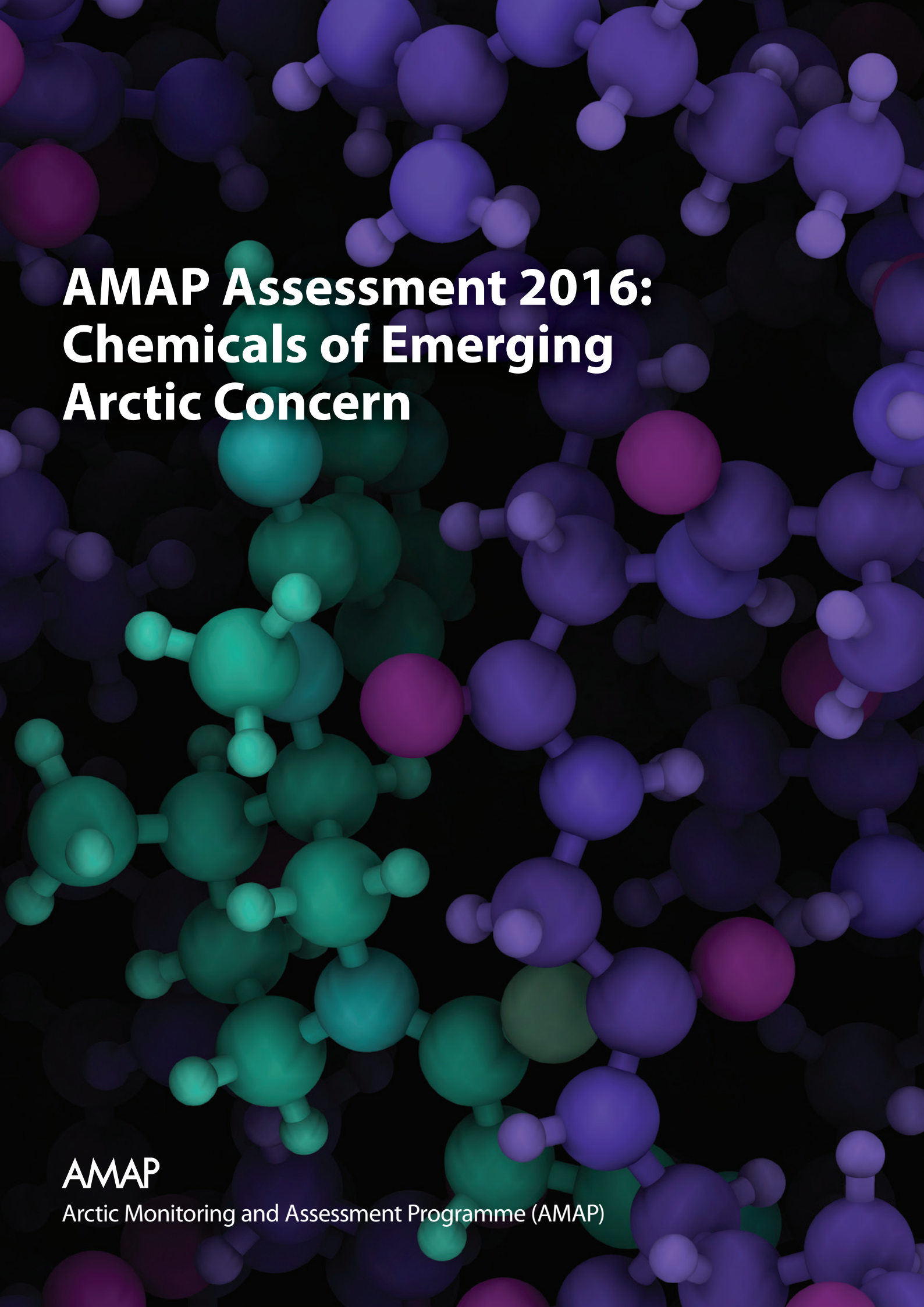

AMAP Assessment 2016: Chemicals of Emerging Arctic Concern

AMAP

Arctic Monitoring and Assessment Programme (AMAP)

Arctic Monitoring and Assessment Programme

The Arctic Monitoring and Assessment Programme (AMAP) was established in June 1991 by the eight Arctic countries (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden and the United States) to implement parts of the Arctic Environmental Protection Strategy (AEPS). AMAP is now one of six working groups of the Arctic Council, members of which include the eight Arctic countries, the six Arctic Council Permanent Participants (indigenous peoples' organizations), together with observing countries and organizations.

AMAP's objective is to provide 'reliable and sufficient information on the status of, and threats to, the Arctic environment, and to provide scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions to reduce adverse effects of contaminants and climate change'.

AMAP produces, at regular intervals, assessment reports that address a range of Arctic pollution and climate change issues, including effects on health of Arctic human populations. These are presented to Arctic Council Ministers in 'State of the Arctic Environment' reports that form a basis for necessary steps to be taken to protect the Arctic and its inhabitants.

This report has been subject to a formal and comprehensive peer review process. The results and any views expressed in this series are the responsibility of those scientists and experts engaged in the preparation of the reports.

The AMAP Secretariat is located in Oslo, Norway. For further information regarding AMAP or ordering of reports, please contact the AMAP Secretariat (Gaustadalléen 21, N-0349 Oslo, Norway) or visit the AMAP website at www.amap.no.

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Preface

This assessment report presents the results of the 2016 AMAP Assessment of Chemicals of Emerging Arctic Concern. This assessment updates the AMAP POPs assessments delivered in 1998, 2002 and 2009, specifically with respect to information on chemicals newly identified in the Arctic environment.

The Arctic Monitoring and Assessment Programme (AMAP) is a Working Group of the Arctic Council. The Arctic Council Ministers have requested AMAP to:

- produce integrated assessment reports on the status and trends of Arctic ecosystems;
- identify possible causes for the changing conditions;
- detect emerging problems, their possible causes, and the potential risk to Arctic ecosystems including indigenous peoples and other Arctic residents;
- recommend actions required to reduce risks to Arctic ecosystems.

This report provides the accessible scientific basis and validation for the statements and recommendations made in the Chemicals of Emerging Arctic Concern Summary for Policy-makers report[1] that was delivered to Arctic Council Ministers at their meeting in Fairbanks, Alaska, USA in May 2017. The present report includes extensive background data and references to the scientific literature, and details the sources for graphics reproduced in the policy-makers summary report. Whereas the Summary for Policy-makers report contains recommendations that focus mainly on policy-relevant actions concerned with addressing contaminant impacts on Arctic human populations, the conclusions and recommendations presented in this report also cover issues of a more scientific nature, such as proposals for filling gaps in knowledge, and recommendations relevant to future monitoring and research work.

This assessment of chemicals of emerging Arctic concern was conducted between 2014 and 2016 by an international group of experts. The expert group members and lead authors were appointed following an open nomination process coordinated by AMAP. A similar process was used to select international experts who independently reviewed this report.

Information contained in this report is fully referenced and based first and foremost on results of research and monitoring undertaken since 2009. It incorporates some new (unpublished) information from monitoring and research conducted according to well established and documented national and international standards and quality assurance/quality control protocols. Care was taken to ensure that no critical probability statements are based on non peer-reviewed materials. Access to reliable and up-to-date information is essential for the development of science-based decision-making regarding ongoing changes in the Arctic and their global implications.

The assessment lead authors have confirmed that both this report and its derivative products accurately and fully reflect their scientific assessment. All AMAP assessment reports are freely available from the AMAP Secretariat and on the AMAP website: www.amap.no, and their use for educational purposes is encouraged.

AMAP would like to express its appreciation to all experts who have contributed their time, efforts and data, in particular the lead authors who coordinated the production of this report. Thanks are also due to the reviewers who contributed to the assessment peer-review process and provided valuable comments that helped to ensure the quality of the report. A list of contributors is included in the acknowledgements at the start of this report and lead authors are identified at the start of each chapter, and each main sub-section of Chapter 2. The acknowledgements list is not comprehensive. Specifically, it does not include the many national institutes, laboratories and organizations, and their staff that have been involved in various countries in contaminants-related monitoring and research. Apologies, and no lesser thanks are given to any individuals unintentionally omitted from the list.

The support from the Arctic countries and non-Arctic countries implementing research and monitoring in the Arctic is vital to the success of AMAP. The AMAP work is essentially based on ongoing activities within these countries, and the countries that provide the necessary support for most of the experts involved in the preparation of the AMAP assessments. In particular, AMAP would like to acknowledge Canada, the Kingdom of Denmark and Sweden for taking the lead country role in this assessment and thank Canada, Norway (Ministry of Foreign Affairs) and the Nordic Council of Ministers for their financial support to this assessment work.

The AMAP Working Group is pleased to present its assessment to the Arctic Council and the international science community.

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Simon Wilson and Jon Fuglestad (AMAP Interim Executive Secretaries)

Oslo, December 2017

[1] AMAP, 2017. Chemicals of Emerging Arctic Concern. Summary for Policy-makers. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. 16 pp.

Extract from *Chemicals of Emerging Arctic Concern: Summary for Policy Makers*

The Arctic Monitoring and Assessment Programme (AMAP) *Chemicals of Emerging Arctic Concern 2016* assessment was presented to Arctic Council Ministers in 2017 in the form of a Summary for Policy-makers document. The following pages (xi-xv) are an extract of that document showing how the content of this report has been interpreted in the form of findings and recommendations for policy-makers. Access to reliable and up-to-date information is essential for the development of science-based decision-making.

The changing face of Arctic pollution

Though distantly located from industrialized centers and agricultural source regions, the Arctic is a sink for global pollutants. The atmosphere, oceans and rivers transport the pollutants released at lower latitudes and deposit them in Arctic ecosystems. Since its establishment in 1991, the Arctic Monitoring and Assessment Programme (AMAP) has documented the extent and effects of pollution in the Arctic and tracked new developments in order to inform policy decisions.

AMAP's initial assessments of these issues in 1997 contributed significantly to the negotiation of international agreements, such as the 'UN ECE's Convention on Long-range Transboundary Air Pollution (LRTAP) Protocol on Persistent Organic Pollutants' and the 'Stockholm Convention on Persistent Organic Pollutants', to restrict and phase out the use of these chemicals on a regional and global scale. As a result of global regulations and other national and regional controls, levels of many Persistent Organic Pollutants (POPs) are now declining in the Arctic and elsewhere. But, the issue of Arctic pollution is not a solved problem.

Chemicals of emerging concern

Tens of thousands of chemicals are presently on the market and new substances continue to enter commerce each year. Many of the chemicals currently registered for use have characteristics similar to legacy pollutants, including a potential to reach the Arctic; however, most are not subject to international (global) regulation. Although international conventions, such as the Stockholm Convention, continue to add new chemicals of concern to the list subject to restrictions, their scope is limited. This, together with the sheer number of chemicals that are in everyday use may constrain their effectiveness in addressing all emerging Arctic pollutants.

Improved analytical technologies, research and screening programmes continue to reveal the presence of chemicals that have previously gone unnoticed, or were not expected to be present in the Arctic. Although newly detected in the Arctic, these so-called 'chemicals of emerging concern', have often been in use and present in the environment for years, even decades. Chemicals found in the Arctic may originate from local sources within the region or come from distant locations. The detection of a new substance in the Arctic that has no local sources is particularly important, as it provides evidence of the chemical's potential to disperse globally. As new substances and their breakdown products continue to be discovered, the notion of what constitutes an 'environmental pollutant' warranting concern also changes, and updated regulatory actions may be needed.

This policy summary refers to the most recent AMAP assessment which looks at a wide range of chemicals newly and recently detected in Arctic ecosystems. These 'chemicals of emerging Arctic concern' should be considered potential candidates for future research or monitoring and possibly for consideration under relevant global and/or regional regulations. In addition, these chemicals of emerging concern contribute to an even broader understanding of how Arctic pollution is changing, which is the primary focus of this summary document and the basis for the recommendations of the AMAP working group given later in this document.

How are new chemicals of emerging concern identified?

There are an estimated 150 000 substances in commerce today, of which less than 1000 are routinely monitored in the environment. Despite the large number of chemicals currently in use, several approaches can be used to recognize those that present a potential concern for Arctic ecosystems.

Database screening

Given the large number of chemicals currently in commerce, initial steps are needed to narrow the pool of potential pollutants to those with the highest probability of being chemicals of concern for the Arctic as well as for the rest of the world. This can be done by screening databases for substances currently in use that have chemical properties similar to known pollutants and the potential for long-range atmospheric transport. The list of chemicals meeting such specifications can then be targeted for possible regulation or additional study. Recent screening of chemical databases in Europe and North America has identified up to about 1200 substances with the potential to reach the Arctic and accumulate in food webs.

Environmental analysis

While database screening can identify chemicals with the potential to be chemicals of emerging Arctic concern, the analysis of environmental samples is required to verify the presence of a suspected chemical and its concentrations in Arctic ecosystems and their inhabitants. Such targeted analysis is responsible for identifying the chemicals of emerging Arctic

concern presented in the current AMAP assessment. New technologies also permit environmental samples to be screened for the presence of unknown or unrecognized pollutants. This type of 'non-target' analysis allows substances to be identified without specifically looking for them and if regularly employed, could hasten the discovery of chemicals of emerging concern in the Arctic.

Long-term monitoring programmes and sample archives

Often, chemicals newly identified in the Arctic have been in use for years, or even decades, prior to their discovery. Thus, additional information is needed to establish how long a chemical has been present in the Arctic and whether its levels have changed through time. Historical levels of many chemicals can be determined through the analysis of archived samples stored specifically for this purpose as well as through the use of natural 'records' such as sediment layers and ice cores. The inclusion of suspected chemicals of concern in long-term monitoring programmes helps to establish trends in environmental levels moving forward, and is useful for informing policies and monitoring the effectiveness of regulations.

Differences between chemicals of emerging concern and 'conventional' pollutants

Four criteria are used to establish whether a chemical qualifies for consideration as a POP according to the Stockholm Convention: chemicals need to persist in the environment for extended periods of time, have the potential to undergo long range transport; accumulate in humans, flora or fauna, and cause adverse effects. Some of the chemicals of emerging Arctic concern meet these criteria and are already under consideration for global regulation or have yet to be assessed. However, other emerging chemicals possess characteristics that fall outside of these criteria or, in some cases information on their environmental behavior and potential to cause adverse health effects is lacking. Such chemicals may therefore not qualify for inclusion under the existing global conventions and may require alternative actions in order to control their releases in a timely manner.

Regional and local sources

Because of the remote location of the Arctic and its small population, the occurrence of chemicals in the region has mostly been attributed to their transport from distantly-located, industrial and agricultural areas. However, several chemicals of emerging concern are being found at elevated levels near Arctic towns and villages, indicating that local settlements may also serve as point sources of chemicals of concern to the Arctic region. Inadequate wastewater treatment in particular seems to be a source of some pharmaceuticals and chemicals used in personal care products, as well as other chemicals found in household products such as some siloxanes and phthalates. Such sources could be addressed through improvement in wastewater treatment in Arctic communities. Targeted monitoring in remote areas can also help to distinguish between long-range transport and local emissions as the main source.

Shorter lifespans

Some chemicals of emerging Arctic concern degrade readily in the hours to weeks following their release into the environment. Despite having shorter lifespans than POPs, these chemicals may still be a concern in the Arctic as a result of their continuous releases in high amounts or transformation into stable degradation products. For example, pharmaceuticals and personal care products released by local wastewater sources are generally not considered to persist in the environment. However, continuous release from northern communities and slow breakdown that results from the colder temperatures and reduced sunlight conditions unique to the Arctic could have consequences for local ecosystems and populations.

Unique chemical makeups

Some emerging pollution threats do not fit the mould of POPs, and thus are not eligible for consideration under current global regulatory practices. For example, plastic debris, and in particular, 'microplastics' are emerging as a major environmental concern world-wide, including in the Arctic. Microplastics are small particles comprised of a wide and diverse range of organic polymers. Although microplastics exhibit some similarities to POPs in terms of long-range transport and potential for harmful effects, because of their complex makeup, they cannot be evaluated with current risk assessment tools and criteria used for POPs, which were developed to focus very specifically on individual chemicals with specific properties.

Unknown toxicity

Owing to their more recent detection in the environment, less data are available on chemicals of emerging concern compared with legacy pollutants. Important information on the toxicity of these chemicals is particularly lacking. Without knowledge of the potential adverse effects of emerging chemicals on Arctic wildlife and human health, regulatory efforts may be delayed.

Sources of chemicals of emerging Arctic concern are changing

The Arctic has unique geographical and climatic characteristics that make it a 'sink' for pollutants transported into the region from distant sources. Atmospheric, riverine and marine pathways carry contaminants from industrialized areas, over long distances where they are deposited in Arctic ecosystems. However, the unique sources and physicochemical properties of emerging pollutants combined with impacts of regulations and environmental changes, are changing where contaminants of Arctic concern originate from and how they are transported into the Arctic.

Climate change

Changes to hydrology, declining sea ice, increased economic development, and changes in air and ocean currents, as well as changes in the way chemicals distribute between air, water and soils are all consequences of a warming climate that are expected to alter how chemicals are released, transported to, and move around within the Arctic. Melting glaciers and sea ice, as well as thawing permafrost and surface soils, could act as an additional source of chemicals of concern as pollutants previously deposited and stored in the Arctic are re-released to the environment. Disruptions to Arctic food webs will also change how Arctic fauna and peoples are exposed to contaminants. These forthcoming ecological changes are uncertain and need to be understood to properly interpret future contaminant data and provide reliable information to policy-makers. An AMAP assessment on the impact of climate change on Arctic pollution is planned for 2017.

New source regions

Prior to the turn of the century, Europe and North America were the major sources for most chemicals entering the market. However, due to new regulations, shifts in production and increasing economic development in regions such as Asia, source regions for chemicals are changing.

Local origins

Many chemicals of emerging Arctic concern are found in consumer products such as electronics, clothing, furniture and building materials, as well as personal care products and pharmaceuticals. Thus, their existence in the Arctic may be due not only to transport from distant regions, but also local sources, such as Arctic towns and villages, community waste sites and sewage outflows. Human presence in the Arctic is also increasing in some areas; as tourism and industrial activities such as mining and gas exploration increase, Arctic regions subject to economic development will also be at a heightened risk of exposure to chemicals of emerging concern.

Long range transport by ocean currents

Our early understanding of POPs considered air to be the primary delivery route of chemicals from distant locations to the Arctic. However, several chemicals of emerging concern, such as PFASs, are more soluble in water than conventional POPs, and appear to be brought to the Arctic via ocean currents to a larger extent.

There is a need for timely and effective action on chemicals of emerging Arctic concern

A large number of unregulated chemicals are already in use and continue to enter commerce each year

As noted, a large number of chemicals are currently in commerce - many in large volumes and with the potential to reach the Arctic – and additional chemicals continue to enter the marketplace each year, often with limited documentation and testing. Given limitations in time and resources, international agreements such as the Stockholm Convention and LRTAP POPs protocol, can only address a fraction of the thousands of chemicals in use. Additional controls, in the form of national and regional actions may therefore be needed to address emerging pollution threats.

Most national regulatory systems do not sufficiently account for a chemical's potential for long range transport

While many countries have environmental regulations in place to restrict the use of chemicals meeting criteria of persistence and bioaccumulation, Canada specifically considers the potential for a chemical to be transported over long distances in air in its national Toxic Substances Management Policy and Persistence and Bioaccumulation Regulations. However, including both atmospheric and oceanic long-range transport potential in national regulatory standards could reduce the number of chemicals with the potential to become Arctic or global pollutants from entering commerce.

The time lag between detection of a harmful chemical and regulation is substantial

History has shown that several decades can pass between the introduction of a new chemical and an eventual agreement to ban or restrict its use. It can take several decades after a chemical has entered the environment before unintended harmful effects on wildlife (or humans) are first noticeable, and many years in addition for regulations to be introduced. Even after a chemical is officially added to the Stockholm Convention, it can take many more years for regulations to take effect and be reflected by declining levels in the environment. The implication is a need for more effective proactive arrangements to reduce risk from chemical pollutants before they are released into the environment.

The timely delivery of scientific information to appropriate regulatory bodies is essential for rapid action

AMAP's primary function is to make scientific knowledge accessible for policy and decision-making processes. Thus, AMAP is uniquely placed to recognize new POPs and other emerging chemical threats and relay such information to appropriate regulatory bodies. Mechanisms to facilitate the timely delivery of AMAP deliverables will be critical in accelerating regional and international actions on emerging chemicals of Arctic concern.

What questions remain unanswered?

The current AMAP assessment confirms that a broad range of chemicals of emerging concern that are being found at lower latitudes are now also present in the Arctic. Given their recent discovery, there is less information available on these chemicals compared to legacy contaminants. Increasing our understanding of these pollutants will be especially important as the Arctic region continues to undergo changes from a warming climate and associated increases in human activity. Environmental monitoring and Arctic-focused studies will be important for filling in current knowledge gaps and assessing the significance of these chemicals to the region.

Current extent of Arctic contamination

Monitoring data for chemicals of emerging concern are not available for large areas of the Arctic, and particularly for Russia and Alaska, US. Thus, the extent and magnitude of contamination of the region is unknown. More information on the levels of these chemicals in different polar ecosystems and over wider geographical areas are needed for a better understanding of the fate of these chemicals in the Arctic environment.

Effects on wildlife and human health

It is largely unknown whether newly identified chemicals of concern will adversely impact the health of the Arctic's human inhabitants and ecosystems. With a few exceptions, most emerging chemicals are being found in the Arctic at concentrations lower than those of legacy POPs. Although their environmental levels may be low, this information is not sufficient to conclude that emerging chemicals present a low risk. There is a general lack of information with regards to the extent to which emerging chemicals may be taken up and accumulated by Arctic fauna or indigenous Arctic peoples whose diets depend heavily on local wildlife.

Cumulative effects

The limited information on the environmental levels combined with a general lack of information regarding effects of individual emerging chemicals make assessing risks to Arctic wildlife and human inhabitants difficult. Even more challenging is understanding the risks from emerging chemicals against a background of exposures to legacy POPs and methyl mercury, as well as additional stressors, such as climate change. This is a focus of a forthcoming AMAP Assessment on Biological Effects.

Next steps: recommendations for future action

Pollution threats to the Arctic are continually evolving. The long-term monitoring data generated by AMAP shows international and national pollution control activities have generally been effective at reducing the occurrence and ecosystem impacts of the chemicals they regulate. Yet, the current AMAP assessment confirms a broad range of new chemicals of emerging concern are now found in the Arctic. Moreover, an even larger number of chemicals with the potential to reach the Arctic are presently in use, with new chemicals continuing to enter commerce each year.

AMAP therefore recommends that:

1. To strengthen efforts under existing global chemicals regulatory systems:

Information on chemicals of emerging Arctic concern be delivered to global and national regulatory bodies in an effective and timely manner.

This recommendation is addressed to the Arctic Council/AMAP to disseminate relevant information on chemicals of emerging Arctic concern to UNECE CLRTAP and the Parties to the Stockholm Convention.

To minimize the time from the discovery of a new chemical of concern in the Arctic to its regulation, it is essential that environmental monitoring data be efficiently delivered to relevant regulatory bodies – both global, for international regulation, and national for regional controls. Currently, national (screening monitoring) programs such as those in Nordic countries (including Greenland) and Canada conduct analyses that document the presence of chemicals of emerging concern in the Arctic and provide this information to relevant parties. The environmental data produced by these national programs and other scientific groups is summarized by AMAP, typically at five-year intervals. Systematized screening monitoring and improved communication between AMAP and relevant regulatory bodies and Parties to Conventions, such as the Stockholm Convention, would streamline this flow of information and accelerate the regulatory review process.

AMAP's 2017-2019 work-plan aims to address the need for more timely provision of information on the presence, levels, and trends in Arctic environmental contamination to global and national regulatory bodies. However, this undertaking will require improved cooperation with the intended recipients of such information, such as the Stockholm Convention Persistent Organic Pollutant Review Committee (POPRC), and commitment at the national level from Arctic States and observer countries in the form of additional nominations of candidate substances and enhanced engagement of scientific experts.

Parties to the Stockholm Convention are encouraged to nominate those chemicals of emerging Arctic concern that exhibit POPs properties.

This recommendation is addressed to governments of Arctic States and observer countries.

The recent AMAP assessment has identified new chemicals that may warrant consideration for regulation under the Stockholm Convention. Only Parties to the Stockholm Convention may propose chemicals for review of their POPs properties by the POPRC. The POPRC review process evaluates whether a chemical meets the criteria for listing it as a POP under the Stockholm Convention, including consideration of whether the chemical is likely, as a result of its long-range transport, to lead to significant adverse human health or environmental effects. Long-range transport resulting in Arctic contamination is an important piece of evidence used by the POPRC when evaluating candidate POPs, but is not the only criteria that is applied.

2. To address chemicals of emerging Arctic concern that may not meet criteria for inclusion under existing international chemicals regulatory systems, or lack information necessary to establish this:

Monitoring programmes and research be continued, with an increased capacity for new pollutants and a focus on documenting long-range transport.

This recommendation is addressed to governments of Arctic States and observer countries, and international and national research funding agencies.

Monitoring data is important in evaluating the effectiveness of international agreements to control pollutants, and providing information needed to evaluate whether new chemicals are causing harm to human health or the environment and should be regulated either nationally or internationally through existing Conventions. In light of the large number of potential chemicals of Arctic concern presently in commerce, a wider application of targeted and non-targeted analytical screening efforts to include candidate POPs and additional contaminants, as well as their long-range transport potential, is needed. Comparable methods and QA/QC need to be developed for chemicals of emerging Arctic concern. Monitoring approaches may need to be modified to cover new POPs and other emerging chemicals, particularly for microplastics, which require new, harmonized methods for assessing their presence and significance in Arctic ecosystems. New research on the 'cocktail effect' of pollutants to assess the long-term effects of pollutant mixtures in the Arctic environment, and the fate and effects of transformation products of chemicals of emerging Arctic concern is needed. Monitoring programmes will need to be coordinated to address both chemicals from local sources associated with Arctic communities, industrial activities and tourism, as well as long-range transport pollutants from global sources, and expanded to cover additional regions. In addition, the continued archiving of samples in specimen banks is critical for assessing risks of new and emerging chemicals of concern.

The Arctic Council engage with relevant global initiatives such as the UN Environment Programme and SAICM to improve the management of chemicals of emerging Arctic concern.

This recommendation is addressed to the Arctic Council (States and Permanent Participants) and governments of observer countries, to further enhance their engagement with the governing bodies of regulatory conventions including UN ECE (LRTAP Convention) and UNEP (the Stockholm, Basel and Rotterdam Conventions), and voluntary international chemical management initiatives, such as the Strategic Approach to International Chemicals Management (SAICM) and the International Programme on Chemical Safety (IPCS).

New approaches to chemicals and waste management should be considered. Many chemicals of emerging Arctic concern, such as the organophosphate-based flame retardants (PFRs), phthalates, some siloxanes, and some current-use pesticides, as well as pollutants that are not chemicals, such as microplastics, may not meet criteria currently applied in the existing mechanisms for the global regulation of long-range transported pollutants. Furthermore, existing global chemicals management systems are addressing chemicals that have already contaminated the environment, However, there is an increased need for proactively preventing the introduction of chemicals with the potential to pollute the Arctic. Consequently, a new generation of policy instruments should be considered to address associated challenges.

Arctic States and observer countries consider the need for additional national and regional actions to control and communicate the risks of pollutants within Arctic communities.

This recommendation is addressed to governments of Arctic States and observers.

There is evidence that some chemicals of emerging Arctic concern – such as pharmaceuticals and personal care products – originate from local sources within the Arctic and therefore their risks may not be adequately managed by international conventions that focus on long-range transported chemicals. In these instances, independent actions by Arctic countries in implementing national and regional controls will be important for protecting the health of Arctic communities and ecosystems.

With regards to pollutants brought to the region via both local and long-range transport, outreach efforts led by Arctic countries will be important for informing local communities of potential health risks and exposure prevention measures until global regulatory controls are effective.

Where they do not already do so, national regulatory systems should be encouraged to take evidence of long-range transport obtained from, e.g., monitoring programmes into account in chemical risk assessment.

Access to information acquired by industry during both research and development as well as chemical manufacturing lifecycle stages be improved

This recommendation is addressed to industry producing chemicals or using them in manufactured products, as well as SAICM for consideration in its Chemicals in Products Programme.

In addition to routine monitoring programmes, non-target approaches – such as database screening and analytical approaches that identify chemicals previously unsearched for can aid the earlier identification of potential chemicals of concern. Such approaches can therefore shorten the time from identification of risk to implementation of regulation. Information on use and chemical properties, including toxicity profiles, from industry is essential for identifying chemicals via database screening and assessing the sufficiency of the existing risk management measures. At present, such information is not always comprehensive or sufficiently accessible to the scientific community and steps should be taken to engage with industry to address this.

1. Introduction

Authors: Jennifer Balmer, Cynthia de Wit, Derek Muir, Simon Wilson

This report presents the fourth in a series of assessments produced by the Arctic Monitoring and Assessment Programme (AMAP) that addresses the presence in the Arctic of environmental contaminants characterized as persistent organic pollutants (POPs). In this regard, this assessment represents something of a departure in that, as well as including 'emerging' chemicals with POP-like characteristics; it also considers some chemicals and groups of substances that may not meet the classical definition of POPs[2]. The term 'chemicals of emerging concern' (CEC) is increasingly being applied to refer to environmental contaminants that are gaining attention, either because they are being newly introduced (in some cases as replacements for chemicals that are being phased out or banned) or because advances in analytical chemistry permit their identification and/or quantification in (environmental) samples with a sufficient degree of reliability. The current assessment is purposely entitled *Chemicals of Emerging Arctic Concern* because the intention here is to consider CECs that are being found in the Arctic.

The report also constitutes the second part of a multi-component assessment that updates information on temporal trends of POPs in the Arctic (AMAP, 2014a, 2016); chemicals of emerging Arctic concern (this report); biological effects of POPs and mercury on Arctic wildlife (2018); and POPs and climate change (to be undertaken in 2018/2019).

AMAP was established as an international program for monitoring and assessing Arctic pollution in 1991, under the Arctic Environmental Protection Strategy (AEPS, 1991). It is now the Working Group of the Arctic Council[3] responsible for monitoring and assessing a range of pollution- and climate change-related issues in order to "*provide reliable and sufficient information on the status of, and threats to, the Arctic environment, and scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions relating to contaminants and adverse effects of climate change*" (see AMAP, 2010a).

AMAP's first assessment report contained a chapter presenting data available up to 1996 that essentially established a baseline for (spatial) trends in POPs in Arctic air, seawater, sediments, soils, plants and biota from terrestrial, freshwater and marine environments (de March et al., 1998). These included polychlorinated biphenyls (PCBs), DDTs, chlordanes, hexachlorocyclohexanes (HCHs), dieldin, endrin, chlorinated benzenes, toxaphene, mirex and polychlorinated dibenzodioxins and furans. Information presented in the first AMAP assessment report (de March et al., 1998) supported national initiatives and was instrumental in stimulating regional and international agreements to regulate 16 selected POPs. In 1998, the Protocol on Persistent Organic Pollutants (POPs) to the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP) was adopted[4]. In 2001 the global Stockholm Convention on Persistent Organic Pollutants was adopted[5] (UNEP, 2001) initially taking action on 12 POPs (often called the 'Dirty Dozen').

Under the Stockholm Convention, there are four screening criteria for establishing that chemicals may be recommended for listing under the annexes to the Convention: they need to be persistent, bioaccumulative, have potential for environmental long-range transport, and display adverse effects. Evidence supporting the criteria of potential for long-range environmental transport include that the chemicals are found at locations "*distant from sources*" or "*where monitoring data show that long-range environmental transport of the chemical…may have occurred*" (UNEP, 2009b: Annex D, paragraph (d) i and ii). Owing to its remoteness from major source areas, the Arctic is important for identifying chemicals that undergo long-range transport in the environment, and thus for identifying substances that may be relevant for listing under the Stockholm Convention. The chemicals listed under the Stockholm Convention when it entered into force in 2004 were aldrin, chlordane, dieldrin, DDT, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, polychlorinated dibenzo-*p*-dioxins and dibenzofurans; these chemicals are referred to by the Convention secretariat as the 'initial POPs'. The term 'legacy POPs' is also commonly applied to several of these chemicals, as their presence in the environment is to a large degree a legacy of past use; however, fresh releases to the environment may continue to occur from, for example, wastes and stockpiles that are not properly stored or disposed of. Also, a number of industrial processes still constitute sources of dioxins and furans.

In 2009, nine more chemicals were added to (listed under) the Stockholm Convention (α- and β-HCHs, lindane, pentachlorobenzene, penta- and octabrominated diphenyl ether mixtures (tetra-, penta-, hexa- and heptabrominated diphenyl ether congeners), hexabromobiphenyl, chlordecone and perfluorooctane sulfonate (PFOS) (UNEP, 2009a). In 2011, endosulfan was added to the Stockholm Convention and hexabromocyclododecane (HBCDD) was added in 2013. At the most recent meeting of the Conference of the Parties of the Stockholm Convention in May 2015, hexachlorobutadiene, pentachlorophenol and polychlorinated naphthalenes were added (UNEP, 2015a). Within the context of the Stockholm Convention, the additional chemicals added are referred to as 'new POPs'. Over time, 'new POPs' will themselves become 'legacy POPs'. DecaBDE, dicofol, short-chain chlorinated paraffins and perfluorooctanoic acid (PFOA) are currently under review by the POPs Review Committee (POPRC) for inclusion under the Stockholm Convention (UNEP, 2015b).[6]

[2] http://chm.pops.int/TheConvention/ThePOPs/tabid/673/Default.aspx (see also Table 5.2)
[3] http://www.arctic-council.org
[4] http://www.unece.org/env/lrtap/pops_h1.htm
[5] http://chm.pops.int
[6] DecaBDE, dicofol and short-chain chlorinated paraffins were listed (2017) at the time of production of this report.

The second AMAP POPs assessment (AMAP, 2004) updated the initial assessment with respect to previously reported POPs; additional data for the period since 1996 allowed some of the first reliable results to be presented for temporal trends for some POPs at Arctic locations. The 2004 assessment also showed that some 'new' contaminants were being found in the Arctic, such as brominated flame retardants (BFRs), and in particular, components (congeners) of the pentaBDE mixture (tetra- and pentaBDEs), and HBCDD (isomers but mainly the sum isomer concentrations), as well as the surfactant PFOS. In 2006, the AMAP POPs Expert Group was tasked by the Arctic Council ministers to produce an updated report on new (or emerging) contaminants in the Arctic, which led to the publication of AMAP's third POPs assessment in 2010 as a series of review articles in a special issue of *Science of the Total Environment* (AMAP, 2010b). These articles covered levels and trends of known BFRs (de Wit et al., 2010), polychlorinated naphthalenes (Bidleman et al., 2010), per-/polyfluoroalkyl substances (PFASs), primarily PFOS and other perfluorinated sulfonic acids as well as perfluorinated carboxylic acids (Butt et al., 2010), endosulfan (Weber et al., 2010), and current use pesticides (Hoferkamp et al., 2010). The articles also reviewed temporal trends in legacy and new contaminants in Arctic air (Hung et al., 2010), temporal trends in legacy POPs in biota (Rigét et al., 2010) and effects of POPs on exposed wildlife and fish (Letcher et al., 2010).

Data from the Arctic can provide evidence for persistence and bioaccumulation, and for assessing long-range transport of chemicals; the Arctic thus has become an important indicator region. AMAP's mandate in relation to POPs is therefore to support the further development and implementation of the Stockholm Convention and similar global agreements, including the Stockholm Convention's POPs Global Monitoring Plan (UNEP, 2007). The information compiled by AMAP feeds into both national and international activities to further develop and refine regulation of harmful chemicals. AMAP results are communicated to groups responsible for evaluating the 'effectiveness and sufficiency' of international agreements, such as the Stockholm Convention and CLRTAP (AMAP, 2014a) as well as to the Stockholm Convention's technical body, POPRC.

Owing to both national and international regulations, environmental concentrations of most legacy POPs are now declining in the Arctic and elsewhere (AMAP, 2016a). However, in many cases, the (relatively few) chemicals which have been phased out are being replaced in production and commercial use by numerous other chemicals that can be used for the same applications. Often, these chemicals have physical-chemical characteristics that are similar to the legacy POPs they substitute; some therefore have the potential to reach the Arctic. It is too early to know whether these chemicals are POPs in the sense that they meet all criteria for persistence, bioaccumulation and adverse effects. Although often referred to as 'new' or 'emerging' chemicals, several of these (groups of) chemicals have been in commerce for many years and are therefore not really new in terms of only now appearing on the market. Their 'emerging concern' is often related to the fact that their production, use and releases to the environment are increasing; and some are now being found in Arctic air, water, biota and humans (Vorkamp and Rigét, 2014). In this respect, they qualify as **chemicals of emerging Arctic concern**.

However, because many CECs are used in consumer products (e.g. electronics, clothing, furniture, plastics) and in building materials and insulation, their presence in the Arctic may be due not only to long-range transport, but also to sources within the region. These 'local sources' are associated with Arctic towns and villages (including community waste sites and sewage disposal) and with resource development and the generally increasing economic activity in Arctic regions.

It is also worth noting that previous focus has been on semi-volatile chemicals that undergo long-range atmospheric transport in the gas-phase or on aerosols/particles as their primary route for transport to the Arctic. However, it is now clear that some substances such as PFOS and perfluorooctane carboxylic acids (e.g. PFOA), undergo long-range transport to the Arctic via ocean currents due to their propensity to partition to water (Prevedouros et al., 2006; Brown and Wania, 2008; Armitage et al., 2009b; Benskin et al., 2012a). Also, PFAS precursors such as fluorinated sulfonamides (FOSAs) and fluorotelemer alcohols (FTOHs) undergo long-range transport via the atmosphere but are subsequently degraded to water-soluble acids.

There are an estimated 150 000 substances in commerce today based on registrations on the European and US chemical inventories over the past 30 years. Screening exercises based on physical-chemical properties and production volumes (etc.) have been performed to identify chemicals with potential to reach the Arctic (Howard and Muir, 2010; Muir and Howard, 2006; Scheringer et al., 2012) (see also Chapter 4). A primary objective of the current assessment is therefore to review both the peer-reviewed and grey literature for existing data on a wide range of CECs that have recently been detected in the Arctic environment. The emphasis is on environmental levels and trends; analytical methods for these new chemicals are not reviewed or evaluated in the current assessment. Most laboratories reporting data to AMAP participate in inter-laboratory studies and inter-comparison exercises for legacy POPs. However, analytical methods for CEC are still at an early stage of development and the authors of the current assessment are very aware of both the limitations that exist and the need for further development of the quality assurance and quality control (QA/QC) methods that are currently lacking for many CECs.

This assessment compiles available Arctic data for many chemicals that have potential for being considered for inclusion in the Stockholm Convention, and some that may need to be addressed under other regulatory arrangements. The chemicals included in this assessment are PFASs, brominated, chlorinated and organophosphorus-based flame retardants, organophosphorus-based plasticizers, phthalates, short-chain chlorinated paraffins, siloxanes, pharmaceuticals and personal care products, polychlorinated naphthalenes, hexachlorobutadiene, current use pesticides, pentachlorophenol/pentachloroanisole, mono- and dibutyltins, polycyclic aromatic hydrocarbons, non-Aroclor and byproduct PCBs, halogenated natural products (HNPs), and microplastics.

Owing to the large number of chemicals covered in Chapter 2, to aid the reader, some sections are structured with shorter sub-sections for specific chemical groups or for individual chemicals. This is the case for BFRs (Section 2.2) and HNPs (Section 2.16).

2.1 Per- and polyfluoroalkyl substances

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2.1.1 Introduction

Butt et al. (2010) reviewed information available for per- and polyfluoroalkyl substances (PFASs) in the Arctic and Letcher et al. (2010) reviewed PFAS exposure in wildlife and fish, both as part of a previous AMAP assessment. This review therefore focuses mainly on data published between about 2009 and early 2015 and on replacement PFASs of emerging concern such as perfluorocarboxylates (PFCAs) and short-chain perfluoroalkyl sulfonates (PFSAs) and their precursors (Table 2.1).

Table 2.2 summarizes the detection of PFASs in Arctic environmental media. It includes all reports to date, i.e. data summarized in previous reviews (Butt et al., 2010) as well as more recent published and unpublished results. Each environmental compartment is discussed separately in the relevant parts of this section.

2.1.2 Physical-chemical properties

The PFAS group is a large suite of highly fluorinated aliphatic compounds, which differ in their functional groups and the length of the carbon chains (Buck et al., 2011). For the perfluoroalkyl substances, all the carbon atoms of the alkyl chain are fully fluorinated as illustrated in Figure 2.1. The high chemical and thermal stability of the C-F bond and the surfactant-like properties of PFASs are the main characteristics that have made this group of compounds suitable for many different uses in industrial and commercial applications.

The PFAS group is further divided into the PFSA and PFCA sub-groups, which include some of the most investigated PFASs over the past 15 years, i.e. perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). Another large subgroup of PFASs is the fluorotelomer alcohols (FTOHs), considered the neutral precursors of the more stable acidic compounds, the PFCAs. PFASs have varying chain lengths. A distinction is often made between long-chain PFASs (with eight or more perfluorinated C atoms) and short-chain PFASs (with seven perfluorinated C atoms or less).

The environmental fate of PFASs is influenced by their physical-chemical properties, which vary depending on their chain length and functional groups. Wang et al. (2011) and Gomis et al. (2015) summarized the limited information available on the physical-chemical properties of PFASs, including newer replacement compounds. Selected physical-chemical properties of the PFASs discussed in this section are provided in Annex Table A2.1/1. The PFCAs and PFSAs have very low acid dissociation constants (pK_A) and are almost fully ionized under most environmental conditions (Cheng et al., 2009; Vierke et al., 2013). As anionic substances, the PFCAs and PFSAs also bind to proteins and phospholipids (reviewed by Armitage et al., 2013). They are typically found at elevated concentrations in tissues with high protein and phospholipid contents (e.g. liver, kidney, blood). Several PFASs have been shown to accumulate in food chains, including those in remote environments such as the Arctic (Butt et al., 2010; Letcher et al., 2010).

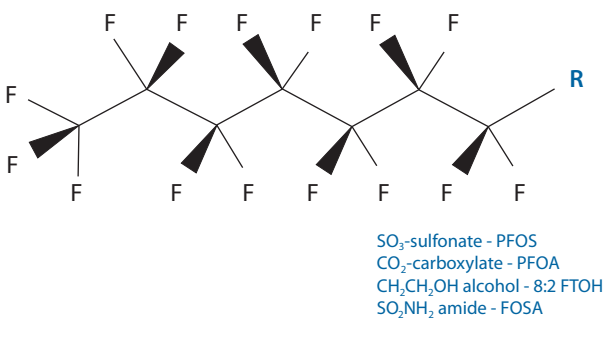

Figure 2.1 Molecular structure of perfluorinated alkyl substances.

Perfluorocarbon chain length and functional group are the predominant parameters influencing the partitioning of PFASs in abiotic environments (Ahrens et al., 2010). The organic carbon partition coefficients (log K_{OC}) of PFCAs and PFSAs are relatively low (Annex Table A2.1/1) ranging from ~1.3 to 3.5 compared to neutral halogenated organics. The short-chain PFCAs ($\leq C_7$ chain length) were exclusively found in the dissolved phase, while long-chain PFCAs ($\geq C_8$ chain length), PFSAs, ethylperfluorooctane sulfonamidoacetic acid (EtFOSAA), and perfluorooctanesulfonamide (PFOSA) appeared to bind more strongly to particles (Higgins and Luthy, 2006; Ahrens et al., 2010). The partitioning also varied depending on the conditions (e.g. organic carbon content, pH, metal ions), for example, increasing sorption was found with increasing organic carbon content (Ahrens et al., 2010). As a consequence, the short-chain PFCAs have a higher potential for long-range transport in aquatic environments, while PFSAs, EtFOSAA and perfluorooctane sulfonamide (FOSA) are preferentially distributed in biota or the abiotic environment such as sediments, which could act as a sink for PFASs. The physical-chemical characteristics also influence the type of long-range transport in the aqueous environment (e.g. sea spray, microlayer, surface water, deep ocean water).

2.1.3 Sources, production, use, and transport

PFASs have been produced since the 1950s and used in surfactants and polymers (Buck et al., 2011). PFASs have been used in polymers developed for stain repellent treatments of textiles and carpets and for use in grease-proof, food-contact paper. As surfactants they have been used (in free acid or salt forms) as the processing aids for fluoropolymer manufacture (e.g. Teflon™), in aqueous film-forming foams and in wetting and leveling agents, emulsifiers, foaming agents, and dispersants due to their ability to lower aqueous surface tension (Prevedouros et al., 2006; Paul et al., 2009; Buck et al., 2011; Wang et al., 2014b). Worldwide production of perfluorooctane sulfonyl fluoride (POSF), the key building block for PFOS-related compounds,

Table 2.1 Per- and polyfluoroalkyl substances (PFASs) referred to in this chapter with nomenclature as recommended by Buck et al. (2011).

Compound	Acronym	CAS number
Perfluorocarboxylates (PFCAs)		
perfluorobutanoate	PFBA	375-22-4
perfluoropentanoate	PFPeA	2706-90-3
perfluorohexanoate	PFHxA	68259-11-0
perfluoroheptanoate	PFHpA	375-85-9
perfluorooctanoate	PFOA	335-67-1
perfluorononanoate	PFNA	375-95-1
perfluorodecanoate	PFDA	335-76-2
perfluoroundecanoate	PFUnDA	2058-94-8
perfluorododecanoate	PFDoDA	307-55-1
perfluorotridecanoate	PFTrDA	72629-94-8
perfluorotetradecanoate	PFTeDA	373-06-7
perfluoropentadecanoate	PFPeDA	141074-63-7
perfluorohexadecanoate	PFHxDA	67905-19-5
Perfluoroalkylsulfonates (PFSAs)		
2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy) -1,1,2,2-tetrafluoroethanesulfonate	6:2-Cl-PFAES or F-53B	756426-58-1
perfluorobutane sulfonate	PFBS	29420-49-3
perfluorohexane sulfonate	PFHxS	432-50-7
perfluoroheptane sulfonate	PFHpS	375-92-8
perfluorooctane sulfonate	PFOS	1763-23-1
perfluorodecane sulfonate	PFDS	335-77-3
perfluorododecane sulfonate	PFDoS	79780-39-5
perfluoroethylcyclohexane sulfonate	PFECHS	335-24-0
1H,1H,2H,2H-perfluorohexanesulfonate	4:2 FTS	414911-30-1
1H,1H,2H,2H-perfluorooctanesulfonate	6:2 FTS	27619-97-2
Perfluorosulfonamides and Sulfonamide Ethanols		
perfluorobutane sulfonamide	FBSA	30334-69-1
perfluorooctane sulfonamide	FOSA	754-91-6
N-methyl perfluorobutanesulfonamide	MeFBSA	68298-12-4
N-methyl perfluorooctanesulfonamide	MeFOSA	122526-47-0
N-ethyl perfluorooctanesulfonamide	N-EtFOSA	4151-50-2
N-ethyl perfluorooctanesulfonamide ethanol	N-EtFOSE	1691-99-2
N-methyl perfluorooctanesulfonamide ethanol	N-MeFOSE	24448-09-7
N-methyl perfluorooctanesulfonamide ethylacrylate	N-MeFOSEA	25268-77-3
N-ethylperfluorooctane sulfonamidoacetic acid	EtFOSAA	
Fluorotelomer Alcohols		
1H,1H,2H,2H-perfluorooctanol	6:2 FTOH	647-42-7
1H,1H,2H,2H-perfluorodecanol	8:2 FTOH	678-39-7
1H,1H,2H,2H-perfluorododecanol	10:2 FTOH	647-42-7
Saturated and Unsaturated Fluorotelomer Acids		
2H-hexadecafluoro-2-decenoic acid	8:2 FTUCA	70887-84-2
2H-octadecafluoro-2-dodecenoic acid	10:2 FTUCA	70887-94-4
2H,2H,3H,3H-pentadecafluoro decanoic acid	7:3 FTCA	812-70-4
2H,2H-heptadecafluoro decanoic acid	8:2 FTCA	27854-31-5
2H,2H-nonadecafluoro dodecanoic acid	10:2 FTCA	53826-13-4

Table 2.2 Summary of Arctic media for which PFAS data have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
PFBA	×	×			×		×	×	×	×
PFPeA	×	×			×		×			
PFHxA	×	×		×	×		×	×		×
PFHpA	×	×		×	×				×	×
PFOA	×	×		×	×	×				×
PFNA	×	×		×	×	×	×			×
PFDA	×	×		×	×	×		×		×
PFUnDA	×	×		×	×	×	×			×
PFDoDA		×		×	×	×				×
PFTrDA				×						×
PFTeDA										×
PFPeDA										×
PFHxDA										×
6:2-Cl-PFAES		×								×
PFBS	×	×		×	×					×
PFHxS	×	×		×	×	×				×
PFHpS	×			×	×					×
PFOS	×	×	×	×	×	×	×	×	×	×
PFDS	×			×						×
PFDoS										×
4:2 FTS					×					
6:2 FTS					×					×
FBSA										×
PFOSA	×	×	×	×	×	×	×	×	×	×
N-EtFOSA	×									
N-EtFOSE	×									
N-MeFOSE	×									
N-MeFOSEA	×									
PFECHS		×			×			×		×
6:2 FTOH	×									
8:2 FTOH	×									
10:2 FTOH	×									
8:2 FTUCA										×
10:2 FTUCA										×
7:3 FTCA										
8:2 FTCA										
10:2 FTCA										

was estimated at 96 000 tonnes (or 122 500 tonnes, when unusable waste production is included) during the period 1972–2002 (Paul et al., 2009). After discovering that several PFASs were globally distributed in the abiotic environment, biota, food items and humans, measures have been taken by international authorities to regulate their production and use. PFOS and related C_8 sulfonate chemicals were included in the Stockholm Convention in 2009 (under Annex B, which allows exemptions for use) owing to their persistence, bioaccumulation and toxicity. PFOA is currently under review for listing.

PFCAs are degradation products of perfluoro- and polyfluoro-substances including fluorotelomer alcohols, perfluoroalkyl phosphates, phosphonates, acrylates, and other compounds with perfluorinated carbon chains (Buck et al., 2011). Some PFCAs, especially PFOA and perfluorononanoate (PFNA), had commercial uses as processing aids for fluoropolymers. Two manufacturing techniques have been used to produce PFOA: (i) electrochemical fluorination (ECF) in which octanoyl fluoride, $C_7H_{15}COF$, undergoes electrolysis in anhydrous hydrogen fluoride, and (ii) telomerization in which pentafluoroethyl

iodide is reacted with tetrafluoroethylene to yield a mixture of perfluoroalkyl iodides. The two manufacturing processes for PFOA and other PFCAs are readily distingannuishable by the isomeric composition of the final commercial products because ECF yields straight-chain and branched isomers while telomerization retains the geometry of the starting material with the majority of the product being straight-chain isomers (Benskin et al., 2010). These differences have been used to identify sources to the Arctic Ocean (Benskin et al., 2012a).

Under the United States Environmental Protection Agency (US EPA) PFOA Stewardship Program (US EPA, 2006), eight leading fluorochemical manufacturing companies agreed to reduce emissions and product content of PFOA and related chemicals in fluorinated polymers (i.e. containing perfluoroalkyl moieties) by 95% by 2010 and to work toward their elimination by 2015 (US EPA, 2015a). Recent trends among the global PFAS producers are to replace the long-chain PFSAs and PFCAs with shorter-chain homologues or other types of fluorinated chemicals (Wang et al., 2014b). However not all global manufacturers have participated in this voluntary agreement and production of C_8-related perfluorinated chemicals continues in China (Jiang et al., 2015) as well as in Russia and India (SAICM/ICCM4, 2015). Wang et al. (2014a) concluded that releases from fluoropolymer production contributed most to historical PFCA emissions (e.g. 55–83% in the period 1951–2002). They also noted that since 2002, there has been a geographical shift in industrial sources (particularly fluoropolymer production sites) from North America, Europe and Japan to emerging Asian economies, especially China.

Wang et al. (2014a) quantified global emissions of C_4–C_{14} -PFCA homologues during the life-cycle of products based on PFOA, PFNA, PFOS and fluorotelomer compounds. Their approach improved upon previous estimates of emissions of PFOA by assigning an average duration to each stage in the product life-cycle, estimating amounts of PFOA- and PFNA-based derivatives used as fluoropolymer processing aids, and incorporating information on the PFOA reduction process under the US EPA Stewardship Program. Their estimated time trends of PFCAs suggest significant ongoing emissions until at least 2020, depending on lower and higher use and emission scenarios (Figure 2.2). These trends can be compared with ongoing monitoring of PFCAs in Arctic wildlife (see Section 2.1.6).

The long-range transport of PFASs to remote areas has been explained by two processes: (i) transport by ocean currents (Armitage et al., 2009b) and (ii) atmospheric oxidative transformations and subsequent wet and dry deposition of airborne precursors, such as FTOHs, FOSAs, and sulfonamido ethanols (FOSEs) (Ellis et al., 2004; D'Eon et al., 2006). PFSAs and PFCAs are persistent and most often found as anions in aquatic environments due to their relatively low pK_A (Armitage et al., 2009a; Butt et al., 2010). The main pathway for PFASs to Northern oceans is transport by ocean currents. However, atmospheric long-range transport, degradation of volatile precursors to PFCAs in the atmosphere (e.g. 8:2 FTOH to PFOA) and secondary sources, such as melting glaciers and snow packs also contribute (Prevedouros et al., 2006; Armitage et al., 2009a,b; Stemmler and Lammel, 2010; Zhao et al., 2012).

2.1.4 Transformation processes

There are multiple pathways in the environment that can account for the presence of PFCAs and other PFASs in Arctic abiotic and biotic compartments. In addition to ocean transport and atmospheric long-range transport of PFCAs and PFSAs (reviewed by Wang et al., 2013b), PFASs can also be produced from perfluoroalkyl-containing precursors that undergo degradation processes such as atmospheric oxidation (Young and Mabury, 2010). A new degradation pathway for FTOHs on metal-rich atmospheric surfaces was recently recognized (Styler et al., 2013).

It is unlikely that Arctic biota are exposed to volatile fluorotelomer precursors of the PFCAs through their tendency to be transported in the atmosphere (Butt et al., 2010). However, fluorotelomers could be present in microplastics transported in ocean waters and released from melting Arctic sea ice (Obbard et al., 2014).

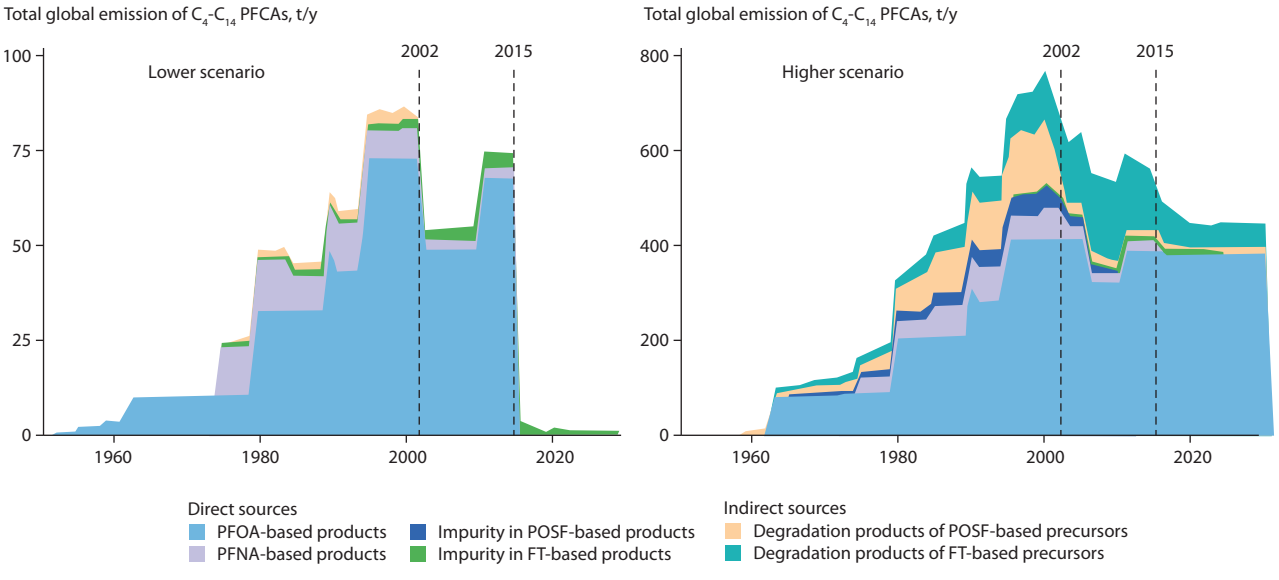

Figure 2.2 Estimated total global annual emissions of C_4–C_{14} PFCAs (1951–2030) (Wang et al., 2014a).

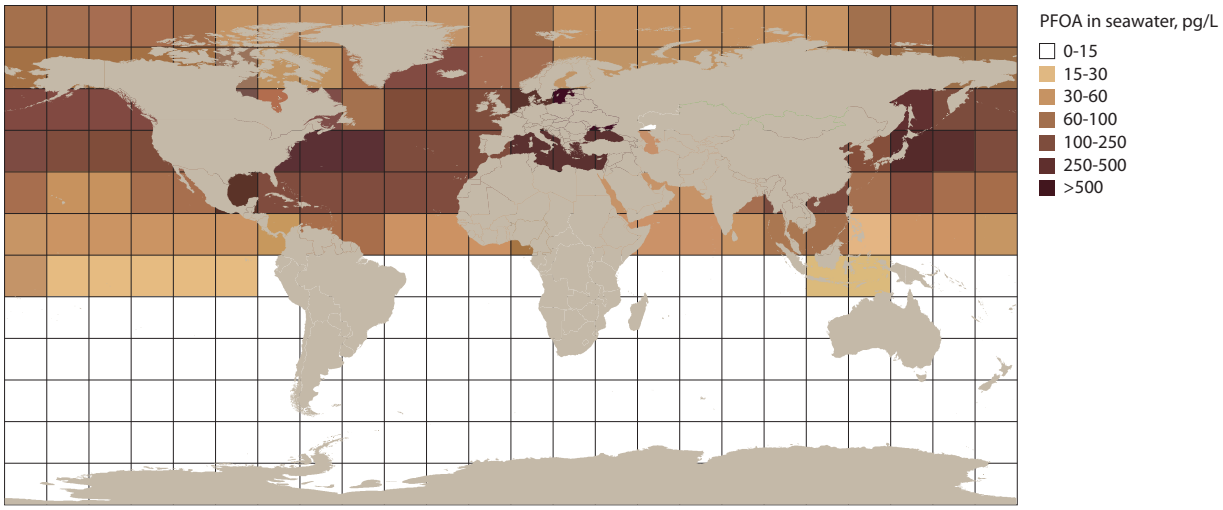

Figure 2.3 Modelled concentrations of PFOA in surface ocean waters in 2005 (Armitage et al., 2009b).

In general, biotransformation pathways are important for explaining the relative proportions of PFCAs and PFSAs in exposed biota (Butt et al., 2014). Controlled studies have not been performed on biotransformation of fluorotelomer-related compounds by Arctic biota. Studies with laboratory animals have shown that the 8:2 FTOH, widely used as starting material for fluoropolymers, and present as a volatile residual in the polymer, undergoes metabolism to PFOA and, to a smaller degree, PFNA and shorter chain-length PFCAs (Butt et al., 2014). There have been a few studies of other fluorotelomer-related products including biotransformation of polyfluoroalkyl phosphates (PAPs), 8:2 fluorotelomer acrylate (8:2 FTAC) and fluorotelomer carboxylates (FTCAs, FTUCAs), all of which yielded PFOA and other PFCAs as persistent degradation products. Galatius et al. (2013) compared PFCA and short-chain PFSAs in three marine mammal species in the North Sea. They found that harbor porpoises (*Phocoena phocoena*) and harbor seals (*Phoca vitulina*) showed lower concentrations of PFCAs than white-beaked dolphins (*Lagenorhynchus albirostris*), and that the seals had higher proportions of perfluorohexane sulfonate (PFHxS) (C_6). The differences were attributed to more rapid excretion in cetaceans. Pinnipeds also appear to have a much higher metabolic capacity for transforming PFOSA to PFOS than cetacean species.

2.1.5 Modelling studies

Global modelling has been used successfully to assess transport of PFASs to the Arctic and to try to explain empirical observations in air, ocean waters and biota (Wania, 2007; Armitage et al., 2009a,b; Stemmler and Lammel, 2010). Processes that transport PFASs to the Arctic include transport of parent compounds in air or water and/or of the precursors that can undergo transformation to the ionic form (PFOS and PFCAs). Butt et al. (2010) reviewed the initial modelling work; here more recent (post-2009) literature that focuses on PFOA and long-chain PFCAs is included. The initial studies showed that ocean transport of directly emitted PFOA is the main source of this compound to the Arctic Ocean and, with continued transport from lower latitudes, concentrations of PFOA are expected to increase over the next couple of decades. However, with the regulation and phase-out of some PFASs, emissions are predicted to decrease and lead over time to reduced levels in the Arctic (Wang et al., 2014a).

Armitage et al. (2009a,b) used the BETR Global model to show that transport via ocean currents is the major pathway to the Arctic for PFOA and long-chain PFCAs that are directly discharged to aquatic environments of urban and industrial areas at mid-latitudes. They predicted PFOA concentrations in the range 30–250 pg/L for the Arctic Ocean and adjacent northern seas (Figure 2.3) which were within the range observed in seawater monitoring (see Section 2.1.6.4).

Stemmler and Lammel (2010) used a global multi-compartment model (MPIMCTM) to assess transport of PFOA to the Arctic. This model allowed a comparison of the relative importance of different ocean pathways and showed that the main source of PFOA to the Arctic Ocean was inflow through the Norwegian Sea and that this was strongly influenced by changes in water transport, which thus determined its interannual variability. The atmospheric component of the model suggested that PFOA deposition occurred via episodic transport events (timescale of days) into the Arctic and that wet deposition occurred over land with maxima in winter (Figure 2.4).

Yamashita et al. (2008) hypothesized that PFASs could be transported globally with the thermohaline circulation system, and that open-ocean water acts as a final sink for PFOS and PFOA. Lohmann et al. (2013) showed that a vertical eddy diffusion model could reproduce the observed depth profile of PFOA concentrations at sites in the Pacific and Atlantic Oceans. This process has not been considered in previous modelling of hydrophobic persistent organic pollutants (POPs) in the ocean, which has assumed they are removed from the water column mainly by settling particles (Lohmann et al., 2006).

However, atmospheric long-range transport and degradation of volatile precursors, such as fluorotelomer alcohols, to PFCAs in the atmosphere are important for Arctic terrestrial environments and could contribute to oceanic inputs via melting glaciers and snow packs (see Section 2.1.6.1). Wallington et al. (2006) used a three-dimensional global atmospheric chemistry model (IMPACT) to show that 8:2 FTOH, a major precursor of PFOA, would be globally distributed, consistent with the measured

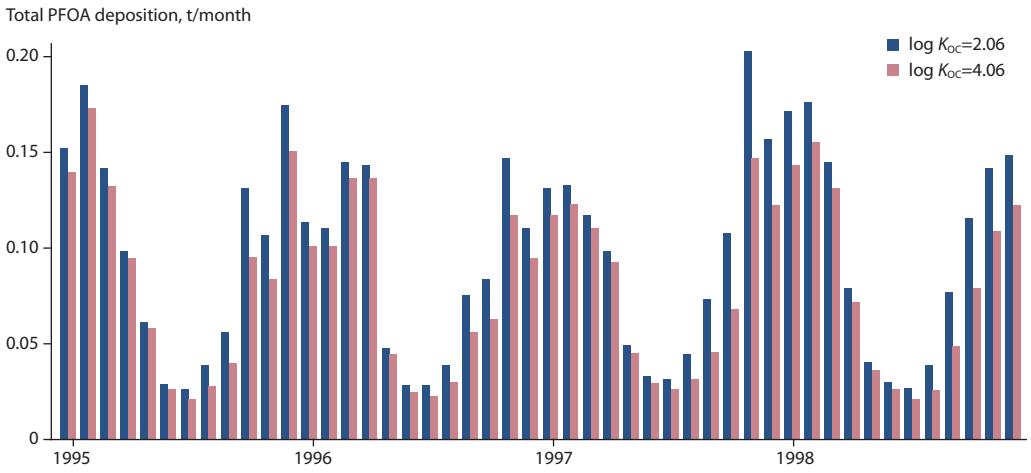

Figure 2.4 Four-year time series of monthly sums of total (wet + dry) deposition of PFOA to the Arctic predicted by the MPIMCTM model (Stemmler and Lammel, 2010). The blue and pink bars represent modelled PFOA deposition assuming a log organic carbon partition coefficient of 2.06 and 4.06, respectively.

half-life of approximately 20 days. PFOA was also predicted to be present at higher atmospheric concentrations during the Arctic summer due to degradation of 8:2 FTOH by photo-oxidants, such as OH radical, and very low concentrations during the Arctic winter due to low light intensity and removal in precipitation. Atmospheric oxidative transformations of other airborne precursors, such as short-chain FTOHs and short-chain FOSAs, and FOSEs (Ellis et al., 2004; D'Eon et al., 2006), and subsequent wet and dry deposition of PFSAs and PFCAs are also likely to occur although they have not been subject to detailed atmospheric deposition modelling.

2.1.6 Environmental concentrations

2.1.6.1 Air and precipitation

Air

To better understand the fate and long-range transport of PFAS to the Arctic, both neutral precursors and ionic PFASs have been measured in the atmosphere at Arctic sites and in the northern Atlantic Ocean. Ionic PFASs are usually measured in the particulate phase, while the neutral precursors are measured in both the gas- and particulate phase.

Results of long-term air monitoring for PFOS and PFOA in airborne particles have been reported for Svalbard (Zeppelin Station) for the period 2006–2012. Recent data show that PFOA continues to be the predominant ionic PFAS in air at Zeppelin (Figure 2.5). PFASs are monitored in air at several locations in Norway, but not many samples have been analyzed and the concentrations of many compounds are below detection limits. For example, 1H,1H,2H,2H-perfluorooctanesulfonate (6:2 FTS), perfluorobutane sulfonate (PFBS), perfluorodecanoate (PFDA), perfluorodecane sulfonate (PFDS), perfluoroheptanoate (PFHpA), perfluorohexanoate (PFHxA) and PFHxS were not detected in samples from any month at Andøya (northern Norway) in 2014. The situation was similar at Zeppelin, although PFDA was found in samples from four months in 2014 (Figure 2.5). PFDA was reported from the southernmost station (Birkenes; southern Norway) as was 6:2 FTS; but they were only found during two months and a single month, respectively (NILU, 2015). There is no clear south-north trend for the number of PFASs detected, or for concentrations of PFOA measured (Figure 2.5). All stations show peak concentrations during summer (NILU, 2015).

Neutral and ionic PFASs were monitored at Alert (Nunavut, Canada) in air (gas and particles) from August 2006 to 2012 (AMAP, 2014a). 8:2 FTOH was the compound measured at highest concentrations at Alert, followed by 10:2 FTOH. PFOS precursors (MeFOSE and EtFOSE) were also detected at Alert.

Atmospheric data for PFASs have also been collected during ship cruises along the northern Atlantic Ocean including Arctic coastal regions. Cai et al. (2012a) investigated the inter-hemispheric gradient of neutral precursors in atmospheric samples, starting from the Japan Sea and then on a transect towards the Arctic Ocean. Samples north of 66°N were taken in the period July–August 2010. 8:2 FTOH was the compound detected at the highest concentrations (range: 83.4–160 pg/m^3) followed by 10:2 FTOH (range: 6.2–31.2 pg/m^3). Other neutral precursors (FOSA and FOSE) were also detected at concentrations in the pg/m^3 range. Concentrations of fluorotelomer acrylates (6:2 FTAC, 8:2 FTAC and 10:2 FTAC) were also reported.

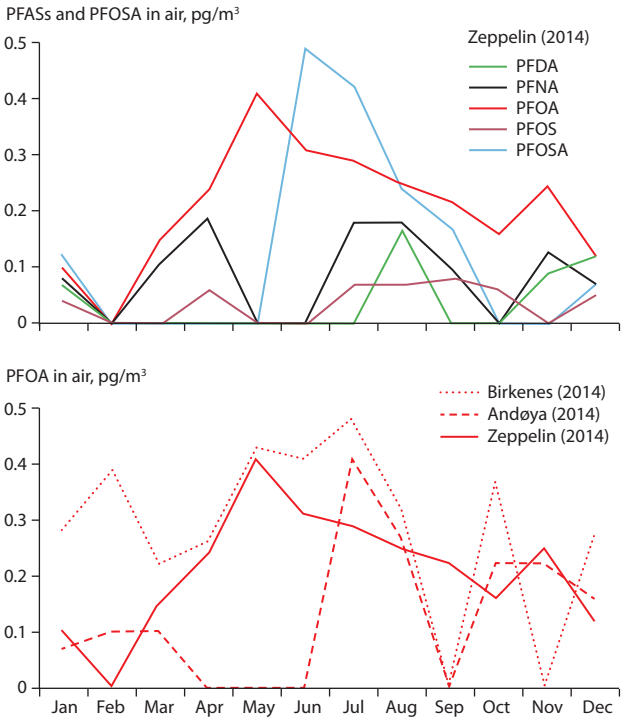

Figure 2.5. Monthly mean concentrations of ionic PFASs and PFOSA in air at Zeppelin in 2014 and mean monthly PFOA at Birkenes, Andøya and Zeppelin in 2014 (NILU, 2015).

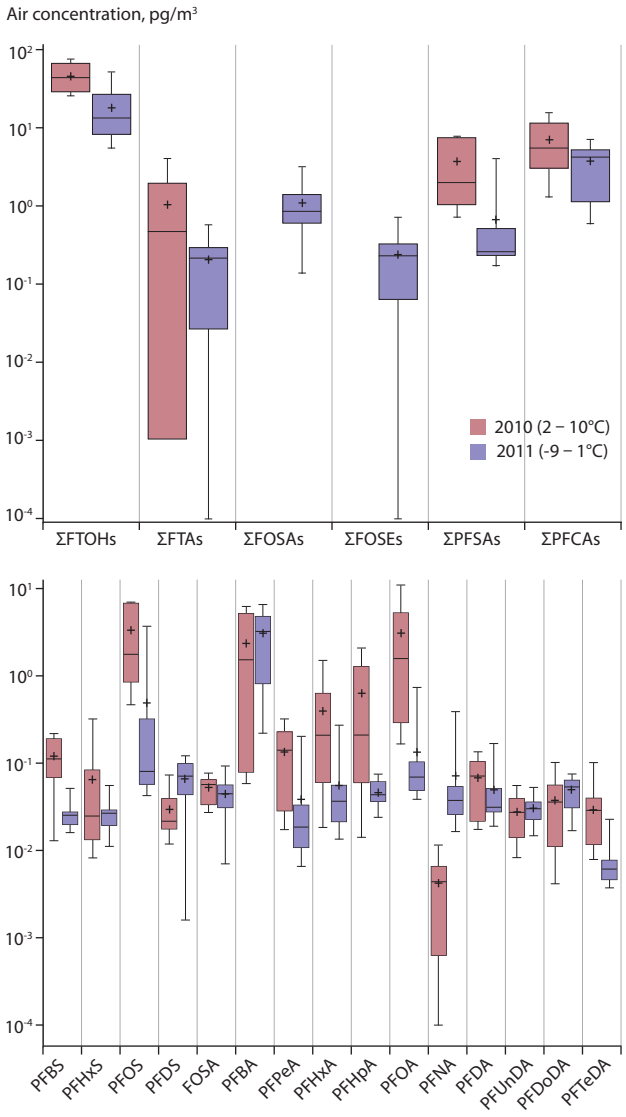

Figure 2.6 Box and whisker plots of PFAS concentrations for PFAS groups and ΣPFSAs (upper) and individual PFSAs and PFCAs in air (sum of particle and gas phases) (lower). Boxes correspond to the interquartile range (25th and 75th percentiles), whiskers to the 5th and 95th percentiles. 2010 FOSAs and FOSEs are excluded owing to contamination in 2010 by MeFOSA and MeFOSEs.

Air samples collected on the *Amundsen* icebreaker during annual cruises in the Canadian Arctic since 2007 have been analyzed for PFASs. These data build on earlier studies of PFAS in the Canadian Arctic using oceanographic cruises (Shoeib et al., 2006; Ahrens et al., 2011). Figure 2.6 shows data for 2010–2011.

Air concentrations of most PFAS compounds measured in the Arctic in 2010 and 2011 were slightly lower or within the same range as those measured in air along a cruise track from coastal Germany to the center of the North Sea in May 2009 by Xie et al. (2013).

Passive air sampling using polyurethane foam (PUF) or sorbent-impregnated polyurethane foam (SIP) has also been used to measure atmospheric concentrations of neutral PFASs at remote sites. The Global Atmospheric Passive Sampling (GAPS) network currently includes about 60 sites, including five in the Arctic: Alert and Little Fox Lake (Canada); Barrow (Alaska, USA); Ny-Ålesund (Svalbard) and Stórhöfði, (Iceland). In the 2009 global-scale pilot study using SIP disk samplers,

Table 2.3 Air concentration (pg/m³) for PFASs measured in Arctic air at GAPS sites. Data show first quarter passive sampling in 2009 using SIP disks (Genualdi et al., 2010).

Chemical	Alert	Barrow	Little.Fox Lake	Stórhöfði	Ny-Alesund
6:2 FTOH	<MDL	0.78	<MDL	<MDL	<MDL
8:2 FTOH	6.4	6.8	16	<MDL	1.72
PFOS	2.0	<MDL	<MDL	<MDL	<MDL

MDL: minimum detection limit

Genualdi et al. (2010) found 8:2 FTOH was the predominant compound and the most abundant of the FTOHs (Table 2.3). EtFOSA and MeFOSA were below detection limits at the four Arctic sites, whereas MeFOSE and EtFOSE were only detected at Barrow with air concentrations of 0.54 and 0.44 pg/m³, respectively. Ionizable PFASs were quantifiable only at Alert. PFOS was the predominant compound with an air concentration of 2.0 pg/m³. Shorter-chain PFSAs were also detected at Alert with concentrations of 0.77 pg/m³ (PFBS) and 0.087 pg/m³ (PFHxS) (Genualdi et al., 2010).

However, in more recent work, a greater number of PFCAs were determined (Rauert and Harner, unpubl. data). Perfluorobutanoate (PFBA) predominated at all locations (Figure 2.7). PFBA has multiple non-fluorotelomer gas-phase sources, including chlorofluorocarbon replacements HFC-329 ($CF_3(CF_2)_3H$) (Young et al., 2009), HFE-7100 ($C_4F_9OCH_3$), and HFE-7200 ($C_4F_9OC_2H_5$) (Wallington et al., 1997; Chen et al.,

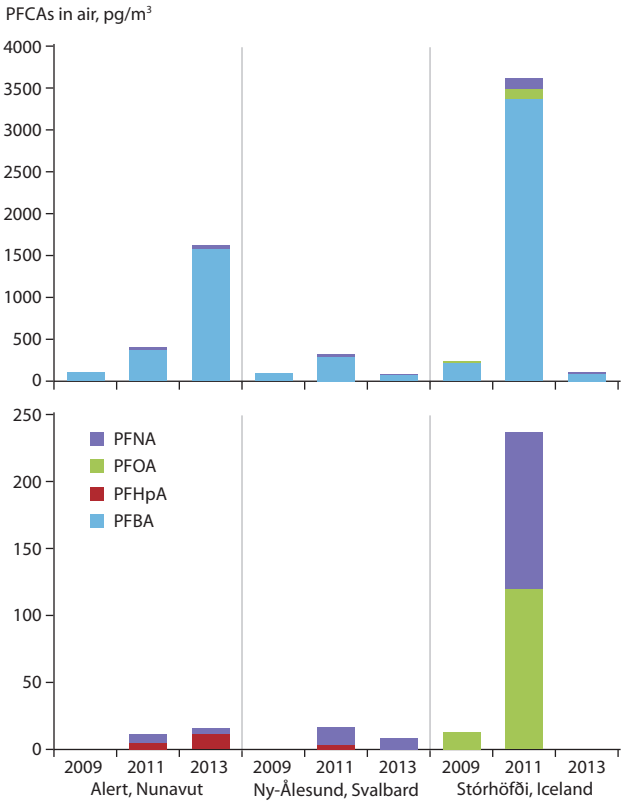

Figure 2.7 Concentrations of PFCAs, including PFBA (upper) and excluding PFBA (lower), measured in the GAPS program in 2009, 2011 and 2013 at three Arctic locations using SIP disks (Rauert and Harner, unpubl. data).

2011b). Among the longer-chain PFCAs, PFNA and PFOA predominated at Stórhöfði and Ny-Ålesund, while PFHpA predominated at Alert (Figure 2.6).

Gawor et al. (2014) reported results for neutral PFASs from XAD-type samplers deployed at a global-scale for one-year intervals during the period 2006–2011. These data include the Arctic sites mentioned above and are reported as ng/sampler to allow for comparable spatial and temporal trends to be assessed. Levels of FOSAs and FOSEs tended to decrease globally during the six years of measurements, whereas an initial decline in the concentrations of FTOHs from 2006 to 2008 did not continue in 2009 to 2011.

Precipitation/snow

The geographical coverage for PFASs in snow or wet precipitation in the Arctic is very limited, with data available for northern Sweden, northern Norway, the Canadian Arctic islands, Svalbard and from ice/snow in the Beaufort Sea. Due to their physical-chemical properties, deposited PFASs accumulate during winter instead of volatilizing back to the atmosphere, and the accumulated PFAS are delivered to the receiving marine systems (from snow on top of sea ice and terrestrial catchment areas) and terrestrial systems (from the snow pack) when the snow/ice melts (AMAP, 2014b; Bertrand et al., 2014).

Kwok et al. (2013) investigated PFAS concentrations in ice cores, surface snow and water samples collected from glaciers and downstream coastal areas of Svalbard. PFBA, PFOA, and PFNA were the predominant compounds found in ice-core samples (Annex Table A2.1/2). Kwok et al. (2013) found an increase in PFAS concentrations in snow and surface water with increasing proximity to Longyearbyen (Svalbard), suggesting the presence of local sources. PFOA was the main PFAS detected in surface snow, while PFBA and perfluoropentanoate (PFPeA) were mainly found in surface water samples from glacial meltwater (Annex Table A2.1/2).

Snow collected in the Lake Hazen (Ellesmere Island) catchment in 2014 had high concentrations of PFBA (1.5 ng/L), PFHpA (1.1 ng/L), PFOA (2.4 ng/L) and PFNA (1.2 ng/L) (St. Louis et al., 2015). Deposition of C_6-C_{12} PFCAs and PFOS in snow has been measured at Station Nord (Greenland) since 2008 (Bossi, unpubl. data) in samples collected three times per year. PFNA and PFOA were the predominant PFASs detected with average concentrations of 0.45 and 0.53 ng/L, respectively (Annex Table A2.1/2).

Veillette et al. (2012) reported 6- to 15-fold lower concentrations of PFHpA, PFOA and PFNA in snow from the Lake A catchment near the northern coast of Ellesmere Island than inland at Lake Hazen. A study of snow collected in 2008 from the Devon Ice Cap in the Canadian Arctic (a follow-up to the original study by Young et al., 2007) also reported concentrations for PFOA (0.07–0.68 ng/L), PFNA (0.03–1.42 ng/L) and PFDA (0.01–0.23 ng/L) which were similar to those at Station Nord (DeSilva and Muir, unpubl. data). Codling et al. (2014) measured PFASs in the snowpack of a boreal forest in northern Sweden (64°N, 19°E). The highest median concentrations ranged from 0.067 to 0.34 ng/L in the order PFBA > PFPeA > PFBS > PFOA. They found evidence of migration to deeper snow layers as melt progressed and a declining proportion of PFBA, the most water-soluble PFAS. They also noted that PFBS and the longer chain C_{10}-C_{12} PFCAs were retained in the melting snow pack. PFBA and PFPeA concentrations in northern Sweden were similar (within a factor of 2) to those found in snow from the Longyearbyen area while C_7-C_{10} PFCA concentrations were more than 5-fold higher at the Swedish site. PFCA concentrations in snow at Station Nord were similar to those found in northern Sweden (Codling et al., 2014) and Svalbard (Longyearbyen; Xie et al., 2015) but lower than for snow from the Lake Hazen (Ellesmere Island) catchment. Overall, the levels of C_4-C_{10} PFCAs in snow in the Canadian Arctic and northern Greenland (Lake Hazen, Devon Ice Cap, Station Nord) appear to be higher than in the European Arctic (Svalbard, northern Sweden).

A study of PFAS compounds in snow in northern Norway (Tromsø area) revealed that ΣPFCAs (C_4–C_{12}) was the major group present with concentrations ranging from 0.294 to 5.206 ng/L. PFHpA dominated the samples with a maximum concentration of 3.866 ng/L. Only two of the PFSAs (PFBS and PFOS) were detected, and levels of PFBS varied from below the limit of detection to 0.178 ng/L. Concentrations of particle-bound PFAS were low and often below the detection limit. Particle-associated PFBA showed levels up to 0.383 ng/L, although the detection frequency was highest in samples near the city of Tromsø (Bertrand et al., unpubl. data). The flux of PFCAs to the snowpack seemed to be related to temperature at the time the snow fell, with higher temperatures linked to larger fluxes. This might be due to greater scavenging of PFCAs from air with wet snow and/or that snowflakes formed a larger surface area during milder conditions, which could facilitate surface-mediated photochemical transformation of PFAS precursors (Bertrand et al., unpubl. data). Hence, snowfall at mild temperatures can lead to a significant contribution of PFAS to the snowpack, where it accumulates through winter to be released to the surrounding environment at snow melt.

Xie et al. (2015) measured neutral PFASs in air and snow collected from Ny-Ålesund (Svalbard) and determined their air-snow exchange fluxes. Concentrations of the ΣFTOHs in air over a one-year period varied from 5.6 to 34 pg/m^3 with a mean of 14 pg/m^3 (Figure 2.8). Among the perfluorosulfonates, MeFBSA, the precursor of PFBS, was the principal component followed by MeFOSA and EtFOSA. In snow, 8:2 FTOH was the predominant species accounting for 45% of ΣFTOHs. Concentrations of ΣFTOHs in snow ranged from 0.218 to 0.507 ng/L (mean: 0.369 ng/L). The composition of PFASs was different in snow compared to air; 10:2 FTOH, MeFOSE and 12:2 FTOH were the three most abundant species in snow. For FTOHs and fluorotelomer acrylateS (FTAs), the total air-snow exchange fluxes were positive indicating exchange back into the atmosphere, whereas fluxes for FOSEs were negative (Xie et al., 2015).

Ice caps

Kwok et al. (2013) reported historical profiles of PFCAs from two ice cores collected on the glacier near Longyearbyen. Consistent patterns were observed in the vertical profiles of PFCAs in both ice cores with PFBA predominating (39%), followed by PFOA (17%) and PFNA (11%). PFCAs were the major PFASs in the ice cores. Fluxes (concentrations in pg/L multiplied by water equivalents in L/m^2 for each

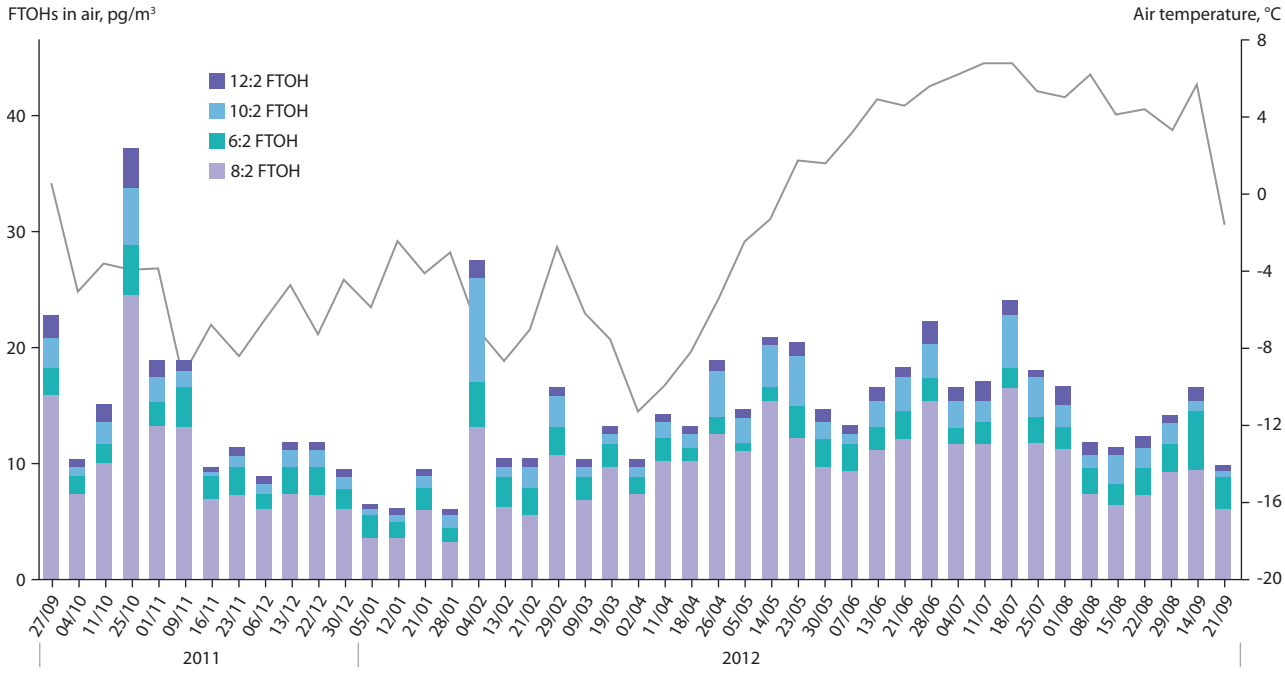

Figure 2.8 FTOHs measured in air at Ny-Ålesund (Svalbard) between September 2011 and September 2012 (Xie et al., 2015). The grey line shows average temperatures during the air sampling.

year) showed maximum PFCA deposition occurred in the late 1990s (Figure 2.9). Young et al. (2007) also observed elevated PFOA and PFNA deposition from the late 1990s in a snow pit from the Devon Ice Cap along with higher deposition in near-surface samples (2005). However, fluxes of PFOA, PFNA, PFDA and perfluoroundecanoate (PFUnDA) found in the Norwegian ice cores (Kwok et al., 2013) were two- to 10-fold lower than in the Canadian Arctic ice cap samples (Young et al., 2007). This result is consistent with higher mean concentrations of PFOA and its volatile precursors (i.e. FTOHs) found in the air masses at Alert and in oceanographic cruise measurements in Nunavut compared to Svalbard (Butt et al., 2010; Hung et al., 2013a).

2.1.6.2 Terrestrial environment

There are currently fewer data available for the terrestrial environment than for the freshwater and marine environments. Müller et al. (2011) detected low levels of PFASs in plants, moss and lichen from locations in the northern Yukon and from western Nunavut near Bathurst Inlet, Canada (Annex Table A2.1/3). Overall, average concentrations of ΣPFCAs in lichen in the two regions were similar. However, the PFAS patterns differed widely between vascular plants and lichen (Figure 2.10). Lowest average ΣPFCA concentrations were found in aquatic sedge (*Carex aquatilis*) and cottongrass (*Eriophorum vaginatum*) in the northern Yukon (0.01–0.02 ng/g ww), while cottongrass in the Bathurst Inlet area had higher

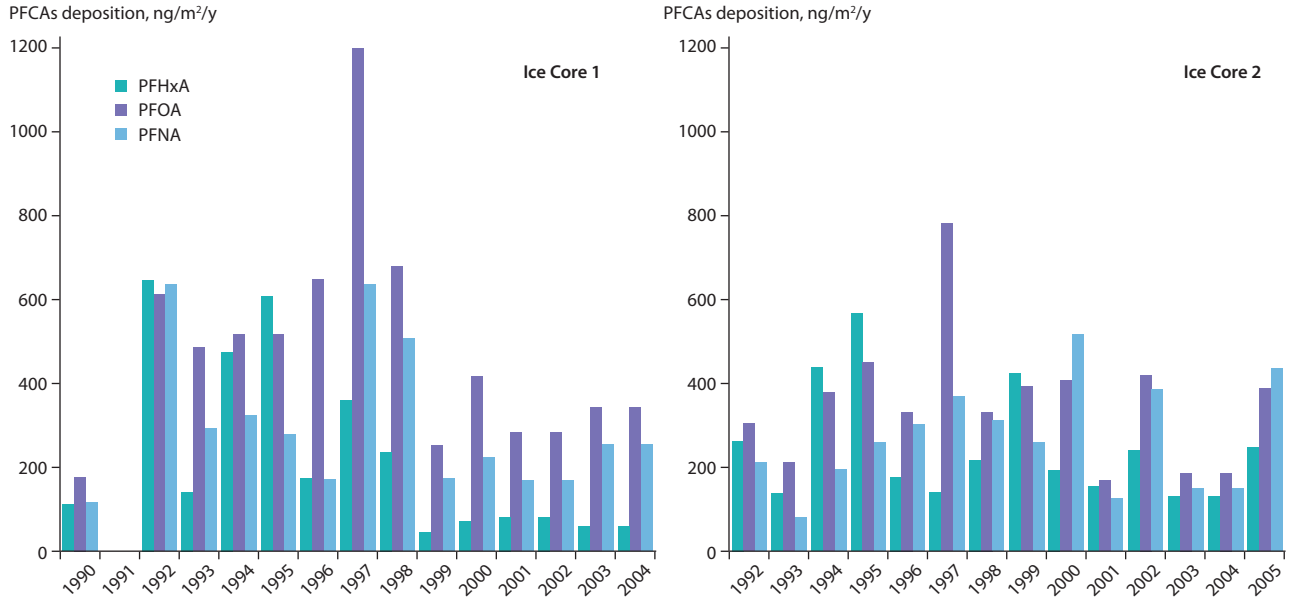

Figure 2.9 Estimated annual fluxes of PFCAs (PFHxA, PFOA, and PFNA) in ice cores from Svalbard, Norway (Kwok et al., 2013). [Note the original graph published by Kwok et al. showed fg/(m² · yr) flux units whereas the correct units are shown here.]

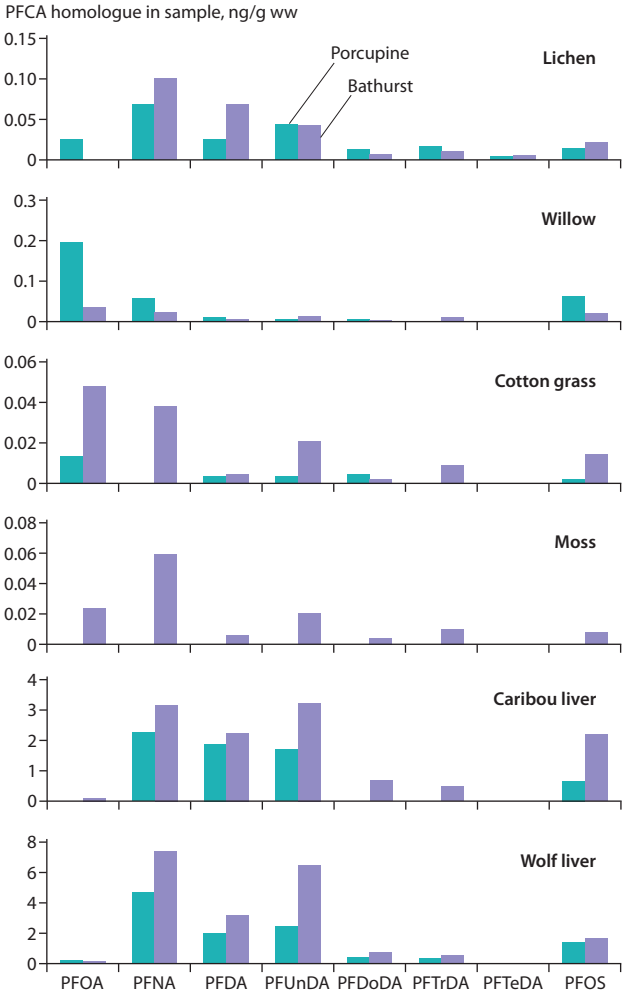

Figure 2.10 PFCA homologue composition of vegetation, caribou and wolf in the Porcupine (Yukon) and Bathurst (Nunavut) caribou summer grazing areas (Müller et al., 2011).

average concentrations (0.12±0.04 ng/g ww). Higher ΣPFCA concentrations were found in lichen (*Cladonia mitis/rangiferina* and *Flavocetraria nivalis/cucullata*) (0.17–0.22 ng/g ww) and Arctic willow (*Salix pulchra*) (0.08–0.26 ng/g ww) and were similar in both areas. The PFCA composition differed among vegetation types. PFOA was the predominant PFCA in all plants (grass, sedge, willow and moss, *Rythidium rugosum*), while both lichen species showed a predominance of odd-carbon-chain lengths (C_8<C_9, C_{10}<C_{11}, C_{12}<C_{13}).

Müller et al. (2011) measured PFASs in liver and muscle of caribou (*Rangifer tarandus*) from the Porcupine herd in the northern Yukon and the Bathurst herd from NWT-western Nunavut as part of a terrestrial food web study. Highest PFAS liver concentrations were found for PFNA (2.2±0.2 and 3.2±0.4 ng/g ww for the Porcupine and Bathurst herds, respectively) followed by PFDA (1.9±0.1 and 2.2±0.2 ng/g ww, respectively) and PFUnDA (1.7±0.1 and 3.2±0.2 ng/g ww, respectively). The Bathurst caribou had relatively high PFOS concentrations (2.2±0.3 ng/g ww) compared to the Porcupine herd. In general, ΣPFCAs and PFOS were about 2-fold higher in the Bathurst herd. This geographical difference may be due to the more remote location of the Porcupine herd relative to PFAS sources although concentrations in lichen were similar (Figure 2.10). Differences in diet may also play a role.

Müller et al. (2011) evaluated the biomagnification of PFAS in vegetation to caribou and wolves (*Canis lupus*). The biomagnification factors were tissue-specific and highest for C_9–C_{11} PFCAs (2.2–2.9) and PFOS (2.3–2.6) although these factors were lower compared to earlier studies of the marine food web (Müller et al., 2011). Not surprisingly, wolf liver contained the highest concentrations of ΣPFAS, followed by caribou liver and ΣPFCAs/PFOS ratios were >10 in vegetation and 5–10 in mammals (Figure 2.10). Muscle and kidney contained 10–20 times lower concentrations (Annex Table A2.1/3).

The distribution pattern of PFAS compounds varied with tissue and trophic level. PFOA predominated in plants (willow, grass) while PFNA and PFDA predominated in lichen and moss. PFNA and PFUnDA predominated in caribou and wolf. The odd-carbon-chain PFCAs predominated in caribou, wolf, grasses and moss.

PFAS concentrations in terrestrial animals are summarized in Annex Table A2.1/3. PFNA predominated in wolf, moose and caribou liver among terrestrial mammals in northern Canada, and in reindeer (*Rangifer tarandus*) from Svalbard (Müller et al., 2011). PFNA was followed by PFOS, PFUnDA, PFDA, perfluorotridecanoate (PFTrDA) and PFHxA as the predominant PFASs, although the pattern varied between these animals.

Concentrations of PFCAs in muscle tissue from Svalbard reindeer were dominated by the long-chained compounds perfluorododecanoate (PFDoDA) and PFTrDA, while PFNA and PFTrDA predominated in liver closely followed by PFOS and PFHxS (Figure 2.11). Long-chain PFCAs were also detectable in reindeer fat. No results for caribou fat or muscle are available from Canada or Greenland. However, comparing data for liver,

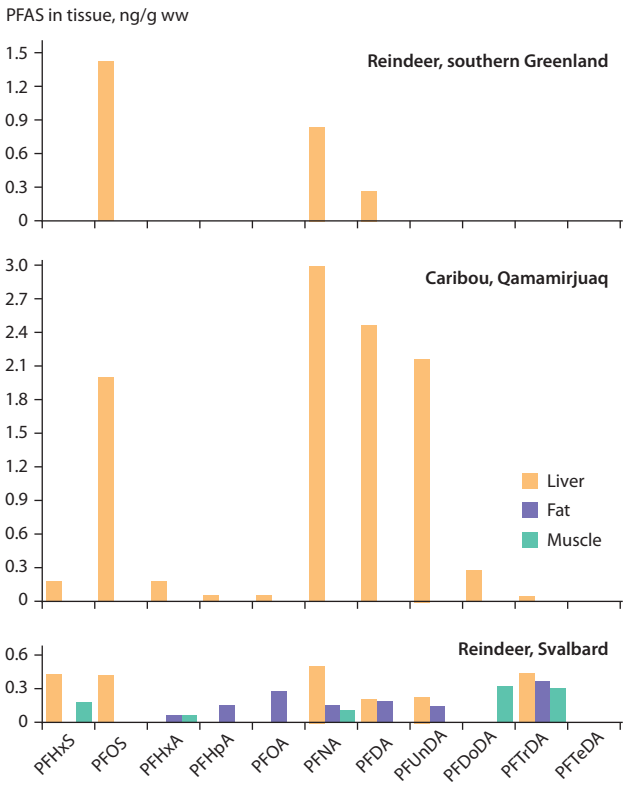

Figure 2.11 Comparison of PFAS profiles in caribou liver from the Qamamirjuaq herd (near Arviat, Canada) (Gamberg and Muir, unpubl. data) and reindeer liver, fat and muscle from Svalbard (Carlsson et al., 2012a). Results from southern Greenland from Bossi et al. (2015).

the Svalbard reindeer differ in having much higher PFTrDA levels (Figure 2.11). PFOS was the PFAS with the highest concentration (1.42 ng/g ww) in reindeer liver from southern Greenland followed by PFNA (0.84 ng/g ww) and PFUnDA (0.45 ng/g ww) (Bossi et al., 2015). A long-term study of reindeer and moose (*Alces alces*) during 1987–2006 from Sweden reported PFOSA, PFOS and PFOA above detection limits in reindeer muscle, but not at concentrations that could be quantified (Danielsson et al., 2008).

Norwegian moose livers showed a slightly different pattern, with PFOS as the predominant compound, followed by PFNA, PFUnDA and PFDA. The PFAS pattern varies with species; liver from wood mice (*Apodemus* sp.) and shrews (Soricidae) from the same area had the highest concentrations of PFTrDA, followed by perfluorotetradecanoate (PFTeDA) and PFUnDA and PFOS (Norwegian Environment Agency, 2013). Liver samples from Arctic fox (*Vulpes lagopus*) from Svalbard had the same PFAS distribution pattern as the Norwegian moose, except that PFTrDA was present at similar levels to PFUnDA (Aas et al., 2014). Concentrations of PFAS in these foxes varied with body condition. Lean foxes had higher wet weight concentrations of ΣPFSA and ΣPFCA in their adipose tissue than fat foxes.

Larter et al. (2017) analyzed PFASs in the liver of moose from the Dehcho Region in the southwestern Northwest Territories. PFASs were the major POPs in moose liver ranking ahead of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs): ΣPFCAs > PFOS > ΣPCBs > ΣPBDEs. Concentrations of PFASs in moose liver ranged from 2.2–4.3 ng/g ww for ΣPFCAs and the C_9–C_{11} PFCAs (PFNA–PFUnDA) predominated.

Bossi et al. (2015) reported PFAS concentrations in liver samples from terrestrial biota (birds and mammals) from Greenland. Samples from ptarmigan (*Lagopus muta*; western Greenland), reindeer (southwestern Greenland) and muskox (*Ovibos moschatus*; eastern Greenland) were analyzed. PFAS concentrations in ptarmigan were mostly below detection limits but PFNA was detected in all samples analyzed (Bossi et al. 2015). The mean PFNA concentration was significantly higher in ptarmigan from Nuuk than from Qeqertarsuaq (ANOVA, $p<0.01$). PFNA, PFDA, PFUnDA and PFDoDA were detected in all samples. Interestingly, ptarmigan had much lower concentrations and different patterns of PFCAs than piscivorus seabirds where long-chain C_9–C_{13} PFCAs predominate in liver. In the three muskox liver samples, PFNA, PFDA and PFUnDA were detected at similar concentrations, ranging from 1.18 to 5.25 ng/g ww. PFDoDA and PFTrDA were found at concentrations between 0.21 and 0.72 ng/g ww, whereas PFTeDA was not detected (Annex Table A2.1/3). Although sample size was limited, muskox had much higher concentrations of PFNA, PFDA, PFUnDA, PFDoDA and PFTrDA than reindeer from the same region of Greenland.

2.1.6.3 Freshwater environment

Lake and river waters

Studies on PFASs in water and sediments from Arctic freshwater environments are very limited. As of 2015, results for water and sediment samples were available for the Canadian Arctic, Faroe Islands, and Norway (Svalbard) and are summarized in Annex Table A2.1/2.

Stock et al. (2007) determined PFASs in water from Amituk, Char, Merretta and Resolute Lakes on Cornwallis Island in Arctic Canada. Further studies were conducted on PFASs in these and other lakes on Cornwallis Island by Lescord et al. (2015). The analyses included C_4–C_6 PFCAs as well as the first report of a new perfluorinated alkyl sulfonate (perfluoro-4-ethylcyclohexane sulfonate) (PFECHS) in the Arctic (Annex Table A2.1/3). Concentrations of all PFAS congeners in the remote lakes on Cornwallis Island were very similar, with mean concentrations of PFOA of 0.20–0.27 ng/L. PFAS ratios of PFOA:PFNA and PFDA:PFUnDA in Amituk and Char Lakes were generally consistent with ratios observed in Arctic glacial ice caps by Young et al. (2007) and in precipitation from rural and remote sites in North America (Scott et al., 2006) suggestive of a common atmospheric source.

The study by Lescord et al. (2015) compared PFAS concentrations in Resolute and Meretta Lakes, which Stock et al. (2007) had shown to be contaminated with high levels of PFOS, with other lakes near Resolute Bay. Other, non-PFOS-related PFASs were identified in Resolute and Meretta Lakes including PFECHS and fluorotelomer sulfonates (FTS) (4:2-, 6:2-, and 8:2 FTS). Stock et al. (2007) concluded that the pattern of contamination observed in water samples from Resolute and Meretta Lakes, with extremely high levels of PFHxS and PFOS, in addition to PFHpA and PFOA, relative to background sites (e.g. Char Lake) was consistent with the use of aqueous fire-fighting foams; these have been detected following spills at airports (Moody et al., 2002) and in groundwater at military bases in Canada (Scott et al., 2007) and the United States (Moody and Field, 2000; Schultz et al., 2004). The 4:2 and 8:2 FTSs may also be associated with fire-fighting foams, while PFECHS is used as an abrasion inhibitor for hydraulic fuels in aircraft and thus also associated with airport emissions.

PFBA was the most prominent PFAS in water from Lake Hazen, a large lake on Ellesmere Island, as well as in snow from the lake surface and nearby catchment (St. Louis and Muir, 2014; St. Louis et al., 2015). The depth profile for total PFCAs in Lake Hazen (Figure 2.12) showed a sharp increase in the near surface waters during snow melt indicative of inflow of snow melt water having much higher concentrations than deeper waters.

Lowest PFAS concentrations in Arctic lakes were found in Lake A, on northern Ellesmere Island (Veillette et al., 2012)

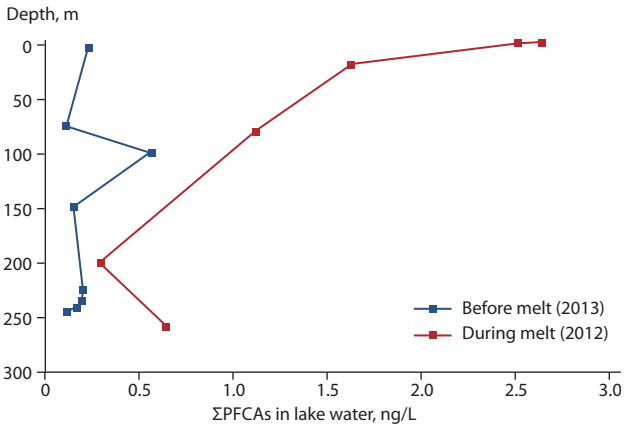

Figure 2.12 Depth profile for total (C_4–C_{12}) PFCAs in Lake Hazen (Ellesmere Island, Nunavut) showing elevated concentrations during snow and ice melt (St. Louis and Muir, 2014).

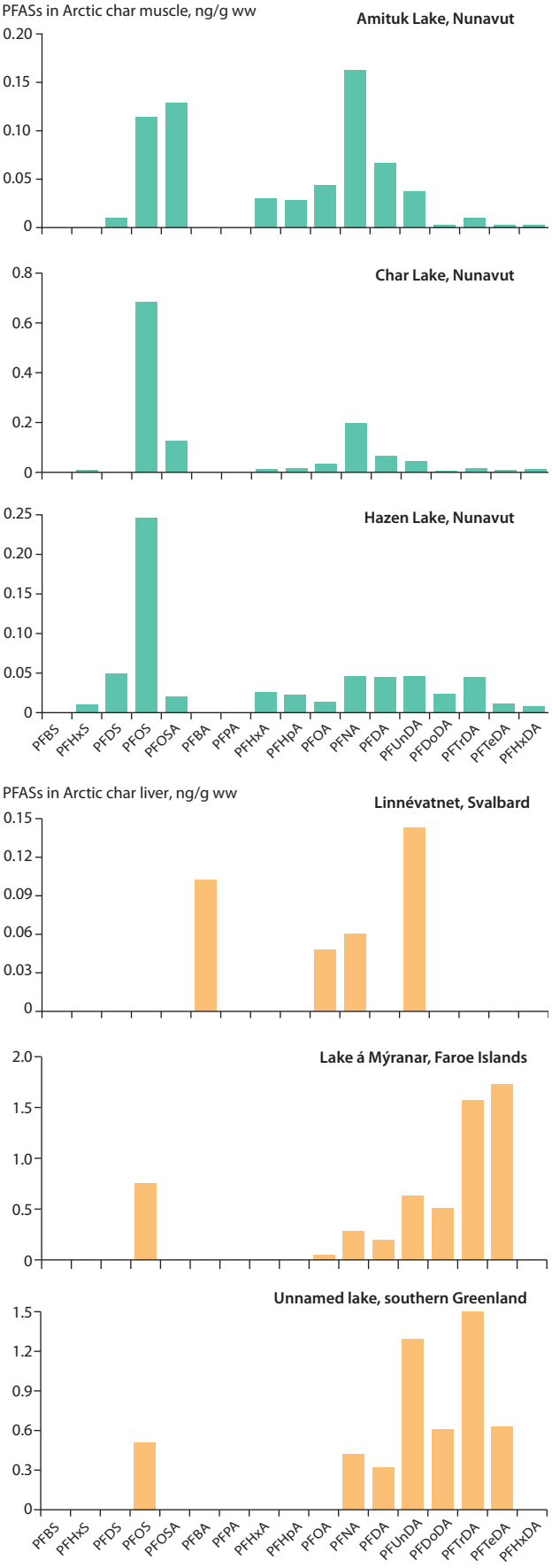

Figure 2.13 Comparison of PFAS concentrations and profiles in landlocked Arctic char from the Canadian Arctic, Svalbard, Faroe Islands and southern Greenland. Results from Canada are for muscle while liver was analyzed at the other sites. All data are for the period 2010–2013 (Annex Table A2.1/4). Data from Garsjø (2014), Bossi et al. (2015) and Muir et al. (unpubl. data).

and in Pingualuk, an isolated crater lake in northern Quebec (Gantner et al., 2012). However, PFAS concentrations in Lake A catchment snow were similar to spring-summer concentrations in accumulated snow from the Devon Ice Cap (8° in latitude south of Lake A) sampled in spring 2006 (Young et al., 2007). Thus, the supply of PFAS from snow melt is likely to be relatively similar at Lake A as it is on lakes on Cornwallis Island (Amituk, Char). Both Lake A and Pingualuk were sampled prior to the snowmelt freshet which would deliver snow-bound PFAS as shown in Figure 2.12.

Four lakes on the Faroe Islands used for drinking water supply had low C_4–C_{10} PFCA concentrations (Eriksson et al., 2013), broadly similar to those in remote lakes on Cornwallis Island (Annex Table A2.1/2).

Kwok et al. (2013) reported a wide range of PFCAs in river water at Longyearbyen. PFBA and PFPeA were predominant in the surface water samples. Approximately 2–3 times higher average PFAS concentrations were detected in both surface snow and water samples collected from the locations downstream of the glacier near Longyearbyen compared to glacial water. Because the river flows near the town of Longyearbyen there may be an influence of local sources in addition to long-range atmospheric transport. St. Louis and Muir (2014) reported PFCAs in water from the Abbe River, which drains a glaciated region near Lake Hazen (Ellesmere Island). PFBA and PFOA were the prominent PFCAs (Annex Table A2.1/2).

Freshwater fish

A large number of measurements have been made on PFASs in freshwater fish, particularly in the Canadian Arctic and Norway, and recently in Greenland and the Faroe Islands (Muir et al., 2013b; Norwegian Environment Agency, 2013; Bossi et al., 2015; Lescord et al., 2015). Detailed results for PFCAs are provided in Annex Table A2.1/4. The long-chained (C_9–C_{12}) PFCAs predominate in freshwater fish, however the pattern differs in the European Arctic compared with Greenland and Canada.

Muscle from Arctic char (*Salvelinus alpinus*) collected in 2010 and 2013 from Lake Linnévatnet, a remote lake near Barentsburg and Longyearbyen on Svalbard showed a different pattern of PFASs compared to other locations. PFBA and PFUnDA were the most prominent congeners detected in more than 50% of samples (Figure 2.13). PFOA was present in lower concentrations than expected; 0.05 ng/g ww in muscle from Arctic char collected in 2010 and 0.02–0.04 ng/g ww in 2013. However, PFOA was only detected in 20–25% of Arctic char muscle samples. Three years earlier (in 2010), PFUnDA was the most was prominent PFAS in char samples from the same lake, together with 6:2 FTS and PFNA. There is insufficient information about local PFAS sources on Svalbard to explain the different PFAS patterns compared to the Norwegian mainland. Longer-chain (C_9–C_{14}) PFCAs predominated in Arctic char from Greenland and the Faroe Islands (Figure 2.13).

Concentrations of PFOS, PFDoDA and PFTrDA were similar in char from Lake á Mýranar (Faroe Islands) and the unnamed lake in southern Greenland, whereas concentrations of PFNA, PFDA and PFUnDA were higher in Greenland. In contrast, landlocked char from the Canadian Arctic had overall lower concentrations of all PFASs than in the Faroe Islands or Greenland and much lower proportions of C_{12}–C_{14} PFCAs.

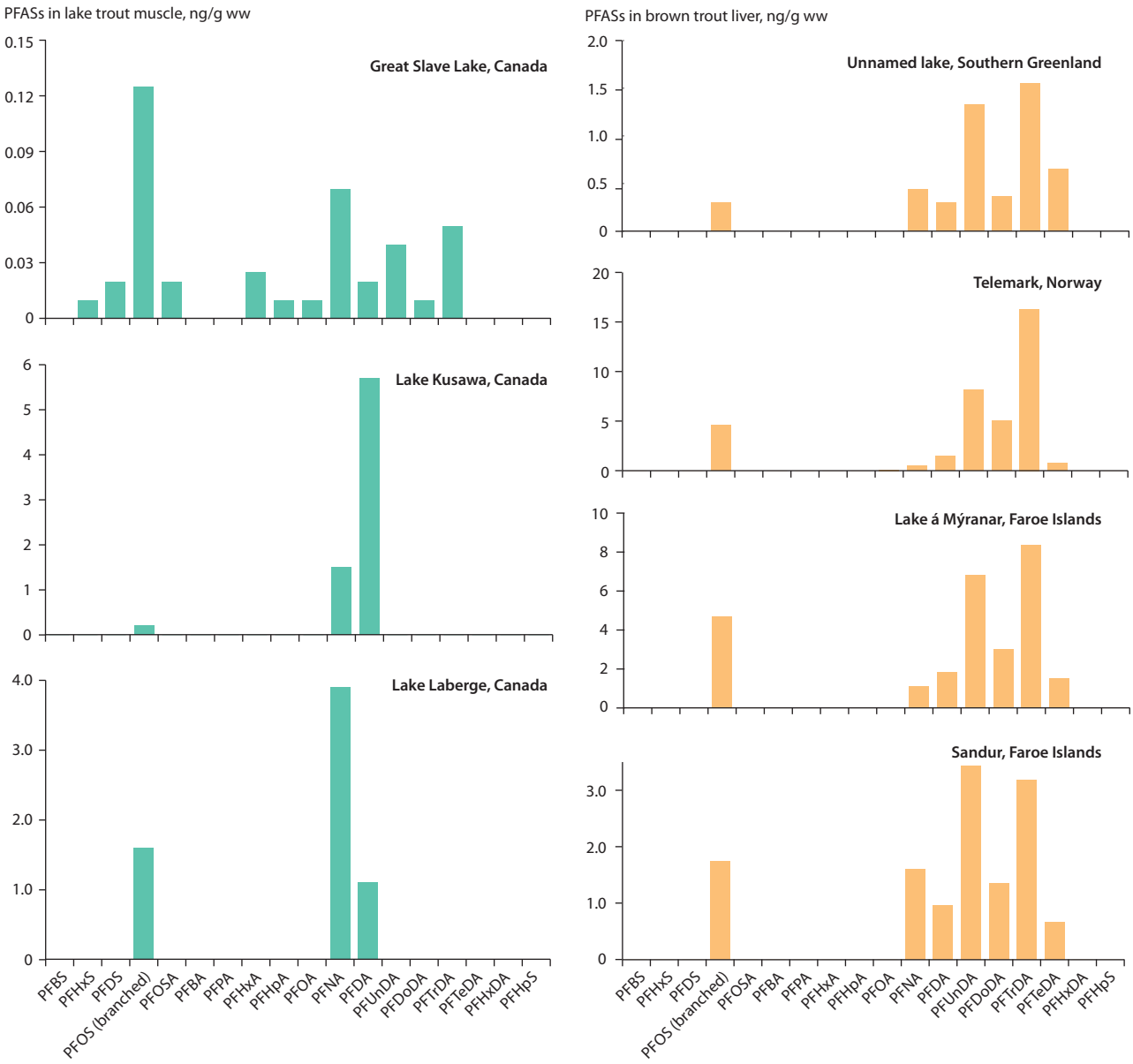

Figure 2.14 Comparison of PFAS concentrations and profiles in brown trout (liver) from northern Norway, the Faroe Islands and southern Greenland, as well as lake trout (muscle) from Great Slave Lake, Kusawa Lake, and Lake Laberge in Canada. Results are from Muir et al. (2013b), Norwegian Environment Agency (2013), Stern et al. (2014b), Bossi et al. (2015) and Evans and Muir (unpubl. data).

Low levels of PFASs in lake trout (*Salvelinus namaycush*) have been reported from Great Slave Lake (Muir et al., 2013b; Evans and Muir, 2015, unpubl. data), Lake Laberge and Kusawa Lake in Canada (Muir et al., 2013b; Stern et al., 2014b) and in brown trout (*Salmo trutta*) from the Faroe Islands and southern Greenland (Bossi et al., 2015) and Telemark, Norway (Norwegian Environment Agency, 2013). PFCAs predominated in all trout samples (Figure 2.14), similar to the pattern found in landlocked char. The pattern differs between the European Arctic and Canada, with C_9–C_{14} PFCAs predominating in Norway, the Faroe Islands and southern Greenland samples (Figure 2.14). The C_{13} and C_{14} PFCAs were not detected (<0.01 ng/g ww) in lake trout from northern Canada. The pattern in brown trout from Telemark was: PFTrDA < PFUnDA < PFDoDA (and PFOS). However, none of these PFCAs were above the detection limits in the water or sediment, and PFTrDA was only detected in 30% of brown trout samples (Norwegian Environment Agency, 2013). For those samples in which it was detected, the levels of PFTrDA were higher (mean: 16.3 ng/g ww) than for other PFCAs, which varied from 5.07 ng/g ww (PFDoDA) to 0.09 ng/g ww (PFOA). Mean ΣPFCA was 32 ng/g ww, which is slightly higher than ΣPFCA reported in liver (mean 5.9–21.0 ng/g ww) from burbot (*Lota lota*) in the Northwest Territories, Fort Good Hope, Canada (Muir et al., 2013b).

PFCAs were also prominent components of total PFASs in burbot liver from Fort Good Hope (Stern et al., 2012) and Great Slave Lake (Muir et al., 2013b; Evans and Muir, unpubl. data). PFNA was the predominant PFCA (2.0 ng/g in burbot from both locations). However, burbot liver from Great Slave Lake differed from lake trout muscle by having detectable long-chain (C_{13}-C_{16}) PFCAs with mean concentrations of 0.05–0.25 ng/g ww (Annex Table A2.1/4).

PFASs were determined in sea-run char muscle from Cambridge Bay, Pond Inlet and Nain in Arctic Canada (Evans and Muir,

unpubl. data). PFOS was detectable in all samples along with PFOA, PFNA, PFDA, PFUnDA, PFDoDA, and PFTrDA (Annex Table A2.1/4). PFOS and ΣPFCA concentrations were very low, averaging 0.04±0.014 and 0.12±0.03 ng/g ww, respectively, at Cambridge Bay and 0.07±0.06 and 0.12±0.15 ng/g ww, respectively, at Pond Inlet. The range in PFAS concentration in sea-run char was 2- to 3-fold lower than in landlocked Arctic char in Lake Hazen and Amituk Lake, which are remote lakes (Annex Table A2.1/4).

2.1.6.4 Marine environment

Seawater

PFASs are globally distributed in the marine environment (Yamashita et al., 2005). The movement of PFASs, from coastal areas influenced by urban emissions, to subarctic and Arctic Ocean waters, was illustrated by Ahrens et al. (2010), who found C_6–C_{10} PFCAs averaging about 700 pg/L in coastal seawater of southern Norway and at detection limits (~10 pg/L) in the open Norwegian Sea. Overall, ocean currents and related dilution effects have a crucial influence on PFAS distribution in seawater, in which industrial and coastal areas and atmospheric deposition are considered as sources of PFASs, and ocean waters are important as sinks and for transportation of these compounds (Ahrens et al., 2010).

Other reports for PFCAs and PFBS in the Arctic Ocean and adjacent waters show higher levels than reported by Ahrens and co-workers with the sum of C_6–C_{10} PFCAs (the PFASs that have been determined in all studies) averaging 80–245 pg/L for the eight studies available as of January 2016 (Annex Table A2.1/5). Benskin et al. (2012a,b) found that PFHxA, PFHpA and PFOA were the major PFASs in seawater in the Canadian Arctic Archipelago and Beaufort/Chukchi Sea waters. However, those studies did not include PFBA and PFPeA. More recent measurements of PFCAs show that PFBA and PFPeA are the major PFAS in seawater at Barrow Strait in the central Canadian Arctic Archipelago (Muir et al., 2015c) and in Chukchi Sea waters (Cai et al., 2012a) with concentrations 2- to 3-fold higher than for PFOA. Kwok et al. (2013) also found PFBA to be the predominant PFAS in Adventfjorden/Isfjorden, Svalbard. However, PFBA was not reported in two seawater studies that sampled the Greenland Sea and Greenland coastal waters (Busch et al., 2010; Zhao et al., 2012) (Figure 2.15). The short-chain sulfonate, PFBS is also widely detected (Ahrens et al., 2010; Cai et al., 2012a; Kwok et al., 2013). In Adventfjorden/Isfjorden, PFPeA was 5-fold higher than PFOA (Kwok et al., 2013), however, this sampling site may have been influenced by the nearby town of Longyearbyen. Analysis of PFBA in water is challenging due to matrix effects, possibly from early eluting natural organic acids (Van Leeuwen et al., 2009).

PFAS concentrations were generally higher in Greenland coastal waters than in open ocean measurements in the northern North Atlantic analyzed in the same studies (Busch et al., 2010; Zhao et al., 2012). This may reflect the influence of freshwater inputs to these nearshore waters, as well as to sampling during the period of ice melt. In the case of the southern Beaufort Sea and Canadian Arctic Archipelago, there are major inflows from the Mackenzie, Coppermine and Back Rivers which peak in June and July (Barrie et al., 1998; Murray et al., 1998). Thus, geographical trends, if any, are obscured by the influence of seasonality. All ship-based sampling has been conducted in open waters or with limited ice cover.

Bertrand et al. (2013, 2014) showed that PFAS concentrations are higher in ice than in the underlying seawater in samples from the Canadian and European Arctic (Figure 2.16). In the southeastern Beaufort Sea ΣPFCAs (C_5–C_{12}) were similar in snow

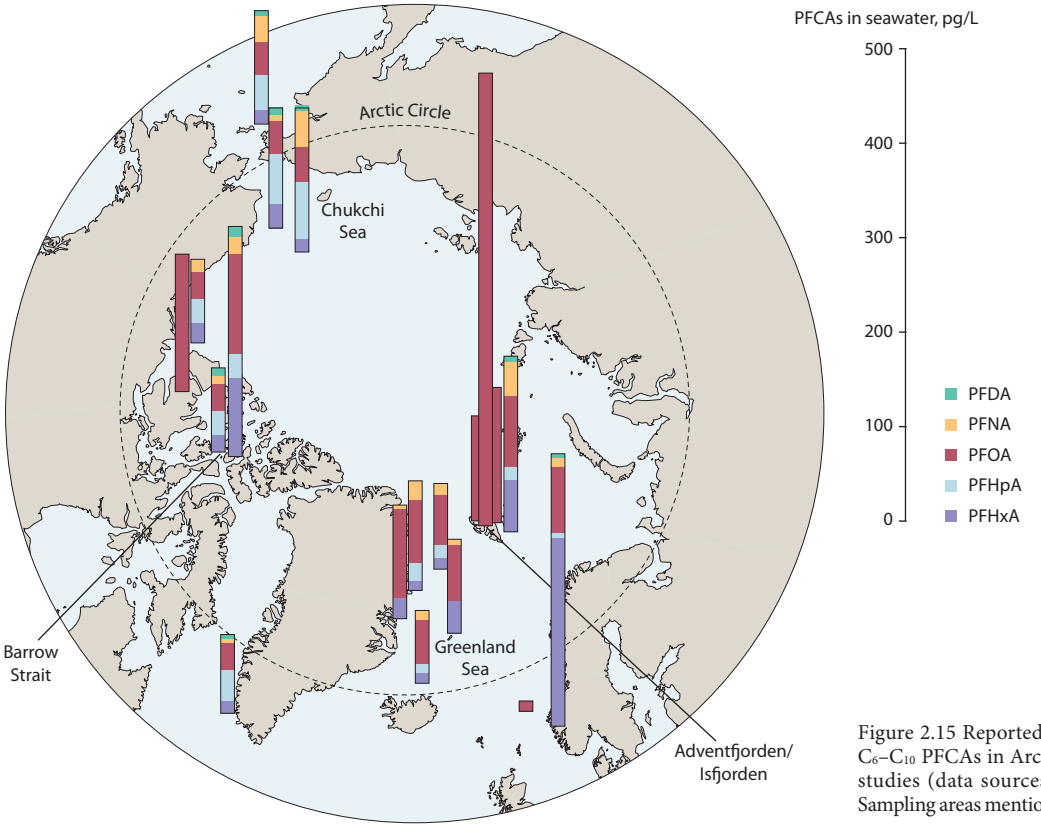

Figure 2.15 Reported average concentrations of C_6–C_{10} PFCAs in Arctic seawater based on eight studies (data sources in Annex Table A2.1/5). Sampling areas mentioned in the text are identified.

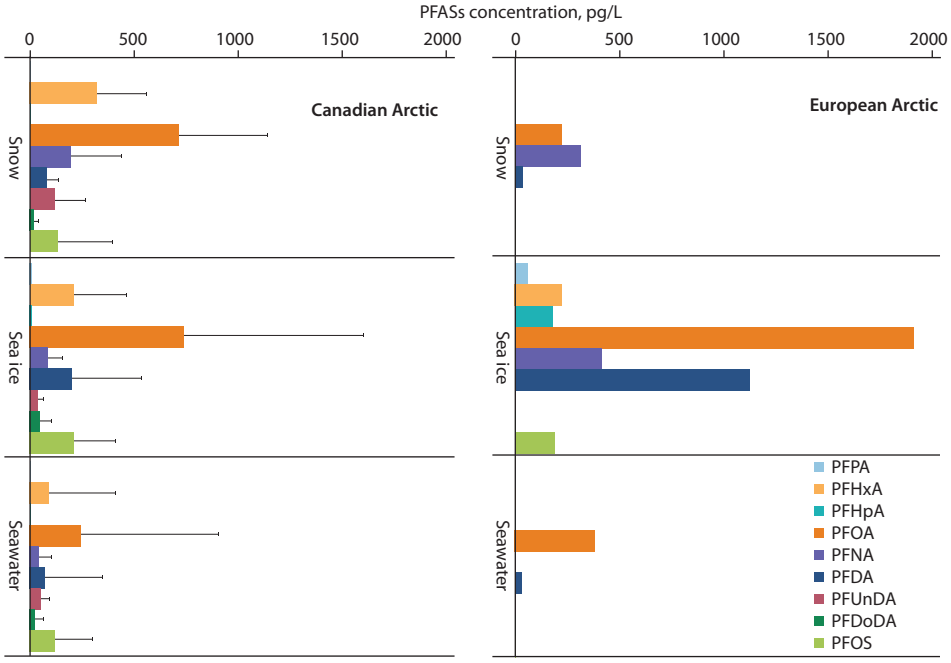

Figure 2.16 Enrichment of perfluoroalkyl carboxylates (C_5–C_{12}) (PFPeA= perfluoropentanoate, PFHxA = perfluorohexanoate etc) and perfluorooctane sulfonate (PFOS) in snow/first-year ice of the Canadian Arctic and snow/multi-year ice of the European Arctic relative to underlying seawater. Data from Bertrand et al. (2014).

and ice but about 4-fold higher than in water. In the Barents Sea near Svalbard, PFOA and other PFCAs were 5- to 10-fold higher in ice than seawater (Figure 2.16). Thus, ice is a source of PFASs to surface waters during spring-summer in polar regions while sealing off surface waters from precipitation inputs during winter.

Ongoing measurements of PFOA and other PFASs in the Canadian Arctic Archipelago have shown that concentrations are often elevated in surface seawaters during ice melt each year (Muir et al., 2015c). This is illustrated in Figure 2.17 for depth profiles of PFCAs (sum of C_6–C_{10}) in waters from Barrow Strait near Resolute collected in May–June 2007, 2008 and 2010.

Benskin et al. (2012a) measured PFOA isomers in seawater from the Canadian Arctic Archipelago and Beaufort/Chukchi Seas. They found a distinct spatial trend whereby PFOA in seawater originating from the Atlantic was predominantly historic (up to 99% ECF), whereas water in the Archipelago along the ship transect from Barrow Strait to the Bering/Chukchi Seas (Figure 2.15) had a significant telomer PFOA contribution indicating that it was predominantly of contemporary origin (Figure 2.18). The percentage ECF was also significantly

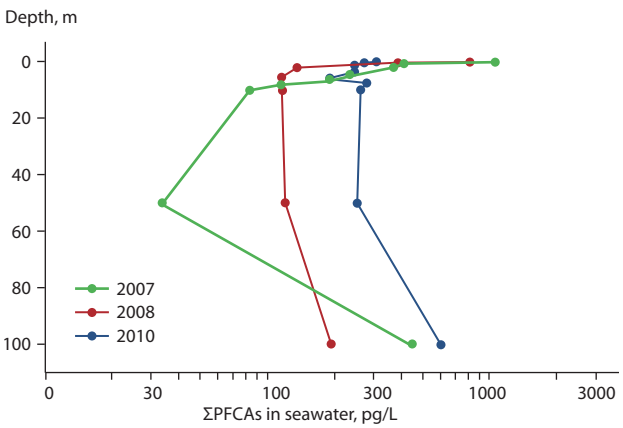

Figure 2.17 ΣPFCAs (sum of C_6–C_{10}-perfluorocarboxylates) in seawater from Barrow Strait (Resolute, Nunavut). Sample collection was conducted from the ice during late May to early June each year (Muir et al., 2015c).

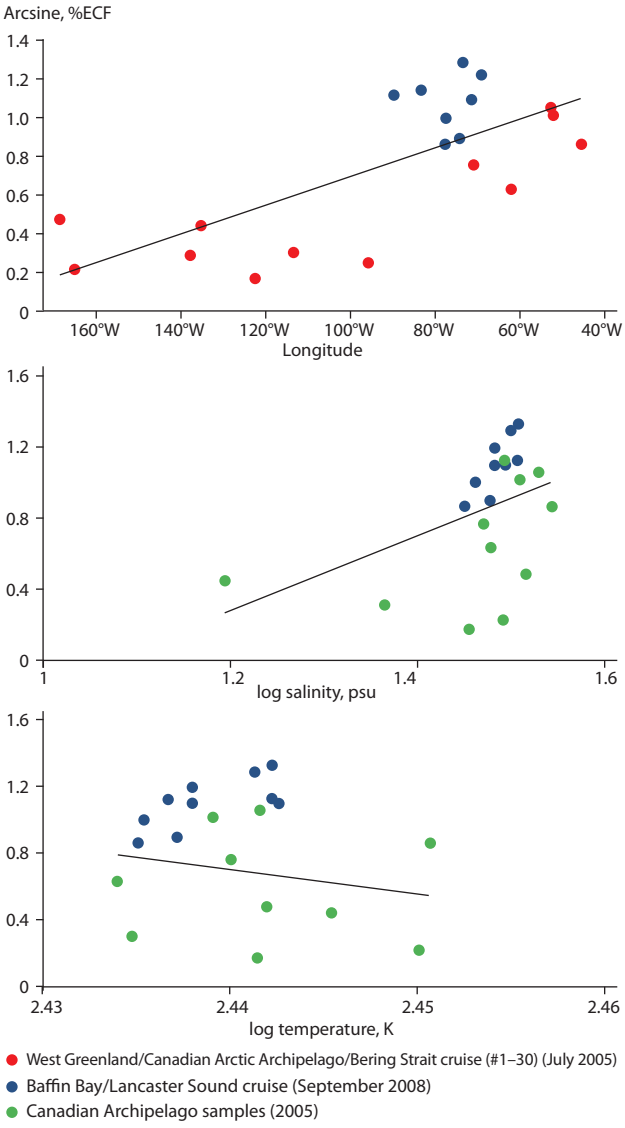

Figure 2.18 Spatial trends in PFOA isomers in seawater from the Canadian Arctic Archipelago and Beaufort/Chukchi Seas. Redrawn from Benskin et al. (2012a).

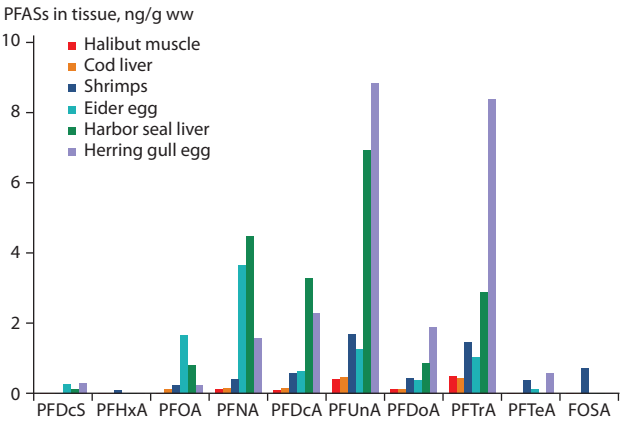

Figure 2.19 Concentrations of PFAS (not including PFOS) in halibut muscle, shrimp, cod liver, eider and herring gull eggs, and harbour seal liver from northern Norway (Norwegian Environment Agency, 2013; Carlsson et al. 2016).

correlated with salinity (r=0.58, p<0.01; Figure 2.18) but not with seawater temperature (Figure 2.18). This suggests that water collected in the Archipelago is more influenced by riverine discharges, which would presumably contain PFOA derived from an atmospheric source (i.e. FTOH). Summer salinity gradients in the Arctic Ocean show a major influence of freshwater inputs in the southern Beaufort Sea and in the southern Archipelago waters (Murray et al., 1998) which supports this hypothesis.

Total extractable organofluorine (EOF) measurements have been made in non-Arctic seawater, which indicates that the PFASs so far identified represent only a small proportion of the EOF (10–40%) (Miyake et al., 2007). The majority of the EOF has not been identified, which suggests the presence of other PFASs in addition to the known PFASs. No EOF measurements appear to have been conducted on Arctic seawaters.

Marine invertebrates

Invertebrates, including copepods and ice amphipods, were included in food web studies conducted in the mid-2000s and reviewed by Butt et al. (2010). There are few recent studies of PFASs in marine invertebrates and plankton. Recent studies of shrimp from northern Norway revealed that they contained higher PFAS levels than found in cod liver or in halibut (*Hippoglossus hippoglossus*) muscle samples from northern Norway (Figure 2.19).

Marine fish

There are few recent studies on PFASs in Arctic marine fish species. Earlier work on marine fish was based mainly on food web studies and was reviewed by Butt et al. (2010). PFAS concentrations were below detection limits in fish from West Greenland, Iceland and the Faroe Islands (Jörundsdóttir et al., 2012; Eriksson et al., 2013; Carlsson et al., 2016). Studies from the Barents Sea (polar cod, *Boreogadus saida*), Beaufort Sea (polar cod) and the Norwegian west coast (halibut) have shown low levels of PFASs in fish (Haukås et al., 2007; Powley et al., 2008; Carlsson et al., 2016). PFOA was not detected in these studies. The levels of PFNA and PFHxA in the Barents Sea samples were 0.19 and 2.06 ng/g ww, respectively (Haukås et al., 2007).

Braune et al. (2014a) determined C_6–C_{15}-PFCAs and PFBS, and PFHxS in forage fish from Coats Island (northern Hudson Bay, Nunavut). PFUnDA and PFTrDA were the most prominent PFCAs, with concentrations (whole fish) of <0.1–0.68 ng/g ww. Arctic cod had the highest concentrations of ΣC_6–C_{15}-PFCAs (1.45, range: 1.0–2.1 ng/g ww) followed by sculpins (1.40, range: 1.0–1.7 ng/g ww) (Annex Table A2.1/6).

Median concentrations of long-chain PFCAs (C_9–C_{13}) in halibut muscle from the Norwegian west coast were 0.07–0.49 ng/g ww, with PFTrDA and PFUnDA present at the highest levels (Figure 2.19). The short-chain PFCAs and PFSAs were below detection limits (Carlsson et al., 2016). Atlantic cod liver from Lofoten (Norway) and Svalbard showed comparable levels of all PFASs analyzed, except for PFOS (0.59 and 0.28 ng/g ww, respectively) and PFTrDA (0.40 and 0.18 ng/g ww, respectively) (Norwegian Environment Agency, 2013). These levels were comparable to PFASs in halibut muscle from northern Norway. PFTrDA concentrations in halibut muscle (0.49 ng/g ww) and cod liver from Lofoten were similar, but PFOS was higher in the halibut than the Lofoten cod; 0.95 and 0.59 ng/g ww, respectively (Norwegian Environment Agency, 2013; Carlsson et al., 2016).

Seals

Early studies on spatial and temporal trends of PFASs in Arctic marine mammals were reviewed by Butt et al. (2010) and temporal trends of PFOS in marine biota have been included in the recent AMAP temporal trend assessment (AMAP, 2014a). This sub-section focuses on more recent reports for PFCAs and on newly detected PFASs. Rigét et al. (2013) reported that in ringed seal (*Pusa hispida*) liver samples collected up until 2010, PFOS was still by far the most predominant compound constituting 92% (West Greenland seals) and 88% (East Greenland seals) of total PFASs. However PFCAs constituted an increasing proportion of total PFASs in ringed seals from Greenland and in the Canadian Arctic.

ΣPFCA concentrations in liver from harbor seal (*Phoca vitulina*) liver from northern Norway were 15 ng/g ww (Norwegian Environment Agency, 2013). The longer, odd-chain PFASs predominated (PFUnDA, PFNA and PFTrDA), which is the commonly observed trend among biological samples in the European Arctic. Other than the investigation by the Norwegian Environment Agency, there are no recent data available for PFASs in seals in the Norwegian part of the Arctic. Data on new PFASs and less reported PFCAs in ringed seals have been reported by Rotander et al. (2012c), Muir et al. (2014) and Gebbink et al. (2016) and are summarized in Figure 2.20 and in Annex Table A2.1/6. Rotander et al. (2012c) reported a suite of PFCAs in liver of ringed seals from northwest Greenland and hooded seals (*Cystophora cristata*) from the Greenland Sea (west ice). They found relatively high levels of PFTriDA especially in hooded seals (21 ng/g ww). Gebbink et al. (2016) found (C_{14})-PFTeDA and (C_{15})-PFPeCA in ringed seal liver from East Greenland and Muir et al. (2015c) detected the C_{16}-PFCA in seal liver (Figure 2.20).

Gebbink et al. (2016) reported the first detection of F53B (also known as 6:2-Cl-PFAES, a chlorinated polyfluorinated ether sulfonic acid) in Arctic biota. This compound has previously been reported in rivers in China (~40 ng/L) and sewage sludge (~2 ng/g) at comparable concentrations to PFOS (Wang et al.,

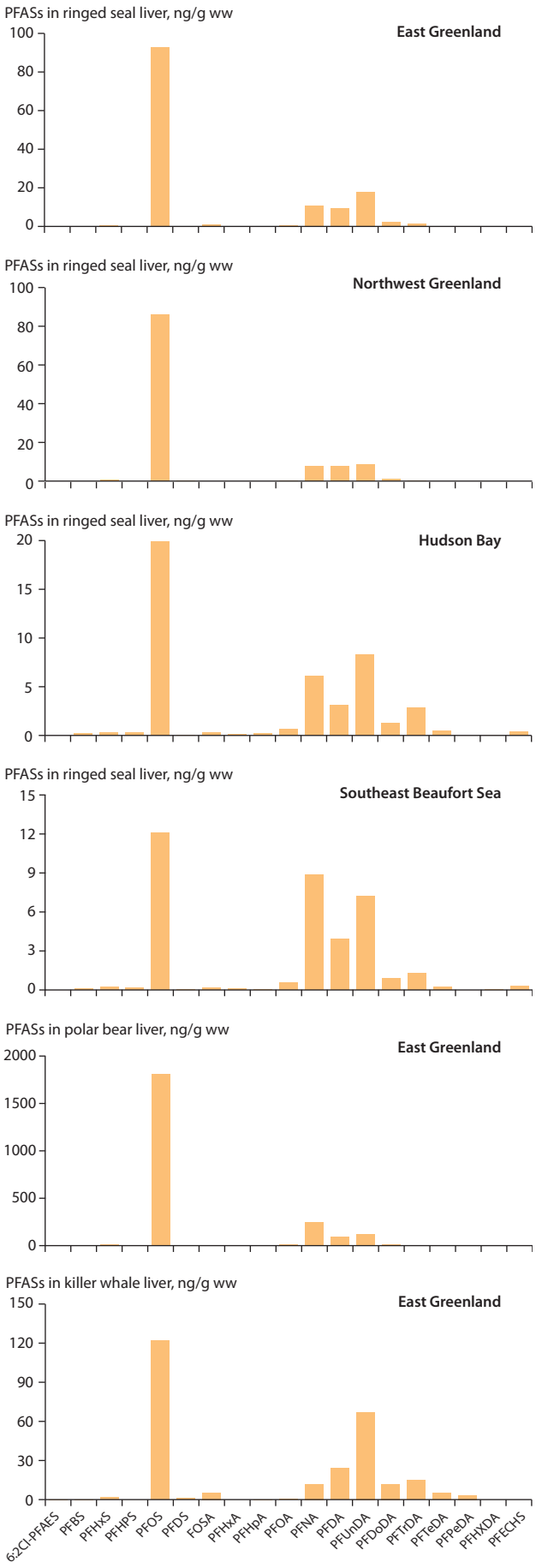

Figure 2.20 Concentrations and patterns of a large suite of PFASs in ringed seal liver from northern Canada and ringed seal, polar bear and killer whale from Greenland. Based on data from Muir et al. (2015c) and Gebbink et al. (2016).

2013a; Ruan et al., 2015). 6:2-Cl-PFAES was detected in ringed seal liver from East Greenland at 0.045±0.004 ng/g ww (Figure 2.20). Muir et al. (unpubl. data) reported the detection of PFECHS, the cyclic analog of PFOS, in ringed seal liver from the Canadian Arctic. This perfluoro-compound was previously reported in lake water and landlocked char (*Salvelinus alpinus*) from Cornwallis Island (Lescord et al., 2015). In seal liver, PFECHS was present at similar concentrations as for PFHxS and PFTeDA.

Gebbink et al. (2016) analyzed seal liver samples for polyfluoroalkyl phosphate esters (mono- and diPAPs) but did not detect them (<0.5 ng/g ww).

Whales

Few new data were available on new or less studied PFASs in whales from the Norwegian or Canadian Arctic beyond what was reviewed by Butt et al. (2010) and reported in the Canadian Arctic POPs assessment (Muir et al., 2013b). Reiner et al. (2011) determined PFASs in liver of beluga (*Delphinapterus leucas*) from Cook Inlet (southeast Alaska) and the eastern Chukchi Sea. The C_9–C_{12}-PFCAs along with PFOS and PFOSA were major PFASs; PFOA, PFHpA, and PFHxA were detected infrequently (<2% of samples). Total C_9–C_{14}-PFCAs were nearly 3-fold higher in Cook Inlet beluga (70.4±46.1 ng/g ww; 2001–2006) than in eastern Chukchi Sea animals (24.0±22.5 ng/g; 1999-2000). Total PFCAs in Cook Inlet beluga were higher than reported for Hudson Bay beluga (Kelly et al., 2009) (Annex Table A2.1/6) mainly due to higher proportions of PFUnDA, PFDoDA, PFTrDA and PFTeDA.

Rotander et al. (2012c) reported concentrations of a suite of PFCAs in liver of whales from the northern North Atlantic, including the Faroe Islands, west Iceland and Greenland, based on samples collected in the mid-2000s as well as older archived samples. PFUnDA was the most prominent PFCA with concentrations ranging from 0.4 ng/g (fin whales, *Balaenoptera physalus*) to 52 ng/g (white-sided dolphin, *Lagenorhynchus acutus*) (Annex Table A2.1/6). Gebbink et al. (2016) reported a suite of PFASs in liver of killer whales (*Orcinus orca*) collected off East Greenland (Figure 2.20); the first report for PFASs in this species. Long-chain (C_9–C_{15})-PFCAs were prominent contaminants in killer whale liver ranging from 3.4 ng/g (PFPeDA) to 67 ng/g (PFUnDA). Gebbink et al. (2016) also detected 6:2-Cl-PFAES in killer whale liver. Levels of PFAES (0.023 ng/g) were about 10-fold lower than in polar bear (*Ursus maritimus*) liver and relatively low compared to PFOA or PFOS.

Polar bears

The information available about new or emerging PFASs in polar bears is scarce for the Norwegian Arctic (Svalbard), but is increasing for bears from sub-populations in East Greenland (Figure 2.20) and in southern and western Hudson Bay in Canada. One recent study investigated levels of PFASs in plasma from Svalbard polar bears. PFOS was the predominant PFAS (205 ng/mL plasma), followed by the longer odd-chained PFCAs; PFNA and PFUnDA at 37.6 and 25.5 ng/mL, respectively (Norwegian Environment Agency, 2013). The same distribution pattern was observed in a polar bear mother-cub pair study with samples from Svalbard in 1998 and 2008 (Bytingsvik et al., 2012). Mean levels of PFOS were 432 and 309 ng/mL plasma in the polar

bear mothers from 1998 and 2008, respectively, while PFNA was present at 28 and 38 ng/mL plasma in 1998 and 2008 (Annex Table A2.1/6). Most of the PFCAs increased over the same period. Maternal transfer is an important exposure pathway for the cubs, although it is less important than for the lipophilic, legacy POPs (Bytingsvik et al., 2012).

In East Greenland polar bears, PFSA and PFCA concentrations were reported to be highest in liver followed by blood > brain > muscle ≈ adipose (Greaves et al., 2012). Also, liver and blood samples contained proportionally more of the shorter/medium-chain (C_6–C_{11}) PFCAs, whereas fat and brain samples were dominated by longer-chain (C_{13}–C_{15}) PFCAs. In different brain region samples for the same bears, PFOS and the longer-chain PFCAs (C_{10}–C_{15}) were found to be significantly and positively correlated with lipid content for all brain regions (Greaves et al., 2013).

C_9–C_{11} PFCAs were prominent, with PFNA dominating, in polar bear liver samples collected in 2014 from the southern and western Hudson Bay sub-populations. This is similar to the pattern found in East Greenland bears. In addition to PFOS, PFHxS and several 'Pre-FOS' precursors (ultimate precursors to PFOS) were quantifiable, for example, N-EtFOSA and PFOSA at low levels (Letcher et al., unpubl. data).

Low ng/g concentrations of C_4 perfluorobutane sulfonamide (FBSA) were reported for the first time in polar bear liver (Letcher et al., unpubl. data). This was the first detection of FBSA, a precursor of PFBS, in an Arctic biota sample. No corresponding PFBS was detectable in any polar bear liver sample. It has been shown that Canadian ringed seal and Icelandic polar bear, but not Canadian beluga, can rapidly dealkylate N-EtFOSA to PFOSA *in vitro* in liver microsomes from these Arctic species (Letcher et al., 2014) and the same pathway probably applies to FBSA.

Gebbink et al. (2016) reported the first detection of F53B (aka 6:2-Cl-PFAES, a chlorinated polyfluorinated ether sulfonic acid) in polar bear liver. Concentrations (0.27 ng/g) were about 6-fold higher than in seal liver but relatively low compared to PFOA or PFOS.

PFBA was measurable at low ng/g levels at almost 100% frequency in all western and southern Hudson Bay bear livers (Letcher et al., unpubl. data). However PFBA was not detected in plasma of Svalbard bears (Bytingsvik et al., 2012). The cyclic analog of PFOS, PFECHS was quantifiable in all Hudson Bay bear liver samples (low ng/g levels). Detection is consistent with its detection in ringed seals from the same region (Muir et al., unpubl. data).

Seabirds

Butt et al. (2010) previously reviewed spatial and temporal trends of PFSAs in seabirds and therefore only reports published after 2009 are considered here. More recent work has involved analyses of seabird liver or eggs from Norway, the Faroe Islands, and Greenland, as well as Nunavut, and is summarized in Annex Table A2.1/6. However, comparing locations is difficult because different species have been sampled. The data are summarized here with an emphasis on the PFCA pattern in liver (Figure 2.21).

Miljeteig et al. (2009) determined PFASs in ivory gull (*Pagophila eburnea*) eggs from four colonies in the Norwegian (Svalbard) and Russian Arctic islands (Franz Josef Land and Severnaya

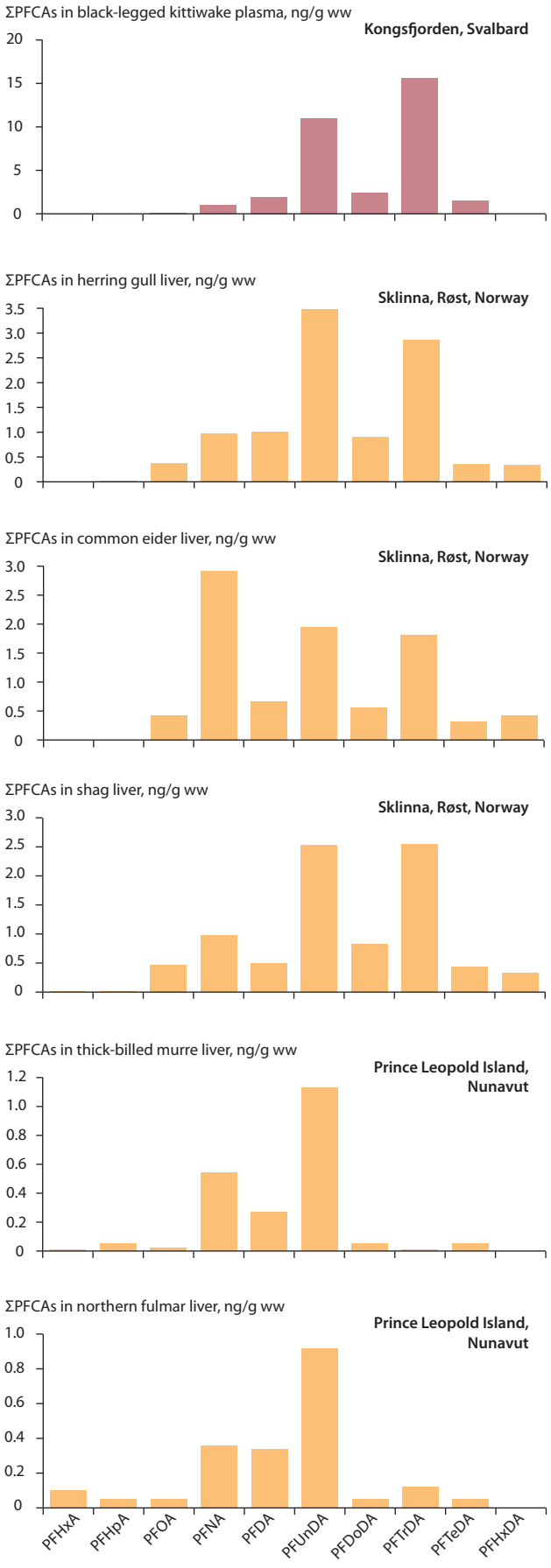

Figure 2.21 Concentrations and patterns of C_6–C_{16}-PFCAs in plasma of black-legged kittiwake (Kongsfjorden, Svalbard) and in liver of common eider (Sklinna, Røst, Norway), herring gull and shag (Sklinna, Røst, Norway), thick-billed murre and northern fulmar (Prince Leopold Island, Lancaster Sound, Nunavut). Results from Norway are from Tartu et al. (2014) and Huber et al. (2015), and for Nunavut from Braune et al. (2014b).

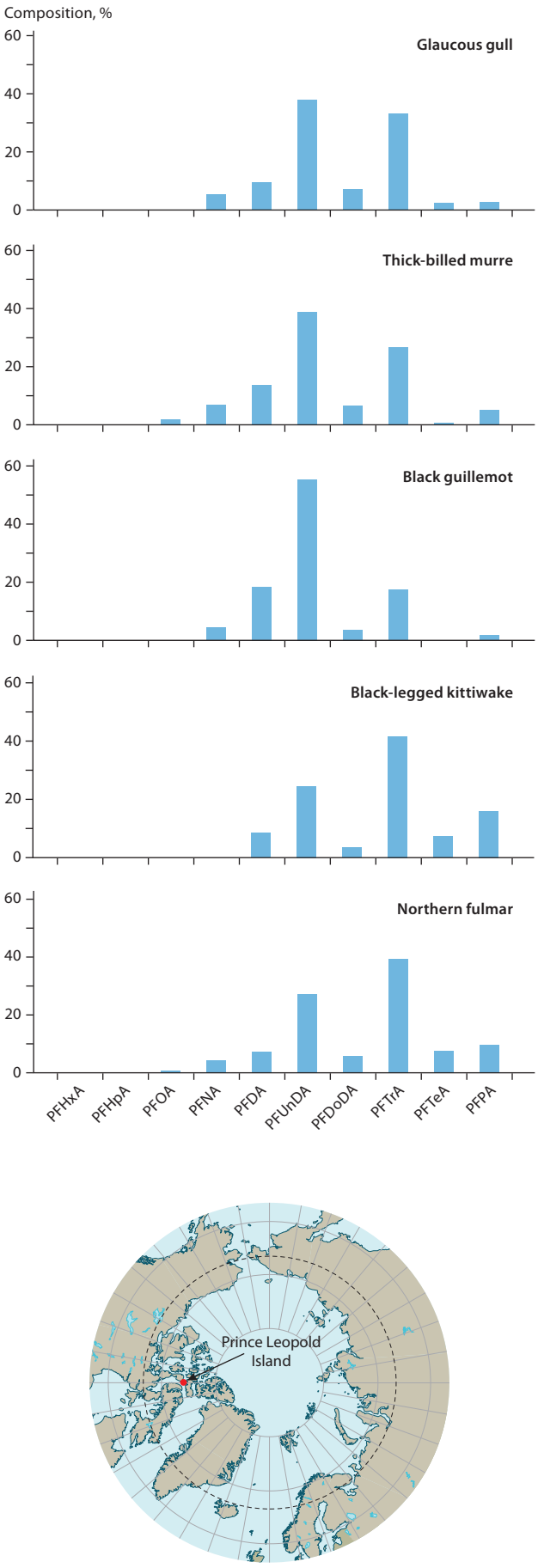

Figure 2.22 Mean contributions of C_6–C_{15}-PFCAs to ΣPFCA in eggs of five seabird species sampled from Prince Leopold Island, Nunavut, 2008 (Braune and Letcher, 2013).

Zemlya). C_{11}–C_{13}-PFCAs predominated at all locations and the range in concentration was similar among colonies (Annex Table A2.1/6). Lucia et al. (2015) analyzed PFOA and PFNA in ivory gull eggs from Station Nord (Greenland) and found that concentrations were significantly higher compared to results from Miljeteig et al. (2009) implying higher exposure further west. However no data for PFASs in ivory gulls are available from the Canadian Arctic or Alaska for comparison.

Nøst et al. (2012) determined PFASs in plasma of black-legged kittiwake (*Rissa tridactyla*) and northern fulmar (*Fulmarus glacialis*) chicks from Kongsfjorden (Svalbard). Median concentrations of total (C_8–C_{14})-PFCAs were 3-fold higher in fulmar than kittiwakes. Tartu et al. (2014) reported on C_4–C_{14}-PFCAs in plasma of adult chick-rearing kittiwakes from the same population on Svalbard. The pattern of PFCAs was similar to that in livers of other seabirds (Figure 2.21) with PFUnDA and PFTrDA predominating.

Braune et al. (2014b) determined PFASs in liver of adult thick-billed murres (*Uria lomvia*) and northern fulmars from several locations in the eastern Canadian Arctic during 2007–2008. ΣPFCA varied significantly among the five murre colonies with the highest concentrations found at Coats Island in Hudson Strait. Patterns varied among colonies and, at some colonies, between sexes, most notably for murres at Akpatok Island. The PFAS patterns and concentrations noted between murres could be at least partially because Pacific waters influence Lancaster Sound while Atlantic waters and freshwater sources influence Hudson Bay. While no results for liver of murres or fulmars are available for the European Arctic there are nevertheless distinct differences when comparing the proportions of PFCAs in common eider (*Somateria mollissima*), shag (*Phalacrocorax aristotelis*), kittiwakes, and herring gull (*Larus argentatus*) from Norway. C_{12}–C_{14} PFCAs are more prominent in the Norwegian species (Figure 2.21).

Braune and Letcher (2013) examined the profile of C_6–C_{15}-PFCAs in eggs of five species of seabird from the Canadian Arctic, collected in 2008. PFUnDA was the predominant congener in glaucous gull (*Larus hyperboreus*), thick-billed murre, and black guillemot (*Cepphus grylle*), while PFTrDA predominated in black-legged kittiwake and northern fulmar (Figure 2.22). Although long-chain PFCAs predominated in eggs, the C_9–C_{11} PFCAs predominated in liver of adult murres and fulmars from Prince Leopold Island (Lancaster Sound) (Braune et al., 2014b). This may be due to preferential accumulation of long-chain PFCAs in egg yolk as demonstrated in herring gull eggs (Gebbink and Letcher, 2012).

Braune and Letcher (2013) also detected PFBS in the murre and fulmar eggs. This was the first detection in these species of PFBS, which is a degradation product of perfluorobutane sulfonyl products, which have replaced PFOS-related chemicals. However, it was detected only in samples from 2010 and 2011 and at low levels ranging from means of 0.04 ng/g (murres) to 0.57 ng/g (fulmars). By comparison, mean PFOS concentrations for 2011 ranged from 19.8 ng/g (fulmars) to 23.8 ng/g (murres).

Tartu et al. (2014) did not detect PFBS or short-chain (C_4–C_6) PFCAs in plasma of chick-feeding black kittiwakes from Svalbard. However the pattern of PFCAs in the kittiwakes from Svalbard was very similar to that for kittiwake eggs from Prince Leopold Island, Nunavut.

2.1.7 Environmental trends

2.1.7.1 Spatial trends

Information on spatial trends is included in Section 2.1.6.

2.1.7.2 Temporal trends

Long-term temporal trend data sets are available for C_8–C_{12}-PFCAs in selected Arctic freshwater and marine biota and for PFOA and FTOH precursors, as well as for MeFOSE and EtFOSE in atmospheric samples. Butt et al. (2010) reviewed temporal trends of PFASs for studies published to 2009. The Canadian Arctic Contaminants Assessment Report on POPs reported temporal trends of PFASs to 2011 in freshwater fish, seabirds and marine mammals (Muir et al., 2013b). This section includes a review of recently published and unpublished trend data with a focus on results for PFCAs reported since 2009. Additional information on temporal trends is available in Section 2.1.6.

Air

The recent AMAP overview of temporal trends in POPs (AMAP, 2014a) included trends for MeFOSE and EtFOSE at Alert (Canada). Both compounds showed non-changing and declining trends, respectively in air (gas + particles) samples collected from August 2006 to 2012. In contrast, 8:2 FTOH and 10:2 FTOH showed increasing tendencies in air at Alert with doubling times of 2.3 to 3.3 years over this period. PFOA did not show any significant decline at Zeppelin (Svalbard) and no consistent seasonality was observed (AMAP, 2014a). Gawor et al. (2014) reported results for neutral PFASs from XAD-type samplers deployed on a global-scale for one-year intervals during the period 2006–2011. Levels of FOSAs and FOSEs tended to decrease globally during the six years of measurements, whereas an initial decline in the concentrations of FTOHs from 2006 to 2008 did not continue in 2009 to 2011.

Freshwater fish

The Canadian Arctic Contaminants Assessment Report on POPs reported temporal trends of PFCAs to 2011 in Arctic char, lake trout and burbot (Muir et al., 2013b). Updated results from that report are provided here. C_7–C_{14} PFCAs appear to be declining in landlocked Arctic char from Lake Hazen, Char Lake and Amituk Lake (Canada), from their peak in the period 2006–2009 (Figure 2.23). The mean annual declines between 2009 and 2013

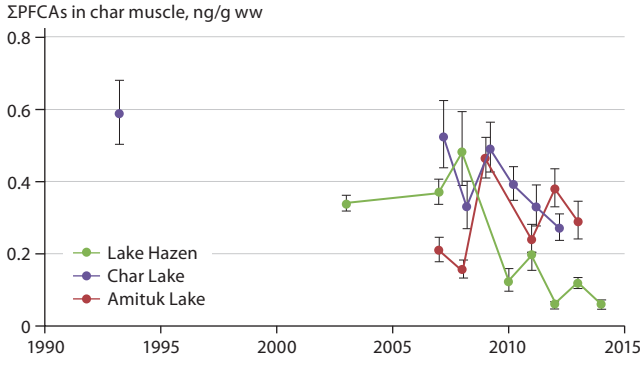

Figure 2.23 Trends of C_7-C_{14} perfluorocarboxylates (ΣPFCAs) in landlocked char muscle from Lake Hazen, Char Lake and Amituk Lake in the Canadian Arctic (Muir, unpubl. data).

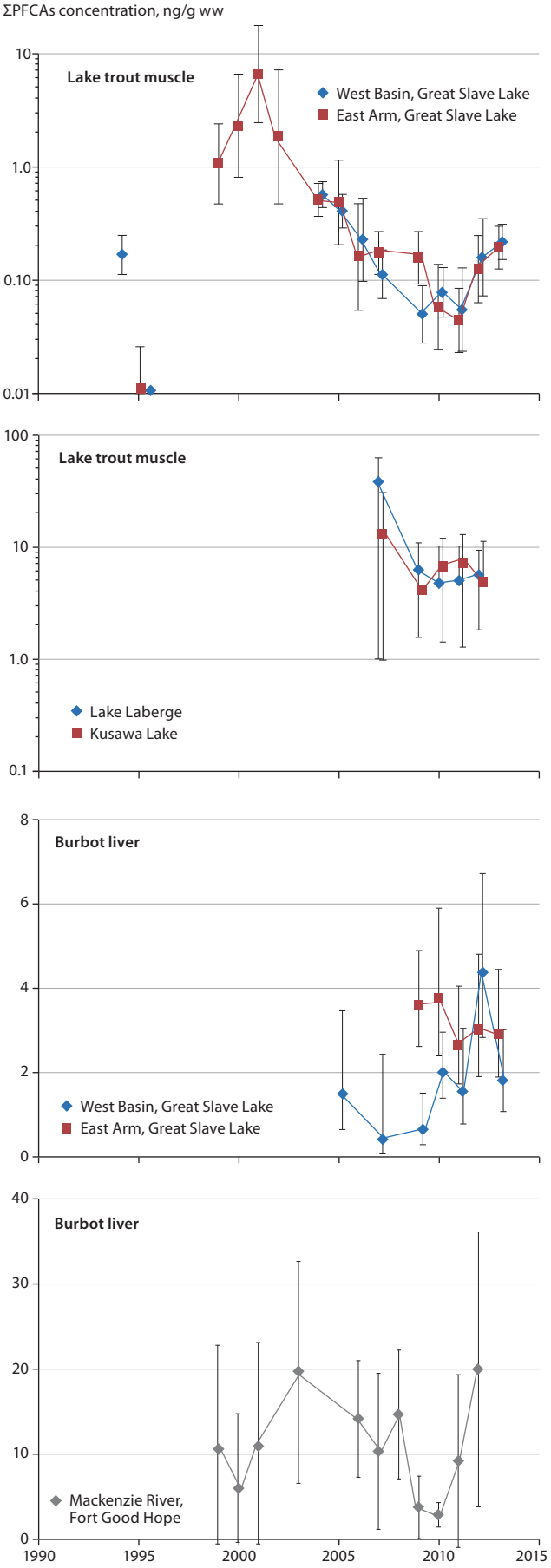

Figure 2.24 Trends in C_7-C_{14} perfluorocarboxylate concentration in lake trout muscle and burbot liver from Great Slave Lake (Muir et al., 2013b; Evans and Muir, unpubl. data), lake trout muscle from Lake Laberge and Kusawa Lake (Stern et al., 2014b), and burbot liver from Fort Good Hope, Mackenzie River (Stern et al., 2014a).

are quite rapid ranging from 8.8% for Lake Amituk to 26% for Lake Hazen using the AMAP PIA program (Bignert, 2007).

Declining trends for C_7–C_{14} PFCAs were also observed in lake trout from Great Slave Lake (Northwest Territories) over the period 2000–2011 (Muir et al., 2013b; Evans and Muir, unpubl. data) (Figure 2.24). These represented declines of about 40% per year from the early 2000s to 2010. Between 2011 and 2013 concentrations levelled off or increased slightly. In lake trout from Lake Laberge and Kusawa Lake (Yukon) total C_9–C_{11}-PFCA concentrations declined over the period 2007–2012 at very similar rates in both lakes.

Trends for PFCAs in burbot liver were distinctly different from those for lake trout (Figure 2.24) possibly reflecting differences in contamination of the benthic versus pelagic food webs. Rising C_7–C_{14}-PFCA concentrations were observed in the West Basin of Great Slave Lake over the period 2007–2012, while concentrations remained the same in burbot from the East Arm. At Fort Good Hope, C_9–C_{11}-PFCA concentrations declined in burbot from 2003 but increased between 2010 and 2013.

Seawater

Time series measurements are lacking for PFASs in seawater although annual measurements at fixed locations such as Barrow Strait (Nunavut, Canada) have begun (Muir et al., 2015c). Additional studies are necessary to investigate seasonality and long-term changes.

Seals

Rigét et al. (2013) found declining trends in PFOA, PFNA, PFDA and PFUnDA in ringed seals from Qeqertarsuaq (West Greenland) over the period 2008–2010 after a steady increase. The decline was particularly striking for PFOA with a clearing half-life of about one year. While PFOA in seal liver also declined (half-life ~ 2 years) at Ittoqqortoormiit (East Greenland), PFNA, PFDA and PFUnDA continued to increase (Figure 2.25).

In the Canadian Arctic, declining trends for total (C_7–C_{14})-PFCAs were observed in ringed seals from four locations in the

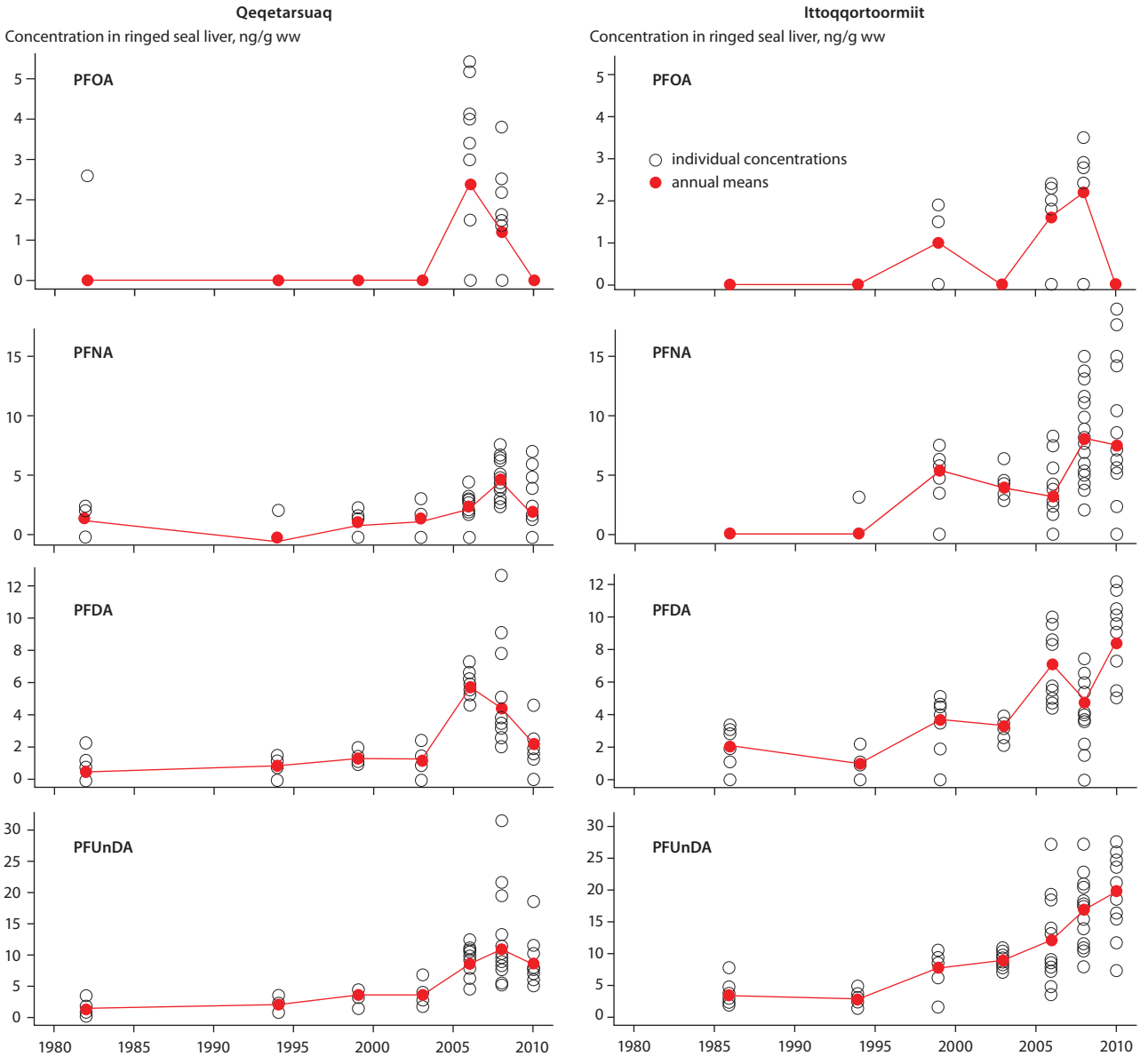

Figure 2.25 Temporal trends in PFOA, PFNA, PFDA, PFUnDA (ng/g ww) in liver tissue of ringed seals from Qeqertarsuaq (West Greenland) and Ittoqqortoormiit (East Greenland). Results reproduced from Rigét et al. (2013).

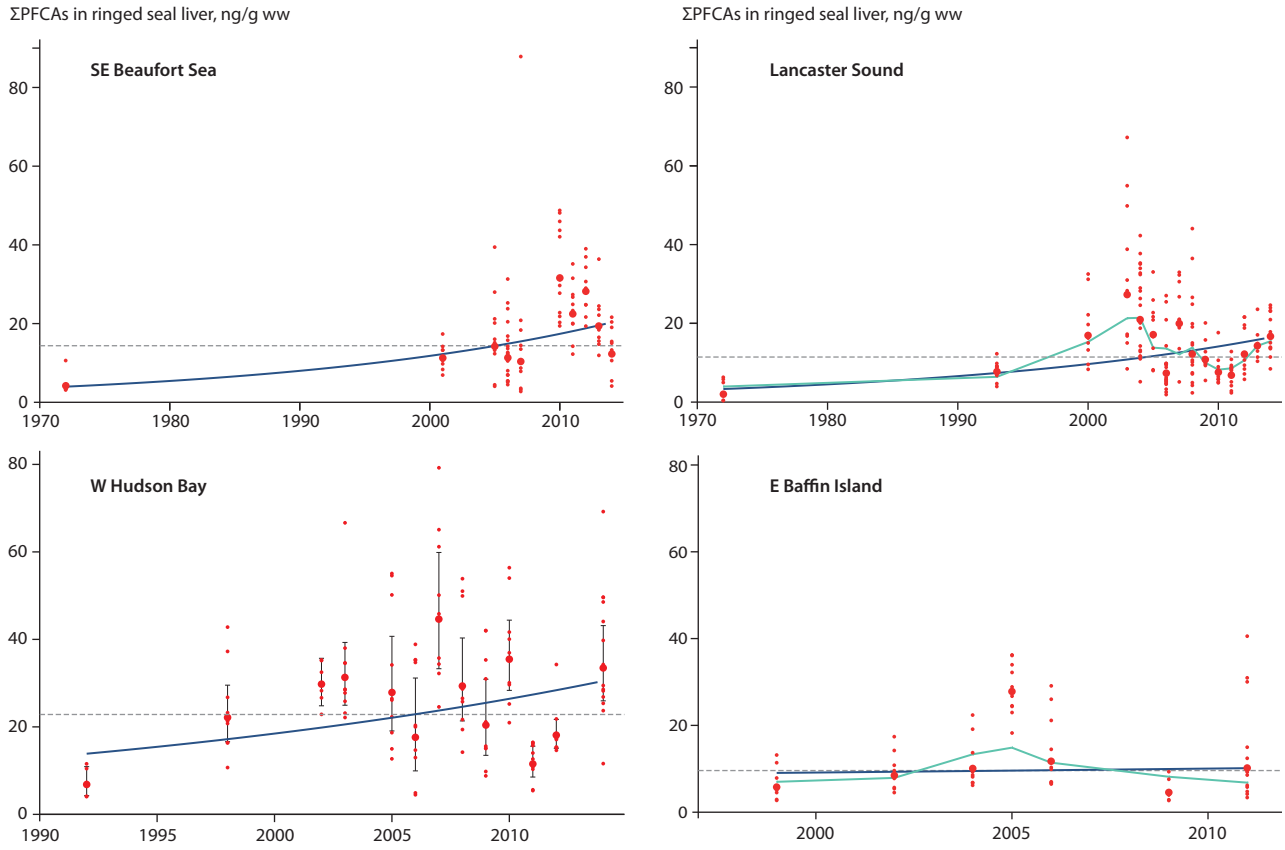

Figure 2.26 Temporal trends of total PFCAs (sum C_7–C_{14}-PFCAs) in ringed seal liver from four locations (SE Beaufort Sea= Sachs Harbour and Ulukhaktok; Lancaster Sound=Resolute, Grise Fiord and Arctic Bay; W. Hudson Bay = Arviat; E Baffin Is = Pangnirtung, Pond Inlet and Qikiqtarjuaq) in the Canadian Arctic (Muir et al., 2014). Blue lines represent trend; green lines represent 2-year moving average; larger red symbols and vertical lines are annual means and standard deviations.

period 2005–2010 (Figure 2.26). However, more recent results suggest an increase in total PFCAs in Hudson Bay and Lancaster Sound; the declining trend occurred later in the southeastern Beaufort Sea seals. The trend for total PFCAs reflects changes in the major components (PFNA, PFDA, PFUnDA; Figure 2.20) which have very similar individual trends (Muir et al. 2014; Muir, unpubl. data). Similar differences in trends between ringed seals in the Beaufort Sea and in Hudson Bay and Lancaster Sound have been observed for β-HCH isomers (Addison et al., 2014). They are thought to reflect the influence of Pacific Ocean waters and Russian rivers as sources for the Beaufort Sea (Li and Macdonald, 2005) whereas sources for western Hudson Bay reflect inflowing rivers and atmospheric deposition from North American sources (Armitage et al., 2009c).

Whales

Rotander et al. (2012c) reported increasing trends for PFNA, PFDA and PFUnDA in pilot whales (*Globicephala melas*) and white-sided dolphins from the Faroe Islands. Samples were from the period 1986–2006 (pilot whales) and 2001–2006 (dolphins). Calculated on an annual basis the increases were generally over 10% per year, reflecting the sharp increases seen for other Arctic marine species up to the mid-2000s. However only three sampling years were available for pilot whales and two for dolphins.

Reiner et al. (2011) examined temporal trends of PFCAs in beluga from Cook Inlet and the Chukchi Sea (northwestern Alaska). Although sample sizes were limited (n=1 or 2 per year

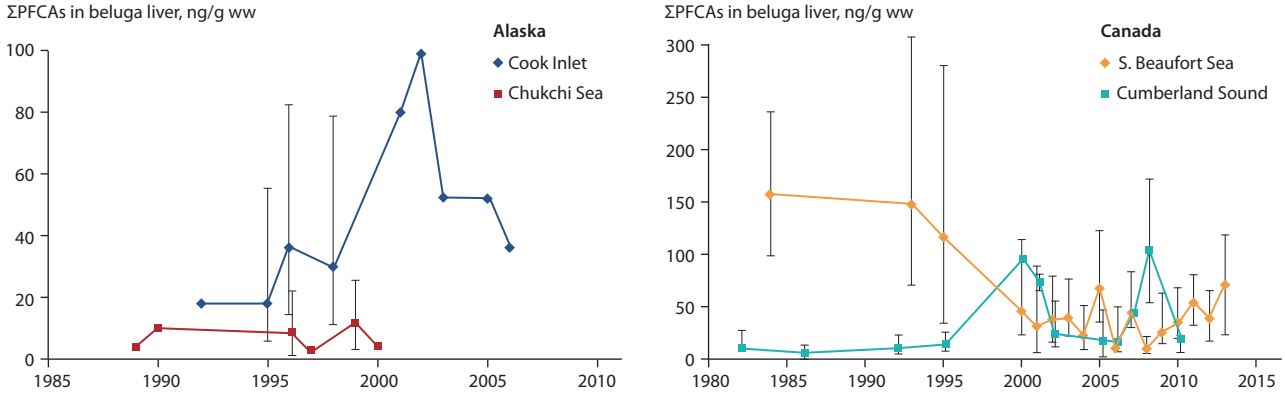

Figure 2.27 Temporal trends in ΣPFCAs in beluga liver samples from the Cook Inlet and Chukchi Sea (northwest Alaska) reported by Reiner et al. (2011) and from the southern Beaufort Sea and Cumberland Sound stocks (Tomy et al., 2011; Tomy and Loseto, 2014). Symbols represent geometric mean concentrations. Vertical bars are 95% confidence intervals for the Alaskan results and minimum and maxima for the Canadian samples.

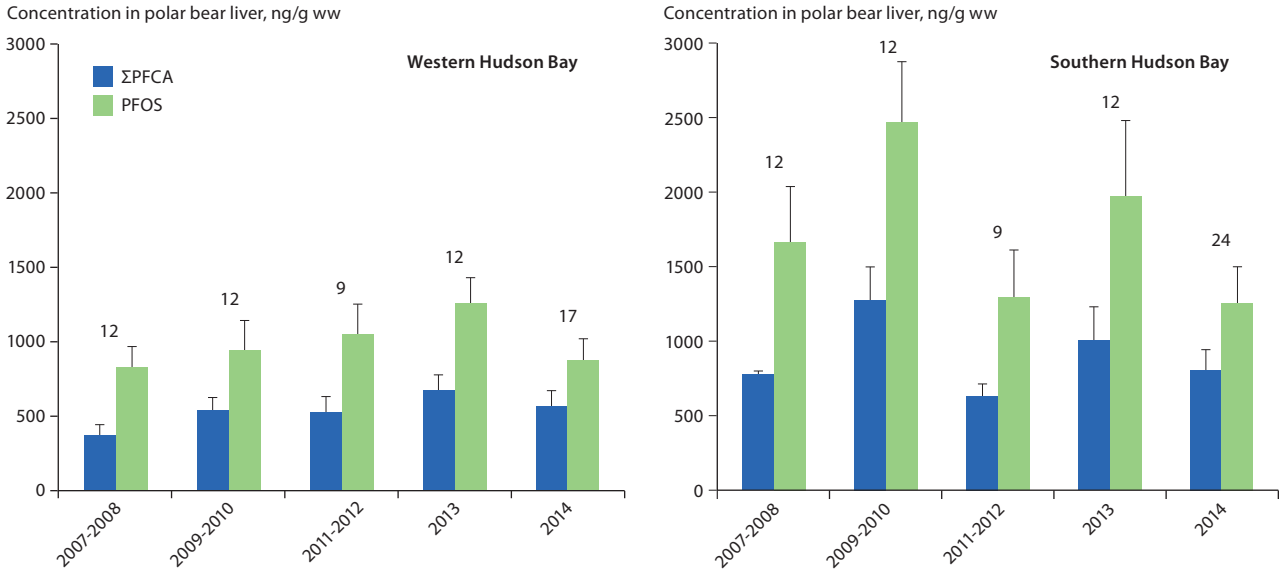

Figure 2.28 Temporal trends in geometric mean concentration of ΣPFCA and PFOS in the liver of western Hudson Bay bears (2007–2014) and southern Hudson Bay bears (2007–2014) (Letcher et al., unpubl. data). Error bars are standard deviations (SDs). Sample numbers are shown above bars. Data not corrected for sex, age or diet.

for Cook Inlet 2001–2006) the overall trend appears to show a rapid increase in concentration of total PFCAs over the period 1993–2003 with a decline thereafter (Figure 2.27). However no significant trend was evident for the Chukchi Sea beluga.

Total (C_8–C_{12})-PFCAs declined over the period 1993–2011 in the southern Beaufort Sea beluga while showing a general decline from 2000–2011 in the Cumberland Sound population (Tomy et al., 2011). More recent results suggest an increasing trend in the southern Beaufort Sea beluga over the period 2010–2013 (Tomy and Loseto, 2014). Total PFCA concentrations in the Beaufort Sea beluga in the 1990s were generally higher than reported for the Chukchi Sea animals.

Polar bears

PFASs have been measured in polar bears in Canada (Figure 2.28) and Greenland (Figure 2.29).

Hudson Bay polar bears appeared to have relatively constant concentrations of ΣPFCAs for the period 2007–2014 while PFOS appears to have declined at least in southern Hudson Bay (Figure 2.28). Even though concentrations were uncorrected for sex, age, and diet, Letcher et al. (unpubl. data) found that in polar bear livers collected for all years between 2007 and 2014, mean concentrations in the Hudson Bay population were continuously very high at >400 ng/g ww (ΣPFCAs) and

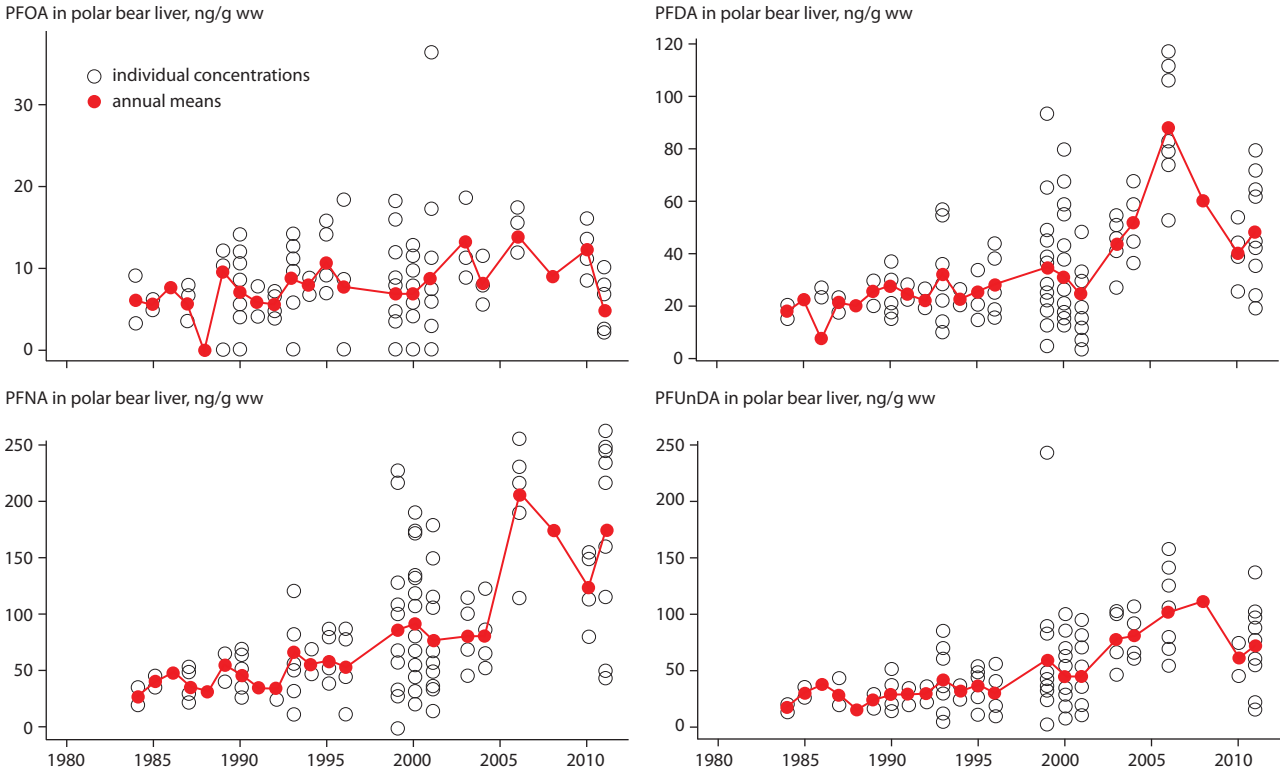

Figure 2.29 Temporal trends in PFOA, PFNA, PFDA, and PFUnDA in polar bear liver from Ittoqqortoormiit (East Greenland), after Rigét et al. (2013).

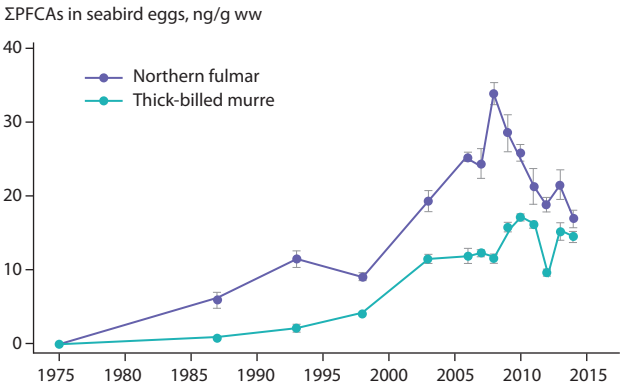

Figure 2.30 Mean (± SE) annual concentrations of total perfluorinated carboxylates (sum of C_6–C_{14}-PFCA) in eggs of northern fulmars and thick-billed murres from Prince Leopold Island, 1975–2014 (Braune, 2015).

>900 ng/g ww (PFOS). This stresses the importance of PFCA and PFOS precursors as sources, which are transported to the Arctic and/or degraded in bears and/or their prey/food web.

Rigét et al. (2013) reported that PFOS was still the most predominant PFAS in polar bear liver samples up to 2010, constituting 85% in East Greenland polar bears, and until 2006 had doubling times of about 14 years. PFOS as well as PFHxS and PFOSA concentrations showed decreasing trends in recent years as did PFDA and PFUnDA. Rigét et al. (2013) updated the temporal trends of PFCAs in East Greenland polar bears that were first reported by Dietz et al. (2008). PFOA, PFNA and PFUnDA all showed declining trends in polar bear liver over the period 2006 to 2011 (Figure 2.29) with annual declines ranging from 6% (PFNA) to 15% (PFOA).

Seabirds

Braune and Letcher (2013) and Braune (2015) examined temporal trends in PFCAs in thick-billed murre and northern fulmar eggs over the period 1975–2014 (14 sampling years including annual samples from 2006 to 2014). Increasing trends were observed in fulmars until 2008 and until 2010 in murres. From 2010 to 2014, PFCAs declined rapidly in fulmar eggs (~12%/y) while remaining more or less constant in murres (Figure 2.30). The long-chain (C_9–C_{15}) PFCAs contributed to the increasing ΣPFCA concentrations in the murres and fulmars during the period 1993–2014. PFUnDA and PFTrDA were the predominant PFCAs and together constituted over 60% of ΣPFCA in all years, with PFTrDA dominating the fulmar PFCA profile (except in 1975) and PFUnDA generally dominating the murre PFCA profile. PFOA (C_8) was detected (>0.08 ng/g ww) in eggs of both species from 2008 onward and comprised <3% of the PFCA profile in murres and northern fulmars.

2.1.8 Conclusions

New data are available for a wider range of perfluoro- and polyfluorinated substances in the Arctic since the previous detailed review (Butt et al., 2010). New PFASs detected include PFECHS (an analog of PFOS), FBSA (a precursor of PFBS), and 6:2-Cl-PFAES (a chlorinated polyfluorinated ether sulfonic acid). Concentrations of these new substances are not elevated relative to PFOS or most PFCAs, however, particularly in the case of 6:2-Cl-PFAES and FBSA, they may be replacement compounds for PFOS-related uses, and so deserve additional scrutiny.

More studies on the partitioning behavior of PFASs are needed, such as between solid/water and air/water phases (Ahrens et al., 2010) to get a better understanding of the relationship between sources, seawater concentrations and the mechanisms of long-range global transport.

Although C_{13}–C_{15}-PFCAs had been reported previously in Arctic marine biota, particularly in seabirds (Butt et al., 2007) additional measurements have shown these compounds to be present in most top predators. Information on the tissue distribution of these long-chain PFCAs, which are more hydrophobic than PFOS or more commonly detected C_8–C_{12} PFCAs, is limited. For example, results from analysis of reindeer showed that C_{13}–C_{15} PFCAs were detectable in fatty tissue. Similarly, in seabirds the eggs have higher proportions of C_{13}–C_{15} PFCAs than liver (Braune and Letcher, 2013). Accumulation of long-chain PFCAs in egg yolk as demonstrated in herring gull eggs (Gebbink and Letcher, 2012) may be the reason. Additional studies of fatty tissues for other mammals are needed. The relative proportions or pattern of the PFCA congeners also differs between the European Arctic, Greenland and Canada. For example, C_{13}- and C_{14}-PFCAs were not detected in lake trout from northern Canada but readily detected in fish in the European Arctic, the Faroe Islands and Greenland. However, additional studies are needed because most analyses of fish from the European Arctic have used liver, while muscle has generally been used in Canada (except for burbot). The differences may thus also reflect tissue distribution.

There are an increasing number of measurements of PFBA in freshwater, seawater, snow and air samples which indicate that it is the most prominent PFCA in these abiotic media. For example, PFBA predominated in all air samples collected by the GAPS program using sorbent-impregnated polyurethane foam or polyurethane foam disks. However, PFBA has multiple non-fluorotelomer gas-phase sources, including chlorofluorocarbon replacements HFC-329 ($CF_3(CF_2)_3H$), HFE-7100162 ($C_4F_9OCH_3$), and HFE-7200 ($C_4F_9OC_2H_5$), and this is likely to explain its predominance. PFBA is also detectable in fish (e.g. in landlocked char from a lake in Svalbard) and in liver of polar bears from Hudson Bay. Although it is expected to be eliminated quickly due to its high water solubility, the predominance of PFBA in abiotic samples suggests that it could be present, particularly in fish and invertebrates that are continuously exposed via gill respiration. Thus further measurements of PFBA in biota are needed.

An extensive dataset exists for long-term trends of long-chain PFCAs in Arctic biota with some datasets including archived samples from the 1970s and 1980s. However, with the exception of air, results are mainly from Canada and Greenland. Trends in PFCAs over time vary across the North American Arctic and between East and West Greenland. Rising levels of some PFCAs have been explained by continued emissions of long-chain PFCAs and/or their precursors (Wang et al., 2014a). Continuing production of precursors of the long-chain PFCAs in Asia (including India and Russia) while reductions in these precursors occur in Europe and North America may explain some of this pattern.

Another temporal pattern that has emerged since 2010 is increasing PFCAs in biota following previous declines from higher concentrations in the early 2000s. This is most evident in ringed seals and beluga in the Canadian Arctic. Annual biological sampling is helping to determine this trend. The trend has not appeared in the data for atmospheric sampling of volatile precursors (FTOHs) or of PFOA on filters.

While the effectiveness of biological sampling for temporal trends in long-chain PFCAs has been demonstrated, this does not apply to the C_4–C_8-PFCAs or PFBS which are generally present at low concentrations in biota. In addition to air sampling, sampling abiotic media such as glacial cores, and annual sampling of lake waters and seawater would appear to be the best approaches for investigating trends in the less bioaccumulative PFASs.

Section 2.1 Annex Contents

Section 2.1 Annex

Table A2.1/1 Physical-chemical properties of selected PFASs. Data based on supporting information given by Wang et al. (2011) except for PFOA, PFOS, PFDS and 6:2-Cl-PFAES for which parameters are estimated by COSMOtherm (Wang et al., 2011; Gomis et al., 2015).

PFAS abbreviation	pK_A	log K_{AW}	log $K_{OW, dry}$	log K_{OA}	log P_L (Pa)	log S_W (mg/L)	log K_{OC}[a] (L/kg)
PFOA	0.9	-1.93	5.3	7.23	0.62		1.31–2.35
PFNA	0.82				0.1		2.39±0.09
PFDA					-0.64		2.76±0.11
PFUnDA					-0.98		3.30±0.11
PFDoDA					-2.29		
PFOS	-3.41	-1.65	6.43	8.07			2.57±0.13
PFDS	-2.86						3.53±0.12
6:2-Cl-PFAES		-1.36	7.03	8.4			3.28
4:2 FTOH		-1.52	3.30±0.04	4.57±0.55	2.33	2.99	0.93
6:2 FTOH		-0.56	4.54±0.01	4.84±0.71	1.26	1.27	2.43
8:2 FTOH		0.58	5.58±0.06	5.58±0.60	0.6	-0.86	3.84
10:2 FTOH		1.6	6.63	5.71±0.47	-0.70	-1.96	6.2
12:2 FTOH				6.20±0.49			
N-MeFOSA		6.3±0.3					
N-EtFOSA		6.4±0.3					
N-MeFOSA		6.6±0.5	-3.40				
N-EtFOSA		6.7±0.2	-2.77				

[a] Organic carbon-water partition coefficient for anionic species

Table A2.1/2 Measured concentrations of selected PFASs in snow, glaciers, sediment and freshwater. Data sources listed below table.

Snow, pg/L						
Area	Longyearbyen glacier	Longyearbyen City	Devon Ice Cap, Canada	Northern Sweden	Lake Hazen catchment	Station Nord
Sample type	Glacial surface snow	Surface snow		Snow pack, median values[a]	Snow pack	Snow pack
Year	2006	2006	2008		2012	2008–2014
Detection limit	5–25	5–25			2–5	
No. samples	4	5	28		8	
PFBA	108	253	120–2020		1485±235	
PFPA	30.2	81.2	40–460		167±116	
PFHxA	75.8	88.7	<10–410		411±474	110
PFHpA	17.1	123.2	<10–690		1141±1411	320
PFOA	112.5	395.7	70–680	66.5	2428±3518	450
PFNA	50.5	245.2	30–1420		1172±1132	530
PFDA	21.8	89.7	10–230		207±191	130
PFUnDA	<MDL	35	10–350		87±43	140
PFDoDA	6.7	15.8	<10–30		22±15	
PFTrDA			<10–30		<MDL	
PFTeDA	<MDL	7.2	<10–10		19±7	
PFHxDA	<MDL	<MDL	<10			
PFOcDA	<MDL	<MDL	<10			
PFBS			<10–230		65±146	
PFHxS	<MDL		<10		222±308	
PFHpS			<10			
PFOS_l			<10–30	20.5		
PFDS			<10–10		<MDL	
PFOS_b			<10–930		161±387	
PFOSA			10–130		6±4	
4:2FTS			<10			
6:2FTS			<10–130			
8:2FTS			<10–10			
pfechs			<10–20		31±14	
Data sources	(1)	(1)	(2)	(3)	(4)	(5)

[a] PFCAs also analyzed, but not presented in abstract.
PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)

Data sources: (1) Kwok et al., 2013; (2) MacInnis et al., 2017; (3) Codling et al., 2014; (4) St. Louis et al., 2015; (5) Bossi, pers comm.

Table A2.1/2 Cont.

Glacier, pg/L			
Area	Longyearbyen glacier		
Sample type	Ice core I	Ice core II	Glacial meltwater
Year	2006	2007	2008
Detection limit	5–25	5–25	5–25
No. samples	13	13	4
PFBA	22.7	80	287
PFPA	6.4	20.9	839
PFHxA	13.5	10.7	104.4
PFHpA	<MDL	<MDL	110.1
PFOA	19.5	24.5	107.1
PFNA	14.3	14.4	77.9
PFDA	4.43	3.97	7.32
PFUnDA	1.69	2.02	4.37
PFDoDA	3.68	0.65	5.72
PFTrDA			
PFTeDA	<MDL	<MDL	<MDL
PFHxDA	<MDL	<MDL	<MDL
PFOcDA	<MDL	<MDL	<MDL
PFBS			
PFHxS	<MDL	<MDL	<MDL
PFHpS			
PFOS_l	8.6	8.59	
PFDS			
PFOS_b			
PFOSA			
4:2FTS			
6:2FTS			
8:2FTS			
pfechs			
Data source	(1)	(1)	(1)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)
Data source: (1) Kwok et al., 2013.

Table A2.1/2 Cont.

Sediment, ng/g dw								
Area	Lofoten, Norway	Telemark, Norway	Cornwallis Is. (Nunavut)					
Sample type	Marine, Flakstad	lake Dalsvatn	Meretta Lake	Resolute Lake	Char Lake	Small Lake	North Lake	9 Mile Lake
Year	2012	2012						
Detection limit			0.001	0.001	0.001	0.001	0.001	0.001
No. samples	3	3	4	3	4	3	4	5
PFBA								
PFPA								
PFHxA			0.67±1.15	0.23±0.21	0.10±0.06	0.05±0.05	<MDL	0.01±0.02
PFHpA			0.81±1.3	0.59±0.26	0.51±0.37	0.14±0.09	<MDL	0.15±0.11
PFOA	0.08	<MDL	1.75±2.42	1.78±0.29	0.74±0.55	0.37±0.05	0.04±0.03	0.33±0.21
PFNA	0.09	<MDL	1.44±1.85	1.47±0.49	0.44±0.3	0.21±0.08	0.08±0.14	0.28±0.14
PFDA	33% 0.09	<MDL	0.14±0.16	0.04±0.04	0.03±0.02	<MDL	0.01±0.02	0.02±0.01
PFUnDA	0.08	0.16	0.16±0.17	0.1±0.17	0.07±0.01	0.09±0.08	0.02±0.02	0.03±0.03
PFDoDA	<MDL	<MDL	0.053±0.095	0.051±0.088	0.004±0.006	0.003±0.005	0.002±0.004	0.001±0.001
PFTrDA	<MDL	<MDL	0.047±0.065	0.073±0.126	<MDL	0.005±0.008	<MDL	<MDL
PFTeDA	<MDL	<MDL	0.035±0.07	0.032±0.054	<MDL	<MDL	<MDL	<MDL
PFHxDA								
PFOcDA								
PFBS			0.01±0.01	0.08±0.07	0.02±0.02	<MDL	0.002±0.001	0.07±0.12
PFHxS			0.95±1.29	0.67±0.17	0.36±0.45	1.00±1.58	<MDL	0.62±1.37
PFHpS			0.11±0.13	0.26±0.32	0.002±0.002	<MDL	<MDL	<MDL
PFOS_l								
PFDS	<MDL	<MDL	0.05±0.07	0.63±1.09	<MDL	<MDL	<MDL	<MDL
PFOS_b	<MDL	<MDL	27.8±42.9	48.5±28.9	0.44±0.08	0.22±0.13	0.02±0.029	0.102±0.122
PFOSA			0.13±0.2	<MDL	0.009±0.007	0.018±0.03	0.007±0.008	<MDL
4:2FTS			0.12±0.24	0.2±0.31	0.002±0.001	<MDL	<MDL	0.002±0.002
6:2FTS	<MDL	<MDL	10.0±11.5	3.41±0.98	<MDL	0.02±0.03	0.008±0.016	0.03±0.05
8:2FTS			13.3±20.8	6.31±5.69	0.002±0.002	0.01±0.02	0.002±0.001	0.01±0.01
pfechs			0.07±0.11	0.01±0.01	<MDL	<MDL	<MDL	<MDL
Data source	(1)	(2)	(3)	(3)	(3)	(3)	(3)	(3)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)

Data sources: (1) NILU, 2013; (2) NILU, 2014; (3) Lescord et al., 2015.

Table A2.1/2 Cont.

	Freshwater, pg/L				
Area	Longyearbyen	Longyearbyen, Isdammen	Faroe Islands	Telemark, Norway	Ellesmere Is. (Nunavut)
Sample type	River	Lake	Lake	Lake Dalsvatn	Lake Hazen
Year	2006		2012	2012	
Detection limit	5–25	5–25			2–5
No. samples	6	1	4	3	4
PFBA	1158	427	560		739±137
PFPA	1047	1388	<LOD		123±5
PFHxA	259	73	<LOD		193±19
PFHpA	153	61	140		285±15
PFOA	305	174	250	560	644±26
PFNA	103	131	150	300	255±27
PFDA	19	18	33.5	200	122±5
PFUnDA	11	12	43	nd	31±3
PFDoDA	8	6		nd	31±11
PFTrDA				nd	24±18
PFTeDA	<MDL	<MDL		nd	24±18
PFHxDA	<MDL	<MDL			
PFOcDA	<MDL	<MDL			
PFBS			<MDL		13±5
PFHxS			<MDL		16±4
PFHpS			440		
PFOS_l			<MDL		
PFDS				nd	<MDL
PFOS_b				nd	97±70
PFOSA					18±10
4:2FTS					
6:2FTS				nd	
8:2FTS					
pfechs					71±39
Data source	(1)	(1)	(2)	(3)	(5)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)

Data sources: (1) Kwok et al., 2013; (2) Eriksson et al., 2013; (3) NILU, 2013; (4) Lescord et al., 2015 ; (5) DeSilva and Muir, unpubl.

Table A2.1/2 cont.

Freshwater, pg/L						
Cornwallis Is. (Nunavut)						
Meretta Lake	Resolute Lake	Char Lake	Small Lake	North Lake	Nine Mile Lake	Amituk Lake
2–5	2–5	2–5	2–5	2–5	2–5	2–5
5	5	5	5	5	5	2
29.6±4.65	22.3±2.97	0.43±0.15	0.60±0.12	0.43±0.33	0.43±0.09	0.087
20.9±3.08	24.9±19.28	0.31±0.04	0.46±0.06	0.30±0.06	0.31±0.02	0.179
16.9±1.25	9.39±1.97	0.62±0.27	0.60±0.22	0.66±0.41	0.69±0.31	0.230
3.8±0.86	2.85±0.95	0.09±0.02	0.17±0.03	0.21±0.01	0.14±0.01	0.180
0.13±0.05	0.11±0.06	0.04±0.04	0.06±0.03	0.08±0.04	0.08±0.03	0.021
0.08±0.01	0.06±0.02	0.006±0.002	<MDL	<MDL	0.009±0.002	0.007
0.003±0.001	0.002±0.001	<MDL	0.002±0.002	0.003±0.002	0.002±0.001	0.005
<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.002
<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.002
4.86±1.01	3.4±0.26	0.17±0.04	0.19±0.03	0.08±0.02	0.07±0.01	0.027
29.72±3.51	19.73±3.87	0.12±0.01	0.11±0.02	<MDL	<MDL	0.010
						0.002
						0.021
0.002±0.002	0.003±0.004	0.001±0.001	<MDL	<MDL	<MDL	0.033
41.1±9.31	26.2±5.15	0.05±0.01	0.09±0.02	<MDL	0.02±0.01	
<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.002
0.183±0.123	0.054±0.068	<MDL	<MDL	<MDL	<MDL	
1.41±1.651	0.20±0.213	0.003±0.003	0.002±0.002	0.001±0.001	0.002±0.002	
0.20±0.26	0.01±0.01	0.001±0.001	<MDL	<MDL	<MDL	
4.3±1.36	2.59±1.16	0.09±0.02	0.13±0.03	0.06±0.01	0.10±0.06	
(4)	(4)	(4)	(4)	(4)	(4)	(5)

Table A2.1/3 Measured concentrations of selected PFASs in terrestrial plants, soil and terrestrial animals. Data sources listed below table.

	Terrestrial plants, ng/g ww				
	Crinkled snow lichen *Flavocetraria nivalis/ cucullata*	Cottongrass *Eriophorum vaginatum*		Reindeer lichen *Cladonia rangiferina*	
Area	Porcupine	Bathurst	Porcupine	Bathurst	Porcupine
Year	2008	2009	2008	2009	2008
Tissue	whole	whole	whole	whole	whole
No samples	10	3	10	9	8
PFBA					
PFPA					
PFHxA					
PFHpA					
PFOA	0.038±0.014	0.020±0.004	0.003±0.002	0.041±0.005	0.049±0.010
PFNA	0.023±0.009	0.047±0.015	0.013±0.009	<0.003	0.025±0.010
PFDA	0.056±0.018	0.038±0.012	<0.004	0.099±0.017	0.083±0.010
PFUnDA					
PFDoDA					
PFTrDA					
PFTeDA					
PFBS					
PFHxS					
PFOS_l	0.014±0.008	0.014±0.007	0.002±0.002	0.021±0.003	0.013±0.006
PFDS					
PFOS_b					
PFOSA	0.025±0.013	0.005±0.003	0.003±0.003	0.067±0.039	0.021±0.010
6:2FTS					
Data source	(1)	(1)	(1)	(1)	(1)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)

Data sources: (1) Müller et al., 2011; (2) NILU, 2014.

Table A2.1/3 cont.

Terrestrial plants, ng/g ww				Terrestrial soils, ng/g ww
Willow *Salix pulchra*		Moss *Rythidium rugosum*	Mushrooms	Soil
Porcupine	Bathurst	Bathurst	Bathurst	Telemark, Norway (Dalsvatn)
2008	2009	2009	2009	2012
whole	whole	whole	whole	
7	3	5	3	1 pooled sample from 3 locations
0.003±0.002	0.013±0.002	0.020±0.009	0.008±0.003	0.25
0.191±0.100	0.034±0.005	0.024±0.004	0.188±0.075	0.12
0.056±0.021	0.021±0.001	0.058±0.018	0.012±0.007	<MDL.
				<MDL.
				<MDL.
				<MDL.
				<MDL.
0.062±0.029	0.018±0.003	0.008±0.002	0.038±0.006	
				0.06
				0.22
0.010±0.010	0.005±0.001	0.006±0.002	<0.005	
				<MDL.
(1)	(1)	(1)	(1)	(2)

Table A2.1/3 cont.

Terrestrial animals, ng/g ww											
	Caribou *Rangifer tarandus groenlandicus*								Moose *Alces alces*	Wolf *Canis lupus*	
Area	Bathurst		Porcupine				Qamanirjuaq		Jean Marie R., Dehcho	Porcupine	
Year	2008	2008	2007	2007	2008	2007	2008	2006	2007	2010	2010
Tissue	Muscle	Liver	Muscle	Liver	Liver	Kidney	Liver	Kidney	Liver	Muscle	Liver
No samples	9	7	7	10	10	10	10	11	7	6	6
PFBA											
PFPA											
PFHxA											
PFHpA											
PFOA	0.18±0.01	3.21±0.23	0.07±0.01	1.72±0.10	0.71	0.02±0.01	1.68	0.02	0.34	0.15±0.02	2.47±0.41
PFNA	0.02±0.01	0.11±0.01	0.02±0.01	<0.01	0.01	<0.01	0.007	<0.002	0.33	0.08±0.01	0.23±0.08
PFDA	0.09±0.01	3.15±0.41	0.06±0.01	2.22±0.23	0.4	0.10±0.02	2.37	0.1	1.02	0.44±0.06	4.68±0.94
PFUnDA											
PFDoDA											
PFTrDA											
PFTeDA											
PFBS											
PFHxS											
PFOS_l	0.08±0.02	2.18±0.29	0.03±0.02	0.67±0.13	0.62	0.02±0.00	1.81	0.04	0.35	0.13±0.02	1.41±0.26
PFDS											
PFOS_b											
PFOSA	0.07±0.01	2.21±0.16	0.03±0.01	1.90±0.11	1.13	0.02±0.01	2.26	0.02	0.38	0.11±0.02	1.98±0.19
6:2FTS											
Data source	(1)	(1)	(1)	(1)	(2)	(1)	(2)	(2)	(3)	(1)	(1)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)

Data sources: (1) Müller et al., 2011; (2) Gamberg et al., 2017; (3) Larter et al., 2017; (4) NILU, 2014; (5) Aas et al., 2014; (6) AMAP, 2016b; (7) Bossi et al., 2015.

Table A2.1/3 cont.

Terrestrial animals, ng/g ww										
Shrew Soricidae	Field mouse *Apodemus*	Arctic fox *Vulpes lagopus*	Moose *Alces alces*	Reindeer *Rangifer tarandus*			Musk-ox *Ovibos moschatus*		Ptarmigan *Lagopus muta*	
Telemark, Norway	Telemark, Norway	Svalbard	Telemark, Norway	Svalbard			South Greenland	South Greenland	Nuuk	Qeqertarsuaq
2012	2012	2010/11	2012	2014	2014	2014	2008	2012	2011	2011
Liver	Liver	Liver, kidney, abdominal adipose tissue, and muscle	Liver	Blubber	Liver	Muscle	Liver	Liver	Liver	Liver
2	8	13	9	8	7	9	10	3	12	10
				<MDL	<MDL	<MDL				
				<MDL	<MDL	<MDL				
				0.08	-	0.07				
				-	-	0.14				
N.D.	<MDL		<MDL	0.28	-	-	1.42 (1.02–2.06)	0.87 (0.67–1.08)	<MDL	<MDL
N.D.	0.62		0.28	0.16	0.49	0.11	0.84 (0.50–1.24)	2.58 (2.0–3.55)	1.04 (0.43–1.82)	0.27 (0.10–0.45)
0.46	0.45		0.29	0.17	0.22	-	0.28 (0.17–0.38)	3.22 (1.59–5.25)	<MDL	<MDL
0.86	0.89		0.25	0.15	0.25	-	0.45 (0.44–0.46)	2.44 (1.18–4.07)	<MDL	<MDL
0.25	0.33		0.08	-	-	0.33	<MDL	0.33 (0.21–0.52)		
0.82	2.34		30% 0.09	0.37	0.44	0.30	<MDL	0.62 (0.52–0.72)		
<MDL	1.22		<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		
				<MDL	<MDL	<MDL				
				-	0.44	0.17				
				-	0.42	-				
<MDL	<MDL		<MDL	<MDL	<MDL	<MDL				
1.21	0.87		0.43				1.273			
				<MDL	<MDL	<MDL	1.42 (1.02–2.06)	0.87 (0.67–1.08)		
<MDL	0.07		<MDL	<MDL	<MDL	<MDL				
(4)	(4)	(5)	(4)	(6)	(6)	(6)	(7)	(7)	(7)	(7)

Table A2.1/4. Measured concentrations of selected PFASs in freshwater fish and invertebrates Data sources listed below table.

	Freshwater fish, ng/g ww							
	Perch	Brown trout	Capelin	Cod	Salmon	Searun char		
Area	Northern Norway		Eastern Hudson Bay			Cambridge Bay	Nain	Pond Inlet
Sample type	Liver	Liver	Whole body	Muscle	Muscle	Muscle	Muscle	Muscle
Year						2010-2012	2010	2010-2012
No. samples	3	10	5	3	6	31	10	20
Statistic	M±SD	M±SD	GM	GM	GM	AM±SD	AM±SD	AM±SD
PFBA								
PFHxA						0.06±0.06	0.07±0.01	0.04±0.04
PFHpA			0.27	<0.06-0.40	1.6	0.06±0.05	0.09±0.01	0.06±0.05
PFOA	N.A	0.09	0.12	0.36	0.3	0.14±0.11	0.28±0.04	0.13±0.11
PFNA	N.A.	0.46	0.09	<0.09-1.3	0.64	0.08±0.17	0.02±0.01	0.04±0.04
PFDA	N.A.	1.45	0.06	0.18	0.19	0.02±0.03	0.01±0.01	0.01±0.01
PFUnDA	N.A.	8.14	0.23	0.3	0.48	0.08±0.1	0.06±0.03	0.05±0.04
PFDoDA	N.A.	5.07	0.1	0.1	0.23	0.01±0.01	0.01±0.01	0.01±0.01
PFTrDA	N.A.	16.3	0.09	<0.04-0.28	<0.03	0.05±0.06	0.03±0.01	0.03±0.02
PFTeDA	N.A.	0.77				0.01±0.02	0±0	0.01±0.01
PFHxDA						<0.01	<0.01	<0.01
PFBS			<0.06	<0.08	<0.2	<0.01	<0.01	<0.01
PFHxS			<0.07	<0.09-3.5	<0.2	0.01±0.01	<0.01	0.01±0.01
PFHpS								
PFOS_l								
PFDS			<0.03	<0.04	<0.08	<0.01	<0.01	<0.01
PFOS_b	N.A.	4.57	<0.1	0.82	<0.3-1.3	0.11±0.06	1.7±5.1	0.12±0.07
PFOSA			0.74	1.5	0.65	0±0	0±0	0±0
42 FTS								
6:2FTS	N.A.	N.D.						
82 FTS								
PFECHS								
Data source	(1)	(1)	(2), (3)	(2), (3)	(2), (3)	(7)	(7)	(7)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)
M: mean, GM: geometric mean, AM: arithmetic mean, SD: standard deviation

Data sources: (1) NILU, 2013; (2) Kelly et al; (3) NCP, 2013; (4) Muir et al., 2015b; (5) Lescord et al., 2015; (6) Bossi et al., 2015; (7) Evans and Muir, unpubl.; (8) Stern et al., 2012; (9) Stern et al., 2014; (10) NILU, 2014; (11) NILU, 2015; (12) Garsjø, 2014, (13) AMAP, 2016b.

Table A2.1/4 cont.

Freshwater fish, ng/g ww									
Landlocked Arctic char									
Amituk Lake	Char Lake	Hazen Lake	9-Mile Lake	Meretta Lake	North Lake	Resolute Lake	Small Lake	Lake á Mýranar (Faroes)	Unnamed lake, South Greenland
Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Muscle	Liver	Liver
2011-2013	2010-2012	2010-2013	2010-11	2010-11	2010-11	2010-11	2010-11	2011-2012	2010
38	18	40	23	21	25	18	21	10	10
AM±SD	AM±SD	AM±SD	AM±SD	AM±SD	AM±SD	AM±SD	AM±SD		
0.03±0.02	0.01±0.01	0.03±0.01	0.001±0.002	0.011±0.03	0.001±0.001	0.01±0.01	0.002±0.004		
0.03±0.02	0.02±0.02	0.02±0.01	0.001±0.002	0.016±0.05	0.001±0.002	0.013±0.005	0.001±0.002		
0.04±0.04	0.03±0.04	0.01±0.03	0.006±0.007	0.028±0.036	0.007±0.009	0.095±0.026	0.007±0.007		
0.16±0.07	0.2±0.08	0.05±0.04	0.04±0.02	0.152±0.067	0.031±0.017	0.34±0.37	0.05±0.02	0.28 (0.12–0.53)	0.42 (0.20–1.23)
0.07±0.04	0.07±0.03	0.05±0.03	0.006±0.003	0.022±0.032	0.013±0.006	0.04±0.04	<MDL	0.2 (0.17–0.22)	0.32 (0.18–0.84)
0.04±0.02	0.04±0.02	0.05±0.05	0.007±0.006	0.014±0.03	0.01±0.007	0.02±0.016	0.006±0.004	0.63 (0.39–0.79)	1.29 (0.73–3.06)
<0.01	0.01±0.01	0.02±0.03	<MDL	0.011±0.028	<MDL	0.003±0.007	0.001±0.002	0.51 (0.43–0.65)	0.61 (0.49–1.04)
0.01±0.01	0.02±0.01	0.05±0.04	<MDL	0.027±0.041	<MDL	<MDL	0.001±0.002	1.57 (0.90–2.52)	1.5 (0.96–3.47)
<0.01	0.01±0.01	0.01±0.01	0.001±0.003	0.016±0.039	<MDL	0.005±0.007	0.001±0.004	1.73 (0.83–2.80)	0.63 (0.44–1.30)
<0.01	<0.01	<0.01							
<0.01	<0.01	<0.01	0.01±0.009	0.021±0.023	0.006±0.008	0.016±0.036	0.01±0.017		
<0.01	0.01±0.01	0.01±0.01	<MDL	0.08±0.03	<MDL	0.33±0.39	<MDL		
			0.001±0.001	0.03±0.03	0.001±0.001	0.14±0.09	0.001±0.002		
0.01±0.01	<0.01	0.05±0.09	<MDL	0.02±0.03	<MDL	<MDL	0.001±0.002		
0.11±0.05	0.68±0.47	0.25±0.84	0.001±0.002	6.59±1.72	<MDL	31.75±16.34	0.009±0.01	0.75 (0.46–1.09)	0.51 (0.38–0.68)
0.01±0.01	<0.01	0.05±0.09	0.003±0.006	0.25±0.08	0.013±0.011	31.78±16.34	0.004±0.004		
			0.002±0.002	0.005±0.009	0.006±0.015	0.02±0.05	0.001±0.002		
			<MDL	0.005±0.011	<MDL	0.003±0.013	<MDL		
			0.011±0.034	0.15±0.17	0.012±0.029	0.11±0.07	0.001±0.001		
			<MDL	<MDL	<MDL	<MDL	<MDL		
(4)	(4), (5)	(4), (5)	(5)	(5)	(5)	(5)	(5)	(6)	(6)

Table A2.1/4 cont.

	Freshwater fish, ng/g ww						
	Burbot			Lake trout			
Area	Fort Resolution	LutselK'e	Ft Good Hope	Hay River	LutselK'e	Kusawa Lake	Lake Laberge
Sample type	Liver	Liver	Liver	Muscle	Muscle	Muscle	Muscle
Year	2010-2013	2010-2013	2011	2010-2013	2010-2013	2011	2011
No. samples	10	10	10	0	0	10	10
Statistic	AM±SD	AM±SD		AM±SD	AM±SD		
PFBA							
PFHxA	0.18±0.21	0.18±0.5		0.04±0.05	0.01±0.01		
PFHpA	0.02±0.02	0.03±0.03		0.01±0.03	0.02±0.02		
PFOA	0.07±0.12	0.11±0.11	1.3±2.1	0.01±0.03	0.01±0.03		
PFNA	1.7±1.6	2.2±1.97	2.0±3.2	0.08±0.11	0.06±0.08	1.5±2.5	3.9±7.5
PFDA	0.42±0.42	0.41±0.34	5.0±6.0	0.02±0.03	0.02±0.02	5.7±5.7	1.1±11.6
PFUnDA	0.54±0.56	0.62±0.5	0.92±2.4	0.04±0.04	0.04±0.04		
PFDoDA	0.07±0.07	0.07±0.06		0.01±0.01	0.01±0.01		
PFTrDA	0.17±0.2	0.19±0.13		0.04±0.03	0.06±0.1		
PFTeDA	0.07±0.03	0.05±0.04		<0.01	<0.01		
PFHxDA	0.15±0.16	0.25±0.33		<0.01	<0.01		
PFBS	0.14±0.19	0.1±0.12		<0.01	<0.01		
PFHxS	0.04±0.03	0.04±0.03		0.01±0.01	0.01±0.01		
PFHpS							
PFOS_l							
PFDS	0.02±0.01	0.02±0.01		0.02±0.02	0.02±0.05		
PFOS_b	2.0±1.4	1.6±1.0	1.7±1.6	0.14±0.09	0.11±0.09	0.21±0.40	1.61±1.62
PFOSA	0.02±0.01	0.02±0.01		0.02±0.02	0.02±0.05		
42 FTS							
6:2FTS							
82 FTS							
PFECHS							
Data source	(7)	(7)	(8)	(7)	(7)	(9)	(9)

PFOS_l: PFOS (linear); PFOS_b: PFOS (branched)
AM: arithmetic mean, SD: standard deviation

Data sources: (1) NILU, 2013 ; (2) Kelly et al; (3) NCP, 2013; (4) Muir et al., unpubl.; (5) Lescord et al., 2015; (6) Bossi et al., 2015; (7) Evans and Muir, unpubl.; (8) Stern et al., 2012; (9) Stern et al., 2014; (10) NILU, 2014; (11) NILU, 2015; (12) Garsjø MSc thesis, 2014; (13) AMAP, 2016b.

Table A2.1/4 cont.

Freshwater fish, ng/g ww						
Trout		Brown trout *Salmo trutta*	Perch *Perca fluviatilis*	Arctic char		
Lake á Mýranar (Faroes)	Unnamed Lake, Sandur (Faroes)	Telemark, Norway		Linnévatnet, Svalbard		
Liver	Liver	Liver	Liver	Muscle	Muscle	Liver
2011-2012	2011-2012	2012	2012	2010	2013	2013
5	5	10	3	20	12	6
		10	3	20	12	6
					0.102	0.132
					ND	ND
				ND	ND	ND
		30% 0.09	N.A.	0.048	ND	ND
1.11 (0.26–1.86)	1.6 (1.02–3.32)	0.46	N.A.	0.061	ND	0.313
1.84 (0.35–2.92)	0.97 (0.47–1.81)	1.45	N.A.	ND	ND	0.665
6.81 (1.31–10.9)	3.44 (1.76–6.13)	8.14	N.A.	0.143	0.03	1.599
3.03 (0.52–4.45)	1.36 (0.84–2.05)	5.07	N.A.	ND	ND	0.147
8.35 (1.09–11.9)	3.19 (2.07–4.72)	30% 16.3	N.A.	ND	ND	0.214
1.52 (1.23–1.9)	0.67 (0.51–0.82)	20% 0.77	N.A.			
				ND	ND	ND
		N.D.	N.A.			
4.71 (4.11–5.51)	1.75 (0.79–2.71)	4.57	N.A.		ND	ND
				ND		
		N.D.	N.A.	0.202	ND	0.771
(6)	(6)	(10)	(11)	(12), (13)	(12), (13)	(12), (13)

Table A2.1/4 cont.

	Freshwater invertebrates, ng/g ww					
	Adult and larval chironomids					
Area	9-Mile Lake	Char Lake	Meretta Lake	North Lake	Resolute Lake	Small Lake
Year	2010-11	2010-11	2010-11	2010-11	2010-11	2010-11
No. samples	6	6	8	10	10	4
Statistic	AM±SD	AM±SD	AM±SD	AM±SD	AM±SD	AM±SD
PFHxA	0.03±0.04	0.01±0.01	0.02±0.02	0.01±0.01	0.04±0.03	0.04±0.08
PFHpA	0.01±0.013	0.004±0.005	0.019±0.018	0.005±0.006	0.013±0.012	0.006±0.005
PFOA	0.12±0.19	0.06±0.07	0.19±0.2	0.05±0.08	0.12±0.1	0.04±0.03
PFNA	0.08±0.14	0.06±0.04	0.84±0.72	0.07±0.07	1.02±1.42	0.32±0.31
PFDA	0.11±0.24	0.02±0.01	0.18±0.16	0.04±0.05	0.28±0.46	0.22±0.23
PFUnDA	0.22±0.47	0.02±0.01	0.08±0.08	0.04±0.06	0.15±0.21	0.29±0.32
PFDoDA	0.03±0.04	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.04±0.04
PFTrDA	0.03±0.05	0.02±0.03	0.01±0.01	0.01±0.01	0.01±0.01	0.03±0.03
PFTeDA	0.005±0.002	0.005±0.004	0.005±0.004	0.003±0.003	0.003±0.003	0.002±0.002
PFBS	<MDL	<MDL	0.017±0.019	0.004±0.009	0.022±0.064	0.003±0.005
PFHxS	0.04±0.06	0.02±0.02	0.13±0.13	0.01±0.01	0.11±0.09	0.01±0
PFHpS	0.007±0.012	0.003±0.005	0.047±0.053	0.004±0.005	0.199±0.37	0.002±0.002
PFDS	0.01±0.02	0.02±0.02	0.006±0.011	0.007±0.01	0.08±0.19	<MDL
PFOS_b	3.08±6.72	3.22±4.88	28.1±30.3	0.96±2.23	77.24±117.64	0.74±0.69
PFOSA	0.05±0.09	0.03±0.04	0.23±0.25	0.04±0.1	0.09±0.12	<MDL
42 FTS	0.001±0.002	<MDL	0.064±0.133	0.077±0.144	0.056±0.082	0.467±0.517
6:2FTS	0.14±0.1	0.07±0.1	0.08±0.1	0.06±0.1	0.07±0.05	0.01±0.02
82 FTS	0.02±0.01	0.14±0.22	3.16±2.09	0.02±0.02	1.11±1.35	0.03±0.01
PFECHS	0.006±0.009	0.005±0.01	0.01±0.017	0.009±0.018	0.06±0.11	0.003±0.006
Data source	(1)	(1)	(1)	(1)	(1)	(1)

PFOS_b: PFOS (branched)
AM: arithmetic mean, SD: standard deviation

Data sources: (1) Lescord et al., 2015.

Table A2.1/4 cont.

Freshwater invertebrates, ng/g ww					
zooplankton					
9-Mile Lake	Char Lake	Meretta Lake	North Lake	Resolute Lake	Small Lake
2010-11	2010-11	2010-11	2010-11	2010-11	2010-11
7	6	13	5	9	7
AM±SD	AM±SD	AM±SD	AM±SD	AM±SD	AM±SD
0.56±0.56	0.009±0.009	0.019±0.019	0.011±0.011	0.006±0.006	0.021±0.021
0.47±0.47	0.004±0.004	0.011±0.011	0.001±0.001	0.004±0.004	0.012±0.012
0.47±0.47	0.002±0.002	0.064±0.064	0.006±0.006	0.015±0.015	0.002±0.002
0.55±0.55	0.002±0.002	0.152±0.152	0.006±0.006	0.026±0.026	0.005±0.005
0.002±0.002	0.011±0.011	0.021±0.021	0.012±0.012	0.004±0.004	0.001±0.001
0.63±0.63	0.55±0.55	0.012±0.012	0.005±0.005	0.003±0.003	0.001±0.001
0.015±0.015	0.01±0.01	0.005±0.005	0.005±0.005	0.005±0.005	0.002±0.002
<MDL	0.01±0.01	0.008±0.008	0.003±0.003	<MDL	<MDL
0.002±0.002	0.01±0.01	0.001±0.001	0.002±0.002	0.005±0.005	0.002±0.002
0.01±0.01	0.02±0.02	0.014±0.014	0.005±0.005	0.004±0.004	0.016±0.016
0.005±0.005	0.08±0.08	0.06±0.06	0.05±0.05	0.03±0.03	0.004±0.004
0.001±0.001	0.005±0.005	0.02±0.02	0.02±0.02	0.01±0.01	<MDL
0.003±0.003	0.05±0.05	0.04±0.04	0.007±0.007	0.007±0.007	0.005±0.005
0.03±0.03	5.71±5.71	7.47±7.47	4.54±4.54	1.25±1.25	0.022±0.022
<MDL	<MDL	0.02±0.02	0.002±0.002	<MDL	0.002±0.002
0.07±0.07	0.02±0.02	0.01±0.01	0.31±0.31	0.07±0.07	0.11±0.11
<MDL	0.04±0.04	0.04±0.04	0.03±0.03	15.95±15.95	<MDL
0.002±0.001	0.116±0.001	0.09±0.001	0.064±0.001	0.082±0.001	0.003±0.001
0.005±0.005	0.15±0.15	0.10±0.10	0.03±0.03	0.01±0.01	0.01±0.01
(1)	(1)	(1)	(1)	(1)	(1)

Table A2.1/5 Measured concentrations of selected PFASs in seawater. Data sources listed below table.

	Ocean water, pg/L						
Area	Adventfjorden	Greenlandic sea	Greenland Sea 75–80°N	Norwegian Sea, 72–75°N	East Greenland, AO–2 surface water	NW Atlantic, east of Newfoundland	Labrador Sea, coastal
Year	2006	2009	2003	2003	2003	2003	2005
No. samples	3						
PFBA	57.2						
PFPA	352	<MDL					
PFHxA	55.7	24.5	<MDL	<MDL		<5.7	
PFHpA	14.6						
PFOA	74.4	85	25–80	45–60	50–55	40–81	8–182
PFNA	38.6	<MDL				<5.1	<MDL
PFDA	<MDL						
PFUnDA	<MDL						
PFDoDA	<MDL						
PFTrDA							
PFTeDA	<MDL						
PFHxDA	<MDL						
PFOcDA	<MDL						
PFBS		<MDL					
PFHxS		25.5	<2–20	5–16			2.3–10
PFHpS		<MDL					
PFOS (branched)		<MDL	12–32	25–80	20–40	<10	24–73
PFDS							
4_2FTS							
6:2FTS							
8_2 FTs							
PFECHS							
Data source	(1)	(2)	(3)	(3)	(4)	(4)	(5)

No data: PFOS (linear)

Data sources: (1) Kwok et al., 2013; (2) Zhao et al., 2012; (3) Caliebe et al., 2005; (4) Yamashita et al., 2005; (5) Rosenberg et al., 2008; (6) Cai et al., 2012a; (7) Benskin et al., 2012b; (8) NILU, 2013; (9) Muir et al., 2015c.

Table A2.1/5 cont.

Ocean water, pg/L							
Chukchi Sea/Arctic Ocean	Northwest Pacific Ocean and Bering Sea	Labrador Sea/ Davis Strait/ North Baffin Bay (59–77°N)	Canadian Arctic Archipelago, 87–124°W	Beaufort Sea/ Chukchi Sea/ Bering Strait, 137–169°W	Flakstad, Lofoten, Norway	Canadian Arctic, Barrow Strait	
2010	2010	2005	2005	2005	2012	2011	2012
					3	7	12
						751 (50–2035)	1630 (50–5370)
						466 (207–805)	49.9 (5–406)
<27–28	<27	0.4–26	3–65	11–45		384 (97.9–1187)	93.6 (41–246)
						117 (56–181)	55.6 (25–135)
<20–67	<20–100	21–41	6–54	26–39	200	321 (42–769)	133 (64.3–275)
<22–51	<22–70	n.d.–13	2–47	5–13	<MDL	24.3 (0–73)	35.6 (13.6–79)
					<MDL	13.7 (1–55)	3.6 (1–20.4)
					<MDL	1 (1–1)	3.5 (1–30.6)
					<MDL	1 (1–1)	1 (1–1)
					<MDL	1 (1–1)	4.1 (1–39)
					<MDL	1 (1–1)	1 (1–1)
						<1	<1
<66	<66	<MDL–15	<MDL–19	n.d.–15		1.6 (1–3.4)	1 (<1–1.5)
						<1	<1
<21–53	<21–60	<MDL–39	<MDL–32	9–27	<MDL	7.8 (1–12.3)	14.5 (1–95)
					<MDL	<1	<1
						<1	<1
						<1	1 (<1–1.3)
						<1	<1
						<1	25.3 (4.2–64)
(6)	(6)	(7)	(7)	(7)	(8)	(9)	(9)

Table A2.1/6 Measured concentrations of selected PFASs in marine sediments, invertebrates, fish, birds and mammals. Data sources listed below table.

	Tissue	Area	Year(s)	No. samples	Statistic	PFBA	PFPA	PFHxA
Cod	Liver	N. Norway		10	M±SD			
Mussel	Pooled	N. Norway		3	M±SD			
Sediment		E. Hudson Bay		9	GM			
Macroalgae		E. Hudson Bay		6	GM			
Capelin	Whole body	E. Hudson Bay		5	GM			
Cod	Muscle	E. Hudson Bay		3	GM			
Salmon	Muscle	E. Hudson Bay		6	GM			
Polar cod *Boreogadus saida*	Whole fish, pooled	Beaufort Sea			M or R			ND
	Liver	Barents Sea			M or R			2.06
Halibut *Hippoglossus hippoglossus*	Muscle	N. Norway	2008-12		M or R	ND	ND	ND
Atlantic cod *Gadus morhua*	Muscle	Faroe Islands			M or R			<0.0063
Saithe *Pollachius virens*	Muscle	Faroe Islands			M or R			<0.0063
Farmed salmon *Salmo salar*	Muscle	Faroe Islands			M or R			<0.0063
Salmon, halibut, seal, whale	?	Nuuk, Greenland						
Atlantic cod *Gadus morhua*	Liver	Lofoten, Norway			M±SD			
Greenland halibut, haddock, lumpfish, mackerel, saithe[a]	Liver, Roe, Sperm	Iceland	2011					
Common eider	Liver?	Sklinna, Røst (Norway)			Med.			<MDL
Shag	Liver?	Toppskarv, Sklinna, Røst (Norway)			Med.			0.012
Herring gull	Liver?	Gråmåke, Sklinna, Røst (Norway)			Med.			0.006
Eider	Egg	N. Norway		10	M±SD			<MDL
Herring gull	Egg	N. Norway		10	M±SD			<MDL
Ivory gull	Egg	Station Nord	2010	10	M (R)			
	Egg	Svenskøya	2007	10	M (R)			
	Egg	Nagurskoe	2006	6	M (R)			
	Egg	Cape Klyuv	2006	7	M (R)			
	Egg	Domashny	2006	12	M (R)			
Black-legged kittiwake	Plasma, female	Kongsfjorden, Svalbard	2012	10	AM±SD	<0.03	<0.03	<0.03
	Plasma, male	Kongsfjorden, Svalbard	2012	10	AM±SD	<0.03	<0.03	<0.03
Northern fulmar	Liver	Cape Vera	2003	10	AM±SD			
	Liver	Prince Leopold Is.	2003	10	AM±SD			
Thick-billed murre	Liver	Coats Is.	2007-08	5	AM±SD			0.15±0.09
	Liver	Digges Is.	2007-08	10	AM±SD			0.07±0.03
	Liver	Akpatok Is.	2007-08	10	AM±SD			0.03±0.03
	Liver	Minarets	2007-08	10	AM±SD			0.11±0.05
	Liver	Prince Leopold Is.	2007-08	10	AM±SD			0.01±0.01
Northern fulmar	Liver	Minarets	2007-08	10	AM±SD			0.07±0.05
	Liver	Prince Leopold Is.	2007-08	10	AM±SD			0.10±0.04

Table A2.1/6 cont.

PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	Data source
	0.09±0.01	0.14	0.13	0.43	0.11	0.40	ND	(1)
	NA	NA	NA	NA	NA	NA	NA	(1)
<0.05	0.05	<0.06-0.14	0.03	0.05	<0.03	0.02		(2), (3)
<0.01-0.09	0.14	<0.2-0.33	<0.03-0.05	0.04	<0.01	<0.03		(2), (3)
0.27	0.12	0.09	0.06	0.23	0.1	0.09		(2), (3)
<0.06-0.40	0.36	<0.09-1.3	0.18	0.3	0.1	<0.04-0.28		(2), (3)
1.6	0.3	0.64	0.19	0.48	0.23	<0.03		(2), (3)
ND	ND	ND	0.3-0.5	ND-0.6	0.1-0.2			(4)
	ND	0.19	ND					(5)
ND	ND	0.08	0.07	0.38	0.08	0.49	ND	(6)
	0.105	<0.035	<0.027	<0.024				(7)
	<0.1-0.12	<0.035	<0.027	<0.024				(7)
	<0.1	<0.035	<0.027	<0.024				(7)
	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL		(8)
	0.09±0.01	0.14	0.13	0.43	0.11	0.40	ND	(9)
								(10)
<MDL	0.425	2.92	0.666	1.95	0.558	1.81	0.322	(11)
0.015	0.468	0.979	0.493	2.525	0.827	2.55	0.438	(11)
0.02	0.369	0.972	1.010	3.475	0.907	2.87	0.362	(11)
<MDL	1.62	3.61	0.59	1.23	0.36	0.98	0.11	(1)
<MDL	0.18	1.55	2.27	8.78	1.85	8.32	0.54	(1)
	1.33 (0.98–1.89)	4.89 (3.32–6.47)						(12)
	<0.05	1.04 (0.40-2.70)	2.41 (0.85-4.35)	12.6 (3.16-19.1)	3.44 (0.94-4.09)	10.7 (2.7-17.7)	0.78 (nd-1.37)	(13)
	0.3 (nd-0.40)	1.34 (0.77-1.48)	3.11 (1.42-5.63)	12.9 (5.82-24.7)	2.29 (1.04-5.71)	8.21 (4.80-19.8)	1.07 (0.80-2.46)	(13)
	0.23 (nd-0.31)	0.99 (0.65-1.21)	3.36 (1.10-4.43)	11.7 (4.66-17.6)	2.12 (0.89-3.98)	7.86 (3.54-15.9)	0.97 (0.31-2.61)	(13)
	0.22 (nd-0.37)	1.49 (0.83-2.15)	3.5 (1.21-5.61)	10.7 (4.84-20.8)	1.51 (0.87-3.65)	5.67 (3.43-13.2)	0.77 (0.43-1.72)	(13)
<0.03	<0.027-0.122	0.97±0.70	1.71±0.46	10.45±2.64	2.19±0.709	12.96±7.33	1.17±0.84	(14)
<0.03	<0.027-0.167	1.24±0.55	2.16±0.53	11.4±2.81	2.66±0.662	18.16±4.02	1.80±0.53	(14)
0.34±1.01	0.52±0.59	1.8±2.22	0.3±0.56	1.25±0.89	1.92±3.43	1.15±0.58	0.97±1.16	(15)
0.01±0.02	1.33±0.52	0.32±0.57	0.33±0.66	0.73±0.66	0.12±0.24	0.97±0.67	0.12±0.23	(15)
0.06±0.04	<0.1	0.30±0.27	0.17±0.17	3.94±0.38	0.25±0.15	0.91±0.38	<0.1	(16)
<0.1	0.01 0.01	0.20±0.05	0.07±0.05	0.64±0.15	<0.1	0.12±0.10	<0.1	(16)
<0.1	0.09±0.09	0.14±0.09	0.11±0.06	0.23±0.08	<0.1	<0.1	<0.1	(16)
0.04±0.02	0.03±0.02	0.30±0.15	0.14±0.08	1.67±0.19	0.09±0.05	0.19±0.13	<0.1	(16)
<0.1	0.02±0.02	0.54±0.13	0.27±0.09	1.13±0.16	<0.1	0.01±0.01	<0.1	(16)
0.04±0.03	0.13±0.06	0.54±0.19	0.33±0.15	2.72±1.09	0.15±0.15	0.96±0.57	<0.1	(16)
<0.1	<0.1	0.36±0.11	0.34±0.07	0.92±0.18	<0.1	0.12±0.08	0.01 0.01	(16)

Table A2.1/6 cont.

	Tissue	Area	Year(s)	No. samples	Statistic	PFPeDA	PFHxDA	PFBS
Cod	Liver	N. Norway		10	M±SD			
Mussel	Pooled	N. Norway		3	M±SD			
Sediment		E. Hudson Bay		9	GM			<0.02
Macroalgae		E. Hudson Bay		6	GM			<0.04
Capelin	Whole body	E. Hudson Bay		5	GM			<0.06
Cod	Muscle	E. Hudson Bay		3	GM			<0.08
Salmon	Muscle	E. Hudson Bay		6	GM			<0.2
Polar cod *Boreogadus saida*	Whole fish, pooled	Beaufort Sea			M or R			
	Liver	Barents Sea			M or R			
Halibut *Hippoglossus hippoglossus*	Muscle	N. Norway	2008-12		M or R		ND	ND
Atlantic cod *Gadus morhua*	Muscle	Faroe Islands			M or R			<0.011
Saithe *Pollachius virens*	Muscle	Faroe Islands			M or R			<0.011
Farmed salmon *Salmo salar*	Muscle	Faroe Islands			M or R			<0.011
Salmon, halibut, seal, whale	Muscle, Meat	Nuuk, Greenland						
Atlantic cod *Gadus morhua*	Liver	Lofoten, Norway			M±SD			
Greenland halibut, haddock, lumpfish, mackerel, saithe[a]	Liver, Roe, Sperm	Iceland	2011					
Common eider	Liver?	Sklinna, Røst (Norway)			Med.		0.416	
Shag	Liver?	Toppskarv, Sklinna, Røst (Norway)			Med.		0.326	
Herring gull	Liver?	Gråmåke, Sklinna, Røst (Norway)			Med.		0.336	
Eider	Egg	N. Norway		10	M±SD		<MDL	
Herring gull	Egg	N. Norway		10	M±SD		<MDL	
Ivory gull	Egg	Station Nord	2010	10	M (R)			
	Egg	Svenskøya	2007	10	M (R)	0.58 (0.14-1.0)		
	Egg	Nagurskoe	2006	6	M (R)	1.19 (0.85-3.50)		
	Egg	Cape Klyuv	2006	7	M (R)	0.91 (0.53-3.07)		
	Egg	Domashny	2006	12	M (R)	0.76 (0.48-1.69)		
Black-legged kittiwake	Plasma, female	Kongsfjorden, Svalbard	2012	10	AM±SD			<0.03
	Plasma, male	Kongsfjorden, Svalbard	2012	10	AM±SD			<0.03
Northern fulmar	Liver	Cape Vera	2003	10	AM±SD	0.33±0.35		<0.01
	Liver	Prince Leopold Is.	2003	10	AM±SD	0.31±0.38		<0.01
Thick-billed murre	Liver	Coats Is.	2007-08	5	AM±SD			0.65±0.40
	Liver	Digges Is.	2007-08	10	AM±SD			0.07±0.04
	Liver	Akpatok Is.	2007-08	10	AM±SD			0.02±0.02
	Liver	Minarets	2007-08	10	AM±SD			0.52±0.19
	Liver	Prince Leopold Is.	2007-08	10	AM±SD			0.07±0.03
Northern fulmar	Liver	Minarets	2007-08	10	AM±SD			0.27±0.11
	Liver	Prince Leopold Is.	2007-08	10	AM±SD			<0.1

Table A2.1/6 cont.

PFHxS	PFOS (linear)	PFDS	PFDoS	PFOS (branched)	PFOSA	6:2FTS	F-53B	Data source
			ND	0.59		ND		(1)
			NA	NA		NA		(1)
<0.03		<0.04		<0.04	<0.01-0.04			(2), (3)
<0.04		<0.02		<0.02-0.21	<0.02			(2), (3)
<0.07		<0.03		<0.1	0.74			(2), (3)
<0.09-3.5		<0.04		0.82	1.5			(2), (3)
<0.2		<0.08		<0.3-1.3	0.65			(2), (3)
		ND	ND					(4)
0.04	2.02					ND		(5)
ND	0.95	ND		0.07	ND			(6)
	0.038							(7)
	0.037							(7)
	<0.004.1							(7)
								(8)
		ND		0.59		ND		(9)
								(10)
0.848	0.15	10.065		13.3	0.050	<0.001		(11)
0.666	0.071	11.6		13.95	0.276	<0.001		(11)
0.518	0.130	21.45	0.038	24.35	0.015	<0.001		(11)
			0.21	10.1		ND		(1)
			0.3	48.2		ND		(1)
				25.8 (10.9–60.8)				(12)
0.37 (0.19-1.46)		0.22 (nd-0.76)		79.2 (24.2-113)	0.05 (0.03-0.20)	<0.1		(13)
0.77 (0.30-1.38)		0.62 (0.25-1.27)		59.1 (25.2-89.9)	<0.05	0.25 (0.22-0.32)		(13)
0.69 (0.24-1.31)		0.86 (0.28-1.32)		66.1 (20.9-97.3)	<0.05	0.28 (0.23-0.37)		(13)
0.79 (0.30-1.90)		0.68 (0.21-1.80)		57.7 (17.7-117)	<0.05	0.37 (0.27-0.47)		(13)
<0.011 - 0.22]	9.30±2.61							(14)
<0.011 - 0.130]	10.23±2.69							(14)
<0.01		<0.01		1.74±1.39	0.04±0.02			(15)
<0.01		<0.01		1.59±0.69	<0.05			(15)
0.29±0.15		0.23±0.17		104±30.4				(16)
0.02±0.02		1.27±0.22		113±30.6				(16)
0.40±0.34		1.36±0.16		230±40.9				(16)
0.13±0.07		0.35±0.15		120±36.4				(16)
0.47±0.17		0.60±0.16		289±87.9				(16)
0.22±0.13		0.40±0.17		349±105				(16)
0.25±0.09		0.24±0.16		657±118				(16)

Table A2.1/6 cont.

	Tissue	Area	Year(s)	No. samples	Statistic	PFBA	PFPA	PFHxA
Narwhal	Skin/ blubber	Nuuk, Greenland			M±SD			<MDL
	Muscle	Nuuk, Greenland			M±SD			
Beluga, female	Blood	E. Hudson Bay		9	GM			
	Muscle	E. Hudson Bay		9	GM			
	Liver	E. Hudson Bay		9	GM			
	Milk	E. Hudson Bay		6	GM			
Beluga, male	Blood	E. Hudson Bay		9	GM			
	Muscle	E. Hudson Bay		9	GM			
	Liver	E. Hudson Bay		13	GM			
	Blubber	E. Hudson Bay		6	GM			
Beluga	Liver	Cook Inlet (SE Alaska)	2001-06		AM±SD			
	Liver	E. Chukchi Sea	1999-2000		AM±SD			
Ringed seal	Liver	Arviat	2010-2012	28	AM±SD			0.11±0.10
	Liver	Pangnirtung	2009-2011	7	AM±SD			0.03±0.07
	Liver	Resolute	2010-2013	46	AM±SD			0.05±0.04
	Liver	Sachs Harbour	2011-2013	29	AM±SD			0.11±0.13
	Liver	Ulukhaktok	2010-2013	9	AM±SD			0.22±0.02
	Liver	Qeqertarsuaq, West Greenland	2010.00	19	AM±SD			
	liver	Ittoqqortoormiit, East Greenland	2010.00	16	AM±SD			
Ringed seal	Liver	NW Greenland	1984		4-5 PI, 3 CS		<0.03	<0.04
	Liver	NW Greenland	1998		4-5 PI, 3 CS		<0.03	<0.05
	Liver	NW Greenland	2006		4-5 PI, 3 CS		<0.03	<0.04
	Liver	East Greenland	2012-13		AM±SD			
	Muscle	Nuuk, Greenland			M±SD			<MDL
Harbour seal *hoca vitulina*	Liver	N. Norway		10	M±SD			
Harbour seal, male	Plasma	Svalbard (Karls Forland)	2009–2010					<0.02–0.04
Harbour seal, female	Plasma	Svalbard (Karls Forland)	2009–2010					<0.02–0.04
Harbour seal, juvenile	Plasma	Svalbard (Karls Forland)	2009–2010					<0.02–0.04
Hooded seal, female	Liver	West Ice	1990		4-5 PI, 3 CS		<0.03	<0.04
	Liver	West Ice	1991		4-5 PI, 3 CS		<0.03	<0.04
Pilot whale, male	Liver	Faroe Islands	1986		3-5 PI, 3 CS		<0.08	<0.04
	Liver	Faroe Islands	2001-02		3-5 PI, 3 CS		<0.03	<0.04
	Liver	Faroe Islands	2006-07		3-5 PI, 3 CS		<0.03	<0.04
Whitesided dolphin, male	Liver	Faroe Islands	2001-02		3-5 PI, 3 CS		<0.04	<0.04
	Liver	Faroe Islands	2006		3-5 PI, 3 CS		<0.02	<0.04
Harbor porpoise, male	Liver	W Iceland	1992		5 PI, 3 CS		<0.02	<0.07
	Liver	W Iceland	1997		5 PI, 3 CS		<0.02	<0.07

Table A2.1/6 cont.

PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	Data source
<MDL	<MDL	<MDL	0.2±0.1	1.1±0.4	<MDL	0.8±0.4	<MDL	(17)
<MDL	<MDL	<MDL	<MDL	0.9±0.2	<MDL	0.8±1.7	<MDL–2.6	(17)
<0.1	0.6	0.82	1.5	2.39	1.32	0.42		(2), (3)
<0.07	<0.03	<0.02	<0.09	<0.38	<0.9	<0.1		(2), (3)
<0.05-0.47	0.54	2.13	6.15	12.3	3.07	0.92		(2), (3)
0.19	0.57	1.16	0.59	1.52	0.39	0.25		(2), (3)
0.27	1.03		1.52	3.96	0.8	0.31		(2), (3)
<0.07	<0.03	<0.02	<0.09	<0.38	<0.9	<0.1		(2), (3)
0.25	0.46	2.05	6.3	11.5	2.47	0.8		(2), (3)
<0.1	1.52	<0.9	<0.01- 0.23	<0.08-0.13	<0.1	<0.6		(2), (3)
		3.13±1.696	3.61±1.603	23.67±8.724	3.29±1.215	30.41±26.154	6.32±7.908	(18)
		1.44±1.21	3.53±3.252	12.09±11.393	1.59±1.316	5.84±5.135	2.33±2.351	(18)
0.23±0.25	0.62±0.6	6.1±3.5	3.16±1.74	8.3±4.6	1.3±0.88	2.8±2.0	0.44±0.4	(19)
0.02±0.01	0.22±0.15	6.0±6.2	3.17±3.53	4.5±4.8	0.44±0.34	0.44±0.17	0.12±0.02	(19)
0.02±0.02	0.23±0.16	4.4±2.6	2.07±1.14	2.6±1.3	0.46±0.19	0.71±0.39	0.12±0.06	(19)
0.05±0.02	0.54±0.36	8.9±3.5	3.9±1.6	7.2±3.1	0.91±0.37	1.3±0.58	0.23±0.07	(19)
0.56±0.04	1.4±0.11	12±4.4	5.6±2.3	8.5±3.6	1.6±0.48	2.4±0.56	0.69±0.15	(19)
	<MDL	2.0±1.9	2.2±0.9	8.5±2.9				(20)
	<MDL	7.6±6.0	8.4±2.5	19.9±5.5				(20)
<0.03	<0.2	0.5-0.8	1.4-1.7	1.0-1.3	0.2-0.4	0.3-0.5		(21)
<0.03	<0.2-0.1	3.3-4.0	3.1-3.8	3.3-4.1	0.5-0.6	0.1-0.7		(21)
<0.03	<0.1-0.1	7.3-15.4	6.4-9.1	7.7-10	1.1-1.7	0.3-0.4		(21)
<0.03–0.071	0.56±0.15	11±1	9.4±0.5	18±1	2.3±0.1	1.3±0.1	0.24±0.02	(22)
<MDL–0.1	0.1–0.2		0.4–0.5	1.6–3.0	0.4–0.6	0.5–1.2	<MDL	(17)
	0.80±0.80	4.43	3.28	6.88	0.83	2.86	ND	(1)
0.03 (0.01–0.04)	0.8 (0.45–1.75)	4.3 (3.6–7.4)	3.9 (3.2–4.2)	10 (8.8–11)	1.3 (1–1.4)	2.9 (2.7–3.2)	0.24 (0.15–0.36)	(23)
0.02 (0–0.02)	0.58 (0.31–0.78)	4 (2.6–5)	3.1 (2.1–4.2)	8.3 (6.7–11)	1.1 (0.8–1.3)	2.2 (1.5–3.2)	0.14 (0.08–0.19)	(23)
0.01 (0–0.01)	0.59 (0.5–0.86)	4.5 (3.4–7.8)	3.7 (2.4–4.1)	9.4 (6.6–10)	1.1 (0.8–1.4)	2.2 (2.1–2.8)	0.12 (0.1–0.19)	(23)
<0.03	0.1-0.2	2.8-4.0	2.4-4.7	12-20	3.0-3.1	21-22		(21)
<0.03	0.2-0.3	4.0-7.0	3.9-6.1	15-22	2.5-3.0	6.5-15		(21)
<0.03	<0.2-0.2	1.3-1.5	2.8-3.9	11-16	3.0-3.9	4.3-8.8		(21)
<0.03	0.2-0.4	2.4-8.8	5.0-16	23-52	6.1-11	15-29		(21)
<0.03	0.2-0.3	5.5-8.3	11-12	46-52	9.4-11	22-49		(21)
<0.03	0.1-0.2	1.4-2.5	6.8-10	22-37	4.2-6.0	13-18		(21)
<0.03	<0.2-0.3	1.3-5.5	11-18	45-68	6.6-10	16-26		(21)
<0.03	<0.2	0.4-0.7	3.9-4.6	22-27	3.5-3.7	2.8-5.4		(21)
<0.03	<0.2	1.3-1.9	3.2-5.4	16-24	2.8-3.7	4.0-5.4		(21)

Table A2.1/6 cont.

	Tissue	Area	Year(s)	No. samples	Statistic	PFPeDA	PFHxDA	PFBS
Narwhal	Skin/ blubber	Nuuk, Greenland			M±SD			
	Muscle	Nuuk, Greenland			M±SD			
Beluga, female	Blood	E. Hudson Bay		9	GM			<0.2
	Muscle	E. Hudson Bay		9	GM			<0.3
	Liver	E. Hudson Bay		9	GM			<0.1
	Milk	E. Hudson Bay		6	GM			<0.1
Beluga, male	Blood	E. Hudson Bay		9	GM			<0.2
	Muscle	E. Hudson Bay		9	GM			<0.3
	Liver	E. Hudson Bay		13	GM			<0.1
	Blubber	E. Hudson Bay		6	GM			<0.1
Beluga	Liver	Cook Inlet (SE Alaska)	2001-06		AM±SD			
	Liver	E. Chukchi Sea	1999-2000		AM±SD			
Ringed seal	Liver	Arviat	2010-2012	28	AM±SD		<0.01	0.18±0.26
	Liver	Pangnirtung	2009-2011	7	AM±SD		<0.01	0.01±0.02
	Liver	Resolute	2010-2013	46	AM±SD		<0.01	0.08±0.11
	Liver	Sachs Harbour	2011-2013	29	AM±SD		0.02±0.01	0.07±0.1
	Liver	Ulukhaktok	2010-2013	9	AM±SD		<0.01	0.22±0.33
	Liver	Qeqertarsuaq, West Greenland	2010.00	19	AM±SD			
	liver	Ittoqqortoormiit, East Greenland	2010.00	16	AM±SD			
Ringed seal	Liver	NW Greenland	1984		4-5 PI, 3 CS			<0.02
	Liver	NW Greenland	1998		4-5 PI, 3 CS			<0.02
	Liver	NW Greenland	2006		4-5 PI, 3 CS			<0.02
	Liver	East Greenland	2012-13		AM±SD		0.16±0.02	<0.002b
	Muscle	Nuuk, Greenland			M±SD			
Harbour seal *hoca vitulina*	Liver	N. Norway		10	M±SD			
Harbour seal, male	Plasma	Svalbard (Karls Forland)	2009–2010					<0.001
Harbour seal, female	Plasma	Svalbard (Karls Forland)	2009–2010					<0.001
Harbour seal, juvenile	Plasma	Svalbard (Karls Forland)	2009–2010					<0.001
Hooded seal, female	Liver	West Ice	1990		4-5 PI, 3 CS			<0.02
	Liver	West Ice	1991		4-5 PI, 3 CS			<0.03
Pilot whale, male	Liver	Faroe Islands	1986		3-5 PI, 3 CS			<0.02
	Liver	Faroe Islands	2001-02		3-5 PI, 3 CS			<0.02
	Liver	Faroe Islands	2006-07		3-5 PI, 3 CS			<0.02
Whitesided dolphin, male	Liver	Faroe Islands	2001-02		3-5 PI, 3 CS			<0.02
	Liver	Faroe Islands	2006		3-5 PI, 3 CS			<0.03
Harbor porpoise, male	Liver	W Iceland	1992		5 PI, 3 CS			<0.04
	Liver	W Iceland	1997		5 PI, 3 CS			<0.04

Table A2.1/6 cont.

PFHxS	PFOS (linear)	PFDS	PFDoS	PFOS (branched)	PFOSA	6:2FTS	F-53B	Data source
<MDL		<MDL		1.2±1.0				(8)
<MDL		<MDL		1.5±0.4				(8)
<0.3		<0.1		10.6	65.5			(2), (3)
<0.2		<0.1		<0.06	16.5			(2), (3)
<0.1		<0.1		27.4	43.7			(2), (3)
<0.1		<0.1		2.78	4.3			(2), (3)
<0.3		<0.1		13.7	78.2			(2), (3)
<0.2		<0.1		1.18	11.4			(2), (3)
<0.1-3.76		<0.1-5.12		37.3	48.3			(2), (3)
<0.1		<0.1		2.23	2.4			(2), (3)
0.46±0.33				25.51±16.637	17.37±7.37			(18)
0.15±0.073				13.43±8.821	34.05±15.24			(18)
0.28±0.21		0.06±0.09		20±7.2	0.06±0.09			(19)
0.27±0.19		<0.01		16±16	0±0			(19)
0.21±0.14		0.02±0.04		6.6±4.2	0.02±0.04			(19)
0.2±0.09		0.01±0.01		12±6.5	0.01±0.01			(19)
0.54±0.06		0.04±0.12		18±8.8	0.04±0.12			(19)
<MDL				16.3±10.0	<MDL			(20)
<MDL				112±37.2	<MDL			(20)
0.1	44-59	<0.02						(21)
0.1-0.2	39-62	<0.02						(21)
0.7	51-87	<0.02						(21)
0.71±0.06	85±5	0.27±0.19		93±6	0.027±0.007		0.045±0.004	(22)
0.2–0.6		<MDL–0.2		5.9–10.2				(17)
			0.11	66.3		0.03±0.04		(1)
1.8 (1.6–2.4)			<0.02	43 (40–52)	<0.05			(23)
1.4 (1.3–2.3)			<0.02	35 (25–39)	<0.05			(23)
2.3 (2.1–3.2)			<0.02–0.22	38 (27–46)	<0.05			(23)
0.1-0.2	58-95	0.1-0.2						(21)
0.2	35-47	0.1-0.2						(21)
0.1-0.2	24-29	0.1						(21)
0.3	51-76	0.3-0.9						(21)
0.2-0.5	40-55	0.4-0.8						(21)
0.3-0.4	95-126	0.5-1.9						(21)
0.4-0.6	104-126	1.3-2.1						(21)
0.1-0.2	38-57	<0.02-0.1						(21)
0.3-0.5	30-67	<0.03-0.2						(21)

Table A2.1/6 cont.

	Tissue	Area	Year(s)	No. samples	Statistic	PFBA	PFPA	PFHxA
Minke whale, female	Liver	CW Greenland	1998		4 PI, 3 CS		<0.04	<0.04
Fin whale, male	Muscle	W Iceland	1986-89		3-5 PI, 3 CS		<0.02	<0.04
	Muscle	W Iceland	2009		3-5 PI, 3 CS		<0.02	<0.04
Killer whale	Liver	East Greenland	2012-13		AM±SD			
Polar bear	Liver	East Greenland	2012-13		AM±SD			
	Plasma, maternal	Svalbard	2008			<MDL	<MDL	<MDL
	Plasma, cub	Svalbard	2008			<MDL	<MDL	<MDL
	Liver	Scoresby Sound, East Greenland	2006	19	AM±SD			18.5±0.6
	Blood	Scoresby Sound, East Greenland	2006	19	AM±SD			nd
	Brain	Scoresby Sound, East Greenland	2006	115	AM±SD			nd
	Muscle	Scoresby Sound, East Greenland	2006	20	AM±SD			0.27±0.05
	Adipose	Scoresby Sound, East Greenland	2006	20	AM±SD			nd
	Liver	Ittoqqortoormiit, East Greenland	2011	10	AM±SD			
Arctic cod		Coats Is., N. Hudson Bay	2007		M (R)			<0.1
Capelin		Coats Is., N. Hudson Bay	2007-08		M (R)			<0.1
Sand lance		Coats Is., N. Hudson Bay	2007		M (R)			<0.1
Arctic shanny		Coats Is., N. Hudson Bay	2007		M (R)			<0.1
Daubed shanny		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Banded gunnel		Coats Is., N. Hudson Bay	2009		M (R)			0.37
Fish doctor		Coats Is., N. Hudson Bay	2007, 2009		M (R)			<0.1
Fourline snake blenny		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Sculpin *Triglops* spp.		Coats Is., N. Hudson Bay	2007, 2009		M (R)			<0.1
Arctic staghorn sculpin		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Snailfish		Coats Is., N. Hudson Bay	2009		M (R)			<0.1

Table A2.1/6 cont.

PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	Data source
<0.03	0.1-0.2	0.6-2.7	2.7-11	9.5-14	1.4-1.7	1.8-4.6		(21)
<0.03	<0.2	<0.05	<0.02-0.1	0.03-0.2	0.1	0.2-0.3		(21)
<0.03	<0.2	<0.05-0.1	<0.02-0.1	0.2-0.7	0.1-0.2	0.5-0.7		(21)
0.16±0.07	0.27±0.09	12±6	24±10	67±23	12±4	15±3	4.8±1.3	(22)
0.74±0.16	13±2	250±30	96±10	122±13	13±2	8.5±1.1	1.5±0.2	(22)
0.4±0.2	4.1±0.3	38.1±3.6	11.9±1.8	28.3±4.3	3.3±0.5	5.8±0.9	0.6±0.03	(24)
1.1±0.2	2.3±0.2	5.6±0.5	1.9±0.2	8.4±1	1.3±0.4	2.5±0.3	<MDL	(24)
8.39±1.36	39.2±3.4	497±44	184±17	276±24	41.5±3.3	82.1±7.2	18.0±0.7	(25)
0.50±0.06	3.53±0.31	17.8±1.6	7.05±0.79	21.8±2.6	5.16±0.57	14.3±1.5	2.66±0.14	(25)
nd	0.27±0.06	1.87±0.14	2.12±0.13	16.0±0.7	7.21±0.33	31.4±1.5	7.45±0.34	(25)
0.19±0.02	0.42±0.05	1.99±0.18	1.00±0.10	3.67±0.37	0.98±0.08	2.96±0.23	1.56±0.22	(25)
nd	0.42±0.10	1.57±0.23	0.74±0.14	3.07±0.45	0.84±0.13	3.05±0.34	1.32±0.15	(25)
	4.8±2.7	174±81.5	48.5±20.0	71.8±36.9				(20)
<0.1	<0.1	0.16	<0.1	0.68	<0.1	0.55	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.26	<0.1	0.14	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.6	<0.1	0.3	<0.1	(16)
<0.1	<0.2	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.18	<0.1	<0.1	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.43	<0.1	0.18	<0.1	(16)
<0.1	<0.1	0.18	<0.1	0.19	<0.1	0.17	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.14	<0.1	<0.1	<0.1	(16)
<0.1	<0.1	0.2	<0.1	0.5	<0.1	0.55	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.19	<0.1	<0.1	<0.1	(16)
<0.1	<0.1	<0.1	<0.1	0.42	<0.1	<0.1	<0.1	(16)

Table A2.1/6 cont.

	Tissue	Area	Year(s)	No. samples	Statistic	PFPeDA	PFHxDA	PFBS
Minke whale, female	Liver	CW Greenland	1998		4 PI, 3 CS			<0.04
Fin whale, male	Muscle	W Iceland	1986-89		3-5 PI, 3 CS			<0.02
	Muscle	W Iceland	2009		3-5 PI, 3 CS			<0.02
Killer whale	Liver	East Greenland	2012-13		AM±SD		3.4±0.7	0.005±0.002
Polar bear	Liver	East Greenland	2012-13		AM±SD		0.72±0.09	0.032±0.008
	Plasma, maternal	Svalbard	2008					<MDL
	Plasma, cub	Svalbard	2008					<MDL
	Liver	Scoresby Sound, East Greenland	2006	19	AM±SD		0.81±0.08	
	Blood	Scoresby Sound, East Greenland	2006	19	AM±SD		1.35±0.13	
	Brain	Scoresby Sound, East Greenland	2006	115	AM±SD		10.4±0.5	
	Muscle	Scoresby Sound, East Greenland	2006	20	AM±SD		0.65±0.07	
	Adipose	Scoresby Sound, East Greenland	2006	20	AM±SD		0.57±0.07	
	Liver	Ittoqqortoormiit, East Greenland	2011	10	AM±SD			
Arctic cod		Coats Is., N. Hudson Bay	2007		M (R)			<0.1
Capelin		Coats Is., N. Hudson Bay	2007-08		M (R)			<0.1
Sand lance		Coats Is., N. Hudson Bay	2007		M (R)			<0.1
Arctic shanny		Coats Is., N. Hudson Bay	2007		M (R)			<0.1
Daubed shanny		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Banded gunnel		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Fish doctor		Coats Is., N. Hudson Bay	2007, 2009		M (R)			<0.1
Fourline snake blenny		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Sculpin *Triglops* spp.		Coats Is., N. Hudson Bay	2007, 2009		M (R)			<0.1
Arctic staghorn sculpin		Coats Is., N. Hudson Bay	2009		M (R)			<0.1
Snailfish		Coats Is., N. Hudson Bay	2009		M (R)			<0.1

[a]No PFAS >MDL in fish. PFOS only compound >MDL in fish liver, roes and sperm.

M: mean, GM: geometric mean, AM: arithmetic mean, Med.: Median, R: range, PI: pooled individuals, CS: composite samples

Data source: (1) NILU, 2013; (2) Kelly et al., 2009; (3) Muir et al., 2013b; (4) Powley et al., 2008; (5) Haukås et al., 2007; (6) Carlsson et al., 2016; (7) Eriksson et al., 2013; (8) Carlsson et al., 2014; (9) NILU, 2014; (10) Jörundsdottir et al., 2012; (11) NILU ORB, 2014; (12) Lucia et al., 2015; (13) Miljeteig et al., 2009; (14) Tartu et al., 2014; (15) Braune et al., 2010; (16) Braune et al., 2014; (17) Carlsson et al., 2014; (18) Reiner et al., 2011; (19) Muir et al., 2014; (20) Riget et al., 2013; (21) Rotander et al., 2012; (22) Gebbink et al., 2016; (23) Routti et al., 2014; (24) Bytingsvik et al., 2012; (25) Greaves et al., 2012.

Table A2.1/6 cont.

PFHxS	PFOS (linear)	PFDS	PFDoS	PFOS (branched)	PFOSA	6:2FTS	F-53B	Data source
0.03-0.3	39-49	0.2-0.6						(21)
<0.03	0.3-0.5	<0.03						(21)
<0.03	0.3-0.5	<0.03						(21)
1.5±0.3	115±40	1.2±0.4		122±42	0.32±0.10		0.023±0.009	(22)
13±2	1597±189	1.5±0.2		1811±218	0.055±0.020		0.27±0.04	(22)
32.6±3.4				309±38.2				(24)
12.2±0.9				65.3±7.4				(24)
30.9±2.1		nd		3270±290	151±32			(25)
18.0±1.1		1.28±0.22		128±17	3.50±0.99			(25)
1.37±0.10		1.30±0.15		35.2±2.0	1.33±0.10			(25)
1.87±0.11		1.40±0.04		15.9±1.7	1.56±0.13			(25)
1.55±0.20		nd		15.4±1.9	0.69±0.10			(25)
5.8±3.8				1061±274	0.5±3.0			(20)
<0.1		1.45 (1.0-2.1)		<3.1				(16)
<0.1		0.11 (nd,1.2)		3.37 (<3.1-23)				(16)
<0.1		0.2		<3.1				(16)
<0.1		0.7		<3.1				(16)
0.16		0.37		6.24				(16)
0.22		0.6		<0.1				(16)
<0.1		<0.1		<0.1				(16)
0.1 (nd,0.21)		<0.1		<0.1				(16)
<0.1		1.45		4.27				(16)
<0.1		<0.1		<3.1				(16)
<0.1		<0.1		<0.1				(16)

2.2 Brominated flame retardants (BFRs)

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Contributor: Crispin Halsall, Tom Harner, Robert Letcher, Jaakko Mannio, Amina Salamova

2.2.1 Introduction

Halogens are effective in capturing free radicals in a combustion process, which hampers the propagation of the flame (Alaee et al., 2003). Hence, halogenated compounds have been widely used as flame retardants and account for about a quarter of the total production of flame retardants. Balancing effectiveness in capturing free radicals and molecule stability at elevated temperatures, only chlorinated and brominated compounds have been used as halogenated flame retardants (Alaee et al., 2003).

Brominated flame retardants (BFRs) cover a large group of chemically diverse compounds, which are additive or reactive substances and part of – or, to a minor extent, bound to – synthetic polymers to delay ignition and thus increase fire safety. The majority of BFRs that are contaminants of emerging concern (CECs) with respect to the Arctic are additive flame retardants. Several BFRs that were previously produced in high volumes, such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs; specifically commercial penta- and octaBDE mixtures) and hexabromocyclododecane (HBCDD) are now globally regulated as they are listed under Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs). Their POP characterization includes an evaluation of long-range transport, for which Arctic data have been of great value. In addition, data from Arctic biota monitoring has provided information on BFR bioaccumulation and biomagnification (de Wit et al., 2010). PBDEs other than decaBDE were addressed in the recent AMAP assessment of temporal trends in POPs (AMAP, 2016a), because these are no longer considered CECs.

The ban on penta- and octaBDE mixtures (added to the Stockholm Convention in 2009), has moved the focus to potential replacement flame retardant products requiring an understanding of their environmental behavior, including in the Arctic. The BFR review of the most recent AMAP assessment included new candidates for which Arctic data were just emerging (de Wit et al., 2010). These included the compounds decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HBBz), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT) and the β-isomer of 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (β-tetrabromocyclohexane, β-TBECH, or β-DBE-DBCH). As of 2009, BTBPE, HBBz, PBEB and PBT had been detected in seabirds, while BTBPE, HBBz and β-DBE-DBCH had been detected in marine mammals, thus providing initial evidence of their long-range transport and accumulation in Arctic biota (de Wit et al., 2010).

The current AMAP assessment reviews the Arctic data that have been published on these and other 'emerging' BFRs between 2009 and the end of 2014. In addition to the compounds just listed, this assessment covers BDE-209 (deca-BDE), HBCDD, tetrabromobisphenol A (TBBPA), 2,4,6-tribromophenyl 2,3-dibromopropyl ether (TBP-DBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)tetrabromo phthalate (BEH-TEBP), 2,3,5,6-tetrabromo-p-xylene (TBX) and pentabromobenzene (PBBz) and related compounds

Table 2.4 Standardized abbreviations adopted for brominated flame retardants referred to in this chapter, as suggested by Bergman et al. (2012).

Standardized abbreviation	CAS number	Chemical name	Other abbreviations commonly used in literature
BDE-209	1163-19-5	polybrominated diphenyl ether 209	DecaBDE, BDE209
BEH-TEBP	26040-51-7	bis(2-ethylhexyl)tetrabromophthalate	TBPH
BTBPE	37853-59-1	1,2-bis(2,4,6-tribromophenoxy)ethane	
DBDPE	84852-53-9	decabromodiphenyl ethane	BDPE-209, DBDE
DBE-DBCH	3322-93-8	1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane	TBECH, TEBC
EH-TBB	183658-27-7	2-ethylhexyl-2,3,4,5-tetrabromobenzoate	TBB
HBBz	87-82-1	hexabromobenzene	HxBBz, HxBrBz
HBCDD	3194-55-6	hexabromocyclododecane	HBCD
OBTMPI	1084889-51-9	octabromotrimethylphenylindane	OBIND
PBB-Acr	59447-55-1	pentabromobenzyl acrylate	PBBA
PBBz	608-90-2	pentabromobenzene	PeBBZ
PBEB	85-22-3	pentabromoethylbenzene	
PBT	87-83-2	pentabromotoluene	
TBBPA	79-94-7	tetrabromobisphenol A	
TBBz	626-39-1	1,3,5-tribromobenzene	TeBBz
TBCT	39569-21-6	tetrabromo-*o*-chlorotoluene	
TBP-AE	3278-89-5	2,4,6-tribromophenyl allyl ether	ATE
TBP-BAE	N/A	2,4,6-tribromophenyl 2-bromoallyl ether	BATE
TBP-DBPE	35109-60-5	2,4,6-tribromophenyl 2,3-dibromopropyl ether	DPTE
TBX	23488-38-2	2,3,5,6-tetrabromo-*p*-xylene	

Table 2.5 Summary of Arctic media for which brominated flame retardants have been reported between 2009 and the end of 2014. The brackets indicate that the compound was sought, but not detected in the respective medium.

	Air		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
BDE-209	×	×		(×)	(×)			×	×	×
BEH-TEBP	×			(×)			×			×
BTBPE	×	×		×			×	×		×
DBDPE	×	×		(×)		(×)	(×)		×	×
DBE-DBCH	×	×					(×)			×
EH-TBB	×			×			×			×
HBBz	×	×		(×)			×	×		×
HBCDD	×	×		(×)	(×)		×			×
OBTMPI	(×)									(×)
PBB-Acr	×									
PBBz	×	×						(×)		(×)
PBEB	×	×		(×)			(×)			×
PBT	×	×		(×)			×	×		×
TBBPA	×						(×)			(×)
TBBz		×								
TBCT	×									(×)
TBP-AE	×						(×)			×
TBP-BAE	×						(×)			×
TBP-DBPE	×						(×)	×		×
TBX	×									×

(Table 2.4). Hydroxy- (OH-) and methoxy- (MeO-) PBDEs are discussed in Section 2.15. BFR data from the Arctic were also recently reviewed by Vorkamp and Rigét (2014). The data in this section cover atmospheric, terrestrial, freshwater and marine environments and originate from peer-reviewed publications, extended conference abstracts and government scientific reports (Table 2.5).

2.2.2 Polybrominated diphenyl ether 209 (BDE-209)

2.2.2.1 Introduction

BDE-209 is the main component of the commercial decaBDE flame retardant mixture (La Guardia et al., 2006). The chemical structure of BDE-209 is given in Figure 2.31. It was added to the Stockholm Convention in 2017. In the EU, BDE-209 is covered by the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive), which restricts the mass percentage of PBDEs to 0.1% in electrical and electronic equipment (EU, 2011). DecaBDE is also included on the candidate list of substances of very high concern (SVHC) of the European Chemicals Agency (ECHA, 2012). The Voluntary Emissions Control Action Programme (VECAP) of the European Flame Retardant Association was initiated in 2004 with a focus on decaBDE in textiles and plastics (EFRA, 2015).

In the most recent AMAP assessment of BFRs in the Arctic (de Wit et al., 2010), BDE-209 concentrations were reported to be increasing in air at Alert, Canada, based on measurements to 2004 (de Wit et al., 2010; Hung et al., 2010). This confirmed atmospheric transport of BDE-209 to the Arctic, probably primarily via association with airborne particles. Deposition in the Arctic environment was reflected by BDE-209 being a predominant PBDE congener in soil and vegetation (de Wit et al., 2010). Results were ambiguous with regard to the accumulation of BDE-209 in biota. While contributing significantly to total PBDE (ΣPBDE) in invertebrates and some fish, BDE-209 had low concentrations in higher trophic level animals, implying low bioaccumulation and biomagnification.

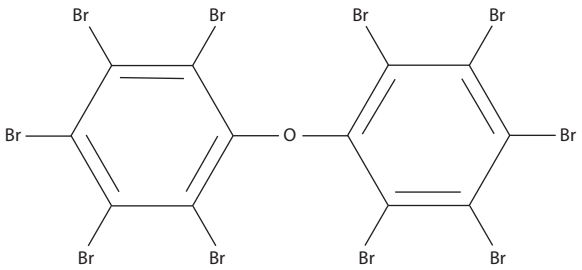


Figure 2.31 Chemical structure of BDE-209.

2.2.2.2 Physical-chemical properties

BDE-209 is very hydrophobic, with several reported log K_{OW} values: 8.70 (Wania and Dugani, 2003), 9.87 (Bao et al., 2011) and 9.97 (Watanabe and Tatsukawa, 1990). BDE-209 has a low volatility and water solubility. It thus adsorbs strongly to organic carbon in sediments and soils and to particulates in air, and partitions to lipids. See Appendix 1 for more detailed information.

2.2.2.3 Sources, production, use and trends

The decaBDE commercial product has been used in hard plastics such as high-impact polystyrene (HIPS) in electrical and electronic devices, such as the back-covers of cathode-ray TV sets and PC monitors (de Wit et al., 2010). It has also been used in textile back-coating in furniture, rubber coating for wiring, and in building, construction and transportation sectors (Abbasi et al., 2015). For the North American market only, Abbasi et al. (2015) calculated a maximum stock of decaBDE of 140 000 tonnes in in-use products in 2008.

Global market demand of decaBDE was about 56 400 tonnes in 2003 (de Wit et al., 2010). Abbasi et al. (2015) estimated total global production to be between 1100 000 and 1250 000 tonnes for the period 1970–2005. They also reported an estimated annual production of 60 000 tonnes by 2005, of which 40% was used in North America. Production has been phased out in North America and Europe, but decaBDE is still manufactured and widely used in China (Ma et al., 2012a; Ni and Lu, 2013). In 2011, production of the decaBDE mixture in China was estimated at 20 500 tonnes (Ni and Lu, 2013). EFRA (2015) reported that two of the three major global producers had stopped selling decaBDE in 2013.

2.2.2.4 Transformation processes

BDE-209 has been shown to degrade to lower brominated BDE congeners via photolysis (e.g. Eriksson et al., 2004; Söderström et al., 2004; Stapleton and Dodder, 2008) and via metabolic debromination (e.g. Kierkegaard et al., 1999, 2007; Stapleton et al., 2003; Van den Steen et al., 2007). In laboratory rats, BDE-209 has been shown to produce several hydroxylated metabolites containing 5–9 bromines (Mörck et al., 2003; Sandholm et al., 2003). In liver microsomes of polar bear (*Ursus maritimus*), beluga (*Delphinapterus leucas*) and ringed seal (*Pusa hispida*), BDE-209 depletion by 14–25% was found, while that of lower brominated congeners was ≤3% (McKinney et al., 2011a). Metabolite identification proved challenging, and no brominated or phenolic metabolites of BDE-209 could be identified.

2.2.2.5 Modeling studies

Breivik et al. (2006) modeled long-range atmospheric transport of BDE-209 on particulates and found that periods of high winds and no precipitation would facilitate transport to the Arctic.

Particle-gas partitioning of BDE-209 in Arctic air was recently addressed in a theoretical approach (Li et al., 2015a). Pointing out that steady state rather than equilibrium states should be applied in these considerations, Li et al. (2015a) showed that BDE-209 was in the maximum partition domain at Arctic temperatures, resulting in a constant partition coefficient (log K_{PSM} of -1.53) and a particle fraction of <1. For a particle concentration of 10 μg/m^3, for example, the particle-phase fraction of BDE-209 was 0.23. Li et al. (2015a) found their predictions agreed well with monitoring data from Alert (Canada) and that the air data reported by Möller et al. (2011b) (see next section), were better described by the steady state model than by the equilibrium model.

2.2.2.6 Environmental concentrations

Air and precipitation

Studies published since the previous AMAP assessments on BFRs (de Wit et al., 2010) have provided more evidence that BDE-209 is an important PBDE congener in abiotic media in the Arctic. BDE-209 has been part of the atmospheric monitoring programs at Alert in the Canadian Arctic and at Zeppelin on Svalbard (Norway) since 2002 and 2006, respectively (Hung et al., 2016). The data measured at Alert until 2010 were reported in the Canadian Arctic Contaminants Assessment Report (Hung et al., 2013a). The data from Zeppelin are published in reports of the Norwegian Institute for Air Research (NILU), the most recent data considered here are for 2014 (NILU, 2015).

At Alert, BDE-209 accounted for 24% of ΣPBDE on average (range 0.66–79%), which is unchanged compared to the previous AMAP assessment of atmospheric monitoring (Hung et al., 2010). While lower brominated PBDE congeners showed a seasonal cycle of higher concentrations in summer than in winter, the correlation with temperature was low for BDE-209. In 2012, concentrations of BDE-209 at Alert ranged from 0.18 to 2.2 pg/m^3, with mean and median concentrations of 0.34 and 0.26 pg/m^3, respectively.

At Zeppelin, concentrations of BDE-209 ranged between 0.10 and 0.67 pg/m^3 in 2012, with mean and median concentrations of 0.30 and 0.25 pg/m^3, respectively (Aas et al., 2013). In 2014, over half the air samples collected at Zeppelin were below detection limit for BDE-209. However, the detection limits were relatively high owing to analytical challenges (NILU, 2015). The highest concentration was 0.80 pg/m^3, while the lowest measurable concentration was 0.34 pg/m^3. In general, concentrations at Zeppelin in 2014 were comparable to those measured during the period 2008–2012. At Pallas in northern Finland, BDE-209 was sought in four air samples from 2009 to 2012 (Kaj et al., 2010; Remberger et al., 2014), but only detected in two: 2011 (0.33 pg/m^3) and 2012 (0.69 pg/m^3) (Remberger et al., 2014). Levels were similar to those measured at Alert and Zeppelin.

BDE-209 was also detected in all air samples collected at Longyearbyen (Svalbard) between September 2012 and May 2013. BDE-209 was only analyzed in the particle phase of these air samples (Salamova et al., 2014). As for the Canadian data, BDE-209 accounted for 24% of ΣPBDE, making it the most abundant PBDE congener. The mean and median concentrations of BDE-209 in the particle phase were 1.3±0.31 and 0.46 pg/m^3, respectively (range 0.12–6.8 pg/m^3). These concentrations appear slightly higher than at Alert and Zeppelin. Salamova et al. (2014) could not rule out that local sources could affect levels of flame retardants at Longyearbyen.

High maximum particle-bound concentrations of BDE-209 (3.43 pg/m^3) were also found on a cruise from the East China Sea to the Arctic (Möller et al., 2011a). Stations at latitudes north of 60°N were considered as Arctic stations. Although mainly detected in the particle phase, BDE-209 was also detected in the gas phase of some samples, at concentrations up to 0.54 pg/m^3. As discussed in Section 2.2.2.5, studies applying a steady state model rather than an equilibrium model have shown that at Arctic temperatures, the majority of BDE-209 might occur in the gas phase (Li et al., 2015a).

BDE-209 was by far the predominant PBDE congener in air in the Bering and Chukchi Sea, accounting for 72% of ΣPBDE, possibly owing to ongoing production and use of commercial decaBDE in Asia (Möller et al., 2011a). Based on data for 2003, about half the global demand for decaBDE occurred in Asia, compared to only 2% of the global demand for pentaBDE (de Wit et al., 2010).

The same study design was applied in a cruise to the East Greenland Sea (Möller et al., 2011b). In these measurements, BDE-209 was not found in the gas phase. In the particle phase, it was only detected in 30% of samples (at 0.05–0.07 pg/m^3). Thus, the results were different to those for Longyearbyen on Svalbard (Salamova et al., 2014). Möller et al. (2011a) discussed the possibility of photolytic degradation of BDE-209 as an explanation for these results.

Atmospheric deposition has been documented by detecting BDE-209 in snow. Snow cores were analyzed from the Devon Ice Cap, Nunavut (Canada) (Meyer et al., 2012). BDE-209 was the main PBDE congener found, accounting for 89% of ΣPBDE. NonaBDE congeners were the second most important congener group, possibly reflecting degradation of BDE-209. This interpretation was supported by correlations between BDE-209 and lower brominated congeners, which were higher with increasing bromine content, as well as by the presence of BDE-201 and BDE-202 in the samples, which are not found in commercial PBDE mixtures (Meyer et al., 2012).

Fluxes determined at the Devon Ice Cap ranged from 90 to 2000 pg/cm^2/y (1993–2008). The mean total flux of BDE-209 to the ice cap was estimated at 7 kg/y. Back trajectories of air masses showed correlations with highly populated areas of North America, which was not the case for other BFRs such as HBCDD (Meyer et al., 2012). Fluxes at the Devon Ice Cap can be compared to those calculated for an ice core at Svalbard (Hermanson et al., 2010). BDE-209 was again the main PBDE congener, and fluxes were 320 pg/cm^2/y between 1995 and 2005, i.e. in the lower end of the range reported for the Devon Ice Cap (Meyer et al., 2012). The input of BDE-209 to the location of the ice core could be traced back to flow from Eurasian sources and was associated with Arctic haze events (Hermanson et al., 2010). Market demand for decaBDE was lower in Europe than in North America (de Wit et al., 2010). Although this is not *per se* equivalent to higher inputs to the Devon Ice Cap, Hermanson et al. (2010) found that the amounts of various BFRs in the Svalbard ice cores were primarily a function of the amounts used in commerce, rather than being determined by vapor pressure or other physical-chemical characteristics of the compounds. The link to particle transport during Arctic haze events discussed in this study is in line with previous findings of BDE-209 being the predominant congener in air in winter, but not in summer (Su et al., 2007). The same pattern is also seen in the monitoring data at Zeppelin, which found the highest concentrations of BDE-47 occur in the summer months, while BDE-209 predominates in other months (Aas et al., 2013). BDE-209 was not detected in two air and deposition samples from Pallas collected in July 2009 and January 2010 (Kaj et al., 2010).

Terrestrial environment

BDE-209 concentrations were below detection limit in a study of bank voles (*Myodes glareolus*) collected in 2001 in Ammarnäs, Vålådalen and Vindeln in northern Sweden (Lind and Odsjö, 2010). Lind (2012) investigated BFRs in Eurasian lynx (*Lynx lynx*), but BDE-209 was below detection limit in a sample from Bydalen in Jämtland (northern Sweden) collected in 2000. BDE-209 was below detection limit in reindeer (*Rangifer tarandus*) muscle from Sweden (Danielsson et al., 2008). As discussed in the previous AMAP assessment (de Wit et al., 2010), BDE-209 was detectable at relatively high (up to 250 ng/g lw) and increasing concentrations in peregrine falcon (*Falco peregrinus*) eggs from Greenland. Although the birds were probably exposed during migration and not necessarily in the Arctic, the results show that some bioaccumulation of BDE-209 can take place. This was supported by studies on peregrine falcon eggs from Sweden and elsewhere (see subsection on marine biota), and could indicate differences in exposure for terrestrial and marine top predators.

Freshwater environment

Surface water samples collected in 2006 from two lakes in northern Sweden – Lake Abiskojaure (background) and Kalixälvens gruvsamhälle (a former mining village, point source) – had no detectable concentrations of BDE-209 (SWECO VIAK, 2007).

Marine environment

Seawater

Seawater samples were analyzed on two cruises, from the East China Sea to the Arctic and in the East Greenland Sea. In agreement with the air samples (see sub-section on air and precipitation), BDE-209 was mainly associated with particles. On the transect from the East China Sea, BDE-209 was below detection limit (0.17 pg/L) in the dissolved phase and ranged from <0.092 to 0.17 pg/L in the particle phase (Möller et al., 2011a). From these data (seawater and air), Möller et al. (2011a) concluded that this indicated atmospheric deposition of BDE-209 to the ocean. In the East Greenland Sea, BDE-209 was only detected in one seawater sample, at concentrations of 0.37 pg/L (dissolved phase) and 0.11 pg/L (particle phase) (Möller et al., 2011b), an unexpected finding given the hydrophobic characteristics of BDE-209.

Sediments

In marine surface sediments sampled in the Bering Sea and Chukchi Sea between July and September 2008, BDE-209 was clearly the predominant PBDE congener, with concentrations 1–2 orders of magnitude higher than summed concentrations of the other PBDEs (Cai et al., 2012b). In Canada Basin, BDE-209 concentrations in sediment were comparable to those for other

Table 2.6 Arithmetic mean and median concentrations (pg/g dw) of BDE-209 and DBDPE in marine surface sediment from three Arctic regions (Cai et al., 2012b).

	Canada Basin			Bering Sea			Chukchi Sea		
	n	Mean	Median	n	Mean	Median	n	Mean	Median
BDE-209	8	39.5	24.7	7	146	15.6	9	141	34.7
DBDPE	8	176	163	7	181	151	9	147	107

PBDEs in total (Cai et al., 2012b). This pattern corresponds to observations by Möller et al. (2011a,b) of higher concentrations of BDE-209 (and a higher contribution to ΣPBDE) in the Bering and Chukchi Sea than in the East Greenland Sea, which is possibly related to the production and use of commercial decaBDE in Asia. Mean concentrations of BDE-209 in the Bering Sea, Chukchi Sea and Canada Basin were much higher than the median concentrations (Table 2.6). Within each area, Cai et al. (2012b) noted a few individual stations with high concentrations of BDE-209 which they assumed were affected by coastal point sources. While there was no correlation with other PBDE congeners, a correlation was found with organic carbon as well as black carbon, which was interpreted as an indication of atmospheric input of BDE-209.

Biota

There is no clear evidence of BDE-209 accumulation in marine biota. A recent study on eggs of white-tailed sea eagle (*Haliaeetus albicilla*) included two samples from Lapland, but all samples (n=44) were below detection limits of about 11 ng/g lw for BDE-209 (Nordlöf et al., 2010). This population of sea eagles mainly feeds on fish, small mammals and carrion (i.e. aquatic, but not necessarily marine prey). BDE-209 levels in the sea eagle eggs were different to the findings for peregrine falcon eggs from Sweden and elsewhere (Lindberg et al., 2004; Johansson et al., 2009; Chen and Hale, 2010), which generally contained more of the highly brominated congeners (Nordlöf et al., 2010). Chen et al. (2010) highlighted that the PBDE pattern was different for fish-eating and terrestrial birds, with the latter containing more highly brominated congeners.

In a study including 96 eggs of herring gull (*Larus argentatus*), Atlantic puffin (*Fratercula arctica*) and black-legged kittiwake (*Rissa tridactyla*), only nine eggs had concentrations of BDE-209 that were significantly above the blank (Helgason et al., 2009). In these samples, BDE-209 ranged from ~0.5 to 15 ng/g ww. In addition, the nonabrominated congeners BDE-206, BDE-207 and BDE-208 were also detected in some samples, but not necessarily in the same ones. Helgason et al. (2009) observed a higher frequency of BDE-209 detection in herring gull eggs from 2003 compared to eggs from 1983 and 1993.

Tomy et al. (2009) studied the trophic dynamics of BDE-209 in a marine food web in the western Canadian Arctic including (in order of increasing trophic level) Arctic copepods (*Calanus hyperboreus*), pelagic amphipods (*Themisto libellula*), Arctic cisco (*Coregonus autumnalis*), Pacific herring (*Clupea pallasi*), Arctic cod (*Boreogadus saida*), ringed seal and beluga. The study complemented a previous one on a marine food web in the eastern Canadian Arctic that had shown trophic dilution of BDE-209 (Tomy et al., 2008b). The concentration data are given in Table 2.7. No trophic magnification factor was calculated for BDE-209, but individual biomagnification factors (BMFs) were generally <1. Exceptions occurred for the Arctic cod / *C. hyperboreus* and Arctic cod / *T. libellula* transitions, which had BMFs of 12.7 and 4.8, respectively. The low concentrations of BDE-209 in the marine mammals do not support biomagnification, which is in agreement with the outcome of the study from eastern Canada (Tomy et al., 2008b).

Previously described *in vitro* metabolism findings for polar bear, ringed seal and beluga (McKinney et al., 2011a) were consistent with recent BDE-209 assessments and with the lack of any detection in polar bear adipose samples from 11 sub-populations spanning Alaska east to Svalbard collected over the 2005–2008 period (McKinney et al., 2011b). BDE-209 in adipose samples collected annually from Hudson Bay bears between 2007 and 2014, was either not detectable or detected at low frequency (NCP, 2015a). The lack of BDE-209 in the adipose samples is probably due to a combination of low exposure and low dietary uptake and to rapid metabolism and debromination (McKinney et al., 2011a).

2.2.2.7 Environmental trends

Spatial trends

Very few data on spatial trends in BDE-209 were available. Air measurements indicated higher concentrations in the Bering and Chukchi Sea than in the East Greenland Sea, which is possibly related to the production and use of commercial decaBDE in Asia (Möller et al., 2011a,b). The same spatial pattern was found in marine sediments (Cai et al., 2012b).

Table 2.7 Concentrations of BDE-209 (ng/g lw) in a marine food web from the western Canadian Arctic, with samples collected between 2004 and 2007 (Tomy et al., 2009).

	Arctic copepods (*Calanus hyperboreus*)	Pelagic amphipods (*Themisto libellula*)	Arctic cisco	Pacific herring	Arctic cod	Ringed seal	Beluga
Median	0.04	0.11	7.23	0.25	1.01	<0.23	<0.23
Range	-	-	2.05–21.67	0.04–0.70	0.23–1.77	<0.23	<0.23–1.13
Mean lipid (%)	0.31	0.07	1.94	6.42	1.62	86.1	81.8

Cai et al. (2012b) also noticed individual sediment samples with elevated concentrations of BDE-209 and attributed these findings to local point sources.

Temporal trends

Although BDE-209 concentrations in air at Alert appeared to peak in 2005, due to the lack of data for 2006 this cannot be confirmed (Figure 2.32) (Hung et al., 2013a). Despite an increasing trend at Alert between 2002 and 2005, six additional years of data show that BDE 209 concentrations declined since the mid-2000s at both Alert and Zeppelin. At Zeppelin, no significant long-term trend was observed for BDE-209 (NILU, 2015). An ice core from Svalbard showed increasing BDE-209 concentrations and fluxes since the 1950s, but measurements in the oldest ice layers may have been affected by downward movement of meltwater (Hermanson et al., 2010) (Figure 2.33). BDE-209 fluxes at the Devon Ice Cap did not show a trend between 1993 and 2008 (Meyer et al., 2012).

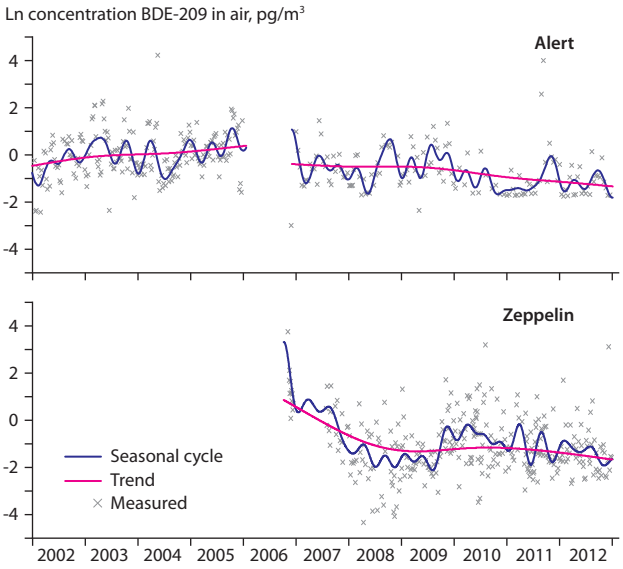


Figure 2.32 Temporal trends and seasonal cycles in BDE-209 concentrations in air at the monitoring stations at Alert (Canada) and Zeppelin (Svalbard, Norway) (Hung et al., 2013a).

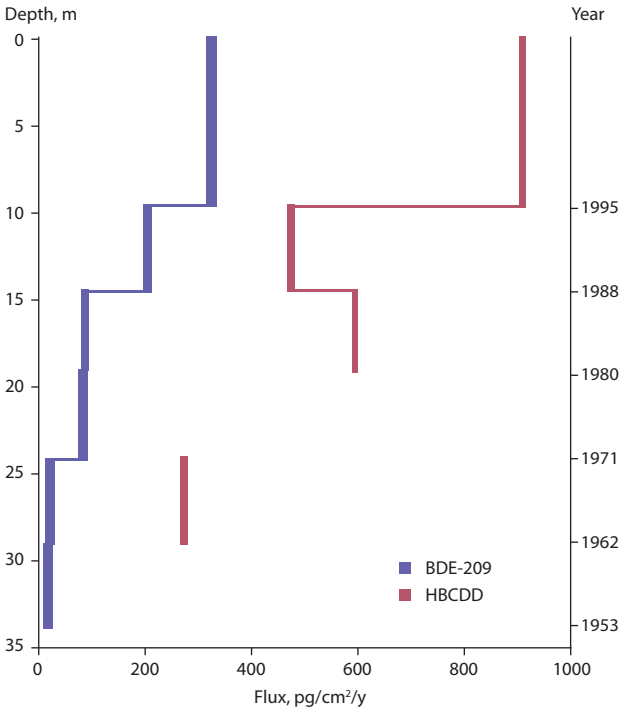


Figure 2.33 BDE-209 and HBCDD fluxes in Svalbard since the 1950s, as determined from ice core measurements (Hermanson et al., 2010).

Observations that BDE-209 concentrations are starting to decrease could be due to voluntary measures to reduce emissions initiated in 2004 (EFRA, 2015) in combination with the phase-out of BDE-209 in two US states (Washington and Maine) in 2007/2008, its ban in Norway in 2008, and its restriction in electrical and electronic equipment in the European Union since July 2008. However, most demand occurs in Asia. BDE-209 was added to the Stockholm Convention in 2017.

2.2.3 Hexabromocyclododecane (HBCDD)

2.2.3.1 Introduction

Hexabromocyclododecane (HBCDD) is an additive BFR used in a commercial mixture mainly consisting of γ-HBCDD (75–89%), α-HBCDD (10–13%) and β-HBCDD (1–12%) (Covaci et al., 2006). Figure 2.34 shows the general chemical structure of HBCDD. Other stereoisomers occur in minor proportions; eight out of the possible 16 stereoisomers of HBCDD have been isolated from the technical mixture (Heeb et al., 2005). As a result, it is more correct to describe HBCDDs as a compound group (analogous to hexachlorocyclohexanes, HCHs), but the singular form is common in the scientific literature and is also the term used in the Stockholm Convention. In the context of the EU Water Framework Directive, hexabromocyclododecane is abbreviated HBCDD (EU, 2013). This avoids confusion with hexabromocyclodecane ($C_{10}H_{14}Br_6$), which is apparent in some publications.

The HBCDD isomers have been of environmental concern for at least ten years (de Wit, 2002). The industrial VECAP and SECURE initiatives have aimed at reducing HBCDD emissions to the environment since about 2006 (VECAP, 2007). As of 2014, EFRA (2015) reported that 98% of 'volumes sold' had joined the programs. A risk assessment prepared for the EU concluded that HBCDD was persistent, bioaccumulative and toxic although some slow biodegradation could occur (EU, 2008a). The assessment also highlighted concerns for HBCDD

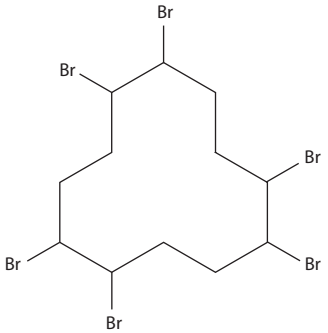


Figure 2.34 General chemical structure of HBCDD.

biomagnification in food chains. HBCDD was subsequently included in both the candidate and the authorization list of Substances of Very High Concern (ECHA, 2008a,b). HBCDD is also on OSPAR's List of Chemicals for Priority Action (OSPAR, 2009c). Following reviews of an HBCDD risk assessment dossier (Peltola-Thies, 2008), the United Nations Economic Commission for Europe (UNECE) concluded that HBCDD was a persistent organic pollutant (POP) in the context of the POP protocol of the UNECE Convention of Long-Range Transboundary Air Pollution (UNECE, 2009a).

HBCDD was proposed to the Stockholm Convention in 2008 and the Conference of the Parties agreed to list it under Annex A in 2013. The Stockholm Convention allows time-limited exemptions of HBCDD use in expanded and extruded polystyrene in buildings (UNEP, 2013b). These products must be easily identified by labelling or other means.

The previous AMAP assessment documented the ubiquitous presence of HBCDD in the Arctic environment, including in air, sediment and various freshwater and marine species (de Wit et al., 2010). Concentrations were usually comparable to or lower than those for PBDEs. Temporal trends were inconclusive, including examples of rising concentrations or tendencies of a levelling off. Results for seabirds suggested higher concentrations in the European Arctic than the North American Arctic, but with the caveat of probable species differences. Local sources of HBCDD may exist in the Arctic, for example in terms of wastewater effluents or waste incineration.

The previous AMAP assessment also showed substantial differences in the isomer composition of HBCDD in the Arctic, depending on the matrix. While abiotic matrices often resembled the commercial HBCDD mixture in terms of a predominance of γ-HBCDD, α-HBCDD was often the only detectable isomer in high trophic level biota (de Wit et al., 2010).

This section summarizes new results for HBCDD in the Arctic (i.e. information published since January 2009). Recent reviews that include HBCDD were published by Marvin et al. (2011) and Law et al. (2014a).

2.2.3.2 Physical-chemical properties

The three diastereomers of HBCDD have slightly different physical-chemical properties, with log K_{OW} values of 4.18 (β-HBCDD) to 4.45 (α-HBCDD) and with higher water solubilities than many other CECs (0.49–1.31 mg/L) (Mariussen et al., 2010). HBCDD diastereomers are chiral molecules and are racemic in the technical product. See Appendix 1 for more detailed information. The variations in physical-chemical properties may partly explain differences in the environmental behavior of the three diastereomers, including bioaccumulation and biomagnification of primarily the α-HBCDD isomer in biota (Law et al., 2005).

2.2.3.3 Sources, production, use and trends

HBCDD is used in expanded (EPS) and extruded polystyrene (XPS) foams that are widely used for insulation purposes in the construction sector (ECHA, 2009). It has also been used in textile back coating and high-impact polystyrene (HIPS) used in electronics housing (US EPA, 2014). In Europe, use of HBCDD in EPS and XPS accounted for 96% of the total use (ECHA, 2009).

Production of HBCDD has been reported in Europe, China, Japan and the USA (UNEP, 2011a). Global production was about 20 000 tonnes in 2003 (de Wit et al., 2010), i.e. roughly half the production volume of commercial decaBDE. UNEP (2011a) gave a global production volume of 28 000 tonnes per year, of which about 13 000 tonnes were produced in the EU and USA. The volume of HBCDD produced in Europe was 6000 tonnes in 2005 (ECHA, 2009).

In contrast to the PBDEs, the majority of HBCDD was used in Europe (UNEP, 2011a), which might have implications for exposure in the Arctic. Use in Europe was estimated at 11 000 tonnes in 2006, and may have been rising. An increase in net import to about 6000 tonnes per year was estimated (ECHA, 2009). According to EFRA (2015), sales of HBCDD are declining and HBCDD is expected to be phased out in Europe 'in the near future'. In Japan, combined production and import values were close to 3000 tonnes per year (UNEP, 2011a).

ECHA (2009) estimated HBCDD emissions in Europe to be roughly 3000 kg/y, half of these to wastewater and about a quarter each to air and surface waters.

2.2.3.4 Transformation processes

A γ- to α-isomerization can occur at elevated temperatures (Heeb et al., 2008) and in biological systems (Law et al., 2006; Szabo et al., 2010) and has also been shown for HBCDD associated with dust particles (Harrad et al., 2009). Furthermore, differences in water solubility and thus bioavailability can have an effect on the HBCDD isomer profile, as well as different metabolism rates for the individual isomers (Szabo et al., 2010, 2011). Liver microsomes from marine mammals have been found to metabolize β- and γ-HBCDD faster than α-HBCDD (Zegers et al., 2005). The study also showed that hydroxylated metabolites were formed (Zegers et al., 2005).

As the carbon–bromine bond is weaker than the carbon–chlorine or carbon–fluorine bond, HBCDD is more susceptible to biodegradation than other POPs (Tomy et al., 2011). In addition, differences in HBCDD accumulation between males and females appear likely because HBCDD activates the pregnane-X-receptor, which is more pronounced in females (Tomy et al., 2011).

Metabolism of HBCDD in Arctic biota was discussed by Vorkamp et al. (2012) who studied differences in the metabolism potential between glaucous gull and ringed seal in enantiomer-specific analyses: larger deviations from racemic mixtures can be considered indicative of a higher degree of biodegradation. While both species showed an accumulation of (-)-α-HBCDD, deviation from a racemic mixture was higher for glaucous gull (Vorkamp et al., 2012). Furthermore, glaucous gull contained relatively low levels of α-HBCDD compared to their organochlorine accumulation. These results from East Greenland might suggest some biodegradation of α-HBCDD in glaucous gull, which is more pronounced than potential biodegradation in ringed seal.

2.2.3.5 Modeling studies

No recent modeling studies were available.

2.2.3.6 Environmental concentrations

Air and precipitation

HBCDD has been monitored in air at Alert in the Canadian Arctic since 2002 and at Zeppelin (Svalbard) since 2006 (NILU, 2015; Hung et al., 2016). Concentrations at Alert were mostly non-detectable (Hung et al., 2016). At Zeppelin, concentrations decreased from 7.13 pg/m^3 (2006) to 0.65 pg/m^3 (2014). However, very few measurements were above detection limits. In 2014, only five samples were above detection limits for α-HBCDD and/or γ-HBCDD (see Table 2.8). The results are based on 48-hour high volume samples collected weekly.

Even lower HBCDD concentrations in air were found in northeastern Greenland, based on weekly high volume air samples collected at Villum Research Station in 2012 (Vorkamp et al., 2015) and 2013 (unpubl. data). Only filters were analyzed because previous studies had reported HBCDD as mainly particle-bound in air (Hoh and Hites, 2005; Yu et al., 2008b). While the 2012 ΣHBCDD concentrations ranged from 0.0057 to 0.13 pg/m^3, 2013 concentrations were considerably lower, with a maximum of 0.016 pg/m^3. There was a tendency towards higher concentrations in winter months, which is comparable to the monitoring data from Zeppelin, but exceptions exist and more data are needed to consolidate potential seasonal trends.

Both studies from Svalbard and northeastern Greenland documented the occurrence of α- and γ-HBCDD in air, while β-HBCDD was of minor importance (NILU, 2015; Vorkamp et al., 2015). On average, α- and γ-HBCDD accounted for 30% and 60%, respectively, of ΣHBCDD in the Greenland samples, but each with a range of 0–100% (Vorkamp et al., 2015).

Passive air samples from the Global Atmospheric Passive Sampling (GAPS) program collected in 2005 were screened for HBCDD. Among the Arctic/subarctic GAPS stations, HBCDD was detected in air at Barrow (<MDL–2.02 pg/m^3), St. Lawrence Island (0.22 pg/m^3), Stórhöfði (<MDL–3.3 pg/m^3) and Ny-Ålesund (<MDL–5.1 pg/m^3) (Annex Table A2.2/2) (Lee et al., 2016).

Deposition of atmospheric HBCDD in the Arctic environment has been studied by means of an ice core from Svalbard and snow cores from Nunavut (Arctic Canada) (Hermanson et al., 2010; Meyer et al., 2012). While HBCDD deposition fluxes exceeded those for PBDEs in the Svalbard ice core (see Figure 2.33), HBCDD was present at much lower concentrations than PBDEs in the snow cores from the Canadian Arctic. The maximum HBCDD fluxes determined from the individual core slices were 910 pg/cm^2/y in Svalbard and about 3.2 pg/cm^2/y in Nunavut (Hermanson et al., 2010; Meyer et al., 2012; Hung et al., 2013a). Meyer et al. (2012) discussed that this may be related to air mass transport from Europe to Svalbard, probably in combination with other factors, while HBCDD present in the Canadian snow cores could not be related to specific areas of origin.

For the Svalbard ice core, the highest HBCDD flux was associated with the uppermost layer representing the 1995-2005 period (Figure 2.33). The oldest slice was dated to 1962, and measurements show the HBCDD flux had increased since then, although not as continuously as for BDE-209 (Hermanson et al., 2010). According to the snow cores from Nunavut, the maximum HBCDD flux occurred in 2004, with variable and lower fluxes in the other years (1993–2008) (Hung et al., 2013a). Given the differences in temporal resolution in the cores, these observations may be consistent. Calculating total contaminant burdens in the ice core, Hermanson et al. (2010) reported a burden of about 1000 ng for HBCDD, which exceeded those for PBDEs (except BDE-209) by a factor of 100. Taken together, the air and precipitation data might indicate a spatial trend of higher concentrations in the European Arctic than the Canadian Arctic.

Table 2.8 Monthly mean concentrations (pg/m^3) of HBCDD in air (with at least one isomer above detection limits) collected in 2014 at the Zeppelin monitoring station (Svalbard) (NILU, 2015). Detection limits were calculated as average blank plus three times the standard deviation of the blank.

	January	February	March	October	December
α-HBCDD	<0.02	0.05	<0.02	<0.21	<0.29
β-HBCDD	<0.02	<0.04	<0.03	<0.45	<1.16
γ-HBCDD	0.03	0.05	0.02	0.55	0.71

Terrestrial environment

Results are scarce for HBCDD in terrestrial species from the Arctic. In Sweden, ΣHBCDD was sought in muscle of moose (*Alces alces*) from central Sweden and reindeer from northern Sweden, but concentrations were below the detection limit of 0.1 ng/g ww in all samples (Danielsson et al., 2008). Lind and Odsjö (2010) found concentrations of HBCDD to be below detection limit in a study of bank voles collected in 2001 in Ammarnäs, Vålådalen and Vindeln in northern Sweden.

Freshwater environment

Water

Ahrens et al. (2014a) found no detectable HBCDD concentrations in water samples from the six most northern Swedish rivers, sampled close to their entry points to the Baltic Sea, and from the Ume älv/Vindelälven river system, including upstream samples. These waters are representative of the Arctic or subarctic areas of Sweden.

Biota

HBCDD concentrations in freshwater fish were generally low (<0.1 ng/g ww) with the exception of burbot (*Lota lota*) liver samples from the Canadian Arctic. Besides burbot, lake trout (*Salvelinus namaycush*) and landlocked Arctic char (*S. alpinus*) from the Canadian Arctic were analyzed for HBCDD (Muir et al., 2013b). Burbot liver samples from the Great Slave Lake in the Yukon had mean ΣHBCDD concentrations of 1.4 and 2.4 ng/g ww for the West Basin and East Arm, respectively, while ΣHBCDD concentrations in lake trout muscle only were about 0.04–0.08 ng/g ww (Great Slave Lake and Great Bear Lake in the Yukon). Concentrations in landlocked Arctic char (muscle and skin) were also low (Muir et al., 2013b). Samples were analyzed from four lakes,

and in two (Hazen and Amituk) the HBCDD detection frequency was 4% and 15%, respectively. In the remaining lakes (Char and Resolute), the ΣHBCDD concentration was higher, at about 0.1 ng/g ww.

For the European Arctic, HBCDD was monitored in perch (*Perca fluviatilis*) from several lakes in Arctic Finland between 2012 and 2014 (Mannio et al., 2016). Ten pooled samples were analyzed, each comprising 10 to 30 individuals. α-HBCDD was detected in two samples (0.010 and 0.012 ng/g ww). In the remaining samples, α-HBCDD was below the level of quantification, as were β- and γ-HBCDD in all ten samples.

Marine environment

Fish

Pelagic marine fish were studied by Tomy et al. (2009), in terms of Arctic cisco, Pacific herring and Arctic cod from the western Canadian Arctic, all collected in 2004 and 2005. HBCDD isomers were determined in whole fish minus the liver. Based on $\delta^{15}N$ values, Arctic cod fed at a higher trophic level than Arctic cisco and Pacific herring, whose trophic levels were comparable. Median concentrations of ΣHBCDD were 0.9 ng/g lw (Arctic cisco), 1.7 ng/g lw (Pacific herring) and 11.8 ng/g lw (Arctic cod). Thus, the lipid normalized concentrations were about 10 times higher in Arctic cod than in ringed seal and beluga from the same area.

Saithe (*Pollachius virens*) and Atlantic cod (*Gadus morhua*) from stations along the Norwegian coast were analyzed for HBCDD, including one station in northern Norway (Øksfjord, 70°N) (Bustnes et al., 2012). Median concentrations of ΣHBCDD in liver samples were 6.3 ng/g lw (saithe) and 6.6 ng/g lw (Atlantic cod) for fish caught at Øksfjord. As the overall POP burden was higher in cod than saithe, HBCDD contributed relatively more to ΣPOP in saithe than cod. This suggests differences in exposure and/or transformation between the two species

Seabirds

Eggs of seabird species from northern Norway, northern Sweden and Iceland were analyzed for HBCDD (Helgason et al., 2009; Nordlöf et al., 2010; Jörundsdóttir et al., 2013). The Norwegian study included eggs of herring gull, Atlantic puffin and black-legged kittiwake, the Swedish study analyzed eggs of white-tailed sea eagle from Lapland, while the Icelandic study included eggs of seven species: common eider (*Somateria mollissima*), Arctic tern (*Sterna paradisaea*), guillemot (*Uria aalge*), fulmar (*Fulmarus glacialis*), lesser black-backed gull (*Larus fuscus*), great black-backed gull (*L. marinus*) and great skua (*Stercorarius skua*). Of these species, the Arctic tern and great skua are migratory birds, with great skuas mainly migrating to Canada. It should be noted that different analytical methods were used in these studies, as indicated in Table 2.9. Although this means that the studies are not directly comparable, the actual differences might be small as the assumption that ΣHBCDD and α-HBCDD have similar concentrations seems reasonable in these samples.

HBCDD was widely detected in the eggs (Table 2.9). For lower trophic level birds, the HBCDD concentration was comparable to that for BDE-47, but was considerably lower than BDE-47 in higher trophic level birds. This might suggest less biomagnification than observed for BDE-47. The Icelandic study showed PBDEs and HBCDD did not group together in principal component analysis, which was explained by their different geographical use patterns (Jörundsdóttir et al., 2013).

Studies on HBCDD in glaucous gull are available from Bjørnøya (Bear Island) in the Norwegian Arctic and from East Greenland (Sagerup et al., 2009; Vorkamp et al., 2012). The study from Norway sought HBCDD in glaucous gulls found dead or dying and observed median concentrations of α-HBCDD of 1.1 ng/g lw (liver) and 0.03 ng/g lw (brain) (Sagerup et al., 2009). Concentrations for glaucous gull liver from East Greenland were much higher, i.e. the median concentration of α-HBCDD

Table 2.9 Mean concentrations (ng/g lw) and standard deviations (±) or ranges (in brackets) of α-HBCDD (from LC-MS/MS determinations) and ΣHBCDD (from GC-MS determinations) in seabirds from the Arctic, collected in 2002–2004. BDE-47 determined in the same samples is given for comparison. β- and γ-HBCDD were below method detection limits (MDL) in the LC-MS/MS analyses unless specified.

Sample type	n	Country	α-HBCDD	ΣHBCDD	BDE-47	Reference
Herring gull eggs	10	Norway	108±48	-	412±191	Helgason et al., 2009
Atlantic puffin eggs	10	Norway	58±20	-	41±17	
Black-legged kittiwake eggs	10	Norway	142±91	-	141±69	
White-tailed sea eagle eggs[a]	12	Sweden (Lapland)	-	60 (40–390)[b]	280 (80–1100)[c]	Nordlöf et al., 2010
Arctic tern eggs	6	Iceland	-	1.3 (0.54–2.3)[b]	73 (60–85)[b]	Jörundsdóttir et al., 2013
Common eider eggs	10	Iceland	-	3.4 (1.3–5.9)[b]	12 (5.5–31)[b]	
Guillemot eggs	10	Iceland	-	19 (7.3–47)[b]	38 (13–96)[c]	
Fulmar eggs	10	Iceland	-	11 (5.0–20)[b]	26 (13–47)[c]	
Lesser black-backed gull eggs	8	Iceland	-	15 (<MDL–320)[b]	660 (360–1600)[c]	
Great black-backed gull eggs	9	Iceland	-	41 (14–180)[b]	550 (360–950)[c]	
Great skua eggs	10	Iceland	-	29 (<MDL–370)[b]	660 (300–2200)[c]	
Glaucous gull liver	21	Bjørnøya (Norway)	1.1 (0.2–15)[c]	-	7.4 (1.2–57)[c]	Sagerup et al., 2009
Glaucous gull brain	21	Bjørnøya (Norway)	0.03 (0.005–0.5)[c]	-	1.1 (0.1–5.9)[c]	
Glaucous gull liver	8	Greenland	68 (11–197)[d]	-	na	Vorkamp et al., 2012

na: Not available; [a]collected 1994–2005; [b]geometric mean; [c]median; [d]β-HBCDD: <MDL–3 ng/g lw; γ-HBCDD: <MDL–1.7 ng/g lw.

in 2010 was 22 ng/g lw (Vorkamp et al., 2012). Glaucous gull liver samples from 2004 showed a median concentration of 38 ng/g lw for α-HBCDD, which was similar to that in glaucous gull plasma from Svalbard for the same year (Verreault et al., 2005a). The reasons for the concentration differences from the study on Bjørnøya are not known, but diet can vary considerably for glaucous gulls.

Studies including samples from lower latitudes generally showed higher concentrations than found in the Arctic samples (Helgason et al., 2009; Nordlöf et al., 2010).

Marine mammals

HBCDD levels in ringed seal blubber were determined for ten locations in the Canadian Arctic, in addition to a western Canadian Arctic food web study (Holman Island) (Tomy et al., 2009; Muir et al., 2013b). HBCDD was also studied in ringed seal from East Greenland (Vorkamp et al., 2011, 2012). Of the ten Canadian locations, ΣHBCDD (in female ringed seals) was below detection limits at three. At the remaining stations, mean concentrations ranged from just above detection limits to about 3 ng/g lw, with indications of the highest concentrations in ringed seal from Hudson Bay (Muir et al., 2013b). Ringed seals from Holman Island (all males) were collected in 2004 and had a median concentration of ΣHBCDD of 1.1 ng/g lw, while the 2004 median concentration of α-HBCDD in juvenile ringed seals from East Greenland was 6.2 ng/g lw (Tomy et al., 2009; Vorkamp et al., 2011). The most recent (2010) median concentration was 11.3 ng/g lw for α-HBCDD in ringed seal from East Greenland (Vorkamp et al., 2012). Thus, the geographical trend for HBCDD in ringed seals is consistent with that described for several sub-populations of polar bears (as discussed in Section 2.2.3.7).

More data have become available on HBCDD in beluga, including concentrations for a sub-population from Hendrickson Island and three other locations in the Canadian Arctic, as well as two sub-populations from Alaska (Cook Inlet and the Eastern Chukchi Sea) (Tomy et al., 2009; Hoguet et al., 2013; Muir et al., 2013b). The HBCDD concentrations in beluga were similar for all sub-populations, with median α-HBCDD concentrations of 1.9 ng/g lw (Hendrickson Island) and 1 ng/g lw (Alaska) (Tomy et al., 2009; Hoguet et al., 2013), and mean concentrations at the other Canadian locations of 0.7–1.7 ng/g lw (Muir et al., 2013b). The Alaskan study noted that the concentrations were semi-quantitative owing to quality assurance issues. Besides, only Alaskan male beluga were considered in this comparison, since females from the Chukchi Sea had concentrations below detection limits for α-HBCDD. While there was no geographical trend for HBCDD in beluga across the Canadian Arctic (Muir et al., 2013b), the beluga from Cook Inlet had significantly higher concentrations of α-HBCDD (and PBDEs) than those from the Eastern Chukchi Sea (Hoguet et al., 2013). Hoguet et al. (2013) explained this difference by the proximity of the Cook Inlet sub-population to more urbanized and industrialized areas.

Adipose samples were collected from polar bears of 11 sub-populations in the period 2005–2008 and screened for various POPs, including HBCDD (McKinney et al., 2011b). Detection frequencies of HBCDD were 100% in polar bears from the European Arctic and Hudson Bay but <80% in the rest of the Canadian Arctic and <20% in Alaska. Figure 2.35 shows the geometric mean concentrations, which range from <0.3 ng/g lw (Alaska and the Gulf of Boothia) to 41.1 ng/g lw

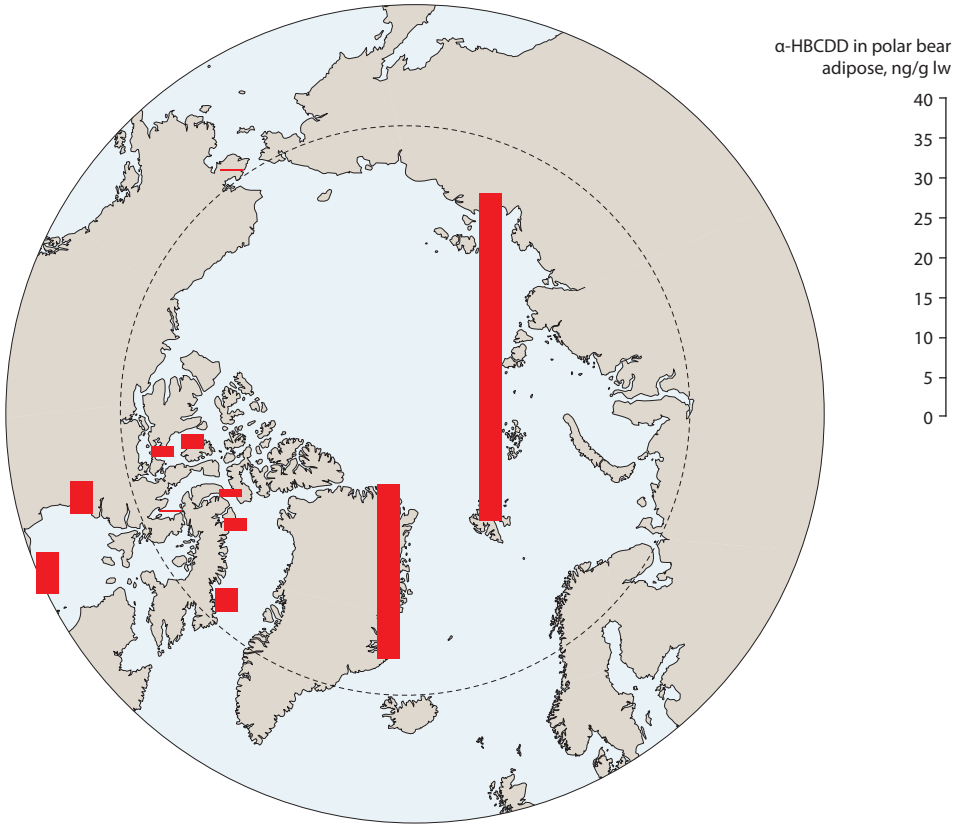


Figure 2.35 Geometric mean concentration of α-HBCDD in adipose of polar bears collected between 2005 and 2008 (data from McKinney et al., 2011b).

(Svalbard). The HBCDD level of 22 ng/g lw reported for polar bears from East Greenland (McKinney et al., 2011b) was confirmed by a subsequent study focusing specifically on this sub-population (Dietz et al., 2013). The most recent study period (2006–2010) showed median α-HBCDD concentrations of 27 ng/g lw (subadults), 19 ng/g lw (adult females) and 26 ng/g lw (adult males). These concentrations are at least double the concentration of α-HBCDD in blubber of ringed seal (a major prey of polar bears) from the same location and time period, indicating biomagnification in this predator-prey relationship (Vorkamp et al., 2011, 2012). As previously discussed, seals had lower lipid-normalized concentrations than Arctic cod and other pelagic fish in the western Canadian Arctic.

2.2.3.7 Environmental trends

Spatial trends

HBCDD levels in polar bears were negatively correlated with longitude (Figure 2.35), which McKinney et al. (2011b) related to the primary use of HBCDD in Europe. This was also supported by a comparison with PBDE concentrations: these were generally higher than HBCDD concentrations in the same samples, except for those from East Greenland and Svalbard. This tendency is consistent with that in snow and ice cores from the Canadian and the European Arctic (Hermanson et al., 2010; Meyer et al., 2012).

Temporal trends

Many studies have addressed temporal trends of HBCDD in the Arctic, as summarized in Table 2.10. Air measured at Zeppelin showed a decline in the first two years of monitoring, i.e. 2006/2007. From 2008 to 2014, the concentrations fluctuated, and no clear temporal trend could be seen (NILU, 2015). Only few samples had concentrations above detection limits.

Increasing HBCDD concentrations and fluxes were found in an ice core from Svalbard dating back to 1962 although some variation occurred (Hermanson et al., 2010) (Figure 2.33).

The trends available for the Canadian freshwater environment generally show increasing concentrations in burbot and lake trout, with maxima of ΣHBCDD within the last two years with data (2010, 2011) (Figure 2.36). Only burbot in the West Basin of the Great Slave Lake showed a maximum in 2008, but similarly high concentrations since then. For landlocked Arctic char (Char Lake), the ΣHBCDD concentration increased until about 2008 and has been relatively constant since then (Muir et al., 2013b).

Table 2.10 Summary of temporal trend studies on HBCDD in the Arctic.

Sample type	Location	Study period	Result	Comments	Reference
Air	Zeppelin (Svalbard)	2006–2014	Inconclusive	Decrease in 2006/2007, fluctuating concentrations subsequently	NILU, 2015
Ice core	Svalbard	1962–1995/2005	Increase	Non-continuous increase, i.e. 1988/1995 lower than 1980/1988	Hermanson et al., 2010
Burbot, lake trout	Yukon, Canada	2007–2011	Increase	Burbot in the West Basin of the Great Slave Lake had a maximum in 2008, but similar concentrations subsequently. Lake trout concentrations peaked in 2010/2011	Muir et al., 2013b
Landlocked Arctic char	Yukon, Canada	1999–2011	Increase	Maximum in 2008, but similar concentrations subsequently	Muir et al., 2013b
Seabird eggs	Northern Norway	1983–2003	Increase	10-year-interval	Helgason et al., 2009
Glaucous gull liver	East Greenland	1994–2010	No trend	-	Vorkamp et al., 2012
Ringed seal	East Greenland	1986–2010	Increase	Annual change +6.4%	Vorkamp et al., 2012
Ringed seal	Canadian Arctic	2000–2011	Increase	Relatively stable concentrations since 2009/2010	Muir et al., 2013b
Beluga	Alaska	1989–2005	Increase	Doubling times of 2.4 and 5 years for two sub-populations	Hoguet et al.. 2013
Beluga	Beaufort Sea (Canadian Arctic)	1993–2009	Increase until 2004	Annual increase of 13% until 2004. Non-significant decrease since 2004	Muir et al., 2013b
Beluga	Cumberland Sound (Canadian Arctic)	1982–2010	Increase	Annual increase 8.7%	Muir et al., 2013b
Polar bear	East Greenland	1983–2010	Increase	-	Dietz et al., 2013
Polar bear	Western Hudson Bay	1991–2014	Increase	Undetectable in samples from 2013 and 2014	McKinney et al., 2010; NCP, 2015a
Polar bear	Southern Hudson Bay	2007–2014	Increase until 2012/2013	Undetectable in samples from 2014	NCP, 2015a

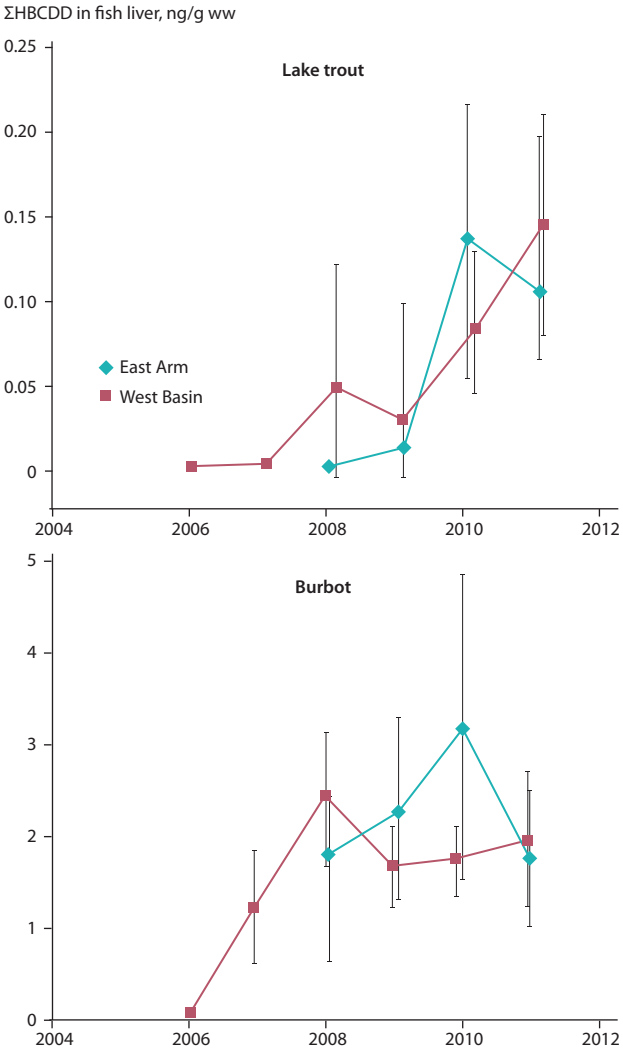


Figure 2.36 Concentration of ΣHBCDD in burbot and lake trout from Great Slave Lake (Yukon, Canada) (Muir et al., 2013b).

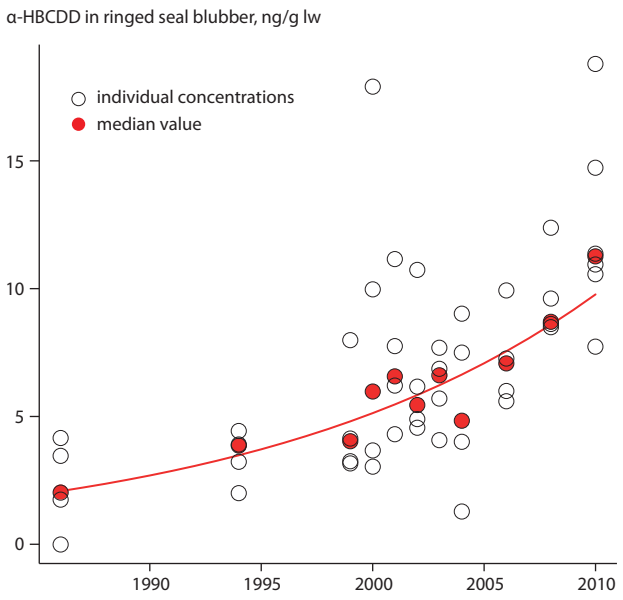


Figure 2.37 Concentration of α-HBCDD in blubber of ringed seal from East Greenland (Vorkamp et al., 2012).

The concentration of α-HBCDD increased significantly over the study period (1983–2003) for eggs of herring gull, Atlantic puffin and black-legged kittiwake from northern Norway (Helgason et al., 2009). These findings differ to those for glaucous gull liver from East Greenland, which did not show any significant trend (p=0.79) between 1994 and 2010 (Vorkamp et al., 2012).

However, ringed seals sampled from the same location in East Greenland did show a significant log-linear increase (p<0.01) in α-HBCDD blubber concentrations between 1986 and 2010, with an annual change of +6.4% (Vorkamp et al., 2012) (Figure 2.37). Increases have also been found for HBCDD in ringed seal blubber from three areas of the Canadian Arctic: Beaufort Sea (2001–2011), Lancaster Sound (2000–2011) and Hudson Bay (2007–2011) (Muir et al., 2013b). At all locations, HBCDD increased rapidly in ringed seals from around 2006/2007, but only until 2009/2010. Since then concentrations have been relatively stable. Owing to the relatively low number of years with samples, only the trend in Lancaster Sound was statistically significant (increase by 162%) (Muir et al., 2013b).

Significant increases of α-HBCDD were also observed in the Alaskan beluga study, which covered the overall period 1989–2005 (Hoguet et al., 2013). Doubling times of 2.4 and 5 years, respectively, were calculated for the two sub-populations from Cook Inlet and the Eastern Chukchi Sea. Significantly increasing concentrations of ΣHBCDD (13% and 8.7% per year) were also reported for the beluga sub-populations in the Beaufort Sea (1993–2009, with a maximum in 2004) and Cumberland Sound (1982–2010) (Muir et al., 2013b).

HBCDD concentrations in adipose for polar bears from Alaska, East Greenland and Svalbard for the period 2005–2008 were compared with concentrations for 1996–2002 and found to be lower in the more recent samples (McKinney et al., 2011b). However, this decrease was not observed in the more detailed trend studies reported for HBCDD in polar bears from East Greenland (Dietz et al., 2013): covering the period 1983–2010, ΣHBCDD was found to increase in all groups of polar bears, i.e. annual changes of 7.6% (subadults), 5.3% (adult females) and 6.7% (adult males). Thus, this temporal trend was very similar to that for ringed seal from the same location and roughly the same period (Vorkamp et al., 2011, 2012).

Although uncorrected for age, sex and diet, the temporal trends in ΣHBCDD relative to PBDEs and BB-153 were recently reported for adipose samples from polar bears from both the western (1991–2014) and southern (2007–2014) Hudson Bay sub-populations (NCP, 2015a). ΣHBCDD concentrations were much lower than ΣPBDE concentrations (BDE-47, BDE-99, BDE-100 and BDE-153 consistently accounted for over 90% of the ΣPBDEs) for both western and southern Hudson Bay bears in all years up to 2013 and non-detectable in 2014 samples (Figure 2.38).

In summary, most of the trend studies recently published on α-HBCDD in the Arctic generally show increasing trends until about 2005–2010. More recent data, where available, show relatively stable or declining concentrations. A decrease was observed in air at Zeppelin in 2006/2007, but not since. Recent findings from Europe indicate a levelling off or decrease

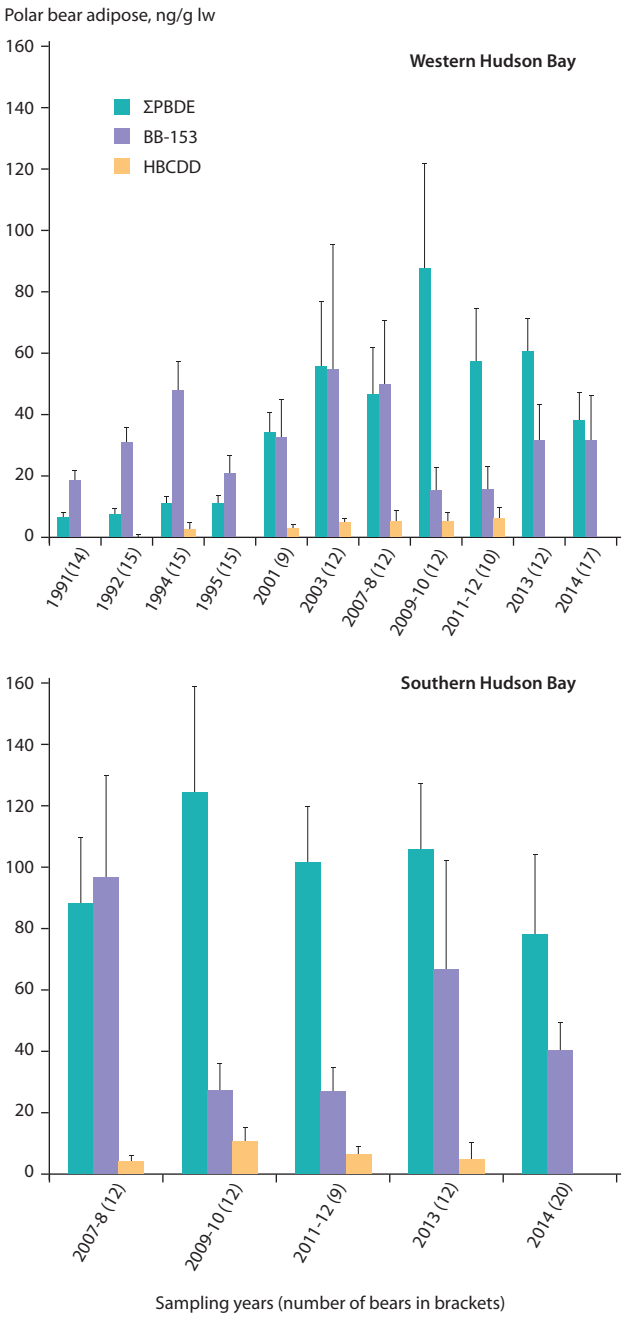


Figure 2.38 Temporal trends in geometric mean concentrations of PBDEs, ΣHBCDD and BB-153 in western Hudson Bay polar bears (upper panel, 1991–2007: McKinney et al., 2010; 2008–2014: NCP, 2015a) and southern Hudson Bay polar bears (lower panel, 2008–2014: NCP, 2015a). Error bars are standard deviations. Data not corrected for sex, age or diet. The absence of ΣHBCDD in the graphic indicates concentrations below detection limits.

in α-HBCDD in biota (e.g. Sellström et al., 2003; Law et al., 2008; Esslinger et al., 2011). Reports from Asia, however, often show increasing concentrations of HBCDD in biota (e.g. Lam et al., 2009).

2.2.3.8 Isomer-specific biomagnification of HBCDD

A food web study from the Canadian Arctic demonstrated the enrichment of α-HBCDD with increasing trophic level. While α-HBCDD only accounted for 20% of ΣHBCDD in Arctic cod and 75% of ΣHBCDD was γ-HBCDD, α-HBCDD made up 95% of ΣHBCDD in beluga (Tomy et al., 2009). As this is a direct predator-prey relationship, γ-HBCDD could be bioisomerized to α-HBCDD in beluga, possibly in addition to α-HBCDD being more recalcitrant than γ-HBCDD (Szabo et al., 2010, 2011). These processes add to those discussed in the previous AMAP assessment, which mainly considered trophic dilution for γ-HBCDD in the food web (de Wit et al., 2010).

Isomer-specific analyses of HBCDD in seabirds from Norway and Greenland also showed that only α-HBCDD was present in detectable amounts (Helgason et al., 2009; Vorkamp et al., 2012). However, slightly deviating results have been reported for the isomer pattern in ringed seal. Although accounting for about 60% (α-HBCDD) and 40% (γ-HBCDD) of ΣHBCDD in the Canadian study, α-HBCDD was the only isomer consistently above detection limits in ringed seal from East Greenland (Tomy et al., 2009; Vorkamp et al., 2011).

In pelagic fish, β-HBCDD was found to account for 10–20% of ΣHBCDD, which is similar to percentages in Arctic air (Tomy et al., 2009; Vorkamp et al., 2015). In high trophic level animals, β-HBCDD was largely absent, suggesting biotransformation of β-HBCDD (Tomy et al., 2009).

The Canadian food web study shows that HBCDD accumulated strongly in lower trophic level animals while some metabolic depletion took place in higher trophic animals (Tomy et al., 2009). Strong biomagnification was also found in a non-Arctic food web study with focus on lower trophic levels, namely invertebrates and fish (Sørmo et al., 2009). In terms of higher trophic levels, however, screening for HBCDD in ringed seals and polar bears from the same location indicated a biomagnification factor of >1 for α-HBCDD (Vorkamp et al., 2011, 2012; Dietz et al., 2013).

The offloading of α-HBCDD to offspring was addressed in a study on beluga in Alaska, which included two mother-fetus pairs (Hoguet et al., 2013). Ratios between fetal (F) and maternal (M) concentrations were F/M = 0.5 for α-HBCDD, indicating a reduced transfer of α-HBCDD to the fetus. For comparison, F/M-ratios >1 were found for HCHs and chlorobenzenes.

2.2.4 Tetrabromobisphenol A (TBBPA)

2.2.4.1 Introduction

Tetrabromobisphenol A (TBBPA) is the flame retardant produced in greatest quantities (de Wit et al., 2010). It is different to other BFRs considered in this assessment in that it is mainly used as a reactive flame retardant (Covaci et al., 2009). The EU has prepared two risk assessments on TBBPA, addressing human and environmental health (EU, 2006, 2008b). The human health risk assessment concluded that no risk was expected because existing risk reduction measures were considered sufficient. The same conclusion was reached for the atmospheric environment and for microorganisms in wastewater treatment plants. However, for the aquatic and terrestrial ecosystems, further information and testing were considered necessary, mainly owing to the potential formation

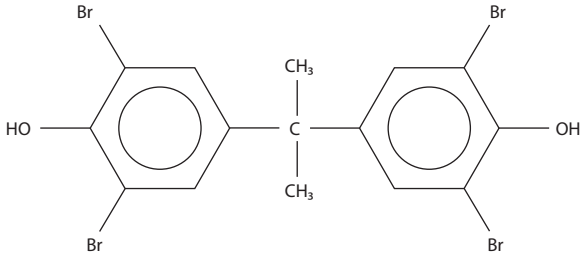


Figure 2.39 Chemical structure of TBBPA.

of bisphenol A or dimethyl-TBBPA, as well as specific risk limitation measures for acrylonitrile butadiene styrene (ABS) compounding sites (EU, 2008b). The European Food Safety Agency concluded that current dietary exposure to TBBPA did not raise a health concern (EFSA, 2011). TBBPA has been registered under REACH since 2011 (BSEF, 2012). While it is not covered by the RoHS Directive, the EU Directive on Waste of Electrical and Electronic Equipment (WEEE) requires that plastics containing BFRs must be removed from separately collected WEEE (EU, 2012). The chemical structure of TBBPA is shown in Figure 2.39.

TBBPA is included on OSPAR's List of Chemicals for Priority Action (OSPAR, 2011). However, Stiehl et al. (2008) reviewed the available TBBPA data and concluded that TBBPA did not meet the criteria for persistence, bioaccumulation and toxicity as defined by OSPAR (Wiandt and Poremski, 2002). TBBPA was added to VECAP in 2006 (VECAP, 2007). According to EFRA (2015), 91% of 'volumes sold' had joined the program in 2014. Environment Canada undertook a screening assessment of TBBPA and concluded that there was a low risk of harm to organisms or the broader integrity of the environment for TBBPA, based on currently available information (Environment Canada, 2013). Furthermore, it concluded that the low environmental concentrations would not endanger human health (Environment Canada, 2013). The report also highlighted the need for re-assessments if the situation changes, for example, increased use of TBBPA.

The previous AMAP assessment noted that few studies had addressed TBBPA in the Arctic (de Wit et al., 2010). While TBBPA had been detected in both the biotic and abiotic environment of the Arctic, several studies had also reported concentrations below detection limits. Thus, with the data available at the time, it was not possible to assess the potential long-range transport of TBBPA, its prevalence in Arctic samples or potential spatial/temporal trends (de Wit et al., 2010). The transformation product dimethyl-TBBPA might also be of interest because it is less polar and so might be more susceptible to bioaccumulation (Covaci et al., 2009).

2.2.4.2 Physical-chemical properties

TBBPA is phenolic in structure and so fairly water soluble, and has a log K_{OW} of 4.5–5.9 (IPCS, 1995; Howard and Muir, 2010). The dimethylated metabolite is more lipophilic. See Appendix 1 for more detailed information.

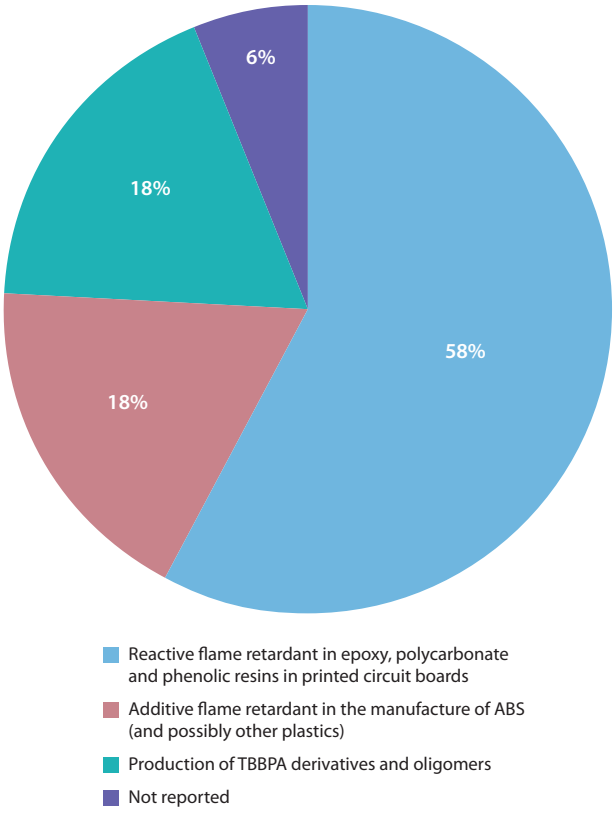


Figure 2.40 Global use of TBBPA in 2007 (data from Covaci et al., 2009).

2.2.4.3 Sources, production, use and trends

TBBPA is the BFR with the largest production volume, with production sites in China, Israel, Japan, Jordan and the USA (BSEF, 2012). The global production volume estimated for 2003 in the previous AMAP assessment was about 150 000 tonnes, which is about three times the production volume for decaBDE (de Wit et al., 2010). This is in line with numbers reported in an EU risk assessment, which also reported increasing production from about 50 000 tons in the early 1990s (EU, 2006). However, given developments in the regulation of BFRs, especially the global ban on PBDEs and HBCDD through the Stockholm Convention, as well as overall trade developments, for example the predominant production of electronics in Asia, production data from 10 to 15 years ago might now be out of date.

One of the main TBBPA applications is the reaction with epoxy resins typically used in laminated printed circuit boards. The main type of reinforced laminated printed circuit boards – the glass fiber based FR4 printed circuit boards – contains TBBPA in 95% of the products (BSEF, 2012). The content of TBBPA in the epoxy resin is typically 15–17% (EU, 2006). Other commercially important applications of TBBPA are reactions with polycarbonate or unsaturated polyester resins used in a wide variety of products (EU, 2006). Besides its main use as a reactive flame retardant, TBBPA is also used as an additive flame retardant mainly for fire proofing of ABS plastics used as plastic casing for TV sets and other electronic devices (BSEF, 2012). The main TBBPA applications are quantified as shown in Figure 2.40 (Covaci et al., 2009). EFRA (2015) reported that emissions of TBBPA to the environment had been 'at default levels', i.e. <2 kg/y, for four consecutive years.

2.2.4.4 Transformation processes

Several studies exist on the microbial and abiotic transformation of TBBPA, as reviewed by Chen et al. (2015). In the context of waste disposal, TBBPA is degraded in the presence of metals and solvents such as acetone (Zhong et al., 2012a). In the environment, TBBPA could be transformed photolytically (Bao and Niu, 2015) and biologically, for example by several species of microalgae (Peng et al., 2014) as well as aerobic and anaerobic microorganisms (Watanabe et al., 1983; Chang et al., 2012). Dimethyl-TBBPA is a transformation product of TBBPA previously detected in peregrine falcons from Greenland (Vorkamp et al., 2005).

2.2.4.5 Modeling studies

No recent modeling studies were available.

2.2.4.6 Environmental concentrations

Air and precipitation

Remberger et al. (2002) investigated TBBPA in air and deposition from Pallas in northern Finland in two samples from August and December 2001. TBBPA was detected in air (2 pg/m^3, August) and deposition (380 pg/m^2/day, December).

Atmospheric concentrations of TBBPA were studied on a cruise from the North Sea to the Arctic in 2004 (Xie et al., 2007a). ΣTBBPA – indicating the sum of gaseous and particle-bound TBBPA – ranged from <0.04 to 0.17 pg/m^3. However, only two out of seven Arctic samples, both collected off the west coast of Norway, had detectable concentrations of TBBPA. In both cases, TBBPA was detected in the gas phase (0.05 and 0.17 pg/m^3). The remaining samples originated from the Greenland Sea and the west coast of Svalbard. An overall decrease in TBBPA concentrations with latitude was observed. For comparison, ΣTBBPA levels at two stations in the North Sea were 0.31 and 0.69 pg/m^3, respectively. Higher concentrations in northern Finland than in the Greenland Sea or near Svalbard might be part of this decrease with increasing latitude.

Terrestrial environment

No recent data were available.

Freshwater environment

TBBPA concentrations were below detection limit in Arctic char muscle samples collected from the lake Ellasjøen on Bjørnøya, Norway (Evenset et al., 2009) (Table 2.11).

Marine environment

Few additional data have been published on TBBPA in Arctic biota since the previous AMAP assessment, and those that have show concentrations below detection limits (Table 2.11). The recent analyses include fish samples from Svalbard and Bjørnøya in the Norwegian Arctic (Evenset et al., 2009), blue mussel (*Mytilus edulis*) and fish from Iceland, and bird eggs and fish from the Faroe Islands (Schlabach et al., 2011).

Table 2.11 Concentrations of TBBPA in Arctic biota (Evenset et al., 2009; Schlabach et al., 2011).

Species	Sample	Location	n	TBBPA, ng/g ww
Atlantic cod	Liver	Svalbard	5	<3.3
Polar cod	Liver	Svalbard	6	<1.9
Polar cod	Whole fish	Svalbard	5	<0.47
Arctic char	Muscle	Bjørnøya (Norway)	5	<0.45
Black guillemot	Egg	Faroe Islands	2[a]	<0.1
Atlantic cod	Liver	Faroe Islands	1[a]	<0.2
Arctic char	Muscle	Faroe Islands	1[a]	<0.03
Cod	Liver	Iceland	1[a]	<0.3
Blue mussel	Tissue	Iceland	1[a]	<0.03

[a]Pooled samples.

2.2.4.7 Environmental trends

Spatial trends

Decreasing air concentrations were observed with increasing latitude (Remberger et al., 2002; Xie et al., 2007a).

Temporal trends

No data were available with which to assess temporal trends.

2.2.5 Bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB)

2.2.5.1 Introduction

Bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) is the brominated analogue of bis(2-ethylhexyl)phthalate (DEHP), which is suspected to be an endocrine disruptor (Latini, 2005). BEH-TEBP is currently assessed under the Community Rolling Action Plan (CoRAP) of the European Chemicals Agency. A tonnage/use of 100–1000 tons per year is given in the justification document for this assessment (Swedish Chemicals Agency, 2015). Moreover, BEH-TEBP is suspected to be persistent, bioaccumulative and toxic or even very persistent/very bioaccumulative and a potential endocrine disrupter (Swedish Chemicals Agency, 2015). Based on the DEHP analogy, the metabolite mono(2-ethylhexyl) tetrabromophthalate might also cause adverse effects in the case of BEH-TEBP exposure (Springer et al., 2012). The US EPA has issued a Data Needs Assessment on BEH-TEBP under the Toxic Substances Control Act because of insufficient data for a quantitative risk assessment (US EPA, 2017a). The Canadian government has also requested information on BEH-TEBP and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) under the Canadian Environmental Protection Act (Canada, 2013). Figure 2.41 shows the chemical structures of BEH-TEBP and EH-TBB.

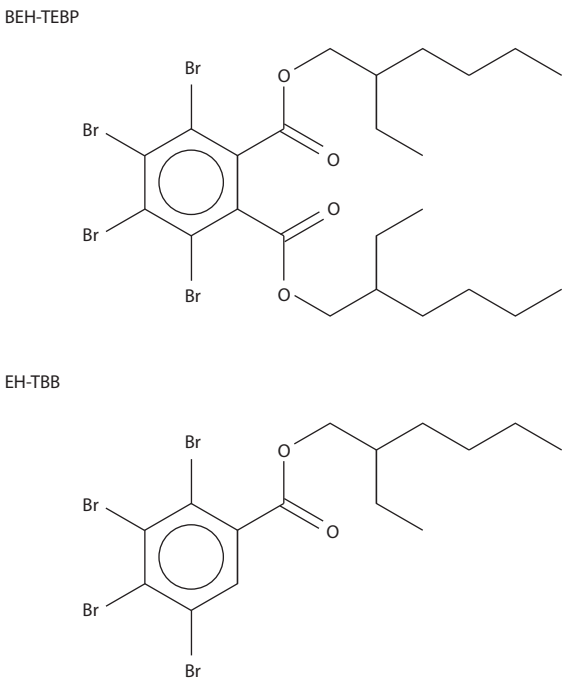


Figure 2.41 Chemical structures of bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB).

Table 2.12 Model results and estimates of parameters related to the long-range transport of BEH-TEBP (Xiao et al., 2012a and references therein).

Log K_{OA}	18
Log K_{AW}	-6.0
Half-life in air	5.9 hours
Half-life in water	1400 hours
Half-life in soil	2900 hours
Overall persistence	170 days
Characteristic travel distance	2900 km
Particle bound fraction in air, Φ_{Air}	1.0

Table 2.13 Percentages of bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) in commercial fire retardant products (Ma et al., 2012b).

	BEH-TEBP	EH-TBB
Firemaster 550[a]	15%	35%
Firemaster BZ-54	30%	70%
DP-45	100%	-

[a]Difference to 100%: aromatic phosphate esters.

2.2.5.2 Physical-chemical properties

BEH-TEBP has relatively high reported log K_{OW} values of 10 (Covaci et al., 2011) and 11.95 (CECBP, 2008) whereas the log K_{OW} for EH-TBB is given as 8.75 (CECBP, 2008). Modeled estimates of parameters related to the long-range transport of BEH-TEBP have been summarized (Xiao et al., 2012a), as shown in Table 2.12. Compared with some of the other flame retardants, such as HBBz (see Section 2.2.9.2) or PBT (see Section 2.2.9.7), the half-life of BEH-TEBP in the atmosphere is relatively short. However, this seems to be overruled by the frequent detection of BEH-TEBP in the Arctic atmosphere. See Appendix 1 for more detailed information.

2.2.5.3 Sources, production, use and trends

BEH-TEBP has been used as a flame retardant on its own and in combination with EH-TBB. Marketed as Firemaster 550 and Firemaster BZ-54, mixtures of BEH-TEBP and EH-TBB have been used as replacements for pentaBDE (Stapleton et al., 2008; Ma et al., 2012b) (Table 2.13). According to Bearr et al. (2010), Firemaster 550 is a mixture of Firemaster BZ-54 and aromatic phosphate esters. BEH-TEBP was also used as an additive flame retardant (DP-45) and as a plasticizer in neoprene and polyvinylchloride (PVC) (Andersson et al., 2006; Stapleton et al., 2008), meaning that its presence in the environment can have multiple sources.

2.2.5.4 Transformation processes

Both BEH-TEBP and EH-TBB have been found to be reductively debrominated in laboratory photodegradation studies (Davis and Stapleton, 2009). This process potentially proceeds to non-brominated degradation products, which for BEH-TEBP would lead to formation of DEHP. The cleavage of BEH-TEBP to yield mono(2-ethylhexyl)tetrabromophthalate has been shown *in vitro* (Springer et al., 2012).

2.2.5.5 Modeling studies

No recent modeling studies were available beyond the modeled parameters summarized in Table 2.12.

2.2.5.6 Environmental concentrations

Air and precipitation

At the western Canadian subarctic site of Little Fox Lake, EH-TBB and BEH-TEBP were detected in 78% and 38% of all air samples collected between August 2011 and December 2014, with median concentrations of 0.28 and 0.38 pg/m^3, respectively (Figure 2.42) (Yu et al., 2015). The average ratio of EH-TBB/BEH-TEBP in Little Fox Lake air was 0.94, based on samples where both compounds were detected. The ratio in the Firemaster 550 mixture is 2.3 (Table 2.13). EH-TBB and BEH-TEBP were weakly correlated with each other (r=0.37, p=0.015), suggesting differences in environmental behavior and/or sources other than the Firemaster technical mixtures. Additional sources of BEH-TEBP were also concluded from measurements at Alert in the Canadian High Arctic, also based on lower EH-TBB/BEH-TEBP ratios than in the Firemaster 550 product (Table 2.13) (Xiao et al., 2012a). This would be in line with the reported use of BEH-TEBP individually, as a plasticizer and/or flame retardant (Andersson et al., 2006).

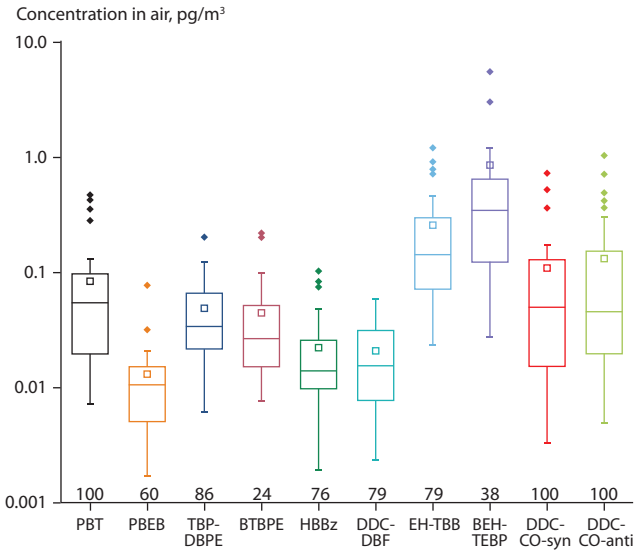


Figure 2.42 Novel brominated flame retardants including EH-TBB and BEH-TEBP in air at Little Fox Lake in the Canadian subarctic (Yu et al., 2015).

Particle phase atmospheric samples collected in Longyearbyen (Svalbard) from September 2012 to May 2013 showed that EH-TBB and BEH-TEBP were among the most abundant non-PBDE BFRs with detection frequencies of 91% (EH-TBB) and 88% (BEH-TEBP) (Salamova et al., 2014) (Annex Table A2.2/3). These concentrations were higher than those previously reported for the Canadian and European Arctic: 0.02–2.7 pg/m³ of EH-TBB and <MDL–2.9 pg/m³ of BEH-TEBP at Alert in 2007–2008 (Xiao et al., 2012a); <MDL–0.08 pg/m³ (in particle phase only) of BEH-TEBP over the East Greenland Sea in August to September 2009 (Möller et al., 2011b), and non-detectable concentrations of EH-TBB and <MDL–0.36 pg/m³ of BEH-TEBP over the Arctic Ocean from June to September 2010 (Möller et al., 2011a).

The relatively high concentrations at Svalbard could be related to increased use of Firemaster 550 (Salamova et al., 2014). The high volume air sampling at Alert in the Canadian High Arctic showed increasing concentrations of BEH-TEBP between 2008 and 2012 (Figure 2.43). Increasing trends have also been observed in air in the Great Lakes region (Ma et al., 2012b).

Recent screening for EH-TBB in air at Alert found concentrations approaching 10 pg/m³, i.e. they had reached the same level as BDE-47 and BDE-99 at their maximum (Hung et al., 2013a) (Annex Table A2.2/1). At Svalbard, the concentration of EH-TBB in particles was higher than that for PBDEs, accounting for 46% of ΣBFR, with PBDEs accounting for 37% of ΣBFR (Salamova et al., 2014) (Annex Table A2.2/3). BEH-TEBP generally had lower concentrations than EH-TBB and accounted for 17% of ΣBFR. The fraction of EH-TBB to total concentration of EH-TBB and BEH-TEBP in Firemaster 550 is 0.77±0.03. In this study, the fraction was found to be 0.65±0.02, close to that of the commercial mixture (Salamova et al., 2014). Xiao et al. (2012a) and Yu et al. (2015) reported lower EH-TBB/BEH-TEBP ratios than for the Firemaster 550 mixture. This could be consistent with the findings

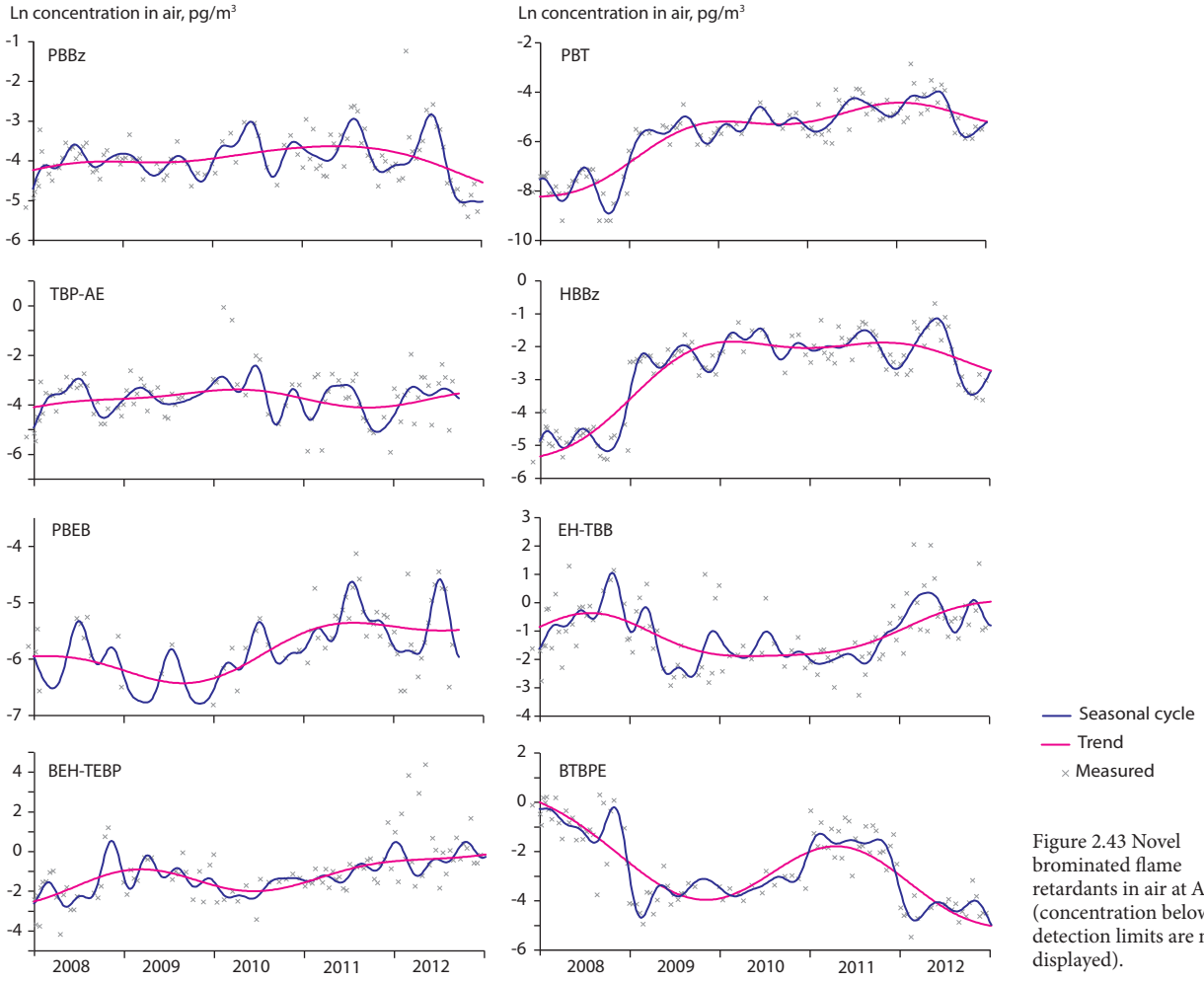


Figure 2.43 Novel brominated flame retardants in air at Alert (concentration below detection limits are not displayed).

Table 2.14 Concentrations (ng/g ww) of bis(2-ethylhexyl)tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) in marine Arctic biota.

Species	Sample	Origin	BEH-TEBP, mean (range)	EH-TBB, mean (range)	Reference
Blue mussel	Tissue	Iceland	0.009[a]	0.0041[a]	Schlabach et al., 2011
Capelin	Whole fish	Svalbard	0.72 (<0.12–1.3)	0.38 (0.16–0.92)	Sagerup et al., 2010
Polar cod	Whole fish	Svalbard	<0.01	na	Harju et al., 2013
Atlantic cod	Liver	Faroe Islands	0.2[a]	0.12	Schlabach et al., 2011
	Liver	Iceland	<0.18	<0.022	Schlabach et al., 2011
	Liver	Svalbard	<0.01–0.07	na	Harju et al., 2013
Common eider	Liver	Svalbard	1.65 (<0.14–3.8)	0.86 (0.25–4.4)	Sagerup et al., 2010
	Egg	Svalbard	0.06 (<0.01–0.21)	Na	Harju et al., 2013
Black-legged kittiwake	Liver	Svalbard/Bjørnøya	0.80 (<0.17–1.4)	0.73 (<0.040–1.2)	Sagerup et al., 2010
	Egg	Svalbard	0.10 (0.04–0.29)	na	Harju et al., 2013
Brünnich's guillemot	Liver	Svalbard	1.8 (<0.16–3.4)	1.2 (<0.032–2.5)	Sagerup et al., 2010
Glaucous gull	Plasma	Svalbard	<0.01–0.03 ng/mL	na	Harju et al., 2013
	Liver	East Greenland	<0.025	0.18 (0.088–0.27)	Vorkamp et al., 2015
Black guillemot	Egg	East Greenland	0.061 (0.055–0.066)	0.076 (0.063–0.090)	Vorkamp et al., 2015
Ringed seal	Liver	Svalbard	0.57 (<0.14–0.73)	0.44 (0.11–1.2)	Sagerup et al., 2010
	Plasma	Svalbard	<0.01–0.04 ng/mL	na	Harju et al., 2013
	Blubber	West Greenland	<0.13	0.19 (<0.064–0.50)	Vorkamp et al., 2015
	Blubber	East Greenland	<0.14	1.02 (0.65–1.46)	Vorkamp et al., 2015
Polar bear	Plasma	Svalbard	<0.29	3.5 (<0.077–7.3)	Sagerup et al., 2010
	Plasma	Svalbard	0.15 (<0.018–0.66)	na	Harju et al., 2013
	Adipose	East Greenland	0.26 (<0.13–0.40)	0.12 (<0.065–0.15)	Vorkamp et al., 2015

na: Not available; [a]no range is given because n=1.

of Salamova et al. (2014), subject to natural variation, but more data are needed to confirm this or to determine potential trends.

EH-TBB was sought, but not detected in bulk deposition samples collected at Abisko and Krycklan in northern Sweden (Newton et al., 2014).

Terrestrial environment

BEH-TEBP and EH-TBB have been included in several screening studies of contaminants in Arctic biota, but most samples originate from the marine environment. For the terrestrial environment, liver samples of Arctic fox (*Alopex lagopus*) from Svalbard had concentrations below detection limit (<0.14 ng/g ww) for BEH-TEBP, but mean concentrations of 0.98 ng/g ww for EH-TBB. Ten samples were analyzed, with a range of <0.037–2.48 ng/g ww (Sagerup et al., 2010).

Freshwater environment

BEH-TEBP and EH-TBB were both detected in Arctic char from a lake on the Faroe Islands, at concentrations of 0.011 ng/g ww (BEH-TEBP) and 0.0031 ng/g ww (EH-TBB) (Schlabach et al., 2011).

Marine environment

Most results for biota are available for the marine environment where EH-TBB and BEH-TEBP were widely detected, albeit at relatively low concentrations (Table 2.14). Although most data sets also include samples below detection limits, it was possible to determine mean values for several species from various locations.

The database is too small to derive trends, but the results show that at lower trophic levels, concentrations of BEH-TEBP exceed those of EH-TBB (Table 2.14). In glaucous gull, ringed seal and polar bear some but not all results showed higher concentrations of EH-TBB than BEH-TEBP (Sagerup et al., 2010; Vorkamp et al., 2015). Vorkamp et al. (2015) pointed out that concentrations of BEH-TEBP and EH-TBB were not statistically different in glaucous gull samples from East Greenland and that they also appeared similar in polar bears.

Sagerup et al. (2010) did not find biomagnification of BEH-TEBP, however, the analyses were based on ringed seal liver and polar bear plasma. For EH-TBB, concentrations were higher in polar bear than ringed seal (Sagerup et al., 2010). In a second study from Svalbard, this was also the case for

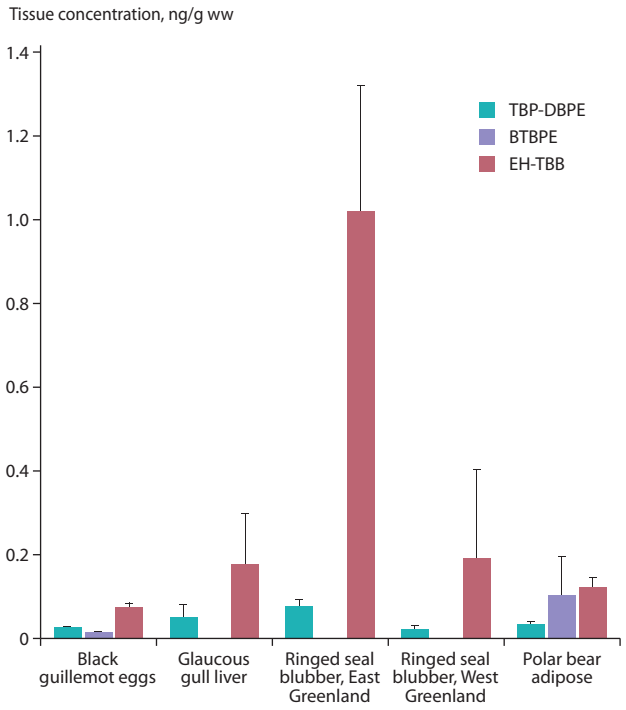


Figure 2.44 Mean concentrations and standard deviations of EH-TBB, TBP-DBPE and BTBPE in marine biota from Greenland (data from Vorkamp et al., 2015).

BEH-TEBP (Harju et al., 2013). It should be noted, however, that results are on a wet weight or volume basis (Table 2.14). Biomagnification studies of lipid-associated compounds usually use lipid-normalized concentrations (Fisk et al., 2001).

While ringed seal samples from East Greenland and Svalbard had similar concentrations of EH-TBB, larger differences occurred in polar bears (Sagerup et al., 2010; Vorkamp et al., 2015). For BEH-TEBP, concentrations were more similar. EH-TBB concentrations in ringed seal were significantly higher in East Greenland than West Greenland ($p<0.05$) (Figure 2.44) (Vorkamp et al., 2015), a pattern also seen for organochlorine POPs (Vorkamp et al., 2008). Concentrations below detection limits prevented comparisons between East and West Greenland for BEH-TEBP, and the results for EH-TBB, based on only 4–5 samples, also require confirmation (Vorkamp et al., 2015).

2.2.5.7 Environmental trends

Spatial trends

The current database is insufficient to assess spatial trends of EH-TBB and BEH-TEBP in the Arctic.

Temporal trends

EH-TBB and BEH-TEBP have been included in the high volume air sampling at Alert in the Canadian High Arctic, and concentrations increased between 2008 and 2012 (Figure 2.43). However, more data are needed to derive temporal trends in the Arctic. For the atmosphere of the Great Lakes region, increases in both EH-TBB and BEH-TEBP have been found (Ma et al., 2012b).

2.2.6 2,4,6-Tribromophenyl 2,3-dibromopropyl ether (TBP-DBPE), 2,4,6-tribromophenyl allyl ether (TBP-AE) and 2,4,6-tribromophenyl 2-bromoallyl ether (TBP-BAE)

2.2.6.1 Introduction

2,4,6-Tribromophenyl 2,3-dibromopropyl ether (TBP-DBPE, formerly abbreviated as DPTE) has been detected in the Arctic, but no information is currently available on its production or use as a flame retardant. The CAS number (35109-60-5) refers to the trade name Bromkal 73-5PE and to synonymously used chemical names (2,3-dibromopropyl-2,4,6-tribromophenyl ether, 1,3,5-tribromo-2-(2,3-dibromopropoxy)benzene; 2,4,6-tribromo-1-(2,3-dibromopropyloxy)benzene).

TBP-DBPE and 2,4,6-tribromophenyl allyl ether (TBP-AE, formerly abbreviated as ATE, CAS number 3278-89-5) were included in a prioritization report on flame retardants for risk assessment (Fisk et al., 2003). For acute toxicity, Fisk et al. (2003) categorized the compounds as A-1/A-2 (lowest acute L(E)C_{50} of <1 and 1–10 mg/L, respectively). They suggested that the risk might be higher in the terrestrial environment than the aquatic environment. Based on chronic ecotoxicity, a medium to very high risk was identified for TBP-AE in aquatic and terrestrial ecosystems in connection with textile and polymer processing, the important industrial sectors for flame retardant use (Fisk et al., 2003). Risk for regional waters was considered low. A preliminary prioritization by Fisk et al. (2003) did not classify TBP-DBPE as persistent, bioaccumulative and toxic, but the authors highlighted that more investigations would be required for TBP-DBPE and TBP-AE.

The chemical structures of TBP-DBPE, TBP-AE and 2,4,6-tribromophenyl 2-bromoallyl ether (TBP-BAE, formerly abbreviated as BATE, no CAS number available) are given in Figure 2.45. The compounds were not included in the previous AMAP assessment on BFRs (de Wit et al., 2010).

2.2.6.2 Physical-chemical properties

The log K_{OW} value for TBP-DBPE was reported as 5.9 (Vetter et al., 2010) and 6.34 (CECBP, 2008). For TBP-AE, the log K_{OW} was reported as 4.97 (Covaci et al., 2011). TBP-AE was defined as a multi-hopper compound with similar partitioning properties as other known Arctic contaminants (Brown and Wania, 2008). See Appendix 1 for more detailed information.

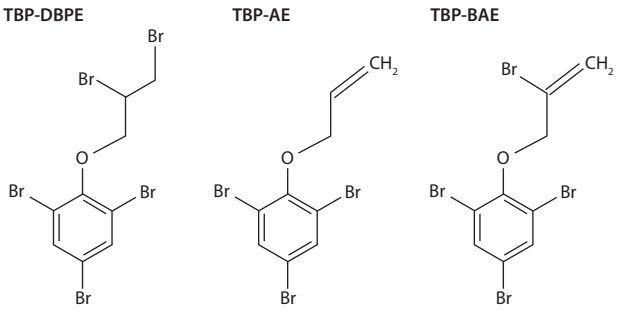


Figure 2.45 Chemical structures of 2,4,6-tribromophenyl 2,3-dibromopropyl ether (TBP-DBPE), 2,4,6-tribromophenyl allyl ether (TBP-AE) and 2,4,6-tribromophenyl 2-bromoallyl ether (TBP-BAE).

2.2.6.3 Sources, production, use and trends

According to Vetter et al. (2010), TBP-DBPE was produced in Germany until 1985 under the tradename Bromkal 73-5PE. The International Programme on Chemical Safety reported that TBP-DBPE was used as a flame retardant in extrusion grade polypropylene (IPCS, 1997). Internet searches show that several suppliers in Europe, North America and Asia offer minor quantities of this compound for sale.

Under the trade name PHE-65, TBP-AE has also been produced and used as a reactive flame retardant and as an additive flame retardant in expandable polystyrene and polystyrene foam (Covaci et al., 2011). Covaci et al. (2011) reported that the US production volume was <227 tons in 2006 and that TBP-AE was listed as a low production volume chemical in the EU.

TBP-BAE has not been produced commercially, based on currently available information.

2.2.6.4 Transformation processes

TBP-AE and TBP-BAE are transformation products of TBP-DBPE (von der Recke and Vetter, 2007). As the chiral molecule TBP-DBPE was still present in nearly racemic fractions, Vetter et al. (2010) concluded that the transformation processes were non-enantioselective.

2.2.6.5 Modeling studies

TBP-AE was found to have Arctic contamination and bioaccumulation potential, based on global transport calculations and a food chain bioaccumulation model (Brown and Wania, 2008). The study also found that the structure of TBP-AE bore some resemblance to known Arctic contaminants. However, TBP-AE was not considered persistent, based on a modelled atmospheric half-life of <2 days (Brown and Wania, 2008).

2.2.6.6 Environmental concentrations

Air and precipitation

TBP-BAE and TBP-AE have been monitored at Alert in the Canadian High Arctic since 2008 (Figure 2.43), while TBP-DBPE was not included. TBP-BAE was only detectable in 2008 and 2012 in <20% of all air samples with concentrations ranging from <MDL–0.020 pg/m^3 (Annex Table A2.2/1). However, TBP-AE was frequently detectable (annual detectability of 65–100%) (Annex Table A2.2/1; Figure 2.43). Passive air samples collected at Arctic/subarctic stations under the GAPS network detected TBP-AE at Barrow and St Lawrence Island (Alaska), Stórhöfði (Iceland), Ny-Ålesund (Svalbard) and Hollola (Finland) with the highest concentrations of about 1 pg/m^3 at St Lawrence Island and Ny-Ålesund; but TBP-BAE was only detectable at Barrow (Annex Table A2.2/2) (Lee et al., 2016).

TBP-DBPE was detected in air samples in two studies following transects into the Bering/Chukchi Sea and the East Greenland Sea, respectively (Möller et al., 2011a,b). On the first cruise, Arctic stations were considered to be those north of 60°N. Concentrations were generally low (Table 2.15), but TBP-DBPE was detected in all gas phase atmospheric samples from the Bering/Chukchi Sea. In the East Greenland Sea, detection frequencies were 89% and 100% for TBP-DBPE in the gas phase and particulate phase of the air samples, respectively.

Compared with the better studied PBDEs, concentrations of TBP-DBPE in the Bering/Chukchi Sea region exceeded those of BDE-47 and BDE-99 (Möller et al., 2011a). In the East Greenland Sea, however, some air samples had lower concentrations of TBP-DBPE than BDE-47 or BDE-99 (Möller et al., 2011b). TBP-AE and TBP-BAE were not included in these studies.

Lower concentrations of TBP-DBPE than BDE-47 or BDE-99 were observed at Little Fox Lake in the Canadian subarctic (Yu et al., 2015). TBP-DBPE was detected in over 75% of the air samples collected monthly over a three-year period from August 2011 to December 2014 by means of a flow-through-sampler containing polyurethane foam (PUF). TBP-AE and TBP-BAE were detected in about 25% of samples (Yu et al., 2015). Mean concentrations at Little Fox Lake were 0.049 pg/m^3 (TBP-DBPE), 0.036 pg/m^3 (TBP-AE) and 0.012 pg/m^3 (TBP-BAE) (Figure 2.42). With a maximum concentration of 0.2 pg/m^3 for TBP-DBPE, these data are comparable to those reported for the East Greenland Sea, but lower than those for the Bering/Chukchi Sea (Table 2.15). Although still occurring at a very low level, TBP-DBPE showed tendencies of increasing concentration at Little Fox Lake (Yu et al., 2015). TBP-DBPE was also sought in air samples collected at Villum Research Station in northeast Greenland in 2012, but was below detection limits of 0.4 pg/m^3 in all samples (Vorkamp et al., 2015). TBP-DBPE was not detected in air samples at Abisko in northern Sweden (Newton et al., 2014). TBP-AE and TBP-BAE were not included in these studies.

Terrestrial environment

No data were available.

Freshwater environment

One pooled sample of Arctic char muscle from a lake on the Faroe Islands was analyzed for TBP-DBPE, TBP-BAE and TBP-AE, but all three were below detection limits (<0.0042, <0.0013, <0.0037 ng/g ww) (Schlabach et al., 2011).

Table 2.15 Concentration ranges of TBP-DBPE in Arctic air and seawater (Möller et al., 2011a,b). The Bering/Chukchi Sea data only include stations north of 60°N.

Bering/Chukchi Sea				East Greenland Sea			
Air, pg/m^3		Seawater, pg/L		Air, pg/m^3		Seawater, pg/L	
Gaseous	Particles	Dissolved	Particles	Gaseous	Particles	Dissolved	Particles
0.1–0.28	<0.21	<0.03–0.078	<0.12	<0.021–1.7	0.005–0.05	<0.028–0.3	<0.076

Marine environment

Sewage sludge

TBP-DBPE, TBP-AE and TBP-BAE were detected in sewage sludge from Reykjavik (Iceland), at concentrations of up to 120 ng/g dw for TBP-DBPE (Schlabach et al., 2011). This suggests that discharges from sewage treatment plants could be a pathway of TBP-DBPE to the Arctic environment.

Seawater

Seawater samples were analyzed for TBP-DBPE on cruises through the Bering/Chukchi Sea and the East Greenland Sea, respectively (Möller et al., 2011a,b) (Table 2.15). TBP-DBPE was only found in the dissolved phase, and only in some samples. Based on the collective data (see also 'Air and precipitation'), a net deposition of TBP-DBPE to Arctic seawater was found (Möller et al., 2011a,b). As was the case for the air samples, the seawater samples had higher concentrations of TBP-DBPE than BDE-47 and BDE-99.

Biota

TBP-DBPE concentrations exceeded PBDE concentrations in harp seals (*Pagophilus groenlandicus*) from the Barents Sea and Greenland Sea, with concentrations of TBP-DBPE of 322–470 and 130–340 ng/g ww in four samples of blubber and brain, respectively (von der Recke and Vetter, 2007). Compared to PCBs and PBDEs, TBP-DBPE was found to be enriched in brain samples by a factor of five in harp seals from the Greenland Sea, and 30 for seals from the Barents Sea. TBP-DBPE was also the predominant brominated compound in blubber samples from hooded seals (*Cystophora cristata*) in the Barents Sea, but the concentration was not determined (Vetter, 2001; von der Recke and Vetter, 2007). While no other harp seal studies are available to confirm the high concentrations, TBP-DBPE was sought in other seal species, as summarized in Table 2.16.

TBP-AE and TBP-BAE were also detectable in harp seal samples (von der Recke and Vetter, 2007). Concentrations were lower than for TBP-DBPE (i.e. ≤10 ng/g ww) (Table 2.16). As TBP-DBPE, TBP-AE and TBP-BAE were the predominant brominated compounds in harp seal brain, von der Recke and Vetter (2007) concluded that these compounds passed the blood-brain barrier more efficiently than PBDEs.

Being a chiral molecule, TBP-DBPE was studied for its enantiomer-specific accumulation in brain and/or blubber of harp and hooded seals from the Barents Sea as well as harp seals from the Greenland Sea (Vetter et al., 2010). TBP-DBPE was found to be close to racemic in all samples, except for a small enrichment (up to 2.5%) of (+)-TBP-DBPE in samples from the Barents Sea and a similarly small (up to 4%) enrichment of (-)-TBP-DBPE in samples from the Greenland Sea. As von der Recke and Vetter (2007) had previously detected TBP-DBPE transformation products in the same samples, Vetter et al. (2010) concluded that this transformation proceeded in non-enantioselective processes.

The screening study by Schlabach et al. (2011) included blue mussel, fish and bird eggs from Iceland and the Faroe Islands. TBP-DBPE was below detection limits in all samples except for blue mussel from Iceland for which a single concentration of 0.049 ng/g ww was found. Likewise, TBP-DBPE was below detection limits of 0.1 ng/g ww in pooled eggs of common eider, European shag and herring gull collected on two Norwegian islands north of 65°N (Huber et al., 2015). TBP-AE and TBP-BAE were also included in the study, but were below detection limits in the samples discussed here.

TBP-DBPE and TBP-AE were also undetectable in capelin, common eider, black-legged kittiwake, Brünnich's guillemot (*Uria lomvia*), ringed seal, Arctic fox and polar bear from Svalbard (Sagerup et al., 2010). According to the Canadian Arctic Contaminants Assessment Report, TBP-DBPE, TBP-AE and TBP-BAE were below detection limits in seals from Canada (Muir et al., 2013a) (Table 2.16). However, TBP-DBPE was detected in ringed seal and polar bear from Greenland, albeit at low concentrations (Vorkamp et al., 2015). Detection frequency for TBP-DBPE was 95% in four species of Greenland wildlife (Figure 2.44). The mean concentrations (ng/g ww) of TBP-DBPE decreased in the order: ringed seal (East Greenland; 0.078) > glaucous gull (0.050) > polar bear (0.034) > black guillemot eggs (0.028) > ringed seal (West Greenland; 0.023) (Vorkamp et al., 2015). Concentrations were higher in ringed seal from East Greenland than West Greenland, which agrees with the geographic trend found for chlorinated compounds and PBDEs (Rigét et al., 2006; Vorkamp et al., 2008, 2011), but more data are needed to derive spatial trends for TBP-DBPE. If the results are lipid normalized, the bird samples have the highest concentrations of TBP-DBPE. TBP-AE and TBP-BAE were not included in this study.

Table 2.16 Concentration ranges (ng/g ww) of TBP-DBPE, TBP-AE and TBP-BAE in seal species from the Arctic.

Species	Tissue	Location	TBP-DBPE	TBP-AE	TBP-BAE	Reference
Harp seal	Blubber	Barents Sea, Greenland Sea	322–470	5.4–9.1	4.9–6.5	von der Recke and Vetter, 2007
	Brain		130–340	3.1–10	1.9–8.0	
Hooded seal	Blubber	Barents Sea	Predominant brominated compound, but not quantified	na	na	Vetter, 2001
Ringed seal	Blubber	Svalbard	<0.0064	<0.0012	na	Sagerup et al., 2010
Seals	Blubber	Canada	<MDL	<MDL	<MDL	Muir et al., 2013a
Ringed seal	Blubber	East Greenland	0.0055–0.0096	na	na	Vorkamp et al., 2015
		West Greenland	<0.0013–0.032	na	na	

na: Not available.

2.2.6.7 Environmental trends

Spatial trends

Insufficient data were available to assess spatial trends in TBP-DBPE, TBP-AE and TBP-BAE.

Temporal trends

While no temporal trend data were available for TBP-DBPE and TBP-BAE, TBP-AE has been included in air monitoring at Alert in the Canadian Arctic since 2008 (Figure 2.43). For the period 2008–2012, no clear change in concentration was observed.

2.2.7 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)

2.2.7.1 Introduction

1,2-Bis(2,4,6-tribromophenoxy) ethane (BTBPE) (CAS number 37853-59-1) is structurally similar to TBP-DBPE, TBP-AE and TBP-BAE in that they all are synthesized from 2,4,6-TBP and consequently, possess a 2,4,6-tribromophenoxy moiety (Ma et al., 2012c). The structure of BTBPE is shown in Figure 2.46.

In a prioritization risk screening, BTBPE was considered to be of high concern in terms of a relatively low tonnage required on the market to reach a risk, but further investigations are warranted (Fisk et al., 2003).

Several studies have indicated that BTBPE can accumulate in biota and biomagnify in food webs. Although not all predator/prey pairs showed biomagnification of BTBPE, the trophic magnification factor in a food web study in Lake Winnipeg (Canada) was 1.86 (Law et al., 2006). BTBPE was readily taken up from the diet by rainbow trout (*Oncorhynchus mykiss*), leading to a biomagnification factor of 2.3 (Tomy et al., 2007). BTBPE was also accumulated in fathead minnow (*Pimephales promelas rafinesque*) in a mesocosm study (de Jourdan et al., 2014).

BTBPE was included in the previous AMAP assessment (de Wit et al., 2010). Based on the detection of BTBPE in seabirds (from the Faroe Islands and the Norwegian Arctic) and marine mammals (from Canada), de Wit et al. (2010) concluded that BTBPE could undergo long-range transport and accumulate in high trophic level biota. Considerably more data from the Arctic are now available including both abiotic matrices and biota studies.

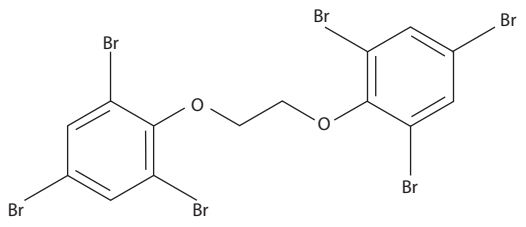


Figure 2.46 Chemical structure of 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE).

Table 2.17 Model results and estimates for parameters related to the long-range transport of BTBPE (Xiao et al., 2012a and references therein).

Log K_{OA}	15
Log K_{AW}	-5.2
Half-life in air	8.6 h
Half-life in water	4300 h
Half-life in soil	8600 h
Overall persistence	520 d
Characteristic travel distance	2800 km
Particle bound fraction in air, Φ_{Air}	1.0

2.2.7.2 Physical-chemical properties

While early studies reported a relatively low log K_{OW} of 3.14 (Karlsson et al., 2006; Verreault et al., 2007b), more recent studies used a considerably higher log K_{OW} of 7.88 (Covaci et al., 2011), 7.9 (Klosterhaus et al., 2012) and 9.15 (CECBP, 2008; Schlabach et al., 2011). As shown in Table 2.17, model results suggest BTBPE has a particle-bound fraction Φ=1 meaning that all atmospheric BTBPE is attached to particles. See Appendix 1 for more detailed information.

2.2.7.3 Sources, production, use and trends

BTBPE is marketed under the trade name FF-680 by Chemtura for use as a polymer additive in thermoplastics, ABS polymer systems and HIPS and was announced in 2005 to replace the commercial octaBDE product (IPCS, 1997; Hoh et al., 2005; Verreault et al., 2007b).

Hoh et al. (2005) reported that BTBPE had been produced in the USA since the early 1970s, reflected by a rapid increase in concentration in sediment core samples of that period. Between 1986 and 1994, 4500–22 500 tons per year were produced in the USA, but annual production decreased to 450–4500 tons after 1998 (Hoh et al., 2005). For 2001, worldwide production/use of BTBPE was estimated at 16 710 tons (Verreault et al., 2007b). These numbers might be outdated if BTBPE now replaces octaBDE, but information on current use and production volumes is unavailable (CECBP, 2008). In the EU, BTBPE is listed as a low production volume chemical (Covaci et al., 2011).

2.2.7.4 Transformation processes

In laboratory experiments with rats, BTBPE could be degraded to 2,4,6-tribromophenol (Hakk et al., 2004), which is an endocrine-disrupting chemical (Hamers et al., 2006; Deng et al., 2010). The majority (94%) of administered radioactive dose was excreted. Besides tribromophenols and tribromophenoxyethanol, hydroxylated and debrominated metabolites were identified (Hakk et al., 2004).

2.2.7.5 Modeling studies

Some physical-chemical characteristics and parameters characterizing the environmental persistence of BTBPE have been modeled, as summarized in Table 2.17 (Xiao et al., 2012a).

2.2.7.6 Environmental concentrations

Air and precipitation

BTBPE has been detected in air at several Arctic monitoring stations (Table 2.18). It has been included in air monitoring at Alert (Canada) since 2006/2007. In high volume air samples from 2006/2007, the median concentration was 0.64 pg/m^3, and the range 0.16–1.9 pg/m^3 (Xiao et al., 2012a). This range was similar to previously reported concentrations from the Great Lakes (Venier and Hites, 2008). No clear seasonal effect was observed in these first BTBPE measurements at Alert. More recent data from Alert are summarized in Annex Table A2.2/1, generally showing slightly lower concentrations (also apparent in Figure 2.43).

At Little Fox Lake, BTBPE was detectable in about 25% of samples between August 2011 and December 2014, with concentrations ranging from non-detectable to 0.22 pg/m^3 (Figure 2.42). BTBPE was detected in passive air samples collected under the GAPS program with the highest concentration found at Ny-Ålesund (up to 5.2 pg/m^3) (Annex Table A2.2/2) (Lee et al., 2016).

BTBPE has a modelled particle-bound fraction Φ=1 meaning that all atmospheric BTBPE is attached to particles. BTBPE was detected in 43% of the 34 samples at Longyearbyen (Svalbard) in 2012/2013 (Salamova et al., 2014). The concentrations were considerably lower than those previously reported from Alert (Xiao et al., 2012a). BTBPE had among the lowest concentrations of the novel BFRs in the study, with concentrations exceeded by BDE-47 and BDE-99 by two orders of magnitude (Salamova et al., 2014).

Similarly low BTBPE concentrations were found in air of the East Greenland Sea, however, in this case BTBPE could also be detected in the gas phase (Möller et al., 2011b), which challenges the model results in Table 2.17 predicting 100% particle adsorption of BTBPE. Möller et al. (2011a) analyzed air samples on a transect in the Bering/Chukchi Sea where a higher maximum concentration of 0.17 pg/m^3 was found. However, this was the only gas phase sample (out of eight samples collected north of 60°N) with a detectable concentration of BTBPE. All remaining samples were <0.031 pg/m^3.

In a study collecting BTBPE and other compounds on Amberlite resins from two months of precipitation at Abisko (Arctic) and Krycklan (subarctic), Sweden, BTBPE was detectable in all bulk deposition samples, but could not be quantified because of insufficient recovery (Newton et al., 2014).

The low atmospheric concentrations of BTBPE at Svalbard are in line with low concentrations and fluxes of BTBPE in an ice core from Holtedahlfonna on Svalbard (Hermanson et al., 2010; Salamova et al., 2014). For BTBPE, the flux was <1 pg/cm^2/y until about 1970 and then increased to 4–5 pg/cm^2/y in the most recent layers, representing the period 1988–2005 (Hermanson et al., 2010) (Figure 2.47). For comparison, the maximum flux of HBCDD was 910 pg/cm^2/y (Figure 2.33). The total burden of BTBPE in the upper 34 m of the ice core was about 10 ng, while that of HBCDD was over 1000 ng. In snow pits in Nunavut (Canada) of 2005, 2006 and 2008, the highest concentration of BTBPE in each snow pit was 70, 2 and 120 pg/L, respectively (Meyer et al., 2012). As several sub-samples had concentrations below detection limits, average concentrations are likely to be lower than those of the Svalbard ice core, which was 92 pg/L in the uppermost layer (Hermanson et al., 2010). No clear trend was observed in the deposition history of BTBPE in the snow pit.

Table 2.18 Concentrations of BTBPE in Arctic air.

Station	Region (Country)	Year	BTBPE concentration, pg/m^3	Reference
Transect marine atmosphere	Bering/Chukchi Sea[a]	2010	Range gas phase: <0.031–0.17 Particle phase: <0.031	Möller et al., 2011a
Transect marine atmosphere	East Greenland Sea	2009	Range gas phase: <0.019–0.06 Range particle phase: <0.0005–0.02	Möller et al., 2011b
Alert	Nunavut (Canada)	2006/2007	Median: 0.64 Range: 0.16–1.9	Xiao et al., 2012a
Longyearbyen	Svalbard (Norway)	2012/2013	Median particle phase: 0.03 Range particle phase: 0.01–0.09	Salamova et al., 2014
Abisko[b]	Northern Sweden (68°N)	2009/2010	Present, but not quantifiable	Newton et al., 2014
Krycklan[b]	Northern Sweden (64°N)	2009/2010	Present, but not quantifiable	Newton et al., 2014
Villum Research Station	Northeast Greenland	2012	<2	Vorkamp et al., 2015
Little Fox Lake	Yukon (Canada)	2011–2014	Median: 0.044 Range: <0.019–0.22	Yu et al., 2015
Barrow[c]	Alaska (USA)	2005/2006	Range: 0.2–1.0	Lee et al., 2016
St. Lawrence Island[c]	Alaska (USA)	2005/2006	0.33	Lee et al., 2016
Ny-Ålesund[c]	Svalbard (Norway)	2005/2006	Range: <0.2–5.2	Lee et al., 2016
Stórhöfði[c]	Iceland	2005/2006	Range: <0.2–0.94	Lee et al., 2016
Hollola[c]	Finland	2005/2006	Range: <0.2–0.21	Lee et al., 2016

[a]Only sampling stations north of 60°N are considered; [b]measurement of bulk deposition, not air concentrations; [c]passive sampling.

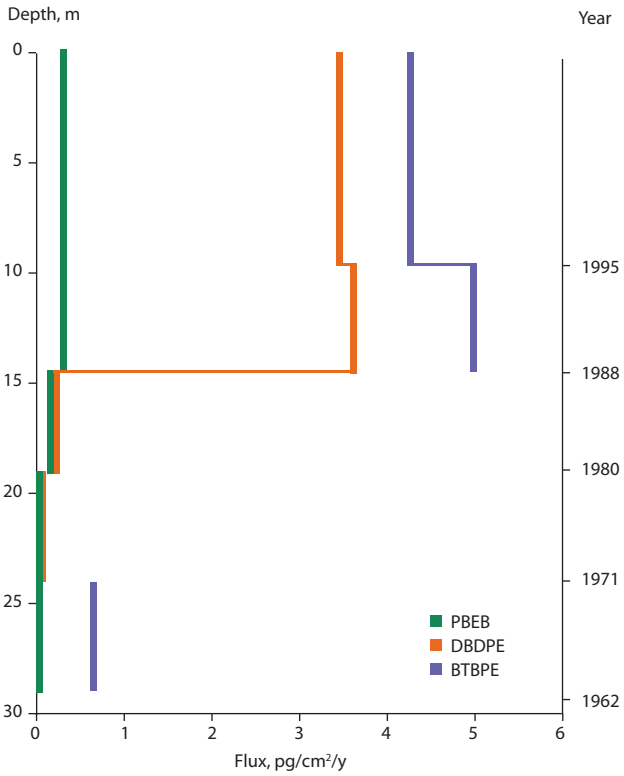


Figure 2.47 Fluxes of BTBPE, DBDPE and PBEB in an ice core from Svalbard (Hermanson et al., 2010).

Terrestrial environment

Results are available for the terrestrial environment of the Canadian Arctic where BTBPE increased in the order caribou < mushrooms < lichen < green plants < wolf (Muir et al., 2013b). The BTBPE concentration in wolf (*Canis lupus*), the top predator of this terrestrial food chain, was about 0.2 ng/g ww, which is comparable to the concentrations reported for polar bear and other high trophic animals of the marine environment. The lowest BTBPE concentration in caribou was about 0.008 ng/g ww. All BTBPE concentrations were exceeded by PBDEs by at least one order of magnitude.

Freshwater environment

BTBPE was detected in muscle of Arctic char from a lake on the Faroe Islands (Schlabach et al., 2011). The pooled sample had a concentration of 0.012 ng/g ww.

Marine environment

Seawater

BTBPE was sought in seawater from the Bering/Chukchi Sea and from the East Greenland Sea. All concentrations were below detection limits (0.017 and 0.0007 pg/L for the Bering/Chukchi and East Greenland Sea, respectively), except for one sample from the East Greenland Sea at 0.002 pg/L in the particle phase (Möller et al., 2011a,b).

Biota

Based on the low concentrations found for BTBPE in Arctic air in combination with indications of bioaccumulation and biomagnification, low concentrations that increase with trophic level could be expected for BTBPE in the Arctic marine food web. A study on BTBPE in liver of Greenland shark (*Somniosus microcephalus*), a high trophic level animal accidentally caught near Iceland, showed a BTBPE median concentration of 0.61 ng/g lw (range: <0.16–8.1 ng/g lw) (Strid et al., 2013). For comparison, the median concentration of BDE-47 was 24 ng/g lw in the same samples, which indicates a lower level of BTBPE even in high trophic level species.

BTBPE was detected in pooled liver samples of Atlantic cod from the Faroe Islands (0.2 ng/g ww) and Iceland (0.0045 ng/g ww) (Schlabach et al., 2011), but was below detection limit (<0.006 ng/g ww) in whole capelin from Svalbard (Sagerup et al., 2010). BTBPE was also detected in a pooled sample of blue mussel from Iceland (0.0085 ng/g ww) (Schlabach et al., 2011).

Several studies have sought BTBPE in seabirds, as summarized in Table 2.19. The black guillemot eggs from East Greenland had comparable concentrations to those from the Faroe Islands (Schlabach et al., 2011). BTBPE was also found in eggs of Brünnich's guillemot from the Norwegian Arctic and in

Table 2.19 Mean concentrations and ranges (in brackets) of BTBPE in Arctic seabird tissues and eggs.

Species	Tissue	Region (Country)	Year	n	BTBPE, ng/g ww	Reference
Common eider	Liver	Svalbard (Norway)	2009	10	<0.006[a]	Sagerup et al., 2010
Black-legged kittiwake	Liver	Svalbard (Norway)	2009	10	<0.007[a]	
Brünnich's guillemot	Eggs	Svalbard and Bjørnøya (Norway)	2008	10	0.664 (<0.0005–1.125)	
Black guillemot	Eggs	Faroe Islands	2008	2[b]	0.022 (0.019–0.024)	Schlabach et al., 2011
Black guillemot	Eggs	East Greenland	2012	4	0.015 (0.013–0.017)	Vorkamp et al., 2015
Glaucous gull	Liver	East Greenland	2012	4	<0.012–0.022[c]	
Common eider	Eggs	Røst (Norway), 67°N	2012	4[b]	<0.03[a]	Huber et al., 2015
European shag	Eggs	Røst (Norway), 67°N	2012	4[b]	<0.03[a]	
Herring gull	Eggs	Røst (Norway), 67°N	2012	4[b]	<0.03	

[a]All samples below detection limits; [b]pooled samples; [c]no mean concentration calculated owing to just one sample above detection limit.

two of five samples of glaucous gull liver from East Greenland (Sagerup et al., 2010; Vorkamp et al., 2015). However, it was below detection limits in liver of common eider and black-legged kittiwake from Svalbard (Sagerup et al., 2010) as well as in eggs of common eider, European shag and herring gull from northern Norway (Huber et al., 2015).

BTBPE was sought in two whale species: pilot whale (*Globicephala melas*) and minke whale (*Balaenoptera acutorostrata*) from the Faroe Islands, but concentrations were below detection limit (<3 ng/g lw) in both cases (Dam et al., 2011). For ringed seal, BTBPE was found in one of five blubber samples from East Greenland, leading to a concentration range of <0.063–0.21 ng/g ww (<0.068–0.23 ng/g lw), while five samples from West Greenland were below detection limit (0.066 ng/g ww, 0.071 ng/g lw) (Vorkamp et al., 2015). Similarly, BTBPE was below detection limits (0.0019 ng/g ww and 3 ng/g lw) in ringed seal liver from Svalbard and ringed seal blubber from the Faroe Islands, respectively (Sagerup et al., 2010; Dam et al., 2011). In the Canadian Arctic, BTBPE was detected in about 20% of ringed seal samples, meaning that these had concentrations above 0.02 ng/g ww (Muir et al., 2013b).

BTBPE was detected in about 25% of polar bear samples analyzed from the Canadian Arctic, but was undetectable in polar bear samples from Alaska, Hudson Bay and the European Arctic (McKinney et al., 2011b). No concentrations were given. BTBPE was also undetectable (<0.013 ng/g ww) in polar bear plasma of animals from Svalbard (Sagerup et al., 2010). In a recent study from East Greenland, polar bears had a mean BTBPE concentration of 0.13 ng/g lw (range: <0.071–0.33 ng/g lw) (Vorkamp et al., 2015).

2.2.7.7 Environmental trends

Spatial trends

Insufficient data were available to assess spatial trends in BTBPE.

Temporal trends

The Arctic air monitoring at Alert does not indicate an increase in BTBPE over time (Figure 2.43). In contrast, BTBPE has been found to increase in landlocked Arctic char in three lakes (Amituk, Char, Resolute) of the Canadian Arctic since about 2005 (Muir et al., 2013b). Concentrations ranged between about 0.001 and 3 ng/g lw and increased at all three locations. Increasing concentrations of BTBPE have also been found in blubber of female ringed seals of the Canadian Arctic since 2005, especially in Lancaster Sound and the Beaufort Sea (Muir et al., 2013b). The ice core and snow pit studies did not show a temporal trend in BTBPE (Hermanson et al., 2010; Meyer et al., 2012), but mainly covered the period before the use of BTBPE as a PBDE replacement was announced.

2.2.8 Decabromodiphenyl ethane (DBDPE)

2.2.8.1 Introduction

Decabromodiphenyl ethane (DBDPE, CAS number 84852-53-9) was introduced in the early 1990s under the tradename Saytex 8010 (Kierkegaard et al., 2004a). The acronym DBDPE has erroneously also been used for BDE-209 in some reports and comments, so the use of CAS numbers for unambiguous identification is advisable. The chemical structure of DBDPE is given in Figure 2.48.

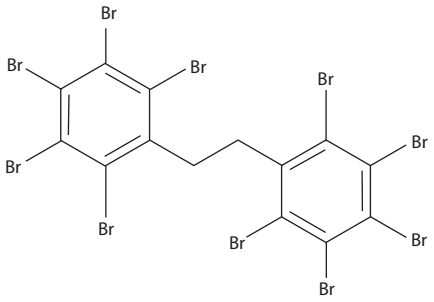


Figure 2.48 Chemical structure of decabromodiphenyl ethane (DBDPE; CAS number 84852-53-9).

The US Toxic Substances Control Act and the Canadian Environmental Protection Control Act regulate DBDPE as a new chemical and include measures to be taken to avoid releases to the environment (Dungey and Akintoye, 2007). In a risk assessment report, Dungey and Akintoye (2007) concluded that the risks from direct toxicity were low but that DBDPE might be persistent. The bioaccumulation potential of DBDPE could not be assessed because of lack of data.

At the time of the previous AMAP assessment, DBDPE had been sought in blubber of ringed seal from the Canadian Arctic, but all samples had been below detection limit (de Wit et al., 2010). As no further data were available at the time, DBDPE could not be assessed in the same way as the better studied BFRs.

2.2.8.2 Physical-chemical properties

Widely varying log K_{OW} values have been reported for DBDPE, ranging from 3.55 to 13.64 (CECBP, 2008; Kuramochi et al., 2014). Both experimentally determined and modeled log K_{OW} values are likely to be uncertain owing to the low water solubility of DBDPE and because of limitations in the model domain (Dungey and Akintoye, 2007). See Appendix 1 for more detailed information.

2.2.8.3 Sources, production, use and trends

DBDPE has the same commercial applications as BDE-209, including addition to HIPS, ABS and polypropylene as well as to textiles (CECBP, 2008; Covaci et al., 2011). DBDPE is industrially produced by two companies in the USA and at least two manufacturers in China (Dungey and Akintoye, 2007; Covaci et al., 2011). In 2006, production in China was 11 000 tons (Ma et al., 2012a and references therein). DBDPE is not produced in Europe, but is imported in volumes over 1000 tons per year, with increasing tendencies (Dungey and Akintoye, 2007). Since its first environmental detection in sewage sludge, sediment and indoor air (Kierkegaard et al., 2004a), DBDPE has gained increasing scientific interest owing to its use as an alternative to BDE-209.

2.2.8.4 Transformation processes

Substantial biotransformation has been reported for DBDPE (McKinney et al., 2011a). Using liver microsomes from several Arctic species (polar bear, beluga, ringed seal), a 44–74% depletion of DBDPE was observed, while maximum depletion of penta- and hexaBDEs was 3%. DBDPE was also transformed to a greater extent than BDE-209, with transformation capacities in the order ringed seal > beluga > polar bear. McKinney et al. (2011a) reasoned that the flexible C-C bond made DBDPE more susceptible to configurations that allow enzymatic reactions. Furthermore, their data suggested that BDE-209 and DBDPE were not substrates for the same enzyme. No simply debrominated metabolites were found, but phenolic metabolites might have been formed, possibly in combination with multiple debromination. These metabolites could not fully account for the depletion of DBDPE (McKinney et al., 2011a).

2.2.8.5 Modeling studies

No modeling studies were available. However, due to similar physical-chemical characteristics to BDE-209, DBDPE is expected to behave similarly to BDE-209 in the environment. Thus it is expected to partition highly to particles in air, to organic carbon in sediments and soil, and to lipids in biota.

2.2.8.6 Environmental concentrations

Air and precipitation

DBDPE was not detected in air samples collected at Pallas (Finland) in the period 2011–2012 (Remberger et al., 2014). However, DBDPE was widely detected in particle samples from air sampling at Longyearbyen, Svalbard (Salamova et al., 2014). The samples were collected from September 2012 to May 2013 by means of high volume air sampling for 48 hours, leading to sampling volumes of 650 m^3. DBDPE was above detection limit in 88% of the 34 samples (Annex Table A2.2/3). The mean concentration of DBDPE (0.53 pg/m^3) was clearly higher than the mean concentrations found for BTBPE (0.04 pg/m^3), and about half the mean concentration for BDE-209, which was 1.3 pg/m^3 in the same samples. As DBDPE concentrations were not statistically different from those of BDE-47, BDE-99 and BDE-209, Salamova et al. (2014) concluded that DBDPE was a significant BFR in the atmosphere of Svalbard.

DBDPE was found in an ice core from Svalbard, but concentrations and fluxes were lower than those for BDE-209 (Figure 2.47) (Hermanson et al., 2010). In the most recent core segment, representing the period 1995–2005, the concentration of DBDPE was 74.4 pg/L, while that of BDE-209 was 6953 pg/L. This corresponded to a DBDPE flux of 3.4 $pg/cm^2/y$, compared to a flux of about 320 $pg/cm^2/y$ for BDE-209 over the same period. Hermanson et al. (2010) related the transport of particle-bound contaminants to Arctic haze phenomena occurring in March and April and found indications of mass transport moving from primarily over-ocean to over-land in this period.

In a snow pit at the Devon Ice Cap in northern Canada, DBDPE was sought in 2005 and 2006, but only detected sporadically, i.e. in non-consecutive snow layers (Meyer et al., 2012). The highest concentration (24 pg/L) occurred in the surface layer of the 2006 snow pit, which is lower than the concentrations observed in Svalbard by Hermanson et al. (2010). The Svalbard > Devon Ice Cap flux was also found for BDE-209 and HBCDD. Meyer et al. (2012) also mentioned the Arctic haze period as a time of contaminant deposition, which in this case lasted from December to April. No links to likely source regions could be established.

Terrestrial environment

A screening study by Sagerup et al. (2010) included liver samples of Arctic fox from Svalbard, but the analysis resulted in undetectable levels of DBDPE (<0.0019 ng/g ww).

Freshwater environment

Ricklund et al. (2009) sought DBDPE in non-Arctic, subarctic and Arctic Swedish lake sediments collected in 2007. The DBDPE concentration in non-Arctic Lake Stor-Björsjön was 95 pg/g dw, but DBDPE was not detected in samples from Lakes Abiskojaure (Arctic), Storvindeln or Tjulträsk (subarctic).

DBDPE was sought in muscle of Arctic char collected on the Faroe Islands, but concentrations were below detection limit (<0.16 ng/g ww) (Schlabach et al., 2011). Although not from the Arctic, it is worth noting that a biota-sediment accumulation factor of 53 000 was found for brown trout (*Salmo trutta*) in lakes of southern Norway (Harju et al., 2013).

Marine environment

Sediment

The concentrations of DBDPE exceeded those for BDE-209 in surface sediments of the Bering Sea, Chukchi Sea and Canada Basin (Cai et al., 2012b). The samples were taken in 2008 and had in common that BDE-209 was the main PBDE congener. Based on arithmetic mean values, the ratio between DBDPE and BDE-209 decreased in the order: Canada Basin > Bering Sea > Chukchi Sea (Table 2.6). For the Bering Sea and the Chukchi Sea, means were much higher than median values for BDE-209, but not for DBDPE. Similarly, although mean values were lower for BDE-209 than for DBDPE, maximum values were higher. Cai et al. (2012b) gave no explanation for this observation, but it is interesting that the two compounds – with presumably exchangeable commercial applications – do not follow the same statistical distribution in their study.

Biota

Since the previous AMAP assessment, several studies have addressed DBDPE accumulation in Arctic biota. While most studies reported DBDPE concentrations below or just above detection limits, a more recent report showed a widespread presence of DBDPE in the marine environment of northern Norway and Svalbard (Harju et al., 2013). Table 2.20 summarizes the concentrations found above detection limits, which have been reported for biota so far.

Arctic marine samples below detection limits included fish (capelin from Svalbard, analyzed as whole fish, and liver of Atlantic cod from Iceland and the Faroe Islands), seabirds (liver of common eider, black-legged kittiwake from Svalbard, eggs of Brünnich's guillemot from Svalbard and eggs of black guillemot from the Faroe Islands, glaucous gull liver and black guillemot

Table 2.20 Arctic biota samples with DBDPE concentrations above detection limits. Studies with 0% detection frequency are described in the text.

Species	Sample	Origin	Detection frequency	Statistic	Concentration, ng/g ww (unless shown otherwise)	Reference
Blue mussel	Tissue	Iceland	-	n=1 (pool)	0.036	Schlabach et al., 2011
		Northern Norway	100%	Mean±SD n=3 (pools)	0.29±0.10	Harju et al., 2013
Atlantic cod	Liver	Northern Norway	100%	Mean±SD n=10	4.29±0.70	Harju et al., 2013
		Svalbard (Norway)	90%	Mean±SD n=3	5.57±1.38	
Polar cod	Whole fish	Svalbard (Norway)	-	n=1 (pool)	0.42	Harju et al., 2013
Common eider	Egg	Northern Norway	100%	Mean±SD n=10	0.33±0.11	Harju et al., 2013
		Svalbard (Norway)	100%	Mean±SD n=12	0.82±0.62	
Brünnich's guillemot	Egg	Svalbard and Bjørnøya (Norway)	10%	n=1	0.581	Sagerup et al., 2010
Black guillemot	Egg	Faroe Islands	50%	n=1 (pool)	0.085	Schlabach et al., 2011
		East Greenland	25%	n=1	0.10	Vorkamp et al., 2015
Herring gull	Egg	Northern Norway	100%	Mean±SD n=10	0.44±0.20	Harju et al., 2013
Black-legged kittiwake	Egg	Svalbard (Norway)	100%	Mean±SD n=12	1.01±1.55	Harju et al., 2013
Glaucous gull	Plasma	Svalbard (Norway)	100%	Mean±SD n=12	6.43±2.62 ng/ml	Harju et al., 2013
Ringed seal	Plasma	Svalbard (Norway)	100%	Mean±SD n=12	5.36±1.94 ng/ml	Harju et al., 2013
	Blubber	East Greenland	17%	n=1	0.16	Vorkamp et al., 2015
		West Greenland	25%	n=1	0.30	
Harbour seal	Liver	Northern Norway	100%	Mean±SD n=10	12.9±6.8	Harju et al., 2013
Polar bear	Plasma	Svalbard (Norway)	100%	Mean±SD n=20	6.94±9.11 ng/ml	Harju et al., 2013

eggs from Greenland) and marine mammals (liver of ringed seal from Svalbard, blubber of minke whale and pilot whale from the Faroe Islands, blubber of ringed seal from Greenland as well as adipose of polar bears from Alaska and the European Arctic) (Sagerup et al., 2010; Dam et al., 2011; McKinney et al., 2011b; Schlabach et al., 2011; Vorkamp et al., 2015).

On the other hand, some of the same species analyzed from northern Norway and Svalbard contained relatively high levels of DBDPE (Table 2.20). For the Arctic biota samples from Svalbard, DBDPE concentrations exceeded those of BDE-47 (Harju et al., 2013). The highest concentrations of DBDPE were found in male polar bear plasma samples, which ranged from 1044 to 4300 ng/g lw (Harju et al., 2013). Unlike most other studies, the analyses by Harju et al. (2013) used labelled DBDPE for quantification, but it is not clear if this had a systematic effect on the results.

Analyzing polar bear adipose, McKinney et al. (2011b) detected DBDPE in about 3% and 10% of polar bears from Hudson Bay and the Canadian Arctic, respectively, but no absolute concentrations were given. In a recent study of wildlife species in Greenland, DBDPE was <0.13 ng/g ww in all five samples of polar bear adipose (Vorkamp et al., 2015). In other Greenland species, DBDPE was detected sporadically (see Table 2.20). Infrequent detections of DBDPE and concentrations close to detection limits have also been reported for ringed seal blubber from the Canadian Arctic (Muir et al., 2013b).

Using log transformed lipid normalized DBDPE concentrations and relative trophic position (nitrogen stable isotope values) for the species analyzed from northern Norway (Atlantic cod liver, common eider eggs, herring gull eggs, seal liver) and Svalbard (polar cod, eider and kittiwake eggs, plasma of glaucous gull, ringed seal and polar bear), trophic magnification factors (TMFs) were calculated (Harju et al., 2013). These were >1 for both food webs and exceeded TMFs calculated for BDE-47 in the same food webs (Harju et al., 2013). Biomagnification of DBDPE is in line with the results of a non-Arctic food web study in Lake Winnipeg, which found a TMF of 8.6 for DBDPE (Law et al., 2006).

2.2.8.7 Environmental trends

Spatial trends

Sediment analyses showed similar concentrations of DBDPE in Canada Basin, the Bering Sea and the Chukchi Sea (Cai et al., 2012b).

Temporal trends

DBDPE concentration increased with time in an ice core from Svalbard (Figure 2.47) (Hermanson et al., 2010). Similarly, DBDPE concentrations in a snow pit in northern Canada were highest in the top layer (Meyer et al., 2012). No further data were available to assess temporal trends.

2.2.9 Bromobenzenes

2.2.9.1 Introduction

Information on the occurrence of bromobenzenes in the Arctic environment is available for 1,3,5-tri-, penta- and hexabromobenzene, with hexabromobenzene (HBBz, CAS number 87-82-1) the best studied compound of this group (Figure 2.49). HBBz is the brominated analogue of hexachlorobenzene, which was among the 'dirty dozen' compounds initially listed for global regulation by the Stockholm Convention.

In a screening assessment by Environment Canada and Health Canada, 1,3,5-tribromobenzene (1,3,5-TBBz) was found to meet the ecological criteria for persistence, bioaccumulation and inherent toxicity to non-human organisms, while it did not meet the human health categorization criteria (Environment Canada, 2010). The European Food Safety Agency identified HBBz as a compound that could raise a concern for bioaccumulation, based on bioaccumulation factors of 3.3–5.5 for several aquatic species (EFSA, 2013). It is pre-registered with the European Chemicals Agency (EFSA, 2013).

HBBz was also assessed in the previous AMAP assessment (de Wit et al., 2010). Based on detection in seabirds and polar bears, HBBz was found to undergo long-range transport and to accumulate in Arctic biota. Concentrations were generally described as low (de Wit et al., 2010).

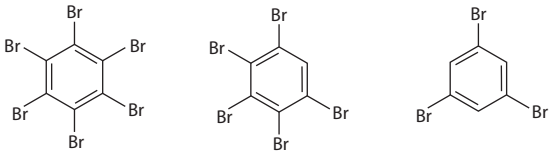


Figure 2.49 Chemical structures of hexabromobenzene (HBBz), pentabromobenzene (PBBz) and 1,3,5-tribromobenzene (1,3,5-TBBz).

2.2.9.2 Physical-chemical properties

Log K_{OW} values reported for HBBz are 5.85 and 6.07 (Kuramochi et al., 2004b; Covaci et al., 2011). No K_{OW} values are available for PBBz or 1,3,5-TBBz, but the log K_{OW} of 1,2,4-TBBz was reported as 4.32 (Kuramochi et al., 2004b). Some parameters characterizing the long-range atmospheric transport of HBBz are summarized in Table 2.21 (Xiao et al., 2012a). The table shows that the predicted half-life in air and the characteristic travel distance are considerably higher than the corresponding values for BEH-TEBP (Table 2.12) and BTBPE (Table 2.17). See Appendix 1 for more detailed information.

2.2.9.3 Sources, production, use and trends

HBBz has been in use since the 1970s for fireproofing of plastics, textiles and woods, but current production and use numbers are unavailable (Arp et al., 2011). In 1998, production and/or import in the USA was 10 000 to 500 000 pounds (4.5–227 tonnes) (CECBP, 2009). In Japan, use of HBBz was 350 tons in 2001 (Watanabe and Sakai, 2003). As of 2007, HBBz was still being produced in Japan and China (Gauthier et al., 2007). Current production volumes in China are about 600 tons per year (Covaci et al., 2011). No information seems to be available on the production and use of pentabromobenzene (PBBz), except that it was mentioned among flame retardants manufactured in the late 1980s (Salamova et al., 2014).

1,3,5-Tribromobenzene (1,3,5-TBBz) on the other hand, has been described as a high production volume chemical (Meyer et al., 2012). It has been used as a motor oil additive and as an intermediate in the manufacturing of various organic chemicals.

Table 2.21 Model results and estimations of parameters related to the long-range transport of HBBz (Xiao et al., 2012a and references therein).

Log K_{OA}	9.9
Log K_{AW}	-3.0
Half-life in air	11 000 hours
Half-life in water	4300 hours
Half-life in soil	8600 hours
Overall persistence	520 days
Characteristic travel distance	11 000 km
Particle bound fraction in air, Φ_{Air}	0.023

2.2.9.4 Transformation processes

Lower brominated benzenes can be formed from HBBz via reductive debromination. PBBz and HBBz can also be formed in pyrolysis processes of BDE-209 (Thoma and Hutzinger, 1987), and PBBz can be a degradation product of DBDPE (Venier et al., 2012). Both HBBz and PBBz were released from pentabromobenzyl acylate oligomers at relatively low temperatures, namely between room temperature and 100°C (Gouteux et al., 2008).

2.2.9.5 Modeling studies

Modelling studies have classified 1,3,5-TBBz as a compound with Arctic contamination and bioaccumulation potential based on a global transport model and a food chain accumulation model (Brown and Wania, 2008). It was also considered persistent in the atmosphere and a potential Arctic contaminant by analogy to known contaminants (Brown and Wania, 2008). HBBz was categorized as a POP of moderate concern based on potential persistence and bioaccumulation (Brown and Wania, 2008; Howard and Muir, 2010). Model data on environmental persistence are summarized in Table 2.21.

2.2.9.6 Environmental concentrations

Air and precipitation

HBBz was found in air samples from Little Fox Lake collected between August 2011 and December 2014 (Figure 2.42) with a mean concentration of 0.023 pg/m^3 (range 0.002–0.10 pg/m^3) (Yu et al., 2015). HBBz was detectable in 76% of all samples. At Alert, the annual mean concentration of HBBz in air was 0.35 pg/m^3 in 2006/2007 (Xiao et al., 2012a), but lower in subsequent years (Figure 2.43) (Annex Table A2.2/1).

Table 2.22 Concentration ranges of HBBz and PBBz in Arctic air and seawater (Möller et al., 2011a,b). The Bering/Chukchi Sea data only include stations north of 60°N.

	Bering/Chukchi Sea				East Greenland Sea			
	Air, pg/m³		Seawater, pg/L		Air, pg/m³		Seawater, pg/L	
	Gaseous	Particles	Dissolved	Particles	Gaseous	Particles	Dissolved	Particles
HBBz	0.13–0.40	<0.002–0.03	<0.001–0.020	<0.001–0.012	0.04–0.66	0.001–0.005	<0.0002– 0.003	<0.001– 0.002
PBBz	0.1–0.28	<0.002	<0.001	<0.001	na	na	na	na

na: Not available.

Higher concentrations of HBBz were found in particle phase air samples from Longyearbyen, Svalbard (Salamova et al., 2014). HBBz was detectable in all samples collected from September 2012 to May 2013 (Annex Table A2.2/3). The study also included PBBz, which was detected in 76% of samples. Mean and median concentrations of PBBz were about half those for HBBz (Annex Table A2.2/3). Under the GAPS program, HBBz was detected in air samples collected at Barrow and St Lawrence Island (Alaska), Stórhöfði (Iceland), Ny-Ålesund (Svalbard) and Hollola (Finland) in 2005/2006 (Annex Table A2.2/2) (Lee et al., 2016). The highest concentrations were observed at Barrow and Ny-Ålesund.

HBBz and PBBz were also sought in air samples on a transect from the East China Sea to the Arctic in summer 2010 (Table 2.22). Slightly higher concentration ranges were observed over the East Greenland Sea in summer 2009, with 100% detectability in all samples (Table 2.22). These concentrations were comparable to or higher than those for BDE-47 and BDE-99 in the same samples (Möller et al., 2011a,b). In both studies, higher concentrations were found in the gas phase than the particle phase, which agrees with the particle bound fractions presented by Xiao et al. (2012a) (Table 2.21). This could imply that the particle phase data from Svalbard might underestimate the total atmospheric concentration of HBBz (Salamova et al., 2014). The PBBz concentration in the gas phase was similar to, but slightly lower than that for HBBz in the same samples. Unlike HBBz, PBBz was not detected in the particle phase of the air samples (Möller et al., 2011a).

HBBz was also sought in air samples collected at Pallas in northern Finland in the period 2011–2012 (Remberger et al., 2014). HBBz was detected in 2011 at 0.10 pg/m³.

1,3,5-TBBz and PBBz were frequently detected in samples from a snow core collected at the Devon Ice Cap in Nunavut, Canada in 2008 (Meyer et al., 2012). HBBz was only detected in one layer corresponding roughly to the years 2003/2004. The highest concentration of PBBz (10 pg/L) was found in the uppermost 50 cm of the snow core representing the years 2007/2008, but the second highest concentration was found in the deepest layer (650–700 cm), representing the years 1993/1994. Converted to fluxes, however, a maximum occurred in 2000 (about 0.15 pg/cm²/y), and no trend was observed for the period 1993/1994 to 2008 (Figure 2.50). Concentrations (8.8–290 pg/L) and fluxes (see Figure 2.50) were relatively high for 1,3,5-TBBz. The maximum 1,3,5-TBBz flux occurred in 1999, which is close to that for PBBz, but fluxes appear to have since declined.

The fluxes of PBBz were clearly lower than for BDE-209 (maximum 2000 pg/cm²/y) and HBCDD (maximum 3.2 pg/cm²/y), while 1,3,5-TBBz fluxes were generally higher than for HBCDD (Meyer et al., 2012). The fluxes of 1,3,5-TBBz were comparable to those for tetra- and pentaBDEs. PBBz and 1,3,5-TBBz concentrations/fluxes could not be related to specific areas of origin. Meyer et al. (2012) noted that PBBz and 1,3,5-TBBz could also be degradation products of HBBz. The general absence of HBBz from the snow pit, which seems to differ from the findings of Salamova et al. (2014) of 100% detection, might also be influenced by higher detection limits for HBBz (6.5 pg/L) compared to PBBz (3.7 pg/L) and 1,3,5-TBBz (0.002 pg/L).

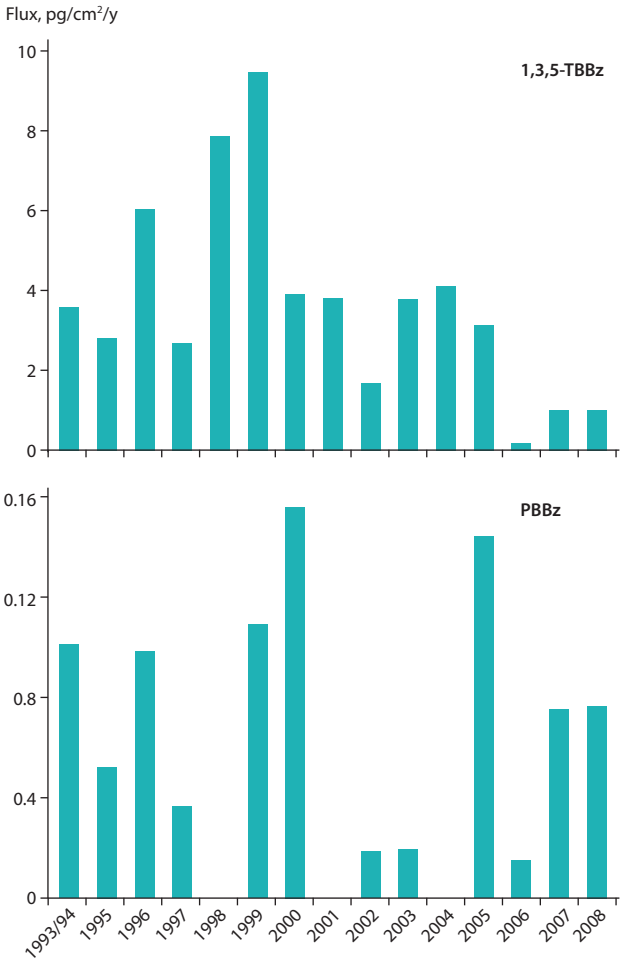


Figure 2.50 Fluxes of 1,3,5-tribromobenzene (1,3,5-TBBz) and pentabromobenzene (PBBz) in a snow core at the Devon Ice Cap in Nunavut, Canada (Meyer et al., 2012).

Table 2.23 Arctic biota samples with concentrations of HBBz above detection limits. Studies including analysis of undetectable levels of HBBz are described in the text.

Species	Sample	Origin	Statistic	HBBz	Reference
Arctic char	Muscle	Faroe Islands	n=1	0.0064 ng/g ww	Schlabach et al., 2011
Blue mussel	Tissue	Iceland	n=1	0.0082 ng/g ww	
Atlantic cod	Liver	Iceland	n=1	0.042 ng/g ww	
Atlantic cod	Liver	Faroe Islands	n=1	0.072 ng/g ww	
Black guillemot	Eggs	Faroe Islands	n=2	0.023 and 0.03 ng/g ww	
Minke whale	Blubber	Norway	Range (n=6)	1.56–8.77 ng/g lw	Dam et al., 2011
Pilot whale	Blubber	Faroe Islands	Range (n=7)	<3.0–13.86 ng/g lw	
Ringed seal	Blubber	Canada	Minimum	>0.02 ng/g[a]	Muir et al., 2013b
Polar bear	Adipose	Canada	Maximum	3.4 ng/g lw	McKinney et al., 2010
Polar bear	Adipose	Alaska, Canada, European Arctic	All samples	<3 ng/g lw	McKinney et al., 2011b

[a]In 5% of samples.

Terrestrial environment

HBBz was determined in Arctic fox liver from Svalbard, but concentrations were below detection limit (<0.0018 ng/g ww) (Sagerup et al., 2010).

Freshwater environment

Data are available for one pooled sample of Arctic char muscle from a lake on the Faroe Islands (0.0064 ng/g ww for HBBz) (Schlabach et al., 2011) (Table 2.23).

Marine environment

Seawater

The studies by Möller et al. (2011a,b) also included seawater analysis (Table 2.22). Unlike the air samples, the seawater samples did not have higher concentrations in the East Greenland Sea. In contrast to the corresponding air data, the results do not indicate differences between concentrations in the dissolved and particle phase. PBBz was undetectable in seawater from the Bering/Chukchi Sea and not sought in the East Greenland Sea.

Biota

HBBz has been included in several screening studies for marine biota from the Arctic. All samples had concentrations below detection limits in a study on marine biota from Svalbard (Sagerup et al., 2010), i.e. marine fish (capelin), seabirds (common eider, black-legged kittiwake, Brünich's guillemot) and marine mammals (ringed seal, polar bear). Detection limits were in the order of 0.002–0.004 ng/g ww. In another screening study, low concentrations of HBBz were found in blue mussel (from Iceland) and Atlantic cod (from Iceland and the Faroe Islands) (Table 2.23).

While ringed seal samples from Svalbard and Greenland had concentrations below detection limits, HBBz was detected in 5% of ringed seal samples analyzed from Canada (Sagerup et al., 2010; Dam et al., 2011; Muir et al., 2013b). These samples had an HBBz concentration of >0.02 ng/g, but a maximum concentration was not given. Higher detection frequencies were found in the analyses of polar bear samples (McKinney et al., 2011b): 50–60% of all polar bear samples (n=163) contained detectable levels of HBBz, and concentrations were <3 ng/g lw. Detection frequencies varied between the sub-populations included in the study and were about 17% (Alaska), 45% (Canadian Arctic), 33% (southern Hudson Bay) and 100% (European Arctic) (McKinney et al., 2011a; Muir et al., 2013b). PBBz was also sought in ringed seals from the Canadian Arctic, but was not detected (Muir et al., 2013a).

2.2.9.7 Environmental trends

Spatial trends

Insufficient data were available to assess spatial trends in HBBz or PBBz.

Temporal trends

HBBz was included in a temporal trend study of contaminants in polar bears from western Hudson Bay covering the period 1991–2007 (McKinney et al., 2010). However, owing to many concentrations below detection limit (Table 2.24), no temporal trend could be calculated. Similarly, although 1,3,5-TBBz, PBBz and HBBz were detected in various layers of a snow core dating back to 1993/1994, no trend was found for any of these compounds with the exception of apparent maxima of 1,3,5-TBBz and PBBz in 1999 and 2000, respectively (Figure 2.50) (Meyer et al., 2012). HBBz and PBBz have also been included in air monitoring from Alert (Canada), but more years with data will be necessary to establish a temporal trend.

Table 2.24 Concentrations of hexachlorobenzene (HBBz) in a temporal trend study on polar bears from western Hudson Bay (McKinney et al., 2010).

	1991	1992	1994	1995	2001	2003	2007
HBBz (ng/g lw)	<0.05	<0.05–3.4	<0.05–0.5	<0.05	<0.05	<0.05–2.6	<0.05–2.6

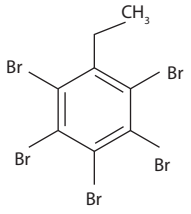
2.2.10 Pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 2,3,5,6-tetrabromo-*p*-xylene (TBX) and 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (DBE-DBCH)

2.2.10.1 Introduction

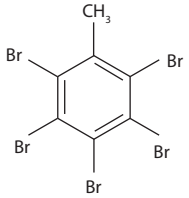
This section covers several compounds for which there is relatively little information. Their chemical structures and CAS numbers are shown in Figure 2.51. Unlike pentabromoethylbenzene (PBEB), pentabromotoluene (PBT) and 2,3,5,6-tetrabromo-*p*-xylene (TBX), 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBE-DBCH) is an aliphatic brominated compound with a cyclohexane structure.

PBEB is included in OSPAR's List of Chemicals for Priority Action, with the comment that there was no current production or use in the OSPAR area (OSPAR, 2013). PBEB, PBT and TBX are pre-registered with the European Chemicals Agency (EFSA, 2013). Being a brominated analogue of ethylbenzene, a known carcinogen, PBEB is suspected to cause adverse effects (CECBP, 2008).

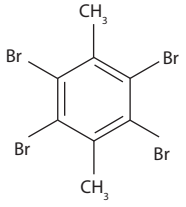
Based on estimated toxicity data, all four compounds are considered to pose a potential aquatic hazard (Fisk et al., 2003). PBEB, PBT and TBX were classified as persistent and bioaccumulative, and DBE-DBCH was classified as very persistent/very bioaccumulative (Fisk et al., 2003). Using predicted toxicity data and production volumes, Fisk et al. (2003) derived small critical tonnages of PBEB and DBE-DBCH, leading to high concern of toxicity in the aquatic environment, while TBX and PBT were found to be of medium and low concern for aquatic toxicity, respectively. A Danish health and environmental assessment concluded that PBT did not present a special hazard to humans, but that PBT was not readily degradable (Danish EPA, 2000). In a study addressing potential persistence and bioaccumulation, DBE-DBCH was among the top ten brominated compounds (Howard and Muir, 2010). Both PBEB and PBT can be degradation products of DBDPE (Arp et al., 2011).



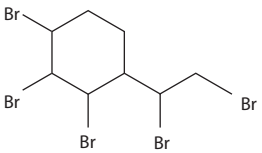
Pentabromoethylbenzene (PBEB)
(CAS no. 85-22-3)



Pentabromotoluene (PBT)
(CAS no. 87-83-2)



2,3,5,6-tetrabromo-*p*-xylene (TBX)
(CAS no. 23488-38-2)



1,2-dibromo-4-(1,2-dibromoethyl)
cyclohexane (DBE-DBCH)
(CAS no. 3322-93-8)

Figure 2.51 Chemical structures and CAS numbers of pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 2,3,5,6-tetrabromo-*p*-xylene (TBX) and 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (DBE-DBCH).

Table 2.25 Model results and estimations of parameters related to the long-range transport of PBT (Xiao et al., 2012a and references therein).

Log K_{OA}	9.5
Log K_{AW}	-3.0
Half-life in air	690 hours
Half-life in water	4300 hours
Half-life in soil	8600 hours
Overall persistence	510 days
Characteristic travel distance	6900 km
Particle bound fraction in air, Φ_{Air}	0.01

With the exception of TBX, these compounds were also assessed in the previous AMAP assessment (de Wit et al., 2010). Based on relatively high detection frequencies of PBEB and PBT in glaucous gull samples and of DBE-DBCH in beluga it was concluded that warning signs existed for long-range transport of these compounds to the Arctic. It was also concluded that PBEB, PBT and DBE-DBCH were potentially bioaccumulative (de Wit et al., 2010).

2.2.10.2 Physical-chemical properties

Log K_{OW} values vary for these chemicals, with reported values of 6.4 for PBEB (Covaci et al., 2011), 5.43–6.99 for PBT (CECBP, 2008; Covaci et al., 2011), 6.2 for TBX (EFSA, 2013) and 5.24 for DBE-DBCH (CECBP, 2008). Based on modeling results, parameters related to long-range transport have been summarized for PBT (Table 2.25). See Appendix 1 for more detailed information.

2.2.10.3 Sources, production, use and trends

PBEB was used in thermoset polyester resins (circuit boards, textiles, adhesives, wire and cable coatings, polyurethanes) and thermoplastic resins (Hoh et al., 2005). The latest production data for the USA are from 1986 when production decreased to 5–225 tons (Hoh et al., 2005). Hoh et al. (2005) also reported the production of PBEB in France, referring to 2002.

PBT is used in a wide range of polymers, textiles and paint emulsions (de Wit et al., 2010; Covaci et al., 2011). Covaci et al. (2011) reported that 600 tons of PBT were produced in China per year.

Synthesis of TBX for use as a flame retardant was patented in the 1970s, but little recent information is available (Venier et al., 2012). TBX might also be used as a starting material for the synthesis of brominated and phosphorus-based flame retardants (Venier et al., 2012), but no production or use numbers seem to be available.

DBE-DBCH is used in polystyrene beads (e.g. in house insulation), extruded polystyrene foam, polyurethane, adhesives, cable coatings and other applications (Andersson et al., 2006; Arsenault et al., 2008; Tomy et al., 2008a). Production volumes were 4–225 tonnes in 2002 (Arsenault et al., 2008). Commercial DBE-DBCH comprises equal amounts of two out of four possible diastereoisomers, i.e. α- and β-DBE-DBCH, but the other diastereoisomers may be formed at elevated temperatures in the manufacturing process and thus may also be present in environmental samples (Arsenault et al., 2008).

2.2.10.4 Transformation processes

According to a modeling study, PBEB, PBT and TBX may undergo reductive and/or photolytic debromination (EFSA, 2013). No corresponding information was available for DBE-DBCH.

2.2.10.5 Modeling studies

Based on a modeling exercise, the European Food Safety Agency classified PBEB, PBT and TBX as compounds of high persistence (>500 days) and with a high potential for bioaccumulation (EFSA, 2013). Modeled parameters describing the persistence of PBT in the environment are given in Table 2.25.

2.2.10.6 Environmental concentrations

Air and precipitation

PBEB and PBT were measured in air samples collected between August 2011 and December 2014 at Little Fox Lake in the Canadian subarctic and detected in 60% and 100% of samples, respectively (Yu et al., 2015). For PBEB, the mean of 0.013 pg/m^3 (range: 0.002–0.078) was the lowest mean concentration of all the novel flame retardants included in this study (Figure 2.42) (Yu et al., 2015). PBT had a mean concentration of 0.084 pg/m^3 (range: 0.007–0.47) in the same samples. For comparison, the mean concentrations for BDE-47 and BDE-99 were 1.2 and 0.96 pg/m^3, respectively. Analysis of potential source regions linked PBT to sources in northern Canada, while no information was given on potential source regions for PBEB (Yu et al., 2015).

PBEB and PBT were also monitored at Alert in the Canadian High Arctic where concentrations appeared to be slightly lower (Annex Table A2.2/1). PBEB, PBT and DBE-DBCH were not detected in air samples collected at Pallas in northern Finland in 2011/2012. TBX was not included in these analyses (Remberger et al., 2014).

On a cruise from East Asia to the Arctic in June to September 2010, air concentrations of PBT were higher than those measured in the Canadian Arctic (Table 2.26). PBT was among the novel flame retardants with the highest concentrations in the study by Möller et al. (2011a) and exceeded the concentrations for BDE-47 and BDE-99 at the same stations. PBT concentrations were comparable to those of BDE-209, with the difference that BDE-209 was particle-bound. Based on air and seawater concentrations, a net flux from air to water was calculated for PBT.

Over the East Greenland Sea in summer 2009, PBT was detectable in 100% of all gas phase samples (Table 2.26) (Möller et al., 2011b). These concentrations are similar to those reported for Alert and lower than those of the study by Möller et al. (2011a). In the particle phase samples, PBT was only detectable in 20% of samples.

Passive air samples collected in the GAPS network were analyzed for PBT, PBEB and TBX (Lee et al., 2016). The compounds were not detectable at Hollola (Finland), and PBT was not detectable at Stórhöfði (Iceland). All three compounds were found at the other Arctic stations (Annex Table A2.2/2).

Focusing on the particle phase of air samples from Svalbard, Salamova et al. (2014) reported atmospheric concentrations of PBEB and TBX in 34 samples collected between September 2012 and May 2013. The results for the two compounds were similar (Annex Table A2.2/3). Mean concentrations were comparable to those for BTBPE. Compared with HBBz, the concentrations of PBEB and TBX were about 5- and 4-fold lower, respectively. Concentrations of PBEB and TBX were an order of magnitude lower than for BDE-47 and BDE-99. Considering the gas-particle distribution described by Möller et al. (2011a,b) and the modelled particle bound fraction (Table 2.25), the focus on the particle phase might underestimate the actual concentration of PBT in the atmosphere.

For PBEB, atmospheric deposition was further studied in ice and snow cores at Svalbard (Norway) and Nunavut (Canada), respectively (Hermanson et al., 2010; Meyer et al., 2012). In both studies, PBEB was found in most core segments, but concentrations were very low. In the ice core from Svalbard, the maximum concentration of PBEB was 0.0063 ng/L, corresponding to a flux of <0.5 pg/cm^2/y (Figure 2.47) (Hermanson et al., 2010). BTBPE and DBDPE had fluxes of 3–5 pg/cm^2/y, while the maximum fluxes were for BDE-209 (320 pg/cm^2/y) and HBCD (910 pg/cm^2/y). In the snow core from Canada, the maximum concentration of PBEB was 0.0026 ng/L, while that of BDE-209 in the same snow pit was 26 ng/L (Meyer et al., 2012). This study also included PBT, which was detected in three unconnected layers of one of the snow pits, at concentrations of 0.000061–0.0013 ng/L (Meyer et al., 2012).

Newton et al. (2014) detected DBE-DBCH in bimonthly bulk deposition (precipitation + dry particle) samples from Abisko (3.1±3.6 ng/m^2/month) and Krycklan (3.5±2.8 ng/m^2/month) in northern Sweden.

Table 2.26 Concentration ranges for PBT in Arctic air and seawater (Möller et al., 2011a,b). The Bering/Chukchi Sea data only include stations north of 60°N.

	Bering/Chukchi Sea				East Greenland Sea			
	Air, pg/m^3		Seawater, pg/L		Air, pg/m^3		Seawater, pg/L	
	Gaseous	Particles	Dissolved	Particles	Gaseous	Particles	Dissolved	Particles
PBT	0.22–0.79	<0.047	<0.001–0.020	<0.001–0.012	0.001–0.02	<0.0001–0.001	<0.0007	<0.0007

Terrestrial environment

PBEB and PBT were included in several studies on Arctic biota, but many results were below detection limits. For the terrestrial environment, both compounds were <0.0006 ng/g ww in Arctic fox liver from Svalbard (Sagerup et al., 2010). Detection limits for PBEB and PBT were the lowest in this study.

Freshwater environment

PBEB, PBT and DBE-DBCH were sought in muscle of Arctic char (Faroe Islands), but were generally below detection limits or at very low levels (Table 2.27) (Schlabach et al., 2011). PBEB was included in studies of lake trout and burbot in the Canadian Arctic, but no concentrations were given (Muir et al., 2013b).

Marine environment

Seawater

PBT was sought in seawater samples on a cruise from East Asia to the Arctic in 2010 (Table 2.26), from which air samples were reported (Möller et al., 2011a). PBT was detected in 78% of seawater samples which made it one of the novel flame retardants with the highest detection frequency. In the East Greenland Sea, however, concentrations of PBT in seawater were below detection limit in all samples (Table 2.26).

Biota

Several marine species have been screened for PBEB and PBT, but many concentrations were below detection limits. Table 2.27 summarizes the concentrations found to be above detection limits. Both PBEB and PBT were below detection limits in capelin, common eider, black-legged kittiwake, Brünnich's guillemot, ringed seal and polar bears from Svalbard (Sagerup et al., 2010). PBEB was undetectable in Atlantic cod from Iceland and the Faroe Islands and blue mussel from Iceland, while PBT had concentrations above detection limits (Table 2.27) (Schlabach et al., 2011). PBT was also below detection limits in minke whale and pilot whale from the Faroe Islands as well as blubber of ringed seal from Greenland, but this study did not include PBEB (Dam et al., 2011).

DBE-DBCH has been found in fish and seabird samples from Iceland and the Faroe Islands (Table 2.27), but was below detection limit in blue mussel (Schlabach et al., 2011). The β-isomer was always present in higher concentrations than the α-isomer, which agrees with the pattern previously reported for herring gull from the Great Lakes and beluga from the Arctic (Tomy et al., 2008a; Gauthier et al., 2009).

A study on Greenland shark included PBEB, PBT and TBX, but owing to low detection frequencies, no results were reported for PBT (Strid et al., 2013). PBEB was detected in 14 of 15

Table 2.27 Concentrations of pentabromoethylbenzene (PBEB), pentabromotoluene (PBT), 2,3,5,6-tetrabromo-*p*-xylene (TBX) or 1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (DBE-DBCH) above detection limits in Arctic biota samples. Results below detection limits are described in the text.

Species	Sample	Origin	Statistic	Concentration, ng/g ww (unless shown otherwise)	Reference
PBEB					
Black guillemot	Eggs	Faroe Islands	n=2 (pooled)	<0.0016; 0.00072	Schlabach et al., 2011
Greenland shark	Liver	Near Iceland	Median (range) (n=15)	3.0 (<0.11–13) ng/g lw	Strid et al., 2013
Polar bear	Adipose	Western Hudson Bay (Canada)	Maximum	1.7 ng/g lw	McKinney et al., 2010
		Hudson Bay	Detection frequency of up to 40–45%		McKinney et al., 2011a
		Canadian Arctic	Detection frequency of about 8%		McKinney et al., 2011a
		Alaska	Detection frequency of about 25%		McKinney et al., 2011a
PBT					
Arctic char	Muscle	Faroe Islands	n=1 (pooled)	0.0015	Schlabach et al. (2011)
Blue mussel	Tissue	Iceland	n=1 (pooled)	0.002	
Atlantic cod	Liver	Iceland	n=1 (pooled)	0.0097	
		Faroe Islands	n=1 (pooled)	0.0021	
Black guillemot	Eggs	Faroe Islands	n=2 (pooled)	0.0063; 0.0054	
TBX					
Greenland shark	Liver	Near Iceland	Median (range) (n=15)	<0.1 (<0.1–2.8) ng/g lw	Strid et al. (2013)
DBE-DBCH					
Atlantic cod	Liver	Iceland	n=1 (pooled)	α: 0.14 β: 0.22	Schlabach et al. (2011)
		Faroe Islands	n=1 (pooled)	α: 0.021 β: 0.037	
Black guillemot	Eggs	Faroe Islands	n=2 (pooled)	α: 0.02 β: 0.066	
				α: 0.018 β: 0.059	

samples (corresponding to 93% of samples), at concentrations up to 13 ng/g lw (Table 2.27). TBX was detected in five of 15 samples (corresponding to 33% of samples), and the maximum concentration was considerably lower (Table 2.27). For comparison, the median concentration of BDE-47 in these samples was 24 ng/g lw.

In addition to the polar bear samples analyzed from Svalbard and found to contain undetectable levels of PBEB and PBT (Sagerup et al., 2010), PBEB and PBT were also sought in polar bears from Alaska, the Canadian Arctic, Hudson Bay and the European Arctic (McKinney et al., 2011a). PBT was undetectable in all samples. PBEB was detected in <14% of all samples. Broken down by polar bear sub-population (Table 2.27), the detection frequency of PBEB was highest in Hudson Bay (40–45%), followed by Alaska (about 25%) and the Canadian Arctic (about 8%). PBEB was undetectable in polar bears from the European Arctic, which agrees with the findings of Sagerup et al. (2010).

PBEB, PBT and DBE-DBCH were also sought in ringed seal from Canada, but levels were below detection limits or very close to detection limits (Muir et al., 2013a,b).

2.2.10.7 Environmental trends

Spatial trends

Insufficient data were available to assess spatial trends in PBEB, PBT, TBX and DBE-DBCH.

Temporal trends

Air measurements at Alert showed the highest concentrations of PBEB and PBT in the most recent years, which could indicate increasing concentrations of these compounds in Arctic air, but more data are needed to establish a temporal trend. Increases in PBEB since 1962 were also found in an ice core from Svalbard (Hermanson et al., 2010), but this observation conflicted with results from snow cores from the Canadian Arctic which did not show increases in PBEB (Meyer et al., 2012). In biota, PBEB was included in a temporal trend study in polar bears from Western Hudson Bay covering the period 1991–2007 (McKinney et al., 2010). No trend could be calculated owing to many concentrations below detection limits. Median concentrations could only be obtained for 1992, 1994 and 2003, and were all 0.1 ng/g lw. No Arctic temporal trend data were available for DBE-DBCH and TBX.

2.2.11 Tetrabromo-*o*-chlorotoluene (TBCT), pentabromobenzyl acrylate (PBB-Acr) and octabromotrimethylphenylindane (OBTMPI)

2.2.11.1 Introduction

Tetrabromo–*o*-chlorotoluene (TBCT, CAS number 39569-21-6) is an additive flame retardant and may be an alternative to decaBDE (López et al., 2011). In some reports, the acronym TB*o*CT has been used, but TBCT was proposed by Bergman et al. (2012). TBCT is a combined brominated/chlorinated flame retardant.

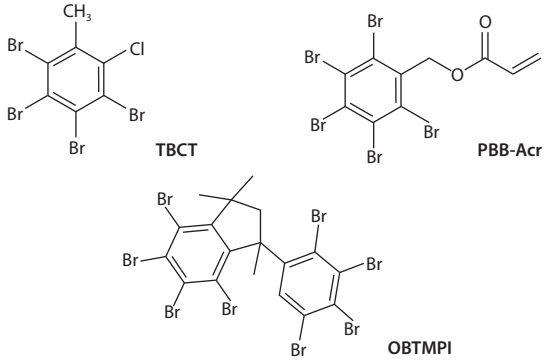


Figure 2.52 Chemical structures of tetrabromo–*o*-chlorotoluene (TBCT), pentabromobenzyl acrylate (PBB-Acr) and octabromotrimethylphenylindane (OBTMPI).

Pentabromobenzyl acrylate (PBB-Acr, CAS number 59447-55-1) is a reactive and intermediate type of BFR. In some reports, the acronym PBBA is use. Octabromotrimethylphenylindane (OBTMPI, CAS number 1084889-51-9/1025956-65-3/893843-07-7/155613-93-7) is an additive flame retardant, also abbreviated to OBIND, Br-Indian and Octalnd. The chemical structures of TBCT, PBB-Acr and OBTMPI are shown in Figure 2.52.

2.2.11.2 Physical-chemical properties

A log K_{OW} of 5.60 has been reported for TBCT (EFSA, 2013). OBTMPI has a high log K_{OW} of 15.11 (Bergman et al., 2012), while no information was available for PBB-Acr. See Appendix 1 for more detailed information.

2.2.11.3 Sources, production, use and trends

According to Chemical Book (www.chemicalbook.com), TBCT is produced by one company in the USA. No information is available on production volume or use (EFSA, 2013).

PBB-Acr is applied in polybutylene terephthalate, polyethylene terephthalate and ABS polymers (Covaci et al., 2011). PBB-Acr is produced by 11 commercial suppliers but no information is available on production volume (EFSA, 2013).

OBTMPI is used in styrenics and engineering thermoplastics (Guerra et al., 2012). The trade name is FR-1808. No information is available on OBTMPI production volumes (Covaci et al., 2011).

2.2.11.4 Transformation processes

No data on transformation processes were available.

2.2.11.5 Modeling studies

No modeling studies were available.

2.2.11.6 Environmental concentrations

Air and precipitation

Very few reports exist on TBCT, PBB-Acr and OBTMPI in the environment. In an earlier screening of Canadian air samples at Alert PBB-Acr was not detected (Hung et al., 2013a; Muir et al.,

2013a). From 2008 to 2012, PBB-Acr was only detectable in 2008, 2010 and 2011 in 8–23% of all air samples collected at Alert (Annex Table A2.2/1). TBCT was not detected in the samples from 2008–2012.

In passive air samples collected in the GAPS network, TBCT was detectable with a maximum concentration of 0.34 pg/m^3 found at Stórhöfði (Iceland) (Annex Table A2.2/2) (Lee et al., 2016). PBB-Acr was not detectable in passive air samples collected at Barrow (Alaska), Ny-Ålesund (Svalbard) and Hollola (Finland) but was found in air at St Lawrence Island (Alaska) and Stórhöfði (Annex Table A2.2/2). OBTMPI was not detected at any of these Arctic GAPS stations.

Terrestrial environment

No data were available.

Freshwater environment

No Arctic data were available, but studies from outside the Arctic have detected TBCT and PBB-Acr in environmental samples (Henny et al., 2011; Yang et al., 2012).

Marine environment

TBCT and OBTMPI were sought in ringed seals from the Canadian Arctic but were not detected (Muir et al., 2013a). TBCT was sought in polar bears from Hudson Bay but not detected (NCP, 2015a).

2.2.11.7 Environmental trends

Although PBB-Acr has been included in Arctic air monitoring at Alert, too few concentrations were above detection limits to indicate a time trend. No data are available for TBCT and OBTMPI to assess temporal or spatial trends.

2.2.12 Conclusions

New data are available for a wider range of new and previously studied BFRs in the Arctic and indicate that many undergo long-range atmospheric transport and deposition and that some have bioaccumulation potential. Some new data were available for BDE-209 and HBCDD. Far fewer data were available for the newer BFRs, including data on production and use.

Most data available for the new BFRs in this assessment were for air and deposition samples (Table 2.5), which come from several Arctic air monitoring programs and a few published research studies. There were additional data from screening of selected, often pooled, samples from biota in the Nordic countries, from monitoring programs in some Arctic countries and from some published scientific studies. There were generally very few or no data for the terrestrial environment and in many cases, only limited information from some freshwater studies. The majority of biota data were for a few species of marine fish, seabirds and mammals. Although the environmental levels of less-studied BFRs (i.e. excluding BDE-209 and HBCDD) are often low, this is not sufficient to conclude low risk. Little is known about toxicology (see Chapter 3) and the significance of their co-occurrence in biota samples (along with legacy POPs and other CECs) has not been studied.

Geographically, there was a lack of data from Arctic Russia and very few data from Alaska so circumpolar trends were not possible to study. Only a few temporal trend studies were available, however those that do exist indicate that environmental concentrations of many of the new BFRs are increasing. Assuming a wide commercial use of PBDE replacement products and considering increases found outside the Arctic (e.g. for EH-TBB and BEH-TEBP in the Great Lakes atmosphere; Ma et al., 2012b), a better understanding of their environmental fate is essential, including their temporal development.

BDE-209 was found at similar concentrations in air samples from Arctic sampling sites in Canada (Alert), Svalbard (Zeppelin, Longyearbyen) and Finland (Pallas). It was found at higher concentrations and with a greater contribution to ΣPBDE in air samples from the Bering and Chukchi Sea than in the East Greenland Sea, which is possibly related to the production and use of commercial decaBDE in Asia. It was also found in snow samples from Canada and Norway and an ice core from Svalbard, in the latter indicating increasing deposition fluxes since the 1950s. BDE-209 was associated with particulates in seawater and was the major PBDE congener in marine sediments. These findings have established BDE-209 as a main BFR component in abiotic matrices in the Arctic. On the other hand, low concentrations were found in seabird eggs and BDE-209 was generally not detected in polar bears, possibly due to its rapid metabolism. BDE-209 did not biomagnify in a food web study except between Arctic cod and zooplankton, so there is little support for BDE-209 biomagnifying in Arctic marine mammals. The previous AMAP assessment showed that exposure and bioaccumulation did occur in terrestrial top predators, but no new data were available to confirm these findings. Temporal trends indicate recently decreasing concentrations in air and deposition, not yet reflected in the ice core from Svalbard.

The database for **HBCDD** was more extensive than in the previous AMAP assessment from 2010. HBCDD (primarily the α- and γ-isomers) has been found in high volume air samples from Zeppelin and Villum Research Station (Station Nord) on northeast Greenland, but was not detected in samples from Alert. It was detected in passive air samples at several Arctic sites from Alaska, Canada, Iceland and Svalbard. Fluxes were higher on Svalbard (ice core) than Nunavut, Canada (snow core). HBCDD was present in low concentrations in freshwater and most marine fish, but higher concentrations were detected in seabirds. Polar bears had higher concentrations than ringed seal from the same area, indicating biomagnification. Food web studies showed enrichment of α-HBCDD with higher trophic level, a process which might involve bioisomerization. Spatial trends in air, ice and biota (ringed seal, polar bear) indicated higher concentrations in the European Arctic than in North America, apparently in line with HBCDD use patterns. The temporal trends recently published on HBCDD in the Arctic generally showed increasing trends, but often only until about 2005–2010 after which concentrations have been relatively stable. Air monitoring on Svalbard showed a decline in 2006/2007 and fluctuating concentrations since then.

There are still surprisingly few environmental data on **TBBPA** given its commercial importance. It was detected in Arctic air, but in so few samples and with a decreasing trend with latitude

that its long-range transport cannot be established with the data presently available. Measurements in water would be relevant given the higher polarity of TBBPA compared with other BFRs. Furthermore, the assessment of the EU of TBBPA causing a potential risk if bisphenol A or dimethyl-TBBPA were formed should trigger corresponding analyses in Arctic media. While previous studies had shown the accumulation of dimethyl-TBBPA in Arctic biota, no new information has been available. The data available on Arctic biota do not indicate bioaccumulation of TBBPA, but it is not clear whether this is a result of availability (i.e. low concentrations in the Arctic) or of biotransformation. Several studies have reported on the degradation of TBBPA and on the formation of bound residues in soil (e.g. Guo et al., 2012; Peng et al., 2014; Sun et al., 2014a), but no information is available on the environmental fate of TBBPA in the Arctic. A non-Arctic study on dolphins and sharks from Florida found TBBPA in 100% of samples and with increasing concentrations over time (Johnson-Restrepo et al., 2008), which suggests some bioaccumulation potential for TBBPA.

More studies have focused on **BEH-TEBP** and **EH-TBB**, which are replacement products of pentaBDE and might thus be applied widely. Although models do not predict a long atmospheric half-life for BEH-TEBP, it is sufficiently stable to reach the Arctic. Levels of BEH-TEBP and EH-TBB in Arctic air are comparable to those of PBDEs and have shown signs of increase. In combination with increasing trends observed in the Great Lakes region, this might reflect the anticipated increase in use as a replacement for pentaBDE. Both compounds have been detected in fish, seabirds and marine mammals from the Arctic indicating that bioaccumulation occurs. Most levels were relatively low, i.e. lower than those of PBDEs, but polar bear plasma from Svalbard, for example, contained slightly higher levels of EH-TBB. The preliminary data do not show biomagnification of BEH-TEBP, but more data will be needed for firm conclusions.

TBP-DBPE has been detected in air and seawater of the Arctic as well as in some biota. TBP-DBPE seems to be widely present in the Arctic environment. Its detection in sewage sludge might indicate additional sources, besides atmospheric long-range transport. While concentrations of TBP-DBPE in abiotic media were roughly comparable to those for PBDEs, most concentrations in biota were lower than those for PBDEs, but exceptions exist. **TBP-AE** and **TBP-BAE** were also widely detected in air, generally with higher detection frequencies and higher concentrations of TBP-AE. The compounds were below detection limits in all biota samples analyzed, with the exception of harp seals from the Barents Sea and Greenland Sea.

The database on **BTBPE** in the Arctic has been extended considerably since the previous AMAP assessment. The air, snow and ice measurements show that BTBPE is transported to the Arctic and deposited in the Arctic environment. Studies from outside the Arctic indicate bioaccumulation and biomagnification of BTBPE. The compound has been detected in Arctic biota (polar bear, seabirds, ringed seal, and several fish species including Greenland shark), but most studies also include non-detectable concentrations. There is no clear link in the present dataset between concentration and trophic level, but it could be masked by the heterogeneity of the data in terms of location and detection limit. Canadian temporal trend studies on landlocked Arctic char and ringed seal indicate increasing concentrations of BTBPE, which would be in line with its increased use as a PBDE replacement. However, the present air time series do not show the same trend.

DBDPE has been widely detected in Arctic air. In marine surface sediments, DBDPE has been found at higher and more uniform concentrations than BDE-209. Ice cores documented an increase in DBDPE between 1971 and 1988, but not since then. Most studies on DBDPE in biota have found concentrations close to detection limits, with the exception of one recent Norwegian study which found DBDPE in biota at concentrations of 5–10 ng/g ww, often exceeding those for BDE-47. As the same type of samples from the same area had shown low or even undetectable concentrations previously, these findings suggest either a rapid increase in DBDPE concentrations or other factors affecting DBDPE concentrations in the analysis. Food web studies have indicated biomagnification of DBDPE. On the other hand, DBDPE also seems to be susceptible to rapid biotransformation. More research will be needed to understand the environmental fate of DBDPE in the Arctic. If used as a commercial alternative to BDE-209, large volumes of DBDPE might be produced and potentially emitted to the environment. Thus, updated information on production and use volumes will also be important.

The previous AMAP assessment concluded that **HBBz** could undergo long-range transport and bioaccumulate in Arctic biota. New data on HBBz in Arctic air show it is widely present, at concentrations similar to BDE-47 and BDE-99, and that it mainly occurs in the gas phase. Some studies have included **PBBz**, which was found in Arctic air at slightly lower levels than HBBz. **1,3,5-TBBz** had relatively high fluxes in snow cores, i.e. again comparable to lower brominated PBDEs. It is unclear whether 1,3,5-TBBz is used as a flame retardant. Other industrial applications have been described as potential sources, as well as the degradation of HBBz. Recent biota analyses have detected HBBz in several species.

PBT was widely detected in Arctic air, at concentrations comparable to PBDEs. **PBEB** and **TBX** were also detectable in abiotic Arctic media, but concentrations were low. **DBE-DBCH** was only included in one atmospheric study and found to be undetectable. All four compounds have been detected at low concentrations in Arctic biota. While PBT was found in some fish and seabirds, it was undetectable in higher trophic level animals such as Greenland shark and polar bear. The opposite was the case for PBEB. DBE-DBCH was present in fish, seabirds and marine mammals, with a predominance of the β-isomer.

TBCT, PBB-Acr and **OBTMPI** have been detected infrequently in Arctic air. In Arctic biota samples, the compounds were generally below detection limits.

Section 2.2 Annex Contents

Section 2.2 Annex

Table A2.2/1 Air concentrations (pg/m^3) for flame retardants measured at Alert, Nunavut, Canada [mean (median, standard deviation; min–max, number of samples) % detection]. Italics indicate <50% of values above detection limit (Hung et al., 2013a).

	2008	2009	2010	2011	2012
PBEB	*(<MDL; <MDL–0.0052, 27) 37%*	*(<MDL; <MDL–0.0032, 22) 9%*	0.0023 (0.0025, 0.0015; <MDL–0.0051, 13) 85%	0.0050 (0.005, 0.0034; <MDL–0.016, 26) 88%	0.0034 (0.0026, 0.0037; <MDL–0.012, 26) 69%
BTBPE	0.58 (0.44, 0.39; 0.023–1.4, 27) 100%	0.024 (0.021, 0.015; 0.0071–0.075, 18) 100%	0.035 (0.033, 0.013; 0.018–0.061, 13) 100%	0.25 (0.17, 0.16; 0.050–0.71, 26) 100%	0.012 (0.011, 0.009; <MDL–0.042, 25) 84%
BEH-TEBP	0.30 (0.099, 0.73; <MDL–3.4, 27) 78%	0.39 (0.35, 0.25; 0.079–0.94, 17) 100%	0.23 (0.21, 0.21; 0.033–0.85, 13) 100%	0.51 (0.39, 0.80; 0.14–4.3, 26) 100%	6.7 (0.89, 18; 0.16–80, 26) 100%
EH-TBB	1.3 (0.63, 2.8; <MDL–15, 27) 96%	0.50 (0.20, 0.71; 0.054–2.7, 21) 100%	0.37 (0.17, 0.52; 0.089–1.8, 13) 100%	0.19 (0.15, 0.18; <MDL–0.89, 26) 88%	1.4 (0.58, 2.0; 0.17–7.7, 26) 100%
TBP-AE	0.025 (0.021, 0.017; <MDL–0.065, 27) 96%	0.027 (0.024, 0.017; <MDL–0.073, 18) 94%	0.16 (0.042, 0.28; 0.0085–0.94, 13) 100%	0.022 (0.011, 0.022; <MDL–0.063, 26) 81%	0.027 (0.017, 0.034; <MDL–0.14, 26) 65%
TBP-BAE	*(<MDL; <MDL–0.0014, 27) 15%*	*(<MDL; <MDL–<MDL, 25) 0%*	*(<MDL; <MDL–<MDL, 13) 0%*	*(<MDL; <MDL–<MDL, 26) 0%*	(<MDL; <MDL–0.020, 26) 19%
PBBz	0.019 (0.017, 0.0075; 0.0072–0.040, 27) 100%	0.018 (0.018, 0.0063; 0.0097–0.036, 19) 100%	0.027 (0.027, 0.013; 0.010–0.048, 13) 100%	0.029 (0.021, 0.018; 0.0097–0.073, 26) 100%	0.033 (0.017, 0.056; 0.0045–0.29, 26) 100%
TBCT	*(<MDL; <MDL–<MDL, 27) 0%*	*(<MDL; <MDL–<MDL, 25) 0%*	*(<MDL; <MDL–<MDL, 13) 0%*	*(<MDL; <MDL–<MDL, 26) 0%*	*(<MDL; <MDL–<MDL, 26) 0%*
PBT	0.0004 (0.0005, 0.0002; 0.0001–0.0008, 27) 100%	0.0038 (0.0035, 0.0021; 0.0012–0.011, 19) 100%	0.0059 (0.005, 0.0025; 0.0034–0.012, 13) 100%	0.0095 (0.0084, 0.0058; 0.0023–0.021, 26) 100%	0.012 (0.0078, 0.012; 0.0028–0.058, 26) 100%
HBBz	0.0088 (0.0084, 0.0032; 0.0044–0.019, 27) 100%	0.097 (0.092, 0.032; 0.057–0.20, 25) 100%	0.16 (0.18, 0.061; 0.061–0.28, 13) 100%	0.15 (0.13, 0.071; 0.059–0.30, 26) 100%	0.15 (0.093, 0.12; 0.027–0.50, 26) 100%
PBB-Acr	*(<MDL; <MDL–0.008, 27) 15%*	*(<MDL; <MDL–<MDL, 25) 0%*	*(<MDL; <MDL–0.018, 13) 23%*	*(<MDL; <MDL–0.011, 26) 8%*	*(<MDL; <MDL–<MDL, 26) 0%*

Table A2.2/2 Concentrations in air (pg/m^3) for emerging chemicals reported at GAPS sites located in the Arctic/subarctic (Lee et al., 2016). Range of values from four consecutive quarterly sampling periods starting in the second quarter of 2005, using PUF disk samplers. MDL: minimum detection limit. na: not available.

Chemical	Barrow	St.Lawr. Isl.	Stórhöfði	Ny-Alesund	Hollola
TBP-AE	0.11–0.22	1.23	<MDL–0.94	0.02–1.1	<MDL–0.059
TBX	<MDL–0.018	0.063	<MDL–0.051	<MDL–0.031	<MDL
TBP-BAE	<MDL–0.039	<MDL	<MDL	<MDL	<MDL
PBBz	<MDL–0.045	0.049	<MDL–0.10	<MDL–1.0	<MDL
TBCT	<MDL–0.04	0.092	<MDL–0.34	<MDL–0.038	<MDL–0.007
PBT	<MDL–0.005	0.0034	<MDL	<MDL–0.005	<MDL
PBEB	<MDL–0.027	0.016	<MDL–0.11	<MDL–0.027	<MDL
TBP-DBPE	<MDL–0.028	<MDL	<MDL–0.79	<MDL–0.11	<MDL–0.012
HBBz	<MDL–0.53	0.14	<MDL–0.25	<MDL–0.67	<MDL–0.034
PBB-Acr	<MDL	0.013	<MDL–0.006	<MDL	<MDL
EH-TBB	<MDL–7.2	<MDL	<MDL–1.0	<MDL–0.21	<MDL
HBCDD	<MDL–2.02	0.22	<MDL–3.3	<MDL–5.1	<MDL
BTBPE	0.15–1.0	0.33	<MDL–0.94	0.1–5.2	0.21
BEH-TEBP	<MDL–1.6	<MDL–0.04	<MDL–6.6	<MDL–0.29	na
OBTMPI	<MDL	<MDL	<MDL	<MDL	<MDL

Table A2.2/3 Concentrations of emerging chemicals on atmospheric particles (pg/m^3) at Longyearbyen, Svalbard (Salamova et al., 2014).

Other BFRs	Mean	Median	Range	% detection, n=34
EH-TBB	7.0±2.02	2.2	0.17–58	91
BEH-TEBP	2.7±0.49	1.8	0.27–14	88
DBDPE	0.53±0.10	0.27	0.04–2.2	88
BTBPE	0.04±0.01	0.03	0.01–0.09	53
HBBz	0.23±0.06	0.12	0.01–1.7	100
TBX	0.07±0.01	0.07	0.01–0.16	65
PBBz	0.14±0.05	0.04	0.01–1.1	76
PBEB	0.04±0.01	0.03	0.01–0.24	71

2.3 Chlorinated flame retardants (CFRs)

Authors: Katrin Vorkamp, Frank Rigét, Jennifer Balmer
Contributors: Hayley Hung, Robert Letcher

2.3.1 Introduction

Brominated compounds (see Section 2.2) and chlorinated compounds have been used as halogenated flame retardants because halogens are effective in capturing free radicals (Alaee et al., 2003). This section summarizes the Arctic data currently available on chlorinated flame retardants (CFRs), specifically *syn*- and *anti*-isomers of Dechlorane Plus (DDC-CO) and related compounds (see Tables 2.28 and 2.29). Chlorinated organophosphate flame retardants and short-chain chlorinated paraffins, which have also been used as flame retardants (Tomy et al., 1997) are discussed in Sections 2.4 and 2.6, respectively.

Dechlorane Plus (DDC-CO; $C_{18}H_{12}Cl_{12}$), also known as bis(hexachlorocyclopentadieno) cyclooctane, is a polychlorinated cycloaliphatic compound that has been used as an additive flame retardant since the 1960s (Feo et al., 2012). DDC-CO was first detected in air, fish, sediment, and bird eggs from the Great Lakes region, close to a production facility in Niagara Falls, NY, USA (Hoh et al., 2006; Gauthier et al., 2007; Sverko et al., 2008; Gauthier and Letcher, 2009). Since then, interest in DDC-CO has increased considerably, and a growing number of publications have addressed its occurrence and fate in the environment. Two reviews of current environmental DDC-CO data conclude that it is a ubiquitous global pollutant with the potential for long-range transport and bioaccumulation (Sverko et al., 2011; Feo et al., 2012). A review with focus on the Arctic confirmed the long-range transport of DDC-CO and presented some evidence of bioaccumulation, but the amount of data was still limited (Vorkamp and Rigét, 2014).

Although not as widely recognized as DDC-CO, three other dechloranes – Dechlorane 602 (DDC-DBF), Dechlorane 603 (DDC-Ant) and Dechlorane 604 (HCTBPH) – were developed by the same manufacturer, Occidental Chemical Corporation (or OxyChem), to be used as flame retardants in materials that require voltage and thermal standards not met by DDC-CO (Sverko et al., 2011). Despite having similar properties to other POPs, there is little information on the production and environmental fate of these analogs. However, evidence of their presence in the Arctic environment and biota is growing, indicating the potential for these alternative dechloranes to undergo long-range transport and bioaccumulation.

Table 2.28 Abbreviations adopted for chlorinated flame retardants, as suggested by Bergman et al. (2012).

Abbreviation	CAS number	Chemical name	Other abbreviations commonly used in the literature
DDC-CO	13560-89-9	Dechlorane Plus; Dechlorane 605	DP
DDC-DBF	31107-44-5	Dechlorane 602	Dec 602
DDC-Ant	13560-92-4	Dechlorane 603	Dec 603
HCTBPH	34571-16-9	Dechlorane 604	Dec 604
$aCl_{11}DP$		Undecachloropentacyclooctadecadiene	
$aCl_{10}DP$		Decachloropentacyclooctadecadiene	
DPMA		Dechlorane Plus monoadducts	

Table 2.29 Summary of Arctic media for which chlorinated flame retardants data have been reported. The brackets indicate that the compound was sought, but not detected in the respective medium.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
DDC-CO	×	×	×	×				×	×	×
DDC-DBF	×		×	×				×	×	×
DDC-Ant	(×)		×	×				×	×	×
HCTBPH	×		×	×				×	×	(×)
$aCl_{11}DP$	×	×								
DPMA										

2.3.2 Physical-chemical properties

DDC-CO is produced by the Diels-Alder condensation of hexachlorocyclopentadiene (HCCPD) and 1,5-cyclooctadiene (1,5-COD) in a 2:1 molar ratio. The resulting material comprises two diadduct stereoisomers, *syn*- and *anti*-DDC-CO, in a ratio of about 1:3 (Figure 2.53) (Hoh et al., 2006). This means that the theoretical proportion of *anti*-DDC-CO is 75% (Sverko et al., 2011), while it was experimentally determined to be 65% (Sverko et al., 2008).

Quantitative structure-activity relationship (QSAR) models (Sverko et al., 2011; Feo et al., 2012) and voluntary testing of DDC-CO by its manufacturer (EHSI, 2004) have indicated that DDC-CO has physical-chemical characteristics typical of other POPs, including high lipophilicity (log K_{OW} ~9), resistance to biodegradation, and bioaccumulation (log BAF ~5 in fish) (EHSI, 2004; Sverko et al., 2011; Feo et al., 2012). Studies are inconclusive with regard to the potential photodegradation of DDC-CO: the manufacturer reported a photolytic half-life of more than 24 years, however this was based on just one study performed in water (EHSI, 2004). Sverko et al. (2008) found indications of photodegradation of DDC-CO when dissolved in solvents. The atmospheric half-life, based on gas phase reactions and not considering particle-bound DDC-CO, was calculated to be about 14 hours (Table 2.30).

In contrast, in a report by the UK Environment Agency, a screening of persistence, bioaccumulation and toxicity (PBT) criteria for DDC-CO concluded that the isomers were 'not PBT'

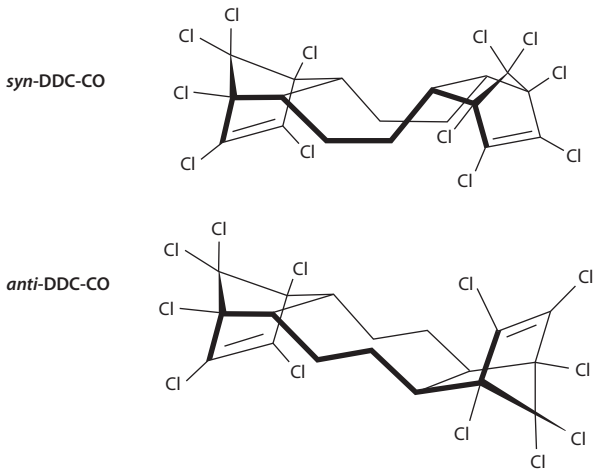


Figure 2.53 Isomers of DDC-CO: *syn*-DDC-CO and *anti*-DDC-CO.

Table 2.30 Environmental half-life estimates used in model calculations of characteristic travel distance and overall persistence for DDC-CO and other dechlorane analogs (Sverko et al., 2011).

	Half-life in air, hr	Half-life in water, hr	Half-life in soil, hr
DDC-CO	13.68	4320	8640
DDC-DBF	18.26	4320	8640
DDC-Ant	18.40	4320	8640
HCTBPH	49.23	4320	8640

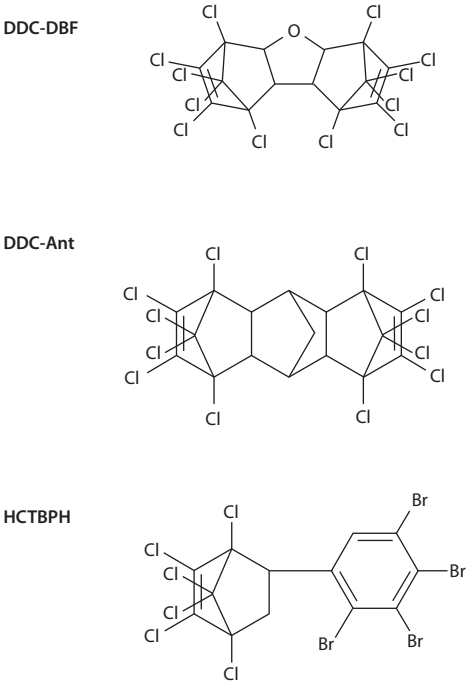


Figure 2.54 Structure of DDC-DBF (Dechlorane 602), DDC-Ant (Dechlorane 603), and HCTBPH (Dechlorane 604), after Bergman et al. (2012).

(Brooke and Burns, 2010). While the persistence criterion was considered provisionally met, the criteria of bioaccumulation and toxicity were not. In an EU PBT assessment, DDC-CO was 'believed to be persistent' and it was concluded that DDC-CO could bioaccumulate in fish (Pakalin et al., 2007).

There is a general lack of measured physico-chemical property data for other dechloranes (Figure 2.54), but estimated values have been derived using QSAR models (Sverko et al., 2011; Feo et al., 2012). Overall, dechloranes are hydrophobic (water solubilities <10 ng/L and log K_{OW} >7), and have very low vapor pressures (<10^{-6} Pa). Properties also vary slightly between compounds. According to estimated properties, DDC-DBF ($C_{14}H_4Cl_{12}O$) has the highest water solubility; whereas HCTBPH ($C_{13}H_4Br_4C_6$) is the least volatile based on its higher molecular weight and low vapor pressure. DDC-Ant ($C_{17}H_8Cl_{12}$) has properties intermediate between the two (Appendix 1) (Sverko et al., 2011; Feo et al., 2012).

2.3.3 Sources, production, use and trends

DDC-CO was introduced in the mid-1960s as a replacement for mirex (otherwise known as Dechlorane; $C_{10}Cl_{12}$) by Hooker Chemical (now part of Occidental Chemical Corporation, or OxyChem) (Hoh et al., 2006). DDC-CO is primarily used as an additive flame retardant in thermoplastic materials such as polyethylene, polyvinyl acetate, and polypropylene, where it can be added at concentrations of 5–35% by weight (ECHA, 2007). Major applications include industrial polymers used in wire and cable coatings, plastic roofing materials, hard connectors in television and computer monitors, and automotive lubricants (Tomy et al., 2008c). Minor applications include use in polyester

and epoxy resins (ECHA, 2007). Unlike its predecessor, mirex, which was used as both a flame retardant and an insecticide, no pesticide use has been reported for DDC-CO. DDC-CO has been mentioned as a potential alternative to DecaBDE (Lassen et al., 2006; Pakalin et al., 2007). These reports refer back to information from the producer OxyChem.

At least two currently operational manufacturing plants are known: the OxyChem facility at Niagara Falls, NY, USA (Hoh et al., 2006) and the Jiangsu Anpon Electrochemical Company, in Huaián, China (Wang et al., 2010b). DDC-CO is not produced in the European Union (ECHA, 2007).

DDC-CO is unregulated for use. It is considered a high production volume chemical by the US EPA, meaning it is produced or imported into the USA in quantities of 450-4500 t/y (Sverko et al., 2011). It is currently classified as a low production volume chemical in the EU, where an estimated 800 t/y are used (metric tonnes assumed but not stated) (ECHA, 2007). Sweden registered a use of 5 tonnes in 2006, after a decrease from 11 tonnes in 2005 (Kaj et al., 2010). DDC-CO is listed on Canada's Domestic Substances List (DSL), meaning it has been manufactured or imported in quantities of 0.1 ton or more (Environment and Climate Change Canada, 2016a). Production in China began in 2005 and is about 300 t/y (Wang et al., 2010a).

Similar to DDC-CO, DDC-DBF, DDC-Ant and HCTBPH were also developed and manufactured by Hooker Chemicals and Plastics, now known as OxyChem (Niagara Falls, NY, USA). Although information on their production is scarce (Sverko et al., 2011), sediment core analysis suggests they have been in use since the 1970s (Shen et al., 2010, 2011a; Yang et al., 2011). None of the three compounds are listed as high production volume chemicals in Europe (OECD, 2009), and at present no information is available from the USA. However, it is likely that DDC-DBF and HCTBPH are currently still in use as evidenced by their presence on the Non-Domestic Substances List published by Environment and Climate Change Canada (Shen et al., 2014; Environment and Climate Change Canada, 2016b). DDC-DBF is used as a flame retardant in fiberglass-reinforced nylon-6, while HCTBPH is used in silicone grease to lubricate metal-to-metal and metal-to-plastic substrates (Sverko et al., 2011). In contrast, no data on the production or use of DDC-Ant are available, but it has been identified as an impurity in formulations of organochlorine pesticides such as aldrin and dieldrin (Shen et al., 2011b) and is generally thought to have entered the environment through past use of these legacy pollutants (Sverko et al., 2011). Although HCTBPH has also been reported as an impurity in commercial products of mirex (NTP, 1990), its presence in the environment, along with DDC-DBF, is thought to be primarily derived from direct commercial production and use (Sverko et al., 2011).

2.3.4 Transformation processes

Although several compounds related to DDC-CO have been detected in a range of abiotic and biotic environmental compartments, without targeted study it is difficult to establish whether these compounds are byproducts of commercial manufacturing or are the result of abiotic degradation and biotransformation processes.

As a diadduct compound, DDC-CO is susceptible to retro reactions that revert the original compound to its monoadduct forms, such as 1,3- and 1,5-Dechlorane Plus monoadducts (1,3-DPMA and 1,5-DPMA) (Sverko et al., 2010). DPMAs may also form as unintended byproducts in the production of DDC-CO, as its starting material HCCPD reacts with feedstock impurities (Sverko et al., 2011). In some cases, DPMAs have been found in the environment and biota at higher concentrations than DDC-CO (Guerra et al., 2011; Tomy et al., 2013), however, results for Arctic media are sparse.

Dechlorinated analogs of DDC-CO have also been widely detected in the environment and biota (Sverko et al., 2008, 2010; Guerra et al., 2011) but only at low levels in the Arctic thus far (see Section 2.3.6). Decachloropentacyclooctadecadiene (*anti*-Cl_{10}DP, aCl_{10}DP) and undecachloropentacyclooctadecadiene (*anti*-Cl_{11}DP, aCl_{11}DP) (Figure 2.55) have been mostly undetectable, but aCl_{11}DP was occasionally identified in Arctic air (Möller et al., 2011a) although the origin of these dechlorinated derivatives remain unclear.

In a small study targeting levels of legacy POPs and screening for new contaminants in polar bears (*Ursus maritimus*) that swam from Greenland to Iceland between 2008 and 2011, DDC-DBF and a potential hydrodechlorinated metabolite were identified in all samples (Vetter et al., 2015). An unknown polyhalogenated compound with a mass spectrum corresponding to DDC-DBF, but with a molecular mass

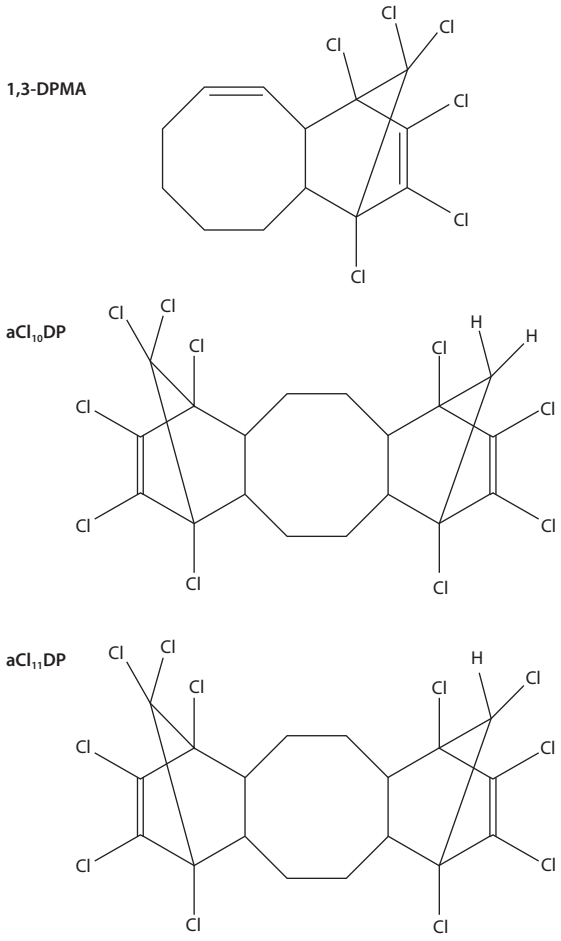


Figure 2.55 Structure of DDC-CO related compounds: 1,3-DPMA, aCl_{10}DP, and aCl_{11}DP.

indicative of one less chlorine ($C_{14}H_5Cl_{11}O$), was tentatively identified as a potential transformation product of DDC-DBF.

In another small study, Shen et al. (2012), identified a monohydro-derivative of DDC-DBF in beluga (*Delphinapterus leucas*) blubber from Hendrickson Island in the Canadian Arctic. It was suggested that the derivative, β-Cl_{11}-DDC-DBF ($C_{14}H_5Cl_{11}O$) is the result of photochemical degradation (rather than biotransformation) of DDC-DBF. Interestingly, the isomer α-Cl_{11}-DDC-DBF was not detected in the beluga samples, suggesting the β-isomer may be more persistent or bioaccumulative than other isomers of DDC-DBF.

2.3.5 Modeling studies

Available models indicate that DDC-CO and its analogs are not readily biodegradable and have transport properties similar to POPs (Wegmann et al., 2009; Sverko et al., 2011). Estimated half-lives ranged from <1 day in air up to 360 days in soil (Table 2.30). The OECD Screening Tool (Wegmann et al., 2009) was also used to calculate the long-range transport potential and overall persistence of DDC-CO and showed it to be comparable to compounds already under regulation by the Stockholm Convention (Figure 2.56) (Sverko et al., 2011). Owing to its high log K_{OW}, model calculations resulted in a low bioconcentration factor for DDC-CO, with the result that DDC-CO was not among the most persistent and bioaccumulative compounds with potential for long-range transport (Muir and Howard, 2006). However, the authors pointed out that this had been overruled by monitoring data. In a subsequent study, Howard and Muir (2010) identified 610 compounds with potential for persistence and bioaccumulation and classified DDC-CO among the top ten chlorinated compounds.

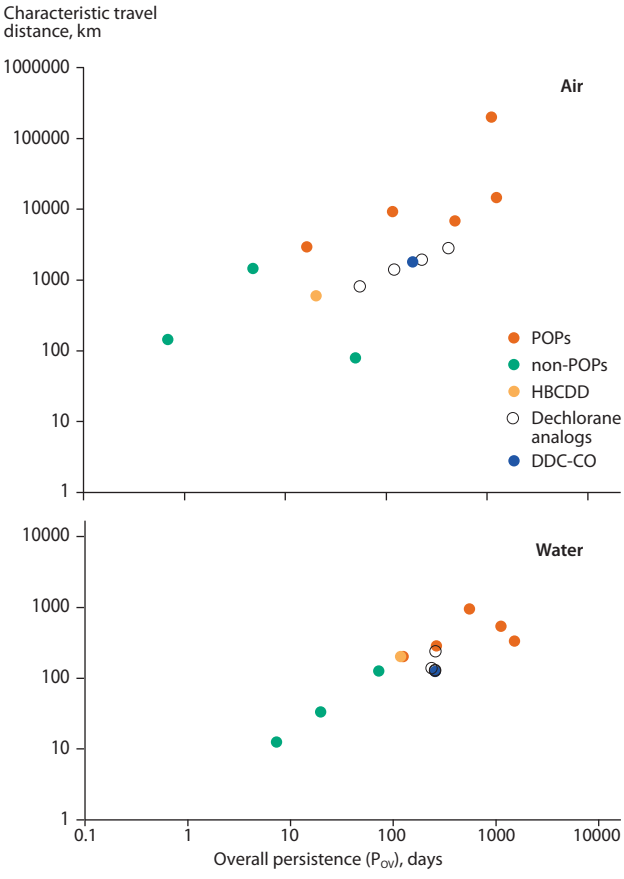


Figure 2.56 Characteristic travel distance and overall persistence (P_{OV}) of dechloranes compared to other environmental contaminants calculated using the OECD Screening Tool assuming 100% of emissions to air and water. Compounds represented include POPs (α-hexachlorocyclohexane, hexachlorobenzene, CB-28, CB-101, CB-180); non-POPs (atrazine, biphenyl; *p*-cresol); hexabromocyclododecane (HBCDD); DDC-CO and dechlorane analogs (DDC-DBF, DDC-Ant, HCTBPH and Chlordene-Plus). (Sverko et al., 2011).

Models indicate that similar to DDC-CO, dechlorane analogs are not readily biodegradable and that the half-lives in water and soil are considerable (Table 2.30) (Sverko et al., 2011). Although most have half-lives in air of less than two days, which does not meet the Stockholm Convention screening criterion for long-range transport, the estimates reported are considered conservative as they are based on the gas phase of air only, when data suggest dechloranes are predominantly (>99%) particle-bound (Möller et al., 2010).

The OECD Screening Tool (Wegmann et al., 2009) was also used to calculate the long-range transport potential and overall persistence of dechloranes in comparison to benchmark chemicals, such as other POPs (Figure 2.56) (Sverko et al., 2011). Although the results are based on estimates of environmental half-lives, rather than measured values, model results generally suggest that, similar to DDC-CO, the dechlorane analogs have transport and persistence properties similar to compounds already under regulation by the Stockholm Convention.

2.3.6 Environmental concentrations

2.3.6.1 Air and precipitation

Measurements of DDC-CO in air showed both isomers were mainly associated with particles (Hoh et al., 2006). For several studies, the concentration of DDC-CO in Arctic air was consistently comparable to that of the major polybrominated diphenyl ether (PBDE) congeners (Möller et al., 2010; Xiao et al., 2012a; Hung et al., 2013a; Salamova et al., 2014), which confirms significant long-range transport of DDC-CO to the Arctic.

DDC-CO was included in the air monitoring at Alert (Nunavut, Canada) in 2007 and detected in 11 of 14 samples, corresponding to a detection frequency of 79% (Xiao et al., 2012a; Hung et al., 2013a). Concentrations of total DDC-CO ranged from <0.05 to 2.1 pg/m^3, and concentrations of *syn*- and *anti*-DDC-CO averaged 0.18 and 0.57 pg/m^3, respectively. However, from 2008 to 2012, the *syn*-isomer was not detectable in most samples (annual detectability of <15%). The *anti*-isomer was detectable in 63% and 90% of samples in 2008 and 2009 with average concentrations of 0.075 and 0.058 pg/m^3, respectively. However, detectability decreased to <30% of samples between 2010 and 2012 with concentrations ranging from below the detection limit (<MDL) to 0.20 pg/m^3. Higher concentrations were observed at Longyearbyen (Svalbard, Norway) where particle phase atmospheric concentrations of DDC-CO were determined between September 2012 and May 2013 (Salamova et al., 2014). The detection frequency was 91% for each isomer, and mean concentrations were 0.29 pg/m^3 (*syn*-DDC-CO) and 1.1 pg/m^3 (*anti*-DDC-CO). The median concentrations were lower at 0.22 pg/m^3 (*syn*-DDC-CO) and 0.55 pg/m^3 (*anti*-DDC-CO), while maximum concentrations

were 0.91 pg/m³ (*syn*-DDC-CO) and 4.2 pg/m³ (*anti*-DDC-CO) (Salamova et al., 2014). Concentrations of *anti*-DDC-CO were not statistically different from those of the most abundant PBDE congeners (BDE-47, BDE-99, BDE-209).

At the Yukon station of Little Fox Lake, from August 2011 to December 2014, *syn*- and *anti*-DDC-CO were detectable in 100% of samples at total concentrations of 0.01–1.8 pg/m³, with means of 0.11 pg/m³ (*syn*-DDC-CO) and 0.14 pg/m³ (*anti*-DDC-CO) (see Figure 2.42) (Yu et al., 2015). *Syn*- and *anti*-DDC-CO were highly correlated (r=0.967, $p<0.0001$), indicating that they had the same source regions and fate pathways. They were also weakly correlated with BDE-47 and BDE-99, but not correlated with other non-BDE flame retardants. DDC-DBF was detectable in over 75% of samples collected at concentrations of 0.004–0.060 pg/m³ (median: 0.016, mean: 0.021). HCTBPH was only detected in 2014 at concentrations of 0.018–0.119 pg/m³ (median: 0.076 pg/m³, mean: 0.071) at 21.4% detectability (Yu et al., 2015).

A single maximum concentration of 4.1 pg/m³ (for *syn*-DDC-CO) was also observed in air over the East Greenland Sea, while the corresponding concentration of *anti*-DDC-CO was 0.14 pg/m³, i.e. a pattern deviating from that at Alert and Svalbard (Möller et al., 2010). Analysis of air mass back trajectories showed mixed air from the Atlantic Ocean, the Arctic Ocean and Greenland. Other concentrations (in the particle phase) were 0.01–0.24 pg/m³ for *syn*-DDC-CO and 0.01–0.07 pg/m³ for *anti*-DDC-CO, which is also different from the isomer composition at Svalbard (Salamova et al., 2014). Möller et al. (2010) reported that about 80% of each isomer was associated with particles, but that the finding of DDC-CO in the gas phase could be an artifact of binding to small particles that can pass through the glass fiber filter.

In air samples collected north of 60°N on a cruise from East Asia to the Arctic in summer 2010, concentrations in the Chukchi/Bering Sea were relatively low, in general <0.1 pg/m³, with the exception of one gaseous sample of 0.17 pg/m³ (*syn*-DDC-CO) and 0.25 pg/m³ (*anti*-DDC-CO) (Möller et al., 2011a) (Table 2.31). Although the maximum concentration was observed in a gas phase sample, the authors again highlighted that DDC-CO mainly occurred in the particle phase. DDC-DBF and DDC-Ant were not detectable in either gas or particle phase samples (Möller et al., 2011a). HCTBPH was non-detectable in either the gas or particle phase samples in general, but was detected in one particle phase sample at 0.05 pg/m³ collected at the most southerly site in the Arctic (62.64°N, 175.12°E) (Table 2.31).

Table 2.31 Atmospheric concentration ranges for DDC-CO and other dechloranes measured in gas and particle phases of the atmosphere along a cruise from East Asia to the Arctic at stations north of 60°N from June to September 2010 (Möller et al., 2011a).

Compound	Gas phase, pg/m³	Particle phase, pg/m³
syn-DDC-CO	0.01–0.17	0.01– 0.08
anti-DDC-CO	<0.003–0.25	0.01–0.05
f_{anti}*	0.23–0.59	0.21–0.56
DDC-DBF	<0.003	<0.011
DDC-Ant	<0.047	<0.065
HCTBPH	<0.008	<0.008–0.05
$aCl_{11}DP$	<0.002–0.003	<0.002

*Fractional abundance of *anti*-DDC-CO, one gas-phase sample excluded with only *syn*-DDC-CO detectable.

For monthly air samples collected at Villum Research Station (Station Nord, northeast Greenland) in 2012, the detection frequency of *syn*- and *anti*-DDC-CO was 46%, with mean concentrations of 2.32 pg/m³ (*syn*-DDC-CO) and 5.24 pg/m³ (*anti*-DDC-CO) (Vorkamp et al., 2015).

Several studies have addressed the *anti/syn* ratio of the DDC-CO concentrations, often expressed as the fraction of *anti*-DDC-CO, i.e. $f_{anti} = anti/(syn + anti)$, based on concentrations. Thus, an *anti/syn* ratio of 3 corresponds to f_{anti}=0.75, which is what is found in the technical product (Sverko et al., 2011). Other studies have given f_{anti} of the technical product as 0.65-0.80 (Sverko et al., 2008; Na et al., 2015).

The studies in Canada, Svalbard and Greenland have in common that *anti*-DDC-CO was the main isomer (Xiao et al., 2012a; Salamova et al., 2014). While f_{anti} could vary widely between individual measurements, it often averaged close to 0.75. In the monitoring at Alert, f_{anti} ranged from 0.54 to 0.93, with an average of 0.72 (Xiao et al., 2012a; Hung et al., 2013a). Similarly, f_{anti} was between 0.43 and 0.90 at Longyearbyen, with an average of 0.75 (Salamova et al., 2014). In East Greenland, f_{anti} ranged from 0.56 to 1.0 and was 0.72 on average (Vorkamp et al., 2015). At the Yukon station of Little Fox Lake, a small change in the *anti/syn* ratio was observed over time: f_{anti} for the first year was 0.61 and decreased in the second (0.56) and third (0.51) year together with the overall concentrations of DDC-CO, indicating that this site may have been more influenced by local emissions in the first year (Yu et al., 2015). In the East Greenland Sea and the Chukchi/Bering Sea, however, *syn*-DDC-CO was often the main isomer and the authors discussed possible stereoselective photodegradation of *anti*-DDC-CO as an explanation (Möller et al., 2010, 2011a).

DDC-CO has also been analyzed in passive air samples of the Global Atmospheric Passive Sampling (GAPS) network, which includes several Arctic stations in Alaska, Canada, Svalbard and Iceland. For DDC-CO, concentrations in Alaska were higher than in Europe and exceeded 50 pg/m³ (Hung et al., 2013a). The authors noted that this was surprisingly high considering the low population density in this region. Although passive samplers usually sample from the gas phase and several studies have highlighted the association of DDC-CO with particles, the GAPS network samplers were found to also collect particles, representative in size and number of ambient air (Markovic et al., 2015).

In 2009–2010, at two Swedish Arctic/subarctic sites, Newton et al. (2014) detected DDC-CO in bulk atmospheric deposition samples (precipitation + dry particles) with mean fluxes (± standard deviation) of 22±21 ng/m²/month at Abisko and 1.1±0.52 ng/m²/month at Krycklan. There were differences in the proportions of the two DDC-CO isomers at the two stations: the fraction of *anti*-isomer f_{anti} was 0.62±0.18 of the total DDC-CO at Krycklan and only 0.25±0.07 at Abisko. The fraction at the more southerly site of Krycklan is closer to the composition of the technical mixture, indicating that it is closer to a source of

DDC-CO (possibly the city of Umeå). The authors discussed that the greater fluxes at Abisko compared to Krycklan might be due to scavenging processes and air transport pathways rather than proximity to sources. Monthly fluxes of DDC-CO at Krycklan were comparable to those reported for Pallas in northern Finland (0.52–0.76 ng/m^2/month) (Kaj et al., 2010).

Meyer et al. (2012) analyzed DDC-CO in the Devon Ice Cap, but both isomers were generally non-detectable, with only one detectable concentration (48 pg/L) and this was found at the 600–650 cm depth in the 2008 snow pit.

2.3.6.2 Terrestrial environment

DDC-CO (*syn*- and *anti*-isomers), DDC-DBF, DDC-Ant and HCTBPH were measured in various environmental matrices, including soil, moss and reindeer dung, collected in July 2012 from Ny-Ålesund, Svalbard (Figure 2.57) (Na et al., 2015). For DDC-CO, concentrations were lowest in moss, at 0.1–2.5 pg/g dw (*syn*-DDC-CO) and <MDL–0.9 pg/g dw (*anti*-DDC-CO). Total DDC-CO concentrations in soil and reindeer dung were higher and more comparable; however levels and ratios of the respective isomers differed. In soil, average concentrations were 284 pg/g dw (range 94–1010) for *syn*-DDC-CO and 42 pg/g dw (range 12–105) for *anti*-DDC-CO, with an f_{anti} ratio of 0.18. In comparison, reindeer dung exhibited average concentrations of 87 pg/g dw (range 3.5–368) for *syn*-DDC-CO and 171 pg/g dw (range 1.7–524) for *anti*-DDC-CO, with an f_{anti} ratio of 0.66. The authors attributed the differences in f_{anti} to the source of DDC-CO to soil and reindeer, with the low ratio observed in soil potentially indicating a long-range transport source with photodegradation and microbial transformation occurring during deposition. Correspondingly, the higher f_{anti} observed in reindeer dung is more similar to that found in commercial products (0.65–0.80), indicating a potential local source of DDC-CO.

For other dechloranes, levels were lowest in moss and highest in reindeer dung and HCTBPH was found at higher concentrations than DDC-DBF or DDC-Ant (Figure 2.57). Reindeer dung exhibited the highest HCTBPH concentrations of the terrestrial samples (12–142 pg/g dw). Concentrations of DDC-DBF (<MDL–17 pg/g dw) and DDC-Ant (<MDL–5.5 pg/g dw) were significantly lower. HCTBPH was also found in all soil samples (1.4–73 pg/g dw), whereas DDC-DBF (<MDL–2.8 pg/g dw) and DDC-Ant (<MDL–8.6 pg/g dw) were measured in about 80% of samples. While DDC-DBF was not detected in moss, DDC-Ant (<MDL–0.9 pg/g dw) and HCTBPH (<MDL–0.4 pg/g dw) were identified in 25% and 87% of samples, respectively.

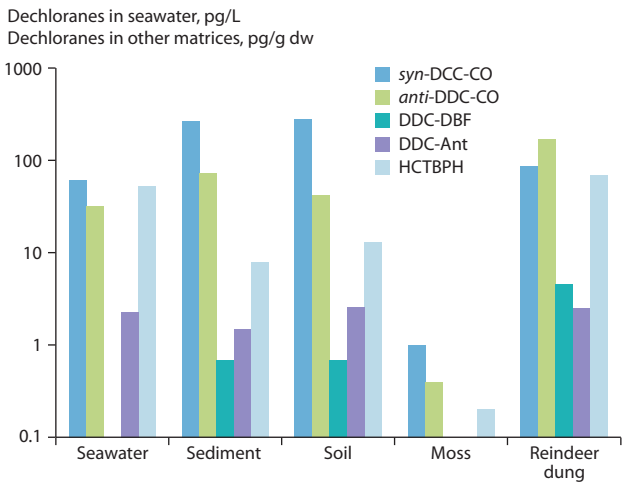


Figure 2.57 Mean concentrations of dechloranes measured in various terrestrial matrices from Ny-Ålesund, Svalbard (based on Na et al., 2015).

2.3.6.3 Freshwater environment

No data available.

2.3.6.4 Marine environment

Seawater and sediment

Measurements in seawater have confirmed the air observations of DDC-CO being mainly associated with particles. In the East Greenland Sea, particle-bound DDC-CO accounted for, on average, 97% of *syn*-DDC-CO and 80% of *anti*-DDC-CO (Möller et al., 2010). Concentrations were <0.002–0.86 pg/L (*syn*-DDC-CO) and <0.002–0.38 pg/L (*anti*-DDC-CO).

On a cruise from East Asia to the Arctic in summer 2010, the predominance of particle-bound DDC-CO in seawater from the Chukchi/Bering Sea was not as clear, with generally low concentrations of *syn*-DDC-CO (≤0.011 pg/L) and *anti*-DDC-CO (≤0.008 pg/L) (Möller et al., 2011a). As discussed for the corresponding air samples of these studies, an enrichment of *syn*-DDC-CO was also observed in seawater (Möller et al., 2010, 2011a). The authors reasoned that the seawater concentrations were a result of dry deposition, which would be reflected in similar isomer compositions for air and seawater. DDC-DBF, DDC-Ant and HCTBPH were mostly non-detectable in seawater samples collected north of 60°N, but were quantifiable in a few isolated samples (Möller et al., 2011a). Of the three dechlorane analogs in the dissolved phase, the most frequently detected was DDC-Ant, being found in four of the nine samples (0.007–0.192 pg/L) and was also detected at the most northerly location at 75.46°N. HCTBPH was detected in two samples (0.016 and 0.046 pg/L), while DDC-DBF was only detected in one (0.021 pg/L). HCTBPH was the only compound detectable in the particle phase, at 0.016 pg/L.

DDC-CO, DDC-DBF, DDC-Ant and HCTBPH were also measured in seawater and sediment collected concurrently from Kings Bay, Svalbard in July 2012 (Figure 2.57) (Na et al., 2015). DDC-CO was detected in all seawater and sediment samples analyzed. Concentrations in seawater were 22–116 pg/L (*syn*-DDC-CO) and 13–88 pg/L (*anti*-DDC-CO). Total dechloranes, which included both DDC-CO isomers as well as dechlorane analogs, DDC-DBF, DDC-Ant and HCTBPH, were highest in seawater found near the inlet of Kings Bay, suggesting that glacial melt water and freshwater input is a potential source of dechloranes to seawater. Concentrations in sediment were 85–648 pg/g dw (*syn*-DDC-CO) and 23–228 pg/g dw (*anti*-DDC-CO). Sediment concentrations did not follow the same spatial pattern observed for seawater, suggesting other factors influence the deposition of DDC-CO isomers to sediment. HCTBPH was detected in all seawater samples (25–106 pg/L), at concentrations similar to those for *syn*-DDC-CO. Conversely, DDC-Ant was detected in just 37.5%

of seawater samples (<MDL–6.3 pg/L) and DDC-DBF was not detectable in any samples. Sediment samples analyzed as part of the same study in Kings Bay, detected DDC-Ant and HCTBPH in all samples, and DDC-DBF in 88% of sediment samples analyzed.

Biota

Few studies have screened or reported DDC-CO and dechlorane analogs in Arctic biota. A screening study of the Nordic environment included biota samples from the Faroe Islands (black guillemot *Cepphus grylle* eggs, Arctic char *Salvelinus alpinus* muscle and Atlantic cod *Gadus morhua* liver) as well as cod liver and blue mussels (*Mytilus edulis*) from Iceland (Schlabach et al., 2011). All samples were pools of several individuals. The fish liver and muscle samples had DDC-CO concentrations that were below detection limits of about 0.03 and 0.004 ng/g wet weight (ww), respectively. DDC-CO was also not detected in blue mussel, at detection limits of about 0.004 ng/g ww. However, DDC-CO was detectable in black guillemot eggs from the Faroe Islands, with concentrations of about 0.01–0.02 ng/g ww (*anti*-DP) and <0.008–0.009 (*syn*-DDC-CO). Thus, the *anti* > *syn* ratio was also observed in these biota samples.

DDC-CO was sought in ringed seal (*Pusa hispida*) and beluga (*Delphinapterus leucas*) blubber from the Canadian Arctic and in liver of Greenland shark (*Somniosus microcephalus*) from around Iceland (Shen et al., 2012; Muir et al., 2013b; Strid et al., 2013). None of these studies found DDC-CO above detection limits. *Syn*- and *anti*-DDC-CO isomers have been routinely screened for in fat samples of western and southern Hudson Bay polar bears each year over the period 2007–2014, and similar to ringed seal and beluga from the Canadian Arctic, neither DDC-CO isomer was consistently detected (Letcher et al., 2018). However, eggs collected from common eider (*Somateria mollissima*), European shag (*Phalacrocorax aristotelis*) and herring gull (*Larus argentatus*) from two remote islands, Sklinna and Røst, north of 65°N on the Norwegian coasts had DDC-CO levels of <MDL–0.08 ng/g ww (Huber et al., 2015). In addition, a 2012 survey of wildlife from East Greenland that included black guillemot eggs, glaucous gull (*L. hyperboreus*) liver, ringed seal blubber, and polar bear fat detected *syn*-DDC-CO and *anti*-DDC-CO in 85% and 100% of samples, respectively (Vorkamp et al., 2015) (Table 2.32). Concentrations in black guillemot eggs as well as the f_{anti} ratio were similar to results for black guillemot eggs from the Faroe Islands (Schlabach et al., 2011). The f_{anti} values were all similar to that of the technical product and not statistically different from each other. Studies from outside the Arctic indicate a stronger biomagnification of the *syn*-isomer than the *anti*-isomer (Wu et al., 2010), but more data are needed to understand the trophic transfer of DDC-CO.

Dechlorane analogs have also been detected in a few samples of marine biota. Fat samples of western Hudson Bay polar bears collected in the period 2012–2013, were screened for several dechlorane-like norbornene derivatives as well as structurally related mirex (Dechlorane) and photomirex (a photodegradation product of mirex). DDC-DBF and DDC-Ant were quantifiable at 2.5±2.4 and 0.3±0.2 ng/g lw, respectively (Letcher et al., 2018.). Concentrations of DDC-DBF and DDC-Ant were the same as for mirex (2.8±2.5 ng/g lw) and less than for photomirex (11±9 ng/g lw). Vetter et al. (2015) also identified DDC-DBF and its tentative metabolite in all four samples of a screening study of polar bears from East Greenland.

In a study of beluga sampled in 2000 and 2010 from Hendrickson Island in the Canadian Arctic, DDC-DBF and β-Cl_{11}-DDC-DBF, a monohydro-derivative of Dechlorane 602, were found in all eight blubber samples, even though DDC-CO, DDC-Ant and HCTBPH were undetectable (Shen et al., 2012). Concentrations of DDC-DBF and β-Cl_{11}-DDC-DBF were similar, ranging from 80 to 300 pg/g lw and 25 to 210 pg/g lw, respectively.

2.3.7 Environmental trends

2.3.7.1 Spatial trends

Following a latitudinal transect in the East Greenland Sea, Möller et al. (2010) observed decreasing air concentrations of DDC-CO with increasing latitude. This trend was not reflected in the seawater samples, which were highest in the northernmost samples. The analysis of air mass back trajectories showed a mix of oceanic, Arctic and continental air masses. The higher levels of DDC-CO in seawater observed at some northern sites were probably due to water masses originating from the Atlantic and Arctic Oceans, in combination with freshwater inputs from melting land ice (Möller et al., 2010). Both water and air concentrations were higher at stations near the coast than in the open sea.

Decreasing DDC-CO concentrations with increasing latitude were also observed in the Chukchi/Bering Sea, however, concentrations were near detection limits (Möller et al., 2011a). The authors also observed correlations with PBDEs, possibly indicating the same source regions.

Table 2.32 Concentrations of DDC-CO in biota from Greenland (Vorkamp et al., 2015).

Species	Tissue	Mean (range), ng/g ww			
		n	*Syn*-DDC-CO	*Anti*-DDC-CO	f_{anti}
Black guillemot	Egg	4	0.014 (0.005–0.030)	0.067 (0.010–0.19)	0.76 (0.67–0.86)
Glaucous gull	Liver	4	0.023 (0.010–0.041)	0.11 (0.066–0.18)	0.83 (0.77–0.88)
Ringed seal (East Greenland)	Blubber	5	0.096 (<0.013–0.42)	0.42 (0.035–1.84)	0.84 (0.74–0.96)
Ringed seal (West Greenland)	Blubber	4	0.019 (0.014–0.030)	0.071 (0.053–0.083)	0.80 (0.73–0.85)
Polar bear	Adipose	5	0.021 (0.013–0.030)	0.055 (0.028–0.079)	0.72 (0.66–0.76)

DDC-CO was not statistically different in ringed seal samples from East and West Greenland although a significant geographical difference was observed for various POPs and some novel brominated flame retardants (Vorkamp et al., 2008, 2015). More data will be needed to derive spatial trends in biota.

No spatial data were available for dechlorane analogs.

2.3.7.2 Temporal trends

No data available.

2.3.8 Conclusions

DDC-CO and its analogs are currently unregulated, yet demonstrate similar properties to POPs, including long-range transport to the Arctic. DDC-CO has consistently been detected in Arctic air. The majority of studies have found an *anti/syn* ratio similar to that of the technical product, but deviations have been reported. Inconclusive observations exist as to whether the *anti/syn* ratio changes with distance from potential sources of DDC-CO.

Although detection in Arctic biota is inconsistent, several recent studies have shown the presence of DDC-CO in terrestrial and marine fauna, including reindeer, seabirds, seals, beluga and polar bears. Concentrations were generally low and challenge analytical detection limits.

Additional monitoring studies are needed to understand the significance of these compounds to the Arctic, specifically regarding freshwater systems for which data are lacking. Including dechlorane transformation products (e.g. dechlorinated derivatives and monoadducts) in screening studies would be useful, because these related compounds have been identified, but not widely screened for in Arctic media and biota, thus their origin and significance remain unclear. Lastly, given the recent detection of dechloranes in apex predators of the Arctic, targeted isomer-specific studies to assess the bioaccumulation potential of these compounds are warranted.

2.4 Organophosphate-based flame retardants and plasticizers

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Contributors: Cynthia de Wit, Hayley Hung, Derek Muir, Katrin Vorkamp

2.4.1 Introduction

Organophosphate esters (OPEs) have been used for a long time as flame retardant and plasticizer chemicals (van der Veen and de Boer, 2012). Aspects of OPE chemistry are informed by the structurally similar organophosphate pesticides for which there is more information. A major group of OPE chemicals are the organophosphate triesters (OP triesters), with various sidechain groups (Figure 2.58). Generally, OPEs that are halogenated are used as flame retardants, while those without halogens are used as plasticizers. However, some OPEs are used in both applications. Aryl OPEs are also used as hydraulic oils and as performance additives to engine oils. Tris(2-butoxyethyl) phosphate (TBOEP) is an example of an OPE that is used in floor polish and waxes, etc.

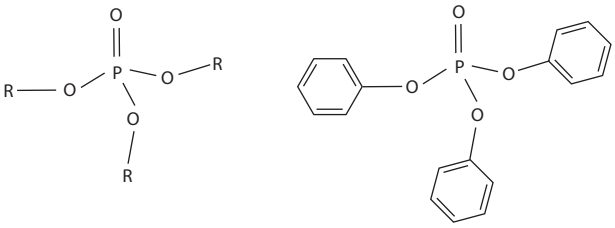

Figure 2.58 Generic chemical structure (left figure) of organophosphate triester flame retardants (also referred to as phosphate flame retardants; PFRs), where the R-substituents can be one of many alkyl groups, which may also be aryl and/or halogenated. On the right is a representative PFR, namely triphenyl phosphate (TPHP). Hydrogen atoms have been omitted for clarity.

For the purposes of this section, the OP triesters used predominantly as flame retardants are referred to as PFRs in accordance with nomenclature suggested by Bergman et al. (2012). In addition to OPEs, other abbreviations seen in the literature are OPFRs and OP triester FRs. PFRs are high production volume chemicals, in use since the 1970s, that are added to plastics, foams, textiles, floor polishes, waxes and furniture (Marklund et al., 2005; Reemtsma et al., 2008; Bergh et al., 2011; van der Veen and de Boer, 2012). In recent years, it has been suggested that the production and use of certain PFRs are increasing, coincident with the regulation and phase-out of many brominated flame retardant (BFR) substances, for example polybrominated diphenyl ethers (PBDEs) such as penta-BDEs and hexabromocyclododecane (HBCDD) (Reemtsma et al., 2008; Schreder et al., 2016). Organophosphate flame retardants and plasticizers that have been shown to be or are predicted to be environmentally relevant are listed in Table 2.33, while

Table 2.33 Summary of organophosphate flame retardants and plasticizers (PFRs) that have been shown to be or are predicted to be environmentally relevant.

PFRs[a]	Abbreviation	CAS#
Tris(2-chloroethyl) phosphate	TCEP	115-96-8
Tripropyl phosphate	TPrP	513-08-6
Tris(2-chloroisopropyl) phosphate[b]	TCIPP	13674-84-5
Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP	13674-87-8
Triphenyl phosphate	TPHP	115-86-6
Tris(2,3-dibromopropyl) phosphate	TDBPP	126-72-7
Tributyl phosphate	TBP	126-73-8
Tricresyl phosphate	TMPP	1330-78-5
2-Ethylhexyl-diphenyl phosphate	EHDPP	1241-94-7
Tris(2-butoxyethyl) phosphate	TBOEP	78-51-3
Tris(2-bromo-4-methylphenyl) phosphate	T2B4MP	35656-01-0
Tris(4-bromo-3-methylphenyl) phosphate	T4B3MP	35656-01-0
Tris(3-bromo-4-methylphenyl) phosphate	T3B4MP	35656-01-0
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2
Tris(tribromoneopentyl)phosphate	TTBP	19186-97-1
Triethyl phosphate	TEP	78-40-0
2,2-bis(chloromethyl_propane-1,3-diyl tetrakis(2-chloroethyl)bis(phosphate)	V6	38051-10-4
Tri-*n*-butyl phosphate	TNBP	126-73-8
Triisobutyl phosphate	TIBP	126-71-6
Butyldiphenyl phosphate	DPhBP	2752-95-6

[a]See Bergman et al. (2012) for a complete listing of PFR triester chemical abbreviations. [b]TCIPP represents tris(2-chloroisopropyl) phosphate as indicated; however, there are seven additional structural isomers of TCIPP with unique CAS# (i.e. 26248-87-3, 76025-08-6, 76649-15-5, 6145-73-9, 137909-40-1, 137888-35-8 and 1067-98-7). See van der Veen and de Boer et al. (2012) for isomer details.

Table 2.34 Summary of Arctic media for which organophosphate flame retardants or plasticizers have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
TCEP	×						×			×
TCIPP	×						×			×
TDCIPP	×						×			×
TPHP	×						×			×
TBP	×						×			×
TMPP										×
EHDPP	×									×
TBOEP	×						×			×
TEHP	×									×
TNBP	×									
TIBP	×									×
DPhBP										×

Table 2.34 lists PFRs for which there is published literature reporting the screening of levels in media from somewhere in the Arctic environment.

2.4.2 Physical-chemical properties

Following the phase-out of PBDEs, due to their persistent, bioaccumulative and toxic properties, PFRs (Figure 2.58, Table 2.33) are increasingly used as alternative flame retardants in many products (van der Veen and de Boer, 2012). In most cases, PFRs are dispersed into the host material but are not chemically bound, and thus can be released from the host material into the surrounding environment. There is wide variation in physical-chemical properties of PFRs.

PFR water solubility decreases with increasing molecular mass. Reemtsma et al. (2008) commented that most PFRs are hydrolytically stable at neutral pH, although this contrasts with OP triesters used as insecticides, which are more hydrolytically unstable. PFR properties of high solubility, relatively high vapor pressures and general resistance to hydrolysis at neutral pH imply relatively high mobility. This is very important when assessing the fate of PFRs with respect to the Arctic. However, in an examination of environmentally relevant PFRs (including those reported in Arctic media), Su et al. (2016) reported on PFR hydrolytic stability at neutral and more basic pH conditions for 16 of the PFRs listed in Table 2.33. Six PFRs (including TPHP, TMPP and TBOEP) showed significant degradation progressing from pH=7 to pH=11 aqueous solutions, over a 35-day period. For 14 PFRs, the hydrolysis half-lives) ranged from 0.0053 days (TPHP) to 47 days (TPrP). A mass balance showed that PFRs that degraded with increasingly basic pH, were mostly transformed to their corresponding OP diester phosphoric acid products. Where hydrolysis half-lives are equal, the PFRs with lower molecular mass are more likely to be found in the aquatic environment than those with higher molecular mass, which is confirmed by the log K_{OW} values of the PFRs. Most of the PFRs have a positive log K_{OW} value, which means they are more lipophilic than hydrophilic. Log K_{OW} values for PFRs range from 0 to 10 (van der Veen and de Boer, 2012). The wide range of Henry's law constant values for PFRs indicates that their distribution in air and water, such as in the oceans, is predicted to be highly variable. There is also a great variety in vapor pressures and bioconcentration factors (BCFs). The vapor pressure at 25°C ranges from 1.9 mm Hg for dimethyl phosphonate (DMHP) to 21 mm Hg for tetrakis-hydroxymethyl phosphonium sulfate (THPS). Predicted BCFs range from 1.37 for tris(2-chloroethyl) phosphate (TCEP) to 1000 000 for trioctyl phosphate and tris(2-ethylhexyl) phosphate (TEHP) (van der Veen and de Boer, 2012).

Overall, there are substantial uncertainties in the physical-chemical properties of PFRs, and not many measured values have been reported. PFR vapor pressures have been reported by Brommer et al. (2014). Also, estimates of physical-chemical properties based on Quantitative Structure-Activity Relationships (QSARs) have been reported using EPI Suite, SPARC and Absolv, but there is high variability between estimates for individual PFRs (e.g. air-water partition coefficients) obtained from these estimation programs. One reason is that the PFRs were not well represented in the training sets for the QSARs (e.g. for EPI Suite) (Zhang et al., 2016).

2.4.3 Sources, production, use and trends

PFRs have been in use for several decades, and contemporary production of PFRs has been continuous and in high volume. For example, the estimated annual consumption of PFRs in Western Europe increased from about 83 000 t/y in 2001 to 91 000 t/y in 2006 (Reemtsma et al., 2008). Production volumes for tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), TPHP, and TCIPP in the USA increased from 500–5000 t in 1990 to 5000–25 000 t in 2006 for each of these chemicals (US EPA, 2012). Schreder et al. (2016) estimated that chlorinated PFR

production (TDCIPP, TCIPP and TCEP) in the USA increased from less than 14 000 t/y in the mid-1980s to about 38 000 t/y in 2012. This increasing production is consistent with reports of very high atmospheric concentrations at sites near urban areas. Specifically, Salamova et al. (2014) reported exceptionally high total atmospheric PFR levels of up to 2100±400 pg/m^3 in the particle phase of air samples from sites in the North American Great Lakes basin. ΣPFR concentrations mainly comprised TCEP, TCIPP, and TDCIPP. ΣPFR concentrations were about 2–3 orders of magnitude higher than all BFRs combined in similar samples. Similarly, relatively high concentrations of PFRs have been reported in Arctic air (see Section 2.4.6).

2.4.4 Transformation processes

There have been few reports on the abiotic and biotic degradation of PFRs in the environment, which means such information that does exist is of great importance when assessing the fate of PFRs in the Arctic. With respect to abiotic transformation, Reemtsma et al. (2008) concluded that most PFRs are hydrolytically stable at neutral pH. However and as mentioned earlier, PFRs are known to be susceptible to hydrolysis as a function of increasingly more basic pH (Su et al., 2016). Liu et al. (2014) reported on heterogeneous reactions between OH radicals and PFRs coated on inert particles. The degradation of these particle-bound PFRs was observed as a result of OH radical exposure, and second-order rate constants were derived for the heterogeneous loss of TPHP, TEHP, and TDCIPP. Atmospheric lifetimes were estimated to be 5.6 (TPHP), 4.3 (TEHP) and 13 (TDCIPP) days. This OH radical oxidation was consistent with the assumption that PFRs can undergo medium- or long-range transport.

There is a growing number of reports on the biotic degradation of PFRs. Data are limited but there are new studies that strongly suggest that PFR residue concentrations in tissues and other body compartments (e.g. blood) and eggs of exposed wildlife are much lower than reported in abiotic environmental samples. This is largely attributed to rapid PFR metabolism in exposed wildlife and fish. The dearth of PFR triester metabolism data has until recently been largely due to an absence of analytical methods for determining PFR diester metabolites and other metabolites in biological samples. Su et al. (2014b) published a method for PFR diesters, applicable to biological samples of varying complexity, for example bovine serum, chicken egg homogenate and pork liver. This method was subsequently applied to plasma samples of six herring gulls (*Larus argentatus*) (2010, Chantry Island, Laurentian Great Lakes), which were found to contain TPHP and TDCIPP as well as the PFR diesters, bis(1,3-dichloro-2-propyl) phosphate (BDCIPP), bis-(2-butoxyethyl) phosphate and di(2-ethylhexyl) phosphate, in the ranges 0.7–3.5, 0.08–29.4 and below detection 0.18 ng/g ww, respectively (Su et al., 2014b).

There is further evidence that the fate and resulting tissue residue levels of PFRs in biota are influenced by degradation/transformation processes such as metabolism. Several *in vitro* and *in vivo* studies have shown that PFR diesters were primary metabolites of PFRs. For instance, BDCIPP was the major metabolite in TDCIPP-exposed Wistar-Han rat liver microsomes (Chu et al., 2011), and the major metabolite eliminated in urine was also BDCIPP in TDCIPP-exposed rats (Lynn et al., 1981). A recent study investigated the metabolism of five PFRs following incubation with human liver S9 fraction and microsomes, and OP diesters were identified as one of the major metabolite groups after treatment with TPHP, TCEP and TDCIPP (Van den Eede et al., 2013). Su et al. (2014a) investigated the *in vitro* metabolism of TPHP by use of a chicken embryonic hepatocyte (CEH) assay. After 36 hours of exposure, rapid degradation of TPHP was observed in CEH exposed to 10 μM, but the resulting concentration of diphenylphosphate (DPHP) accounted for only 17% of the initial TPHP dosing concentration. Monohydroxylated-TPHP (OH-TPHP) and two $(OH)_2$-TPHP isomers were identified in TPHP-exposed CEH, and concentrations of these metabolites increased over a 36-hour period. In a follow-up study, Su et al. (2015) reported the phase I hydroxylation and phase II conjugation metabolic pathways (either *in vitro* or *in vivo*) of TPHP. They also reported DPHP metabolite formation using the same CEH assay. TPHP was phase I metabolized to *p*- and *m*-hydroxy-TPHP metabolites, which were largely present in the assay medium and cells as phase II conjugates with glucuronic acid. Overall, in TPHP-exposed organisms, this study demonstrated the importance of phase I and II metabolic processes in the biological fate of TPHP. Greaves et al. (2016a) studied the *in vitro* biotransformation and kinetics of six environmentally relevant PFRs (TNBP, TBOEP, TPHP, TEP, TDCIPP and TCIPP) in herring gulls from the North American Great Lakes using a hepatic microsomal assay. Rapid metabolism and depletion were found for all the PFRs except TEP. Following the Michaelis-Menten enzyme kinetics model, TNBP was metabolized most rapidly followed by TBOEP, TCIPP, TPHP and TDCIPP. Furthermore, the proportion of OP diesters formed metabolically from their corresponding OP triesters varied greatly between compounds, ranging from 90% (TDCIPP to BDCIPP) to 9% (TBOEP to BBOEP). *In vitro* biotransformation of OP triesters was clearly structure-dependent where non-halogenated alkyl OP triesters (i.e. TNBP, TBOEP) were metabolized more rapidly than halogenated alkyl triesters (i.e. TDCIPP, TCIPP).

These *in vivo* and *in vitro* study findings consistently demonstrated rapid PFR metabolism and a dependence on PFR structure. In most cases, PFR diester and other metabolites are formed in PFR triester-exposed organisms. There remains a dearth of studies on PFR biotransformation and fate in Arctic biota.

2.4.5 Modeling studies

Recent modeling exercises have examined the long-range transport potential of PFRs to the Arctic and related gas phase-particle partitioning (Sühring et al., 2016b; Zhang et al., 2016). Zhang et al. (2016) estimated the long-range transport of 29 PFRs using the OECD Screening Tool. They found that PFRs partition mainly to the water compartment (e.g.68–99% of the mass of TCEP and TCIPP, respectively) and that Cl-PFRs have a longer characteristic travel distance in water enabled by their higher persistence in water (due to resistance to neutral hydrolysis). This suggests that PFRs may be travelling to the Arctic via ocean currents and Arctic river inputs, enabled by their high solubility and persistence in water. The OECD Tool

also estimated high atmospheric long-range transport potential for nine of the tested PFRs (IDDPP, MC984, PIP, TEHP, TTBNPP, TTBPP, TPPP, TDMPP and TXP). Sühring et al. (2016b) noted that while model predictions (e.g. using the OECD Tool) suggest that PFRs partition into the gas phase, the partitioning on particles could be systematically underestimated due to strong seasonal effects such as the low temperatures that are typical in the Arctic.

2.4.6 Environmental concentrations

A comprehensive review by van der Veen and de Boer (2012) documents concentrations of PFRs in various matrices, as well as more recent studies reporting PFRs in indoor dust (Ali et al., 2012), drinking water (Li et al., 2014b) and sediment (Cristale et al., 2013; Brandsma et al., 2015). PFR information is much more limited for biota (Chen et al., 2012; Brandsma et al., 2015; Greaves et al., 2016b). For example, although there are some reports of PFRs in birds these do not include species that are resident or breed in the Arctic. Previous reviews of contaminants in the Arctic have not mentioned PFRs (de Wit et al., 2010; Vorkamp and Rigét, 2014) owing to very limited information on PFRs in Arctic media.

2.4.6.1 Air and precipitation

Haglund and Marklund (2004) determined PFRs in air and deposition samples collected in 2004 from Pallas in northern Finland. PFRs with detectable air concentrations were TDCIPP (20 pg/m^3), TPHP (12 000 pg/m^3), TBP (280 pg/m^3), TCEP (1.6 pg/m^3), and TCIPP (810 pg/m^3). No concentrations in air were found for TEHP, TPrP, TMPP and TBOEP. In deposition, detectable PFRs were TDCIPP (20 ng/m^2/day), TNBP (230 ng/m^2/day), TCEP (550 ng/m^2/day) and TCIPP (510 ng/m^2/day). No detectable concentrations were observed in deposition for TEHP, TPrP, TMPP and TBOEP.

Green et al. (2008) detected TIBP, TCEP, TCPP, TDCP, TBOEP and EHDPP in air samples from Ny-Ålesund in Svalbard at concentrations ranging from <10 to 330 pg/m^3. A similar suite of PFRs was detected in air samples from Birkenes, a remote site in southwestern Norway although detection frequency was lower. The PFRs were present in a combined polyurethane-foam and filter extract.

PFRs were investigated in airborne particles over the Pacific, Indian, Arctic, and Southern Ocean on cruises of the Chinese research ice-breaker R/V *Xuelong* (Möller et al., 2012). Samples taken during two polar expeditions in 2010/11, one from East Asia to the High Arctic, were analyzed for TCEP, TCIPP, TDCIPP, TNBP, TiBP, TBOEP, TEHP and TPHP. The sum of the eight PFRs ranged from 230 to 2900 pg/m^3. TCEP and TCIPP were the predominant compounds, with concentrations ranging from <1 to 1980 pg/m^3 (Table 2.35). This study was the first to show the long-range atmospheric transport of PFRs over the global oceans toward the Arctic.

PFRs were determined in high volume air (glass fiber filter) samples in the Canadian Arctic taken on board the *Amundsen* Icebreaker between 2007 and 2013 as well as at two land-based sites (Sühring et al., 2016a) (Table 2.35, Figure 2.59). PFRs identified in Arctic air were: TDCPP, TCEP, TCIPP, TPHP, TNBP, EHDPP, TBOEP, and TEHP. Generally, the highest concentrations were found for TCEP, followed by TCIPP, TPHP, TDCIPP and EHDPP (Table 2.35). Concentrations of Cl-PFRs and most non-Cl PFRs did not change significantly over time, apart from a significant annual increase from 2007–2013 of TPHP. Concentrations at land-based sites were within the same range as ship based measurements except for TNBP which was elevated at a sampling site located near the Resolute Bay airport. TNBP is used in various aircraft hydraulic fluids and the nearby airport is the likely source. Levels that were found compared well with levels found by Möller et al. (2012) in the North Pacific and Chukchi Sea area (shown in red in Figure 2.59).

Table 2.35 Atmospheric particle concentrations of PFRs in air from monitoring in the Canadian Arctic (Sühring et al., 2016a), in Svalbard at Longyearbyen (Salamova et al., 2014) and Ny-Ålesund (Green et al., 2008) and the Chukchi Sea (Arctic Ocean) (Möller et al., 2012).

	PFRs in air, median (range) pg/m^3				
	Sühring et al. 2016a		Salamova et al 2014	Möller et al 2012	Green et al 2008
	Ship-based	Land-based	Land-based	Ship-based	Land-based
TNBP	<1 (<1–97)	416 (<1–2340)	56 (5.6–1000)	11 (<MDL–36)	<200
TCEP	133 (<1–1980)	72 (<1–433)	15 (4.0–63)	289 (126–585)	100 (<200–270)
TCIPP	57 (<1–1670)	53.5 (<1–276)	57 (10–186)	281 (85–529)	100 (<200–330)
TDCIPP	1.8 (<1–19)	5 (<1–46)	10 (2.3–294)	<10 (<MDL–5)	230 (0.087–250)
TPHP	5.1 (<1–1934)	12.5 (1.2–96)	17 (1.1–52)	19 (10–60)	<100
TBOEP	<1 (<1–157)	<1.0	63 (47–208)	<10 (<MDL–11)	100 (<100–150)
EHDPP	5.3 (<1–11)	3.7 (0–40)	85 (5.6–298)	<10	260(<100–260)
TEHP	<1 (<1–7.5)	<1.0	9 (1.0–42)	1 (<MDL–6)	<100
Σnon-Cl-PFRs	5.5 (<1–1940)	7.8 (<1.0–2400)	239 (19–1351)	31 (<MDL–102)	360 (<100–410)
ΣCl-PFRs	190 (<1–3670)	30.5 (2.7–720)	70 (14–385)	570 (211–1120)	430 (<200–850)

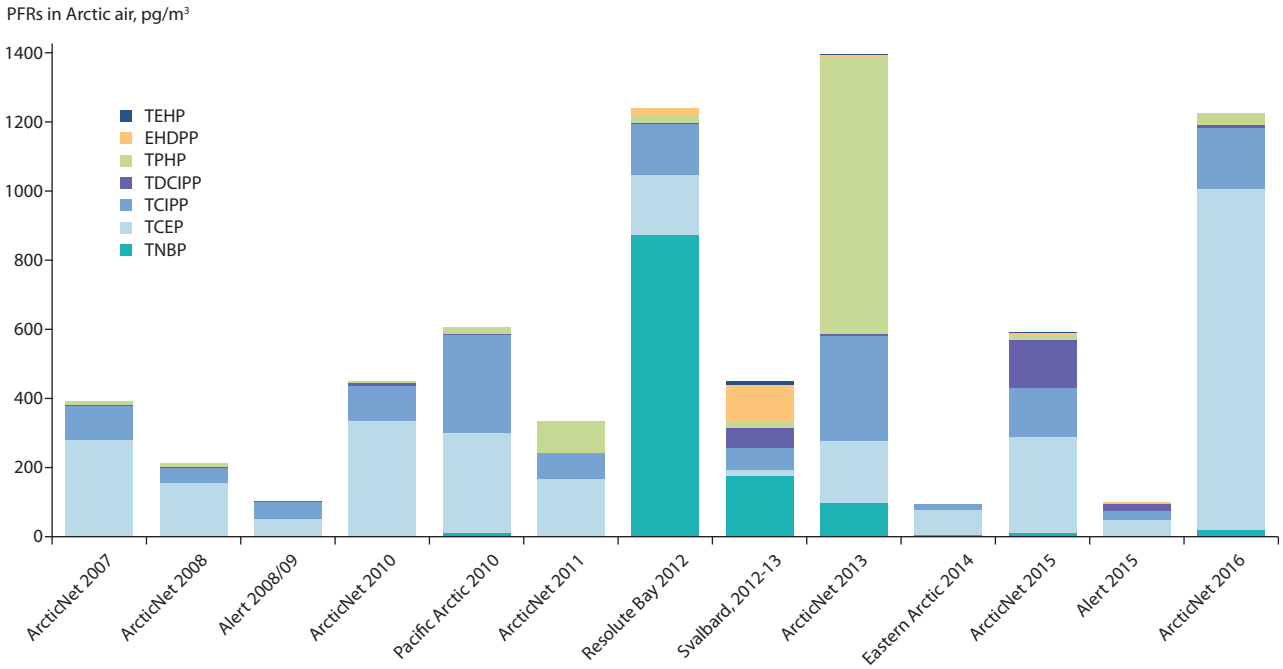

Figure 2.59 Average concentrations of PFRs in Arctic air for the period 2007–2016. Canadian Arctic: ArcticNet 2007 (shipboard August in the Labrador Sea and Hudson Bay areas), ArcticNet 2008 (shipboard Beaufort Sea in May-June), ArcticNet 2010 (central and eastern Canadian Archipelago, August), ArcticNet 2011 (shipboard central and east archipelago), ArcticNet 2013 (shipboard in Barrow Strait and McClure Strait), ArcticNet 2015 (central and eastern Canadian Archipelago, August), ArcticNet 2016 (central and eastern Canadian Archipelago, August). Alert 2008/09: land-based December 2008 to August 2009 (blank problems for TPHP), Alert 2015 (land-based, summer). Pacific Arctic 2010: ship-based Bering-Chukchi-Beaufort Seas summer 2010. Svalbard (Longyearbyen) 2012-2013. Eastern Arctic, 2014. Data sources: ArcticNet 2007, ArcticNet 2008, ArcticNet 2010, ArcticNet 2011, ArcticNet 2013 (Sühring et al., 2016a); ArcticNet 2015, ArcticNet 2016 (Jantunen pers. comm.); Pacific Arctic 2010 (Möller et al., 2012); Resolute Bay 2012 (Sühring et al., 2016a); Svalbard, 2012-13 (Salamova et al., 2014); Eastern Arctic 2014 (Li et al., 2017 EST).

Salamova et al. (2014) reported particle phase air concentrations of 13 PFRs at Longyearbyen, Svalbard, from September 2012 to May 2013 in 34 samples (Table 2.35). The range in Σnon-Cl-PFR concentrations was 19–1351 pg/m^3, with a mean of 239 pg/m^3. The range in ΣCl-PFR concentrations was 14–3851 pg/m^3, with a mean of 70 pg/m^3. The highest concentrations were observed for non-chlorinated TNBP with a mean of 56 pg/m^3 and EHDPP with a mean of 85 pg/m^3. Both PFRs were detectable in all samples. Non-chlorinated PFRs comprised ~75% of all PFRs. The most abundant chlorinated PFR was TCIPP with a mean of 57 pg/m^3.

The combined results for airborne PFRs to date show that TCEP concentrations are much greater in the North American Arctic, including the Chukchi Sea, than at Svalbard or at Pallas in northern Finland. This reflects the continued use of TCEP in North America and Asia, whereas it has been restricted under REACH in Europe and production is being phased out in the United States (Schreder et al., 2016). Several PFRs including TNBP, TBOEP, EHDPP and TDCIPP were higher on Svalbard than at other Arctic locations, which may be due to sampling in close proximity to a community (Table 2.35). The levels of PFRs in all high volume measurements to date were much higher than ΣPBDEs at Arctic monitoring stations (Figure 2.59).

PFRs were analyzed retrospectively in archived passive air samples collected in 2009 under the GAPS program. This was carried out to establish whether detection of PFRs was possible using pre-existing sample preparation and treatment protocols and to provide a preliminary assessment of air concentrations (Harner et al., 2014b). Of the 18 sites included in the analysis, results are available for five Arctic sites including Alert, Barrow, Ny-Ålesund, Stórhöfði, and Little Fox Lake. Compounds analyzed included TPHP, TCEP, TCIPP, TDCIPP and EHDPP. Highest concentrations in air at Arctic sites were observed for TDCIPP at Barrow (238 pg/m^3) and Stórhöfði (504 pg/m^3). These results are from four consecutive quarterly sampling periods starting in the second quarter of 2005, using PUF disk samplers (Lee et al., 2016).

2.4.6.2 Terrestrial environment

There do not appear to be any published reports on PFRs in the terrestrial Arctic environment, such as in biota and soil.

2.4.6.3 Freshwater environment

As of June 2016, reports on PFRs in Arctic freshwater environments are very limited. Evenset et al. (2009) analyzed PFRs in muscle of landlocked Arctic char (*Salvelinus alpinus*) from Lake Ellasjøen (Bjørnøya). EHDPP was the predominant PFR (1.3–16 ng/g ww), followed by TDCIPP (<0.6–6.7 ng/g ww) and TCEP (<0.5–5 ng/g ww). This lake is well known for contamination introduced by guano from a seabird colony (Evenset et al., 2007). However, data for char from unimpacted lakes were not available to assess whether this biovector transport pathway was important for PFRs. McGoldrick et al. (2014b) investigated PFRs in whole body homogenates of lake trout (*S. namaycush*) and walleye (*Theragra chalcogramma*) collected from Canadian lakes, including Great Bear Lake just above the Arctic Circle. Six PFRs (TCEP, TBOEP, TCIPP, TDCIPP, TPHP, TNBP) were detected above quantitation limits in at least one individual fish from the sampled lakes. TCEP and TBOEP were most frequently quantified with concentrations of <0.07–9.8 ng/g ww. Levels of TBOEP were highest in fish from the Great Lakes region while TCEP was detected only in fish from the northern-most lakes (including Great Bear Lake).

2.4.6.4 Marine environment

Seawater

The importance of riverine and ocean transport of PFRs was highlighted by Sühring et al. (2016a). Based on measured air concentrations they inferred contamination 'hotspots' around mouths of major rivers, notably the Nelson and Churchill Rivers (with a drainage basin of over 1000 000 km^2 in the provinces of Alberta, Saskatchewan and Manitoba) as well as the Churchill River and Lake Melville (drainage area of 80 000 km^2 in Labrador) that discharges into the North Atlantic at the Labrador coast. Sühring et al. (2016a) noted that increased rates of volatilization would be expected at the river mouth as Cl-PFRs are 'salted-out' (i.e. their solubility decreases in saline water compared to freshwater. Moreover, the OECD Screening Tool predicts that Cl-PFRs have a long characteristic travel distance in water enabled by their higher persistence in water than air.

As of June 2016, there were very few data in the scientific literature on PFRs in Arctic seawater. Jantunen (2014) and Jantunen et al. (2015a) reported relatively high levels of six PFRs (TNBP, TCEP, TCIPP, TDCIPP, TPHP, EHDPP) in seawater collected via ship-based sampling in the Arctic archipelago in 2013, during the same cruise described by Sühring et al. (2016a). TCIPP was the most prominent PFR (6–13 ng/L), followed by TCEP (4.4–4.5 ng/L) and TNBP (4.2–8 ng/L). Concentrations of PFRs in Arctic waters were high compared to PBDEs, organochlorine pesticides (OCPs) and current-use pesticides (CUPs). However, levels were comparable to measurements by Bollmann et al. (2012) who found TCIPP was the most prominent Cl-PFR (3–28 ng/L) in the eastern North Sea.

Marine biota

Reports on PFRs in wildlife in general, and particularly in the Arctic are limited as of June 2016. The first study that included measurements of PFRs in Arctic marine biota was by Evenset et al. (2009). They analyzed whole fish homogenates of Atlantic cod (*Gadus morhua*) and polar cod (*Boreogadus saida*), as well as livers of kittiwake (*Rissa tridactyla*) and common eider (*Somateria mollissima*) from Svalbard (Kongsfjorden, Liefdefjorden and Billefjorden). EHDPP was the predominant compound in both fish samples (up to 50 ng/g ww) and seabird samples (up to 28 ng/g ww). Of the chlorinated PFRs, TCEP, TCIPP and TDCIPP were detected in the fish samples (<0.6–26 ng/g ww), while only TCEP and TCIPP were detected in the seabird samples (<0.5–4.7 ng/g ww). On a wet weight basis the concentrations of most compounds were higher in Atlantic cod than in Arctic char from Lake Ellasjøen (see Section 2.4.6.3) and polar cod. PFR concentrations were lower in seabird livers compared to fish (homogenates) on a wet weight and lipid basis.

Eulaers et al. (2014) screened for six PFRs in feathers and blood plasma samples of white-tailed sea eagle (*Haliaeetus albicilla*) nestlings from Trøndelag, Norway (just below the Arctic Circle). TCEP and TCIPP were the predominant PFRs in feathers (110 and 91 ng/g dw, respectively), while TCIPP and TDCIPP were the only PFRs detected in plasma (0.22 ng/g ww, each). Huber et al. (2015) reported on PFRs in the eggs of three seabird species, common eider, European shag (*Phalacrocorax aristotelis*), and European herring gull from the Norwegian marine environment. Among the various chemicals that were analytically screened for and found to be quantifiable (ΣPAHs, ΣPCBs, ΣCPs, ΣPFASs, ΣBFRs), ΣPFRs were among the predominant chemical classes, and were found at similar or higher concentrations than the legacy POPs.

Another recent screening study measured PFRs in eight Arctic species, including fish, birds and mammals, from the Svalbard Archipelago, Norway (Table 2.36) (Hallanger et al., 2015). Of the 14 PFRs examined, only ten were detectable. The most frequently detected PFR was TCEP (detected in 17% of samples and five species), followed by EHDPP (detected in 14.9% of the samples of three species) and TEHP (12.8% of samples from six species). Capelin (*Mallotus villosus*), the only fish species analyzed in the study, had the highest number of detectable PFRs. However, liver from Arctic fox (*Alopex lagopus*) was found to have the greatest ΣPFR concentrations, mainly due to levels of TBOEP, which was detected in five of ten samples at levels up to 2198 ng/g lw (median ± SD; 955±294 ng/g lw).

Table 2.36 Range of PFR concentrations (ng/g lw) detected in biota from Svalbard, Norway, 2007-2010 (Hallanger et al., 2015).

Species	Capelin (whole body)	Kittiwake (liver)	Brünnich's guillemot (egg)	Glaucous gull (egg)	Ringed seal (blubber)	Harbour seal (plasma)	Arctic fox (liver)	Polar bear (plasma)
n	10	12	10	12	10	10	10	20
TIBP	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL–7.44	<MDL	<MDL–10.0
TCEP	<MDL–9.41	<MDL–13.0	<MDL	<MDL–10.8	<MDL	<MDL–3.51	<MDL	<MDL–52.5
TCIPP	36.6–92.9	<MDL	<MDL	<MDL	<MDL	<MDL–372	<MDL	<MDL
TDCIPP	<MDL–9.56	<MDL	<MDL	<MDL–29.5	<MDL	<MDL	<MDL	<MDL–6.89
TBOEP	<MDL–537	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL–2198	<MDL
TEHP	<MDL–26.4	<MDL–8.86	<MDL–7.11	<MDL–6.79	<MDL–3.16	<MDL	<MDL–8.75	<MDL
TPHP	15.8–78.6	<MDL	<MDL	<MDL	<MDL	<MDL–15.4	<MDL	<MDL–5.36
EHDPP	11.1–485	<MDL–136	<MDL	<MDL	<MDL–9.60	<MDL	<MDL	<MDL
TMPP	<MDL–23.7	<MDL	<MDL	<MDL	<MDL	<MDL–14.9	<MDL	<MDL
DPhBP	<MDL–9.85	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL–0.67	<MDL

Polar bear (*Ursus maritimus*) adipose samples from 2013–2014 collected from western and southern Hudson Bay were screened for a suite of 17 PFRs (Letcher et al., 2018). The only PFR that was quantifiable in polar bear fat was TEHP, with concentrations of 0.163–0.308 ng/g lw. TEHP concentrations were relatively uniform, as no within- or between-subpopulation differences were noted. Trace (detectable) amounts of TPHP, TCIPP, TBOEP and TNBP were also found in the fat of the present bears but with <50% frequency of detection. Nevertheless, for all Hudson Bay polar bears collected in 2013–2014, the mean TEHP concentration in adipose was extremely low compared to other emerging chemicals, and extremely low compared to legacy POPs. This is probably due to low level exposure (via the diet) and rapid metabolism of accumulated PFRs.

2.4.7 Environmental trends

As there is a dearth of knowledge regarding PFRs in the Arctic environment, with the exception of air monitoring, spatial or temporal trends of PFRs in the Arctic are currently unknown.

2.4.8 Conclusions

There is currently a dearth of information on PFRs in abiotic and biotic media of the Arctic. However, there is strong evidence of long-range transport of PFRs to the Arctic because they have been reported in Arctic air (particles). The chlorinated PFR, TCEP, which has been restricted in Europe, was present at much higher concentrations in the Canadian Arctic and Chukchi Sea than in Svalbard and at northern Finland monitoring sites. TCIPP was the predominant Cl-PFR in European Arctic air. Measurements of PFRs in air during oceanographic cruises in the Canadian Arctic from 2007 to 2013 did not show any temporal trends, apart from a significant annual increase from 2007 to 2013 in TPHP. Airborne PFR concentrations have been reported to be two orders of magnitude higher than for PBDEs, which should be considered of concern in the Arctic.

Limited measurements of PFRs in seawater suggest concentrations are much higher than CUPs, PBDEs and legacy POPs. However the preliminary results reported to date may be confounded by shipboard contamination.

In biota, PFRs have been detected in Hudson Bay polar bears, in lake trout as well as in plasma, feathers and eggs from birds at the fringe of the Arctic Circle (i.e. northern Norway), and in fish, seabirds, Arctic fox and polar bear from Svalbard.

2.5 Phthalates

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2.5.1 Introduction

Phthalates (esters of phthalic acid) are high production volume chemicals used in a wide variety of applications. The most common use of high-molecular-weight phthalates is as plasticizers in polyvinyl chloride (PVC) plastics while low molecular weight phthalates are used in many personal care products. Di(2-ethylhexyl) phthalate (DEHP) and other phthalates have received increasing scientific and public interest due to their widespread occurrence in products and in the environment, and owing to the suspicion of exposure risk (Vorkamp and Rigét, 2014). The World Health Organization (WHO) and United Nations Environment Programme (UNEP) have identified some phthalate esters as likely endocrine disruptors (WHO/UNEP, 2013).

DEHP is among the Priority Substances listed in the EU Water Framework Directive (WFD; EU, 2000) and both DEHP and di-n-butyl phthalate (DnBP) are on OSPAR's List of Chemicals for Priority Action (OSPAR, 2013). Under the EU REACH regulations several phthalates have been identified as substances of very high concern (on the EU Candidate List) and some of these – butylbenzyl phthalate (BBP), DEHP, DnBP and diisobutyl phthalate (DIBP) – have also been included in the authorization list. Six phthalates (DEHP; DnBP; BBP; diisononyl phthalate, DINP; diisodecyl phthalate, DIDP; and di-n-octyl phthalate, DnOP) are restricted in toys and childcare articles (ECHA, 2015). Several phthalates, dimethyl phthalate (DMP), diethyl phthalate (DEP), DnBP, BBP, DEHP and DnOP are also among the priority pollutants listed by the US Environmental Protection Agency. Canada has also implemented restrictions on certain phthalates in child care products under the Hazardous Products Act (www.laws-lois.justice.gc.ca/eng/regulations/SOR-2010-298/page-1.html).

Several screening studies on phthalate levels in the environment have recently been undertaken in the Nordic countries and in Arctic areas, and these provide important data sources for this assessment (Vorkamp et al., 2004; Evenset et al., 2009; Schlabach et al., 2009; Remberger et al., 2013). The aim of screening in this context is to measure environmental concentrations but also to highlight important transport pathways and to identify current emission sources. However, there are limitations and uncertainties in screening studies. Measurements of selected chemicals are carried out in several media at several sites but only in a few samples at each site and the results must thus be considered a 'snap shot' of the situation. The selection of phthalates for this assessment was based on availability of environmental data from AMAP monitoring. The phthalates considered here are listed in Table 2.37 together with abbreviations and CAS numbers for each compound. Table 2.38 provides a summary of Arctic media for which phthalate concentration data have been reported.

Table 2.37 Name, abbreviation and CAS-number of phthalates considered in this section.

Dimethyl phthalate	DMP	131-11-3
Diethyl phthalate	DEP	84-66-2
Di–n-butyl phthalate	DnBP (DBP)	84-74-2
Diisobutyl phthalate	DIBP	84-69-5
Butylbenzyl phthalate	BBP	85-68-7
Di(2-ethylhexyl) phthalate	DEHP	117-81-7
Di-n-octyl phthalate	DnOP (DOP)	117-84-0
Diisononyl phthalate	DINP	28553-12-0
Diisodecyl phthalate	DIDP	26761-40-0
Diundecyl phthalate	DUP	3648-20-2
Di-n-hexyl phthalate	DnHP (DHP)	84-73-3

Table 2.38 Summary of Arctic media for which phthalate concentration data have been reported.

	Air		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
DMP	×							×		×
DEP	×							×	×	×
DnBP	×							×	×	×
DIBP	×							×		
BBP	×							×	×	×
DEHP	×				×	×	×	×	×	×
DnOP										×
DINP									×	×
DIDP									×	×
DUP									×	
DnHP									×	×

Sampling and analyses of phthalates set high requirements on quality assurance (QA) and quality control (QC) procedures owing to their ubiquity in the environment. Phthalates are generally detected even in ultra-pure water, organic solvents used for extraction, and laboratory equipment (Tienpont et al., 2005).

Blank problems in trace analyses of DEHP and DBP were investigated by Fankhauser-Noti and Grob (2007), who showed that analytical results are often too high because of contamination during sample preparation and analysis. Methods for analyzing DBP and DEHP must be designed taking into account system contamination. Special laboratory procedures are therefore essential to minimize the risk of sample contamination.

Inter-laboratory comparison studies were undertaken by Ikonomou et al. (2012) to assess phthalates. The results demonstrated that analytical methods used in environmental monitoring of phthalates such as DEHP often show high detection limits due to high levels in procedural blanks. These findings highlight the need to address the issue of background contamination.

All stages of the determination process must be carefully checked for contamination, and the potential for contamination must be considered when evaluating environmental data.

2.5.2 Physical-chemical properties

The phthalate esters have physical-chemical properties that are dependent on the length of the carbon chains. In a review from the late 1990s, Staples et al. (1997) stated that the octanol-water partition coefficients (K_{ow}) for phthalates span over eight orders of magnitude and their vapor pressures over four orders of magnitude, depending on the number of carbons attached. They also concluded that true solubilities were significantly overestimated in the literature, particularly for the longer chain phthalates. The general structure of phthalate esters and some examples are shown in Figure 2.60. A compilation of physical-chemical properties is given in Appendix 1.

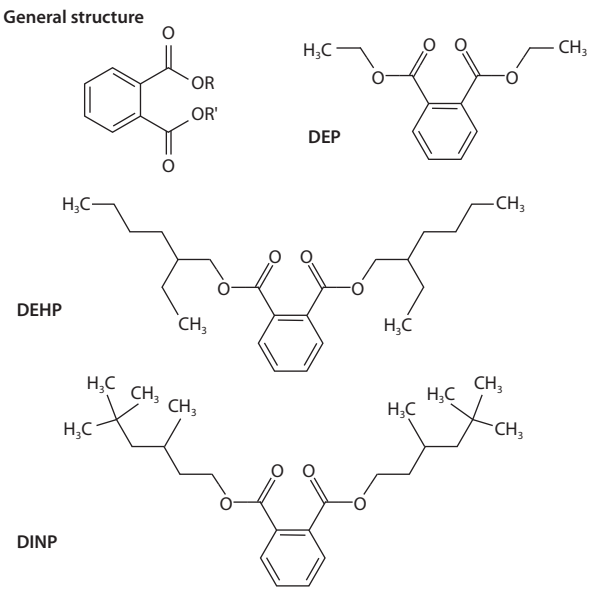

Figure 2.60 General structure of phthalate esters together with some examples: DEP, DEHP and DINP.

Several phthalates have log K_{ow} values of >4 and most of the substances have relatively low water solubility. Phthalates have several degradation pathways in the environment, including photodegradation in the atmosphere (see Section 2.5.4).

2.5.3 Sources, production, use and trends

Phthalates are the most commonly used plasticizers and so are present in a wide variety of industrial and consumer products and packaging materials. The main use of long-chain phthalates is as additives to PVC. Of the amount produced in Europe, 93% is used for that purpose. The low-molecular-weight phthalates are used in different personal care products.

China is the largest market for plasticizers and accounted for almost 38% of world production in 2012 (Jebens et al., 2013). Other Asian countries including Japan accounted for the second largest share (21%), followed by Western Europe (16%) and North America (13%) (Jebens et al., 2013).

According to Vorkamp and Rigét (2014), the major individual phthalate produced is DEHP with a worldwide production volume of 2 million t/y. However the market has gradually shifted towards longer chain, higher molecular weight phthalates such as DINP, DIDP and others. High-molecular-weight phthalates now represent over 80% of the amount produced in Europe (ECPI, 2012).

Use of some phthalates in the Nordic countries in 2012 is shown in Figure 2.61. DINP had the highest use (1600 t/y) followed by DEHP (1100 t/y), DIDP (500 t/y) and DBP (100 t/y). It should be noted that SPIN (a database on the use of Substances in Products in the Nordic Countries based on data from the Product Registries of Norway, Sweden, Denmark and Finland) only lists ingredients in chemical preparations and not in finished consumer articles, which is the predominant use of the phthalates. Reporting to the SPIN database can also vary between countries, which results in uncertainties in the

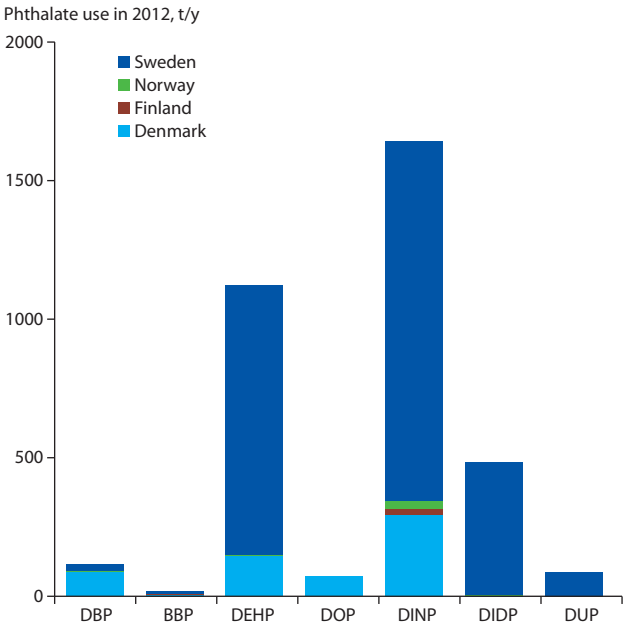

Figure 2.61 Use of phthalates in the Nordic countries in 2012 (Nordic Council of Ministers, 2014).

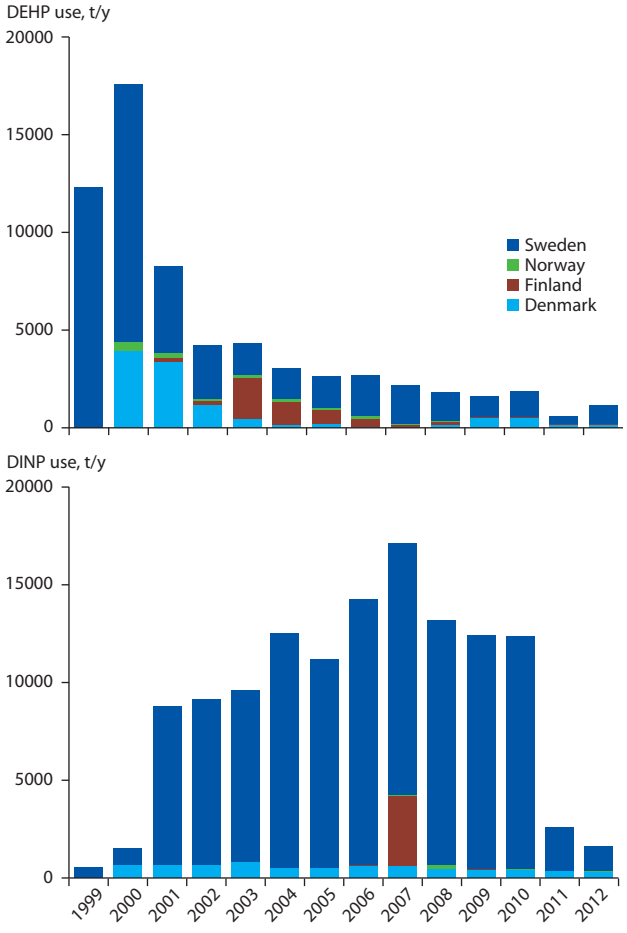

Figure 2.62 DEHP and DINP use in the Nordic countries (Nordic Council of Ministers, 2014).

numbers and means comparisons between countries may not be completely relevant. Thus the data only indicate relative use and distribution among the phthalates.

A change in phthalate use over the past decade is clearly evident in the usage data for Nordic countries, exemplified for DEHP and DINP in Figure 2.62. There has been a substantial decline in the use of DEHP since 2001 while DINP use shows a marked increase between 2001 and 2010. Another example of change in usage is di(2-propyl heptyl) phthalate DPHP (CAS 53306-54-0) which increased substantially between 2010 and 2012 according to SPIN, and usage in Sweden in 2012 was more than 2000 t.

Phthalates can enter the environment from industrial processes and from articles, household products and waste handling. Phthalates in plastics are not physically bound to the polymer and can diffuse out of the plastic and leach into the environment or be released from the use and disposal of materials.

Emissions to air occur both from point sources and via diffuse emissions from chemical products and articles. Direct release to the atmosphere is an important route for phthalate entry into the environment (Xie et al., 2007b).

Phthalates enter aquatic systems through releases from industrial point sources and municipal waste water treatment plants (MWWTPs), as well as through leaching from landfills (Staples et al., 1997). Wastewater treatment may be inadequate or completely lacking in some Arctic regions, making MWWTPs potentially important point sources to the environment (Gunnarsdottir et al., 2013).

Table 2.39 Concentrations of phthalates in effluents from municipal wastewater treatment plants (data from Remberger et al., 2013).

Phthalate	Average for Faroe Islands, ng/L	Average for Sweden, Norway, Finland, Denmark, ng/L
	n=2	n=12
BBP	120	220
DnBP	170	200
DEHP	13 000	1700
DIDP	2700	350
DINP	18 000	140

Results from a recent Nordic screening study showed that release of phthalates from municipal sewage systems can be an important pathway to the environment (Remberger et al., 2013). Phthalates were frequently detected in effluents from MWWTPs in all Nordic countries. Of the phthalates included in the screening, DEHP was the predominant plasticizer in most of the samples followed by DINP and DIDP while DnBP, BBP and DnOP occurred in lower concentrations. Effluent samples from the Faroe Islands (two samples) had the highest concentrations of phthalates compared to effluents from the other Nordic countries and these samples predominantly contained DINP followed by DEHP. Effluent concentrations of phthalates from the Nordic screening are shown in Table 2.39, where concentrations from the Faroe Islands are compared to averages for the other Nordic countries.

Although MWWTP effluents primarily contained DEHP, sewage sludge from the MWWTP usually had higher concentrations of DINP. All sewage sludge samples contained DINP, DEHP and DIDP and together comprised 96–99.7% of the summed concentration of all measured phthalates. The lower molecular weight phthalates, DnBP, BBP and DnOP mostly occurred in much lower concentrations and Diundecyl phthalate (DUP) was not detected at all. Phthalate concentrations in sewage sludge from Iceland (three samples) and the Faroe Islands (two samples) were comparable to concentrations from other Nordic countries, but there were differences among substances as shown in Table 2.40.

Although the number of samples was too small to draw conclusions on differences between countries it is striking that the highest concentrations in effluents were found in samples from the Faroe Islands, where low concentrations in sludge could indicate an inefficient treatment plant process (Remberger et al., 2013).

A discrepancy exists between current phthalate consumption patterns and what was found to be released in MWWTP effluents, for example DEHP is still the predominant plasticizer in the effluents despite the significant decline in DEHP usage in the Nordic counties in recent years (see Figure 2.62). This indicates that the total amount of DEHP that has accumulated in the technosphere over several decades may still be the predominant

Table 2.40 Concentrations of phthalates in sewage sludge from Nordic municipal wastewater treatment plants (data from Remberger et al., 2013).

Phthalate	Faroe Islands Average, ng/g dw	Iceland Average, ng/g dw	Sweden, Norway, Finland, Denmark Average, ng/g dw
	n=2	n=3	n=11
BBP	210	390	310
DnBP	120	320	88
DEHP	13 000	18 000	31 000
DIDP	5200	13 000	77 000
DINP	56 000	99 000	19 000

pool of phthalates, and may explain why phthalates still occur in high concentrations in MWWTP effluents. For example, phthalate-containing materials in buildings constitute a large reservoir of DEHP, and in-use release from this reservoir may be a significant environmental source (Batterman et al., 2009). However DINP which is more recently used and with higher molecular weight than DEHP is the predominant phthalate in sewage sludge (Remberger et al., 2013).

In a recent screening DEP, which is widely used in cosmetics, was measured in MWWTP samples from the Faroe Islands, Iceland and Greenland (Huber et al., 2013). DEP was detected in all influent (0.44–3.0 µg/L) and effluent samples (0.17–2.1 µg/L). The DEP concentrations in the effluents were in the same range as previously reported for Norway by Schlabach et al. (2009). Two out of eight de-watered sewage sludge samples contained low concentrations of DEP (68–78 ng/g dw; MDL 8 ng/g dw). The authors suggested that the low detection frequency in sludge was due to the high water solubility of DEP. The concentrations of DEP in sludge found by Huber et al. (2013) agreed with the results from a previous study in Norway by Schlabach et al. (2009).

One possible transport route for phthalates to the Arctic is via atmospheric long-range transport, with phthalates entering Arctic ecosystems via atmospheric deposition. Evaluative models indicate that phthalates have moderate long-range atmospheric transport potentials (Cousins et al., 2003). Several phthalates are regarded as semi-volatile substances and as such will be transported in the atmosphere both in the gas and particle phases. Based on physical-chemical properties it is expected that DEHP in the atmosphere will occur partly associated with particles and partly in the gas phase (Xie et al., 2007b).

Deposition of semi-volatile organic substances in general may take place via precipitation as well as via gas exchange and dry particle deposition (Bidleman, 1988).

To improve understanding of the distribution and transport mechanisms of selected phthalates to the Arctic, especially the role of air-sea gas exchange, Xie et al. (2007b) carried out a study in 2004 that included measurement of six phthalates in air and surface water along a transect from the Norwegian Sea to the Arctic. Phthalate air-sea gas exchange fluxes were calculated from paired air/water samples. Results showed that overall deposition predominated in the air-sea gas exchange of DEHP at five out of six sites while volatilization of DEHP from seawater occurred at the most southern site in the Norwegian Sea. The authors suggested that atmospheric transport and deposition of some phthalates is a significant pathway for their occurrence in the remote Atlantic and Arctic Ocean and that the major input of phthalates to the Norwegian Sea and the Greenland Sea is from western and northern European countries. However, input to the Arctic might also be highly influenced by atmospheric transport from North America, Russia, and the Pacific Ocean (Xie et al., 2007b).

Deposition of semi-volatile phthalates may occur via precipitation and dry particle deposition and as the Arctic is covered by ice and snow throughout the year, atmospheric phthalates will presumably deposit onto the snow and ice, which could act as a cold trap.

2.5.4 Transformation processes

Phthalates have several degradation pathways, for example, photodegradation in the atmosphere, biodegradation in water, and anaerobic degradation in sediments and soil. Monoalkyl phthalate esters (MPEs) are primary degradation and/or biotransformation products of dialkyl phthalate esters which can be formed via abiotic and microbial degradation of DPEs in sediments, soils, and water (Blair et al., 2009). Blair et al. (2009) found several MPEs including mono-(2-ethylhexyl)-phthalate (MEHP), a metabolite of DEHP, in surface waters, sediments, and biological tissues in a marine system near Vancouver, Canada.

DEHP and DIDP have also been identified as persistent in the environment (ECB, 2003, 2008; Lambert et al., 2010) while other phthalates are not expected to persist in most environments. Longer half-lives are likely under anaerobic conditions, low concentrations, and in cold and nutrient-poor environments.

2.5.5 Modeling studies

A wide range of environmental behaviors is expected from the physical and chemical properties of phthalates (see Section 2.5.2). Multimedia mass balance models have been used to understand the environmental fate and distribution of phthalates (Cousins et al., 2003). As previously mentioned, one possible route for phthalates to reach the Arctic is via atmospheric long-range transport. Although photodegradation of phthalates may occur, modelling results suggest that some phthalates have moderate long-range atmospheric transport potentials (Cousins et al., 2003).

2.5.6 Environmental concentrations

2.5.6.1 Air and precipitation

In an air-sea exchange study in 2004, Xie et al. (2007b) determined air concentrations of phthalates at six sampling sites along a transect from the Norwegian Sea to the Arctic. Air concentrations at one site in the North Sea were used for comparison. The study included six phthalates (DMP, DEP, DIBP, DnBP, BBP, DEHP) and these were measured in the gas and particle phases.

There was a slightly declining latitudinal trend in phthalate concentrations from the North Sea to the Arctic. The declining trends in phthalate concentration from the source regions to the remote Arctic followed the sequence DEHP > BBP > DnBP = DIBP > DEP > DMP. DMP and DEP were predominantly found in the gas phase, DIBP and DnBP were mostly in the gas phase and BBP and DEHP were also found in the particle phase. Averages for the summed concentrations of the six phthalates from the six sample sites were 1300 pg/m^3 (gas phase) and 790 pg/m^3 (particle phase). The corresponding averages for DEHP were 220 pg/m^3 (gas phase) 540 pg/m^3 (particle phase).

In a screening study from 2006, phthalates were measured in air at Swedish background, urban and industrial sites (Palm Cousins et al., 2007). Phthalates were detected in all air samples and the most abundant substance in the atmosphere was DEHP, which generally occurred at higher concentrations than for iso-phthalates, DINP and DIDP. DEHP concentrations at a background site on the Swedish west coast were 500–1100 pg/m^3 (sum of gas and particle phases), which is close to the level found by Xie et al. (2007b) in the Arctic atmosphere.

2.5.6.2 Terrestrial environment

No data were available for phthalates in the Arctic terrestrial environment.

2.5.6.3 Freshwater environment

Priority substances listed in the WFD have been detected in water and some sediment samples from Lake Abiskojaure in northern Sweden (SWECO, 2009). DEHP was analyzed in monthly water samples during 2008 and was detected in the March sample at 3.4 µg/L. The one sediment sample collected in 2008 contained DEHP at 74 ng/g dw.

The Nordic screening by Remberger et al. (2013) included measurements of phthalates in sediment from Þingvallavatn, a background lake in southwestern Iceland. No phthalates were detected and the MDLs are given in Table 2.41. In the same screening, DEHP was detected in Arctic char (*Salvelinus alpinus*) muscle from the Faroe Islands (53 ng/g ww), and in one of three brown trout (*Salmo trutta*) samples from Iceland (7.9 ng/g ww) from remote areas without direct influence from discharges.

Table 2.41 Concentrations of phthalates in sediments from Iceland and the Faroe Islands (data from Remberger et al., 2013).

	Sediment type		Concentration, ng/g dw	Number of samples
Iceland				
Þingvallavatn	Freshwater	BBP	<4	1
		DnBP	<8	1
		DEHP	<80	1
		DIDP	<20	1
		DINP	<30	1
Reykjavik	Marine	BBP	25–56	2
		DnBP	110–400	2
		DEHP	1100–2100	2
		DIDP	880–1300	2
		DINP	5000–5200	2
Faroe Islands				
Kollafjord	Marine	BBP	17	1
		DnBP	40	1
		DEHP	320	1
		DIDP	110	1
		DINP	590	1
Klaksvik/ Torshavn, harbor	Marine	BBP	410–3000	3
		DnBP	31–410	3
		DEHP	1000–9500	3
		DIDP	<1200–36000	3
		DINP	<1300–17000	3

2.5.6.4 Marine environment

Seawater

Xie et al. (2007b) determined phthalate levels in seawater during summer 2004 on a transect from the Norwegian Sea to the High Arctic. The sum of all six phthalates (DMP, DEP, DIBP, DnBP, BBP, DEHP) in the dissolved phase ranged from 80 to 5030 pg/L (average 705 pg/L). DEHP occurred in the highest concentrations (<24–3330 pg/L), followed by DEP (<8–797 pg/L), DnBP (8–349 pg/L), DMP (<13–312 pg/L), DIBP (<5–204 pg/L) and BBP (<0.2–48 pg/L). The phthalates occurred almost exclusively in the dissolved phase except for DEHP, which was also detected in the total suspended particle phase. Phthalate concentrations showed a latitudinal gradient, with higher levels along the Norwegian coast than in the central Arctic. A regional maximum occurred near Bergen where concentrations were comparable to the average level determined in the German Bight, while concentrations of DEHP in the High Arctic were an order of magnitude lower than detected in the German Bight (Xie et al., 2005). The authors debated whether freshwater from snowmelt on the mountains might be a source of phthalates to the coastal waters in the Arctic as well as the North Sea current that moves along the

Dutch, German, and Danish Coast and could thus transport contaminants from Western Europe to the Norwegian coast.

DEP has recently been found in seawater from sites such as harbors and near MWWTPs on the Faroe Islands, Iceland and Greenland (Huber et al., 2013). Two of 10 recipient water samples contained DEP in quantifiable concentrations (MDL 30 ng/L) in the range 45–140 ng/L. The highest concentration (140 ng/L) was detected in Torshavn. DEP occurrence in recipient waters outside MWWTPs shows this may be an important pathway to the environment. DEP was also detected in water samples from Oslofjord and Tromsøsund by Schlabach et al. (2009), with reported levels of 14–22 ng/L (Oslofjord) and 17–140 ng/L (Tromsøsund), which is in the same order of magnitude as reported by Huber et al. (2013).

Sediment

In a previous screening by Vorkamp et al. (2004), phthalates were detected in sediment (duplicate samples) from Greenland at a location far from human settlements: DEP (43, 49 ng/g dw), BBP (6.3, 14 ng/g dw), DnBP (2.5, 9.6 ng/g dw) and DEHP (119, 120 ng/g dw). Di-n-hexyl phthalate (DnHP) was detected in one sample (2.5 ng/g dw) while DMP was not detected (<1.5 ng/g dw). In a screening study by Evenset et al. (2009), DEHP was analyzed in sediments from the Norwegian Arctic collected around Svalbard (including Bjørnøya). DEHP was below the detection limit in all five samples (MDL, 60 ng/g dw). Bakke et al. (2008) analyzed 11 sediment samples from the southern and eastern Barents Sea for DEHP. DEHP concentrations in the same sediment samples varied from 1160 to 57 690 ng/g dw, which is much higher than measured in sediment from the Svalbard fjords (Evenset et al., 2009). Thus, it is likely that the Barents Sea samples have been contaminated during sampling or storage (Bakke et al., 2008).

In the Nordic screening by Remberger et al. (2013), phthalates were found in sediments from the entire Nordic region. The highest concentrations generally occurred in samples from potentially affected areas, such as urban areas, harbors and near WWTPs. The quantitatively predominant phthalates were in declining order: DINP, DEHP and DIDP. DUP was not detected in any of the sediment samples. The relative concentrations of the phthalates in sediments showed a similar pattern to that found in sewage sludge samples in the same study. The two samples from the Faroe Islands (Torshavn Harbor; Table 2.41) contained the highest concentrations and were different to the other sediment samples, which contained predominantly DIDP. Phthalates in the sediment from Reykjavik were detected at similar concentrations or slightly higher than in urban sediments from southern Scandinavia. This series of sediment samples showed clearly decreasing phthalate concentrations moving from urban to background areas. Phthalate concentrations in marine sediments from the Faroe Islands and Iceland are summarized in Table 2.41.

In the screening by Huber et al. (2013), DEP was detected in one of six sediment samples at the Faroe Islands and Greenland. The DEP concentration in sediment from Torhavn marina was 9.9 ng/g dw.

Biota

Vorkamp et al. (2004) detected phthalates in a range of fish and wildlife samples (liver and fatty tissues) from the marine environment around Greenland and the Faroe Islands. Sampling was undertaken between 1999 and 2002. Samples from Greenland represented different trophic levels: polar bear (*Ursus maritimus*), minke whale (*Balaenoptera acutorostrata*), ringed seal (*Pusa hispida*), and shorthorn sculpin (*Myoxocephalus scorpius*). The Faroese samples included long-finned pilot whale (*Globicephala melas*) and fulmar (*Fulmarus glacialis*). Phthalates were detected in almost all samples, with the highest concentrations in polar bear liver from East Greenland, fulmars from the Faroe Islands and ringed seals from East and West Greenland. No geographical trends were seen between East and West Greenland. Of the phthalates included in the screening, levels were highest for DEHP (75–161 ng/g ww). The general trend was: DEHP > BBP ≈ DEP > DnHP ≈ DnBP ≈ DnOP > DMP. However, concentration differences between species were small, usually smaller than observed for the halogenated compounds in the same study. Furthermore, the duplicate analyses showed relatively large variation, which introduces uncertainty into any comparison of the species.

Most samples in the screening study by Evenset et al. (2009) were collected in the marine environment in regions far from potential sources in the Norwegian Arctic. In this study, DEHP was analyzed in Atlantic cod (*Gadus morhua*; liver) and polar cod (*Boreogadus saida*; liver or whole fish) and in the seabirds, kittiwake (*Rissa tridactyla*; liver) and common eider (*Somateria mollissima*; liver). DEHP was detected in 11 of the 16 fish liver samples. The highest concentration (293 ng/g ww) occurred in liver from polar cod collected in Billefjorden, Svalbard. Measurable concentrations of DEHP were also found in liver from three of the Atlantic cod sampled in Kongsfjorden, Svalbard (<88–203 ng/g ww) and in liver from polar cod from Liefdefjorden, Svalbard (126–142 ng/g ww). No DEHP was found in polar cod (whole fish) from Moffen, Svalbard. DEHP was also found in six of 10 kittiwakes (four from Kongsfjorden and two from Liefdefjorden), and in one of five common eiders (Evenset et al., 2009). Concentrations were <88–155 ng/g ww and there were no apparent differences between the two areas (Kongsfjorden versus Liefdefjorden) or between species.

Remberger et al. (2013) analyzed five fish liver samples from cod caught 30 km off the Faroe Island coast (background). The samples contained DEHP at levels of 17–92 ng/g ww and two samples contained DBP at 8.8 and 30 ng/g ww, respectively.

In the screening by Remberger et al. (2013), black guillemot (*Cepphus grylle*) eggs were sampled from two remote islands at the Faroe Islands. The eggs were analyzed as pooled homogenates (five eggs) from each site. One sample contained 5.3 ng/g ww DBP which was close to the MDL. Although DINP was also found in the eggs from the Faroe Islands, the authors could not exclude contamination from the sampling equipment. DEHP was not detected in the black guillemot eggs.

Concentrations of DEHP, the most frequently detected phthalate in birds and fish, reported in recent screening studies are summarized in Table 2.42.

Table 2.42 Concentrations of DEHP in seabirds and fish from the Arctic and the Faroe Islands.

Species	Location	Tissue	Period	No. samples	DEHP, ng/g ww	Reference
Seabirds						
Kittiwake	Kongsfjorden	Liver	2008	5	<88–111	Evenset et al., 2009
	Liefdefjorden	Liver	2008	4	<88–155	
Eider	Kongsfjorden	Liver	2008	5	<88–100	Evenset et al., 2009
Black guillemot	Faroe Islands	Egg	2010	2	<4	Remberger et al., 2013
Fish						
Arctic cod	Kongsfjorden	Liver	2008	5	<88–203	Evenset et al., 2009
Polar cod	Liefdefjorden	Liver		2	126–142	Evenset et al., 2009
	Billefjorden	Liver		4	<60–293	
Atlantic cod	Faroe Islands	Liver	2012	5	17–92	Remberger et al., 2013

Eggs of three seabird species; common eider, European shag (*Phalacrocorax aristotelis*) and European herring gull (*Larus argentatus*) have been surveyed for a broad mixture of chemicals including phthalates. Eggs were collected at two remote marine locations in Norway; Sklinna and Røst. Phthalates were detected in all species, and concentrations were <3–42 ng/g ww, in the form of DEHP only (Huber et al., 2015).

2.5.7 Environmental trends

Available information on phthalate levels in the environment is mainly based on screening and research-based studies which provide data on selected phthalates during particular periods, in various media, at several sites and with few samples at each site. There is no temporal monitoring program for phthalates in the Arctic or in Nordic countries. There are also issues with quality requirements for the analytical methodology, such as limited method comparability and few inter-laboratory exercises. It is therefore not possible to make trend assessments.

2.5.7.1 Spatial trends

Higher phthalate concentrations generally occur in samples from populated areas but phthalates are found in the remote Arctic. Measurements from 2004 showed a slightly declining latitudinal trend in phthalate levels in air and seawater from the Norwegian Sea to the Arctic (Xie et al., 2007b).

The highest concentrations of phthalates in sediment generally occurred in samples from areas close to MWWTPs on the Faroe Islands and Iceland (Remberger et al., 2013), while DEHP concentrations in sediments from the Norwegian Arctic collected around Svalbard were below the MDL (Evenset et al., 2009).

Phthalates are present in marine biota from Greenland, the Faroe Islands, and Iceland and in the Norwegian Arctic. But due to the variety of species and few data at different locations and because samples were collected during different periods, it is not possible to determine spatial trends.

2.5.7.2 Temporal trends

It is not possible determine temporal trends in phthalate concentrations due to lack of data.

2.5.8 Conclusions

Various screening and research-based studies have confirmed the presence of phthalates in the Arctic environment. Phthalates were found in air, seawater and biota in the Arctic environment. The highest concentrations occurred near populated areas. Phthalates were also detected, but at lower concentrations in remote Arctic locations.

The most frequently measured phthalate is DEHP but some data are also available for other phthalates, such as DEP and DINP. Phthalates have physical-chemical properties that are dependent on the length of the carbon chains, which affect their transport and behavior in the environment. Important pathways to the Arctic environment are via long-range atmospheric transport and deposition, and locally via release from wastewater treatment plants.

There has been a change in the use of different phthalates in the Nordic countries, for example use of DEHP has declined substantially in recent years due to substitution with other plasticizers. However there is a discrepancy between current use and what is detected in the environment, such as in sediments which may indicate that DEHP has accumulated in the technosphere and will continue to be part of the pool of phthalates found in the environment.

There is a general lack of data on environmental levels of phthalates in the Arctic. Medium- and long-term monitoring data are not available and most data are from the European Arctic. More data are needed to assess the environmental distribution and toxicological consequences of phthalates in the Arctic, which can be different compared to temperate regions.

Change in usage and substitution with other phthalates must be taken into account in future monitoring programs and research. Future phthalate monitoring efforts should also include relevant phthalate metabolites. Because some degradation is certain to occur, metabolites may be more representative of the total loading or exposure. Owing to the potential for contamination during measurement procedures, inter-laboratory comparisons are required to achieve comparable data, such as between regions. Establishing spatially-distributed monitoring with a longer time perspective would allow for future evaluation of spatial and temporal trends and as a basis for assessing the outcome of changes in use and emissions.

2.6 Short-chain chlorinated paraffins (SCCPs)

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2.6.1 Introduction

Chlorinated paraffins (CPs), also called polychlorinated alkanes, are synthetic chlorinated hydrocarbons produced since the 1930s. Although their manufacture has declined in some regions, it has increased in others and they remain high volume production compounds. They are among the last industrially produced high molecular weight organochlorine compounds in commerce (Muir et al., 2000b; OECD, 2009; UNEP, 2015d).

Analytical challenges associated with the complexity of CP mixtures have limited their detection in the environment. Reports of their occurrence in the Arctic, and elsewhere, have been scarce in comparison to other persistent organic pollutants (POPs) (Sverko et al., 2012). In spite of limited environmental data, foresight for the potential environmental and human health hazards of short-chain chlorinated paraffins (SCCPs) has prompted international regulatory action. SCCPs are recognized as POPs by the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP), and included on the list of harmful substances issued by the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) and the Baltic Marine Environment Protection Commission (HELCOM) (UNEP, 2015d). SCCPs have been placed on the United States Environmental Protection Agency (EPA) Toxic Release Inventory (TRI), and in Canada are considered Priority Toxic Substances under the Canadian Environmental Protection Act (Muir et al., 2000b). SCCPs are classed as Substances of Very High Concern by the European Chemical Agency in the European Union (ECHA, 2008c) and included as Priority Hazardous Substances in the European Water Framework Directive (EU, 2013). The International Agency for Research on Cancer has classified CPs with an average carbon chain length of twelve and an average chlorine content of approximately 60% as possibly carcinogenic to humans (class 2B) (IARC, 1990).

SCCPs were included as POPs under the Stockholm Convention at the eighth meeting of the Conferences of the Parties in 2017, with several specific exemptions (UNEP, 2017). Following nomination for POP candidacy in 2006, a draft risk profile for SCCPs was prepared and underwent several rounds of revision (UNEP, 2006, 2010, 2012c, 2015d), until it was adopted in 2015. The risk management evaluation was adopted at the 2016 meeting of the Persistent Organic Pollutant Review Committee (POPRC), and the committee decided to recommend to the Conference of the Parties to list SCCPs in Annex A (elimination) of the Convention (UNEP, 2016a).

Although the general lack of environmental data has precluded the inclusion of SCCPs in previous AMAP reports, the growing number of publications produced in the last few years, possibly in response to their candidature for listing under the Stockholm Convention, now allows for a first review of their status in the Arctic. The current assessment summarizes all known SCCP data reported for the Arctic region through September 2015, using data from peer-reviewed publications and government scientific reports (Table 2.43). Unless specified otherwise, SCCPs include chain lengths of 10 to 13 carbon atoms. Due to the complexity of CP mixtures, reported concentrations of SCCPs are likely to be more uncertain than for those POPs with established routine analyses. As multiple methods have been applied, inter-laboratory comparability must also be expected to be lower. However, most data have been obtained by a few laboratories, offering comparability between studies performed by the same laboratory.

2.6.2 Physical-chemical properties

Chlorinated paraffins are commercially produced as complex technical mixtures of polychlorinated alkanes that vary in the length of their carbon chains and degree of chlorination (Figure 2.63). They can be subdivided into three groups based on carbon chain length: short-chain CPs (SCCPs) comprising 10 to 13 carbon atoms, medium-chain CPs (MCCPs) comprising 14 to 17 carbon atoms and long-chain CPs (LCCPs) with 18 or more carbon atoms, and may be further subdivided by their chlorine content by

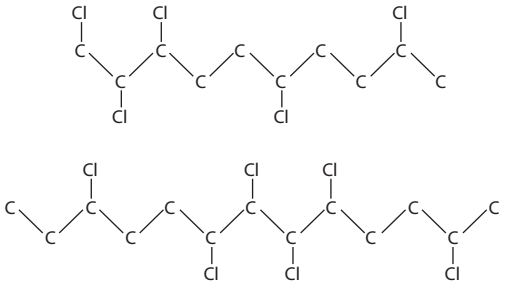


Figure 2.63 Structure of two SCCPs ($C_{10}H_{17}Cl_5$ and $C_{13}H_{22}Cl_6$) (UNEP, 2015b).

Table 2.43 Summary of Arctic media for which SCCPs have been reported.

		Atmosphere		Terrestrial		Freshwater			Marine		
Chemical	CAS#[1]	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
SCCPs	85535-84-8	×		×	×	×	×	×		×	×

[1]The CAS number provided represents the commercial SCCP mixture produced from n-alkanes with chain lengths of 10 to 13 carbon atoms. The Stockholm Convention listing is specific for SCCP products containing more than 48% by weight chlorination, which is not indicated by the CAS number. Note that other CAS numbers (e.g. CAS No 63449-39-8) may contain SCCPs and several countries, including the United States, use multiple CAS numbers to identify SCCPs (UNEP, 2012c).

weight: 40–50%, 50–60% and 60–70% (Muir et al., 2000b). SCCPs (C_{10}–C_{13}) with greater than 48% chlorination are those listed as POPs under the Stockholm Convention (UNEP, 2017).

Physical-chemical properties vary widely among CPs. SCCPs have physical-chemical properties similar to legacy POPs, and thus are the most likely to pose environmental concern (Drouillard et al., 1998a,b). With low water solubilities (Drouillard et al., 1998a) and log K_{OW} values generally greater than 5 (Hilger et al., 2011; Glüge et al., 2013), SCCPs are both hydrophobic and lipophilic and may therefore bioaccumulate and biomagnify through food chains (Tomy et al., 2000; Houde et al., 2008). SCCPs are also considered semi-volatile, making them comparable to other POPs with regards to their ability to volatilize from water and soils (Drouillard et al., 1998b). Specifically, SCCPs with 3 to 9 chlorines are considered 'multi-hoppers' with the potential to cycle continuously between the atmosphere and surface media in response to temperature, and therefore have the highest potential for long-range transport to the Arctic (Gawor and Wania, 2013). Those with 4 to 6 chlorines are thought to have the highest Arctic contamination potential (Gawor and Wania, 2013), as further described in Section 2.6.5.

2.6.3 Sources, production, use and trends

Chlorinated paraffins are synthetic compounds used worldwide in diverse applications, ranging from high temperature and pressure additives in metalworking fluids, plasticizers, and flame retardants, to additives in adhesives, paints, rubber, and sealants (Muir et al., 2000b; van Mourik et al., 2015). Produced from the free radical chlorination of n-alkanes (paraffins) derived from petroleum distillation (Bayen et al., 2006), it is estimated that more than 200 commercial CP formulations have been made available on the market (Alcock et al., 1999). The technical SCCP mixtures do not contain isomers with more than one chlorine atom at a carbon in relevant amounts because the industrial production process with low positional selectivity does not favor second chlorine substitutions at a carbon atom (Rusina et al., 2011; van Mourik et al., 2015). Van Mourik et al. (2015) also reported that 1,2-chlorine substitution is less favored than 1,3-chlorine substitution. There are no known natural sources of CPs (Fiedler, 2010).

While the CPs all have similar industrial applications, LCCPs and MCCPs are more frequently used as plasticizers in flexible polyvinylchloride (PVC) and as industrial metalworking fluids, whereas SCCPs are mainly used in metalworking applications, in sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings (Fiedler, 2010). The recent addition of SCCPs to the Stockholm Convention contains several exemptions and still allows their use in the rubber and leather industry, as lubricant additives, and in metal processing etc. (UNEP, 2017).

Large-scale production of CPs began in the 1930s (Muir et al., 2000b). Historically, world production grew from 38 000–50 000 t/y in 1961 to 300 000 t/y in 1993 (Muir et al., 2000b). Sverko et al. (2012) indicated total production estimates for SCCPs in the USA and Europe of 7500 to 11 300 t/y. Although production in the USA, Europe, and Japan remained relatively constant throughout the 1990s (Muir et al., 2000b), China has seen an exponential increase in CP production, so much so, that it is currently the largest producer and user globally (UNEP, 2015d). Production in China increased from a few thousand tonnes in the early 1990s to 600 000 tonnes in 2006 (Fiedler, 2010) and about one million tonnes in 2009 (Chen et al., 2011a). More than 80% of the CPs produced in China in 2008 were the commercial formulations CP-42 and CP-52, with a chlorine content of 42% and 52%, respectively (Cao et al., 2015). Both mixtures contain SCCPs, but also MCCPs and LCCPs (Yuan et al., 2010; Cao et al., 2015). CPs are still produced in Russia, India, Japan and Brazil (UNEP, 2015d). Production of SCCPs in Brazil was reported at 150 t/y in 2015 (UNEP, 2015d).

Beginning in the mid-1990s, numerous domestic and international regulations were implemented to reduce or eliminate SCCP production and use (UNEP, 2015d). Norway banned SCCP use in 2002. Both the United States and the EU ceased production in 2012 (UNEP, 2015d). In Japan, metal-working industries voluntarily phased out the use of SCCPs by 2007 (Harada et al., 2011).

It is important to note that SCCPs represent a fraction of the world's total production of CPs. Owing to the regulations imposed on SCCPs production over time, usage of MCCPs increased and eventually superseded SCCP use (Stern and Tomy, 2000). Given their use as flame retardants, it has been suggested that the ban on polybrominated diphenyl ethers (PBDE) mixtures could result in an increased use of SCCPs (Stiehl et al., 2008). Furthermore, it was also recommended that CPs be used as replacements for phthalates and phosphate-based plasticizers in polymer industries (Chaemfa et al., 2014) and a range of patents point to the potential use of SCCPs in fluids for oil and gas exploration (UNEP, 2015d).

Anthropogenic releases of SCCPs may occur at any one of the various stages of manufacture, use and disposal of SCCP-containing products. Direct introduction of SCCPs into water may occur through industrial spills, improper disposal of metalworking fluids, facility cleanings and stormwater run-off (Fiedler, 2010). Leaching of SCCPs from products during their use and disposal are other potential sources of SCCPs to the environment. Discarding of SCCP-containing products in landfills could facilitate slow leaching of SCCPs into the environment for centuries after disposal (IPCS, 1996). Recycling activities involving the washing and grinding of plastics could also contribute to the release of SCCPs into water and air (Fiedler, 2010).

Several studies have documented low levels of SCCP contamination in abiotic media and biota from remote Arctic sites (Tomy et al., 1999a; NILU, 2002; Stern et al., 2005), suggesting atmospheric transport is a major route of SCCP to the Arctic. However, elevated SCCP concentrations near urban centers and one Arctic community emphasize the significance of local sources to environmental SCCP levels (Tomy et al., 1999a; Dick et al., 2010; Halse et al., 2015).

2.6.4 Transformation processes

The literature has been reviewed with regard to studies addressing physical or biological transformation of chlorinated paraffins in the Arctic environment. There do not appear to be any recently published empirical data. Atmospheric half-lives

of SCCPs, including degradation reactions by hydroxyl radicals (OH·) (Li et al., 2014a) have been addressed in modeling studies (see next section). Atmospheric half-lives are predicted to range from <1 day to about two months, depending on the SCCP congener in question (Vulykh et al., 2007; Li et al., 2014a).

2.6.5 Modeling studies

Modeling has been used to predict which substances are likely to have physical-chemical properties typically associated with persistence, long-range transport and/or bioaccumulation, for example, a sufficiently long atmospheric half-life and a high bioconcentration factor. Several modeling exercises have identified SCCPs as persistent and bioaccumulative chemicals warranting future monitoring. Strempel et al. (2012) conducted a theoretical screening of about 95 000 chemicals for persistence, bioaccumulation, and toxic properties. The analysis identified four SCCP mixtures with chlorine contents of 46%, 54%, 60%, and 61% as having all three properties. To prioritize chemicals for long-term atmospheric monitoring, Palm-Cousins et al. (2012), used empirical atmospheric monitoring data in conjunction with estimates of atmospheric persistence, long-range transport, and bioaccumulation potential to identify chemicals of concern. Using this approach, SCCPs were identified as having the highest priority for future monitoring efforts.

Focusing on long-range transport and persistence, Wegmann et al. (2007) examined SCCPs and other POP candidates using the OECD overall persistence and long-range transport Screening Tool which had previously been used to provide information on candidate substances for inclusion in the Stockholm Convention. The results indicated that SCCPs have properties similar to those of established POPs.

An extensive analysis of SCCP physical-chemical properties has also been used to determine the likelihood of long-range atmospheric transport to the Arctic and subsequent bioaccumulation (Gawor and Wania, 2013). The analysis identified most SCCPs with up to four chlorines as 'fliers', but despite their high volatility, they were considered to have low Arctic contamination potential as they would not effectively deposit to surface media. Similarly, SCCPs with more than 9–10 chlorine atoms were predicted to act as 'single hoppers' that may volatilize from point source areas, but are likely to be deposited at lower latitudes prior to reaching the Arctic, and thus also have a low Arctic contamination potential. However, SCCPs with an intermediate degree of chlorination were considered 'multiple hoppers' with the potential to cycle between the atmosphere and surface media in response to changes in temperature, and therefore were found to have the highest potential for long-range atmospheric transport to the Arctic (Gawor and Wania, 2013). Those with 4–6 chlorines are thought to have the highest Arctic contamination potential as they are the most persistent in the atmosphere, with estimated half-lives greater than five days (Gawor and Wania, 2013).

To better understand the influence of degradation on the atmospheric lifetimes of SCCPs, a Quantitative Structure-Activity Relationship (QSAR) model that accounts for reaction with hydroxyl radicals was employed (Li et al., 2014a). Based on the global average hydroxyl radical concentration of 9.7×10^5 molecules/cm^3, atmospheric lifetimes of the selected SCCPs analyzed ranged from 0.4 to 67 days and were positively correlated with the percentage of chlorine atoms, implying that highly-chlorinated SCCPs are most persistent in the atmosphere (Li et al., 2014a).

The long-range atmospheric transport potential and persistence of SCCPs was also evaluated using the EMEP/MSCE-POP multi-compartment hemispheric transport model using three SCCP isomers that vary in carbon chain length (C_{10}, C_{12}, C_{13}) and chlorine content (Cl_5, Cl_6, Cl_7) (Vulykh et al., 2007). The model calculates the atmospheric transport of SCCPs from a conventional emission point source located in Europe (5°E; 47.5°N) for a one-year period using atmospheric half-lives of 2–4 days, and resulting in transport distances of 1756–2609 km. The model predicted that whereas 87% of $C_{10}H_{17}Cl_5$ was degraded in the atmosphere over the one-year study period with only 13% being deposited to land and sea surfaces, the other isomers ($C_{12}H_{20}Cl_6$ and $C_{13}H_{21}Cl_7$) underwent less degradation and experienced higher rates of deposition to surfaces (45% and 66%, respectively). Transport distances were defined as the average distance from the source at which the annual mean atmospheric concentration is 1000-fold lower compared to the point source (Vulykh et al., 2007).

The same multi-compartment model was also used to evaluate the environmental residence times of these three isomers. Residence time takes into account the distribution of SCCP isomers between the main environmental compartments (air, soil, water, sediment, vegetation) and the amount degraded in each media throughout the year. The overall calculated environmental half-lives of the three isomers ranged from 6.8 d ($C_{10}H_{17}Cl_5$) to 42.6 d ($C_{12}H_{20}C_6$), and modeled persistence was 180 days in soil, 60 days in water and ~2 days in air (Vulykh et al., 2007).

The environmental fate of SCCPs in the Nordic environment and their potential for bioaccumulation was assessed using a mechanistic, integrated, dynamic multimedia model (CoZMoMAN21) consisting of 12 environmental compartments including air, freshwater, seawater, sediments, soils and forest canopies, as well as a marine food chain (zooplankton, herring, cod), an agricultural food chain (grass, cow milk, beef), and humans (Krogseth et al., 2013c). SCCP emission scenarios were estimated and used to predict the composition and concentrations of SCCPs in the environment and food chains (Figure 2.64).

SCCPs with long chain lengths (C_{11}–C_{13}) and a high degree of chlorination (Cl_8–Cl_9) were predicted to be the predominant isomers in sediments, whereas SCCPs with medium carbon chain lengths (C_{11}–C_{12}) and chlorination degrees (Cl_6-Cl_7) were predicted to predominate in the atmosphere.

Modeled profiles also suggested that SCCPs with longer chain lengths and a higher degree of chlorination may have a greater bioaccumulation potential; SCCPs with 11–12 carbons and 7–8 chlorines were predicted to predominate in the agricultural food chain, while those with longer carbon chains and higher chlorination degrees were predicted to be more prevalent in the aquatic food chain (Krogseth et al., 2013c). Krogseth et al. (2013c) cautioned however, that the model's overestimation of heavy SCCPs in fish and humans might bias bioaccumulation trends. They also highlighted that model predictions would be greatly improved by better analytical methods and more

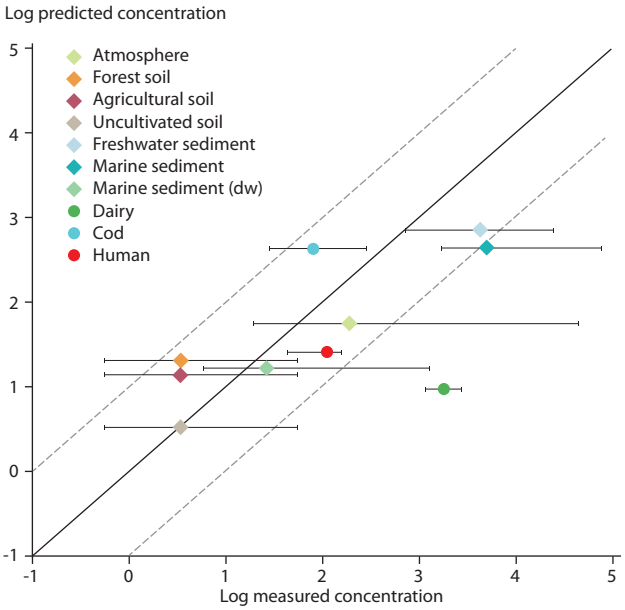


Figure 2.64 Measured versus modeled SCCP concentrations in various environmental compartments of the Nordic environment (Krogseth et al., 2013c). Error bars show the range in measured concentrations. The solid line is the one-to-one line, while the dashed lines mark deviations of one order of magnitude. Numerical concentration data and units not specified.

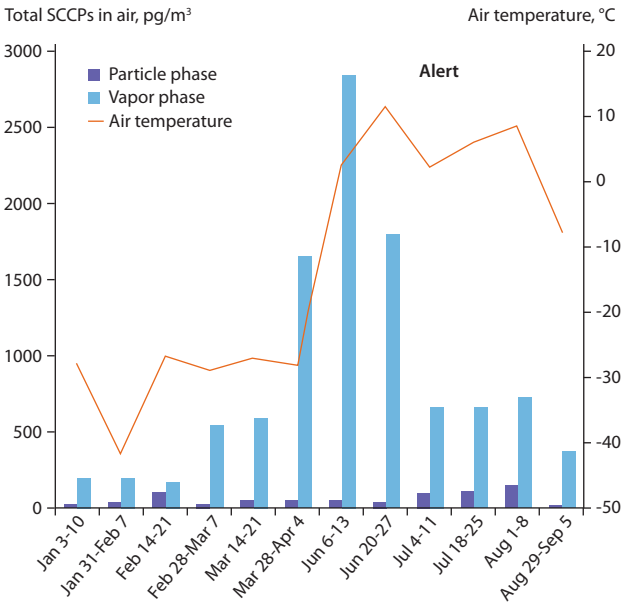


Figure 2.65 SCCP high volume air concentrations at Alert, Canada in 2011 (NCP, 2015a).

strategic sampling, especially for remote regions representing background concentrations.

In summary, several modeling studies have pointed at SCCPs as a candidate for environmental monitoring, mainly on the grounds of their predicted persistence and/or bioaccumulation potential. Not all SCCPs might enter the Arctic equally, as those with a medium chlorine content (4–9 chlorines) might be most prone to long-range transport and deposition. However, their stability versus degradation in the atmosphere was also predicted to depend on the carbon chain length, as well as other factors. Model predictions indicate SCCPs with longer carbon chain lengths and higher chlorine contents have a greater bioaccumulation potential; however, validations with monitoring data are limited due to the high uncertainty of the chemical analysis of SCCPs.

2.6.6 Environmental concentrations

2.6.6.1 Air and precipitation

Levels of SCCPs were determined in high volume active air samples from Alert in the Canadian Arctic collected between September and December, 1992. Mean total concentrations were 20 pg/m^3 (range <1.7–67 pg/m^3) (Peters et al., 2000). Levels of SCCPs in air from Alert have also been reported by Bidleman et al. (2001). Air samples collected from January 1994 to January 1995 exhibited SCCP concentrations of 1.1–7.3 pg/m^3 and were highest in the late summer months.

From January through August 2011, air samples were again collected from Alert and screened for SCCPs. Results showed SCCPs were found mostly in the gas phase, with particle concentrations being similar to levels in blanks, except during the haze season (i.e. February) and summer (Figure 2.65). The mean and median concentrations were 910 and 680 pg/m^3, respectively, with a range of 210 to 2900 pg/m^3, with the C_{10} and C_{11} groups predominating (Hung, 2015). These concentrations were much higher than those measured in the 1990s (Tomy, 1997; Bidleman et al., 2001). The results from the three studies are summarized in Figure 2.66. For comparison, the atmospheric concentration of ΣPCB_{10} (sum of ten congeners) at Alert was about 5 pg/m^3 in 2005 (Hung et al., 2010).

Several measurements of SCCPs have been made in air from the Norwegian Arctic. From March to May 1999, Borgen et al. (2000) measured SCCPs in the gas and particulate phases from Mt. Zeppelin (Svalbard) in the range 9.0–57 pg/m^3. However, they cautioned that the levels detected were of a similar order of magnitude to those detected in field blanks, and that the presence of other contaminants may have interfered with the analysis.

One year later, from May to November 2000, Borgen et al. (2002a) measured SCCPs in ambient air from Bjørnøya, a remote island between Svalbard and mainland Norway, and detected gas and particulate phase concentrations of 1800–11 000 pg/m^3 (Borgen et al., 2002a). Most recently, in 2013 and 2014, SCCPs were measured in air from Mt. Zeppelin with mean annual

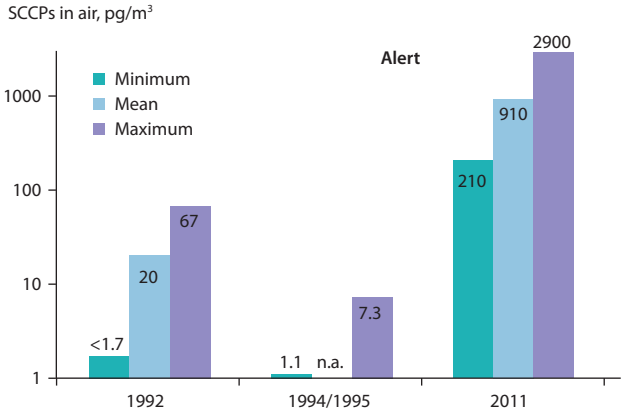


Figure 2.66 SCCP concentrations in air at Alert (Canadian Arctic). The numbers in or above the bars are measured concentrations. Data sources: 1992 (Peters et al., 2000), 1994/1995 (Bidleman et al., 2001) and 2011 (NCP, 2015a).

Table 2.44 Annual mean concentrations of SCCPs in air at Mt. Zeppelin, Svalbard for 2014 in comparison to other contaminants (NILU, 2014).

Contaminant class	Air, pg/m³
SCCP	240
HCB	83
ΣHCH	5.7
Σ_7PCB	3.3
DDT	0.6
PBDE	1.1
Σ_{16}PAH	1433

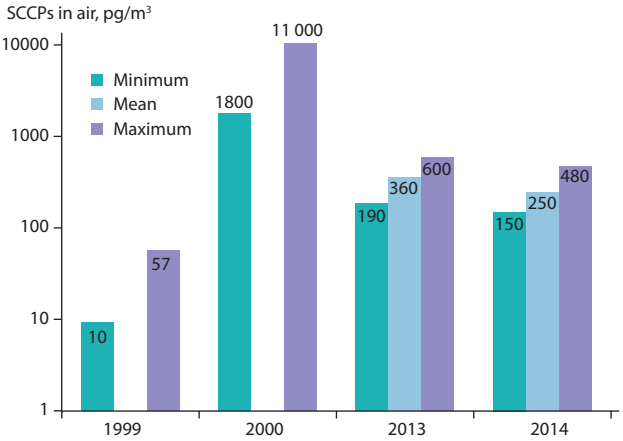


Figure 2.67 SCCP concentrations in air at Mt. Zeppelin (Svalbard) in 1999, 2013 and 2014, and at Bjørnøya in 2000. The numbers in or above the bars are measured concentrations. Data sources: 1999 (Borgen et al., 2000), 2000 (Borgen et al., 2002a), 2013 (NILU, 2014) and 2014 (NILU, 2015).

concentrations of 360 and 240 pg/m³, respectively (NILU, 2014, 2015). Although levels of CPs detected in 2013 blanks were high, resulting in high limits of detection, only 3% of SCCP measurement were below detection limits. Furthermore, SCCP concentrations were up to three orders of magnitude higher than levels of legacy POPs, and at similar concentrations to individual PAHs (NILU, 2014) (Table 2.44). An overview of the Svalbard and Bjørnøya data is presented in Figure 2.67.

The results of the 2009 GAPS retrospective study included four Arctic sites. SCCPs were analyzed using high resolution GC/MS and concentrations in PUF disk samples are given in Table 2.45 (Harner et al., 2014a,b), in comparison to previously determined PCB concentrations. As shown for the Arctic atmospheric monitoring stations Alert and Mt Zeppelin, SCCP concentrations exceeded those of PCBs.

Table 2.45 SCCPs in air at four Arctic stations determined by passive sampling under the GAPS network (Harner et al., 2014a,b) in comparison to previously determined PCB concentrations (Pozo et al., 2009).

Location	SCCP (from 2009), pg/m³	ΣPCB$_{48}$ (from 2005), pg/m³
Barrow, Alaska, USA	220	45
Ny-Ålesund, Svalbard, Norway	81	2
Stórhöfði, Iceland	1000	40
Little Fox Lake, Yukon, Canada	87	n.a.

n.a. not analyzed

2.6.6.2 Terrestrial environment

In 2008, Halse et al. (2015) measured SCCPs and other POPs in background surface soil samples along a transect from the UK (50.58°N) to the Norwegian Arctic (70.47°N). Twenty-three remote Norwegian sites were sampled, including woodland and grassland soils. The average concentration of SCCPs detected in Norwegian soils was 22 ng/g soil organic matter (SOM). For comparison, the average ΣPCB$_{31}$ concentration was 8 ng/g SOM in the same samples. There was a steep decline in SCCP concentrations with increasing latitude and no sites north of 62°N had concentrations of SCCPs above the detection limit. In addition, unlike other POPs measured, SCCP levels were not correlated to any of the soil parameters measured, including bulk density, black carbon and organic matter content. SCCPs were correlated with PBDEs in the same samples, but not with other POPs, suggesting different sources and/or environmental behavior. Taken together, these data suggest soil SCCP levels are influenced primarily by proximity to source regions, rather than soil characteristics (Halse et al., 2015). SCCP concentrations ranging from 13 to 140 ng/g were determined in terrestrial soils taken near the landfill site in Iqaluit, Nunavut, in the Canadian Arctic (Dick et al., 2010), suggesting the landfill may act as a local source of SCCP contamination in Iqaluit.

Chlorinated paraffins of unspecified chain length were found at 140 ng/g lw in pooled fat samples collected from reindeer from Ottsjö, Sweden in 1986 (Jansson et al., 1993).

2.6.6.3 Freshwater environment

Surface waters

Surface water samples collected from several freshwater sources near the community of Iqaluit, Nunavut, the largest community in Arctic Canada, had SCCP concentrations that ranged from non-detectable to 98 ng/L. These levels were low compared to those detected in a local sewage lagoon (150–240 ng/L), indicating local contamination sources, in addition to atmospheric transport that may influence environmental SCCP exposure in the Arctic (Dick et al., 2010). Surface water from Lake Abiskojaure in northern Sweden was investigated for SCCPs in 2006 (SWECO VIAK, 2007) and 2008 (Törneman et al., 2009b), but concentrations were below detection limits. Likewise SCCPs were not detected in surface water from Kalixälven gruvsamhälle (SWECO VIAK, 2007), a former mining village with contamination potential.

Sediments

Several studies have confirmed the presence of SCCPs in the sediments of remote lakes in the Canadian Arctic. Tomy et al. (1999a) determined SCCPs in sediment cores collected from Hazen Lake on Ellesmere Island, Nunavut and Ya Ya Lake in the Mackenzie Delta, in the Northwest Territories. Total sediment SCCP concentrations were 1.6 and 4.5 ng/g dw, respectively (Tomy et al., 1999a). At Lake DV09 on Devon Island, Nunavut, SCCP concentrations of up to 18 ng/g dw were detected in the surface layer of a sediment core and exceeded levels of all other POPs measured by one to two orders of magnitude (Stern et al., 2005). While contamination from local boat traffic is theoretically possible, it is unlikely given the remote nature of the lakes. Tomy et al. (1999a) suggested that the presence

of SCCPs is most likely the result of long-range atmospheric transport and deposition. In addition to surface water samples, sediments from streams, rivers and lakes at Iqaluit, Nunavut were analyzed for SCCPs. Concentrations ranged from 5.2 to 140 ng/g (no information given on whether this is on a wet weight or dry weight basis). Areas associated with waste disposal sites, including a sewage lagoon, a city landfill, and an abandoned military dumpsite, had the highest levels, confirming that local inputs, in addition to long-range atmospheric transport from southern industrialized nations, are sources of SCCPs to Iqaluit (Dick et al., 2010). In contrast, sediment from Lake Abiskojaure in northern Sweden was investigated for SCCPs in 2006 (SWECO VIAK, 2007) and 2008 and, as was also the case for SCCPs in surface water, concentrations were below detection limits.

Fish

In 1986, CPs of unspecified chain length were detected in pooled whitefish (*Coregonus* sp.) muscle from Lake Storvindeln, Sweden at 1000 ng/g lw (Jansson et al., 1993). Borgen et al. (2002b) measured SCCPs in burbot (*Lota lota*), Arctic char (*Salvelinus alpinus*) and trout (species not given) from various freshwater bodies throughout Norway, including those in the Norwegian Arctic. Total SCCP concentrations were 110–1700 ng/g lw in trout muscle, 500–600 ng/g lw in Arctic char muscle, and 230–3700 ng/g lw in burbot liver. Liver and muscle samples from two Arctic char caught in 2001 from Lake Ellasjøen on Bjørnøya, Norway, had concentrations of 7–27 ng/g ww (89–540 ng/g lw) (Reth et al., 2006).

In Canada, SCCPs have been measured in fish from many freshwater lakes (Muir et al., 2013c; Basconcillo et al., 2015). A preliminary analysis of landlocked Arctic char collected from Resolute Lake in the Canadian Arctic in 2010 detected relatively low levels of SCCPs in muscle (0.12 ng/g ww; SD or range not specified) (Muir et al., 2013c). For comparison, the ΣPCB concentration in landlocked Arctic char from Resolute Lake was 93 ng/g ww, averaged over the period 2003–2009 (Muir et al., 2013c). Another study from 2010 and 2011 analyzed SCCPs and MCCPs in predatory fish species from nine Canadian freshwater bodies, including Lake Kusawa in the Yukon (Basconcillo et al., 2015). Long-range atmospheric transport was considered the only source of SCCPs to this lake (Basconcillo et al., 2015). SCCPs were detectable in whole body homogenates of lake trout (*Salvelinus namaycush*) from Lake Kusawa, with a mean concentration (± SD) of 2±3 ng/g ww (22±18 ng/g lw). These levels were the lowest compared of the eight freshwater bodies included in the study. However, concentrations of SCCPs in lake trout from the Great Lakes were not much higher. Lake trout from Lake Superior, Lake Huron, and Lake Erie had mean concentrations of 3±3 ng/g ww each (22±19 ng/g lw, 26±24 ng/g lw, 12±7 ng/g lw, respectively), while lake trout from Lake Ontario had a mean SCCP concentration of 5±3 ng/g ww (37±21 ng/g lw). Furthermore, the observation that Lake Kusawa fish had higher concentrations of SCCPs than MCCPs was suggestive of an atmospheric source (Basconcillo et al., 2015). ΣPCB concentration in lake trout from Lake Kusawa was about 10 ng/g ww averaged over the period 2003–2009 (Muir et al., 2013c). Dick et al. (2010) measured SCCPs in two pooled samples from ninespine stickleback (*Pungitius pungitius*) (n=30 per pool) from various locations around Iqaluit, Canada, as well as in a single landlocked Arctic char from Iqalugaajuruluit lake. SCCP concentrations were 12 ng/g ww for the landlocked Arctic char and a mean of 12±2.2 ng/g ww (range 11–14 ng/g ww) for ninespine stickleback.

2.6.6.4 Marine environment

Seawater

No data are currently available for SCCPs in seawater.

Sediment

In 2007, a total of 11 sediment samples from the Barents Sea were screened for SCCPs and MCCPs (SFT, 2008). SCCPs were quantifiable in all sediment samples, with concentrations of 8–92 ng/g dw, whereas MCCPs could only be quantified in one sample. In 1997 and 1998, marine sediment cores and grab samples were collected from various regions of the Canadian Arctic Archipelago. SCCP concentrations were 4.79–77.41 ng/g dw. Similar to the PCBs and other organochlorine pesticides measured, SCCP concentrations tended to decrease from southern to northern latitudes (Stern and Evans, 2003).

Biota

In 2012 and 2013, blue mussels (*Mytilus edulis*) were collected from sites in northern Norway. In 2012, median concentrations (±SD) of 2.2 ng/g ww and 5.5 ng/g ww SCCPs were found at Husvaagen, Svolvær on Lofoten and in Bodø harbor, respectively (NIVA, 2013). In 2013, median concentrations of 1.6, 2.8 and 1.2 ±0.5 ng/g ww, were found in blue mussels from Outer Trondheimsfjord, Bodø harbor, and Svolvær (on Lofoten), respectively (NIVA, 2014).

In 2003 and 2004, a total of six individual Atlantic cod (*Gadus morhua*) were sampled from various regions in the European Arctic including the northern Norwegian coast, and southern and northern Iceland (Figure 2.68). SCCP concentrations in liver were 11–70 ng/g ww and were comparable to previously detected levels of CB-153 (31–120 ng/g ww) and BDE-47 (7–32 ng/g ww, median 15 ng/g ww) in the same fish (Reth et al., 2006).

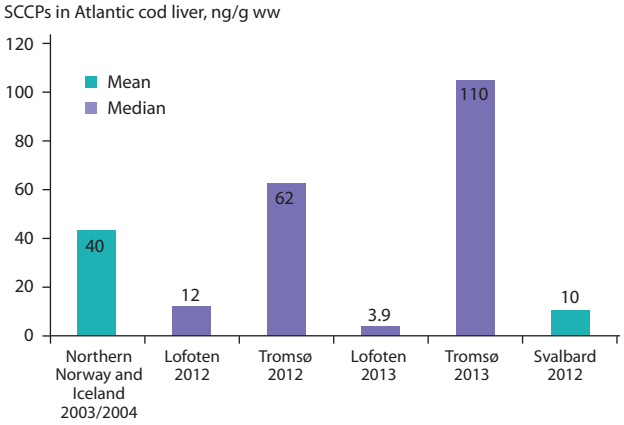


Figure 2.68 Concentrations of SCCP in Atlantic cod from the Arctic. The numbers in or above the bars are measured concentrations. Data sources: northern Norway and Iceland 2003/2004 (Reth et al., 2006), Lofoten 2012 and Tromsø 2012 (NIVA, 2013), Lofoten 2013 and Tromsø 2013 (NIVA, 2014), and Svalbard 2012 (NILU, 2013).

In 2012 and 2013, additional samples of Atlantic cod were analyzed from northern Norway. In 2012, median SCCP concentrations of 12 and 62 ng/g ww were found in cod liver from Lofoten (Skrova harbor) and Tromsø harbor, respectively (NIVA, 2013). In 2013, median concentrations of 3.9 and 110 ng/g ww were detected in cod liver from these same two locations (NIVA, 2014). The higher concentrations near Tromsø might be indicative of local sources contributing to SCCP levels in Atlantic cod. The analysis of cod liver from the non-Arctic areas Ålesund and Inner Trondheimsfjord in 2013 found median concentrations of 70 and 110 ng/g ww, respectively (NIVA, 2014). Additionally, Atlantic cod from Svalbard, was reported with a mean SCCP concentration of 10 ng/g ww (range 3–36 ng/g ww) (NILU, 2013) (Figure 2.68). A pooled sample of polar cod (*Boreogadus saida*) from Svalbard had an SCCP concentration of 2.3 ng/g ww (NILU, 2013) (Figure 2.69).

Strid et al. (2013) measured SCCPs in 15 Greenland sharks (*Somniosus microcephalus*) accidentally caught in waters around Iceland between 2001 and 2003 and found a median concentration of 430 ng/g lw in liver (range <MDL–5200).

Chlorinated paraffins were determined in 30 anadromous Arctic char collected near the community of Iqaluit, in Nunavut, Canada (Dick et al., 2010). Char collected near the town had a mean concentration (±SD) of 7.8±17 ng/g ww (range, <MDL–96). In comparison, three char collected from Peterhead Inlet, to the east of Iqaluit, had lower concentrations, with a mean of 1.6±2.8 ng/g ww (range <MDL–4.9). In line with findings for SCCPs in sediment and surface water, the SCCP concentrations in fish from near the larger settlements of Tromsø and Iqaluit were higher than in the same species caught far from settlements. This suggests that local sources may contribute to SCCP levels near larger settlements. However, SCCPs were also present in fish from locations where long-range atmospheric transport was the only possible source, indicating that this is probably the main source of these compounds to the Arctic in general.

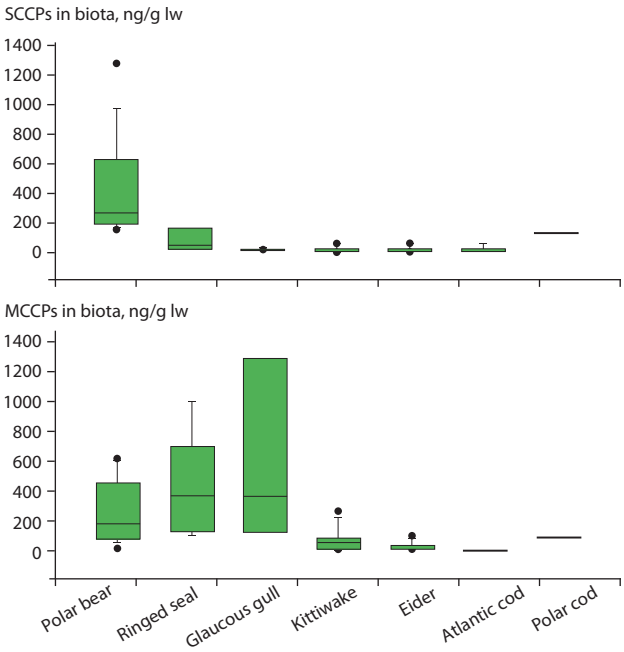


Figure 2.69 Box and whisker plots comparing SCCP and MCCP concentrations in biota from Svalbard, Norway in 2012. Tissues sampled include plasma (polar bear, ringed seal, glaucous gull), eggs (common eider, kittiwake), liver (Atlantic cod) and pooled whole body homogenate (polar cod). The box indicates the 25th and 75th percentiles and the horizontal line marks the median. Lines without statistics are below three valid data points (> detection limits) (NILU, 2013).

Muscle and liver were collected from two little auks (*Alle alle*) and two black-legged kittiwakes (*Rissa tridactyla*) from Bjørnøya, Norway in 2001 and analyzed for SCCPs and MCCPs. Concentrations of SCCPs ranged from 5 to 88 ng/g ww (Table 2.46) and MCCPs from 5 to 370 ng/g ww. With the small sample size, no clear trends between species or tissues were apparent (Reth et al., 2006). SCCPs and MCCPs were sought in Svalbard glaucous gulls (*Larus hyperboreus*) (plasma, brain, liver) but were consistently below the method detection limits (Knudsen et al., 2007) (Table 2.46).

Table 2.46 Summary of SCCP concentrations reported for Arctic seabirds.

Species	Location	Year	Tissue	n	Lipid, %	Statistic	SCCP, ng/g ww unless otherwise noted	Reference
Little auk	Bjørnøya, Norway	2001	Liver	2	10	Range	18–88	Reth et al., 2006
			Muscle	2	4.5	Range	7–16	
Kittiwake	Bjørnøya, Norway	2001	Liver	2	5.5	Range	6–44	Reth et al.. 2006
			Muscle	2	8.5	Range	5	
Glaucous gull	Svalbard, Norway	2003-2005	Liver	10	-	-	<MDL	Knudsen et al., 2007
Common eider	Sklinna/Røst, Norway	2012	Egg	18[a]	NR	Range	<2.0–4.8	Huber et al., 2015
European shag	Sklinna/Røst, Norway	2012	Egg	18[a]	NR	Range	<2.0	Huber et al., 2015
Herring gull	Sklinna/Røst, Norway	2012	Egg	18[a]	NR	Range	<2.0–2.7	Huber et al., 2015
Black guillemot	East Greenland	2012	Egg	4	10.2	Mean±SD (range)	710±200 (490–940)	Vorkamp et al., 2017
Glaucous gull	East Greenland	2012	Liver	4	5.3	Mean±SD (range)	230±110 (170–390)	Vorkamp et al., 2017
Glaucous gull	Svalbard, Norway	2012	Plasma	12	14.4[b]	Mean±SD (range)	4.0±2.0 ng/mL (<0.24–6.7)	NILU, 2013
Kittiwake	Svalbard, Norway	2012	Egg	12	8.1	Mean±SD (range)	7.8±8.3 (<1.6–25)	NILU, 2013
Common eider	Svalbard, Norway	2012	Egg	12	17.4	Mean±SD (range)	3.2±1.8 (<1.6–8.1)	NILU, 2013

NR: not reported; [a]pooled into six samples ; [b]not measured, value taken from literature data as reported by authors.

Table 2.47 Concentrations of SCCPs detected in Arctic marine mammals.

Species	Location	Year	Tissue	n	Lipid, %	Statistic	ng/g ww unless otherwise noted	Reference
Ringed seal	Nunavut, Canada	1994	Blubber	6	90.3	Mean (range)	520 (370–770)	Tomy et al., 2000
		2002	Blubber	8	NR	GM	35	Muir et al., 2013b
		2004	Blubber	18	NR	GM	180	Muir et al., 2013b
	West Greenland	1999–2001	Blubber	6	92.2	AM±SD	11±13	Johansen et al., 2004
	East Greenland	2012	Blubber	5	93.1	AM±SD	1400±370	Vorkamp et al., 2017
	Svalbard, Norway	1981	Blubber	7	88	AM	130[a] ng/g lw	Jansson et al., 1993
	Svalbard, Norway	2012	Plasma	10	0.7[b]	AM (range)	5.0 ng/mL (2.1–10)	Muir et al., 2013b
Harp seal	West Greenland	1999–2001	Blubber	5	88.9	AM±SD	2.4±1.4	Johansen et al., 2004
Walrus	NW Greenland	1978	Blubber	2	83.5	AM (range)	430 (360–490)	Tomy et al., 2000
Minke	West Greenland	1999–2001	Skin	5	45.0	AM±SD	4.0±6.6	Johansen et al., 2004
Narwhal	West Greenland	1999–2001	Blubber	5	77.1	AM±SD	97±49	Johansen et al., 2004
Beluga	Northwest Territories, Canada	1993	Blubber	10	NR	GM	340 ng/g lw	Muir et al., 2013b
		1995	Blubber	10	NR	GM	250 ng/g lw	Muir et al., 2013b
		2000	Blubber	10	NR	-	<MDL	Muir et al., 2013b
		2001	Blubber	11	NR	GM	205 ng/g lw	Muir et al., 2013b
		2002	Blubber	10	NR	-	<MDL	Muir et al., 2013b
		2003	Blubber	11	NR	-	<MDL	Muir et al., 2013b
		2004	Blubber	10	NR	-	<MDL	Muir et al., 2013b
		2005	Blubber	10	NR	GM	250 ng/g lw	Muir et al., 2013b
		2006	Blubber	10	NR	GM	4.0 ng/g lw	Muir et al., 2013b
		2007	Blubber	10	NR	-	<MDL	Muir et al., 2013b
		2008	Blubber	10	NR	-	<MDL	Muir et al., 2013b
	Nunavut, Canada	1982	Blubber	8	NR	GM	200 ng/g lw	Muir et al., 2013b
		1986	Blubber	7	NR	GM	160 ng/g lw	Muir et al., 2013b
		1992	Blubber	8	NR	GM	330 ng/g lw	Muir et al., 2013b
		1995	Blubber	10	NR	GM	120 ng/g lw	Muir et al., 2013b
		2000	Blubber	4	NR	-	<MDL	Muir et al., 2013b
		2002	Blubber	8	NR	GM	120 ng/g lw	Muir et al., 2013b
		2005	Blubber	10	NR	GM	17 ng/g lw	Muir et al., 2013b
		2006	Blubber	4	NR	GM	3.0 ng/g lw	Muir et al., 2013b
		2007	Blubber	5	NR	-	<MDL	Muir et al., 2013b
		2008	Blubber	4	NR	-	<MDL	Muir et al., 2013b
		2010	Blubber	3	NR	-	<MDL	Muir et al., 2013b
	NW Greenland	1989	Blubber	4	88.3	AM (range)	190 (110–250)	Tomy et al., 2000
	West Greenland	1999–2001	Blubber	5	87.9	AM±SD	280±140	Johansen et al., 2004
Polar bear	Northwestern Hudson Bay, Canada	2011	Fat	23	80	AM±SD	493±300	Letcher, 2013
	Western Hudson Bay, Canada	2014	Fat	17	84	AM±SD	175±100	Letcher et al., 2018
	Southern Hudson Bay, Canada	2014	Fat	24	86	AM±SD	160±84	Letcher et al., 2018
	Svalbard, Norway	2012	Plasma	20	0.9[b]	AM (range)	4.0 ng/mL (<0.12–12)	Muir et al., 2013b
	Svalbard, Norway	2002	Fat	15	56.3	AM±SD (range)	0.5±1.0 (0.004–2.6)	Gabrielsen et al., 2004
	East Greenland	2012	Adipose	5	86.4	AM±SD	2200±580	Vorkamp et al., 2017

NR: not reported. [a]Concentration refers to total chlorinated paraffins; [b]not measured, value taken from literature data as reported by authors.

Eggs of black guillemot (*Cepphus grylle*) and liver of glaucous gull, both collected in East Greenland in 2012, were included in a recent screening study of SCCPs in Greenland biota (Vorkamp et al., 2017) (Table 2.46). The compound identification and quantification was based on gas chromatography combined with low resolution mass spectrometry (GC-LRMS) and followed the methods of Reth and Oehme (2004) and Reth et al. (2005). For comparison, ΣPCB_{10} in glaucous gulls from East Greenland was present at 1900 ng/g ww in 2004 (Vorkamp et al., 2012). Vorkamp et al. (2017) noted that although they had succeeded in removing PCBs and several organochlorine pesticides from the extracts prior to analysis, a risk of interference from non-SCCPs remained.

Northern fulmar (*Fulmarus glacialis*) eggs collected in 2003 from Prince Leopold Island and Cape Vera on Devon Island, Nunavut, Canada were analyzed for SCCP and MCCP concentrations. Both were below detection limits (Muir et al., 2004a). Eggs from common eiders (*Somateria mollissima*), European shags (*Phalacrocorax aristotelis*) and herring gulls (*Larus argentatus*) were collected from two remote islands, Sklinna and Røst on the Norwegian coast,

during 2012 and analyzed for SCCPs and MCCPs (Huber et al., 2015) (Table 2.46). Although CPs were measurable in all samples, MCCPs (<MDL–17 ng/g ww) were detected more frequently than SCCPs (<MDL–4.8 ng/g ww). ΣPCB_7 concentrations in herring gull eggs were as high as 876 ng/g ww (Huber et al., 2015).

SCCPs and MCCPs were also measured in glaucous gulls, black-legged kittiwakes and common eiders from Svalbard in 2012 (NILU, 2013) (Figure 2.69). Mean concentrations of SCCPs in kittiwake and common eider eggs were 7.8 ng/g ww (range <MDL–25) and 3.2 ng/g ww (range <MDL–8.1), respectively. The mean SCCP concentration in plasma from glaucous gulls was 4.0 ng/mL (range <MDL–6.7) (Figure 2.69).

Evidence of SCCP accumulation in Arctic marine mammals is growing, but data are still sparse (Table 2.47). The largest SCCP concentration dataset for Arctic marine mammals exists for beluga (*Delphinapterus leucas*) with concentration ranges of 3.0–340 ng/g lw. SCCPs were measured in beluga from Greenland and various regions of Canada in multiple studies over the period 1982–2001 (NCP, 2013). SCCP concentrations in beluga were generally lower than for other legacy POPs, including PCBs, DDT and toxaphene, implying that SCCPs may be less bioaccumulative in similar exposure situations. However, SCCP concentrations in beluga pre-2000 exceeded those of other emerging contaminants, including PBDEs, HBCDD and PFASs (Tomy et al., 2010). In 1993, geometric mean concentrations of SCCPs in beluga blubber were about 65 and 1000 times greater than for PBDE and HBCDD, respectively. Post-2000, SCCP levels have appeared to decrease; beluga samples from Hendrickson Island, NWT, and Pangnirtung, Nunavut, Canada were also used to assess temporal trends in SCCPs (see Section 2.6.7).

Recently, a suite of 24 SCCP congeners was screened in adipose samples from northwestern Hudson Bay polar bears (*Ursus maritimus*) harvested in 2011 (Letcher, 2013). Each SCCP carbon chain contained 5 to 10 chlorines. Seventeen of the 24 SCCPs were quantifiable in all samples. The mean $\Sigma SCCP_{24}$ concentration in the 2011 samples was 493±300 ng/g ww (Table 2.47). In 2014, fat samples were collected from both the southern (n=24) and western (n=17) Hudson Bay polar bears (Letcher et al., 2018). For the 24 SCCPs analyzed, the same contaminant pattern was found as in the 2011 northwestern Hudson Bay samples. The mean $\Sigma SCCP_{24}$ concentration in the 2014 samples was 175±100 and 160±84 ng/g ww, for western and southern Hudson Bay bears, respectively. These concentrations were among the highest of the POPs measured. For example, in the southern Hudson Bay samples, SCCP concentrations were similar to those of ΣDDT, ΣHCH and Σchlorobenzenes. SCCPs were also detectable in 95% of plasma samples from 20 polar bears sampled in Svalbard during 2012, with a mean concentration of 4.0 ng/mL plasma (Figure 2.69) (NILU, 2013).

Polar bear adipose and ringed seal blubber from East Greenland were included in a recent screening study for SCCPs (Vorkamp et al., 2017). The analytical method was the same as described above for black guillemot eggs and glaucous gull liver (see Reth and Oehme, 2004; Reth et al., 2005). Compared with levels reported for Canadian polar bears, concentrations measured in East Greenland bears appear higher (Table 2.47). In addition to geographic influences, differences in analytical

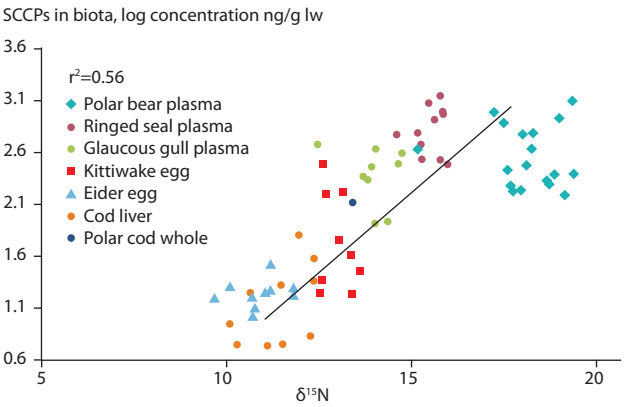


Figure 2.70 Relationship between SCCP concentrations and isotopic nitrogen signature (NILU, 2013).

methods may also contribute to the spatial variations observed for SCCP concentrations in Canadian and East Greenland biota. Canadian samples were analyzed by gas chromatography-high resolution mass spectrometry (GC-HRMS), and higher selectivity might result in less interference and thus lower concentrations (Tomy et al., 1999b).

A screening study conducted by NILU (2013) included high-trophic level marine mammals in addition to lower-trophic level seabirds and fish from Svalbard (Figure 2.69) and simultaneously measured isotopic nitrogen signatures to determine the relationship between SCCP concentrations and trophic level in Arctic biota (Figure 2.70). A positive relationship between log normalized SCCP concentration and isotopic nitrogen was found, indicating a potential for SCCP biomagnification and resulting in a trophic magnification factor of 2.3 (NILU, 2013).

Isolated analyses of SCCPs in other Arctic marine mammals have been reported (Table 2.47). However, small sample sizes and differences in the reporting of concentrations as wet weight or lipid normalized data preclude direct comparisons between these data. One finding common among many of the marine mammals with detectable SCCP concentrations was that shorter carbon chain length congeners (i.e. the C_{10} and C_{11} SCCP groups) tended to predominate (Tomy et al., 2000; Johansen et al., 2004; Letcher, 2013), in some cases constituting up to 91% of total SCCP abundance (Tomy et al., 2000). Previous work has indicated that the shorter carbon chain length congeners are the most volatile (Drouillard et al., 1998b), suggesting that the source of SCCP bioaccumulation is their long-range atmospheric transport to the Arctic.

2.6.7 Environmental trends

2.6.7.1 Spatial trends

Tomy et al. (1999a) measured SCCPs in sediment cores from six lakes in Canada to examine spatial (and temporal – see next section) trends in deposition. SCCP concentrations declined significantly with latitude, with the lowest concentrations being detected in remote, high latitude lakes Ya Ya (NWT) and Hazen (High Arctic). In 2008, Halse et al. (2015) measured SCCPs and other POPs in background surface soil samples along a transect from the UK (50.58°N) to the Norwegian Arctic (70.47°N). The data show a steep decline in SCCP concentration with increasing latitude and no sites north of 62°N had concentrations of SCCPs

above the detection limit (see Section 2.6.6.2 for greater detail). In 1997 and 1998, marine sediment cores and grab samples were collected from various regions of the Canadian Arctic Archipelago. SCCP concentrations tended to decrease from southern to northern latitudes (Stern and Evans, 2003).

2.6.7.2 Temporal trends

Tomy et al. (1999a) also used the study of SCCPs in sediment cores from six lakes in Canada (see previous section) to examine temporal trends. In mid-latitude lakes, maximal SCCP concentrations were measured in slices representative of the 1980–1990 period. However, the trend was less apparent in high latitude lakes, probably owing to low sedimentation rates and near detection limit concentrations (Tomy et al., 1999a).

Stern and colleagues have also reported SCCPs in a sediment core from a high latitude lake in the Canadian Arctic (Stern and Evans, 2003; Stern et al., 2005). Sediment from Lake DV09 on Devon Island (Nunavut) showed maximal SCCP concentrations in surface sediment corresponding to 1997, with a smaller peak in the slice dated to 1956/1957 (Figure 2.71). The increase in the 1990s concurs with the doubling of the production volume in China from 1993 to 2006, while production in other countries remained relatively constant (Muir et al., 2000b; Fiedler, 2010).

Air measurements at Alert showed a considerable increase in SCCP concentrations from the 1990s (mean 20 pg/m^3) to 2011 (mean 910 pg/m^3) (Peters et al., 2000; Hung, 2015). Likewise, SCCP concentrations increased about 10-fold at Mt Zeppelin on Svalbard from 1999 to 2013/2014 (Borgen et al., 2000; NILU, 2014, 2015). However, samples from Bjørnøya taken in 2000 exceeded both measurements on Svalbard (Borgen et al., 2002a).

The data available on SCCPs in beluga allow a first assessment of the temporal development of SCCPs in Arctic biota (Figure 2.72). Blubber samples collected between the early 1980s and mid-2000s from the southern Beaufort Sea (Hendrickson Island) and Cumberland Sound (Pangnirtung) beluga stocks indicate that SCCPs reached the highest levels in the 1990s and declined thereafter (Tomy et al., 2010; Muir et al., 2013b), which contrasts with the concentration development found in the sediment core and air measurements. Muir et al. (2013b) discussed that this might reflect the reduced use of SCCPs in North America and Western Europe. They did not provide any information as to whether the decline observed in beluga is statistically significant.

2.6.8 Conclusions

Although data on the occurrence of SCCPs in the Arctic remain scarce, a growing body of evidence indicates that SCCPs can be found in a wide range of Arctic environments and in biota, thus providing evidence of long-range transport and bioaccumulation of SCCPs.

Several spatial analyses of soil, and sediment show that SCCP concentrations decrease with increasing latitude and that proximity to urban source regions may influence Arctic SCCP concentrations. Air monitoring and a sediment core study indicate increases in SCCP concentrations in the Arctic atmosphere since the 1990s. This trend is not paralleled by SCCPs in beluga from the Canadian Arctic. However, no systematic time trend analysis exists as yet for SCCPs in the Arctic.

SCCPs have been detected in polar bears, the top predator of the marine Arctic food chain. Studies involving several prey species in the polar bear food chain indicate biomagnification of SCCPs.

Although the manufacture of SCCPs has declined in some regions since the 1990s it has increased in others. Also, there has been speculation that their use could increase in the future if CPs are used as replacement chemicals for restricted flame retardants, phthalates and plasticizers (Stiehl et al., 2008; Chaemfa et al., 2014). This could change however, as SCCPs have recently been included in Annex A of the Stockholm Convention (UNEP, 2017).

Although analytical challenges associated with the complexity of CP mixtures might lead to lower accuracy in the determination of SCCPs compared to better-studied POPs, their general level is often similar to or even higher than that for PCBs and other chlorinated POPs. Limited comparability between laboratories still prevents the establishment of reliable trends across studies, especially for spatial trends. Therefore, understanding of the environmental fate and significance of these compounds in the Arctic would be greatly enhanced by improved analytical capabilities and strategic sampling of remote Arctic regions representative of background concentrations.

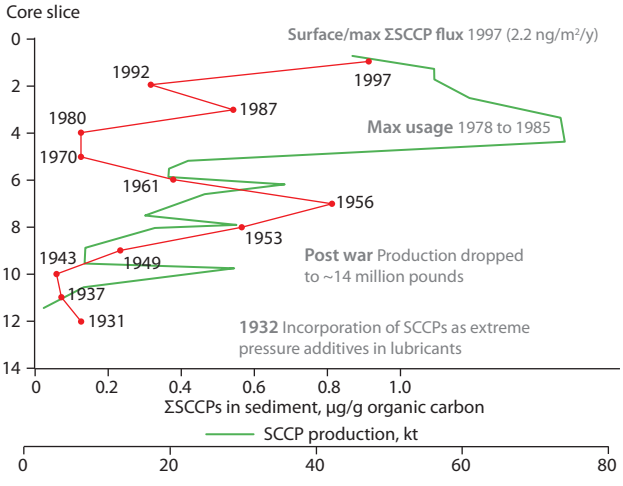


Figure 2.71 Profile of SCCP concentrations in a dated sediment core from Lake DV09 on Devon Island, Nunavut, Canada (Stern and Evans, 2003).

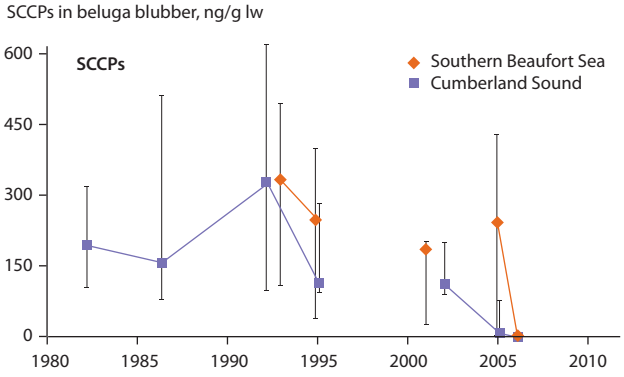


Figure 2.72 Change in SCCP concentration in beluga blubber from the southern Beaufort Sea and Cumberland Sound stocks. Symbols represent arithmetic mean and vertical bars represent minimum and maximum concentrations (NCP, 2013).

2.7 Siloxanes

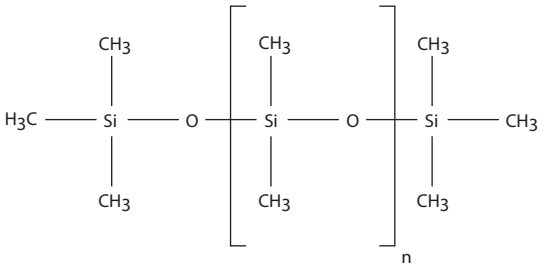
Author: Nicholas A. Warner

2.7.1 Introduction

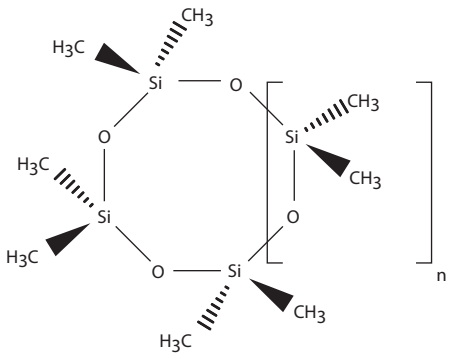
Siloxanes consist of a large class of compounds characterized by their alternating silicon and oxygen backbone substituted with various organic side chains to the silicon atoms. Although this class of chemicals contains many compounds with molecular weights ranging over several thousand atomic mass units (u), most attention has focused on the lower molecular weight (<600 u) dimethylsiloxane oligomers comprising 2–6 units of O-Si$(CH_3)_2$-monomers (Table 2.48). This particular group of compounds exists both as linear (L) and cyclic (D) forms (Figure 2.73). Several of these compounds are present in environmental media in Arctic regions (Table 2.49) and are receiving close attention from regulatory agencies. Cyclic siloxanes can also be referred to according to the number of dimethylsiloxane units (n), more commonly referred to as D units. For example, D (or n) = 4 may be known as D4 (octamethylcyclotetrasiloxane).

2.7.2 Physical-chemical properties

Dimethylsiloxanes, more commonly referred to as volatile methylsiloxanes (VMS) are characterized as highly volatile compounds due to their high vapor pressures (Flaningam, 1986; Lei et al., 2010) (see also Appendix 1). Thus, the majority of environmental releases are to the atmosphere. Once in the atmosphere, VMS can undergo degradation through reactions



General structure of linear volatile methylsiloxanes: (2n+6)methyl-(n+1) siloxane (e.g., n=1; L2)



General structure for cyclic volatile methylsiloxanes

Figure 2.73 Structure of linear and cyclic methylsiloxane oligomers (based on Dewil et al., 2006).

Table 2.48 Summary information for siloxanes.

Name	Abbreviation	CAS#	MW
Hexamethyldisiloxane	L2	107-46-0	162.4
Octamethyltrisiloxane	L3	107-51-7	236.5
Decamethyltetrasiloxane	L4	141-62-8	310.7
Octamethylcyclotetrasiloxane	D4	556-67-2	296.61
Decamethylcylopentasiloxane	D5	541-02-6	370.77
Dodecamethylcyclohexasiloxane	D6	540-97-6	445.00

Table 2.49 Summary of Arctic media for which siloxane data have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
L2										
L3										
L4										
D4	×					×	×		×	×
D5	×					×	×		×	×
D6	×					×	×		×	×

with hydroxyl radicals with half-lives ranging from 6 to 15 days (Atkinson, 1991; Markgraf and Wells, 1997). Evaluation criteria listed under the Stockholm Convention (half-lives >2 days; UNEP, 2001) suggest that these compounds possess long-range transport potential, which has been confirmed by atmospheric measurements in Arctic regions (Genualdi et al., 2011; Krogseth et al., 2013a). Partitioning of VMS to atmospheric particles has been shown in previous work, particularly at lower temperatures (Latimer et al., 1998). However, gas phase concentrations are several orders of magnitude greater than for the particle phase within the same study, which indicates low atmospheric deposition potential for VMS even under Arctic conditions (Wania, 2003).

The environmental behavior of VMS released into aquatic environments will also be dictated by their volatility. Air-water partition coefficients (K_{AW}) (Appendix 1) (Xu and Kropscott, 2014) indicate that partitioning to the atmospheric compartment is preferred. However, VMS also possess intrinsically low water solubility (Appendix 1) (Varaprath et al., 1996; Mazzoni et al., 1997) and favorably partition to organic carbon (log K_{OC} >4) (Whelan et al., 2009, 2010; Kozerski et al., 2014; Panagopoulos et al., 2015) hindering volatilization from surface waters. Sedimentation of contaminated particulate matter to the sediment provides an exposure pathway for VMS to aquatic biota where high octanol-water partition coefficients (log K_{OW} >5; Bruggeman et al., 1984; Mazzoni et al., 1997; Xu and Kropscott, 2014) indicate a risk for bioaccumulation.

Bioconcentration factors (BCFs) for some VMS oligomers were reported in earlier studies (log BCF: 1.5–4.1; Annelin and Frye, 1989; Fackler et al., 1995). However, due to their physical-chemical properties (high hydrophobicity and volatility), detecting dissolved phase concentrations at trace levels is difficult, contributing to large uncertainties in experimentally-derived BCF values (Arnot and Gobas, 2006). In addition, analytical challenges associated with the analysis of this class of chemical (high background levels) introduces high variation in experimental results, creating more uncertainty in previously measured BCFs. Estimating BCF values for VMS using their K_{OW} (Mazzoni et al., 1997) is useful when empirical data are absent. However, the estimates may also may be subject to uncertainty. Recent improvements in experimental design and measurement techniques for determining partitioning properties have shown K_{OW} values to be much higher than earlier measurements suggest and these recent estimates of K_{OW} are considered more accurate.

2.7.3 Sources, production, use and trends

VMS are synthetic intermediates in the production of silicone polymers, but also have various other industrial applications. The main use of VMS is in cosmetic and personal care product formulations (e.g. deodorants, skin and hair care products) (Allen et al., 1997; Horii and Kannan, 2008) where they aid in the application (or spread) of products on skin surfaces. These chemicals are also used in mechanical fluids and lubricants, biomedical products, and cleaning and surface treatment agents (Brooke et al., 2009a,b,c; Environment Canada and Health Canada, 2008a,b).

VMS production volumes are difficult to estimate because they represent thousands of different chemicals intended for various uses and are often reported as total silicone fluid production. In addition, production volumes for some VMS are considered proprietary or confidential information by industry and thus difficult to determine. For example, industry reports worldwide consumption of all silicone fluids (including VMS) reaching 2000 kilotonnes (kt) in 2002 (Brooke et al., 2009b,c). This amount is much larger compared to recent reports where worldwide consumption of silicone fluids in 2012 reached 639 kt (Jebens et al., 2013). China, as the world's largest producer of silicone fluids reported outputs of polydimethylsiloxane (PDMS) alone of 195 kt (2008) and 270 kt (2009) (Wang et al., 2013c).

Owing to widespread findings of these chemicals within the Nordic environment (Kaj et al., 2005), attempts have been made to determine production volumes of specific VMS oligomers, particularly the cyclic volatile methylsiloxanes (cVMS) (e.g. D4, D5 and D6) (Environment Canada and Health Canada, 2008a,b; Brooke et al., 2009a,b,c). Production volumes reported in the United States in 2006 were in the kt range for D4 (45–225 kt), D5 (22.5–45 kt) and D6 (0.045–4.5 kt) (Wang et al., 2013c). Although not produced in Canada, imports for D4, D5 and D6 were 0.1–10 kt (Wang et al., 2013c). These production and import volumes for cVMS are comparable to estimates reported for Europe in 2003: D4 (9.5 kt), D5 (19 kt), D6 (2 kt) (Brooke et al., 2009a,b,c).

The largest releases to the environment occur around manufacturing sites where VMS are used as intermediates in the synthesis of other products (Allen et al., 1997). However, due to dominant usage in cosmetics and personal care products, wastewater effluents are also sources of VMS to the aquatic environment (Kaj et al., 2005; Sparham et al., 2008). Higher discharges of VMS from wastewater effluents occur around urban centers with large populations. However, concentrations also depend on the level of treatment applied to wastewater influent. Wastewater treatment plants that incorporate secondary or tertiary treatment remove the majority of VMS (>90%) from wastewater influent (Allen et al., 1997). Because many communities located within Arctic or northern regions have minimal or no treatment of their wastewater, greater discharge of VMS on a per capita basis can occur in these regions. This has already been observed in the Arctic with elevated concentrations of cVMS (i.e. D4, D5, D6) detected in sediment and fish around Arctic communities (Warner et al., 2010, 2014; Krogseth et al., 2017a,b).

2.7.4 Transformation processes

Despite their properties of high thermal stability and inertness, VMS are subject to both abiotic and biotic transformation/degradation processes (see review by Rücker and Kümmerer, 2015). Degradation within the atmosphere occurs via hydroxyl radicals (Atkinson, 1991; Markgraf and Wells, 1997). Cleavage of the Si-C bond results in the replacement of a CH_3 group by an OH group where various silanol by-products are produced (Sommerlade et al., 1993; Latimer et al., 1998). Reaction half-lives for atmospheric degradation are between 6 and 15 days depending on the VMS oligomers investigated.

In the aquatic environment, VMS will undergo hydrolysis and subsequently degrade to smaller linear dimethylsiloxane-diol byproducts (Brooke et al., 2009a,b,c). For the cVMS oligomers

D4 and D5, hydrolysis data reported by Brooke et al. (2009a,b) indicate both pH and temperature dependence. Hydrolysis rates were catalyzed under both acidic (pH ≤5) and alkaline (pH ≥9) conditions (half-lives: 0.2 hours to 15 days) compared to neutral pH conditions (half-lives, pH 7: 2.2 to 449 days) with longer half-lives observed at lower temperatures. Similar findings have also been reported for the linear VMS (lVMS) with half-lives comparable to or lower (5 to 30 days) than those observed for cVMS under similar environmental conditions (Rücker and Kümmerer, 2015).

Bio-amended soils can also contain considerable amounts of VMS due to high concentrations present within the applied sludge. Removal from soils can occur through both volatilization and/or transformation processes, depending on soil characteristics. Hydrolysis to various linear dimethylsiloxane-diol by-products is the predominant removal mechanism in dry soils where half-lives for cVMS are between 50 minutes and 5 days depending on soil characteristics and cVMS molecular weight (Xu, 1999; Xu and Chandra, 1999). However, reformation of cVMS (i.e. D3 and D4) from dimethylsiloxane-diols through condensation reactions was observed with increasing moisture content within soils in laboratory experiments (i.e. simulating rain events) (Xu, 1999). The presence of bacteria in contaminated soils will also catalyze degradation of VMS. Hydrolysis of D4 in sewage sludge only proceeded in the presence of living cells in which 3% of initial D4 concentration was degraded after 100 days (Grümping et al., 1999) and no degradation occurred in autoclaved sludge.

Metabolism of VMS has also been reported in living organisms. Laboratory exposure studies identified the hydrolysis reaction product $(CH_3)_2Si(OH)_2$ (Si-O bond cleavage) as the major urinary metabolite in rodents exposed to D4 and D5 (Varaprath et al., 1999, 2003). However, the reaction product $CH_3Si(OH)_3$ was also observed in considerable amounts along with other similar reaction products, indicating that metabolic processes involving Si-C bond cleavage were also occurring. Similar findings have been reported in fish, where exposure to cVMS produced several polar metabolites (Woodburn et al., 2013). However, one metabolite of D4 in fish was found to be less polar compared to the parent compound. This metabolite could not be identified but warrants further research regarding its bioaccumulation potential.

Metabolism of D4 and D5 in rodents occurs quickly. Experimental half-lives were 55 to 548 hours (D4) and 50 to 475 hours (D5), with the slowest elimination occurring in fat and lung tissue (Plotzke et al., 2000; Tobin et al., 2008). Longer half-lives were observed in fish, ranging from 17 to 20 days for D4 and D5 (Woodburn et al., 2013). These are shorter than the metabolic half-lives estimated by Arnot et al. (2008) of 27 to 46 days (D4) and 198 to 770 days (D5) in fish. Differences in half-lives between aquatic and terrestrial organisms are likely to be attributed to (or to lack of) air respiration, which has been shown to be an important elimination route for cVMS (Sarangapan et al., 2003; Tobin et al., 2008). Similar to rats, metabolism has also been found to occur in humans, where the metabolite $(CH_3)_2Si(OH)_2$ together with the parent cVMS and lVMS were detected in the plasma of Chinese workers within a silicone manufacturing plant (Xu et al., 2012).

2.7.5 Modeling studies

Owing to their inherent volatility, the dominant fate of VMS will be to volatilize to the atmosphere where they will undergo atmospheric degradation (Atkinson, 1991; Markgraf and Wells, 1997) to their silanol reaction products (Sommerlade et al., 1993; Latimer et al., 1998). Simple equilibrium partitioning modelling employed by Whelan et al. (2004) demonstrated that maximum concentrations of both L4 and D4 and their single OH-substituted silanol reaction products would occur in the vapor phase. Concentrations of silanols with two or more substituted OH groups were found to dominate in the dissolved and adsorbed (i.e. particle) phases, where wet and dry deposition accounted for 99% and 1% of total atmospheric removal of the original VMS (e.g. L4 and D4). Partitioning to the dissolved phase was favored at lower atmospheric temperatures for both L4, D4 and their reaction products due to a decrease in Henry's law constant (Whelan et al., 2004). However, this is unlikely to cause deposition of L4 and D4 due to their inherent volatility and hydrophobicity. This is supported by work from Wania (2003) where the Arctic accumulation potential was estimated using a global distribution model (Globo-POP) to identify specific combinations of chemical partitioning properties under different emission scenarios. The VMS fall within the range of other volatile chemicals (log octanol-air partition coefficient (K_{OA}) <6.5 and log K_{AW} >-0.5), which were predicted to remain in the atmosphere even under Arctic conditions (Wania, 2003).

Long-range transport potential of specific VMS has been confirmed by recent field investigations. Elevated atmospheric concentrations of D5 were detected at a rural site near Stockholm (Sweden) and showed a clear seasonal dependence (McLachlan et al., 2010). Higher concentrations in winter were attributed to lower atmospheric hydroxyl radical concentrations during this seasonal period, thus lower photo-degradation of D5. Measured values agreed well with model estimates of D5 atmospheric concentrations using the Danish Eulerian Hemispheric Model (DEHM) (Figure 2.74).

Within the same study, D5 concentrations were also estimated for the entire Northern Hemisphere. Highest simulated atmospheric concentrations of D5 within the Arctic occurred in winter (2–5 ng/m^3), which agrees with recent air measurement data in Arctic regions (Genualdi et al., 2011; Krogseth et al.,

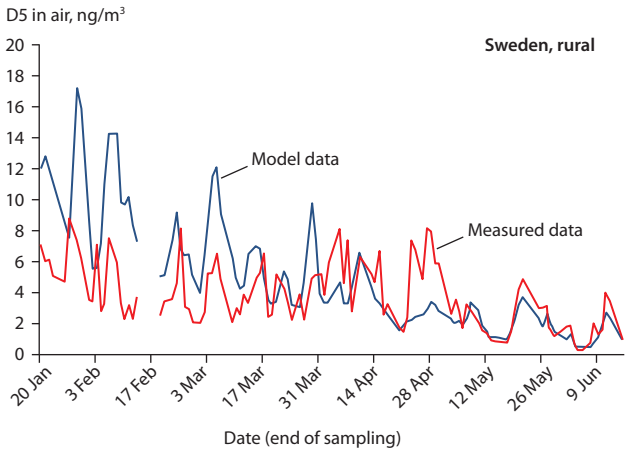


Figure 2.74 Comparison between measured and modelled (Danish Eulerian Hemispheric Model, DEHM) results for D5 atmospheric concentrations at a rural site in Sweden (McLachlan et al., 2010).

2013a; Bohlin-Nizzetto et al., 2014, 2015). Similar estimates were generated in other modelling exercises for atmospheric concentrations of D5 within the Arctic using the Berkeley-Trent Global Contaminant Fate Model (BETR) (0.5–5 ng/m^3; Genualdi et al., 2011) and the Globo-POP model (0.6–6 ng/m^3; Xu and Wania, 2013). Good correlation between measured and modelled results indicates that atmospheric transport pathways for D5 are reasonably well understood.

Fate and residence times of cVMS (e.g. D4, D5, D6) in the global environment have also been estimated by Xu and Wania (2013) using the Globo-POP model under the hypothetical scenario of emissions cessation. An initial phase of rapid elimination was predicted to occur within the first few months as most of the total mass of cVMS present within the atmosphere is removed via photo-degradation (Atkinson, 1991; Markgraf and Wells, 1997). This was followed by slow elimination from the sediment with predicted half-lives of 1 to 2 years. These estimates are significantly shorter than degradation half-lives within sediment stated in non-published industry reports (i.e. 8 years; Xu et al., 2010). Xu and Wania (2013) attributed this difference to desorption from sediments and subsequent hydrolysis within the water phase. However, sediment half-lives estimated on the basis of hydrolysis in the freely dissolved phase of sediment pore water may be as long as 63 years (Whelan and Breivik, 2013). Environmental residence times of VMS will be dependent on the environmental compartment within which the emissions occur. Recent work by Whelan (2013) used a Quantitative Water Air Sediment Interaction (QWASI) model to estimate residence times of cVMS between two contrasting lake systems: Lake Ontario (Canada) and Lake Pepin (USA). Water column residence times of D4, D5 and D6 were predicted to be shorter in Lake Pepin (2 to 9 days) than Lake Ontario (4 to 209 days) due to faster water turnover (11.8 days versus 7.2 years) and shallower depth (5.5 m versus 86 m), which enhances the role of volatilization from the water column. Likewise, chemical residence times within the sediment were shorter in Lake Pepin (109–126 days versus 2.4–7.2 years) due to higher sediment burial rates and re-suspension to the water column. These model results indicate that environment-specific characteristics can significantly affect residence times for siloxanes within specific environmental compartments as well as the environment as a whole. This may explain the discrepancy between studies for estimates of environmental residence time of siloxanes.

Model predictions on the biological fate of methylsiloxanes were carried by Whelan and Breivik (2013). Using the Oslofjord POP Model (Breivik et al., 2004) and the marine component of the ACC-Human model developed by Czub and McLachlan (2004), Whelan and Breivik (2013) explored the fate of cVMS (e.g. D4, D5, D6) within the pelagic food web of the Inner Oslofjord. As suggested by earlier model simulations, volatilization was the most important removal process for D5 and D6 from the water column, whereas hydrolysis was the main process affecting the overall fate of D4. The model underestimated concentrations for D4 and overestimated those for D5 and D6 compared to measured values in biota (Schlabach et al., 2007; Powell et al., 2010), but predicted trophic dilution to occur for all cVMS investigated. This agrees with un-published industry reports for the aquatic food web of Lake Pepin and Oslofjord (Powell et al., 2009, 2010) as well as recent findings for Lake Erie (McGoldrick et al., 2014a). However, trophic magnification of D5 and D6 has been observed within Norwegian lakes (Borgå et al., 2012, 2013). The reasons for conflicting findings between modelling and field studies is unclear but may be attributed to site-specific differences in emissions/discharges and environmental residence times (Whelan, 2013) resulting in different exposure profiles for aquatic biota. Food web structure and how well it has been defined (i.e. inclusion/exclusion of specific species) can also have a significant impact on biomagnification of cVMS (Borgå et al., 2012). Including migratory fish that represent variable exposure profiles compared to non-migratory fish will also introduce greater variation in biomagnification assessments (McLeod et al., 2015).

2.7.6 Environmental concentrations

2.7.6.1 Air and precipitation

Most attention has been given to determining atmospheric concentrations of VMS, as the majority of emissions are to the atmospheric compartment due to their volatile nature. cVMS (e.g. D4, D5, D6) were detected in urban air collected in Iceland and the Faroe Islands, with concentrations of 0.08–2.1 μg/m^3 for D4, D5 and D6 (Kaj et al. (2005). Higher concentrations were observed in air collected within wastewater/sewage treatment plants. Air concentrations of D4, D5 and D6 within a sewage treatment plant in Torshavn, Faroe Islands (4.1, 2.4 and 2.1 μg/m^3, respectively) were twice those collected in an urban downtown area (2.1, 0.93 and 0.39 μg/m^3, respectively). Comparison of cVMS concentration profiles between the two locations shows a difference in dominance between D4 and D5. In sewage sludge collected from the Torshavn sewage treatment plant, D5 was the dominant cVMS. This is a typical observation due to D5 being the dominant cVMS currently used in cosmetic and personal care products (Horii and Kannan, 2008). One explanation for higher D4 concentrations in air may be the higher volatility and lower hydrophobicity of D4 compared to D5. During wastewater treatment, D5 will have greater affinity for sewage sludge than D4, making it less available for volatilization from the dissolved phase. However, this does not explain elevated levels of D4 compared to D5 in the urban downtown area. Recent studies have identified sorbents as potential sources of D4 through degradation mechanisms involving D5 and D6 (Kierkegaard and McLachlan, 2013; Krogseth et al., 2013a). Although it is unclear if similar degradation mechanisms would occur on the type of sorbent (Tenax TA) used by Kaj et al. (2005), this may also have contributed to elevated levels of D4 compared to D5.

Development of sorbent impregnated polyurethane foam (SIP) disk passive samplers (Shoeib et al., 2008) has improved sorption capacity for volatile contaminants. These samplers have been used for global atmospheric monitoring of contaminants through the Global Atmospheric Passive Sampling (GAPS) network and were used to monitor VMS in 2009 (Genualdi et al., 2011). The cVMS (D3, D4, D5, D6) were detected at the Arctic monitoring stations of Zeppelin (Ny Ålesund, Svalbard) and

Alert (Nunavut, Canada), whereas the lVMS investigated (L3, L4, L5) were not detected (method detection limits: 0.5–11 pg/m³). Concentrations of D3 (10–12 ng/m³) and D4 (16–17 ng/m³) were higher than D5 (0.6–4 ng/m³) and D6 (0.3–0.5 ng/m³) in air sampled at Zeppelin and Alert. As previously mentioned, this profile is unexpected because production/emission estimates show D5 to be the predominant cyclic oligomer produced/emitted compared to the other cVMS (Environment Canada and Health Canada, 2008a,b; Brooke et al., 2009a,b,c).

Recent work by Krogseth et al. (2013a) detected air concentrations of cVMS (e.g. D4, D5, D6) at Zeppelin in 2011 using the SPE-AAS method previously developed by Kierkegaard and McLachlan (2010). Seasonality was observed with higher average (±SD) concentrations detected for D5 and D6 in winter (2.94±0.46 and 0.45±0.18 ng/m³, respectively) than summer (0.73±0.46 and 0.23±0.17 ng/m³, respectively) (Krogseth et al., 2013a). In addition, measurements of D5 agreed well with model estimates for atmospheric D5 in the Arctic using the DEHM (Figure 2.75), previously applied by McLachlan et al. (2010).

No clear conclusions can be drawn regarding D4 concentrations as results may be affected by degradation/formation kinetics on the sampling SPE sorbents used in studies. Formation of both D3 and D4 through degradation of D5 and D6 on ENV+ sorbent has been observed by Krogseth et al. (2013a), where 80% of ^{13}C-D5 and ^{13}C-D6 internal standard had degraded after 30 days in storage experiments. This sorbent-mediated transformation has been confirmed by other studies (Kierkegaard and McLachlan, 2013) and may explain why concentrations reported by Genualdi et al. (2011) for D3 (10–12 ng/m³) and D4 (16–17 ng/m³) were higher than upper concentration limits reported by Krogseth et al. (2013a) for D3 (2.98 ng/m³) and D4 (2.13 ng/m³). Similar storage effects were not observed with XAD-2 sorbent after 28 days (Krogseth et al., 2013b) and this sorbent has been recently used for atmospheric passive sampling of VMS in urban areas (Krogseth et al., 2013b; Ahrens et al., 2014b).

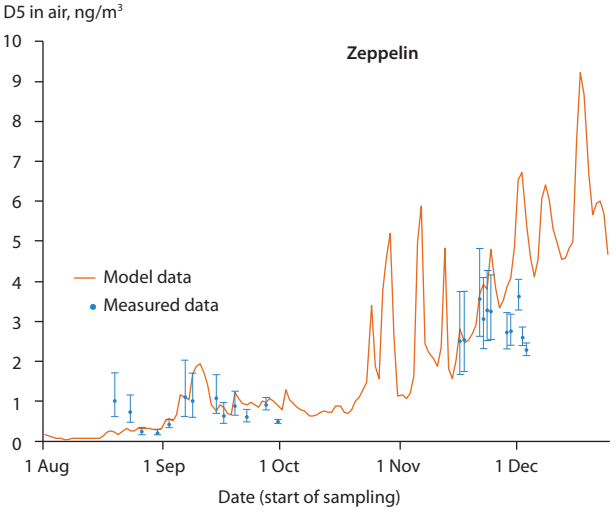


Figure 2.75 Measured and modelled (Danish Eulerian Hemispheric Model, DEHM) concentrations for D5 at Zeppelin (Svalbard, Norway) in 2011 (based on Krogseth et al., 2013a).

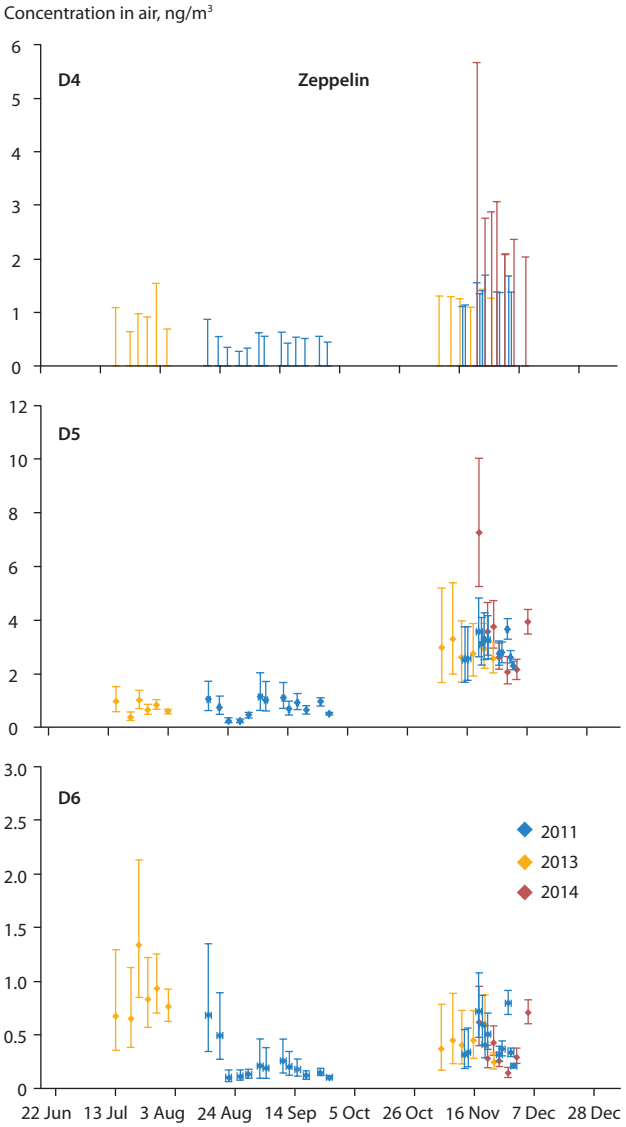


Figure 2.76 Measured concentrations of D4, D5 and D6 at Zeppelin station in 2011 (Krogseth et al., 2013a), 2013 and 2014. Concentrations of D4 are reported as a range from non-detected to the upper limited detected. Concentrations reported for D5 and D6 are storage-corrected with a range representing the 95% confidence interval of the storage correction. Figure from Bohlin-Nizzetto et al. (2015).

Continued monitoring campaigns at Zeppelin in 2013 and 2014 (Bohlin-Nizzetto et al., 2014, 2015), further support earlier findings for D5 by Krogseth et al. (2013a) and Genualdi et al. (2011) (Figure 2.76). However, higher concentrations were reported for D4 and D6 during summer than winter in 2013, in contrast to observations in 2011 by Krogseth et al. (2013). This profile is surprising because greater degradation is expected to occur during summer (due to the higher atmospheric concentration of hydroxyl radicals) compared to winter. Elevated D6 concentrations in summer could be due to changes in atmospheric circulation as large concentration variations have been shown to occur for D5 over short periods (Figure 2.74). However, this is unlikely because an increase in D5 concentration should also be observed (D5 is more prevalent in the atmosphere than D6) and it was not. The elevated levels could be due to a local source of D6 as higher concentrations of D6 compared to D5 have been reported in fish from the nearby community of Ny Ålesund (Warner et al., 2010). This suggests that a different emission profile for D5 and D6 may occur locally to the aquatic

environment, but it is unclear if this source would affect atmospheric measurements. However, problems with sampling logistics during summer 2014 meant it was not possible to confirm the findings observed in 2013. Nevertheless, D5 and D6 measurements at Zeppelin in 2014 during winter did agree well with those made in earlier years (Figure 2.76).

2.7.6.2 Terrestrial environment

Fewer studies have investigated the fate of VMS in the terrestrial environment than in atmospheric and aquatic compartments. Due to their high Henry's Law constants, VMS are expected to be removed rapidly from the soil through volatilization (Hughes et al., 2012; Xu and Wania, 2013), resulting in short residence times in the terrestrial environment. This is supported by earlier findings by Kaj et al. (2005) where VMS were not detected in soil collected from landfills from the Faroe Islands.

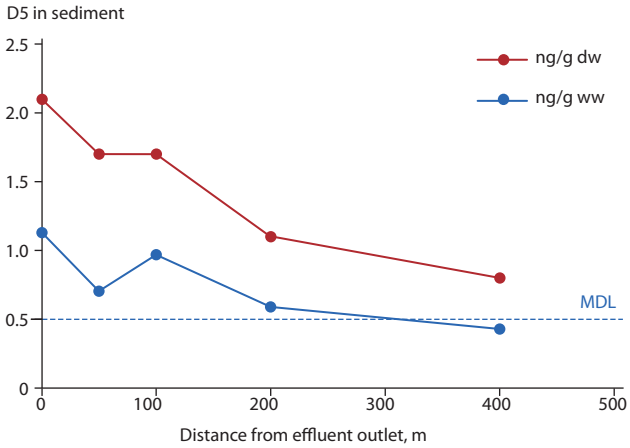


Figure 2.77 D5 concentration in sediment from Advenfjorden, Svalbard. Concentrations are presented on a wet and dry basis. Dashed horizontal line represents method detection limit on a ng/g ww basis (Warner et al., 2010).

2.7.6.3 Freshwater environment

Data on VMS in Arctic freshwater environments is extremely limited, as greater attention has been placed on freshwater environments from temperate regions. However, data on the fate of VMS in Arctic lakes are starting to emerge. Krogseth et al. (2017a,b) recently reported cVMS contamination in an Arctic lake receiving unintentional discharges of raw sewage from leaking pipes and overflow events in high precipitation periods. Although D4 (<8–50 ng/L), D5 (20–1400 ng/L) and D6 (<15–100 ng/L) were detected within the sewage, cVMS were all below detection and/or quantification limits in the lake surface water, indicating rapid removal through volatilization, hydrolysis, advection or sedimentation processes. Despite the lake receiving intermittent inputs and there being a relatively low population in the surrounding area (roughly 3600 inhabitants), high levels of cVMS were found within the lake sediment. D5 showed the highest concentrations (38–121 ng/g ww; 2800–5300 ng/g organic carbon, OC), followed by D6 (9.0–26.2 ng/g ww; 600–1200 ng/g OC) and D4 (2.5–5.5 ng/g ww; 160–240 ng/g OC) (Krogseth et al., 2017a). These levels are comparable to concentrations in sediment impacted by wastewater effluent in more populated regions (Powell et al., 2010; Kierkegaard et al., 2011, 2013a; Sparham et al., 2011). High levels of contamination were also observed in several fish species (e.g. brown trout, *Salmo trutta*; Arctic char, *Salvelinus alpinus*) where D5 was found at concentrations of up to 8 µg/g lw (muscle) and 24 µg/g lw (liver) (Krogseth et al., 2017b).

2.7.6.4 Marine environment

Population within Arctic communities is lower than in urban centers within Europe and North America. However, Arctic communities often have limited or no treatment for their wastewater and so discharges may significantly affect the local marine environment. Human settlements are known sources of VMS to the Arctic environment (Warner et al., 2010). Sediment concentrations of D5 were found to decrease from 2.1 ng/g dw (152 ng/g OC) to 1.1 ng/g dw (53 ng/g OC) along a 400-m transect from wastewater outlets at Longyearbyen, Svalbard (Figure 2.77). This indicates that wastewaters were the main source of cVMS to the local marine environment.

Elevated cVMS concentrations were also found in fish from Adventfjorden, into which wastewaters from Longyearbyen are released. Highest average concentrations in Adventfjorden were detected for D5 in Atlantic cod (*Gadus morhua*; 57 ng/g ww; 180 ng/g lw) and shorthorn sculpin (*Myoxocephalus scorpius*; 86 ng/g ww; 530 ng/g lw). Average concentrations of D6 were considerably lower in Atlantic cod (3.1 ng/g ww; 10 ng/g lw) and sculpin (2.4 ng/g ww; 15 ng/g lw), while D4 was not detected in any fish (Warner et al., 2010). Within the same study, D5 median biota-sediment accumulation factors (BSAFs) were >1 for Atlantic cod and shorthorn sculpin from Adventfjorden, indicating bioaccumulation potential for D5. Multi-media bioaccumulation factors (mmBAFs) – which reflect the ratio of the amount of chemical accumulated within an organism over the amount of chemical present within the surrounding environment – for the Humber Estuary (UK) and Swedish lakes also indicate bioaccumulative behavior of cVMS (Kierkegaard et al., 2011, 2013a). Comparing mmBAFs of cVMS to those for known persistent organic pollutants with a propensity for bioaccumulation (e.g. CB-180), higher mmBAFs were observed for D4 and D5 than for CB-180 in the Humber Estuary, indicating that D4 and D5 are also strongly bioaccumulative chemicals (Kierkegaard et al., 2011). This contradicts earlier findings in which D4 and D5 were found to biodilute (i.e. with a trophic magnification factor, TMF, of <1) within various aquatic food webs (Powell et al., 2009, 2010; McGoldrick et al., 2014a). Differences between mmBAFs for D4, D5 and CB-180 could be due to differences in sorption affinity between biological tissues and sediment. Chemical distribution between the environment and biota is driven by the ratio K_{OW}/K_{OC}. Although K_{OW} (1.5×10^{7}) and K_{OC} (4.0×10^{6}) values for CB-180 are similar, the respective values for D4 (9.5×10^{6} and 1.2×10^{5}) and D5 (1.2×10^{8} and 1.2×10^{5}) (Panagopoulos et al., 2015) differ by more than two orders of magnitude. The ratio of K_{OW}/K_{OC} for D4 and D5 is over 20 times greater than for CB-180, highlighting stronger partitioning affinity to lipids than organic carbon (i.e. sediment) for D4 and D5. Although this indicates that a greater fraction of D4 and D5 will be transferred to biota from the sediment compartment, biodilution may still occur for D4 and D5 as these chemicals are transferred

up food chains. However, several studies have shown trophic magnification for cVMS (Borgå et al., 2012, 2013), indicating that biomagnification will be both site- and food-chain specific.

High exposure to cVMS has also been shown to occur in the marine environment within the Norwegian Arctic with concentrations reaching the µg/g level in Atlantic cod. The highest concentrations were observed for D5 (200–1110 ng/g ww, 340–2500 ng/g lw), followed by D6 (17–66.5 ng/g ww, 29–139 ng/g lw) and D4 (9.2–45.6 ng/g ww, 16–110 ng/g lw) in Atlantic cod liver collected near Tromsø, Norway (Warner et al., 2014). Concentrations of D5 in Atlantic cod around Tromsø are surprisingly high considering the small population of this Arctic community (72 000 inhabitants). Larger urban cities within Europe and North America often employ a combination of mechanical, biological and/or chemical wastewater treatment, which has been shown to remove over 90% of VMS from the influent (Allen et al., 1997). However, in many Arctic communities only mechanical treatment is used, potentially resulting in higher per capita discharges and exposure of VMS to the local aquatic environment. Wastewater concentrations of D5 alone were 1–20 µg/L from various wastewater outlets (Warner, unpubl. data) around Tromsø. The highest concentrations observed are comparable to concentrations in wastewater influent for cities within Europe and North America (van Egmond et al., 2013; Wang et al., 2013d), which can be attributed to the lack of treatment employed in Tromsø. D4 and D6 were also detected in wastewater effluent in Tromsø but at much lower concentrations (0.1–0.33 µg/L and 0.9–0.18 µg/L, respectively). Similar findings have been reported for D5 and D6 in wastewater effluent in the Faroe Islands (5.2 and 0.33 µg/L, respectively) (Kaj et al., 2005), highlighting Arctic communities as significant sources of cVMS to the marine environment.

Allometric parameters (e.g. length and weight) are also important variables. Warner et al. (2014) showed concentrations of D4 and D6 in Atlantic cod liver to be negatively correlated to fish length and weight (Figure 2.78). However, similar correlations were not observed for D5. This is probably due to the high variation observed in D5 concentrations detected, which has been observed in previous studies investigating aquatic biota (Warner et al., 2010; Kierkegaard et al., 2011; Borgå et al., 2012). In addition, emission/exposure of D5 is considered to be much higher than for D4 and D6 in the environment (Brooke et al., 2009b,c) and so may offset elimination that occurs with growth. Borgå et al. (2012) also found no relationship between fish size and D5 concentration, but did find higher concentrations of D5 in small fish (e.g., smelt, *Osmerus eperlanus*) occupying similar trophic positions to large fish (e.g. trout, *Salmo trutta*), suggesting that bioaccumulation may be both size- and species-dependent.

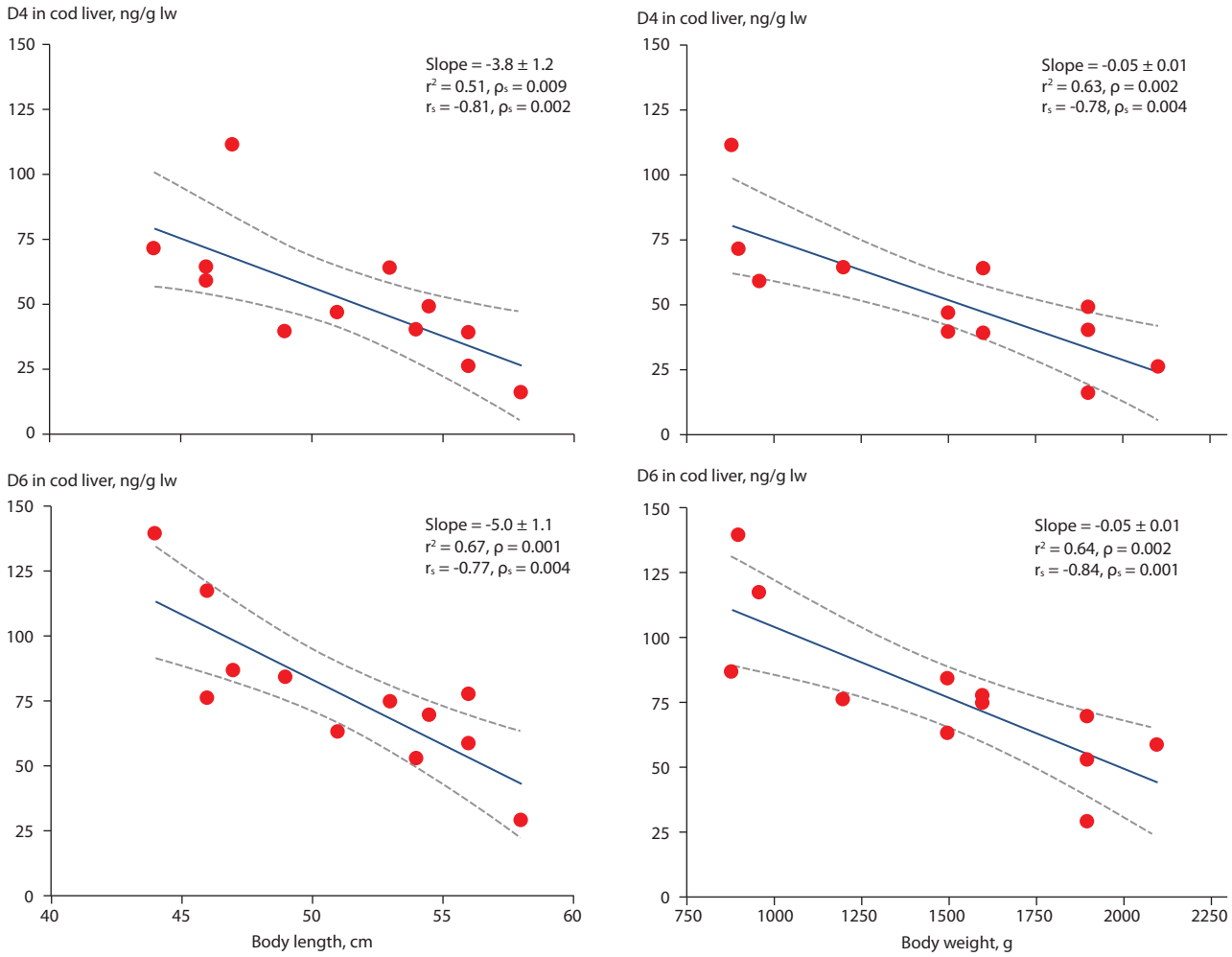


Figure 2.78 Linear regressions and Spearman correlations between D4 and D6 liver concentrations and fish length and weight for Atlantic cod collected from Tromsø. Dashed line represents 95% confidence interval of linear regression; r^2 and r_s represent correlation coefficient for linear and Spearman regression tests, respectively; ρ and ρ_s represent probability for linear and Spearman correlation to be caused by random sampling, respectively (Warner et al., 2014).

Biomagnification potential of cVMS in aquatic food webs has been shown in several studies (Warner et al., 2010; Kierkegaard et al., 2011; Borgå et al., 2012, 2013). However, studies investigating top (air-breathing) predators in marine food webs have found lower concentrations compared to concentrations in fish. cVMS detected in bearded seals (*Erignathus barbatus*) from Svalbard (0.8–1.1 ng/g lw) were 10 to 50 times lower than in fish from the same area (Warner et al., 2010) and this is supported by similar findings for grey seals (*Halichoerus grypus*) from the Baltic Sea region (Kierkegaard et al., 2013b). Low concentrations are also observed in Arctic seabirds where D4 liver concentrations in kittiwakes (*Rissa tridactyla*) from Svalbard were 1.5–3.2 ng/g ww (Evenset et al., 2009). This agrees well with findings for eggs of common eider (*Somateria mollissima*), European shag (*Phalacrocorax aristotelis*) and herring gull (*Larus argentatus*) collected from remote seabird colonies along the Norwegian coastline. cVMS were below detection limits in most of the samples collected, although some individuals had detectable levels of both D5 (1.4–3.6 ng/g ww) and D6 (0.7–0.8 ng/g ww) (Huber et al., 2015).

Lower concentrations in top (air-breathing) predators of marine food chains can be attributed to enhanced elimination capabilities. Previous laboratory studies with rodents have shown that more than half the D4 and D5 absorbed via inhalation or oral exposure, was eliminated by exhalation (Sarangapan et al., 2003; Tobin et al., 2008). In addition to exhalation, 10–20% of absorbed exposure was eliminated via urine excretion within the same studies. Elimination from exposed tissues is likely to be aided by metabolism as metabolites of D4 and D5 accounted for most of the burden found in urine in rodent exposure studies (Varaprath et al., 2003). These results in combination with findings from field studies indicate that top marine predators, especially those that are air breathing, are at low risk of VMS bioaccumulation.

2.7.7 Environmental trends

2.7.7.1 Spatial trends

Information regarding spatial variation of VMS in the Arctic is sparse although some studies have been made. Concentrations of cVMS in fish (i.e. Atlantic cod) have been shown to decrease with distance from human settlements on Svalbard (Warner et al., 2010). The highest average concentrations were observed in fish collected near Longyearbyen, Adventfjorden (2000 inhabitants) (D5: 180 ng/g lw; D6: 10 ng/g lw), whereas concentrations were up to 20 times lower (D5: 18 ng/g lw; D6: 26 ng/g lw) in fish collected near Ny Ålesund, Kongsfjorden (40 to 150 inhabitants). This is supported by findings from Kierkegaard et al. (2013a) where higher environmental concentrations were directly related to the number of inhabitants connected to wastewater systems.

Warner et al. (2010) also reported findings for cVMS in shorthorn sculpin collected from Liefdefjorden (Svalbard). While most of the fish collected showed no detectable levels of cVMS. Two (out of five) individuals did have detectable levels of D5 (2.2 ng/g ww, 11.3 ng/g lw) and D6 (0.9–1.7 ng/g ww, 8.8–9.2 ng/g lw). These findings agree with results for fish from Liefdefjorden analyzed in industry laboratories (Warner et al., 2013), suggesting that exposure to cVMS has occurred in this fjord. The sources of exposure are still unknown as no human settlements are present. However, seasonal tourism shipping traffic entering this fjord may present a potential source that warrants future investigation.

Similar spatial trends have been observed in the Norwegian Arctic where average concentrations of cVMS (e.g. D4, D5, D6) detected in Atlantic cod decreased by a factor of 5 within a 30-km radius of Tromsø (Warner et al., 2014). Reduction in cVMS concentration in Atlantic cod can be attributed to elimination mechanisms (i.e. metabolism/physical elimination) because metabolic half-lives are relatively short (i.e. 20 days; Woodburn et al., 2013) compared to those for legacy POPs (i.e. PCBs ≥ 90 days; Bruggeman et al., 1984; de Boer et al., 1994). However, a similar spatial decrease in PCB body burden was also observed, indicating that spatial trends in cVMS and PCBs in Atlantic cod near Tromsø are largely driven by different exposure profiles (Warner et al., 2014). Despite a decrease in cVMS exposure with distance from dense populated centers, D5 dominated over concentrations for recalcitrant PCB congeners (i.e. CB-153 and CB-180) in Atlantic cod from all locations (Warner et al., 2014). Efficient uptake of D5 from the surrounding environment is due to its higher transfer efficiency between sediment and biota (Kierkegaard et al., 2011) in combination with higher current discharges of D5 compared to PCBs.

2.7.7.2 Temporal trends

Current air monitoring campaigns at Zeppelin represent the only data currently available for investigating temporal trends in cVMS concentrations within the Arctic. Concentrations of D5 measured by Krogseth et al. (2013a) in 2011 are in very good agreement with those obtained in 2013 (Bohlin-Nizzetto et al., 2014) and 2014 (Bohlin-Nizzetto et al., 2015) with no increasing trend in annual atmospheric concentrations of D5 in either summer or winter. Similar findings were observed for D6 between 2011 and 2014 in winter. However, higher D6 concentrations were detected in summer 2013 compared to summer 2011, and were higher than concentrations detected in winter. This contrasts with the trends observed by Krogseth et al. (2013a) in 2011 who showed D6 concentrations to increase in winter. However, this increase could not be confirmed in 2014 due to logistical problems in the summer sampling campaign. However, monitoring of cVMS at Zeppelin will continue in future years to compare against the established baseline and to provide insight into seasonal patterns for D6.

2.7.8 Conclusions

Volatile methylsiloxanes are ubiquitous in the natural environment and have been reported in various environmental matrices from Arctic regions. Although lVMS and cVMS are both released into the natural environment, only cVMS have been detected in Arctic matrices, indicating greater emissions and/or environmental persistence compared to lVMS. Long-range atmospheric transport of cVMS to the Arctic has been demonstrated and monitoring data show that annual concentration trends have remained stable in recent years. Higher atmospheric concentrations of cVMS occur during

winter due to lower atmospheric concentrations of hydroxyl radicals, resulting in lower photo-degradation during winter. However, even under Arctic conditions, atmospheric deposition of cVMS is unlikely to occur due to its inherent volatility. Exposure to cVMS in Arctic regions is primarily from local sources such as human settlements. Due to limited wastewater treatment in such settlements, wastewater inputs are major sources of cVMS to aquatic environments in the Arctic. High discharges translate into high environmental exposure with tissue concentrations in biota reported at parts per million levels, which is similar to or higher than levels reported for legacy POPs. Exposure and accumulation of cVMS will also be dictated by the characteristics of the receiving environment. cVMS concentrations within sediment and biota from the Arctic lake Storvatn, which receives accidental wastewater/sewage discharges from the community of Hammerfest, are comparable to or higher than in marine environments that receive greater inputs. This is supported by model simulations, which indicate that characteristics of the physical environment play an important role in dictating the overall persistence of cVMS. Taking into consideration that degradation mechanisms (i.e. hydrolysis) decrease at lower temperatures, longer environmental residence times of cVMS may occur in Arctic regions receiving high cVMS inputs and this requires further investigation. Considering the wide range of applications for cVMS and the potential for an increase in their use through new applications, there is a need to continue monitoring this class of compounds. Recent proposals have been made by the UK and the EU to reduce the use of D4 and D5 to less than 0.1% in washed-off personal care products. If the proposals are accepted, monitoring data will be crucial to assess changes in environmental concentrations of cVMS due to potential future restrictions on D4 and D5 use.

Acknowledgements

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2.8 Pharmaceuticals and personal care products (PPCPs)

Authors: Roland Kallenborn, Eva Brorström-Lunden

2.8.1 Introduction

Pharmaceuticals are substances used in the diagnosis, treatment, or prevention of disease and for restoring, correcting, or modifying organic functions in veterinary and/or human medical therapeutic treatments. Personal care products are non-medicinal consumable products that are used in the topical care and grooming of the body. The only common characteristic of these organic substances is that they are directly applied to humans or animals for the purpose of maintaining health and physiological fitness. As a result they express a great heterogeneity in terms of chemical properties including polarity, solubility and volatility, with significant consequences for their environmental fate. Pharmaceuticals and personal care products (PPCPs) as environmental pollutants and xenobiotics in ecosystems have been a focus of pollutant research for the past 20 years (Kummerer, 2009c). The first evidence of PPCP presence in a waste-receiving environment was reported more than 20 years ago, when Ajmal et al. (1980) reported on hazardous effects of a pollution mixture from pharmaceutical industries on microorganisms. Direct release from wastewater treatment plants (WWTPs) and diffusive seeping from deposition sites are currently considered the major sources of environmental contamination. WWTPs in densely populated regions are reported to have medium to high retention properties for selected PPCPs (Hirsch et al., 1999; Lee et al., 2003; Fatta-Kassinos et al., 2011a; Kallenborn et al., 2008a). However, because most Arctic WWTPs only provide primary treatment (filtration) minimal PPCP retention is expected.

The aquatic system has been identified as the most important recipient for PPCPs in the environment. PPCPs are usually readily degraded after entering the environment and in general are not considered persistent. They are currently considered relevant environmental pollutants only near human activities and point sources (domestic areas, industrial production sites, animal husbandry, and other agricultural activities). However, the continuous high volume releases into aquatic environments mean transformation rates in the receiving ecosystem can sometimes be exceeded. When this occurs, these chemicals are considered permanently present and thus 'pseudo-persistent' in this specific ecological context.

PPCPs are not yet considered priority chemicals for monitoring in Arctic environments. Because most of the PPCPs studied are not considered persistent, are relatively immobile and not expected to be transported over long distances, they are only expected to be found in close proximity to human activities. However, their toxicological potential is usually very well defined due to their target-specific application range in therapeutic usage. In contrast to conventional POPs, PPCPs are designed and manufactured to have particular biochemical and physiological functions during specific medical treatment. These biochemical properties expressed under uncontrolled environmental conditions have the potential to result in toxicological effects. Thus, for pharmaceutical agents, effect thresholds related to their targeted physiological and biochemical processes can be assumed to be very low due to their specifically designed application range under controlled therapeutic conditions. For example, Brodin et al. (2013) found wild perch (*Perca fluvialis*) exposed to the benzodiazepine anxiolytic drug oxazepam at concentrations measured in effluent-influenced surface waters had altered behavior and feeding rates. Such effects are of ecological relevance.

From well-known and comprehensively studied legacy POPs, polycyclic aromatic hydrocarbons (PAHs) and trace metals, it is clear that general ambient environmental conditions (e.g. air temperature, radiation, microbiology, geology) and the physical-chemical properties of the target chemical can play an important role in determining the environmental behavior of contaminants. As a result, high environmental stability can be assumed for pollutants in the low ambient temperatures of northern environments. This assumption is also valid for pharmaceutical residues and other less studied environmental contaminants in the Arctic (Burkow and Kallenborn, 2000; Kallenborn et al., 2012). Due to low annual average ambient temperatures and the extremes of seasonal daylight conditions in the Arctic (midnight sun during summer to polar night during winter), conditions exist for deposition and prolonged environmental stability of anthropogenic pollutants. The long Arctic half-lives (i.e. very reduced degradation rates) inevitably result in elevated environmental levels as well as increased exposure potential for organisms and humans in the northern regions.

The Norwegian State Pollution Control Authorities (now the Norwegian Environment Agency) commissioned a comprehensive literature-based survey to help generate a priority list of PPCPs for environmental monitoring (Grung et al., 2007). Following the recommendations arising, the Norwegian and Nordic screening programs initiated and funded a series of screening studies to identify PPCP-related priority substances in environmental matrices in northern regions. Together with several published research studies, this information forms the basis for the present summary (Lee et al., 2003; Metcalfe et al., 2003; Weigel et al., 2004a; Lindqvist et al., 2005; Servos et al., 2005; Lishman et al., 2006; Vasskog et al., 2006, 2008; Dye et al., 2007; Vieno et al., 2007; Kallenborn et al., 2008a; Kleywegt et al., 2011; Carlson et al., 2013; Huber et al., 2013; Kaj et al., 2014; Kankaanpää et al., 2014; Mutter, 2014; Thomas et al., 2014). In addition to the High Arctic, this first review covers adjacent subarctic regions (i.e. south of 66°N) such as Hudson Bay, Ontario, Manitoba, Alaska, the northwestern coast of Norway, southern and western Greenland, Finland, the Faroe Islands and Iceland, Sweden and Finland (Figure 2.79). There was no information available for the eastern Arctic regions.

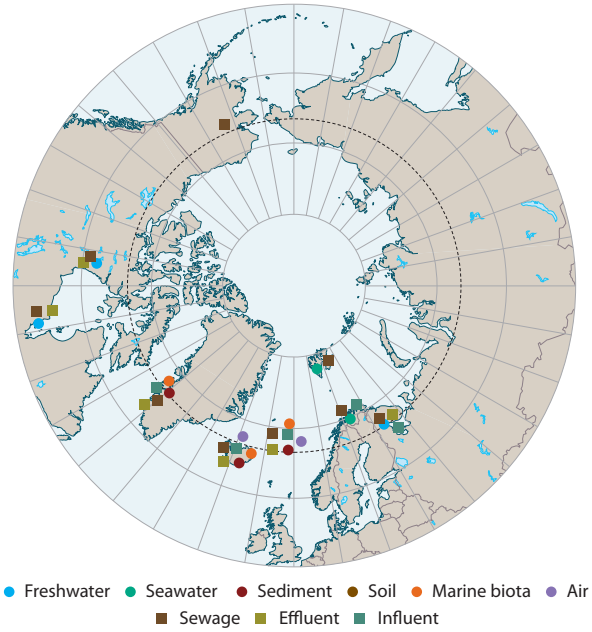

Figure 2.79 Arctic regions where PPCP contamination has been confirmed in environmental samples.

This first comprehensive literature survey confirms the presence of many PPCPs in the Arctic environment. PPCPs are shown to occur in a range of environmental compartments (Figure 2.79) and the compound groups identified are listed in Table 2.50. Detailed information on levels and locations is provided in Annex Tables 2.8/1 to 2.8/3.

2.8.2 Physical-chemical properties

As environmental xenobiotics, PPCPs are a highly diverse group of target substances for environmental chemical analysis. Physical-chemical properties span a large range with respect to polarity, solubility and volatility (see Appendix 1). Due to excess dosing, which is common practice in medical applications, excretion rates (parent compounds as well as metabolic products) are often reported in the range of 60–80% of the respective therapeutically active compound (or metabolite) based on the compound-specific pharmacokinetic studies required for permission to market the pharmaceutical products (Kummerer, 2009c). Thus, a major proportion of the therapeutic agent is excreted

Table 2.50 Summary of Arctic media and compound groups for which PPCP data have been reported (see Annex Table A2.8/1 for more detailed information). The number of compounds analyzed for each compound group is given in parentheses.

	Atmosphere		Terrestrial		Freshwater			Marine			Waste
Compound group	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	Sewage
NSAIDs (11)					×	×		×			×
Antidepressants/SSRI (10)					×	×		×			×
β(beta)-blockers (5)					×	×					×
Calcium channel blockers (1)						×					×
ACE blockers (3)						×					×
Angiotensin receptor antagonists (3)						×					×
Antiepileptics (1)					×						×
Antimicrobials (4)					×			×			×
Antibiotics (14)					×			×			×
Additives (5)	×		×		×					×	×
Fragrances (5)					×						×
Steroid hormones (5)					×	×					×
Lipid regulators (3)					×						×
Illicit drugs (4)					×						×
Stimulants (2)					×			×			×
Anti-cancer (2)											×
Artificial sweeteners (2)					×						×
Surface tension suppressors (6)					×	×	×				×
Hypnotics (1)											×
Antidiabetics (1)											×
Anticoagulants (2)						×					×
Diuretics (4)						×					×
Chelating agents (1)						×					×
UV-filters (3)											×
Bisphenol monomers (5)											×

NSAIDs: non-steroidal anti-inflammatory and antipyretic analgesic drugs; SSRI: selective serotonin re-uptake inhibitors; ACE: acetylcholine esterase.

Table 2.51 Selected classes of pharmaceuticals and personal care products identified in Arctic environments (for a complete list of compounds, including CAS registry numbers and IUPAC nomenclature, see Annex Table A2.8/1).

Compound group	Effect/Application area	Relevant examples
NSAID	Painkillers and anti-inflammatory effect	Ibuprofen, diclofenac, acetylsalicylic acid, naproxen, paracetamol and others
Antimicrobials/Antiseptics	Additives to personal care products	Triclosan, Bronopol, Resorcinol, m-Cresol
Antibiotics and antiseptics	Antimicrobial agents	Benzyl penicillin, Sulfomethizole and others
Antidepressants	Neuro-regulatory agents	Paroxetine, Sertraline, Citalopram and others
Antidiabetics	Insulin regulators	Metformin, Gliclazide
Anti-cancer drugs	Cancer therapy and treatment	Ifosfamide, Cyclophosphamide
Antiulcer drugs	Gastric system controlling drugs	Omeprazole and others
Cardiovascular drugs	Blood circulation controlling agents	Anti-arrhythmic drugs
Anticoagulants	Blood clotting control	Coumarin derivatives, Amlodipin, Warfarin, Dipyridamole
Steroids/Hormones	Endocrine functions	Ethinylestradiol, Mestrone, Estrone and others
Hypnotics	Consciousness control	Zopiclone, Lidocaine
Complexing agents	Additives to cosmetic products	Ethylene diamine tetraacetic acid (EDTA)
Detergents	Sebum removal	Sodium dodecyl sulfate (SDS) and others
Surfactants	Reducing surface tension pressure	Cetrimonium salts and others
Synthetic fragrances	Additives to perfumes, soap etc.	Polycyclic musks, nitro musks
Angiotensin II receptor antagonists	Blood pressure regulation	Losartan, Candesartan and others
Additives/stabilizers	Added to personal care products	Butylparaben, Siloxanes, Bisphenol A
Lipid regulators	Regulating cholesterol levels	Fenofibrate, Clofibric acid
Illicit drugs	Illegal drugs	Cocaine, metamphetamine and others
Stimulants	Added to drinks and pharmaceutical products	Caffeine, 1,7 dimethylxanthine
Diuretics	Liquid regulation	Furosemide, Hydrochlorothiazide and others
UV-filters	Sun screen	Benzophenone, Octocrylene and others
Bisphenol monomers	Monomer for polymers (packing materials and additives)	Bisphenol A, methylenebisphenols and others
Artificial sweeteners	Food additives	Sucralose, Cyclamate

unchanged and enters the sewage system, where a proportion of the PPCP load is retained and/or eventually degraded into transformation products. As a result, risk assessments of PPCPs in the Arctic environment must include properties of the major transformation products as well as those of the target parent compounds (Daughton, 2003).

Pharmaceuticals are usually characterized by their therapeutic effects during medical treatment. A selection of pharmaceutical groups and personal care products already studied in Arctic environments is listed in Table 2.51.

A total of 112 different PPCP-related substances have been identified in Arctic samples in research and screening studies published as scientific articles and reports (see Annex Table A2.8/1). This already relatively large number of compounds can only reflect the capability of current analytical methods. Future technological developments will inevitably lead to the identification of new, as yet unidentified PPCPs.

Most of the compounds have been identified in raw sewage or related matrices (i.e. effluent, recipients). However, a large number of compounds were also found in freshwater, seawater and biota, illustrating the inherent environmental risk posed by these contaminants. Due to the high concentrations of target PPCPs expected in WWTP-related samples, most of the studies reported here focused on sewage and effluent. The very low concentrations of PPCPs expected in the receiving environmental media (including seawater) are still a challenge for many of the presently applied analytical methods.

2.8.3 Sources, production, use and trends

Pharmaceuticals and personal care products are produced as active agents for supporting general health and hygiene as well as for disease treatment and therapeutic applications in medicine and veterinary medicine. No PPCP production is reported from western Arctic environments, so potential release from production sites can be excluded as a source. Human population structure in the Arctic is characterized by a decentralized, scattered distribution of minor settlements with a few cities as cultural and social centers. This situation in the Arctic is very different to population structures in, for example, mid-latitude European countries. These structural differences have major implications for the release of pharmaceutical residues. Installing modern small- to medium-scale WWTPs is not usually economically viable for the small communities of the Arctic (Gunnarsdottir et al., 2013). As a result, sewage is often released

more or less untreated from single households directly or via collecting processes into the aquatic environment. Due to their generally low environmental mobility, the presence of PPCP-related substances in the Arctic environment usually indicates local anthropogenic sources. However, recent evidence suggests a few PPCP-related substances (such as volatile siloxanes) may be transported long distances via the atmosphere or ocean currents, possibly even as far as the Arctic (Vorkamp and Rigét, 2014). Nevertheless, the majority of PPCP residues identified in Arctic media are directly associated with human activities in the Arctic region (i.e. through usage and application). Direct release from WWTPs, as well as release from households and leaching from disposal sites is still considered the predominant source for the majority of PPCP release into Arctic aquatic environments (Kummerer, 2009c; Gunnarsdottir et al., 2013). Thus, most published studies on the fate and distribution of PPCPs in the Arctic have focused on the compound-specific distribution originating from their direct release via sewage into receiving waters (Metcalfe et al., 2003; Weigel et al., 2004a,b; Lindqvist et al., 2005; Servos et al., 2005; Lishman et al., 2006; Vieno et al., 2007; Vasskog et al., 2008; Mutter, 2014). Some recent studies have confirmed the presence of PPCPs in biota, sediment, soil and air, thus indicating the potential for their transfer between environmental compartments (Bakke et al., 2008; Huber et al., 2013; Vorkamp and Rigét, 2014). The preferred medium in which target substances are likely to be found will depend on the environmental conditions and the substance-specific physical-chemical properties (volatility, reactivity, solubility, environmental stability etc.).

In a first survey for an Arctic location, sewage sludge, sewage effluents and receiving seawater samples were analyzed for PPCPs in the vicinity of several sewage treatment sites in Tromsø (northern Norway) (Weigel et al., 2004a). Levels of ibuprofen, its metabolites and caffeine in the seawater samples were very high (in the medium ng/L range) despite strong currents in the receiving waters (Tromsø Sound). These currents were originally expected to dilute and disperse the target compounds (Weigel et al., 2004a). However, year-round low ambient water temperatures and so low degradation rates in combination with high emission volumes, have led to the permanent presence of the target PPCPs in the seawater surrounding the WWTPs (Weigel et al., 2004a). Because hospital sewage is physically separated from household sewage by different sewage systems, source-specific emission differences could be identified. The PPCP patterns from the hospital sewage, which contained SSRI (selective serotonin re-uptake inhibitor) antidepressants and other therapeutic agents, were significantly different to those of sewage effluents predominantly influenced by domestic waste water, which were dominated by caffeine and NSAID (non-steroidal anti-inflammatory and antipyretic analgesic drug) over-the-counter products (Weigel et al., 2004a). This first study confirmed the hypothesis that the cold northern ambient conditions have considerable influence on the environmental properties (including transformation) of environmental pollutants such as PPCPs.

In Tromsø, sewage samples were collected from three WWTP facilities. All Tromsø WWTPs process sewage using primary treatment only. The caffeine concentration in Tromsø sewage effluent was considerably higher than reported for sewage effluent and river water from a major German City (Hamburg, 900 000 inhabitants) (Weigel et al., 2004a). Concentrations of ibuprofen-related compounds for the Tromsø samples were of the same order of magnitude as reported for the Hamburg WWTP effluent samples. However, the distribution profile of the ibuprofen-related residues (ibuprofen, carboxy-ibuprofen and hydroxy-ibuprofen) showed distinct differences compared to the German data (Figure 2.80). No carboxy-ibuprofen was identified in the effluent sample from the Hamburg WWTP whereas all effluent samples from Tromsø showed an even distribution between the parent compound and the carboxy- and hydroxy-transformation products. All freshwater samples from the River Elbe adjacent to the Hamburg WWTP predominantly contained hydroxy-ibuprofen, whereas the parent compound and the carboxylated transformation product contributed

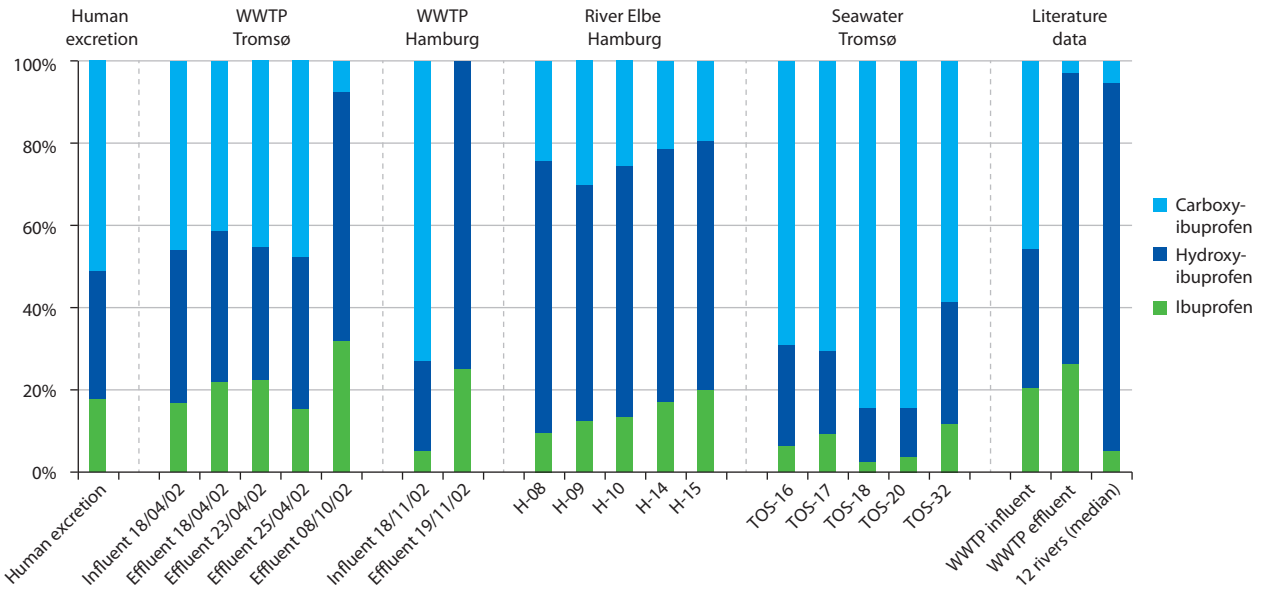

Figure 2.80 Distribution profile of ibuprofen and its major degradation products in sewage influents, sewage effluents and in the receiving seawater near Arctic waste water treatment plant (WWTP) facilities (Tromsø, Norway) compared to data for a more southerly latitude (Hamburg, Germany) (Weigel et al., 2004a). 'Human excretion' data from Bruchhausen et al. (1994) and 'Literature data' from Stumpf et al. (1996).

Table 2.52 Concentration ranges for PPCP compounds in samples collected during the Pharmafate pilot study in 2007 (Kallenborn et al., 2008a).

Target PPCP	Concentration range, ng/L					
	Oslo (VEAS)		Tromsø		Longyearbyen	
	Effluent (n=1)	Seawater (n=2)	Effluent (n=8)	Seawater (n= 8)	Effluent (n=5)	Seawater (n=2)
Ibuprofen	10	nd–52	448	na	30–403	0.4–1
Hydroxy-ibuprofen	126	188–243	3614	na	8–1398	2–34
Carboxy-ibuprofen	42	109–213	70 170	na	411–34 028	6–26
Diclofenac	25	nd–48	78	na	30–1074	1–4
Triclosan	11	nd	350	na	28–803	2–2.3
Caffeine	23	5–96	na	na	501–50 704	24–41
Citalopram	238	na	63–102	<MDL	<MDL	nd
Desmethyl-citalopram	310	nd	118–215	<MDL	<MDL	nd
Didesmetyl-citalopram	10	na	6–10	nd	nd	nd
Fluoxetine	8	na	1–5	nd	nd	nd
Norfluoxetine	2	na	0.7– 2.5	nd	nd	nd
Fluvoxamine	1	na	0.8–1.7	nd	nd	0.5–0.8
Sertraline	8	na	8–90	nd	nd	<MDL
Desmethylsertraline	6	na	nd	nd	nd	nd
Paroxetine	4	<MDL	3–13	nd	nd	0.6–1.4
Tetracycline	nd	nd	na	na	0.6–1.1	nd
Trimethoprim	0.8–0.9	nd	na	na	0.07–0.15	nd
Sulfamethoxazole	0.2–0.3	nd	na	na	nd	nd

MDL: Limit of quantification; na: not analyzed; nd: not detected.

not more than 35% of the total Ibuprofen group burden. In contrast to these findings, carboxy-ibuprofen dominated all seawater samples from Tromsø, comprising up to 80% of the total ibuprofen burden.

In a follow-up study, PPCP levels were determined in effluent and receiving seawater for three typical WWTPs on a longitudinal gradient through Norway from Oslo (60°N), to Tromsø (70°N) to Longyearbyen, Svalbard (78°N) (Kallenborn et al., 2008a). Average levels for all target PPCPs from this study are summarized in Table 2.52. Location-specific differences were found for all compounds analyzed. High concentrations (including antibiotic residues) in the receiving seawater samples from Longyearbyen sometimes exceeded the PPCP levels found in Tromsø. In addition to ambient conditions, the technological standard of sewage treatment plays a major role in the release profile and concentration levels found in this latitudinal study.

Based on these pilot investigations, the Norwegian Pollution Control Authority (SFT) conducted a national literature survey on the occurrence of selected PPCPs in the environment. The survey provided a first overview of the current state of knowledge regarding usage, distribution patterns and occurrence of these compounds in the Norwegian environment (Grung et al., 2007). The final report included recommendations on which PPCPs to prioritize for inclusion in future monitoring programs, as well as recommendations on sampling strategy. The report also included information on sales volumes for the selected compounds in Norway and the other Nordic countries (Grung et al., 2007).

The issue of PPCPs as environmental pollutants was recognized by the Nordic Council of Ministers (NCM) who initiated a series of screening programs. The results have been published in several reports (Dye et al., 2007; Grung et al., 2007; Huber et al., 2013; Kaj et al., 2014). Monitoring covered the following: influent, effluent and sludge for several WWTPs; surface water, including seawater and freshwater; and freshwater and marine sediments (se The screening exercise included water samples upstream and downstream of fish farms, other freshwaters or seawaters, and groundwater, especially near hospitals and farms (NCM, 2012). Nevertheless, the numbers of samples and PPCP compounds covered are still relatively few compared to what would be needed for developing sound regulation strategies.

The majority of the data generated by the NCM screening programs (NCM, 2012) is based on samples collected in Finland, the Faroe Islands, Greenland and Iceland. Most of the monitoring and screening programs are based on samples from WWTPs, receiving aqueous compartments and related aqueous environments (see also Table 2.50). Results from biotic and abiotic matrices further from large human settlements are still

scarce (Vorkamp and Rigét, 2014). The focus of that study was on WWTPs, including sewage, sewage influent, sewage effluent water, and sediment, and water samples and biota associated with the receiving environment. Of the target PPCPs selected, a few (e.g. diclofenac and ibuprofen) were detected in all samples at significant levels. Estrone (both a synthetic and naturally occurring estrogen) was detected in most samples analyzed.

2.8.4 Transformation processes

Transformation of PPCP compounds is mainly governed by their physical-chemical properties and the underlying environmental conditions. Studies investigating PPCP transformation have reported a range of relevant processes, including photochemical transformation, hydrolyses, and various microbial pathways (Xia et al., 2005; Kagle et al., 2009; Oulton et al., 2010; Fatta-Kassinos et al., 2011b; Dodgen et al., 2014; Rudd et al., 2014; Zenker et al., 2014; Evgenidou et al., 2015; Petrie et al., 2015; Aus der Beek et al., 2016; Hijosa-Valsero et al., 2016; Mathon et al., 2016). As previously discussed, low seawater temperatures seem to delay the breakdown of PPCPs. The comparison of ibuprofen patterns in Tromsø with published data from Germany (Figure 2.80) showed the carboxylated transformation product (carboxy-ibuprofen) was about 2-fold higher in the Arctic than at the mid-latitude locations. It can thus be assumed that carboxy-ibuprofen is more stable in the cold seawater environment around Tromsø (annual average 4–6°C) than in temperate mid-latitude environments. On the basis of current knowledge, the carboxylated metabolite (carboxy-ibuprofen) is considered the predominant transformation product following human excretion (Paxeus, 2004). However, following microbial degradation in the receiving (waste)waters (via directed waste water treatment or direct exposure in the aqueous environment), the hydroxylated transformation product (hydroxy-ibuprofen) seems to predominate in mid-latitude aquatic environments, which implies carboxy-ibuprofen is readily hydrolyzed to hydroxy-ibuprofen (Weigel et al., 2004a; Quintana et al., 2005; Hijosa-Valsero et al., 2016). This suggests a complex combination of metabolic (in the organism), abiotic and biotic (i.e. microbial after excretion) transformation processes result in a final predominating transformation product that is released and detectable in the aqueous environment. These transformation processes are strongly influenced by ambient conditions including the temperature, microbiological environment, abiotic environment (i.e. receiving water and sediment characteristics) and light conditions along the release pathway. These influences were also found to be important for the PPCPs identified in a subsequent study in Tromsø (Vasskog et al., 2006) where selected SSRI antidepressants including their transformation products were found in ng/L concentrations in sewage effluent samples. Similar SSRI levels as reported from the WWTP in Tromsø were also found in untreated sewage effluent collected in Longyearbyen (Svalbard; around 2200 inhabitants in 2008) in a comparative study (Vasskog et al., 2008).

The influence of ambient temperature on the microbial transformation of an antibacterial pharmaceutical was studied in a controlled laboratory experiment. This focused on the temperature-dependent microbiological transformation of benzyl-penicillin (a β-lactam antibiotic) applying the Zahn-Wellens test (OECD 302B) for microbiological degradation in raw sewage sludge (Bergheim et al., 2010). The temperature-dependent degradation of benzyl-penicillin was studied at 5°C, 12.5°C and 20°C ambient conditions during an experimental period extending from the OECD recommended standard 28-day testing period to a final duration of 42 days. Concentrations of benzyl-penicillin as well as the major transformation products identified were monitored continuously by chromatography coupled to mass spectrometric detection over the entire experimental period. Dissolved organic carbon (DOC) was monitored to control microbial carbon consumption during the experiments. Benzyl-penicillin is expected to serve as a secondary carbon source after the primary carbon source is completely consumed. Maximum DOC loss was slowest at 5°C and total DOC degradation (considered a measure of the available total microbial carbon source in the experiment) was not reached even after 42 days (Bergheim et al., 2010), in contrast to the 20°C set up for which total carbon consumption occurred after about 8 days (12.5°C = carbon consumption after 32 days). A first preliminary structure elucidation was undertaken for the major microbial transformation products for benzyl-penicillin based on available full-scan mass spectra (m/z) and complementary mass spectra library research. From these results, Bergheim et al. (2010) concluded that transformation under the three temperature regimes resulted in different predominant final transformation products. The consequences of these findings are currently under investigation but again demonstrate the importance of ambient temperature for PPCP transformation processes; indicating that transformation pathways as well as environmental stability may differ significantly between Arctic conditions (strong seasonality in light conditions, low year-round temperatures, permafrost in soil, and ice cover in freshwater systems for more than eight months a year) and mid-latitude environments, with major consequences for direct human exposure risk and hazardous environmental effects (Kallenborn et al., 2008b).

In addition to a changed transformation pathway, effects on organisms may be altered or even enhanced under Arctic conditions. For antibiotics, a longer half-life in the Arctic environment may affect the local microbial community in the exposed location. This could even lead to bacterial and viral resistance with severe consequences for human populations and the environment at concentrations already observed at the ng/L range. Various mechanisms are described in the literature for enzymatic inactivation of antibiotics. Conventional mechanisms include chemically changing the structure of the antibiotic, inactivating the substance through physical removal from the cell, or modifying the target location to make it unavailable for the antibiotic (Alekshun and Levy, 2007; Aarestrup et al., 2008; Boerlin and Reid-Smith, 2008; Acar and Moulin, 2012; Voolaid et al., 2012; Cox and Wright, 2013; Gaze et al., 2013; Corno et al., 2014; Keeney et al., 2014).

Research over the past decade confirms that antibiotic resistance can transfer between microbial strains since this property is encoded by several transitional genes. New resistance mechanisms are constantly being described, and new genes and vectors of transmission were identified recently (Blair et al., 2015). Thus, the continued environmental release of antimicrobial

substances in Arctic aqueous and marine coastal environmental will ultimately result in a shift in bacterial populations from those predominantly sensitive to pharmaceutically-produced antimicrobials to predominantly resistant phenotypes. Such a shift could potentially lead to the transfer of genetic information (resistance determinants) into microbial pathogens (Kallenborn et al., 2008b), which could be harmful for patients treated with conventional antibiotics for infectious diseases.

A recent study explored these mechanisms by using functional metagenomics to investigate the resistomes (pool of genes responsible for resistance) of bacterial communities isolated from different layers of permafrost in the Canadian High Arctic (Perron et al., 2015). The resistome may be considered as the bacterial 'tool box' for responding with resistance strategies to exposure from chemical poisoning (quite common in natural processes). Eight genes conferring clinical levels of resistance against aminoglycoside, β-lactam and tetracycline antibiotics were isolated from bacteria strains sampled from ancient permafrost layers. In bacteria sampled from the active layer (the top layer of soil that thaws during summer and refreezes during autumn), another ten genes were isolated and characterized conferring resistance to the six antibiotics tested. The study concluded that antibiotic resistance genes are functionally diverse microbial defense mechanisms that existed even prior to the anthropogenic use of antibiotics, contributing to the evolution of natural reservoirs of resistance genes (Perron et al., 2015).

Many antimicrobial agents, including antibiotics, are semi-synthetic or synthetic derivatives of naturally occurring biologically active substances (i.e., antibiotics, hormones etc.) and are persistent in the environment (Andersson and Hughes, 2011; Clarke and Smith, 2011; Alm et al., 2014; Batchu et al., 2014; Sun et al., 2014b; Dorival-Garcia et al., 2015; Qiu et al., 2016). These anthropogenic synthetic substances are persistent in the environment because they have been specifically developed to retain activity and resist degradation by the biochemical activities of the organism until they reach the target location within the treated organism (Dooley et al., 2003; do Nascimento et al., 2013). An excess of antibiotics consumed during treatment is usually excreted chemically unchanged and then enters the sewage system (Hirsch et al., 1999; Kummerer, 2003, 2009a,b; Ding and He, 2010; Braschi et al., 2013; Milic et al., 2013; Bergheim et al., 2015). Modern WWTPs are typically able to retain and degrade this type of pollution effectively (Carballa et al., 2007; Yu et al., 2009; Zorita et al., 2009; Le-Minh et al., 2010; Schaar et al., 2010; Schroder et al., 2012).

Even triclosan, a chlorinated antimicrobial agent used in various consumer products is associated with the development of microbial multidrug resistance when present in the aqueous environment (Carey and McNamara, 2015). Triclosan has also been identified in the direct release of sewage to the Arctic environment (see Annex Table A2.8/2). Although reliable research is still required for assessing the consequences of triclosan release to the aqueous environment, direct physiological risks for biota at higher trophic levels in the terrestrial Arctic are not expected in relation to the levels reported here (Reiss et al., 2009).

2.8.5 Modeling studies

Development of model-based environmental risk assessment of PPCPs has been a major challenge due to the many compound-specific 'modes-of-action', the heterogeneity of their physical-chemical properties, the compound-specific source characterization and their specific toxicity features. For scientifically appropriate modeling tools, it is necessary to develop theoretical descriptors as completely and accurately as possible. Such parameters are usually based on combining physical-chemical properties, source characterization, transformation profiles, and environmental toxicological parameters.

The scientific literature contains two relevant studies on model-based evaluation of risk and environmental fate in northern environments (Wajsman and Ruden, 2006; Zukowska et al. 2006). Specific environmental toxicity parameters, such as the predicted environmental concentrations (PEC) and predicted no-effect concentrations (PNEC) are difficult to establish in a scientifically reliable manner without adequate and calibrated models. One such study considered release to the aquatic environment via effluent and sludge from WWTPs. From a large number of information sources, a set of 181 potentially relevant exposure models were identified (Wajsman and Ruden, 2006). Assessing and testing the chosen models resulted in a final selection of two priority models. However, the authors concluded that there is still much potential for developing exposure model(s) specifically designed for pharmaceutical inputs to the Nordic environment (Wajsman and Ruden, 2006).

Multimedia box models have been successfully applied for establishing the environmental fate of pollutants in many regions, including the Arctic. This approach has good potential for use in modelling the fate of PPCPs (Barrie et al., 1992; Macdonald et al., 2000; Toose et al., 2004; Wania, 2006; Brown and Wania, 2008; Mackay and Reid, 2008; Reid and Mackay, 2008; Hung et al., 2010; Armitage et al., 2011; Mackay et al., 2011; Krogseth et al., 2013a). A first assessment has been reported aimed at expanding the traditional box model approach toward PPCPs (Zukowska et al., 2006). Poly-parameter linear free energy relationships (PP-LFERs) were used as new characteristic parameters to account for the large polarity range that PPCPs cover in their physical-chemical properties. The PP-LFER-based fugacity model was then used to calculate overall persistence, concentrations and inter-media fluxes for typical polar and non-polar organic chemicals including PPCPs between air, water, soil and sediments at steady-state. Model results suggest that an accurate description of the partitioning equilibrium is essential for generating reliable predictions of environmental fate. The PP-LFER-based modeling approach also confirms that the greatest mobility for this type of substances distributed in aqueous phases may be expected for pharmaceutical residues combining small molecular size with strong H-acceptor properties (Zukowska et al., 2006).

2.8.6 Environmental concentrations

In total, 112 different substances from 26 different PPCP groups were identified in atmospheric, terrestrial, freshwater and marine samples from Arctic locations. The majority of the data reported are from studies and screening activities associated with human settlements, release via WWTPs and analyses of receiving

waters. The data are from around 20 reports and peer-reviewed scientific articles and form the basis of the following sections. This information is summarized in detail in Annex Table A2.8/2. All supporting references are also given.

2.8.6.1 Air and precipitation

Only two studies reported PPCPs in atmospheric samples. Cyclic volatile polysiloxanes (D4, D5, D5) were detected in atmospheric samples collected during a Nordic screening exercise (Kaj et al., 2005). The levels for D4, D5 and D6 were determined and confirmed in Icelandic air samples as well as air from the Faroe Islands. A detailed assessment of this information is provided in Section 2.7 (on siloxanes).

2.8.6.2 Terrestrial environment

The terrestrial environment is still not considered a major focus for research and monitoring of PPCPs in the Arctic. Only one report noted the presence of PPCPs in soil. In a recent Nordic screening study, *m*-cresol (96 ng/g dw) was identified and quantified in Faroe Island soil (Dye et al., 2007).

2.8.6.3 Freshwater environment

The freshwater environment is considered the major recipient for PPCPs. The majority of PPCPs identified as contaminants in Arctic environments have been identified in freshwater-related samples including sewage influent, sewage effluent, sewage and sludge samples (Kümmerer, 2010).

Sewage-related samples

Based on current scientific understanding, sewage-related samples including sewage effluents and sludge are considered the main sources of PPCPs as environmental contaminants (Huber et al., 2013). Consequently, the freshwater environment is the focus for studies on PPCP fate and distribution processes in the Arctic.

Sewage influent

Fifty-five of the 112 (49%) reported PPCPs were identified in sewage influent samples. Most of the data are from reports to the Nordic Council of Ministers. PPCP concentration data from sewage influent is reported from nine Arctic regions (northern Norway, Finland, Faroe Islands, Iceland, Greenland, Svalbard, Ontario, Manitoba, and Alaska). The highest measured concentrations were reported for prescription-free, over-the-counter NSAIDs including salicylic acid (874 µg/L, Ontario, Canada), acetominophen/paracetamol (506 µg/L, Faroe Islands), naproxen (109 µg/L, Iceland) and the anticoagulants dipyridamole (166 µg/L, Faroe Islands). Most of the PPCP compounds in the sewage influent samples analyzed were found in the low ng/L (0.03 ng/L Diclofenac, Ontario) to µg/L concentration range (506 µg/L Acetaminophen/paracetamol, Faroe Islands) (Huber at al., 2013).

Sewage and sludge

Fifty-two of the 112 (46%) reported PPCPs were identified in sewage and sludge samples. Most of the data are from Nordic reports and peer-reviewed research publications. PPCP concentration data from sewage and sludge are reported from nine Arctic regions (northern Norway, Finland, Faroe Islands, Iceland, Greenland, Svalbard, Ontario, Manitoba, and Alaska). In general, water-soluble residues are enriched in sewage, whereas less polar compounds are found mainly in sludge. Consumption volumes directly reflect the amount of active PPCP substances found in sewage-related samples. The average levels of all compounds identified were found in the 10–100 ng/L range for sewage and 10–1000 ng/g dw range for sewage sludge. In sewage sludge, SSRI antidepressants were found at the highest concentrations (metoprolol 549 µg/g dw and propranolol 680 µg/g dw in Iceland). For sewage, the highest levels were found for additives and surfactants (siloxane D5 4.3 µg/L in Faroe Islands and DDAC type 25 µg/L in Iceland) (Huber et al., 2013).

Sewage effluent

Concentrations of PPCP in sewage effluent represent the combined result of biochemical transformation in the treated organisms, biotic and abiotic transformation in the WWTP and the effects of WWTP technology on PPCP residues. Seventy-three of 112 (65%) reported PPCPs were identified in Arctic sewage effluent samples. Thus, the majority of the PPCP-related compounds were confirmed in sewage effluent. This supports the importance of sewage-related matrices as primary sources for PPCPs.

In addition, many PPCP compounds are immobilized by the exposed organism (humans and wildlife) through Phase II metabolization such as glutathione-*S*-transferase induced conjugation (Bidlack and Smith, 1984; Yu et al., 2010; Jeon et al., 2013; Mathews and Reinhold, 2013). The conjugates are not easily quantified using standard analytical procedures without direct cleavage during the preparation method (prior to quantitative analysis) as an additional sample treatment step. However, during the passage of sewage through WWTPs the conjugates are often cleaved, making the original substance available again. Thus, PPCP levels identified in effluent samples are considerably higher for those compounds than in inflow or sewage (Lishman et al., 2006). All PPCP substances identified in sewage effluent were present at concentrations from 0.01 ng/L to 70 µg/L. The predominant compounds were quantified in the 1–10 µg/L range (such as NSAIDs, caffeine, surfactants, anticoagulants etc). The ibuprofen metabolite carboxy-ibuprofen was found at levels up to 70 µg/L in Tromsø (Norway) and 38 µg/L in Longyearbyen (Svalbard). Acetominophen/paracetamol was found at levels up to 71 µg/L in Faroe Island effluents. The surfactant BAC was found at levels up to 60 µg/L in effluent samples from Greenland (for references see Annex Table A2.8/2).

Freshwater

Of the reported 112 PPCPs, 26 (23%) were identified in freshwater samples collected close to the waste water source. Detected concentrations were usually in the 1–20 ng/L range and the highest concentrations were found in the high 700 ng/L to 2 µg/L range. Naproxen was found at a maximum level of 199 ng/L in Ontario (Canada) surface freshwater samples, carbamazepine was found at a maximum level of 749 ng/L in Ontario (Canada) surface water samples. However, the

antibiotics lincomycin (maximum 1413 ng/L) and monensin A (maximum 810 ng/L) dominated Ontario surface water samples, and the levels are only slightly lower than in the respective effluent samples (for references see Annex Table A2.8/2).

Freshwater sediment

Of the reported 112 PPCPs, 30 (26%) were identified in freshwater sediment samples. Most data are reported on a wet weight basis. Detected concentrations were usually in the low ng/g ww range and the highest levels were found in the 100 ng/g to 10 µg/g range. Sertraline was found at a maximum of 1 µg/g in sediment from the Faroe Islands. The angiotensin II receptor antagonist losartan was found at 392 ng/g in Icelandic sediment. 17β(beta)-estradiol was found at a maximum level of 302 ng/g in Greenlandic sediment. However, surfactants such as benzalkonium chloride (1.3 µg/g) in Faroe Island sediment and alkyl trimethyl ammonium chloride (1 µg/g) in sediment from Iceland were the dominant PPCPs in freshwater sediments. It was mainly surface-active substances and the less polar compounds that were associated with sediment as the carrier and storage matrix (for references see Annex Table A2.8/2).

Freshwater biota

There was no information on PPCPs in freshwater biota in the available literature.

2.8.6.4 Marine environment

The marine (coastal) environment is considered an important recipient for PPCPs, especially in the Arctic. Most Arctic settlements are located in the coastal zone and so discharge sewage-related waste directly to the adjacent coastal waters.

Seawater

Of the reported 112 PPCPs, 22 (20%) were identified in seawater samples. Detected concentrations were usually in the low ng/L range and the highest in the 10–500 ng/L range. Citalopram (SSRI antidepressant) was found at a maximum level of 612 ng/L in surface seawater from Tromsø (influenced by direct hospital effluent). Carbamazepine was found at a maximum of 47.7 ng/L in Manitoba seawater (Hudson Bay, Canada). The stimulant caffeine was found at concentrations of up to 126 ng/L in receiving seawater samples from Tromsø (Norway) (for references see Annex Table A2.8/2).

Marine sediment

Only one screening study reported PPCPs in marine sediments from the Barents Sea. The substances found were bisphenol A (maximum 11 ng/g dw) and the artificial fragrance musk xylene (maximum 4.1 ng/g dw) (Vorkamp and Rigét, 2014).

Marine biota

Of the reported 112 PPCPs, 11 (10%) were identified in marine biota samples. Detected concentrations were usually in the high pg/g to low ng/g dw range with the highest levels found in the low ng/g range. The siloxanes D5 (maximum 10 ng/g in Icelandic marine mammals) and D6 (maximum 5.2 ng/g in Faroe Island fish) were quantified in a comprehensive Nordic study (Kaj et al., 2005). ATAC type of surfactants were found up to 6.7 ng/g in marine fish from Greenland. The synthetic musks phantolide (2.5 ng/g Ontario), cashmeran (2.5 ng/g in Greenland) and musk tibetene (maximum 6 ng/g in Greenland) were found in polar bear (*Ursus maritimus*) liver tissue (Vorkamp and Rigét, 2014).

Samples of whole polar cod (*Boreogadus saida*) and capelin (*Mallotus villosus*), seal blubber (*Phoca hispida*), kittiwake (*Rissa tridactyla*) and glaucous gull (*Larus hyperboreus*) blood/plasma, and common eider (*Somateria mollissima*) and common guillemot (*Uria aalge*) eggs collected from Arctic Norway in 2010–2011 contained levels of nonylphenol, nonylphenol monoethoxylate, octylphenol, and octylphenol monoethoxylate (OP1EO) below limits of detection (NIVA, 2012). In 2013, Atlantic cod (*Gadus morhua*) fillet and liver from Tromsø harbor (Norway) were screened for several nonylphenol and octylphenol related compounds (NIVA, 2014). All levels were below detection limits, with the exception of 4-*tert*-nonylphenol which was found in liver at 24.2–39.2 ng/g ww. It was mainly personal care products that were reported in biota. No reports of pharmaceuticals in Arctic biota are yet available.

2.8.7 Environmental trends

2.8.7.1 Spatial trends

A qualitative attempt at a first spatial distribution assessment is presented in Table 2.53. Since the majority of PPCP-related compounds are released into the environment via direct application, consumption and/or disposal of consumer products, long-distance distribution processes can mostly

Table 2.53 Maximum concentrations (ng/L) of selected PPCPs in Arctic sewage effluent samples reported for the period 2003–2013.

Location/Region	Ibuprofen	Diclofenac	Acetominophen/ Paracetamol	Sertraline	Paroxetine	Citalopram
Ontario, Canada	4000		740			
Greenland	2800		25 800	2	20.8	192
Iceland	5800	390	8540	299	89.3	69.2
Faroe Islands	4500	597	71 500	23	149	540
Longyearbyen, Svalbard, Norway	403	1074				
Tromsø, Norway	448	48		90	13	102

be excluded as diffusive secondary sources. The regional distribution pattern in the data mainly reflects consumption profiles, population density and mobility, WWTP infrastructure, and local environmental transformation and distribution processes. In addition, as confirmed by studies outside the Arctic region, concentration variability in primary emission sources (sewage, sewage effluent) can be large, spanning several orders of magnitude (Ort et al., 2010). This is dependent on application profile, consumer habits, and seasonality etc. Therefore, the comparison presented here must be considered indicative only. The most frequently reported PPCP compounds were determined in more than four areas (see Table 2.53).

The data are compiled from a comprehensive Nordic screening study, national project reports and several research reports (Lee et al., 2003; Metcalfe et al., 2003; Weigel et al., 2004a; Vasskog et al., 2006, 2008; Kallenborn et al., 2008a,b; Huber et al., 2013) reporting data for the period 2003–2013. As a result, temporal changes in consumption and application, which directly affect release profiles, cannot be inferred from available data.

The data show that for PPCPs consumed in high volumes (i.e. ibuprofen, acetominophen/paracetamol and others), determining factors for the overall concentration in the aquatic environment are population density and product availability (i.e. prescription or purchase over-the-counter) and not necessarily environmental stability and mobility only. The highest concentrations of prescription-free substances (ibuprofen and acetominophen/paracetamol) were found in locations with the highest population density: Ibuprofen (Canada and Iceland) and Acetominophen (Iceland and Faroe Islands), and the lowest in less populated locations (such as Longyearbyen, Svalbard). However, for prescribed compounds the application strategy (dose, oral, injected etc.) may also contribute to the release profile. For diclofenac (usually prescribed as an anti-inflammatory NSAID in northern Europe), the highest concentrations were reported in Longyearbyen (Svalbard). Diclofenac concentrations were much higher in Longyearbyen (2000 inhabitants) than Tromsø (northern Norway, 60 000 inhabitants), an Arctic city with considerably higher population density. Similar profiles were found for prescribed antidepressants (i.e. SSRI agents) where national regulations for drug application schemes influence the respective release profiles (in effluent samples). In Iceland, sertraline is the predominant SSRI in effluent samples, whereas citalopram is the predominant SSRI residue in effluent samples from the Faroe Islands. Detected concentrations were usually in the high pg/g to low ng/g dw range.

2.8.7.2 Temporal trends

Although an impressively high number of PPCP-related substances (n=112) are reported to be present in the Arctic environment, trends over time are not yet available because the data are widely scattered. Most of the available information is based on seasonal screening and research-based studies without a temporal monitoring component (on either an annual or seasonal scale). In addition, method related quality control protocols applied by different laboratories for similar target substances (limited method comparability, no inter-laboratory exercises performed for the respective methods) make it difficult, if not impossible to compare available data along a relevant timeline. At least five years of consecutive monitoring and analyses preferably performed by the same laboratory and under good quality control protocols, are required for a scientifically sound evaluation of temporal trends (Katsoyiannis et al., 2010; Travaglini et al., 2013). None of the data sets reported here fulfil these requirements.

2.8.8 Conclusions

Over the past decade, various national and international research and screening studies have confirmed the presence of PPCPs in the Arctic environment. Although pharmaceutical usage in the Arctic is low compared to densely populated regions of the globe, the lack of modern WWTP installations even in the larger settlements, as well as low ambient temperatures, slow microbiological transformation and no photochemical degradation during winter, results in surprisingly high concentrations of some pharmaceuticals in the Arctic environment (Weigel et al., 2004a,b; Vasskog et al., 2006, 2008; Green et al., 2008; Kallenborn et al., 2008a,b; Gunnarsdottir et al., 2013; Huber et al., 2013).

Pharmaceuticals are designed to express a specific biochemical function at low concentrations as a part of an integrated therapeutic procedure. This biochemical effect, desirable during therapy, may cause unwanted environmental toxicological effects on non-target organisms when the compound is released into the environment. In the Arctic, pharmaceutical residues are released into low- to very low ambient temperatures in receiving aqueous environments which results in a long half-life for most PPCPs released. This is especially critical when significant amounts of antibiotic/antimicrobial agents are released in a low temperature environment and so enhance the potential for resistance against these substances in local microbial communities.

The environmental toxicological consequences of continuous releases into the Arctic environment are expected to differ from those in temperate regions. An impact on human populations due to consumption of contaminated local fish and invertebrates or through exposure to resistant microbial communities cannot be excluded.

Scientific results so far available through published papers and reports must be considered as indicative only. Comprehensive environmental studies on the fate, environmental toxicology and distribution profiles for pharmaceuticals applied in high volumes and released into the aquatic environment under cold northern climate conditions should be given high priority by national and international authorities. This is also necessary to ensure that local food sources can be harvested by future generations of indigenous populations without concern for health and well-being.

Section 2.8 Annex Contents

Section 2.8 Annex

Table A2.8/1 Supplementary information concerning Arctic media and compound groups for which PPCP data have been reported. Abbreviations and data sources listed at the end of the table.

Group Compound	IUPAC	CAS no.	Location identified
NSAIDs			
NSAID general	See below		
Salicyclic acid	2-Hydroxybenzoic acid	69-72-7	Nordic, Can-Ont
Ibuprofen	*RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid*	15687-27-1	Can-Ont, Nor-Tro, Nor-Lon, Nordic
Hydroxy-Ibuprofen	2-[4-(1-Hydroxy-2-methylpropyl)phenyl]propanoic acid	51146-55-5	Nor-Tro, Nor-Lon, Nordic
Carboxy-Ibuprofen	2-[4-(2-Carboxypropyl)phenyl]propionic acid	15935-54-3	Nor-Tro, Nor-Lon, Nordic
Gemfibrozil	5-(2,5-dimethylphenoxy)-2,2-dimethyl-pentanoic acid	25812-30-0	Can-Ont, Can-Man
Naproxen	(S)-2-(6-methoxynaphthalen-2-yl)propanoic acid	22204-53-1	Can-Ont, Can-Man, Nordic
Ketoprofen	RS)-2-(3-benzoylphenyl)propanoic acid	22071-15-4	Can-Ont, Nor-Tro, Nor-Lon, Nordic
Diclofenac	2-(2,6-dichlorophenyl)amino]phenylacetate	15307-86-5	Nor-Tro, Nor-Lon, Nordic, Can-Ont
Indomethacin	[1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl]acetic acid	53-86-1	Can-Ont
Fenoprofen	2-(3-Phenoxyphenyl)propanoic acid	31879-05-7	Can-Ont
Paracetamol/Acetaminophen	4-(Acetylamino)phenol	103-90-2	FI, Ic, Gr, Can-Ont
Antidepressants/SSRI			
Sertraline	(1*S*,4*S*)-4-(3,4-dichlorophenyl)-*N*-methyl-1,2,3,4-tetrahydronaphthalen-1-amine	79617-96-2	Nor-Tro, Nor-Lon, Nordic
Fluoxetine	N-methyl-γ-[4-(trifluoromethyl)phenoxy]benzenepropanamine	54910-89-3	Nor-Tro, Nor-Lon, Nordic
Paroxetine	(3S,4R)-3-[(2H-1,3-benzodioxol-5-yloxy)methyl]-4-(4-fluorophenyl) piperidine	61869-08-7	Nor-Tro, Nor-Lon, Nordic
Citalopram	(RS)-1-[3-(Dimethylamino)propyl]-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile	597-33-8	Nor-Tro, Nor-Lon, Nordic
Fluvoxamine	2-{[(E)-{5-Methoxy-1-[4-(trifluoromethyl)phenyl]pentylidene}amino]oxy} ethanamine	61718-82-9	Nor-Tro, Nor-Lon
Desmethylcitalopram	RS/S)-1-[3-(methylamino)propyl]-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile	144010-85-5	Nor-Tro, Nor-Lon, Nordic
Didesmethylcitalopram	(RS or S)-1-[3-aminopropyl]-1-(4-fluorophenyl)-1,3-dihydroisobenzofuran-5-carbonitrile	1189694-69-5	Nor-Tro, Nor-Lon, Nordic
Norfluoxetine	S)-3-Phenyl-3-[4-(trifluoromethyl)phenoxy]propan-1-amine	126924-38-7	Nor-Tro, Nor-Lon, Nordic
Desmethylsetraline	(1S,4S)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-amine	87857-41-8	Nor-Lon
Venlafaxine	RS)-1-[2-dimethylamino-1-(4-methoxyphenyl)-ethyl]cyclohexanol	93413-69-5	Ala, FI, Ic, Gr
Betablockers			
Acebutolol	(RS)-N-{3-acetyl-4-[2-hydroxy-3-(propan-2-ylamino)propoxy]phenyl} butanamide	37517-30-9	Fin
Atenolol	(RS)-2-{4-[2-Hydroxy-3-(propan-2-ylamino)propoxy]phenyl}acetamide	29122-68-7	Fin, Can-Man, FI, Ic, Gr
Metoprolol	(RS)-1-(Isopropylamino)-3-[4-(2-methoxyethyl)phenoxy]propan-2-ol	51384-51-1	Fin, Can-Man, FI, Ic, Gr
Propranolol	(RS)-1-(1-methylethylamino)-3-(1-naphthyloxy)propan-2-ol	525-66-6	Nor-Tro
Sotalol	(RS)-N-{4-[1-hydroxy-2-(propan-2-ylamino)ethyl]phenyl} methanesulfonamide	3930-20-9	Fin
Calcium channel blocker			
Amlopidine	(RS)-3-ethyl 5-methyl 2-[(2-aminoethoxy)methyl]-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate	88150-42-9	FI, Ic, Gr
ACE-blocker			
Enalaprilat	(2S)-1-[(2S)-2-{[(1S)-1-carboxy-3-phenylpropyl]amino}propanoyl] pyrrolidine-2-carboxylic acid	76420-72-9	FI, Ic, Gr

Table A2.8/1 cont.

Atmosphere		Terrestrial		Freshwater				Marine				Data sources
Air	Snow	Soil	Biota	Sewage	Water	Sediment	Biota	Water	Sediment	Biota	Comments	
				×		× (Gr, Ic, FI)					influent/ effluent	(1), (2), (3), (4), (5), (6)
				×	×	× (Gr, Ic, FI)		×				(1), (4), (5), (6), (7)
				×	×							(6), (7)
				×	×							(6), (7)
				×								(1), (8), (9)
				×	×							(1), (3), (4), (5), (9)
				×								(10)
				×	×							(1), (4), (5), (6), (7)
				×								(1)
												(8)
				× (Gr, FI)	×	× (Gr, Ic, FI						(3), (5)
				×	×			×				(5), (7), (11), (12)
				×	×			×				(5), (7), (11), (12)
				×	×			×				(5), (6), (7), (11), (12)
				×				×				(5), (11), (12)
				×				×				(6), (11), (12)
				×				×				(12)
				×				×				(12)
				×				×				(12)
				×				×				(12)
				×								(5), (13)
				×	×							(14), (15)
				×	×							(5), (9), (14), (15)
				×	×	× (Gr, Ic, FI)						(5), (7), (9), (14), (15)
					×							(7)
				×	×							(14), (15)
				× (Gr, Ic, FI)								(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)

Table A2.8/1 cont.

Group Compound	IUPAC	CAS no.	Location identified
Perindopril	(2S,3aS,7aS)-1-[(2S)-2-{[(2S)-1-ethoxy-1-oxopentan-2-yl]amino} propanoyl]-octahydro-1H-indole-2-carboxylic acid	82834-16-0	FI, Ic, Gr
Perindoprilat	(2S,3aS,7aS)-1-[(2S)-2-{[(1S)-1-carboxybutyl]amino}propanoyl]-octahydro-1H-indole-2-carboxylic acid	95153-31-4	FI, Ic, Gr
Angiotensin II receptor antagonists			
Losartan	2-Butyl-4-chloro-1-{[2'-(1*H*-tetrazol-5-yl)(1,1'-biphenyl)-4-yl]methyl}-1*H*-midazole-5-methanol	124750-99-8	FI, Ic, Gr
Candesartan	2-ethoxy-1-({4-[2-(2H-1,2,3,4-tetrazol-5-yl)phenyl]phenyl}methyl)-1H-1,3-benzodiazole-7-carboxylic acid	139481-59-7	FI, Ic, Gr
Enalapril	(2S)-1-[(2S)-2-{[(2S)-1-ethoxy-1-oxo-4-phenylbutan-2-yl]amino}propanoyl] pyrrolidine-2-carboxylic acid	75847-73-3	FI, Ic, Gr
Antiepileptics			
Carbamazepine	5H-dibenzo[b,f]azepine-5-carboxamide	298-46-4	Fin, Can-Ont Can-Man, FI, Ic, Gr
Antimicrobials/Antiseptics			
Triclosan	5-chloro-2-(2,4-dichlorophenoxy)phenol	3380-34-5	Nor-Tro, Nor-Lon, Nordic, Can-Ont, FI, Ic, Gr
Bronopol	2-bromo-2-nitropropane-1,3-diol	72625-97-9	FI, Ic
Resorcinol	Benzene-1,3-diol	108-46-3	FI, Ic
m-Cresol	3-Methylphenol	108-39-4	FI, Ic
Antibiotics			
Ciprofloxacin	1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-quinoline-3-carboxylic acid	85721-33-1	Fin, FI, Ic, Gr
Ofloxacin	(RS)-7-fluoro-2-methyl-6-(4-methylpiperazin-1-yl)-10-oxo-4-oxa-1-azatricyclo[7.3.1.05,13]trideca-5(13),6,8,11-tetraene-11-carboxylic acid	82419-36-1	Fin
Norfloxacin	1-ethyl-6-fluoro-4-oxo-7-piperazin-1-yl-1H-quinoline-3-carboxylic acid	70458-96-7	Fin
Tetracyclines (sum)	(4S,4aS,6S,12aS)-4-(Dimethylamino)-3,6,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydro-2-tetracencarboxamidhydrochlorid	60-54-8	Nor-Lon, Nordic, Can-Ont
Lincomycin	(2S,4R)-N-[(1R,2R)-2-hydroxy-1-[(2R,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(methylsulfanyl)oxan-2-yl]propyl]-1-methyl-4-propylpyrrolidine-2-carboxamide	154-21-2	Can-Ont, Can-Man, Ala, Nor-Lon
Sulfamethazine	4-amino-N-(4,6-dimethylpyrimidin-2-yl)benzenesulfonamide	57-68-1	Can-Ont, Can-Man
Tylosin	[[(2R,3R,4E,6E,9R,11R,12S,13S,14R) -12- {[3,6-dideoxy-4-O-(2,6-dideoxy-3-C-methyl-α-L-ribo-hexopyranosyl) -3- (dimethylamino)-β-D-glucopyranosyl]oxy}-2-ethyl-14-hydroxy-5, 9,13-trimethyl-8, 16-dioxo-11-(2-oxoethyl)oxacyclohexadeca-4,6-dien-3-yl]methyl 6-deoxy-2,3-di-O-methyl-β-D-allopyranoside		Can-Ont
Erythromycin	(3*R*,4*S*,5*S*,6*R*,7*R*,9*R*,11*R*,12*R*,13*S*,14*R*)-6-(2*S*,3*R*,4*S*,6*R*)-4-(dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy}-14-ethyl-7,12,13-trihydroxy-4-{[(2*R*,4*R*,5*S*,6*S*)--hydroxy-4-methoxy-4,6-dimethyloxan-2-yl]oxy}-3,5,7,9,11,13-hexamethyl-1-oxacyclotetradecane-2,10-dione	114-07-8	Can-Ont, Can-Man
Enrofloxacin	1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid	93106-60-6	Can-Ont
Lincomycin	(2S,4R)-N-[(1R,2R)-2-hydroxy-1-[(2R,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(methylsulfanyl)oxan-2-yl]propyl]-1-methyl-4-propylpyrrolidine-2-carboxamide	154-21-2	Can-Ont
Roxithromycin	[3R,4S,5S,6R,7R,9R,11S,12R,13S,14R)-6-{[(2S,3R,4S,6R)-4-(Dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy}-14-ethyl-7,12,13-trihydroxy-4-{[(2R,4R,5S,6S)-5-hydroxy-4-methoxy-4,6-dimethyloxan-2-yl] oxy}-3,5,7,9,11,13-hexamethyl-10-(2,4,7-trioxa-1-azaoctan-1-ylidene)-1-oxacyclotetradecan-2-one	80214-83-1	Can-Ont
Sulfamethoxazole	4-Amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide	723-46-6	Can-Ont, Can-Man
Monensin Na	4-[2-[5-ethyl-5-[5-[6-hydroxy-6-(hydroxymethyl)-3,5-dimethyl-oxan-2-yl]-3-methyl-oxolan-2-yl]oxolan-2-yl]- 9-hydroxy-2,8-dimethyl-1,6-dioxaspiro[4.5]dec-7-yl]-3-methoxy-2-methyl-pentanoic acid	17090-79-8	Can-Ont
Trimethoprim	5-(3,4,5-Trimethoxybenzyl)pyrimidine-2,4-diamine	738-70-5	Can-Ont, Nor-Lon, Nordic
Sulfmethizole	4-amino-N-(5-methyl-1,3,4-thiadiazol-2-yl)- benzenesulfonamide	144-82-1	Nordic
Additives			
Siloxanes (General)	see below		Nordic
D4	Octamethylcyclotetrasiloxane	556-67-2	Nordic

Table A2.8/1 cont.

Atmosphere		Terrestrial		Freshwater				Marine				Data sources
Air	Snow	Soil	Biota	Sewage	Water	Sediment	Biota	Water	Sediment	Biota	Comments	
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				×	×							(3), (4), (7), (9), (14), (15)
				×	×			×				(1), (6), (7), (8)
				×	×			×				(16)
				×	×			×				(16)
				×	×			×				(16)
				×	×							(14), (15), (17)
				×	×							(14), (15), (17)
				×	×							(14), (15), (17)
				×	×							(3), (6)
					×							(3)
					×							(3), (4), (9)
					×							(3)
					×							(3), (4), (9)
					×							(3)
					×							(3)
					×							(3)
					×							(3), (4), (9), (17)
					×							(3)
				×	×							(3), (4), (6), (9), (17)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
×		×		×	×					×		(18), (19), (20)
×		×		×	×					×		(19)

Table A2.8/1 cont.

Group Compound	IUPAC	CAS no.	Location identified
D5	Decamethylcyclopentasiloxane	541-02-6	Nordic
D6	Dodecamethylcyclohexasiloxane	540-97-6	Nordic
Butylparaben	Butyl 4-hydroxybenzoate	94-26-8	FI, Ic, Gr
Fragrances			
Celestolide	1-[1,1-Dimethyl-6-(2-methyl-2-propanyl)-2,3-dihydro-1H-inden-4-yl] ethanone	13170-00-1	Can-Ont
Phantolide	1-(1,1,2,3,3,6-Hexamethyl-2,3-dihydro-1H-inden-5-yl)ethanone	15323-35-0	Can-Ont
Traseolide	1-(3-Isopropyl-1,1,2,6-tetramethyl-2,3-dihydro-1H-inden-5-yl)ethanone	68140-48-7	Can-Ont
Galaxolide	4,6,6,7,8,8-Hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene	1222-05-5	Can-Ont
Cashmeran			
Tonalide			
Musk Tibetene			
Musk xylene			
Musk keton			
Steroid hormones			
Estrone	(8R,9S,13S,14S)-3-hydroxy-13-methyl- 6,7,8,9,11,12,13,14,15,16-decahydrocyclopenta[a]phenanthren- 17- one	53-16-7	Can-Ont, FI, Ic, Gr
Ethinyl Estradiol (EE2)	19-nor-17α-pregna-1,3,5(10)-trien-20-yne-3,17-diol	57-63-6	Can-Ont, Can-Man, FI, Ic, Gr
Estriol	(16α,17β)-Estra-1,3,5(10)-triene-3,16,17-triol	50-27-1	FI, Ic, Gr
Levothyroxine	(S)-2-Amino-3-[4-(4-hydroxy-3,5-diiodophenoxy)-3,5-diiodophenyl] propanoic acid	51-48-9	FI, Ic, Gr
Estradiol/17b-Estradiol	(8R,9S,13S,14S,17S)-13-methyl-6,7,8,9,11,12,14,15,16,17-decahydrocyclopenta[a]phenanthrene-3,17-diol	50-28-2	Can-Ont, Can-Man, FI, Ic, Gr
Lipid regulators			
Gemfibrozil	5-(2,5-dimethylphenoxy)-2,2-dimethyl-pentanoic acid	25812-30-0	Can-Ont
Fenofibrate	propan-2-yl 2-{4-[(4-chlorophenyl)carbonyl]phenoxy}-2-methylpropanoate	49562-28-9	Can-Ont
clofibric acid	2-(4-Chlorophenoxy)-2-methylpropanoic acid	882-09-7	Can-Ont, FI, Ic, Gr
Illicit drugs			
MDMA (3,4-metylendioxymetamfetamin	(+/−)-*N*,α-dimethyl-3,4-(methylene-dioxy)phenethylamine,	64057-70-1	Fin (Oulo, Rovaniemi)
Metamphetamine	N-methyl-1-phenylpropan-2-amine	537-46-2	Fin (Oulo, Rovaniemi)
Amphetamine	(RS)-1-phenylpropan-2-amine	300-62-9	Fin (Oulo, Rovaniemi)
Cocaine	methyl (1R,2R,3S,5S)-3- (benzoyloxy)-8-methyl-8-azabicyclo[3.2.1] octane-2-carboxylate	50-36-2	Fin (Oulo, Rovaniemi)
Stimulants			
Caffeine	1,3,7-Trimethylpurine-2,6-dione	58-08-2	Nor-Tro, Nor-Lon, Nordic, Canada, Ala
1,7-dimethylxanthine/Paraxanthine	1,7-dimethyl-3H-purine-2,6-dione	611-59-6	Ala
Anti-cancer			
Ifosfamide	N-3-bis(2-chloroethyl)-1,3,2-oxazaphosphinan-2-amide-2-oxide	3778-73-2	Can-Ont
Cyclophosfamide	(RS)-N,N-bis(2-chloroethyl)-1,3,2-oxazaphosphinan-2-amine 2-oxide	50-18-0	Can-Ont
Surface tension supressors			
Quaternary ammonium compounds (QACs)	see below		Nordic (FI, Gr, Ic
ATAC	hexadecyl(trimethyl)azanium	112-02-7	FI, Ic, Gr
BAC	dimethyldioctadecyl-ammonium bromide	3700-67-2	FI, Ic, Gr
DDAC	didecyldimethylammonium chloride	713-51-5	FI, Ic, Gr
Sodium dodecyl sulphate (SDS)	Sodium lauryl sulfate	151-21-3	FI, Ic, Gr
Sodium laureth sulphate (SDSE-1-14)	Sodium lauryl ether sulfate	9004-82-4	FI, Ic, Gr

Table A2.8/1 cont.

Atmosphere		Terrestrial		Freshwater				Marine				Data sources
Air	Snow	Soil	Biota	Sewage	Water	Sediment	Biota	Water	Sediment	Biota	Comments	
×		×		×	×					×		(19)
×		×		×	×					×		(19)
				× (Gr, Ic, FI)								(19)
				×	×					×		(8), (21)
				×						×		(8), (21)
				×	×					×		(8), (21)
				×	×					×		(8), (21)
										×		(8), (21)
										×		(8), (21)
										×		(21)
									×			(22)
												(22)
				×		× (Gr, Ic, FI)						(5), (8)
					×	× (Gr, Ic, FI)						(5), (9)
				×	×							(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				×	×							(3), (4), (8)
												(8)
				×	×							(4), (7), (8)
				×								(23)
				×								(23)
				×								(23)
				×								(23)
				×	×							(6), (7), (13)
				×								(13)
												(4)
												(4)
				× (Gr, Ic, FI)	× (Ic, FI)	× (Gr, FI)	× (Gr, FI)					(24)
				× (Gr, Ic, FI)	× (Gr, Ic, FI)	× (Gr, FI)	× (Gr, FI)					(5), (24)
				× (Gr, Ic, FI)	× (Gr, Ic, FI)	× (Gr, FI)	× (Gr, FI)					(24)
				× (Gr, Ic, FI)	× (Gr, Ic, FI)	× (Gr, FI)	× (Gr, FI)					(24)
				× (Gr, Ic, FI)	× (Gr, Ic, FI)	× (Gr, FI)						(5)
				× (Gr, Ic, FI)	× (Gr, Ic, FI)	× (Gr, FI)						(5)

Table A2.8/1 cont.

Group Compound	IUPAC	CAS no.	Location identified
Cocoamidopropyl betaine (CAPB)	{[3-(Dodecanoylamino)propyl](dimethyl)ammonio}acetate	61789-40-0	FI, Ic, Gr
Hypnotics			
Lidocaine	2-(diethylamino)-2-(diethylamino)-N-(2,6-dimethylphenyl)acetamide	137-58-6	FI, Ic, Gr
Antidiabetics			
Metformin	N,N-Dimethylimidodicarbonimidic diamide	657-24-9	FI, Ic, Gr
Gliclazide	N-(hexahydrocyclopenta[c]pyrrol-2(1H)-ylcarbamoyl)-4-methylbenzenesulfonamide	21187-98-4	FI, Ic, Gr
Anticoagulant			
Warfarin	(RS)-4-Hydroxy-3-(3-oxo-1-phenylbutyl)- 2H-chromen-2-one	81-81-2	FI, Ic, Gr
Dipyridamole	2,2',2",2'"-(4,8-di(piperidin-1-yl)pyrimido[5,4-d]pyrimidine-2,6-diyl) bis(azanetriyl)tetraethanol	58-32-2	FI, Ic, Gr
Diuretics			
Furosemide	4-chloro-2-(furan-2-ylmethylamino)- 5-sulfamoylbenzoic acid	54-31-9	FI, Ic, Gr
Hydrochlorothiazide	6-chloro-1,1-dioxo-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide	58-93-5	FI, Ic, Gr
Bendroflumethiazide	3-Benzyl-1,1-dioxo-6-(trifluoromethyl)-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide	73-48-3	FI, Ic, Gr
Amiloride	3,5-diamino-6-chloro-N-(diaminomethylene)pyrazine-2-carboxamide	2609-46-3	FI, Ic, Gr
Complexation agents			
EDTA	2-({2-[Bis(carboxymethyl)amino]ethyl}(carboxymethyl)amino)acetic acid	94108-75-5	FI, Ic, Gr
UV-filters			
Benzophenone-3 (BP3)	Diphenylmethanone	131-57-7	Nor
Ethylhexylmethoxycinnamate (EHMC)	(*RS*)-2-Ethylhexyl (2*E*)-3-(4-methoxyphenyl)prop-2-enoate	5466-77-3	Nor
Octocrylene (OC)	2-ethylhexyl 2-cyano-3,3-diphenyl-2-propenoate	6197-30-4	Nor
Bisphenol-monomers			
4,4'-methylenebisphenol (4,4-BPF)	4,4'-Methylenediphenol	620-92-8	Nor
2,2'-methylenebisphenol (2,2-BPF)	2,2'-Methylenebis[4-methyl-6-(2-methyl-2-propanyl)phenol]	2467-02-9	Nor
Bisphenol A	4,4'-(propane-2,2-diyl)diphenol	80-05-7	Can-Ont
4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene] bisphenol (BPAF)	4,4'-(1,1,1,3,3,3-Hexafluoro-2,2-propanediyl)diphenol	1478-61-1	Nor
4,4'-(diphenylmethylene)bisphenol (BP-BP)	4,4'-(2,2-Propanediyl)diphenol	1844-01-5	Nor
Artificial sweeteners			
Cyclamate	cyclohexylsulfamic acid	139-05-9	FI, Nor, Ic
Sucralose	1,6-Dichloro-1,6-dideoxy-β-D-fructofuranosyl-4-chloro-4-deoxy-α-D-galactopyranoside	56038-13-2	FI, Nor, Ic

Abbreviations. Ala: Alaska, Can-Ont: Canada (Ontario); Can-Man: Canada (Manitoba); Gr: Greenland; Ic: Iceland; FI: Faroe Islands; Fin: Finland; Nor-Tro: Norway (Tromsø); Nor-Lon: Norway (Svalbard, Longyearbyen).

Data sources: (1) Lee et al. 2003, (2) Lindqvist et al. 2005, (3) Kleywegt et al. 2011, (4) Metcalfe et al. 2003, (5) Huber et al. 2013 (Nordic), (6) Kallenborn et al. 2008a, (7) Weigel et al. 2004a, (8) Lishman et al. 2006, (9) Carlson et al. 2013, (10) Lee et al. 2003, (11) Vasskog et al. 2006, (12) Vasskog et al. 2008, (13) Mutter 2014, (14) Vieno et al. 2007, (15) Vieno et al. 2007, (16) Dye et al. 2007 (Nordic study), (17) Lindberg et al. 2005, (18) Huber et al. 2015, (19) Kaj et al. 2005 (Nordic), (20) Krogseth et al. 2013a, (21) Vorkamp et al. 2004a, (22) Bakke et al. 2008, (23) Kankaanpää et al. 2014, (24) Kaj et al. 2014 (Nordic study), (25) Thomas et al. 2014 (Norway), (26) Remberger et al. 2013.

Table A2.8/1 cont.

Atmosphere		Terrestrial		Freshwater				Marine				Data sources
Air	Snow	Soil	Biota	Sewage	Water	Sediment	Biota	Water	Sediment	Biota	Comments	
				× (Gr, Ic, FI)	× (Gr, Ic, FI)	× (Gr, FI)						(5)
				× (Gr, Ic, FI)								(5)
				× (Gr, Ic, FI)								(5)
				× (Gr, Ic, FI)								(5)
				× (FI)								(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (Gr, Ic, FI)						(5)
				× (Gr, Ic, FI)		× (FI)						(5)
				× (Nor)								(25)
				× (Nor)								(25)
				× (Nor)								(25)
				× (Nor)								(25)
				× (Nor)								(25)
				× (Nor)		× (Can-Ont)			×			(3), (22), (25)
				× (Nor)								(25)
				× (Nor)								(25)
				× (Nor, Ic, FI)	× (Nor, Ic, FI)							(26)
				× (Nor, Ic, FI)	× (Nor, Ic, FI)							(26)

Table A2.8/2 Supplementary information concerning Arctic media and compound groups for which PPCP data have been reported. Abbreviations and data sources listed at the end of the table.

Characteristics			Terrestrial	Freshwater		
Group Compound	Location	Air, ng/m^3	Soil, ng/g	Sewage influent, ng/L	Sewage effluent, ng/L	Sewage sludge, ng/g
NSAID						
General						
Salicyclic acid	Can-Ont, FI, Ic, Gr			150–87 4000 (Can-Ont), <MDL–30 500 (Ic), 21 700–38 400 (FI)	3600 (med, Can-Ont), <MDL–6030 (Ic), 605–1050 (Gr)	
Ibuprofen	Can-Ont, Nor-Tro, FI, Ic, Gr			38 700 (med, Can-Ont), 1.62–48 800 (Ic), 10.2–3530 (FI), <MDL–6050 (Gr)	<MDL–4000 (med, Can-Ont), <MDL–5800 (Ic), 3380–4500 (FI), 2810 (Gr), 448 (Nor-Tro), 30–403 (Nor-Lon)	
Hydroxy-Ibuprofen	Nor-Tro				3614 (Nor-Tro), 8–1298 (Nor-Lon)	50–5010 (Nor-Tro)
Carboxy-Ibuprofen	Nor-Tro				70 170 (Nor-Tro), 411–34 028 (Nor-Lon)	4–18 400 (Nor-Tro)
Gemfibrozil	Can-Ont, Can-Man			700 (med, Can-Ont)	<MDL–0.54	
Naproxen	Can-Ont, Can-Man			1.1–6.06,1300 (med, Can-Ont), 175–109 000 (Ic), <MDL–102 (FI)	0.21–1.21, 12 500 (med, Can-Ont), 525–1920 (Ic), <MDL–7.88 (FI)	
Ketoprofen	Can-Ont			5700 (med, Can-Ont)	0.03–0.15	
Diclofenac	Can-Ont, Nor-Tro, Nor-Lon, FI, Ic, Gr			0.03–0.2, 1300 (med, Can), 24.3–697 (Ic), 58.8–190 (FI)	0.02–0.21, 0.1–0.2 (northern Swe), 33.4–390 (Ic), 1.84–597 (FI), <MDL–3.55 (FI), <MDL–48 (Nor-Tro), 30–1074 (Nor-Lon)	
Indomethacin	Can-Ont			0.05–0.2	0.03–0.24	
Fenoprofen	Can-Ont			1800 (med, Can)		
Acetaminophen/Paracetamol	FI, Ic, Gr, Can-Ont			9790–251 000 (Ic), 42.3–506 000 (FI), <MDL–698 (Gr), 0.37–3.24 (Can-Ont)	3660–8540 (Ic), 40 300–71 500 (FI), 20 600–25 800 (Gr), 0.03–0.74 (Can-Ont)	
Fenoprofen	Ontario (Can)			1800 (med, Can-Ont)		
Pentoxyfylline	ontario (Can)				250 (med, Can-Ont)	
SSRI						
Sertraline	Arctic Norway and Svalbard, FI, Ic, Gr			9.4, <MDL–121 (Ic), <MDL–2.10 (FI), <MDL–7.09 (Gr)	3.7–14.6, 33.5–299 (Ic), <MDL–22.7 (FI), <MDL–1.96 (Gr), 8–90 (Nor-Tro),	33.6–141 (Ic), <MDL–28.8 (Gr)
Fluoxetine	Arctic Norway and Svalbard, FI, Ic, Gr			1.4, <MDL–382 (Ic),	0.6–3.9, <MDL–5.29 (Ic), 3.46–30.6 (FI)	7.05–49.4 (Ic), <MDL–0.13 (Gr)
Paroxetine	Arctic Norway and Svalbard, FI, Ic, Gr			11.5–12.9 (Nor-Tro), 70.9–783 (Ic), <MDL–91.5 (FI), <MDL–1.76 (Gr),	1.9–11.7, 3.04–89.5 (Ic), <MDL–149 (FI), 2.7–20.8 (Gr), 3–13 (Nor-Tro)	6.72–27.4 (Ic), 49.4–120 (FI)
Citalopram	Arctic Norway and Svalbard, FI, Ic, Gr			101.5, 130–1040 (Ic), 0.61–151 (FI), <MDL–6.25 (Gr), 62.9–303.6 (Nor-Tro)	24.9–89.3, 12.2–69.2 (Ic), 101–540 (FI), 130–192 (Gr), 63–102 (Nor-Tro), 24.9–64.1 (Nor-Tro)	46,1–86.7 (Ic), 255–383 (FI), 51.6 (Gr)
Fluvoxamine	Nor-Sva, Nor-Tro			0.8	<MDL–2.4, 1.5 (Nor-Tro), 0.8–1.7 (Nor-Tro),	

Table A2.8/2 cont.

Freshwater			Marine			Comments	Data source
Sewage, ng/L	Water, ng/L	Sediment, ng/g	Water, ng/L	Sediment, ng/g	Biota, ng/g		
							(1: Canada)
110–535 (Ic), 162 (Gr), 159 (FI)		7.69 (FI)					(2: Can-Ont), (3: Nordic)
0.3–17 (Ala), 0.02–0.38 ug/L (Nor-Tro), 15.8–130 (Ic), 53.5 (FI), 48.2 (Gr)	0.5–79 (Can-Ont)	2.57 (Ic), 0.18 (Gr)	0.15–0.6 (Nor-Tro), 0.4–1 (Nor-Lon)				(2: Can-Ont), (3: Nordic), (4: Can-Ont), (5: Ala), (6: Can), (7)
			0.21–1.32 (Nor-Tro), 2–34 (Nor-Lon)				(7)
			0.07–1.63 (Nor-Tro), 6–26 (Nor-Lon)				(7)
	1–9 (Can-Ont)		<MDL–40.6 (Can-Man)				(1), (2: Can-Ont), (4: Can-Ont), (8: Can-Man)
01.3–120 (Ic), 0.32 (FI)	2–199 (Can-Ont)	0.85 (Ic)	<MDL–2.1				(1: Can), (2), (3: Nordic), (4: Can-Ont), (8: Can-Man)
							(1: Can), (2: Can-Ont), (9: Nordic)
0.006–4.47 (Nor-Tro), 1.65–19.4 (Ic), 26.9 (FI)		0.26–1.04 (Ic), 0.26 (FI), 0.19 (Gr)	0.03 (Nor-Tro), 1–4 (Nor-Lon)				(1: Can), (2: Can-Ont), (3: Nordic), (7)
							(2: Can-Ont)
	17						(1: Can), (4: Can-Ont)
22.4 (FI), 85.2 (Gr), 1.2–27 (Ala)							(2: Can-Ont), (4: Can-Ont), (5: Ala), (3: Nordic)
100 (Nor-Tro),		28.1 (Ic), 418–1070 (FI), 0.16–0.27 (Gr)	0.9–16.3*				(3: Nordic), (7), (10: Nor), (11: Nor)
		10.8 (Ic), 0.16–0.27 (Gr)	<MDL–2.4*				(3: Nordic), (7), (10: Nor), (11: Nor)
20 (Nor-Tro)		6.91 (Ic), <MDL–0.34 (FI), <MDL–1.15 (Gr)	0.5–12.3*, 0.6–14 (Nor-Lon)				(3: Nordic), (7), (10: Nor), (11: Nor)
		44.2–82.2 (Ic), 0.14–0.82 (FI), 1.2–3.69 (Gr)	9.2–612*				(3: Nordic), (10: Nor), (11: Nor)
			0.04–2.4*				(10: Nor), (11: Nor), (12)

Table A2.8/2 cont.

Characteristics			Terrestrial	Freshwater		
Group Compound	Location	Air, ng/m^3	Soil, ng/g	Sewage influent, ng/L	Sewage effluent, ng/L	Sewage sludge, ng/g
Desmethylcitalopram	Nor-Sva, Nor-Tro			118–425.7 (Nor-Tro)	<MDL–10.6, 118–215 (Nor-Tro), 36.3–300.5 (Nor-Tro)	
Didesmethylcitalopram	Nor-Sva, Nor-Tro			5.6–20 (Nor-Tro)	0.9–8.5, 6–10 (Nor-Tro), 0.9–10 (Nor-Tro)	
Norfluoxetine	Nor-Sva, Nor-Tro			2.5	<MDL–2.4, 0.7–2.6 (Nor-Tro)	
Desmethylsetraline	Nor-Sva, Nor-Tro			<MDL	<MDL–10.6	
Venlafaxine	Ala, FI, Ic, Gr			29.3–30 200 (Ic), 0.54–1071 (FI), <MDL–5.58 (Gr)	24–149 (Ic), 647–746 (FI), 21.3–1020 (Gr)	48.5–11 400 (Ic), 53.4–282 (FI), 7.01–20.6 (Gr)
Bupropion	Ala					
Betablockers						
Acebutolol	Fin			390–510	80–280	
Atenolol	Fin, Can-Man, FI, Ic, Gr			510–800, 501–1650 (Ic), <MDL–36.8 (FI)	40–440, 707–1730 (Ic), <MDL–188 (FI), <MDL–470 (Gr)	
Metoprolol	Fin, Can-Man, FI, Ic, Gr			980–1350, 14.3–350 (Ic), <MDL–319 (FI), <MDL–2.16 (Gr)	910–1070, <MDL–135(Ic), 356–810 (FI), 136–251 (Gr)	549 000 (Ic), 108 000 (FI), 41 400 (Gr)
Propranolol	FI, Ic, Gr					
Sotalol	Fin			640–830	160–300	
Calcium channel blockers						
Amlodipine	Faroe Islands, Iceland, Greenland			<MDL–11.4 (IS), <MDL–247 (FO),	<MDL–72.9 (IS), 98.1–448 (FO), 12.8–121 (GL)	
ACE–blocker						
Enalaprilat	FI, Ic, Gr			<MDL–26.2 (Ic),	10.1–27.9 (IS)	
Perindopril	FI, Ic, Gr			<MDL–190 (Ic), <MDL–18.4 (FI)	<MDL–11.8 (FI)	0.13–1.05 (FI)
Perindoprilat	FI, Ic, Gr			>MDL–2.98 (Ic), <MDL–2.49 (FI), <MDL–2.91 (Gr)	<MDL–2.90 (Ic), <MDL–13.3 (FI)	
Angiotensin II receptor antagonists						
Losartan	FI, Ic, Gr			189–8700 (Ic), <MDL–98.5 (FI), <MDL–5.03 (Gr)	162–327 (Ic), 22.9–292 (FI), 21.5–165 (Gr)	22.9–39.9 (Ic), 14.4–33 (FI), 1.8–1.92 (Gr)
Candesartan	FI, Ic, Gr			<MDL–1040 (Ic), <MDL–53.8 (FI)	<MDL–64.8 (Ic), 111–251 (FI)	<MDL–49.7 (FI)
Enalapril	FI, Ic, Gr			<MDL–522 (Ic), <MDL–112 (FI), <MDL–2.98 (Gr)	1.58–22.7 (Ic), 57.4–135 (FI)	<MDL–2.39 (Ic), 0.13–1.05 (FI), 26.1–322 (Gr)
Antiepileptics						
Carbamazepine	Fin, Can-Ont, Can-Man, FI, Ic, Gr			290–310, 700 (med, Can-Ont)	380–470, 700 (med, Can-Ont)	
Bezafibrate	Can-Ont			600 (med, Can-Ont)	200 (med, Can-Ont)	
Antibacterials/Antiseptics						
Triclosan	Can-Ont, FI, Ic, Gr			0.37–3.24	0.03–0.74, 0.04–0.13 (FI), 350 (Nor-Tro), 28–803 (Nor-Lon)	
Bronopol	FI, Ic					
Resorcinol	FI, Ic			<MDL–0.05 (FI)		
m-Cresol	FI, Ic		96 (FI)			

Table A2.8/2 cont.

Freshwater			Marine			Comments	Data source
Sewage, ng/L	Water, ng/L	Sediment, ng/g	Water, ng/L	Sediment, ng/g	Biota, ng/g		
							(11: Nor), (12)
							(11: Nor), (12)
							(11: Nor), (12)
							(11: Nor), (12)
		73.6 (Ic), <MDL–0.3 (FI), 1.68–2.97 (Gr)					(3: Nordic), (5: Ala)
0.23–0.84 (Ala)							(5: Ala)
	<MDL–8						(13: Fin), (14: Fin)
161–1650 (Ic), 9.82–13.4 (FI),	<MDL–25	58.6 (Ic)	<MDL–15.2 (Can-Man)				(3: Nordic), (13: Fin), (14: Fin)
270 (Nor-Tro)	<MDL–116	62.8 (Ic), 7.39 (Gr)	<2.11 (MDL) (Can-Man), 0.7 ug/L (Nor-Tro)				(3: Nordic), (7), (8: Can-Man), (13: Fin), (14: Fin)
0.34 µg/L (Nor-Tro)			0.01 µg/L (Nor-Tro)				(3: Nordic), (7)
	<MDL–52						(13: Fin), (14: Fin)
13.1 ng/L (IS), 214–286 ng/L (FO), 37.5–45.7 ng/L (GL)		9.58 (IS), 1.47 (GL)					(3: Nordic)
		2.13 (IS)					(3: Nordic)
							(3: Nordic)
							(3: Nordic)
		392 (Ic)					(3: Nordic)
							(3: Nordic)
							(3: Nordic)
0.27 (Nor-Tro)	<MDL–66 (Fin), 1–749 (Can-Ont)		<MDL–47.1 (Can-Man)				(1: Can), (3: Nordic), (4: Can-Ont), (7), (13: Fin), (14: Fin)
	0.5–3.6 (Can-Ont)						(2: Can), (4: Can-Ont)
44 (FI), <MDL–79 (Ic), 0.69–2.38 (Nor-Tro)			0.16–0.48 (Nor-Tro), 2–23 (Nor-Lon)				(2: Can-Ont), (3: Nordic), (7)
							(15: Nordic)
219 (FI), <MDL–107(Ic)			0.01–0.08 (Ic)				(15: Nordic)
106 (FI)							(15: Nordic)

Table A2.8/2 cont.

Characteristics		Terrestrial		Freshwater		
Group Compound	Location	Air, ng/m^3	Soil, ng/g	Sewage influent, ng/L	Sewage effluent, ng/L	Sewage sludge, ng/g
Antibiotics						
Ciprofloxazine	Fin, FI, Ic, Gr					
Ofloxazine	Fin			<MDL–130	<MDL–50	
Norfloxazine	Fin					
Tetracyclines	Can-Ont, Nor-Lon				0.6–11 (Nor-Lon)	
Lincomycin	Can-Ont					
Sulfamethazine	Can-Ont, Can-Man					
Tylosin	Can-Ont					
Erythromycin	Can-Ont, Can-Man					
Enrofloxacin	Can-Ont					
Lincomycin	Can-Ont					
Roxithromycin	Can-Ont					
Sulfamethoxazole	Can-Ont, Can-Man					
Trimethoprim	Can-Ont, Can-Man, Ala, Nor-Lon				0.07–0.15 (Nor-Lon)	
Monensin Na	Can-Ont					
Additives						
Siloxanes (General)	Nordic					
Fluorinated Siloxanes	Nor-Tro					
D3	Nor_Sva	<MDL–2.8				
D4	Ic, FI	2.1–4 (FI), 0.3–2.1(Ic), <MDL–2.13 (Nor-Sva)				
D5	Ic, FI	0.9–2.4 (FI), 0.1–1.6 (Ic), <MDL–3.74 (Nor-Sva)				
D6	Ic, FI	0.39–2.1 (FI), 0.08–0.57 (Ic), 0.11–0.82 (Nor-Sva)				
Butylparabene	FI, Ic, Gr			0.016–0.048 (Ic), <MDL–0.053 (FI),	0.021–0.054 (Ic), 0.012–0.025 (FI), 0.081–0.109 (Gr)	<MDL–440 (Ic), 5–22.8 (FI)
Fragrances						
Celestolide	Can-Ont, Gr, FI					
Phantolide	Can-Ont					
Traseolide	Can-Ont					
Galaxolide	Can-Ont					
Cashmeran	Gr, FI Islands					
Tonalide	Can-Ont					
Musk tibetene	Gr, FI					
Musk xylene	Gr, FI					
Musk ketone	Gr, FI					
Steroid hormones						
Estrone	Can-Ont, FI, Ic, Gr			2.04–141 (Ic), 1.69–11.6 (FI), <MDL–2.09 (Gr)	<MDL–13.3 (Ic), 7.44–18.5 (FI), 7.82–21 (Gr)	17.9–18.8 (Ic), 15.4–61.4 (FI), 6.89–210 (Gr)

Table A2.8/2 cont.

Freshwater			Marine			Comments	Data source
Sewage, ng/L	Water, ng/L	Sediment, ng/g	Water, ng/L	Sediment, ng/g	Biota, ng/g		
	<MDL–25						(13: Fin), (14: Fin), (16: Swe)
	<MDL						(13: Fin), (14: Fin), (16: Swe)
	<MDL						(13: Fin), (14: Fin), (16: Swe)
	5–35 (Can-Ont)					dry weight	(4: Can-Ont)
	0.5–143 (Can-Ont)						(4: Can-Ont)
	1–34 (Can-Ont)		<MDL–8.8 (Can-Man)				(4: Can-Ont), (8: Can-Man)
	5–39 (Can-Ont)						(4: Can-Ont)
	10–145 (Can-Ont)		< 3.0 (MDL (Can-Man)				(4: Can-Ont), (8: Can-Man)
	5–13 (Can-Ont)						(4: Can-Ont)
	0.5–1413 (Can-Ont)						(4: Can-Ont)
	5–66 (Can-Ont)						(4: Can-Ont)
0.2–5 (Ala)	1–34 (Can-Ont)		<MDL–9.2 (Can-Man)				(4: Can-Ont), (5: Ala), (8: Can-Man), (16: Swe)
0.5–1 (Ala),	1–25 (Can-Ont)		<MDL–4.4 (Can-Man)				(4: Can-Ont), (8: Can-Man), (5: Ala), (16: Swe)
	10–810 (Can-Ont)						(4: Can-Ont)
					3.4	dry weight	(3: Nordic), (17: Nordic)
							(18)
					2.9–3.7 (Nor-Sva)		(19), (20)
190 (FI), 96–120 (Ic)	<MDL–1.1 (Ic)				2.6–3.2 (Nor-Sva)		(17: Nordic), (19), (20)
4300 (FI), 1100–1600 (Ic)	<MDL–5.2 (FI), <MDL–5.4 (Ic)				<MDL–10 (mammals)		(17: Nordic), (19)
1000 (FI), 220–240 (Ic)	<MDL–0.33 (FI), <MDL–1.3 (Ic)				<MDL–5.2 (FI, fish)		(17: Nordic), (19)
		<MDL–93 (FI)					(3: Nordic)
							(21), (22), (23)
					2.5 (PB)		(21), (22), (23)
							(21), (22), (23)
							(21), (22), (23)
					2.5 (PB)		
							(21), (22)
					2.5–6 (PB)		(23)
				2.8–4.1 (Barents Sea)			(23)
							(23), (24)
		1.11 (Ic), <MDL–1.42 (FI), <MDL–0.8 (Gr)					(21)

Table A2.8/2 cont.

Characteristics		Terrestrial		Freshwater		
Group Compound	Location	Air, ng/m^3	Soil, ng/g	Sewage influent, ng/L	Sewage effluent, ng/L	Sewage sludge, ng/g
Estradiol/Ethinyl estradiol (EE2)	Can-Ont, Can-Man, FI, Ic, Gr				<3 (MDL)	
Levothyroxine	FI, Ic, Gr			<MDL–2.74 (Ic)	<MDL–1.72 (Ic), <MDL–1.72 (FI)	<MDL–2.26 ng/g (IS), 1.32–1.48 ng/g (FO)
17b-Estradiol	FI, Ic, Gr			<MDL–474 (Ic), <MDL–75.9 (FI)	<MDL–249 (Ic), 342–375 (Gr)	58.8–77.7 ng/g (IS), 6.4 ng/g (FO)
Lipid regulators						
Fenofibrate	Can-Ont					
Clofibric acid	Can-Ont, FI, Ic, Gr					
Illicit drugs						
MDMA (3,4-metylendioxymetamfetamin)	Fin-Oul, Fin-Rov				30–100 (Fin-Oul, Fin-Rov)	
Metamphetamine	Fin-Oul, Fin-Rov				20–100 (Fin-Oul, Fin-Rov)	
Amphetamine	Fin-Oul, Fin-Rov				20–100 (Fin-Oul, Fin-Rov)	
Cocaine	Fin-Oul, Fin-Rov				<MDL (Fin-Oul, Fin-Rov)	
Stimulants						
Caffeine	Ala				501–5074 (Nor-Lon)	
1,7-dimethylxanthine	Ala					
Anti-cancer						
Ifosfamide	Can-Ont					
Cyclophosfamide	Can-Ont					
Surfactants						
Quatarnary Ammonium Compounds (QACs)	FI, Gr, Ic					
ATAC	FI, Gr, Ic			1.3–61 (Ic), <MDL–87 (FI), <MDL–7.5 (Gr)	<MDL–13 000 (FI), 34–6800 (Gr), 41–2000 (Ic); 1.3–61 (Ic); 1.6–31 (Ic), 5.2–29 (FI), 3.4–3.8 (Gr)	4000–680 000 (Ic); 44 000–79 000 (FI), 1700–76 000 (Gr)
BAC	FI, Gr, Ic				<MDL–18 000 (FI), 13–60 000 (Gr), 390–6800 (Ic)	
DDAC	FI, Gr, Ic				<MDL–1300 (FI), <MDL–15 000 (Gr), 2.5–25 000 (Ic)	
Sodium dodecyl sulphate (SDS)	FI, Gr, Ic			1.6–4.1 (Ic), 0.13–7.9 (FI), <MDL–0.41 (Gr)	0.79–4.2 (Ic), 0.79–5.6 (FI), 0.96–2.4 (Gr)	
Sodium laureth sulphate (SDSO-1-14)	FI, Gr, Ic			2.7–970 (Ic), 0.28–510 (FI), <MDL–19 (Gr)	0.84–67 (Ic), 33–120 (FI), 330–450 (Gr)	510–17 000 (Ic), 4300–180 000 (FI), 20 000–40 000 (Gr)
Cocoamidopropyl betaine (CAPB)	FI, Gr, Ic			<MDL–22 (Ic), <MDL–0.27 (FI), <MDL–7.5 (Gr)	<MDL–5.5 (Ic), <MDL–47 (FI), 85–89 (Gr)	
t-nonylphenol						
4-t-nonylphenol						
4-n-nonylphenol						
Nonylphenol monoethoylate						
4-t-octylphenol						
4-n-octylphenol						
Octylphenol monoethoxylate						

Table A2.8/2 cont.

Freshwater			Marine			Comments	Data source
Sewage, ng/L	Water, ng/L	Sediment, ng/g	Water, ng/L	Sediment, ng/g	Biota, ng/g		
			<4.5 (MDL)				(8: Can-Man)
		<MDL–1.68 (FI)					(3: Nordic)
		302 (Gr)					(3: Nordic)
							(21)
							(1: Can), (21)
						mg/1000p/d	(25)
						mg/1000p/d	(25)
						mg/1000p/d	(25)
						mg/1000p/d	(25)
0.2–112 (Ala), 20.3–293 (Nor-Tro)			30.2–126 (Nor-Tro), 24–41 (Nor-Lon)				(5: Ala), (7)
23.–54 (Ala)							(5: Ala)
							(1: Can)
							(1: Can)
							(3: Nordic), (26: Nordic)
140–9300 (FI), 160–15 000 (Ic)		<MDL–1300 (FI), 0.5–28 (Gr), 1000 (Ic), <MDL–340 (FI),<MDL–190 (Gr)			<MDL–7.6 (FI), <MDL–6.7 (Gr)		(3: Nordic), (26: Nordic)
450–20 000 (FI), 110–23 000 (Ic)		13–1300 (FI), 0.4–320 (Gr)			<MDL–4.8 (FI),<MDL–1.4 (Gr)		(26: Nordic)
67–50 000 (FI), 2.5–25 000 (Ic)		0.5–480 (FI), 0.16–51 (Gr)			MDL–1.3 (FI), <MDL–0.53 (Gr)		(26: Nordic)
210–3100 (Ic), 1000–1100 (FI), 580–2000 (Gr)		110 (Ic), <MDL–93 (FI)					(3: Nordic)
		360 (Ic)					(3: Nordic)
510–5000 (Ic), 350–630 (FI), 2100–2300 (Gr)		360 (Ic)					(3: Nordic)
					< MDL (Nor)		(27)
					24.2–39.2 ng/g ww (Nor)		(28)
					< MDL (Nor)		(27), (28)
					< MDL (Nor)		(27)
					< MDL (Nor)		(27), (28)
					< MDL (Nor)		(27), (28)
					< MDL (Nor)		(27)

Table A2.8/2 cont.

Characteristics		Terrestrial		Freshwater		
Group Compound	Location	Air, ng/m³	Soil, ng/g	Sewage influent, ng/L	Sewage effluent, ng/L	Sewage sludge, ng/g
Hypnotics						
Lidocaine	FI, Ic, Gr			1.16–144 (Ic), <MDL–183 (FI), <MDL–0.86 (Gr)	>MDL–5.25 (Ic), <MDL–2.97 (FI), 0.64 (Gr),	
Antidiabetics						
Metformin	FI, Ic, Gr			<MDL–59 000 (Ic), <MDL–9660 (FI), <MDL–62 (Gr)	234–4830 (Ic), 7560–7950 (FI), 3580–5900 (Gr)	
Glicazide	FI, Ic, Gr			<MDL–538 (Ic), <MDL–3.68 (FI)	22.6–29.6 (FI)	0.56 (Gr)
Anticoagulant						
Warfarin	FI, Ic, Gr			<MDL–1.48 (Ic), <MDL–3.21 (FI)	<MDL–0.83 (Ic)	<MDL–0.83 (FI)
Dipyridamole	FI, Ic, Gr			836–69 600 (Ic), <MDL–166 000 (FI), 4630 (Gr)	64.8–12 500 (Ic), 1700–24 600 (FI)	29.7–55.6 (Ic), 1330–1880 (FI), 3.26–326 (Gr)
Diuretics						
Furosemide	FI, Ic, Gr			237–1250 (Ic), <MDL–532 (FI), <MDL–48.6 (Gr)	120–909 (Ic), 1140–11 400 (FI), 47.3–87.3 (Gr)	2.23–38.8 (Ic), 97.7–686 (FI), 2.96–6.18 (Gr)
Hydrochlorothiazide	FI, Ic, Gr			232–1960 (Ic), <MDL–90.4 (FI)	410–984 (Ic), <MDL–354 (FI), 6.26–22.6 (Gr)	<MDL–168 (Ic), <MDL–7.52 (FI)
Bendroflumethiazide	FI, Ic, Gr			<MDL–1.23 (Gr)	<MDL–1.26 (Ic), MDL–7.00 (FI)	
Amiloride	FI, Ic, Gr			30.6–1260 (Ic)	40.9–217 (Ic)	35.9–95.6 (Ic)
Complexation agents						
EDTA	FI, Ic, Gr			9–49 (Ic), 1.6–16 (FI), <MDL–1.3 (Gr)	18–29 (Ic), 11–630 (FI), 37–420 (Gr)	
UV-filters						
Benzophenone-3 (BP3)	Nor				721–1915	
Ethylhexylmethoxycinnamate (EHMC)	Nor				4–37	
Octocrylene (OC)	Nor				1701–6969	
Bisphenol-monomers						
4,4'-methylenebisphenol (4,4-BPF)	Nor				<MDL–1148	
2,2'-methylenebisphenol (2,2-BPF)	Nor				<MDL–257	
Bisphenol A	Can-Ont, Nor				<MDL–991	
4,4'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene] bisphenol (BPAF)	Nor				<MDL–2.5	
4,4'-(diphenylmethylene) bisphenol (BP-BP)	Nor				<MDL–6	
Artificial Sweeteners						
Cylamate	FI, Ic				<MDL–870	1700–6900 (Ic)
Sucralose	FI, Ic				<MDL–690	<MDL–5700 (FI)

MDL: Minimum detection limit. * Direct emission into coastal seawater (effluent).
Country abbreviations. Ala: Alaska, Can-Man: Canada (Manitoba); Can-Ont: Canada (Ontario); FI: Faroe Islands, Fin-Oulo: Finland (Oulo); Fin-Rov: Finland (Rovaniemi); Gr: Greenland; Ic: Iceland; Nor-Lon: Norway (Svalbard, Longyearbyen), Nor-Sva: Norway (Svalbard), Nor-Tro: Norway (Tromsø); Se: Sweden.

Data sources: (1) Metcalfe et al. 2003; (2) Lee et al. 2003; (3) Huber et al. 2013; (4) Kleywegt et al. 2011; (5) Mutter 2014; (6) Metcalfe et al., (7) Weigel et al. 2004a, (8) Carlson et al. 2013, (9) Andersson et al, 2006, (10) Vasskog et al. 2006, (11 Vasskog et al. 2008, (12) Kallenborn et al., 2008a, (13) Vieno et al. 2007, (14) Vieno et al. 2008, (15) Dye et al. 2007, (16) Lindberg et al. 2005, (17) Kaj et al. 2005, (18) Thomas et al. 2014; (19) Krogseth et al. 2013a, (20) Evenset et al. 2009, (21) Lishman et al 2006, (22) Vorkamp and Rigét, 2014, (23) Vorkamp et al. 2004a, (24) Bakke et al. 2008, (25) Kankaanpää et al. 2014, (26) Kaj et al. 2014, (27) NIVA, 2012, (28) NIVA, 2014, (29) Thomas et al 2014, (30) Remberger et al. 2013.

Table A2.8/2 cont.

Freshwater			Marine			Comments	Data source
Sewage, ng/L	Water, ng/L	Sediment, ng/g	Water, ng/L	Sediment, ng/g	Biota, ng/g		
0.85 (Ic), 46.5 (FI), 15.4 (Gr)		0.73 (Ic)					(3: Nordic)
149 (Ic), 239 (FI), 553 (Gr)		56.7 (Ic), 2.45 (Gr)					(3: Nordic)
							(3: Nordic)
							(3: Nordic)
		14.2 (Ic), 1.52–1.86 (FI), 4.04 (Gr)					(3: Nordic)
		2.75 (Ic)					(3: Nordic)
							(3: Nordic)
<MDL–3.28 (FI), 0.96–0.97 (Gr)		<MDL–1.32 (FI)					(3: Nordic)
		21 (Ic)					(3: Nordic)
9–49 (Ic), 1.6–16 (FI), <MDL–1.3 (Gr)							(3: Nordic)
							(29: Nor)
							(29: Nor)
							(29: Nor)
							(29: Nor)
							(29: Nor)
	2–99 (Can-Ont)			3–11 (Barents Sea)	<1.0 (MDL, Nor)		(4), (24), (28: Nor), (29: Nor)
							(29: Nor)
							(29: Nor)
						Only Arctic locations compared	(30)
						Only Arctic locations compared	(30)

Table A2.8/3 Supplementary information concerning PPCPs in sewage (maximum reported values).

Sewage influent, ng/L

Location/Region	Salicyclic acid	Ibuprofen	Naproxen	Diclofenac	Acetaminophen/ Paracetamol	Sertraline
Alaska						
Ontario	874 000	38 700	1300	1300	3240	
Manitoba						
Greenland		6050			25 800	7
Iceland	30 500	48 800	109 000	697	251 000	121
Faroe Islands	38 400	3530	102	190	506 000	2
Svalbard						
Tromsø (northern Norway)						

Sewage, ng/L

Location/Region	Salicyclic acid	Ibuprofen	Naproxen	Diclofenac	Acetaminophen/ Paracetamol	Sertraline
Alaska		17			27	
Ontario						
Manitoba						
Greenland	162	48			85.2	29
Iceland	535	130	120	19.4		141
Faroe Islands	159	54	0.3	26.9	22.4	
Svalbard						
Tromsø (northern Norway)		380		4.5		100

Sewage sludge, ng|g

Location/Region	Salicyclic acid	Ibuprofen	Naproxen	Diclofenac	Acetaminophen/ Paracetamol	Sertraline
Alaska						
Ontario						
Manitoba						
Greenland						
Iceland						
Faroe Islands						
Svalbard						
Tromsø (northern Norway)						

Sewage effluent, ng/L

Location/Region	Salicyclicacid	Ibuprofen	Naproxen	Diclofenac	Acetaminophen/ Paracetamol	Sertraline
Alaska						
Ontario	3600	4000	12 500		740	
Manitoba						
Greenland	1050	2800			25 800	2
Iceland	6030	5800	1920	390	8540	299
Faroe Islands		4500	8	597	71 500	23
Svalbard		403		1074		
Tromsø (northern Norway)	448		48		90	

Table A2.8/3 cont.

Fluoxetine	Paroxetine	Citalopram	Atenolol	Metoprolol	Estrone	17b-Estradiol	ATAC
	1.8	6.25		2.16	2.09		7.5
382	783	1040	1650	1350	141	474	61
	91.5	151	36.8	319	11.6	78	87
	12.9	304					

Fluoxetine	Paroxetine	Citalopram	Atenolol	Metoprolol	Estrone	17b-Estradiol	ATAC
0.1		51.6			21.1		3.8
49.4		86.7	150		13.3		31
		283	13.4		18.5		29
	20			270			

Fluoxetine	Paroxetine	Citalopram	Atenolol	Metoprolol	Estrone	17b-Estradiol	ATAC
		20.6		41 400			15 000
	27.4	11 400		549 000		2.26	680 000
	120	282		108 000		1.48	9300

Fluoxetine	Paroxetine	Citalopram	Atenolol	Metoprolol	Estrone	17b-Estradiol	ATAC
	20.8	192	470	251	21	375	6800
5.29	89.3	69.2	1730	1070	13.3	249	2000
30.6	149	540	188	810	18.5		13 000
	13	102					

Table A2.8/3 cont.

Sewage effluent (ng/L); relevant comparison

Location/Region	Ibuprofen	Diclofenac	Acetaminophen/ Paracetamol	Sertraline	Paroxetine	Citalopram
Alaska						
Ontario	4000		740			
Greenland	2800		25 800	2	20.8	192
Iceland	5800	390	8540	299	89.3	69.2
Faroe Islands	4500	597	71 500	23	149	540
Longyearbyen (Svalbard)	403	1074				
Tromsø (northern Norway)	448	48		90	13	102

2.9 Polychlorinated naphthalenes (PCNs)

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2.9.1 Introduction

Chlorinated naphthalenes include 75 theoretical congeners with one to eight chlorine atoms substituting the hydrogen atoms of the naphthalene ring (Figure 2.81). Strictly speaking, polychlorinated naphthalenes (PCNs) only include molecules with more than 1 chlorine atom (Table 2.54). As the naphthalene ring has a planar structure, PCNs can exhibit dioxin-like effects through aryl hydrocarbon (Ah) receptor-mediated mechanisms. In contrast to dioxins and other dioxin-like compounds, however, no official toxic equivalency factors (TEFs) exist (Wyrzykowska et al., 2009). Instead, Relative Potency Factors (RPFs) have been suggested for some PCN congeners, relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), which is the most potent Ah-receptor agonist (Blankenship et al., 2000; Falandysz et al., 2014) (Table 2.55). Most TEFs or RPFs are based on in vitro cell-based assays using ethoxyresorufin-*O*-deethylase (EROD) responses and dioxin-receptor-chemical activated luciferase gene expression (DR-CALUX). For CN-66 and CN-67, additional information is available from in vivo studies (Falandysz et al., 2014).

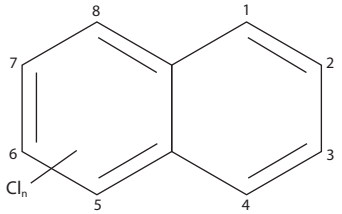

Figure 2.81 Chemical structure and ring numbering system of polychlorinated naphthalenes (PCNs) (Falandysz et al., 2014).

In 2011, the European Union proposed PCNs for inclusion in the Stockholm Convention (UNEP, 2011d). Following the review process, the POP Review Committee (POPRC) recommended in 2013 to list PCNs (i.e. di- through octachlorinated naphthalenes) in Annexes A and C (UNEP, 2013a). The Conferences of the Parties to the Stockholm Convention followed this recommendation at their seventh meeting in May 2015 (UNEP, 2015j). The listing of PCNs in Annex A includes the exemption that PCNs can still be used or produced in the manufacture of polyfluorinated naphthalenes (UNEP, 2015j). Tri- to octaCNs are also on OSPAR's List of Chemicals for Priority Action, Group C (i.e. no current production or use interest in the OSPAR region).

The occurrence of PCNs in the Arctic was previously reviewed by Bidleman et al. (2010). The present report updates the previous assessment and only repeats previously reported findings if necessary for context. A summary of the old data and those reviewed by Bidleman et al. (2010) is given in Table 2.56. ΣPCN usually comprises a different suite of congeners for each study, with a potential risk of limited comparability. Given the low concentrations of some CN congeners, the treatment of values below detection limits (i.e. replacing them by the detection limit, half the detection limit or zero) might further influence ΣPCN. Parallel analyses of the same samples by low resolution and high resolution mass spectrometry have further indicated systematic differences in PCN quantification (Muir, pers. comm.). These details have therefore been provided where available.

2.9.2 Physical-chemical properties

The PCN congeners are solids at room temperature. The trade name 'Halowax' reflects their wax-like texture. Water solubility decreases with increasing degree of chlorination, ranging from 137 µg/L for CN-3 to 0.08 µg/L for CN-75. Data on melting points and water solubility were compiled by Jakobsson and Asplund (2000).

The PCN congeners have log K_{OW} values of 4.42–6.48 (Jakobsson and Asplund, 2000). In combination with experimentally derived bioconcentration factors and bioaccumulation factors, PCNs were evaluated to possess bioaccumulation potential by the POPRC (UNEP, 2012a). Detailed physical-chemical properties are given in Appendix 1. The risk profile report of the

Table 2.54 Overview of PCN homolog groups and the theoretical number of individual congeners per homolog group.

Homolog group	CAS no.	Molecular formula	Number of congeners	Congener nomenclature
MonoCNs	25586-43-0	$C_{10}H_7Cl$	2	CN-1, CN-2
DiCNs	28699-88-9	$C_{10}H_6Cl_2$	10	CN-3 – CN-12
TriCNs	1321-65-9	$C_{10}H_5Cl_3$	14	CN-13 – CN-26
TetraCNs	1335-88-2	$C_{10}H_4Cl_4$	22	CN-27 – CN-48
PentaCNs	1321-64-8	$C_{10}H_3Cl_5$	14	CN-49 – CN-62
HexaCNs	1335-87-1	$C_{10}H_2Cl_6$	10	CN-63 – CN-72
HeptaCNs	32241-08-0	$C_{10}HCl_7$	2	CN-73, CN-74
OctaCNs	2234-13-1	$C_{10}Cl_8$	1	CN-75

Table 2.55 Relative potency factors (RPFs) suggested for polychlorinated naphthalenes (PCNs) as summarized by Falandysz et al. (2014).

Congener (congener number)	CAS no.	RPF
1,2-DiCN (CN-3)	2050-69-3	$<2.9\times10^{-7}$
1,4-DiCN (CN-5)	1825-31-6	5.1×10^{-9} – 3.5×10^{-5}
1,5-DiCN (CN-6)	1825-31-6	$<6.6\times10^{-7}$ – $<1.2\times10^{-6}$
1,8-DiCN (CN-9)	2050-74-0	$<1.7\times10^{-6}$ – 1.5×10^{-5}
2,3-DiCN (CN-10)	2050-75-1	$<5.9\times10^{-6}$ – 2.7×10^{-5}
2,7-DiCN (CN-12)	2198-77-8	$<4.2\times10^{-7}$
1,2,3-TriCN (CN-13)	50402-52-3	$<2.0\times10^{-6}$ – $<4.4\times10^{-6}$
1,2,7-TriCN (CN-17)	55720-34-8	$<8.4\times10^{-7}$
1,2,3,4-TetraCN (CN-27)	20020-02-4	$<1.6\times10^{-6}$ – $<2.3\times10^{-6}$
1,2,4,7-TetraCN (CN-34)	67922-21-8	$<4.2x10^{-7}$ – $<6.9x10^{-7}$
1,2,5,6-TetraCN (CN-36)	67922-22-9	$<4.1x10^{-7}$
1,2,6,8-TetraCN (CN-40)	67922-24-1	1.6×10^{-5}
1,3,5,7-TetraCN (CN-42)	53555-64-9	$<1.9\times10^{-6}$ – 7.5×10^{-6}
2,3,6,7-TetraCN (CN-48)	34588-40-4	4.1×10^{-5}
1,2,3,4,6-PentaCN (CN-50)	67922-26-3	4.3×10^{-5} – 6.8×10^{-5}
1,2,3,5,7-PentaCN (CN-52)	53555-65-0	$<1.8\times10^{-6}$ – 4.2×10^{-6}
1,2,3,5,8-PentaCN (CN-53)	150224-24-1	$<1.2\times10^{-6}$ – $<1.8\times10^{-6}$
1,2,3,6,7-PentaCN (CN-54)	150224-16-1	9.2×10^{-5} – 5.8×10^{-4}
1,2,3,7,8-PentaCN (CN-56)	150205-21-3	2.4×10^{-6} – 4.9×10^{-4}
1,2,4,5,6-PentaCN (CN-57)	150224-20-7	1.7×10^{-6} – 3.7×10^{-6}
1,2,4,6,7-PentaCN (CN-60)	150224-17-2	$<4.2\times10^{-7}$ – $<2.8\times10^{-5}$
1,2,4,6,8-PentaCN (CN-61)	150224-22-9	$<4.2\times10^{-7}$
1,2,3,4,5,6-HexaCN (CN-63)	58877-88-6	2×10^{-3}
1,2,3,4,5,7-HexaCN (CN-64)	67927-27-4	2×10^{-5}
1,2,3,4,6,7-HexaCN (CN-66)[a]	103426-93-3	5.4×10^{-4} – 3.9×10^{-3}
1,2,3,5,6,7-HexaCN (CN-67)[b]	103426-97-7	2.8×10^{-4} – 2×10^{-3}
1,2,3,5,6,8-HexaCN (CN-68)	103426-95-5	1.5×10^{-4} – 2×10^{-3}
1,2,3,5,7,8-HexaCN (CN-69)	103426-94-4	6.9×10^{-6} – 2×10^{-3}
1,2,3,6,7,8-HexaCN (CN-70)	17062-87-2	5.9×10^{-4} – 9.5×10^{-3}
1,2,4,5,6,8-HexaCN (CN-71)	90948-28-0	$< 1.1\times10^{-6}$
1,2,4,5,7,8-HexaCN (CN-72)	103426-92-2	7.1×10^{-6} – 6.0×10^{-5}
1,2,3,4,5,6,7-HeptaCN (CN-73)	58863-14-2	4×10^{-4} – 3×10^{-3}
1,2,3,4,5,6,8-HeptaCN (CN-74)	58863-15-3	4.1×10^{-6}
1,2,3,4,5,6,7,8-OctaCN (CN-75)	2234-13-1	$< 4.3\times10^{-6}$ – 1.0×10^{-5}

[a]RPF based on in vivo studies: 1.5×10^{-3} – 4.1×10^{-3}; [b]RPF based on in vivo studies: 2.9×10^{-4} – 6.7×10^{-4}.

POPRC further concluded that tri- to octaCNs were persistent. This conclusion was based on predicted half-lives in water of at least 180 days, predicted half-lives in soil of at least one year, and monitoring data from polar regions (UNEP, 2012a). Furthermore, photolysis was evaluated to be of minor relevance (UNEP, 2012a). Although fewer data exist for diCNs, these congeners were also considered to be persistent. Long-range transport classification for PCNs was based on atmospheric half-lives of 3–417 days, model predictions characterizing most PCNs as 'multi hoppers' and the detection of PCNs in polar regions (UNEP, 2012a). The dioxin-like toxicity of PCNs has been recognized for several years (Blankenship et al., 2000).

2.9.3 Sources, production, use and trends

PCNs had industrial applications similar to those of polychlorinated biphenyls (PCBs), namely in capacitor dielectrics, cutting oils, wood and paper preservatives, cable insulation, and dye carriers (Yamashita et al., 2000). Production and use preceded that of PCBs and stopped in the 1970s and 1980s. The total production volume was estimated at 150 000 tonnes (Falandysz, 1998), which is considerably lower than the total PCB production volume of about 1.3-1.5 million tonnes (Falandysz, 1998; Breivik et al., 2002). The main PCN usage between the 1920s and 1985 occurred in the USA, Europe and Japan. Between 1998 and 2000, cases of illegal trade of PCNs and PCN-contaminated products occurred in Japan (Yamashita et al., 2003; Falandysz et al., 2008).

PCNs have been detected as impurities of PCB formulations (Yamashita et al., 2000). They can also be formed in combustion processes (*de novo* synthesis), for example during waste incineration (Benfenati et al., 1991; Schneider et al., 1998). Emissions of chlorinated naphthalenes formed in coking processes were estimated at 1.8–125 µg per ton of coke production, with 20–80% being monoCNs. (Liu et al., 2010). This was extrapolated to 430–692 mg TCDD toxic equivalents (TEQ) globally, comparable to dioxin-like PCBs inadvertently formed in the same processes.

Several studies have addressed the composition of commercial PCN mixtures (Falandysz et al., 2006a,b; Noma et al., 2006), recently also applying comprehensive two-dimensional gas chromatographic separation to resolve co-eluting congeners (Hanari et al., 2013). Other congeners, absent or of little abundance in the commercial products, have been identified as indicators of combustion, especially CN-13, CN-26, CN-29, CN-44 and CN-54 (Helm and Bidleman, 2003; Orlikowska et al., 2009). More specifically, CN-24 was further identified as an indicator of coal and wood burning (Lee et al., 2005). In addition to specific markers, diagnostic fractions or ratios have been used to indicate PCN sources, as well as multivariate statistical methods such as principal component analysis (Bidleman et al., 2010).

Table 2.56 Summary of Arctic media for which polychlorinated naphthalenes (PCNs) have been reported. '×' indicates new data, i.e. available since the previous AMAP assessment (Bidleman et al., 2010) and '+' indicates older data as reviewed by Bidleman et al. (2010). In the case of older and new data, only '×' is used.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
PCNs	×	+				+ (subarctic)	+			×

An early study from Sweden reported that most PCN profiles in environmental samples were similar to the profile of PCN impurities found in PCB formulations, and showed little similarity with low and medium chlorinated Halowax mixtures (Järnberg et al., 1997). More recently, PCNs in pine needles in Poland were found to reflect multiple sources, including the burning of wood and fossil fuels (Orlikowska et al., 2009). Helm and Bidleman (2003) concluded that about 54% of PCNs in air at Toronto had originated from combustion sources. Along with the discontinuation of the industrial use of PCNs, there has been an increase in combustion-related congeners in the overall profile of PCNs in the UK since the 1950s, indicating the increasing importance of combustion processes as sources of PCNs to the environment (Meijer et al., 2001).

With regard to the Arctic, combustion-related PCN congeners were detected in air at Svalbard and Alert (Canada) (Lee et al., 2007). The congener pattern at Ny-Ålesund (Svalbard) in particular also showed some resemblance to the profile of Halowax 1014, suggesting evaporation of the technical mixture from past use as one of the PCN sources in the atmosphere of Svalbard. Lee et al. (2007) also noted that the homolog profile at Ny-Ålesund was more similar to urban locations than that of, for example, Alert in the remote High Arctic. Based on measurements at Dunai (Russia) and Alert and Tagish (Canada), Helm et al. (2004) concluded that evaporation was the main source of PCNs in Arctic air although some combustion markers could be identified in the PCN profile. They confirmed that CN-54 was the most reliable indicator of combustion sources in Arctic air samples.

2.9.4 Transformation processes

There do not appear to be any recently published data on the transformation of PCNs in the Arctic environment. Based on quantitative structure-property relationships (QSPRs), model results on the reaction of PCNs with atmospheric hydroxyl radicals (OH·) lead to predicted atmospheric half-lives of a few days for lower chlorinated congeners to nearly one year for octaCN (Puzyn et al., 2008; Table 2.57). Besides the degree of chlorination, the substitution pattern of the molecule affects the atmospheric stability.

Biological transformation reactions have also been described for PCNs as reviewed by Falandysz et al. (2014): Lower chlorinated PCNs (i.e. up to tetraCNs) can undergo metabolic transformation by hydroxylation via arene oxide intermediates or by hydroxylation-dechlorination. In animals, several phase II metabolites have been detected, such as conjugates with glucuronic acid and mercapturic acid, for these lower chlorinated congeners. For tetra- to hexaCNs, partial transformation to methylthio and methyl sulfoxide metabolites has been found.

2.9.5 Modeling studies

Several modeling studies have been published on the prediction of physical-chemical properties of PCNs including the QSPRs (Chen et al., 2003; Puzyn and Falandysz, 2007; Puzyn et al., 2008). Based on QSPR and an atmospheric concentration of 9.4×10^5 OH· radicals/cm^3, Puzyn et al. (2008) calculated atmospheric half-lives for all PCN congeners (Table 2.57). Even for the most volatile congeners, the persistence criterion for defining POPs according to the Stockholm Convention was met ($t_{½} > 2$ days). Recently, new quantum-mechanical models were developed to calculate the vapor pressure, water solubility and partition coefficients of PCNs (Vikas and Chayawan, 2014; Chayawan and Vikas, 2015). Electron-correlation contributions were found to have a central role in these predictions, which showed significant correlations with experimentally determined values. Using multi-linear regression, a QSPR was developed to predict the enthalpy of vaporization for a large number of POPs, including some PCNs (Sosnowska et al., 2014). From these results, vapor pressures were estimated for a wide temperature range (213–323K).

Table 2.57 Average atmospheric half-lives determined by quantitative structure-property relationships (QSPRs) and based on a concentration of 9.4×10^5 OH· radicals/cm^3 (Puzyn et al., 2008).

Homolog group	Half-life, d
MonoCNs	2
DiCNs	5
TriCNs	10
TetraCNs	19
PentaCNs	39
HexaCNs	79
HeptaCNs	163
OctaCN	343

2.9.6 Environmental concentrations

2.9.6.1 Air and precipitation

The previous AMAP assessment showed PCNs were widespread in Arctic air, with the highest concentrations of up to 40 pg/m^3 in the European Arctic (Bidleman et al., 2010). Concentrations could differ between locations by a factor of 10–100, which was much larger than the difference observed for chlorinated pesticides, which usually differed by a factor of 2–3. Roughly half of the PCN concentration in Arctic air was attributed to triCNs, while tetraCNs accounted for about a third of ΣPCN.

PCNs were monitored in air at Alert (Canada) and Dunai (Russia) as part of the Canadian Northern Contaminants Program (Harner et al., 1998) and have also been included in other projects and campaigns in Canada, Russia and Greenland (Helm et al., 2004; Bossi et al., 2008). However, no new data have been reported for PCNs from these programs and campaigns since the previous AMAP assessment by Bidleman et al. (2010).

PCNs were measured in passive air samples of the Global Atmospheric Passive Sampling (GAPS) Network collected in 2005 (Lee et al., 2007) and were in the order of a few pg/m^3 for Arctic stations (Table 2.58). PCNs were measured again in GAPS samples as part of the 2009 GAPS retrospective study (Harner et al., 2014b). ΣPCN was generally in the same range as reported for the 2005 samples (Table 2.58). While the analyses from 2005 used low resolution mass spectrometry (LRMS) for detection, the samples from 2009 were analyzed using high resolution mass spectrometry (HRMS).

Table 2.58 Air concentrations of ΣPCN in samples collected at Arctic sites as part of the Global Atmospheric Passive Sampling (GAPS) Network. In the study by Lee et al. (2007) ΣPCN includes the following congeners: CN-14, CN-15, CN-16, CN-17/25, CN-19, CN-23, CN-24, CN-25, CN-27/30/39, CN-28/43, CN-32, CN-33/34/37, CN-36/45, CN-38/40, CN-42, CN-46, CN-47, CN-49, CN-50, CN-51, CN-52/60, CN-53, CN-54, CN-57, CN-58, CN-59, CN-61, CN-62, CN-63, CN-64/68, CN-65, CN-66/67, CN-69, CN-71/72, CN-73, CN-74 and CN-75. Harner et al. (2014b) gave no information on the composition of ΣPCN.

Year	ΣPCN in air, pg/m³					Method	Reference
	Alert	Barrow	L.Fox Lake	Stórhöfði	Ny-Alesund		
2005	1.2	2.3	na	0.86	7.6	GC-LRMS	Lee et al., 2007
2009	4.9	0.46	1.1	3.5	na	GC-HRMS	Harner et al., 2014b

na: not analyzed; GC: gas chromatography: LRMS: low resolution mass spectrometry. HRMS: high resolution mass spectrometry.

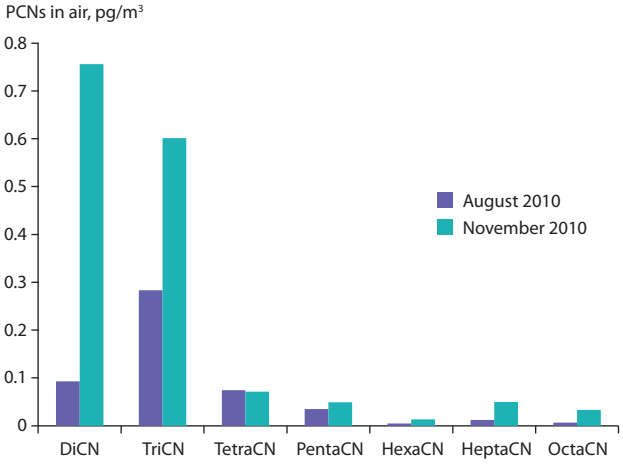

Figure 2.82 Concentrations of PCN homolog groups at Pallas (northern Finland) in August and November 2010 (Haglund et al., 2011).

At the Pallas air monitoring station in northern Finland, ΣPCN was 0.5 and 1.6 pg/m³ in samples from August and November 2010, respectively (Haglund et al., 2011). Individual congeners ranged between 0.00035 and 0.046 pg/m³. Homolog groups (not further defined on a congener basis) were detected at the following concentrations: ΣdiCNs at 0.093 and 0.76 pg/m³, ΣtriCNs at 0.280 and 0.600 pg/m³, and ΣtetraCNs at 0.071 and 0.074 pg/m³ (Figure 2.82).

2.9.6.2 Terrestrial environment

No terrestrial data were presented on PCNs in the previous AMAP assessment (Bidleman et al., 2010) and there do not seem to be any recent reports on PCNs in the terrestrial environment of the Arctic.

2.9.6.3 Freshwater environment

No new data have been reported on PCNs from Arctic freshwater environments since the assessment by Bidleman et al. (2010), which included PCN data on biota from Bjørnøya in the Norwegian Arctic and from lakes and rivers in northern Scandinavia (e.g. Evenset et al., 2005; Isosaari et al., 2006). Arctic char (*Salvelinus alpinus*) from lakes on Bjørnøya had ΣPCN mean concentrations of 4.6–38 pg/g ww (about 290–850 pg/g lw) (ΣPCN included the following congeners: CN-42, CN-52 and CN-66/67; Evenset et al., 2005), while various freshwater fish species from the subarctic Scandinavian locations had ΣPCN concentrations in the range 2–7 pg/g ww (140–3540 pg/g lw) (ΣPCN included the following congeners: CN-27, CN-36, CN-42, CN-48, CN-52, CN-53, CN-54, CN-66/67, CN-68, CN-70, CN-71/72, CN-73, CN-74 and CN-75; Isosaari et al., 2006). On a lipid weight basis, some of these concentrations were higher than those found in marine mammals, most of which are <1000 pg/g lw (see next section). However, as Bidleman et al. (2010) also pointed out, ΣPCN concentrations are not always directly comparable because of different suites of congeners included in the analysis.

2.9.6.4 Marine environment

New data are available for PCNs in seabirds eggs (thick-billed murre *Uria lomvia*) from the Canadian Arctic, for pinnipeds (ringed seal *Pusa hispida*) from Canada and Greenland, for pinnipeds and cetaceans from the Northeast Atlantic and Arctic Ocean as well as for beluga (*Delphinapterus leucas*) and polar bears (*Ursus maritimus*) from the Canadian Arctic. As for other POPs, the PCNs detected in the animals are likely to reflect an accumulation over time. For migratory species this might also mean an integration in space, depending on their migration range.

Seabirds

New results have become available on PCN concentrations in seabird eggs from the Canadian Arctic. The mean annual ΣPCN_{67} concentration in eggs of thick-billed murre collected at Prince Leopold Island, Lancaster Sound over the period 1975–2014 ranged from 364 to 995 pg/g ww (Braune and Muir, 2017). The main congeners were CN-42 and CN-52/60, which accounted for 42–57% annually of ΣPCN_{67}. The composition for all years was pentaCNs (41–50%) > tetraCNs (36–45%) > hexaCNs (5–10%) > triCNs (2–7%), while other homolog groups only contributed marginally. The suite of PCN congeners was the same as described for ringed seals in Table 2.59 (note b). Based on comparisons with the literature, Braune and Muir (2017) concluded that PCNs seemed to accumulate in seabirds to a greater extent than in marine mammals. Asia was considered as the main source region of the PCNs detected in biota from the Canadian High Arctic (Braune and Muir, 2017).

Marine mammals

PCNs have been monitored in ringed seal blubber from Greenland and from several locations in the Canadian Arctic (Table 2.59), thus expanding and updating the dataset presented by Bidleman et al. (2010). Arithmetic means of ΣPCN_{67} in animals collected between 2008 and 2013 ranged between 495 and 2718 pg/g lw at individual locations in Canada, being

Table 2.59 Arithmetic mean concentrations of PCNs in ringed seal, beluga and polar bear from the Arctic.

Species	Location	Year of sampling	n	Method	ΣPCN, pg/g lw	Reference
Ringed seal	East Greenland	2006	3 (pooled samples)	HRMS	220[a]	Rotander et al., 2012b
	Sachs Harbour, Canada	2011–2013	32	HRMS	2433[b]	Houde et al., 2016; Muir et al. unpubl. data
	Kugaaruk, Canada	2012	14	HRMS	1971[b]	
	Pangnirtung, Canada	2008–2010	12	HRMS	2718[b]	
	Resolute, Canada	2011–2013	33	HRMS	2588[b]	
	Arviat, Canada	2011–2012	23	HRMS	1055[b]	
	Nain, Canada	2013	9	HRMS	495[b]	
Beluga	Hendrickson Island, Canada	2000, 2008	18	LRMS	118–430[c]	Muir et al., 2013b
Polar bear	Western Hudson Bay	2014	5	HRMS	20 200 (adult males)[d]	Letcher et al., 2018
	Southern Hudson Bay	2014	5	HRMS	26 100 (adult females) 14 800 (adult males) 48 500 (subadults)[d]	

HRMS: High resolution mass spectrometry. LRMS: Low resolution mass spectrometry. [a]Congeners CN-13, CN-28/36, CN-27, CN-48, CN-46, CN-52, CN-50, CN-53, CN-66, CN-69, CN-72, CN-73 and CN-75 were analyzed. ΣPCN is the sum of CN-52/60, CN-53/55, CN-66/67 and CN-69, with values below detection limit divided by two. [b]ΣPCN included the following congeners: CN-1, CN-2, CN-3, CN-4, CN-5/7, CN-6/12, CN-8/11, CN-9, CN-13, CN-14, CN-15, CN-16, CN-17, CN-18, CN-19/20, CN-21/24, CN-23, CN-27/30/39, CN-28/43, CN-32, CN-33/34/37, CN-35/48, CN-36/45, CN-38/40, CN-41, CN-42, CN-46, CN-47, CN-49, CN-50, CN-51, CN-52/60, CN-53/55, CN-54, CN-56, CN-57, CN-58, CN-59, CN-61, CN-62, CN-63, CN-64/68, CN-65, CN-66/67, CN-69, CN-70, CN-71/72, CN-73, CN-74 and CN-75. [c]Tri- to octaCNs, no congeners specified. [d]Geometric mean concentrations. A total of 68 congeners were analyzed, i.e. CN-1, CN-2, CN-3, CN-4, CN-5/7, CN-6/12, CN-9, CN-11/18, CN-13, CN-14, CN-15, CN-16, CN-17, CN-18, CN-20/19, CN-21/24, CN-23, CN-28/43, CN-30/27/39, CN-32, CN-33/34/37, CN-36/45, 38/40, CN-41, CN-42, CN-46, CN-47, CN-48/35, CN-49, CN-50, CN-51, CN-52/60, CN-53/55, CN-54, CN-56, CN-57, CN-58, CN-59, CN-61, CN-62, CN-63, CN-64/68, CN-65, CN-66/67, CN-69, CN-70, CN-71/72, CN-73, CN-74 and CN-75.

highest at Pangnirtung and lowest at Nain (Figure 2.83). These concentrations were derived from HRMS analyses (Houde et al., 2016; Muir et al., unpubl. data), while those reviewed by Bidleman et al. (2010) and published by Muir et al. (2013b) were based on LRMS detection. According to Muir (pers. comm.), the LRMS method had underestimated the PCN concentration and misclassified some PCN congeners.

The PCN congener composition in these ringed seals generally showed highest percentages of tetra- and pentaCNs, representing 89–94% of ΣPCN (Houde et al., 2016). The PCN profiles were relatively similar at the different locations, with pentaCNs accounting for (on average) 53% of ΣPCN at Nain to 72% of ΣPCN at Sachs Harbor. The difference from typical profiles in air indicates a congener-specific uptake and accumulation in the

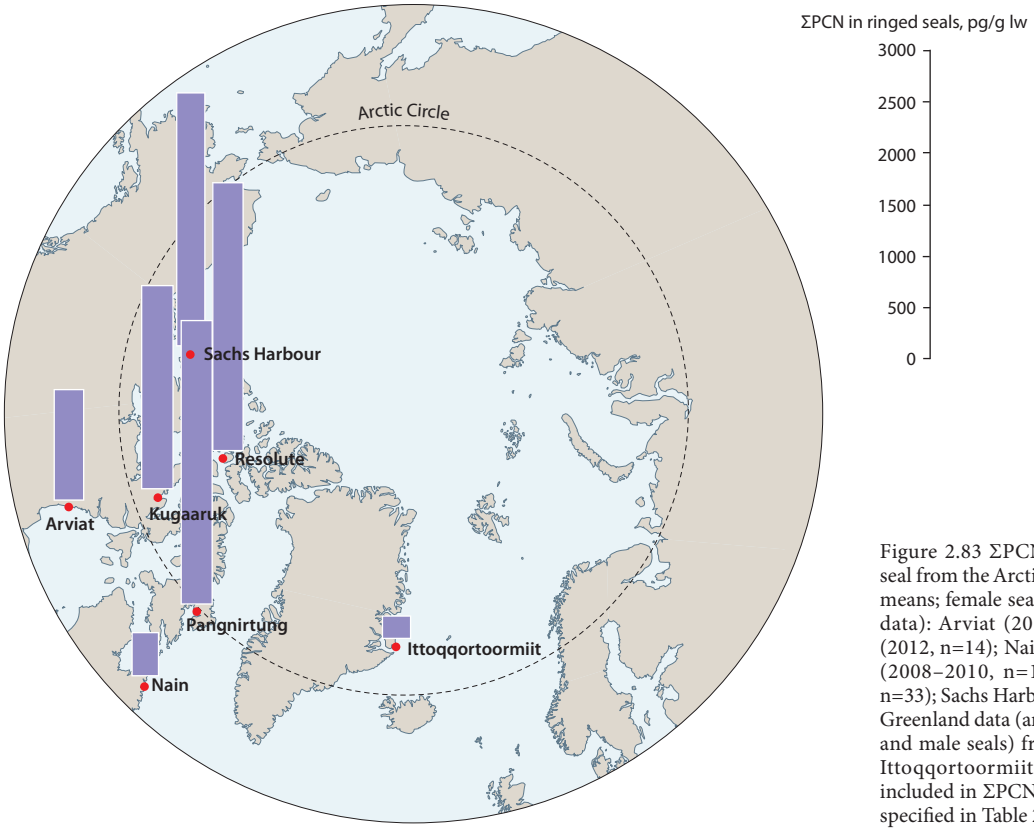

Figure 2.83 ΣPCN concentrations in ringed seal from the Arctic. Canadian data (arithmetic means; female seals) from Muir et al. (unpubl. data): Arviat (2011–2012, n=23); Kugaaruk (2012, n=14); Nain (2013, n=9); Pangnirtung (2008–2010, n=12); Resolute (2011–2013, n=33); Sachs Harbour (2011–2013, n=32). East Greenland data (arithmetic mean; 2006; female and male seals) from Rotander et al. (2012b): Ittoqqortoormiit. Note that the congeners included in ΣPCN differ for the two studies as specified in Table 2.9/6.

marine food chain. However, the profiles were similar in seabird eggs collected at the same location (Braune and Muir, 2017).

The concentrations reported for ringed seal are generally higher than those reviewed by Bidleman et al. (2010) in the previous AMAP assessment. For example, the arithmetic mean concentration of ΣPCN at Pangnirtung was 230 pg/g lw for female ringed seal for the period 1999–2002 (Bidleman et al., 2010), compared to 2718 pg/g lw in animals collected in the 2008–2010 period (Muir et al., unpubl. data). Rather than reflecting a real trend, these differences might be caused by changes in analytical methods including the suite of congeners sought (Houde et al., 2016; Muir, pers. comm.). As the new data are mainly for female and juvenile seals, age is not expected to be an important factor in the comparison with older data.

Three pooled blubber samples from ringed seals collected from Ittoqqortoormiit (central East Greenland) for each of three years (1986, 2000, 2006) were included in the study by Rotander et al. (2012b). Each pool consisted of 4–5 individuals. Of the 13 congeners included in the analysis, only CN-48/35, CN-52/60, CN-53/55 and CN-69 were above detection limits (20–300 pg/g lw for individual congeners) in at least one of the samples as determined by HRMS. Minimum and maximum ΣPCN concentration defined as CN-52/60 + CN-53/55 + CN-66/67 + CN-69, with values below detection limits divided by two, ranged from about 200 to 800 pg/g lw. This seems slightly higher than the value <130 pg/g lw previously reported for ringed seal from the same location, but collected in 2002 and determined by LRMS (Vorkamp et al., 2004a). Besides the different detection techniques, different congeners included in the analytical methods as well as the handling of values below detection limits again restricts comparability.

As well as ringed seal, the study by Rotander et al. (2012b) included long-finned pilot whale (*Globicephala melas*) and Atlantic white-sided dolphin (*Lagenorhynchus acutus*) (both from the Faroe Islands), minke whale (*Balaenoptera acutorostrata*) from West Greenland, Norway and Iceland, hooded seal (*Cystophora cristata*) and fin whale (*B. physalus*), both from Iceland, and harbor porpoise (*Phocoena phocoena*) (Norway and Iceland). Considering samples from the last ten years, concentrations increased in the order fin whale < ringed seal < hooded seal < minke whale < white-sided dolphin ~ pilot whale (Table 2.59). This is in line with toothed whales such as pilot whale feeding at a higher trophic level than baleen whale species, thus suggesting biomagnification of PCNs in the marine food web. Concentrations in pilot whale from the Faroe Islands are very similar to those of a previous study including samples from 2001 although different detection techniques had been applied (Vorkamp et al., 2004a). They were also similar in terms of TEQ concentrations, with concentrations of 4–17 pg/g lw and 8–13 pg/g lw in the studies by Rotander et al. (2012b) and Vorkamp et al. (2004a), respectively. Rotander et al. (2012b) suggested that these concentrations were not likely to induce toxic effects in marine mammals, but may contribute to dioxin-based toxicity.

PCNs were also analyzed in beluga blubber collected at Hendrickson Island in the Canadian Arctic in 2000 and 2008 (Table 2.59). Beluga are long-lived species feeding on fish and invertebrates (Muir et al., 2013b). The ΣPCN concentrations ranged from 118 to 430 pg/g ww (Muir et al., 2013b), which is slightly lower than the concentration reported by Rotander et al. (2012b) for minke whales from the European Arctic (Table 2.60). The concentrations were not statistically different between 2000 and 2008 and were comparable to previously published results for the same species and the same location, which had ranged from 36 to 380 pg/g ww (Helm et al., 2002). The results were also comparable in terms of TEQ concentration, which was 0.29 pg/g on average in the recent data and ranged from 0.028 to 0.43 pg/g in the study by Helm et al. (2002). Compared with dioxin-like PCBs, the PCN contribution to total TEQs was disproportionally high (Helm et al., 2002). The PCN pattern was clearly dominated by higher chlorinated congeners, i.e. hexaCNs > pentaCNs > tetraCNs (Figure 2.84). This is different to the pattern described above for ringed seal from Canada, which showed pentaCNs > tetraCNs > hexa/triCNs. Besides differences in exposure, selective transformation processes seem likely in different species. The main congeners in beluga were CN-42, CN-52/60 and CN-66/67.

Table 2.60 Range of polychlorinated naphthalene (PCN) concentrations in marine mammals from the Northeast Atlantic and the Arctic as reported by Rotander et al. (2012b). The table summarizes concentrations in the samples collected within the last 10 years. ΣPCN includes the following congeners: CN-52/60, CN-53/55, CN-66/67 and CN-69.

Species	Location	Year of sampling	ΣPCN, pg/g lw
Fin whale	West Iceland	2006; 2009	100–300
Ringed seal	East Greenland	2006	200–300
Hooded seal	Greenland Sea	2007	400–500
Minke whale	West Iceland	2003–2006	500–900
White-sided dolphin	Faroe Islands	2006	1600–3000
Pilot whale	Faroe Islands	2006/2007	1800–4100

Polar bear fat samples collected in 2014 from western and southern Hudson Bay animals were screened for a suite of 68 mono- to octaCN congeners (Letcher et al., 2018). The study included ten individuals: Five males from western Hudson Bay and three

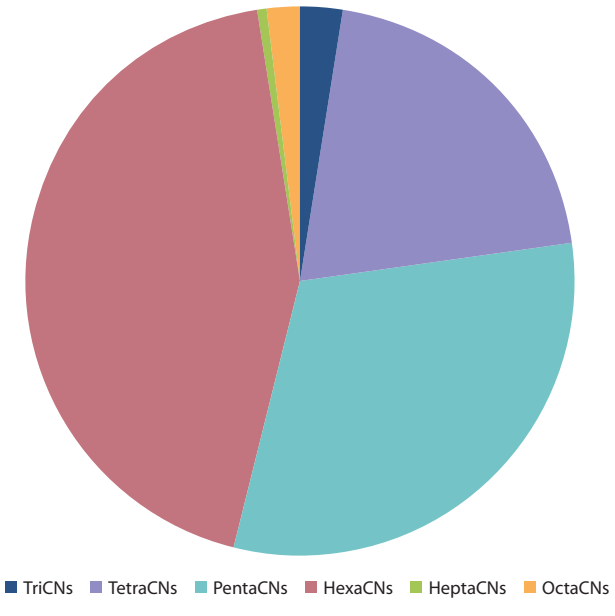

Figure 2.84 Relative distribution of PCN homolog groups in blubber of beluga from Hendrickson Island, Canada (Muir et al., 2013b).

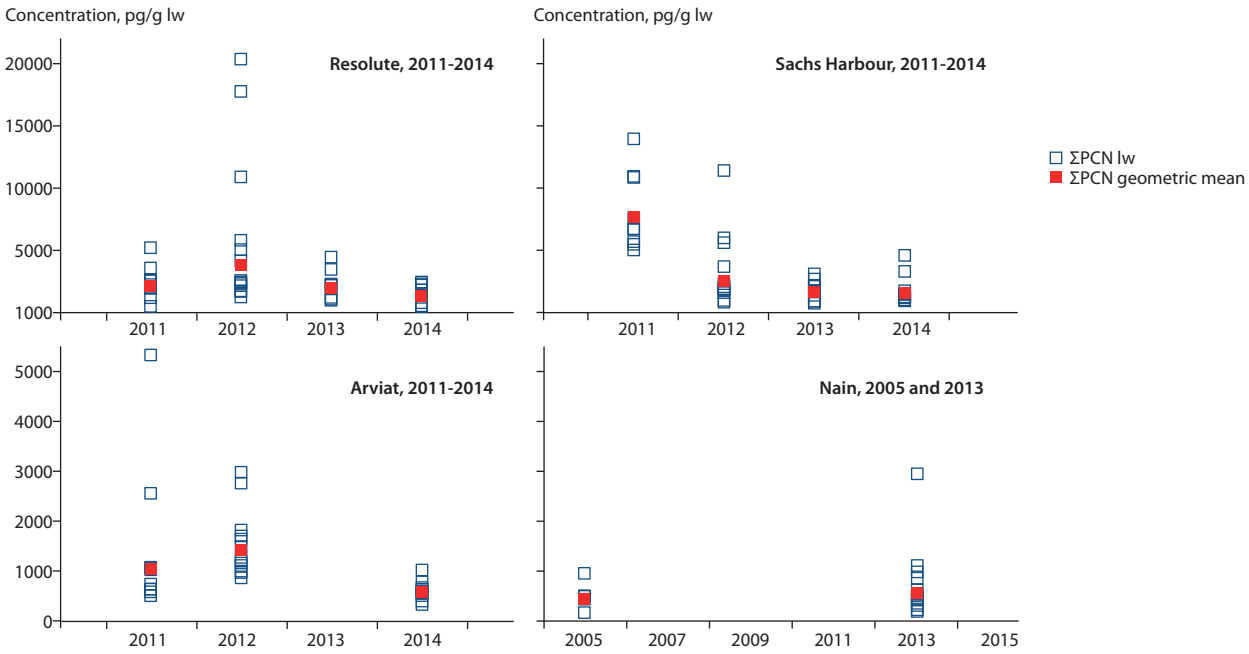

Figure 2.85 ΣPCN concentrations in female ringed seals from the Canadian Arctic (Houde et al., 2016).

females (of which two were subadults) plus two males from southern Hudson Bay. The geometric mean ΣPCN concentrations were 20 200 pg/g ww for the western Hudson Bay animals and between 14 800 and 48 500 pg/g ww in the southern Hudson Bay samples (Table 2.59). The concentrations were not significantly different for western and southern Hudson Bay samples. They seem higher than those summarized by Bidleman et al. (2010) for polar bears, including polar bear liver samples from Alaska and polar bear fat samples from East Greenland. In the Hudson Bay bears, tetra- to hexaCNs accounted for >95% of the ΣPCN concentrations, with penta-CNs accounting for >80% of the ΣPCN concentrations. On a lipid weight basis, the concentrations in polar bears are similar to those in seabird eggs from the Canadian Arctic (Braune and Muir, 2017).

2.9.7 Environmental trends

2.9.7.1 Spatial trends

No circumpolar spatial trend can be assessed for PCNs owing to a lack of data from large parts of the Arctic. Figure 2.83 shows the combined results of ΣPCN concentrations in ringed seals from Greenland (Rotander et al., 2012b) and the Canadian Arctic (Houde et al., 2016; Muir et al., unpubl. data). The concentrations in East Greenland are lower than those in the Canadian Arctic. The spatial trend for air showed the opposite, i.e. higher values in the European Arctic than in Canada (Bidleman et al., 2010), but more data will be needed to deduce geographic trends. Furthermore, and as described above, the comparability between studies can be affected by different suites of congeners and other methodological differences.

2.9.7.2 Temporal trends

Temporal trends in PCNs have been studied for seabirds and marine mammals. Time trends are available for ringed seals from the Canadian Arctic, including locations in the southern Beaufort Sea (Ulukhaktok, Sachs Harbour), Lancaster Sound (Arctic Bay, Resolute, Grise Fjord), Hudson Bay (Arviat, Inukjuaq) and Baffin Island (Pangnirtung). The Lancaster Sound time series includes one data point for 1972, but the majority of data have been collected since the mid-1990s (Helm et al., 2002; Muir et al., 2013b). With the exception of Baffin Island, all concentrations measured since the early 2000s were considerably lower than the older data, which indicates a decrease in PCN concentration.

Examining the most recent data, Figure 2.85 shows geometric means of ΣPCN in ringed seals at four locations in the Canadian Arctic (Houde et al., 2016). The results also indicate decreasing rather than increasing concentrations, although the concentrations at Resolute and Arviat were highest for the intermediate samples. A considerable year-to-year variation in biological samples is well-known in time trend monitoring (Rigét et al., 2010).

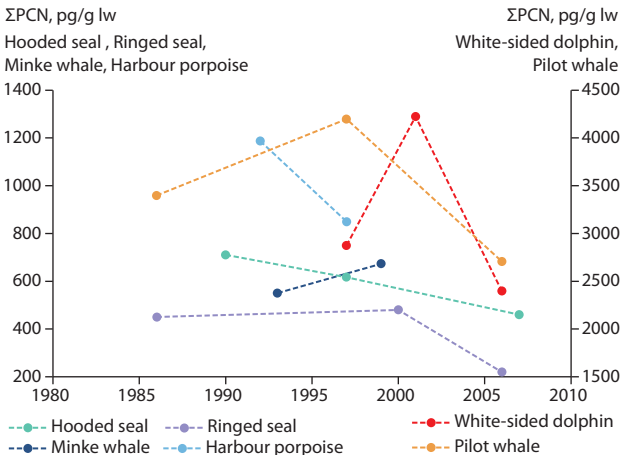

Figure 2.86 ΣPCN concentrations in marine mammals from the European Arctic (Rotander et al., 2012b). Concentrations in pilot whale and white-sided dolphin refer to the secondary y-axis. ΣPCN includes the following congeners: CN-52/60, CN-53/55, CN-66/67 and CN-69. The graphic shows mean concentrations for n=3, each of these samples comprising a pool of 3–6 individuals.

The study by Rotander et al. (2012b) also produced three years of data for most of the species included in the study (Figure 2.86). Continuously decreasing concentrations were only observed for hooded seals. For some of the other species, the most recent data point had the lowest concentrations. However, the fact that some species had the highest concentration in the intermediate sample, as was the case for the Resolute Bay ringed seals, indicates considerable year-to-year variation. As remarked by Rotander et al. (2012b), the migratory nature of some of the species in their study is likely to have increased variation because of varying exposure.

Monitoring of seabird eggs in the Canadian Arctic has resulted in a time series of PCNs in eggs of thick-billed murre from Prince Leopold Island, Lancaster Sound, for the period 1975–2014 (Braune and Muir, 2017). ΣPCN and the 40 individual congeners which could be analyzed statistically decreased significantly over this period, from an annual mean concentration for ΣPCN of 978 pg/g ww (1975) to 364 pg/g ww (2014). This development is in line with the observations for ringed seal from most sampling locations in the Canadian Arctic. As the concentration followed a linear decrease with no signs of levelling off, they are likely to continue to decrease (Braune and Muir, 2017). Converted to TEQ concentrations, the annual mean decreased from 0.89 pg/g in 1975 to 0.20 pg/g ww in 2014. Although the overall composition of ΣPCN, in terms of a predominance of penta- and tetraCNs, did not change over time, the penta- and tetraCN contribution increased over the study period. According to Braune and Muir (2017), this suggested an increasing influence of PCN combustion sources over those associated with PCB mixtures.

2.9.8 Conclusions

Compared with other compounds of emerging concern in the Arctic, relatively few data have been generated for PCNs since the previous AMAP assessment. Few new reports have become available on PCNs in air and no new data have been published for the terrestrial or freshwater environment. Recently conducted studies confirm the accumulation of PCNs in seabirds and marine mammals.

Analyses of PCN patterns can give indications of the likely sources of emissions, namely historical PCN use, PCNs as impurities, or unintentionally formed PCNs in combustion processes. These have been pursued in a few studies, which showed widely varying profiles between locations, matrices and animal species. Further research into PCN profiles might contribute to a better understanding of the environmental fate of PCNs in the Arctic. Moreover, little information on PCN-based toxicology in Arctic animals is available. While TEQ-based concentrations might be below thresholds for effects, they could contribute to dioxin and dioxin-like PCBs in the same samples.

The assessment of spatial trends for the past five years is limited to ringed seal data from the Canadian Arctic and Greenland. Results indicate higher concentrations in the Canadian Arctic by a factor of 2–10, although differences in methodology may play a role. There are currently no biota data from Russia or Alaska. Air measurements from Canada, Russia, Greenland and Finland have provided few recent data.

Comparisons between studies are generally limited by the different suites of congeners, making the selection of common 'indicator PCNs' advisable. Other methodological differences, for example regarding selectivity in PCN detection, might also affect comparability.

Some progress has been made in terms of temporal trend studies, for which no data were available at the time of the previous AMAP assessment. All recent temporal trend studies show decreasing concentrations for PCNs. The decrease was particularly clear for PCNs in seabird eggs from the Canadian Arctic studied from 1975-2014. Ringed seal from the Canadian Arctic generally show lower concentrations post-2000 than pre-2000. Concentration decreases were also found in the majority of pinnipeds and cetaceans studied in the European Arctic, but the three years of data available also showed large year-to-year variation.

2.10 Hexachlorobutadiene (HCBD)

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2.10.1 Introduction

Hexachlorobutadiene (HCBD) is a halogenated aliphatic hydrocarbon that historically was manufactured for industrial use, but is currently generated in much larger quantities as an unintentional by-product in the manufacture of other chlorinated hydrocarbons (UNEP, 2012b). Similarities between HCBD and other POPs have made it an environmental and health concern for some time, as evidenced by the many international regulations and treaties already in place to govern its production and use (UNEP, 2012b). Yet, despite this concern, data on its occurrence in the environment are limited. HCBD cannot be discounted as a threat to the Arctic, due to its high propensity for long-range atmospheric transport and its toxicity to aquatic organisms and birds.

In 2009, HCBD was added to Annex I (prohibition of production and use) of the UNECE Protocol on Persistent Organic Pollutants under the Convention on Long-Range Transboundary Air Pollution (UNECE, 2009b). This amendment has not yet entered into force, but will do so when two-thirds of the Parties have adopted the decision (www.unece.org/env/lrtap/pops_h1.html). In 2011, HCBD was proposed as a new POP under the Stockholm Convention (UNEP, 2011c). Following evaluation by the Persistent Organic Pollutants Review Committee (POPRC) (UNEP, 2012b, 2013c), the Conference of the Parties adopted HCBD as a persistent organic pollutant under Annex A (elimination) in May 2015 (UNEP, 2015h), however its listing under Annex C (unintentional production) is deferred and will be reconsidered at the eighth meeting of the Conference of the Parties in 2017 (UNEP, 2015g).

Amid concern for environmental releases of HCBD the amount of data on its occurrence in the Arctic is growing but still scarce (Table 2.61). This assessment provides a comprehensive review of HCBD levels reported for the Arctic to date using information collected from peer-reviewed publications, government scientific reports and unpublished data when necessary.

2.10.2 Physical-chemical properties

Hexachlorobutadiene (CAS registry number 87-68-3) is a halogenated aliphatic compound with an empirical molecular formula of C_4Cl_6 (Figure 2.87; Appendix 1) (IPCS, 1994). Compared with other POPs, HCBD has a low water solubility and is lipophilic (Chiou, 1985; Mackay et al., 2006). It has a high vapor pressure, allowing it to volatilize from water and wet surfaces (Pearson and McConnell, 1975; Shen, 1982). Owing to its hydrophobic and volatile nature, HCBD will not remain in water for long and will partition into the atmosphere or adsorb onto sediments (US EPA, 1980).

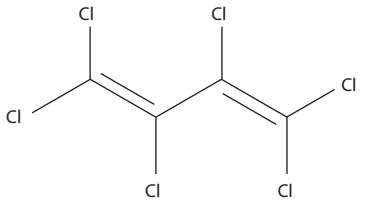

Figure 2.87 Hexachlorobutadiene (HCBD).

Several experimental studies on invertebrates and fish have indicated that HCBD has the potential to bioaccumulate with reported bioconcentration factors ranging widely from 17 to 71 000 (reviewed by UNEP, 2012b). However, HCBD does not appear to biomagnify through food chains, probably owing to its high depuration rate (Environment Canada, 2000).

2.10.3 Sources, production, use and trends

Although HCBD was historically manufactured for use as a solvent and other industrial purposes, it is no longer intentionally produced or used in the United States, Canada, or the UNECE region (UNEP, 2012b). Data on the production of HCBD outside these areas is not available. Generally, larger quantities of HCBD are generated as an inadvertent byproduct in the manufacture of other chlorinated hydrocarbons; in 1982 intentional production of HCBD was estimated at 10 000 tons worldwide, whereas an estimated 14 000 tons were generated as a waste byproduct in the United States alone (Lecloux, 2004).

Today, HCBD is primarily generated as an unintended waste product in the production of chlorinated hydrocarbons such as perchloroethylene, trichloroethylene and carbon tetrachloride (Lecloux, 2004). While some reports indicate the possibility of HCBD forming as a byproduct in the production of vinyl chloride, allyl chloride and epichlorohydrin, the likelihood of HCBD production under these circumstances has been questioned (Lecloux, 2004). HCBD may also be formed in the manufacture of magnesium and during incineration processes (Lecloux, 2004). There are no natural sources of HCBD in the environment (Environment Canada, 2000).

Table 2.61 Summary of Arctic media for which HCBD data have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
HCBD	×			×		×	×			×

The inadvertent production of large amounts of HCBD as an industrial by-product prompted its development into marketable applications (Lecloux, 2004). HCBD has had a variety of uses: it has been used as a solvent for rubber and other polymers; as a 'scrubber' to recover chlorine and other volatile organic components from gas; in hydraulic, heat transfer, transformer and gyroscopic fluids; and in the production of aluminum and graphite rods. Outside its technical applications, HCBD was used as an insecticide in vineyards in Argentina, Mediterranean Europe and the former Soviet Union, where it was also used as a fungicide (UNEP, 2012b).

It is currently believed that HCBD is no longer intentionally produced for commercial use in the 55 UNECE member countries, plus the United States and Canada (UNEP, 2013c). Intentional production in Europe and the United States ceased in the 1970s (Mumma and Lawless, 1975; Van der Honing, 2007) and HCBD was never intentionally produced in Canada. The production of HCBD outside these regions is unknown, although there is some evidence that intentional production may still occur, especially in southeast Asia (Li et al., 2008; Juang et al., 2010; UNEP, 2013c). Estimates for the global volume of HCBD production and use are scarce and out-of-date, but according to UNEP (2013c) large volumes of HCBD were produced between 1970 and 1980. In 1982, worldwide production of HCBD was estimated at 10 000 tonnes (IPCS, 1994).

Although the intentional production of HCBD in the UNECE region appears to have ceased, there is still potential for its unintentional production during the manufacture of chlorinated solvents in most parts of the world (Lecloux, 2004; UNEP, 2012b). HCBD is generated as a by-product during the production of chlorinated solvents and other industrial processes, but specific information on the volume of HCBD unintentionally produced globally is scarce. Relatively recent estimates are available for Europe and the United States, for which releases to air and surface water are within the same order of magnitude (up to several hundred kilograms per year) for the period 2007 to 2010 (UNEP, 2013c). Estimates of HCBD production from unintentional sources in Canada are comparatively low (less than 100 g in 2004) (UNEP, 2013c). Current estimates for the UNECE regions are orders of magnitude lower than for previous decades, suggesting that although unintentional production of HCBD is still likely, the amount generated has decreased significantly (UNEP, 2013c). Data on unintentional production in countries outside the UNECE region is sparse.

The discharge of HCBD from stockpiles, waste sites and landfills remains a concern globally (UNEP, 2013c). Although local contamination sites have been identified in the United States, the UK, and Australia, there is no estimate of the total number of potential sites or their releases worldwide (Crump et al., 2004), which means the relevance of disposal sites as a source of HCBD to the Arctic is not known.

2.10.4 Transformation processes

HCBD is susceptible to abiotic and biotic transformation processes. Because HCBD absorbs light within the solar spectrum it is expected to undergo photo-degradation (IPCS, 1994), photo-oxidation by hydroxy radicals (OH·) (Atkinson, 1987) and, less significantly, photo-oxidation by ozone (Atkinson and Carter, 1984). However, having a structure lacking hydrolysable functional groups, HCBD is not expected to undergo hydrolysis (UNEP, 2012b).

There is conflicting evidence regarding the conditions required for the biotransformation of HCBD in soil – some evidence points to reductive chlorination of HCBD under anaerobic conditions while other studies indicate no degradation occurs under anaerobic conditions (reviewed by UNEP, 2012b). HCBD is probably recalcitrant in soil under aerobic conditions, unless preceded by a dechlorination step (UNEP, 2012b). However, biotransformation of HCBD under aerobic and anaerobic conditions in wastewater has been reported (also reviewed by UNEP, 2012b). There are very few studies on the metabolism of HCBD in vertebrates, but several studies on fish show HCBD is quickly eliminated and unlikely to biomagnify (IPCS, 1994; Environment Canada, 2000).

There do not appear to be any recently published data on the transformation of HCBD specifically in the Arctic environment.

2.10.5 Modeling studies

The potential for HCBD to partition into the atmosphere, persist for long periods, and undergo long-range atmospheric transport has been identified by various models. The general trends of cumulative modeling efforts are briefly summarized here. UNEP (2012b) provides a more comprehensive review.

Most models suggest that a significant fraction of the HCBD released ends up in the atmosphere. Air is the main environmental compartment in which HCBD is found according to several sources. An air:water:solid partitioning ratio of 78:2:20 and a theoretical distribution of >99% in air have been reported (UNEP, 2012b). Furthermore, a non-equilibrium steady state Equilibrium Criterion Level III model used by Environment Canada and the US EPA shows that HCBD tends to remain in the environmental compartment into which it is released. More than 98% of atmospheric HCBD releases will remain in the air (Environment Canada, 2000). Although discharges of HCBD to soil are thought to stay predominantly in soil, owing to its hydrophobic nature, HCBD releases to water have the potential to repartition into air or sediment (Environment Canada, 2000). Inter-compartmental transfer is thought to occur primarily through volatilization, adsorption to particulate matter, and subsequent deposition or sedimentation (IPCS, 1994).

Estimates of HCBD half-lives in the atmosphere vary widely but most indicate a high degree of persistence. HCBD persists in air until it is either degraded photochemically or adsorbed onto particulate matter and deposited to water or soil (Environment Canada, 2000). The MSCE-POP multi-compartment chemistry transport model estimated the half-life of HCBD in the environment overall at 13 months. But half-lives vary among environmental compartments, with HCBD persistence greater in air (14 months) than water (three months) and soil (six months), indicating that its half-life in air is the most critical for assessing residence time in the environment (Vulykh et al., 2005). Other estimates for the atmospheric half-life of HCBD range from 60 days (ATSDR, 1994) to three years (Howard et al., 1991).

Of particular concern for the Arctic is that several models have shown HCBD has a high potential for long-range transport. According to Vulykh et al. (2005), the MSCE-POP model predicted HCBD would travel 8784 km with an atmospheric half-life of 118 days (roughly four months). These authors emphasized that a transport distance of this magnitude would enable atmospheric pollution to disperse over very wide areas. The OECD multimedia fate model also showed HCBD to have high potential for long-range transport (MacLeod et al., 2007). Measuring HCBD in abiotic and biotic media in remote areas of the Arctic (see Section 2.10.6) is also evidence of long-range transport.

2.10.6 Environmental concentrations

2.10.6.1 Air and precipitation

In 2003, HCBD was analyzed in air at the Arctic background station Pallas in Finland. HCBD was detected in both air samples analyzed (120 and 150 pg/m^3) and concentrations were similar to those in air at a background station in southern Sweden (Kaj and Palm, 2004).

HCBD was also analyzed in air at Alert, a High Arctic station in Nunavut, Canada from 2002 to 2012. Samples were obtained using a super-high-volume air sampler. This involves air being pulled through a glass fiber filter and two polyurethane foam plugs (PUFs) capture samples of the gas and particle phases, respectively, using a pump. Each sampler is deployed continuously at seven-day intervals for 52 weeks per year. Each seven-day integrated sample is representative of concentrations in 13 000 m^3 of air. More volatile compounds, such as HCBD (and chlorobenzenes and hexachlorocyclohexanes) often break through the sampling train, resulting in chemical loss. Break through occurs when the sampling medium, in this case PUF, becomes saturated with a specific analyte before the end of the sampling interval and a proportion of the compound passes through the PUFs and is lost. For each air sample taken at Alert, break through is defined as: (amount on second PUF)/(amount on front PUF) >33.3% (i.e. over a third of the chemical captured on the first PUF moved onto the second PUF). Break-through analysis for 23 samples taken in 2006 and 2007 showed break through of HCBD in the vapor phase for 22 of the 23 samples. Concentrations of HCBD reported at Alert may therefore be underestimated.

Each year, 56–100% of air samples had HCBD concentrations that were at least three times higher than method detection limits (MDL range, 0.025–0.37 pg/m^3). Concentrations were lower in 2008 and 2009, but in winter 2010/2011 and 2011/2012 levels returned to those seen in earlier years (Figure 2.88). Between 2002 and 2012, HCBD air concentrations measured at Alert ranged from non-detectable to 21 pg/m^3.

Air concentrations appeared to follow a cyclical pattern that peaked in winter and fell to a minimum in summer (Figure 2.88). This cyclical seasonal pattern may be partly because HCBD has a higher tendency to break through PUFs in the warmer months. However, no relationship between ambient temperature and percentage break through was observed in the break-through analysis. Alternatively, peak concentrations in winter could be due to a reduction in photodegradation processes during the darker winter months. The episodically high air concentrations of HCBD (>10 pg/m^3) observed in winter may reflect long-range transport of HCBD from Eurasian source regions, as general winter air patterns flow from Eurasia to the Arctic (Hung, unpubl. data).

2.10.6.2 Terrestrial environment

There are no data available on HCBD in soil.

A survey of contaminants in Greenlandic biota in 1999–2001 targeted several terrestrial animals, including ptarmigan (*Lagupus mutus*), Arctic hare (*Lepus arcticus*), lamb (*Ovis* sp.), caribou (*Rangifer tarandus*), and muskox (*Ovibos moschatus*) (Vorkamp et al., 2004b). Of the terrestrial biota, only ptarmigan, sheep and muskox had measurable concentrations. Overall, the range of median HCBD concentrations for terrestrial species (<MDL–4.9 ng/g lw) was greater than for all marine biota analyzed, including marine mammals (<MDL–0.8 ng/g lw) and

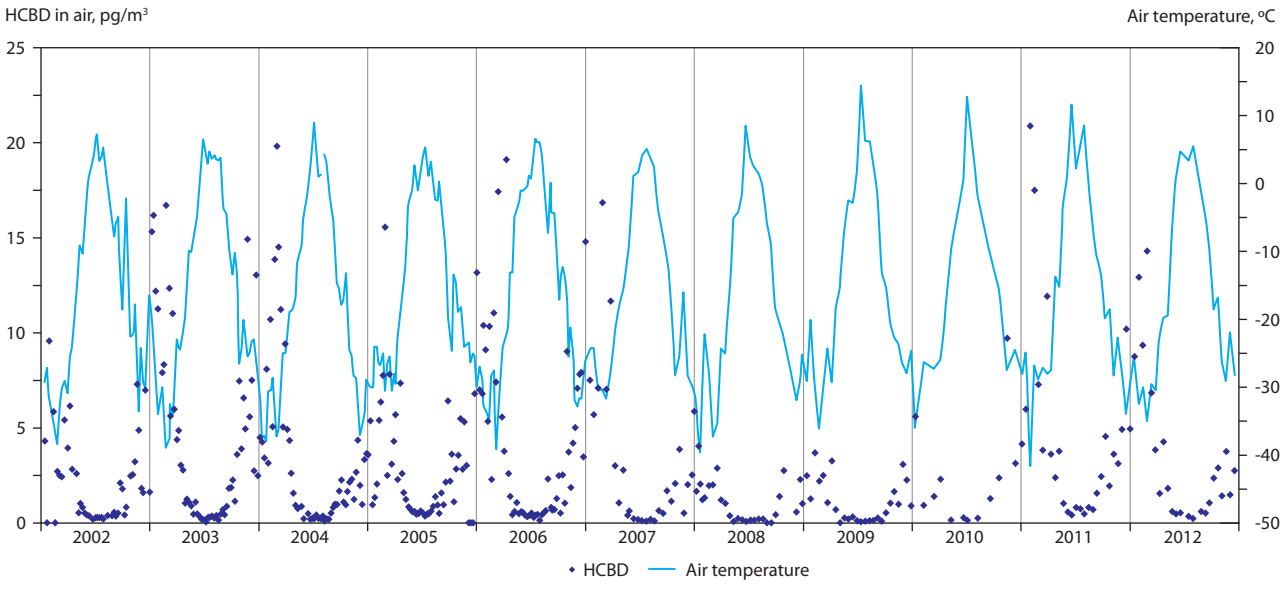

Figure 2.88 Temperature and HCBD concentrations measured in air (gas and particle phase together) at Alert station in Nunavut, Canada over the period 2002–2012 (Hung, unpubl. data).

seabirds (<MDL–3.4 ng/g lw). Ptarmigan muscle contained the highest median concentrations of HCBD of all terrestrial and marine biota included in the study.

A long-term study of reindeer (*Rangifer tarandus*) and moose (*Alces americanus*) during 1987–2006 from Sweden reported HCBD below the detection limit in reindeer muscle (Danielsson et al., 2008). Analysis of moose liver from the Dehcho region of the southwestern NWT found no detectable concentrations of HCBD (<0.2 ng/g lw) (Larter et al., 2017). However, mountain goat (*Oreamnos americanus*) liver from the same region had median concentrations of 6.8 ng/g lw (5.1–8.2 ng/g lw) (Larter et al., 2014).

2.10.6.3 Freshwater environment

Monitoring of water in Lake Abiskojaure (background) and Kalixälvens gruvsamhälle (old mining village, point source) in northern Sweden showed no detectable concentrations of HCBD (limit of quantification <10 ng/L) as analyzed by headspace gas chromatography/mass spectrometry (SWECO VIAK, 2007; Törneman et al., 2009b).

In 1987, HCBD was detected in all sediment samples collected from Great Slave Lake in the Northwest Territories (Canada) with concentrations of 0.01–0.23 ng/g dw (Murdoch et al., 1992). The city of Yellowknife, and several small towns and mining operations for gold and lead-zinc deposits, are located along the lake shore. The lake is also a major component of the Mackenzie River Basin, which contains heavy oil and tar sand deposits and one million hectares of farmland.

HCBD was detected in landlocked Arctic char (*Salvelinus alpinus*) from four lakes in the Canadian Arctic based on annual sampling over the period 2011–2013 using analysis by high resolution mass spectrometry (Muir et al. unpubl. data, 2015b). Median concentrations in skin-on muscle samples ranged from 0.17 to 0.64 ng/g lw (Table 2.62), and showed no relation to latitude or possible sources near the lakes (Resolute and Char Lake are near the Resolute Bay airport). HCBD was also detected in lake trout (*Salvelinus namaycush*) and burbot (*Lota lota*) from Great Slave Lake (Table 2.62; Muir and Evans, unpubl. data, 2015). Median concentrations of HCBD were similar in lake trout (muscle) in the eastern basin and western basin of Great Slave Lake (0.68 and 0.52 ng/g lw, respectively). In burbot (liver), HCBD concentrations were higher in samples from the western basin compared to the eastern basin (0.50 and 0.15 ng/g lw, respectively). The western basin is influenced by large inflowing rivers and several lakeside communities.

HCBD was monitored in perch from several lakes in Arctic Finland from 2012 to 2014 (Mannio, unpubl. data, 2015). Nine pooled samples was analyzed, each comprising 10 to 30 individuals. HCBD was below the limit of quantification in each pooled sample.

2.10.6.4 Marine environment

There were no data on HCBD in seawater or marine sediments.

A survey of Greenlandic biota in 1999–2001 included three species of invertebrate: Iceland scallop (*Chlamys islandica*), snow crab (*Chionoecetes opilio*) and shrimp. Median concentrations of HCBD were <MDL–0.57 ng/g lw (Vorkamp et al., 2004b).

Sheefish (*Stenodus leucicthys*), a common subsistence food harvested from Kotzebue (Alaska), had HCBD levels below the limit of detection in 2004–2005 (Moses et al., 2009). In contrast, HCBD was detectable in marine fish from Greenland. Concentrations were measured in seven species collected between 1999 and 2001: Atlantic cod (*Gadus morhua*), redfish (Sebastes sp.), Atlantic salmon (*Salmo salar*), Greenland halibut (*Reinhardtius hippoglossoides*), wolfish (*Anarichas minor*), capelin (*Mallotus villosus*), and shorthorn sculpin (*Myoxocephalus scorpius*), and were found in the range <MDL–2.6 ng/g lw (Vorkamp et al., 2004b). The highest concentrations were found in cod and redfish muscle (2.6 and 2.1 ng/g lw, respectively), while the lowest occurred in cod liver (0.13 ng/g lw) (Vorkamp et al., 2004b).

Searun Arctic char sampled near Cambridge Bay and Pond Inlet in the Canadian Arctic had similar low concentrations of HCBD in muscle (0.49 and 0.45 ng/g lw, respectively) (Muir and Evans, unpubl. data, 2015). These levels are within the range observed in landlocked char (Table 2.62) despite the differences between the two in terms of dietary sources, age and growth rates.

HCBD was analyzed in plasma and egg samples of glaucous gulls (*Larus hyperboreus*) collected from major breeding colonies on Bjørnøya in the Norwegian Arctic, but levels were consistently below method detection limits (Verreault et al., 2005b).

Conversely, HCBD was measurable in several species of seabird from Greenland in 1999 (Vorkamp et al., 2004b). Concentrations were <MDL–3.4 ng/g lw for muscle and liver samples from common eider (*Somateria mollisima*), king eider (*S. spectabilis*), black-legged kittiwake (*Rissa tridactyla*), and thick-billed murre (*Uria lomvia*). Muscle generally had higher concentrations than liver. Muscle concentrations were lowest in thick-billed murre (1.4 ng/g lw) and highest in common eider (3.4 ng/g lw) (Vorkamp et al., 2004b).

HCBD was measured in blubber, liver, muscle and kidney of five spotted seals (*Phoca largha*) harvested during subsistence hunts in Kotzebue (Alaska) during 2004–2005. Concentrations were only above the detection limit in blubber (0.012–0.184 ng/g ww) (Moses et al., 2009). Similar levels have also been reported for ringed seals (*Pusa hispida*) from the Hudson Strait area of northern Quebec, Ungava Bay and Labrador, with blubber concentrations of 0.03–0.33 ng/g ww (Lecloux, 2004).

HCBD concentrations were measurable in beluga (*Delphinapterus leucas*) and narwhal (*Monodon monoceros*) blubber from Greenland collected in 1999–2001, with median concentrations of 0.41 and 0.80 ng/g lw, respectively. Lower concentrations were also detectable in beluga liver (0.05 ng/g lw) (Vorkamp et al., 2004b).

HCBD was detectable in five of 15 fat samples from polar bears collected on Svalbard in 2002. Concentrations were 1.2–8.9 ng/g ww with a mean of 3.7 (Gabrielsen et al., 2004). However, HCBD was below detection limits in blood and fat of 57 polar bears from the Alaskan Beaufort Sea coast in 2003 (Bentzen et al., 2008). HCBD was consistently not detected in fat samples from western and southern Hudson Bay polar bears collected in 2012–2014 (Letcher et al., 2018).

Table 2.62 Concentrations of HCBD detected in Arctic biota.

Species	Location	Year	Tissue	n	Statistic	Concentration	Source
Marine invertebrates							
Iceland scallop, snow crab, shrimp	Nanortalik and Nuuk, Greenland	2000, 2001	Muscle; liver	29	median (range)	<MDL–0.57 ng/g lw	Vorkamp et al. (2004b)
Marine and freshwater fish							
Atlantic cod	Nuuk, Greenland	2000	muscle	9	median	2.6 ng/g lw	Vorkamp et al. (2004b)
			liver	3	median	0.13 ng/g lw	
Redfish	Nuuk, Greenland	2000	muscle	5	median	2.1 ng/g lw	Vorkamp et al. (2004b)
Sheefish	Alaska, US	2004–2005	muscle	8		<MDL	Moses et al. (2009)
Searun Arctic char	Cambridge Bay, Nunavut, Canada	2011–2013	muscle	11	median	0.49 ng/g lw	Muir and Evans (unpubl. data, 2015)
	Pond Inlet, Nunavut, Canada	2011–2013	muscle	10	median	0.45 ng/g lw	
Landlocked Arctic char	Lake Hazen, Nunavut, Canada	2011–2013	muscle	43	median	0.64 ng/g lw	Muir et al. (unpubl. data, 2015b)
	Amituk Lake, Nunavut, Canada	2011–2013	muscle	29	median	0.28 ng/g lw	
	Resolute Lake, Nunavut, Canada	2011–2013	muscle	29	median	0.28 ng/g lw	
	Char Lake, Nunavut, Canada	2011–2013	muscle	9	median	0.17 ng/g lw	
Lake trout	Great Slave Lake, Lutzel'ke, NWT, Canada	2012–2013	muscle	19	median	0.68 ng/g lw	Muir and Evans (unpubl. data, 2015)
	Great Slave Lake, Hay River, NWT, Canada	2012–2013	muscle	21	median	0.52 ng/g lw	
Burbot	Great Slave Lake, Lutzel'ke, NWT, Canada	2012–2013	liver	11	median	0.15 ng/g lw	Muir and Evans (unpubl. data, 2015)
	Great Slave Lake, Ft Resolution , NWT, Canada	2012–2013	liver	31	median	0.50 ng/g lw	
Seabirds							
Glaucous gull	Bjørnøya, Norway	2002, 2004	plasma	107		<MDL	Verreault et al. (2005b)
		2002, 2004	egg	30		<MDL	
Thick-billed murre	Nuuk, Greenland	1999	muscle	19	median	1.4 ng/g lw	Vorkamp et al. (2004b)
King eider	Nuuk, Greenland	1999	muscle	10	median	2.3 ng/g lw	
Common eider	Nuuk, Greenland	1999	muscle	10	median	3.4 ng/g lw	
Terrestrial Birds							
Ptarmigan	Nuuk, Greenland	1999	muscle	5	median	4.9 ng/g lw	Vorkamp et al. (2004b)
Terrestrial mammals							
Lamb	Narsaq, Greenland	1999	kidney	5	median	0.66 ng/g lw	Vorkamp et al. (2004b)
Muskox	Kangerlussuaq, Greenland	1999	kidney	5	median	1.3 ng/g lw	Vorkamp et al. (2004b)
Moose	Dehcho region, NWT, Canada	2012	liver	11	median	<0.20 ng/g lw	Larter et al. (2017)
Mountain goat	Dehcho region, NWT, Canada	2013	liver	3	median	6.8 ng/g lw	Larter et al. (2014)
Marine mammals							
Ringed seal	Beaufort Sea/Sachs Harbour, NWT, Canada	2011–2013	blubber	27	median	0.33 ng/g ww	Muir and Evans (unpubl. data, 2015)
	Hudson Bay/Arviat, Nunavut, Canada	2011–2013	blubber	17	median	0.13 ng/g ww	
	Lancaster Sound/Resolute Bay, Nunavut, Canada	2011–2013	blubber	34	median	0.40 ng/g ww	
Spotted seal	Alaska, US	2004	blubber	5	mean	0.092 ng/g ww	Moses et al. (2009)
			muscle	5		<MDL	
			liver	5		<MDL	
			kidney	5		<MDL	
Beluga	Saqqaq, Greenland	2000	blubber	10	median	0.41 ng/g lw	Vorkamp et al. (2004b)
			liver	5	median	0.05 ng/g lw	
Narwhal	Saqqaq, Greenland	2000	blubber	3	median	0.80 ng/g lw	Vorkamp et al. (2004b)
Polar bear	Svalbard, Norway	2002	adipose	15	mean	3.7 ng/g ww	Gabrielsen et al. (2004)
	Alaska, US	2003	adipose	57		<MDL[a]	Bentzen et al. (2008)
			blood	46		<MDL[a]	
	Hudson Bay, Canada	2012–2014	adipose	100		<MDL	Letcher et al. (2018)

[a] Summary statistics not reported because concentrations were below detection limits in more than 50% of samples.

2.10.7 Environmental trends

2.10.7.1 Spatial trends

There is some information on spatial trends in landlocked Arctic char in Section 2.10.6.3.

2.10.7.2 Temporal trends

HCBD was detected (>1 pg/g dw) in a dated sediment core from Lake Hazen on northern Ellesmere Island (Muir et al. unpubl. data, 2015g). Maximum concentrations were present in horizons dated to the 1970s and 1980s (2–10 pg/g dw).

2.10.8 Conclusions

Although HCBD has been shown to disperse via long-range atmospheric transport, and has been measured consistently in Arctic air, data on its occurrence in other Arctic media and biota are scarce. Measurements of HCBD in abiotic media such as glacier cores, seawater and freshwaters, and soils and sediments are particularly lacking. The relatively low HCBD concentrations measured in all Arctic terrestrial and marine biota to date are consistent with laboratory bioaccumulation studies which indicate that HCBD has the potential to bioaccumulate, but not to biomagnify due to its relatively fast biotransformation and elimination. Available data for Arctic biota suggest that terrestrial birds and mammals and seabirds, have higher HCBD concentrations than fish and marine mammals. As a result, future monitoring of the former and their food sources should be strongly considered.

Spatial and temporal trends in HCBD concentrations in the Arctic are sparse and would be useful for identifying sources, transport pathways, and the impact of newly-imposed regulations. Continued monitoring will be important because HCBD is primarily generated as an unintended by-product in the production of other industrial solvents, which means environmental releases may continue despite new regulations.

2.11 Current-use pesticides (CUPs)

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Contributors: Hayley Hung, Liisa Jantunen, Frank Rigét, Katrin Vorkamp

2.11.1 Introduction

Since legacy pesticides such as DDT began to be regulated in the 1970s and 1980s, there has been a massive increase in the use of replacement chemicals that serve similar purposes to the chemicals they replace (i.e. reducing exposure to insect-borne diseases, protecting crops, and maintaining agricultural yields). In theory, these so-called current-use pesticides (CUPs) are only licensed for use if they do not persist in the environment long after their period of use and have low bioaccumulation potential, and thus have less environmental impact than the legacy pesticides they are replacing (US EPA, 2007). Nevertheless, many CUPs continue to be discovered in remote regions, including the Arctic, indicating that they are sufficiently persistent to undergo long-range transport and present an environmental concern (Hoferkamp et al., 2010). Recent studies also indicate that several CUPs bioaccumulate in Arctic biota (Morris et al., 2014, 2016).

Because CUPs were the subject of several recent reviews examining contaminants of emerging Arctic concern (Hoferkamp et al., 2010; Weber et al., 2010; Vorkamp and Rigét, 2014), the present assessment serves primarily as an update, summarizing recently published and unpublished information for CUPs previously identified in the Arctic and several pesticides newly identified in the Arctic environment. For comparison purposes, Table 2.63 provides a summary of CUP data currently and previously reported in Arctic media (i.e. air, water, sediment, and biota).

2.11.2 Physical-chemical properties

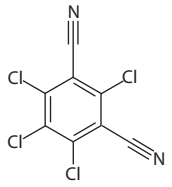
The CUPs currently reported in the Arctic span diverse structural classes (Figure 2.89 and Table 2.64), making it difficult to describe them as a group based on similar physical-chemical properties. However, owing to their occurrence in remote, high-latitude regions, they do share several general characteristics (Hoferkamp et al., 2010). Many exhibit a moderate to low solubility in water and relatively low air-water partitioning (log K_{AW} values ranging from -3.5 to -6), allowing them to reach the Arctic, primarily through long-range atmospheric transport, with some contribution possible via ocean currents (Wania, 2003; Muir et al., 2004b; Matthies et al., 2009; Zarfl et al., 2012). In addition, intermediate lipid solubility (log K_{OW} values ranging from 3 to ~5) and high octanol-air partitioning (log K_{OA} values ranging from 7 to 11) impart the potential for many CUPs to bioaccumulate in aquatic food chains, especially marine and terrestrial food chains that contain multiple air-breathing consumers (Kelly and Gobas, 2003; Kelly et al., 2007; Morris et al., 2014, 2016).

Table 2.63 Summary of Arctic media for which CUP data have been previously (+) and newly (×) reported.

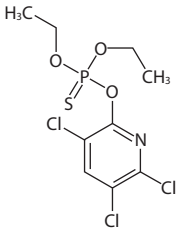
Common name	Air		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
Chlorothalonil	+,×	+		×	+			+, ×		
Chlorpyrifos	+,×	+		×	+		+	+, ×		+
Dacthal	+,×	+		+, ×	+	+	+	+, ×		+, ×
Diazinon		+			+					
Dicofol	+,×							+, ×		
Endosulfan	+,×	+		+, ×	+		+	+, ×	×	+, ×
MCPA	×									
Methoxychlor	+	+		+	+		+	×		+
Metribuzin	×									
Pendimethalin	×									
Pentachloro-nitrobenzene (PCNB)	×	+,×		×	+			×		×
Phosalone	×									
Quizalofop ethyl	×									
Tefluthrin	×									
Triallate	×									
Trifluralin	+,×	+			+	+		+, ×	×	

Historical data summarized from Hoferkamp et al. (2010); Weber et al. (2010) and Vorkamp and Rigét (2014).

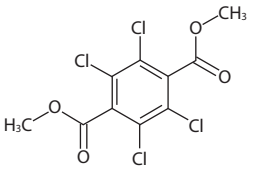
Chlorothalonil
CAS no: 1897-45-6



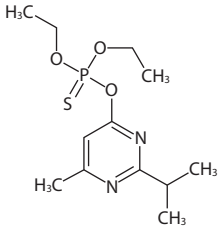
Chlorpyrifos
CAS no: 2921-88-2



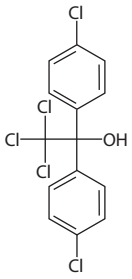
Dacthal
CAS no: 1861-32-1



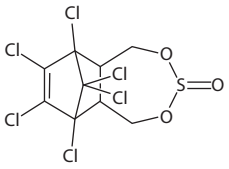
Diazinon
CAS no: 333-41-5



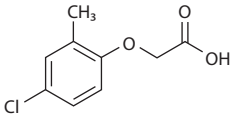
Dicofol
CAS no: 115-32-2



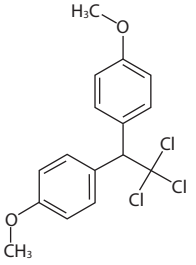
Endosulfan
CAS no: 115-29-7



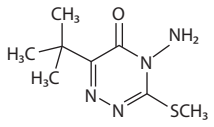
MCPA
CAS no: 94-74-6



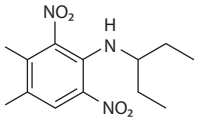
Methoxychlor
CAS no: 72-43-5



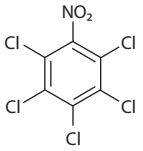
Metribuzin
CAS no: 21087-64-9



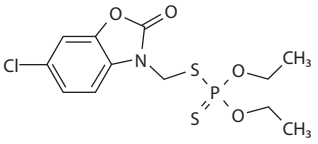
Pendimethalin
CAS no: 40487-42-1



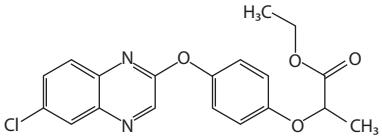
Pentachloro-
nitrobenzene (PCNB)
CAS no: 82-68-8



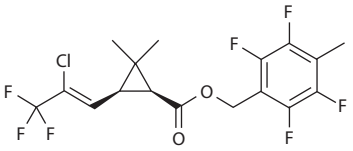
Phosalone
CAS no: 2310-17-0



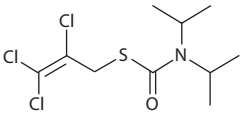
Quizalofop ethyl
CAS no: 76578-14-8



Tefluthrin
CAS no: 79538-32-2



Triallate
CAS no: 2303-17-5



Trifluralin
CAS no: 1582-09-8

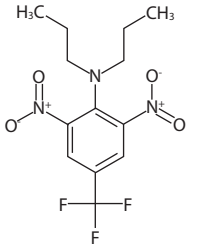


Figure 2.89 Structure of current-use pesticides detected in Arctic media.

Table 2.64 Current-use pesticides detected in Arctic media.

Common name	CAS#	High production volume (HPV) chemical[a]	Class
Chlorothalonil	1897-45-6	×	Organochlorine fungicide
Chlorpyrifos	2921-88-2	×	Organothiophosphate insecticide
Dacthal (DCPA) Dimethyl tetrachloro-terephthalate	1861-32-1		Organochlorine herbicide
Diazinon	333-41-5	×	Organothiophosphate insecticide
Dicofol	115-32-2 (*p,'p*-dicofol); 10606-46-9 (*o,p'*-dicofol)	×	Organochlorine insecticide
Endosulfan	115-29-7	×	Organochlorine insecticide
MCPA (2-methyl-4-chloro-phenoxyacetic acid)	94-74-6	×	Phenoxy herbicide
Methoxychlor	72-43-5		Organochlorine insecticide
Metribuzin	21087-64-9		Triazinone herbicide
Pendimethalin	40487-42-1	×	Dinitroaniline herbicide
PCNB or Quintozene	82-68-8		Organochlorine fungicide
Phosalone	2310-17-0		Organothiophosphate insecticide
Quizalofop ethyl	76578-14-8		Aryloxyphenoxypropionic herbicide
Tefluthrin	79538-32-2		Pyrethroid insecticide
Triallate	2303-17-5	×	Thiocarbamate herbicide
Trifluralin	1582-09-8	×	Dinitroaniline herbicide

[a] Produced or imported in quantities greater than 1000 tonnes per year (OECD, 2009).

2.11.3 Sources, production, use and trends

According to the most recent report from the US Environmental Protection Agency (US EPA), roughly 2.4 million tonnes of pesticides were used globally in 2007, with herbicides accounting for the largest proportion of total use (Figure 2.90) (US EPA, 2011b). Published records reporting chemical-specific uses are scarce, making it difficult to identify sources and global trends of their production and use. However, most CUPs of Arctic concern have been recognized as high production volume (HPV) chemicals being produced or imported in amounts greater than 1000 tonnes per year by at least one of the 34 OECD member nations (Table 2.65) (OECD, 2009). The CUPs detected in Arctic media mainly originate from agricultural applications. None of the chemicals listed in Table 2.64 were identified in a recent global survey of pesticides used to control insect-borne diseases, such as malaria or dengue fever (van den Berg et al., 2012).

The CUPs presently detected in the Arctic fall under varying levels of regulation (Table 2.65). Most are still approved for use in the United States, Canada and Europe; however, some have restrictions on their use and others are beginning to be subject to domestic and international regulations. In 2011, endosulfan was added to the UN Stockholm Convention on POPs (Annex A) and is currently in the process of being phased out globally (UNEP, 2011b). Dicofol is also currently under consideration for inclusion in the Stockholm Convention following a decision by the POPs Review Committee that dicofol met the criteria set out in Annex D to the Convention (UNEP 2016b).

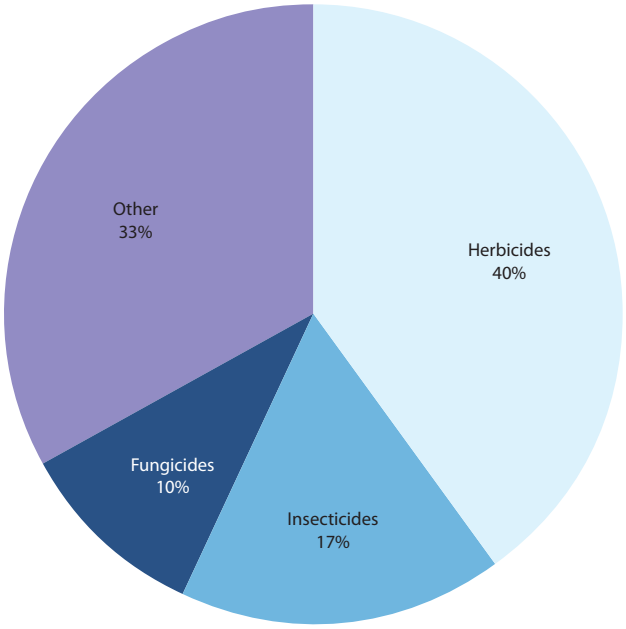


Figure 2.90 Global pesticide market by type as estimated for 2007 (US EPA, 2011b). 'Other' includes nematicides, fumigants, and miscellaneous conventional chemicals used as pesticides such as sulfur, petroleum oil, and sulfuric acid.

Table 2.65 Regulatory status of current-use pesticides of relevance to the Arctic as of 2015.

	United States (US EPA, 2015b)	Canada (Health Canada, 2015)	European Union (EC, 2015)	Stockholm Convention	LRTAP Convention
Chlorothalonil	Approved	Approved	Approved		
Chlorpyrifos	Approved for restricted use	Approved for restricted use	Approved for restricted use		
Dacthal	Approved	Approved	Approved		
Diazinon	Approved	Approved	Not approved		
Dicofol	Voluntarily phased out 2011	Not approved	Not approved	Under review	Under review
Endosulfan	Phase out underway, all uses expire July 2016	Phase out in process, all uses expire December 2016	Not approved	Listed, Annex A (2011)	Under review
MCPA	Approved	Approved	Approved		
Methoxychlor	Not approved	Not approved	Not approved		
Metribuzin	Approved	Approved	Approved		
Pendimethalin	Approved	Approved	Approved		
PCNB	Approved for restricted use	Approved for restricted use	Not approved		
Phosalone	Not approved	Not approved	Not approved		
Quizalofop ethyl	Approved	Approved	Not approved		
Tefluthrin	Approved	Approved	Approved		
Triallate	Approved	Approved	Approved		
Trifluralin	Approved	Approved	Not approved		Under review

2.11.4 Transformation processes

In agricultural and urban settings, pesticides are directly and extensively applied to large land areas. Therefore, degradation and transformation represents an important pathway for the removal of CUPs from the environment. As a group, pesticides span a wide range of structural conformations and physical-chemical properties, therefore the type(s) of transformation processes a given pesticide will undergo depends on its molecular configuration as well as the environmental conditions to which it is exposed.

Although degradation of pesticides can involve both abiotic and biotic transformation processes, biodegradation by micro-organisms is generally recognized as the most important route of removal from the environment (Fenner et al., 2013). Organophosphate pesticides (i.e. chlorpyrifos, diazinon), phenoxy-herbicides (MCPA); pyrethroids (i.e. tefluthrin) and carbamates (i.e. triallate) are primarily degraded via microbial transformation. Several of the CUPs including chlorpyrifos (US EPA, 2011a), dacthal (US EPA, 1998), endosulfan (Dorough et al., 1977), and pentachloro-nitrobenzene (PCNB) (Larsen et al., 1998) are biotransformed and residues are depurated from the tissues of mammals relatively rapidly, particularly in comparison to recalcitrant organochlorine pesticides (OCPs). Chlorothalonil also seems to be eliminated rapidly from mammals, but this is more likely to be due to poor absorption across the gut epithelium than to biotransformation (Wilkinson and Killeen, 1996). Although the CUPs are effectively metabolized, in some cases the biotransformation products can be bioaccumulative (endosulfan sulfate) (Morris et al., 2014) and in the case of chlorpyrifos-oxon, a more potent toxicant than the parent compound (Sams et al., 2004). For some CUPs, abiotic processes such as chemical and photochemical reactions can also be important degradation pathways. Pyrethroids, carbamates and dinitroaniline derivatives (i.e. trifluralin) are particularly susceptible to phototransformation, especially when discharged into surface waters. The primary degradation routes of the major pesticide classes are reviewed by Fenner et al. (2013).

2.11.5 Modeling studies

Modeling efforts have been used to assess the influence of a warming climate on the delivery of CUPs to the Arctic Ocean (Pućko et al., 2015). Legacy OCPs and CUPs were measured in air and surface seawater in the Beaufort Sea in 2008 and used to predict levels in sea-ice melt pond water. Predicted melt water concentrations were higher for CUPs (ranging from 27±28 pg/L for dacthal to 258±443 pg/L for chlorothalonil) than for legacy OCPs (ranging from 0.7±0.4 pg/L for trans-chlordane to 41±18 pg/L for dieldrin). The total annual release via melt water was estimated at 6 kg for dacthal, 16 kg for chlorpyrifos, 6 kg for α-endosulfan, and 54 kg for chlorothalonil, which equates to 2% of dacthal, 4% of chlorpyrifos, 10% of α-endosulfan, and 4% of chlorothalonil found in the standing stock of CUPs present in the upper mixed layer of the Beaufort Sea. Overall, the data suggest that sea ice meltwater is an important route for CUPs to the Arctic Ocean, one that will influence contaminant pathways as the Arctic's ice-scape changes under a warming climate.

Modeling efforts have been used to determine the global inventory, distribution, environmental fate, and Arctic contamination potential of dicofol (Li et al., 2015b). Data compiled from literature and field surveys suggest that 28 200 tonnes of dicofol were released into the environment between 2000 and 2012, with east and southeast Asia, the Mediterranean coast, and northern and central America the major sources. Applying the BETR-Global simulation and Globo-POPs model, shows dicofol was transported northward via atmospheric and oceanic transport and exhibits an Arctic contamination potential greater than for several POPs, such as heptachlor, aldrin, and hexabromocyclododecane (HBCDD).

2.11.6 Environmental concentrations

2.11.6.1 Air and precipitation

In 2005 and 2007, passive air samplers were installed at nine Canadian locations, including three sites within the Canadian Arctic (Messing et al., 2014). Samplers were deployed at Coral Harbour, Cape Dorset and Arviat (Nunavut) for 90 days and screened for seven currently used herbicides, including 2,4-D, bromoxynil, ethalfluralin, MCPA, mecoprop, triallate and trifluralin. Although most of the target analytes, including trifluralin, were undetectable; both triallate and MCPA were detected in samples from Arviat, providing the first evidence of these CUPs in the Arctic region.

Starting in August 2006, air samples were collected at Alert using a high volume air sampler (separate from the routine monitoring using super high volume air samplers) equipped with a glass fiber filter and a PUF-XAD sandwich to collect CUPs (in both the particulate and gas phases). Thirteen CUPs were sought and confirmed with dual column analysis in these samples (gas and particulate phases were analyzed together). Table 2.66 summarizes results from August 2006 to October 2009. The air concentrations of all CUPs were low (<1 pg/m^3). Only dacthal, α-endosulfan, endosulfan sulfate, trifluralin and tefluthrin were detectable in more than 40% of samples.

Table 2.66 Air concentrations measured at the Canadian High Arctic station of Alert between August 2006 and October 2009 under the Northern Contaminants Program (Hung et al., 2013a; Hung, 2015). Samples obtained using a high volume air sampler. Data shown are field and laboratory blank-corrected.

Chemical	Mean ± SD (n=68)	Range	% Detection
Chlorpyrifos	0.27±1.0	<MDL–6.8	19
Chlorothalonil	0.076±0.15	<MDL–0.65	31
Dacthal[a]	0.041±0.057	<MDL–0.23	66
α-Endosulfan[a]	3.4±3.5	0.0060–14	100
β-Endosulfan	0.16±0.54	<MDL–3.2	37
Endosulfan sulfate[a]	1.9±4.1	<MDL–24	56
Metribuzin	0.029±0.089	<MDL–0.49	32
Pendimethalin	0.087±0.19	<MDL–1.1	25
PCNB	0.19±0.80	<MDL–5.5	26
Phosalone	0.12±0.41	<MDL–2.6	13
Quizalofop Ethyl	0.042±0.23	<MDL–1.9	28
Trifluralin[a]	0.043±0.056	<MDL–5.5	76
Tefluthrin[a]	0.029±0.041	<MDL–0.15	59

[a] Detectable in more than 40% of samples.

CUPs have been determined in Arctic air using PUF and XAD passive samplers (see Tables 2.67 and 2.68). During a GAPS (Global Atmospheric Passive Sampling) network special pilot study both PUF disks and SIP disks measured seven CUPs at five locations (Koblizkova et al., 2012): Alert (Canada), Little Fox Lake (Canada), Barrow (Alaska, USA), Ny-Ålesund (Svalbard, Norway), and Stórhöfði (Iceland). Concentrations in air were reported for dacthal, trifluralin, chlorpyrifos, pendimethalin and chlorothalonil. The highest concentrations of chlorothalonil, dacthal and pendimethalin were found at Stórhöfði. CUPs were also sought at several GAPS network

Table 2.67 Arctic air concentrations (pg/m^3) of current-use pesticides measured via passive sampling at eight locations by Shunthirasingham et al. (2010). Conversion: ng/sampler converted to pg/m^3 using days of deployment and sampling rate of 0.5 m^3 per day (Wania et al., 2003) for Arctic locations.

		Trifluralin	Chlorothalonil	Dacthal	Pendimethalin	α-Endosulfan	β-Endosulfan	Endosulfan sulfate
Alert, Canada	2006–2007	<MDL	<MDL	<MDL	<MDL	<MDL–8.8	<MDL	<MDL
Barrow, Alaska, USA	2004–2007	<MDL– 0.3	<MDL–1.1	<MDL–0.3	<MDL	<MDL–13	<MDL	<MDL
Dyea, USA	2005–2008	<MDL–0.3	<MDL–6.3	<MDL–0.3	<MDL	<MDL–2.8	<MDL	<MDL
St. Lawrence Island, USA	2004–2007	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Little Fox Lake, Canada	2006–2008	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Ny-Ålesund, Norway	2004–2007	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Pallas, Finland	2005–2008	<MDL	<MDL–99	<MDL–1.1	<MDL	<MDL–15.6	<MDL–0.3	<MDL–0.6
Stórhöfði, Iceland	2004–2008	<MDL	<MDL–64	<MDL–2.7	<MDL	<MDL–17.2	<MDL–0.5	<MDL–0.5

Method detection limit (MDL) = ~0.5 pg/m^3.

Table 2.68 Arctic air concentrations (pg/m³) of current-use pesticides measured via passive sampling at five GAPS network sites (Koblizkova et al., 2012). Range of values based on PUF disk and SIP disk passive air samples deployed for about three months during May–June, 2009. Malathion, chlorpyrifos and trifluralin were also sought by Koblizkova et al. (2012) but were not detected (<MDL) and so are not included in the table.

		Chlorothalonil	Dacthal	Pendimethalin	Metribuzin
Alert, Canada	May–June 2009	<MDL	<MDL	<MDL	<MDL
Barrow, Alaska, USA	May–June 2009	<MDL–110	4.7–9.4	<MDL	<MDL
Little Fox Lake, Canada	May–June 2009	<MDL	<MDL–37	<MDL	<MDL–190
Stórhöfði, Iceland	May–June 2009	47–870	8.8–28	<MDL–270	<MDL
Ny-Alesund, Norway	May–June 2009	<MDL	19–37	<MDL	<MDL

Method detection limit (MDL) = ~1-5 pg/m³.

sites as well as at other Arctic sites by Shunthirasingham et al. (2010) over the period 2004–2008. These data were determined based mainly on 1-year deployments using XAD samplers and were reported by the authors as ng/sampler. Results in Table 2.67 are expressed as pg/m³ for comparison with the results of Koblizkova et al. (2012) in Table 2.68. Dacthal and chlorothalonil, along with endosulfan were the most widely detected compounds. Endosulfan is another CUP that is detected routinely at Arctic sites using PUF disks deployed quarterly since 2005 (Pozo et al., 2009) and these endosulfan data were reviewed in a previous assessment of endosulfan in the Arctic (Weber et al., 2010).

Air concentrations of CUPs were measured onboard the *Oden* Icebreaker in July 2005 in the North Atlantic and the Canadian Arctic Archipelago (Hung et al., 2013a). CUPs analyzed in these samples include dacthal, trifluralin, chlorothalonil, metribuzin, pendimethalin and endosulfans (α-, β-isomers and endosulfan sulfate). Back-trajectory analysis showed that during the entire sampling period there was no strong atmospheric input from potential source regions at lower latitudes. Although the samples were collected in summer when CUP use is generally high, the intrusion of air masses into the Arctic was minimal. Thus, these samples represent background Arctic concentrations. Metribuzin and pendimethalin were not detectable in blanks and rarely in samples. Dacthal concentrations exceeded the method detection limit (MDL) of 0.6 pg/m³ in two out of 20 samples and all concentrations found were higher than those observed at Alert (Table 2.66). One of the two episodes was associated with transport from the United Kingdom where there was ongoing use of dacthal (Hung et al., 2013a). α-Endosulfan concentrations only exceeded the MDL of ~9 pg/m³ once and the trifluralin concentration was also high in this sample. The β-endosulfan concentration was very low and endosulfan sulfate was not detectable.

Air samples collected from oceanographic cruises in the Bering and Chukchi Seas, northern Canada Basin, and Canadian Arctic Archipelago have also been monitored for some CUPs (Table 2.69) and are discussed further in Section 2.11.7.2.

Dicofol, which is currently under review by the Stockholm Convention, was recently added to the target analyte list and was measured in air samples taken on board the *Amundsen* icebreaker in the Canadian Arctic Archipelago in 2011–2013 following modification of analytical methods (Jantunen, pers. comm.). Average levels of dicofol in air were 1.9 pg/m³. Global dicofol use is thought to have decreased over the period 2000–2012, from 3400 tonnes (2000) to 730 tonnes (2012) (Li et al., 2015b), and dicofol data for the Arctic are sought because there are few data available to provide evidence of long-range atmospheric transport.

Air and seawater samples were collected during a research cruise extending from the East China Sea to the High Arctic between June and September 2010 and analyzed for six CUPs: chlorpyrifos, chlorothalonil, dacthal, dicofol, endosulfan and trifluralin (Table 2.70; Zhong et al., 2012b). Levels of α-endosulfan, chlorpyrifos and dicofol were one to two orders

Table 2.69 Average air concentrations (pg/m³) of current-use pesticides measured during oceanographic surveys in the western Arctic Ocean between 1999 and 2007–2013 (Jantunen, 2014; Jantunen et al., 2015b).

Chemical	1999 Mean ± SD	2007–2013 Mean ± SD
Chlorpyrifos	NA	1.1±1.3
Chlorothalonil	0.30±0.30	0.90±1.8
Dacthal	2.1±1.6	1.1±1.6
α-Endosulfan	4.3±3.7	2.5±1.5
β-Endosulfan	0.31±0.54	0.12±0.19
Endosulfan sulfate	NA	0.26±0.55
Trifluralin	NA	0.39±0.69

Table 2.70 Concentration range of current-use pesticides in Arctic air and seawater measured during an oceanographic cruise from the North Pacific to the Arctic Ocean in 2010 (Zhong et al., 2012b).

Chemical	Air (gas phase; pg/m³)	Seawater (dissolved; pg/L)
Chlorpyrifos	0.50–2.0	0.08–0.85
Chlorothalonil	0.1–2.1	<MDL–0.17
Dacthal	0.03–0.1	<MDL–4.0
Dicofol	0.9–2.5	<MDL–2.3
α-Endosulfan	0.40–1.6	0.04–0.4
β-Endosulfan	<MDL	<MDL
Trifluralin	0.9–2.2	<MDL–0.009

of magnitude higher in East Asia and the North Pacific than in the Arctic, indicating Asian countries as potential sources. Gaseous concentrations of chlorothalonil, dacthal and dicofol also increased with latitude from the North Pacific toward the Arctic, which Zhong et al. (2012b) attributed to direct input from Russia and North America and/or transport via ocean currents.

Endosulfan and mirex were investigated in air and deposition samples from Pallas in northern Finland. Cousins et al. (2005) found concentrations of α-endosulfan of 2.5–8.6 pg/m³ in all four air samples from 2004, but β-endosulfan and mirex were not detected. α-Endosulfan and mirex were also not detected in the four deposition samples from Pallas 2004. Kaj et al. (2007) investigated the concentrations of endosulfan in monthly air and deposition samples during 2006. α-Endosulfan was detected in all air samples with concentrations of 3.2–19 pg/m³ and β-endosulfan was found in 8 of 12 samples at 0.12–0.36 pg/m³. In deposition, α-endosulfan was detected in 12 of 13 samples at 0.01–0.4 ng/m²/d, β-endosulfan at 0.006–0.26 ng/m²/d. No seasonal differences were found in air or deposition samples for α- or β-endosulfan. Bossi et al. (2016) measured α-endosulfan in air (sum of gaseous and particulate phases) at Villum Research Station, Station Nord in northern Greenland over the period 2008–2013 and found no significant temporal trends. α-Endosulfan was detected in all 61 samples at a mean concentration of 3.3 pg/m³ (range 0.09–14.1 pg/m³).

From 2009 through 2010, bi-monthly bulk atmospheric deposition samples (precipitation + dry particle) were taken at an Arctic site near Abisko National Park (68°20'N, 19°30'E) in Stordalen mire, Sweden (Newton et al., 2014). Two CUPs were detected: trifluralin was detected in 75% of samples, with an overall mean monthly deposition flux of 0.57 ng/m² and chlorothalonil was detected in 33% of samples, at levels just above the instrument detection limit so an average monthly flux could not be calculated.

Ruggirello et al. (2010) reported the historical profiles of CUPs in the Holtedahlfonna ice cap, one of the major ice fields on Svalbard, Norway. The ice core and snow samples were collected in 2005 and analyzed for 47 CUPs as well as legacy OCPs. Nine CUPs were observed in at least one of six core segments dating to 1953 and chlorpyrifos, dacthal, trifluralin and endosulfan-related compounds were the most prominent (Figure 2.91).

Chlorpyrifos had the highest fluxes of the CUPs peaking at 808 pg/cm²/y compared to 12.4 pg/cm²/y for total endosulfan. Ruggirello et al. (2010) also compared fluxes from the Holtedahlfonna ice cap with earlier results in the Austfonna ice cap (220 km east-northeast of Holtedahlfonna) for the same time horizon (Hermanson et al., 2005). They found that the α-endosulfan and chlorpyrifos burdens at Austfonna were much higher by factors of about 60 and 13, respectively. The β-endosulfan burden had the opposite trend, being roughly 12 times greater at Holtedahlfonna. The burdens of methyl parathion were very similar, and occurred at about the same time. The dacthal burden at Holtedahlfonna was almost 3-fold higher than at Austfonna, although the peak inputs occurred over the same periods. The divergence of burdens or peak input periods of these compounds between these sites suggested that the general sources of these pesticides were different at least part of the time, and that Austfonna generally received

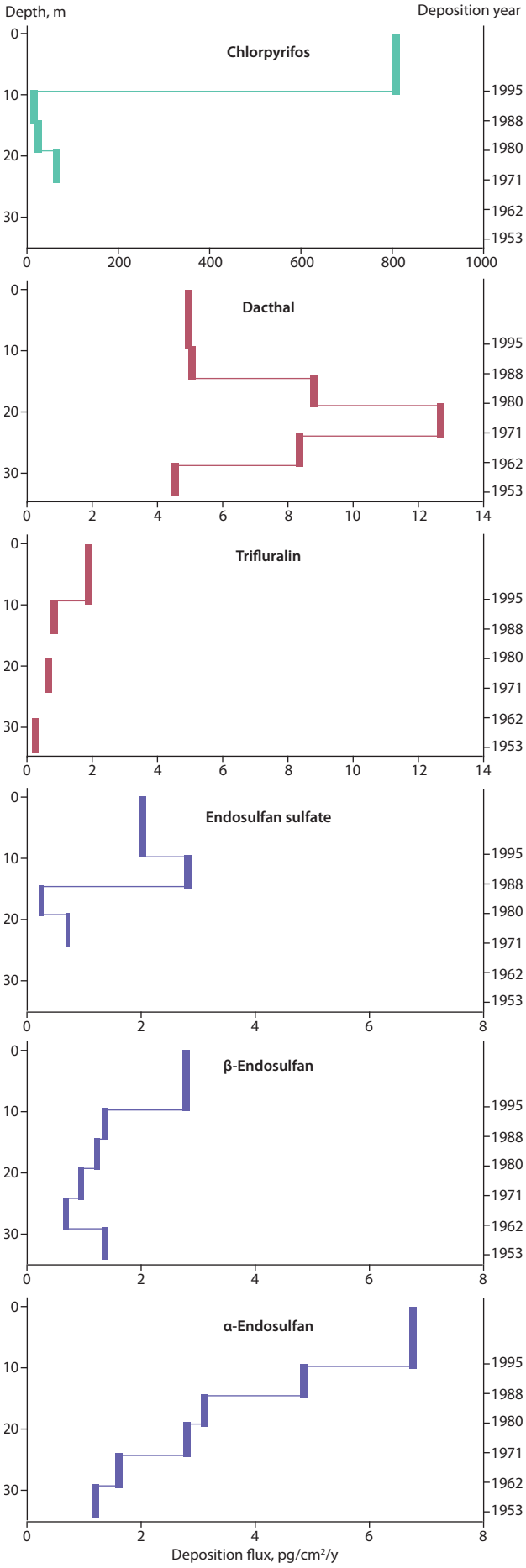


Figure 2.91 Trends in the deposition of current use pesticides in the Holtedahlfonna ice cap (Svalbard) (Ruggirello et al., 2010).

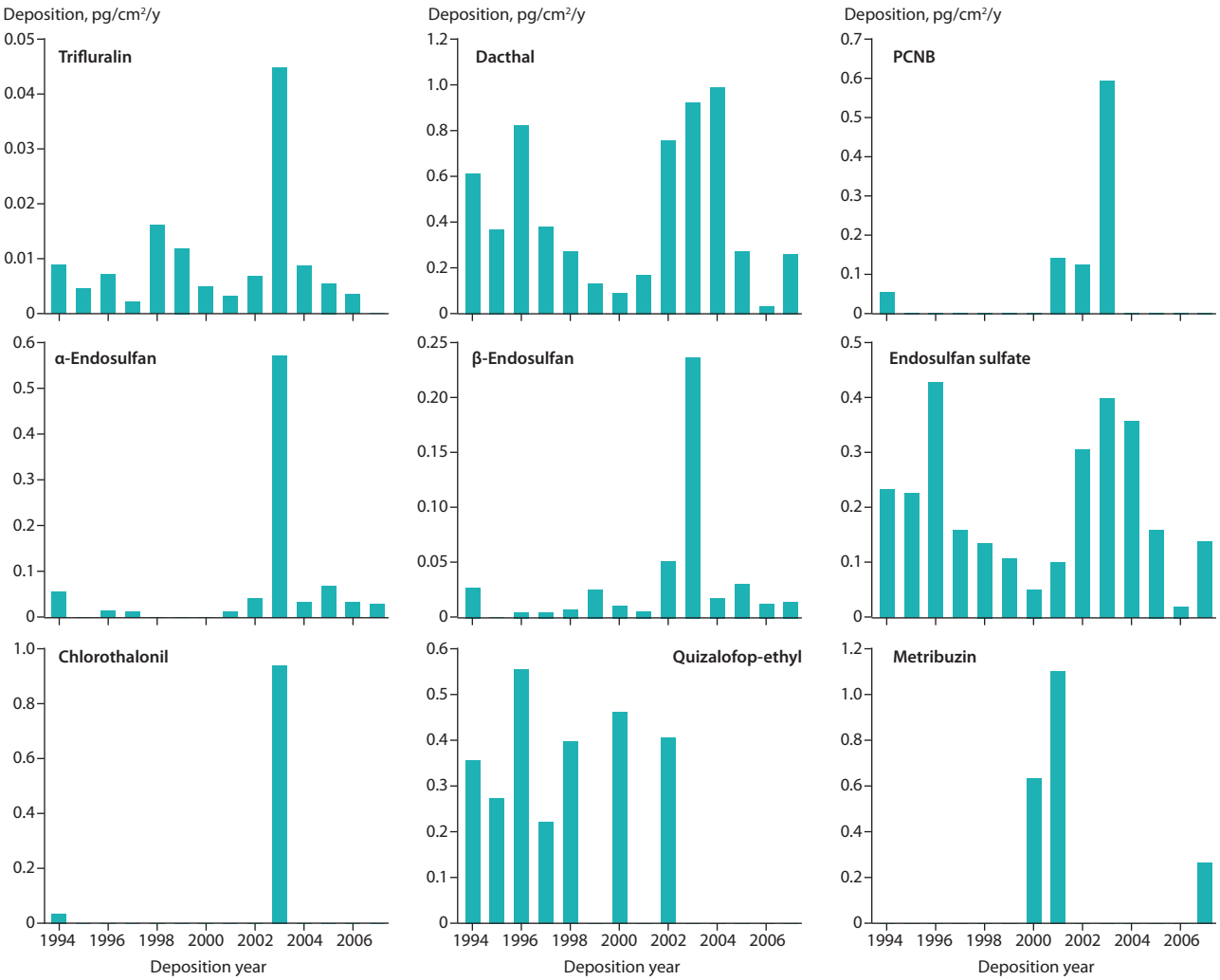


Figure 2.92 Annual net deposition fluxes of CUPs in snow segments from a snow pit dug on the Devon Island Ice Cap in 2008 (Zhang et al., 2013).

the greater input. Air mass back trajectories over a 10-year period of comparison (1986–1995) showed air mass flow from Eurasia 74% of the time to Austfonna and 45% of the time to Holtedahlfonna, which may account for some of the differences.

Zhang et al. (2013) reported annual deposition profiles of CUPs in the Devon Ice cap (Devon Island, Nunavut) based on a 6-m snow pit sampled in 2008. Dacthal and endosulfan sulfate were the most frequently detected CUPs with peak deposition fluxes of 1.0 and 0.4 pg/cm^2/y (Figure 2.92). Endosulfan (sum of α and β isomers) predominated in 2003 and 2006, which together with air mass back trajectories suggested ongoing use in Eurasia as a possible origin. Comparison of results for deposition of CUPs in Arctic ice caps showed generally higher fluxes in Holtedahlfonna and Austfonna than in the Canadian Arctic (Ruggirello et al., 2010; Zhang et al., 2013). This may be due to the proximity of the Svalbard glaciers to populated and agricultural regions in northern Eurasia of the Svalbard glaciers, compared to the Canadian High Arctic.

2.11.6.2 Terrestrial environment

Current-use pesticides were investigated in a terrestrial food chain on the border of the Northwest Territories and Nunavut, Canada (Morris et al., 2014). Between 2008 and 2010, samples were collected from regional flora and fauna, including lichens (*Cladonia* sp. and *Flavocetraria* sp.), crumpled leaf moss (*Rhytidium rugosum*), Arctic willow (*Salix pulchra*), cotton grass (*Eriophorum vaginatum*), aquatic sedge (*Carex aquatilis*), brown mushrooms (an unknown species), caribou (*Rangifer tarandus*), and wolves (*Canis lupus*). Samples were analyzed for seven CUPs, including chlorothalonil, chlorpyrifos, dacthal, pentachloronitrobenzene (PCNB), and endosulfans (α-endosulfan, β-endosulfan, and endosulfan sulfate).

Low ng/g, lipid-equivalent corrected concentrations of the CUPs were detected in all vegetation species analyzed (Table 2.71). Mean concentrations of PCNB, chlorothalonil, dacthal, and total endosulfans were highest in lichens > green plants > mushrooms. Concentrations of chlorpyrifos were highest in mushrooms > lichen > green plants (Table 2.71). CUPs tended to bioconcentrate effectively (on a volumetric basis) in lichens and moss, which have the greatest surface area to volume ratio of the vegetation and are relatively long-lived compared to the other species investigated. There was a positive correlation between the log K_{OA} and the bioconcentration factors for the CUPs, although dacthal did not fit this pattern and showed higher bioconcentration than would be predicted from its lipophilicity (Morris et al., 2014).

Concentrations of CUPs were lower in mammalian tissues than in vegetation (Table 2.72). The highest concentrations detected were for Σendosulfan in caribou liver, chlorothalonil

Table 2.71 Lipid equivalent (L_{eq})-normalized concentrations (ng/g lw) of current-use pesticides detected in vegetation of the Bathurst caribou herd region on the border of the Northwest Territories and Nunavut (geometric mean and 95% confidence interval). Values that share capital superscript letters, or where no superscripts are indicated, are not significantly different (one-way ANOVA or Kruskal-Wallis ANOVA on ranks, $p > 0.05$). Selected results from Morris et al. (2014).

	Lichen		Moss	Willow[a]	Grass and Sedge[a]	Mushroom
	(*Cladonia* sp.)	(*Flavocetraria* sp.)				
Samples (n)	6	6	6	6	8	5
L_{eq} (%)	1.7±0.12	2.0±0.18	0.61±0.039	1.9±0.40	1.2±0.096	1.4±0.67
PCNB	0.73^{AB} (0.19–2.9)	0.89^{A} (0.13–6.1)	0.10^{BC} (0.065–0.17)	0.14^{ABC} (0.052–0.40)	0.48^{ABC} (0.23–0.98)	0.072^{C} (0.023–0.23)
Chlorothalonil	0.20 (0.039–0.98)	0.38 (0.18–0.79)	0.69 (0.29–1.7)	0.12 (0.045–0.34)	0.21 (0.074–0.57)	0.12 (0.043–0.32)
Chlorpyrifos	0.20 (0.053–0.75)	0.32 (0.051–2.0)	0.49 (0.22–1.1)	0.18 (0.075–0.43)	0.17 (0.073–0.42)	0.85 (0.11–6.4)
Dacthal	0.74^{AB} (0.26–2.1)	0.99^{B} (0.56–1.7)	0.19^{ABC} (0.074–0.48)	0.14^{AC} (0.043–0.45)	0.085^{C} (0.036–0.20)	0.043^{C} (0.012–0.16)
ΣEndosulfan	7.7^{A} (4.5–13)	7.4^{A} (4.1–13)	2.1^{B} (0.94–4.5)	2.0^{B} (1.4–3.0)	0.92^{B} (0.56–1.5)	<MDL (0.13–0.36)

[a]Only leaves of willow and leaves and stems of grasses were included in the extractions.

Table 2.72 Lipid-normalized tissue and body burden concentrations (ng/g lw) of current-use pesticides detected in caribou and wolves sampled from the Bathurst caribou herd region on the border of the Northwest Territories and Nunavut, Canada (geometric mean and 95% confidence interval). Mammalian total body burden concentrations were compared using Student's *t*-tests (α = 0.05); where significant differences were detected in pair-wise concentrations, the significantly greater concentration is marked by an asterisk. Differences in concentration between tissues were tested using one-way ANOVA or Kruskal-Wallis ANOVA on ranks, with appropriate post-hoc tests; values that have capital superscript letters in common or have no superscripts are not significantly different. Selected results from Morris et al. (2014).

	Caribou		Wolf		Caribou	Wolf
	Muscle	Liver	Muscle	Liver	Total body burden	Total body burden
Samples (n)	6	6	7	7	6	7
Lipid (%)	2.1±0.85	4.4±1.2	3.1±1.5	4.2±1.2	-	-
PCNB	0.044^{A} (0.019–0.10)	0.21^{B} (0.11–0.39)	0.11^{AB} (0.054–0.21)	0.13^{B} (0.075–0.23)	0.032 (0.015–0.069)	0.069 (0.037–0.13)
Chlorothalonil	0.38^{A} (0.25–0.56)	0.038^{B} (0.015–0.098)	0.44^{A} (0.12–1.5)	0.20^{AB} (0.13–0.3)	0.25 (0.16–0.37)	0.27 (0.076–0.92)
Chlorpyrifos	0.40^{A} (0.20–0.79)	<MDL (0.035–0.060)	<MDL (0.045–0.11)	0.060^{B} (0.030–0.12)	0.26* (0.14–0.52)	0.023 (0.015–0.035)
Dacthal	0.069 (0.037–0.13)	0.024 (0.0092–0.060)	0.018 (0.009–0.036)	0.023 (0.012–0.042)	0.046* (0.024–0.085)	0.0079 (0.0049–0.013)
ΣEndosulfan	0.57^{A} (0.36–0.84)	2.0^{B} (1.1–3.6)	0.17^{C} (0.11–0.27)	0.14^{C} (0.071–0.26)	0.40* (0.27–0.6)	0.10 (0.058–0.17)

in wolf muscle, as well as chlorpyrifos and Σendosulfan in caribou muscle (Morris et al., 2014). A long-term study of reindeer and moose for the period 1987–2006 in Sweden reported endosulfan concentrations below the detection limit in reindeer muscle (Danielsson et al., 2008).

Although measurable concentrations and bioconcentration factors demonstrated that these CUPs can effectively enter the terrestrial Arctic food chain, a subsequent calculation of trophic magnification factors by Morris et al. (2014) indicated significant trophic dilution for all CUPs investigated, probably through biotransformation and excretion of these compounds, particularly in wolves. There was no intertrophic-level biomagnification from vegetation to caribou or caribou to wolves on total body burden bases, and only limited tissue-specific biomagnification of some of the CUPs.

2.11.6.3 Freshwater environment

Törneman et al. (2009a) investigated the presence of chlorothalonil in surface water, sediment and soil samples collected in 2008 at Lake Abiskojaure (a background site) in northern Sweden but found no detectable concentrations. In another study, Törneman et al. (2009b) sought EU Water Framework Directive (WFD) priority substances, mostly in water but also in some sediment samples from Lake Abiskojaure. Chlorpyrifos was not detected in water. α- and β-endosulfan and trifluralin were not detected in water or sediment. Endosulfan was sought but not detected in water samples collected in 2006 from Lake Abiskojaure and Kalixälvens gruvsamhälle (an old mining village on River Kalixälven, point source) (SWECO VIAK, 2007). However, trifluralin was detected in Lake Abiskojaure (4.5 pg/L) and Kalixälvens gruvsamhälle (2.5 pg/L) water samples while no chlorpyrifos was detected at either site (SWECO VIAK, 2007).

CUPs have been determined in lake trout (*Salvelinus namaycush*), burbot (*Lota lota*), landlocked char and sea-run char (*S. alpinus*) from the Canadian Arctic and results to 2011 were summarized by Muir et al. (2013b). Endosulfan was detected in burbot liver and lake trout muscle from Great Slave Lake (Figure 2.93). Burbot liver had higher concentrations of endosulfan-related compounds than lake trout. Endosulfan sulfate, the stable degradation product of endosulfan was the main component, accounting for 95% of total endosulfan in burbot liver and 89% of total endosulfan in lake trout muscle. In landlocked char, α-endosulfan and endosulfan sulfate were present at similar sub-ng/g concentrations, while β-endosulfan was below detection limits unlike in lake trout and burbot liver. Mean concentrations of α-endosulfan and endosulfan sulfate were higher in sea-run char (Figure 2.93) than in landlocked char.

Dicofol was sought in perch (*Perca fluviatilis*) from several lakes in Arctic Finland in 2014 (Mannio, unpubl. data). Four pooled samples were analyzed, each comprising 10 to 20 individuals. Dicofol was below the limit of quantification in each one.

2.11.6.4 Marine environment

Seawater

Surface seawater samples were collected during oceanographic cruises in the western Arctic ocean and monitored for selected OCPs and CUPs between 1993 and 2013 (Figure 2.94). Across all years, the detection rate for CUPs was highest for dacthal (98%), followed by α-endosulfan (97%), chlorpyrifos (95%), chlorothalonil (78%), β-endosulfan (76%), endosulfan sulfate (68%) and trifluralin (60%). Chlorothalonil, which exhibited the highest maximum concentration, was also highly variable. In 2011, a year with high variation, the highest concentrations were associated with samples taken in regions with no ice cover and low salinity, indicating a potential relationship with recent melt episodes (Jantunen et al., 2015b).

Surface seawater samples from a research cruise extending northward from the Sea of Japan into the Chukchi Sea and western Arctic Ocean in 2008 were also analyzed for α- and β-endosulfan, endosulfan sulfate, and methoxychlor (Cai et al., 2010). Concentrations of α-endosulfan (<MDL–0.0980 ng/L), β-endosulfan (<MDL–0.0265 ng/L), endosulfan sulfate (<MDL–0.0875 ng/L) and methoxychlor (<MDL–0.0353 ng/L) in the Chukchi sea were comparable to those found in the Arctic Ocean: α-endosulfan (0.0192–0.0528 ng/L), β-endosulfan (<MDL–0.0398 ng/L), endosulfan sulfate (<MDL–0.1225 ng/L) and methoxychlor (<MDL–0.0523 ng/L).

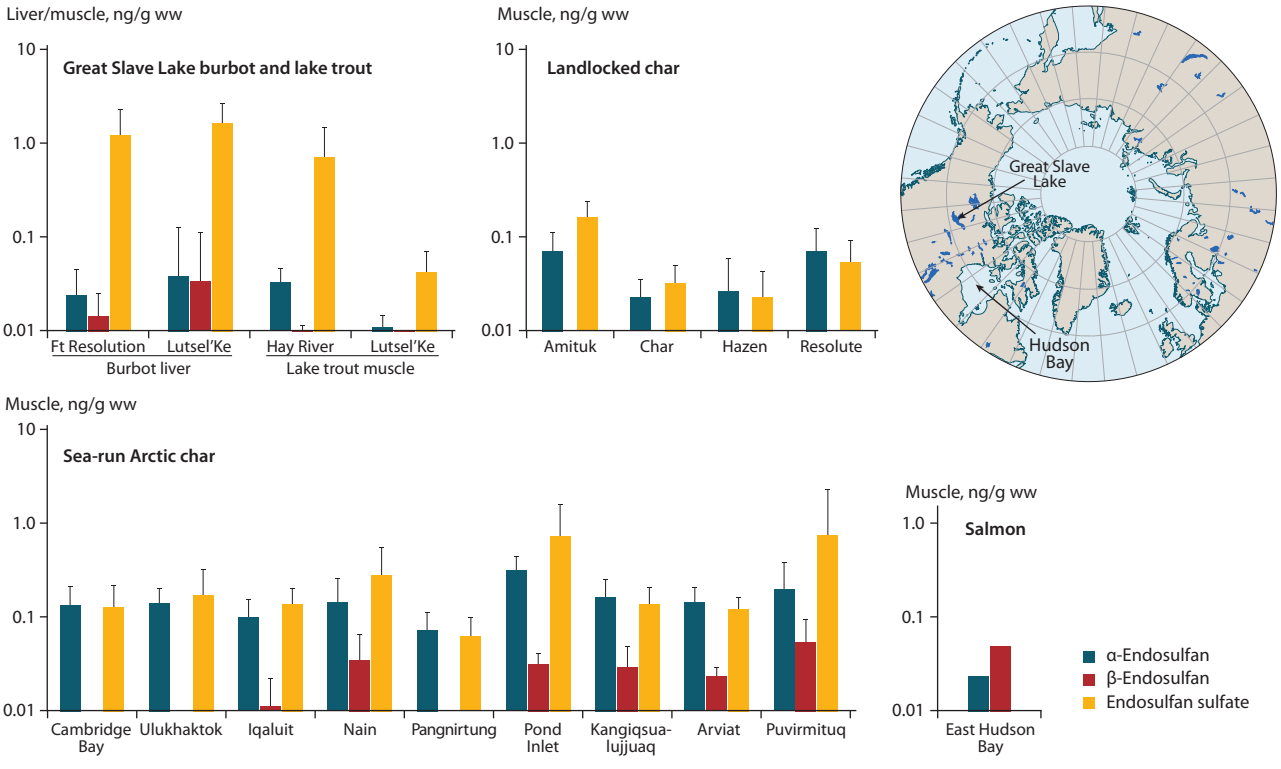


Figure 2.93 Mean concentrations (± standard deviation) of α- and β-endosulfan and endosulfan sulfate in Great Slave Lake burbot liver and lake trout muscle and sea-run char muscle (Evans and Muir, unpubl. data), landlocked Arctic char (*Salvelinus alpinus*) muscle (and salmon from east Hudson Bay; Kelly et al. 2007). Results from Kelly et al. (2007) are geometric means converted to wet weight. Reproduced from Muir et al. (2013b).

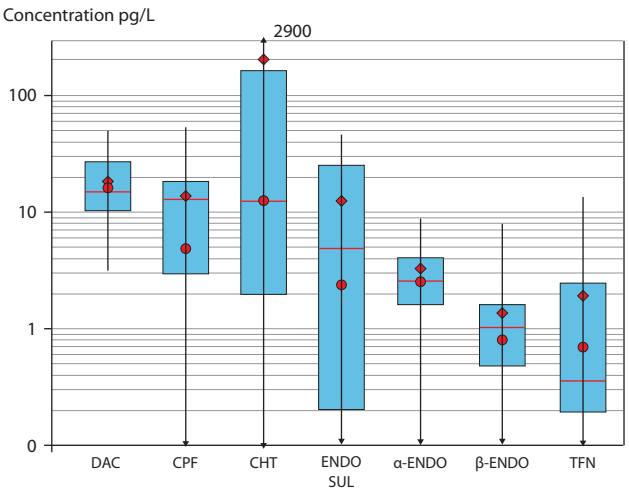


Figure 2.94 Organochlorine pesticides and current-use pesticides in Arctic surface seawater collected between 1993 and 2013. Red bars are median concentrations, while red diamonds and dots are arithmetic means and geometric means, respectively. Vertical bounds of blue boxes indicate 25th and 75th percentiles, whiskers indicate the range, with lower arrows for samples below the instrument detection limit. Dacthal (DAC), chlorpyrifos (CPF), chlorothalonil (CHT), endosulfan sulfate (ENDO SUL), α-endosulfan (α-ENDO), β-endosulfan (β-ENDO), trifluralin (TFN) (after Jantunen et al., 2015b).

Air and seawater samples were collected on a research cruise extending from the East China Sea to the High Arctic between June to September 2010 and analyzed for six CUPs: chlorpyrifos, chlorothalonil, dacthal, dicofol, endosulfan and trifluralin (see Table 2.70). Spatial trends for CUPs seawater were generally consistent with those observed in air as discussed in greater detail in Section 2.11.6.1.

The distribution of CUPs in seawater was also investigated at three Canadian Arctic locations: Rae Strait, Cumberland Sound, and Barrow Strait (Figure 2.95) (Morris et al., 2016). Overall, endosulfan sulfate (<MDL–19 pg/L) and dacthal (0.76–15 pg/L) were found in the highest concentrations and were the most consistently detected CUPs in the dissolved phase, followed by chlorpyrifos (<MDL–8.1 pg/L), PCNB (<MDL– 2.6 pg/L) and α-endosulfan (0.20–2.3 pg/L).

Chlorpyrifos was detected in all particulate phase samples and had the highest concentrations in that phase (1.3–4.1 pg/L) (Figure 2.95). In contrast to the dissolved phase, endosulfan sulfate was detected in only two particulate phase samples, at the lowest concentrations (<MDL–0.079 pg/L). Generally, the CUPs with the highest detection frequencies and concentrations in the particulate phase were those with higher K_{OW} values. However, environmental transformation of the endosulfans affected the consistency of this trend (e.g. β-endosulfan was detected in only three samples at low concentrations despite a relatively large K_{OW} value) (Morris et al., 2016).

Sediments

Some emerging contaminants were recently analyzed in surface sediments from a glacial fjord in Svalbard, Norway (Ma et al., 2015). α-Endosulfan was detected in all samples (range 0.1–9.5 pg/g dw), while β-endosulfan was detected less frequently and at lower concentrations (range <MDL–3.0 pg/g dw). Both α- and β-endosulfan increased in concentration from the outer fjord to the inner fjord, suggesting

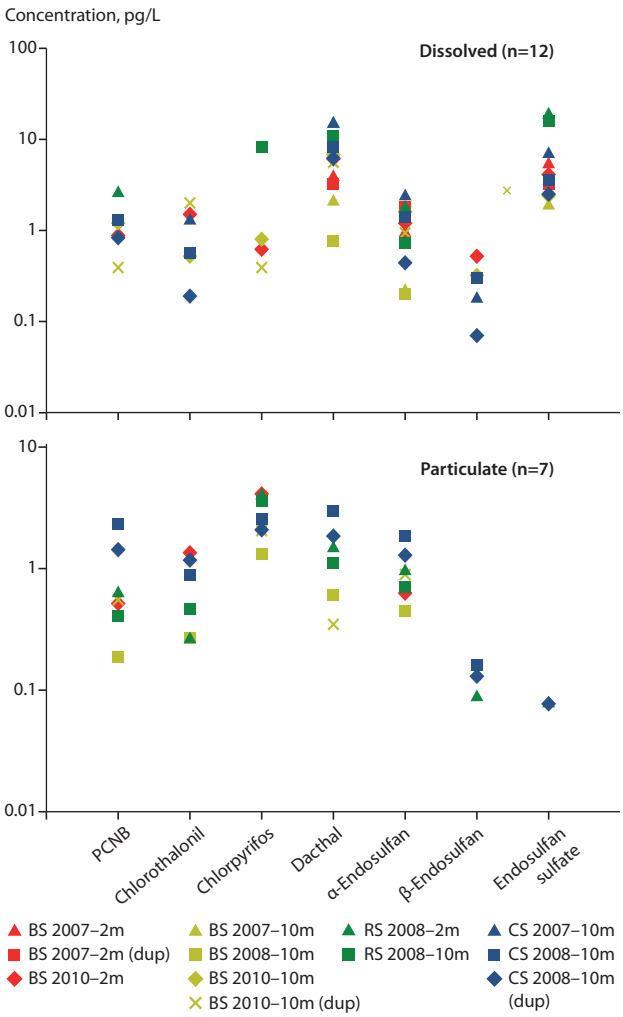


Figure 2.95 Concentrations of current-use pesticides in the unbound and dissolved phase and particulate phase of seawater collected from three Arctic locations between 2007 and 2010. Only concentrations above the method detection limit (MDL) are shown. Modified from Morris et al. (2016).

that runoff of glacial melt water may influence concentrations within the fjord. Trifluralin was also detected in fjord sediments but at lower concentrations, averaging 0.14 pg/g dw. With the exception of an elevated concentration of 1.97 pg/g dw at a single station, trifluralin concentrations were all <0.15 pg/g dw.

Biota

With the exception of endosulfan, very few studies have reported CUP concentrations in Arctic marine animals.

In 2012, eggs from common eider (*Somateria mollisima*), European shag (*Phalacrocorax aristotelis*), European herring gull (*Larus argentatus*) and American herring gull (*Larus smithsonianus*) were collected from the remote island Røst on the Norwegian coast and analyzed for three CUPs: pendimethalin, trifluralin, and methoxychlor; however all were below the limit of detection (Huber et al., 2015). Blood/plasma samples from polar cod (*Boreogadus saida*), capelin (*Mallotus villosus*), kittiwake (*Rissa tridactyla*) and glaucous gull (*L. hyperboreus*) and eggs from eider duck (*Somateria* sp.) and common guillemot (*Uria aalge*) collected from Arctic Norway in 2010–2011, contained no detectable levels of chlorpyrifos, dacthal, methoxychlor, or trifluralin. However, one ringed seal (*Pusa hispida*) blubber sample contained 1.4 ng/g of chlorpyrifos (NIVA, 2012).

Table 2.73 Concentrations of current-use pesticides (ng/g lw) in Canadian Arctic marine biota from three locations (geometric mean and 95% confidence interval). Lipid-equivalent (%L_{eq}) normalization was applied for algae and plankton, all other animals were normalized to lipid content alone (% lipid) (Morris et al., 2016). Values that have capital superscript letters in common or have no superscripts are not significantly different (One way ANOVA or Kruskal-Wallis ANOVA on Ranks with appropriate post hoc tests, p <0.05). Trophic level calculations after Jardine et al. (2006).

Barrow Strait	Ice-algae	Plankton	Amphipods	Arctic cod	Seal blubber	Polar bear fat
n	10	18	8	23	18	8
ϕL_{eq} (%)	1.5±0.82	2.4±0.73	2.7±1.6	7.0±3.9	84±13	84±5.9
Trophic Level	1.5±0.29	2.1±0.29	2.5±0.31	3.6±0.18	4.2±0.18	5.4±0.11
PCNB	0.24^{A} (0.11–0.53)	0.25^{A} (0.14–0.45)	0.15^{A} (0.068–0.34)	0.35^{A} (0.21–0.58)	0.011^{B} (0.0039–0.029)	<MDL -
Chlorothalonil	1.1^{A} (0.65–2.0)	<MDL -	<MDL -	0.10^{B} (0.072–0.15)	<MDL -	<MDL -
Chlorpyrifos	<MDL -	0.41^{A} (0.33–0.51)	<MDL -	<MDL -	<MDL -	0.022^{B} (0.013–0.035)
Dacthal	<MDL -	0.15^{A} (0.075–0.29)	0.16^{A} (0.089–0.29)	0.13^{A} (0.076–0.22)	0.017^{B} (0.011–0.027)	<MDL -
ΣEndosulfan	0.74^{A} (0.45–1.2)	1.3^{AB} (0.87–1.8)	2.9^{B} (1.9–4.4)	1.8^{B} (1.4–2.4)	0.070^{C} (0.054–0.092)	0.13^{C} (0.048–0.36)

Rae Strait	Plankton	Polar cod	Seal blubber	Polar bear fat
n	4	6	6	7
ϕL_{eq} (%)	3.82±0.018	6.62±2.61	90.1±2.94	68.7±8.24
Trophic Level	2.3±0.25	3.6±0.48	4.6±0.32	5.6±0.19
PCNB	0.50^{A} (0.13–1.9)	0.071^{B} (0.026–0.20)	0.059^{B} (0.044–0.081)	0.011^{C} (0.0056–0.021)
Chlorothalonil	0.28 (0.00095–85)	0.40 (0.27–0.60)	<MDL -	0.16 (0.096–0.28)
Chlorpyrifos	0.33^{A} (0.11–0.95)	<MDL -	<MDL -	0.032^{B} (0.013–0.076)
Dacthal	1.7^{A}	0.075^{B}	<MDL	0.015^{C}
ΣEndosulfan	11^{A} (5.3–24)	0.79^{B} (0.58–1.1)	0.082^{C} (0.043–0.16)	0.27^{D} (0.11–0.65)

Cumberland Sound	Plankton	Char	Capelin	Ringed seal blubber	Polar bear fat
n	3	5	5	8	8
ϕL_{eq} (%)	3.9±0.11	8.9±4.2	1.5±0.36	90±11	82±13
Trophic Level	2.1±0.075	3.1±0.039	2.8±0.065	3.3±0.13	4.4±0.25
PCNB	0.28^{ABC} (0.046–1.7)	0.058^{B} (0.033–0.10)	0.49^{C} (0.063–3.9)	NM -	0.0093^{D} (0.0037–0.023)
Chlorothalonil	0.47^{AB} (0.12–1.8)	0.11^{AB} (0.048–0.24)	1.4^{A} (0.81–2.3)	NM -	0.082^{B} (0.039–0.17)
Chlorpyrifos	1.1^{A} (0.010–131)	0.11^{AB} (0.013–0.93)	0.31^{A} (0.017–5.5)	NM -	0.016^{B} (0.0078–0.033)
Dacthal	0.074^{AB} (0.00033–17)	0.49^{AB} (0.15–1.6)	2.1^{A} (1.3–3.5)	NM -	0.010^{B} (0.0047–0.020)
ΣEndosulfan	8.7^{A} (3.1–25)	2.2^{A} (1.0–5.0)	5.1^{A} (2.2–12)	0.22^{B} (0.14–0.27)	0.22^{B} (0.099–0.49)

NM: not measured.

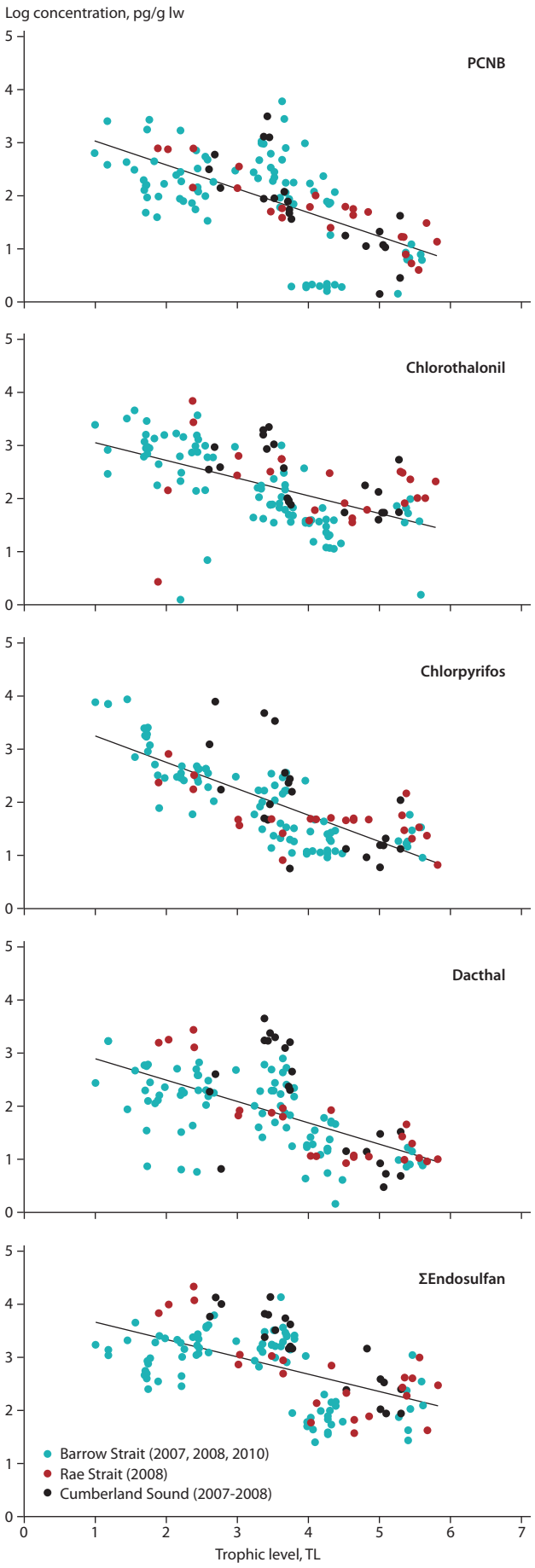


Figure 2.96 Trophic dilution of current-use pesticides (CUPs) in the polar bear-ringed seal food web, based on data from three food chains sampled across the Canadian Arctic, illustrated by log plots of CUP concentration versus trophic level (Morris et al., 2016).

In a study of ringed seal from eastern Greenland between 1986 and 2012, α-endosulfan was above the detection limit (0.10 ng/g ww) in only 9 of 54 blubber samples, and none had concentrations of β-endosulfan above detection limits (0.10–0.25 ng/g ww) (Vorkamp et al., 2017). In contrast, the majority of blubber samples had detectable levels of endosulfan sulfate, which was found at a mean concentration of 0.24 ng/g ww.

PCNB, chlorothalonil, chlorpyrifos, dacthal, α-endosulfan, β-endosulfan and endosulfan sulfate were measured in biota from three marine food chains in the Canadian Arctic Archipelago collected over the period 2007–2010 (Morris et al., 2016). Samples comprised ice algae, plankton, amphipods, Arctic/polar cod, char, capelin, ringed seal tissues and polar bear fat (Table 2.73). Generally, low to sub-ng/g (lipid-equivalent normalized) concentrations of CUPs were observed, with lower trophic level biota such as ice algae, plankton and fish having the highest concentrations within the marine food web (Table 2.73). All of the bioaccumulation factors (BAFs) calculated for the CUPs (in water-respiring organisms only) indicate that CUPs are bioaccumulative with log BAFs ranging from 3.8±2.7 to 7.4±7.1 (arithmetic means ± SEs, L/kg lipid weight). The lowest detectable concentrations were found in polar bear (*Ursus maritimus*) fat; PCNB, chlorpyrifos and dacthal were detected at very low concentrations (0.0061–0.032 ng/g lw). Endosulfan sulfate was not detected in polar bear fat, but both α- and β-endosulfan were detected (Σendosulfan <0.13–0.27 ng/g lw).

Combining the results for all three food chains into a food web spanning across the three locations showed that these CUPs all underwent trophic dilution (i.e. concentrations were highest in invertebrates and lowest in marine mammals, decreasing with increasing trophic level; Figure 2.96). The relative consistency of marine mammal concentrations, lack of detection of endosulfan sulfate in polar bears, and the poor absorption and rapid depuration of many of the CUPs previously observed in laboratory studies (Dorough et al., 1977; Wilkinson and Killeen, 1996; Larsen et al., 1998; US EPA, 1998, 2011a) and trophic dilution of the CUPs through the food web together suggest significant metabolic modification of CUPs in mammals. Endosulfan sulfate is a biotransformation product of the isomers of endosulfan, and is bioaccumulative in a range of terrestrial and aquatic biota (seen in all lower trophic level biota reported by Morris et al., 2016), however, it can also be further metabolized in some mammals to polar products that are more easily excreted (endosulfan ether, diol and lactone for example) (Dorough et al., 1977; Weber et al., 2010). Given that polar bears must be exposed to endosulfan sulfate from their diet of seal blubber, as well as it forming through metabolism of endosulfan isomers, lack of detection of this compound in polar bear fat indicates further metabolism of endosulfan sulfate. This seems particularly likely given their high capacity to metabolize other organohalogen compounds (Letcher et al., 2009).

Although the CUPs underwent food web dilution, it is important to note the significant biomagnification of some CUPs in specific consumer-prey interactions. The Σendosulfan biomagnified in several of these, including plankton-algae, amphipod-plankton and polar bear-ringed seal blubber, with biomagnification factors (BMFs) ranging from 1.5 to 3.8. The highest BMFs observed were for the trophic transfer of β-endosulfan from seal blubber polar bear fat (bear-seal) at

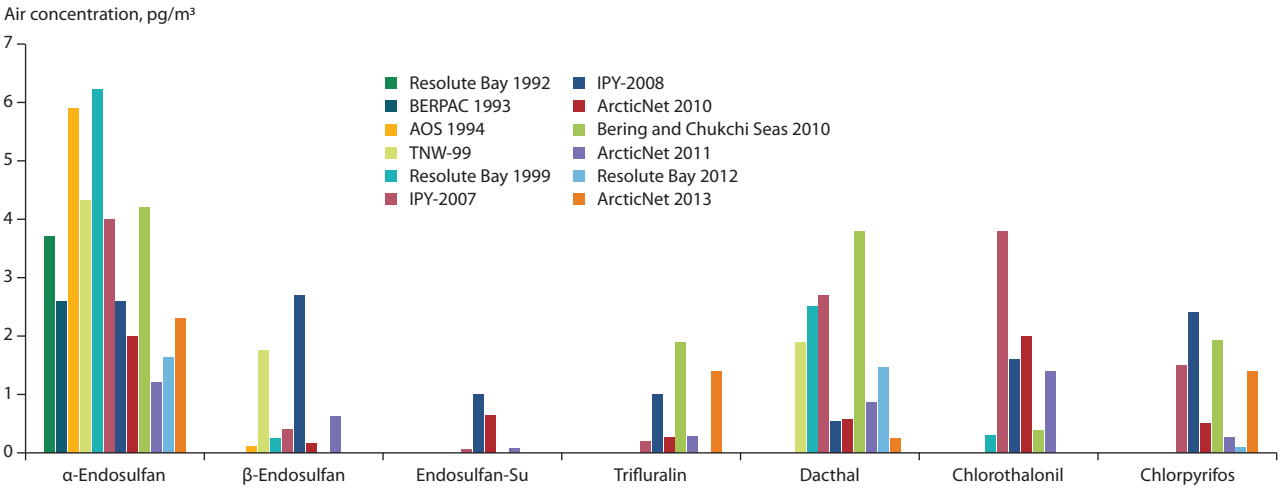


Figure 2.97 Temporal trends of current use pesticides measured in air in the western Arctic Ocean collected during oceanographic surveys between 1999 and 2013. Data show arithmetic mean concentrations. Graphic from Jantunen (2014) and data from Jantunen et al. (2015b). Expeditions, listed by year, traversed the Bering-Chukchi Seas (BERPAC-1993), central Canada Basin to the North Pole (AOS-1994) and the Canadian Archipelago (TNW-1999, IPY-2007, IPY-2008, ArcticNet-2010, ArcticNet-2011, ArcticNet-2013).

Barrow Strait (BMF = 16±4.9), dacthal in capelin-plankton from Cumberland Sound (BMF = 13±5.0) and α-endosulfan in bear-seal from Rae Strait (BMF = 9.3±2.8). Chlorothalonil also exhibited a small amount of biomagnification in bears from Rae Strait (BMF = 3.7±0.63) and in capelin (BMF = 2.7±0.70) (Morris et al., 2016).

2.11.7 Environmental trends

2.11.7.1 Spatial trends

Section 2.11.6 contains some information on spatial trends.

2.11.7.2 Temporal trends

Air and seawater

Trends in atmospheric concentrations of α-endosulfan at Alert (Canada) were reported in the recent AMAP Trends overview (AMAP, 2014a). At Alert, α- and β-endosulfan were sought in the routine air monitoring samples obtained with a super-high volume air sampler. β-endosulfan was mostly below detection limits. The time series of α-endosulfan from 1993 to 2011 shows little change or a slightly declining trend with a half-life of 37 years (Yu et al., 2015). Recent restrictions on endosulfan use in Europe and North America and its recent addition to the Stockholm Convention are not yet reflected in its temporal trend in Arctic air. At Pallas (Finland), α-endosulfan was monitored between 2009 and 2011 with no consistent trend or seasonality evident. At Station Nord (Greenland), α-endosulfan measured between 2008 and 2010 did not show any correlation with temperature indicating direct transport from primary sources as the origin (Bossi et al., 2013).

Several CUPs have been monitored in air and surface water samples collected from oceanographic cruises in the Bering and Chukchi seas, northern Canada Basin, and Canadian Arctic Archipelago between 1993 and 2013 (Jantunen, 2014; Jantunen et al., 2015b). In surface water, concentrations of some CUPs increased (e.g. α-endosulfan, chlorothalonil, trifluralin), while concentrations of others showed no significant change over time (e.g. chlorpyrifos, dacthal). In air, α-endosulfan

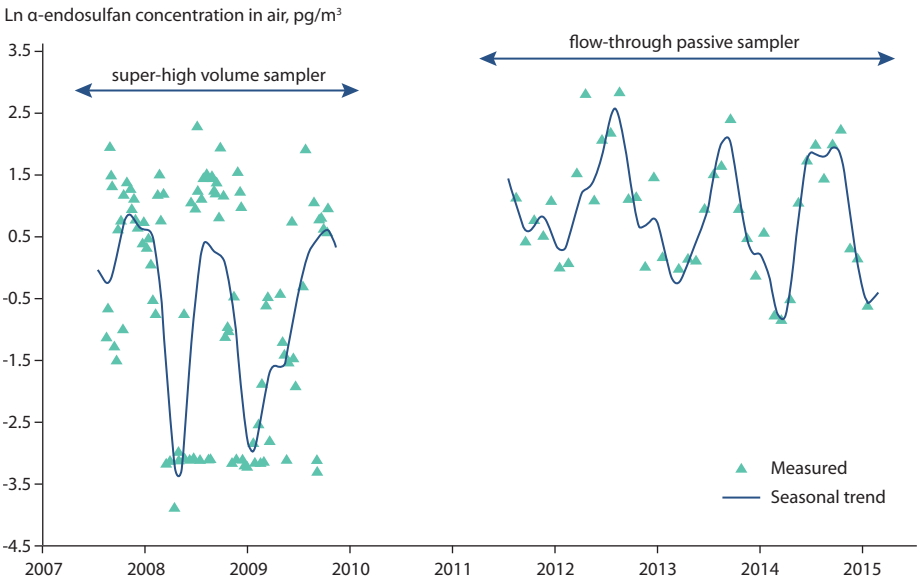


Figure 2.98 Trends in concentration of α-endosulfan at Little Fox Lake (Yukon) from 2007 to 2014 using a super-high volume sampler and a flow-through passive sampler (Yu et al., 2015).

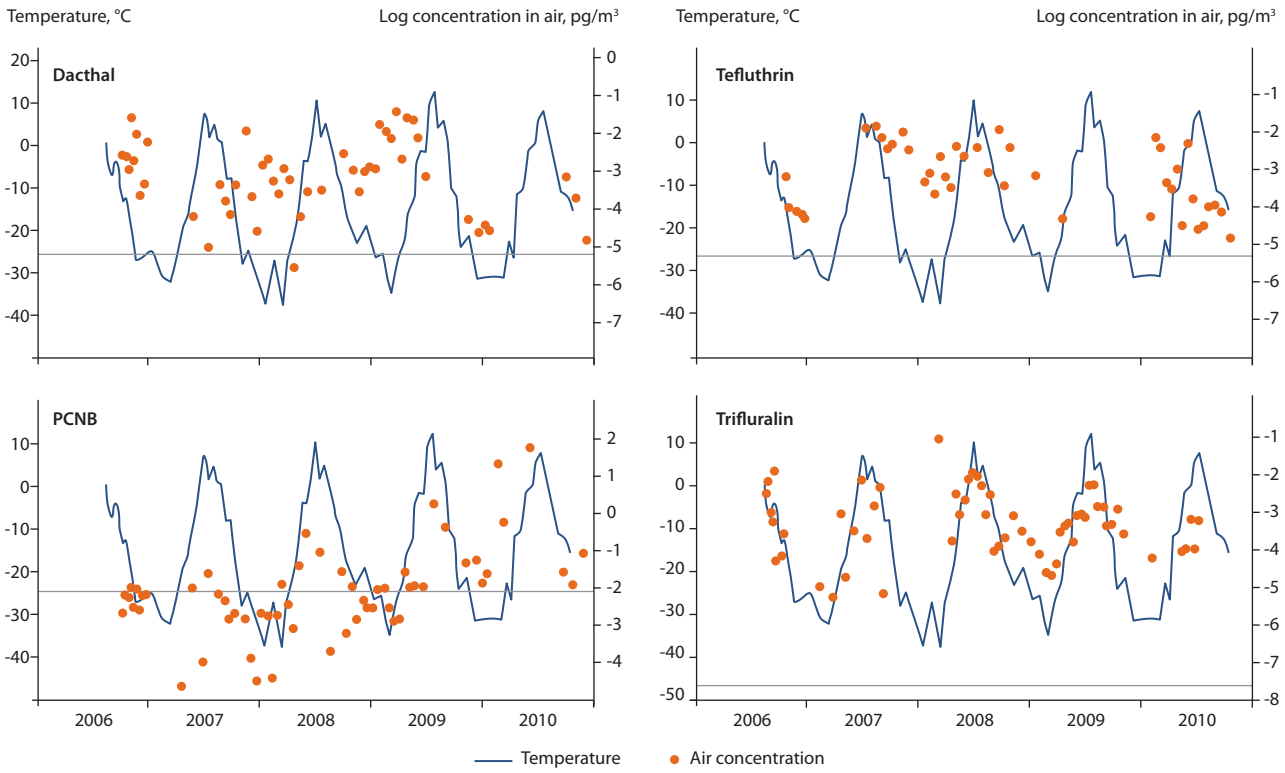


Figure 2.99 Trends in concentration of dacthal, PCNB, tefluthrin, and trifluralin in air at Alert (2006–2010). Horizontal grey lines indicate mean blank concentrations (Hung et al., 2013a).

concentrations in 1993 and 1999 were about 2-fold higher than in the period 2010–2013, in the same region. Concentrations of most other CUPs in air were stable or had lower concentrations in 2010–2013 compared to earlier sampling cruises (Figure 2.97).

Yu et al. (2015) determined α-endosulfan in air at Little Fox Lake (Yukon) using a flow-through sampler with collection on polyurethane foam (Xiao et al., 2012b) as well as a high-volume sampler similar to the one used at Alert. Concentrations of α-endosulfan showed a decrease during the period in which the flow-through sampler was used (2011–2014). In the earlier period, in which a high-volume sampler was used (2007–2009), average concentrations determined using a digital filter technique were relatively constant (Figure 2.98). Potential source contribution function calculations indicated that endosulfan originates mainly from the Pacific, East Asia, and northern Canada during the warm seasons while in cold seasons, the Pacific Rim region is the predominant source.

Trends of dacthal, PCNB, tefluthrin, and trifluralin have been monitored in air at Alert since mid-2006. Concentrations of dacthal and trifluralin were high in summer, whereas PCNB concentrations were high in winter (Figure 2.99). No apparent seasonality was seen for air concentrations of chlorpyrifos, endosulfan sulfate, and tefluthrin.

Freshwater fish

Long-term monitoring of burbot, lake trout, and landlocked char has yielded temporal trends of endosulfan for several Canadian lakes (Muir et al., 2013b). In lake trout from the Great Slave Lake, total endosulfan (sum of α-endosulfan, β-endosulfan and endosulfan sulfate determined by GC-NCIMS) concentrations generally increased between 2006 and 2010 and then declined, although more recent measurements indicate a shift to higher concentrations in west basin lake trout (Figure 2.100). In burbot, total endosulfan declined between 2008 and 2011 but showed an increase from 2011 to 2013.

Landlocked Arctic char from Resolute, Char and Amituk Lakes on Cornwallis Island and from Lake Hazen in Quttinirpaaq

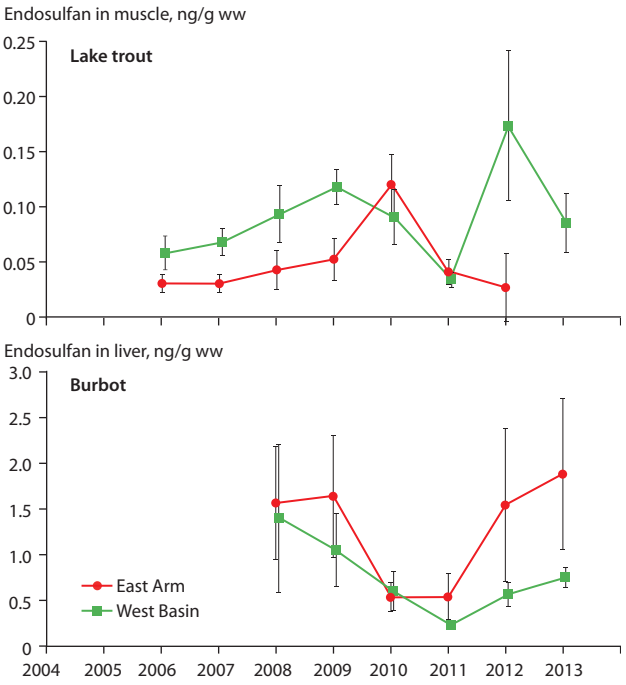


Figure 2.100 Temporal trends in the concentration of total endosulfan (sum α, β and endosulfan sulfate) in lake trout muscle and burbot liver (± 95% confidence intervals) from two sites in the Great Slave Lake in the Canadian Arctic (Evans and Muir, unpubl. data).

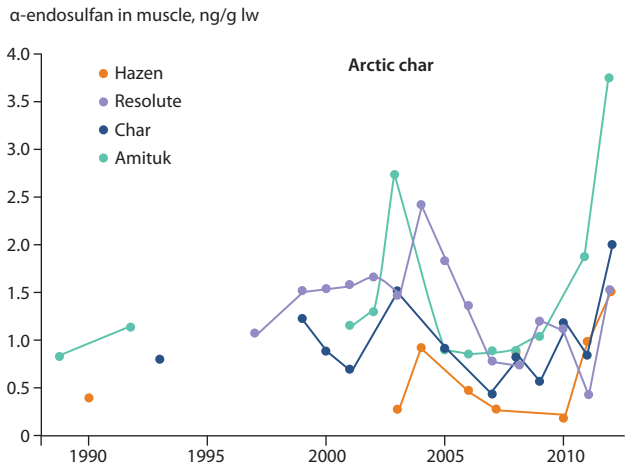


Figure 2.101 Temporal trends in concentration of α-endosulfan (geometric means, ng/g lw) in landlocked Arctic char from Canadian lakes. From Muir et al. (2013b) and Muir (unpubl. data). Error bars are omitted for clarity.

National Park on Ellesmere Island have been consistently monitored for endosulfan isomers since the early 1990s; measurements prior to 2009 did not include endosulfan sulfate. Although no temporal trend for α-endosulfan was apparent in char from Lake Hazen, fish from other lakes, notably Amituk and Resolute, showed increases until 2003–2004 and then declined. More recent data show striking increases in lipid-normalized concentrations of α-endosulfan in Amituk, Char and Resolute Lakes (Figure 2.101).

Marine mammals

Endosulfan was also sought in a temporal study of ringed seal from eastern Greenland between 1986 and 2012 (Vorkamp et al., 2017). Although concentrations of endosulfan sulfate appeared to decrease over this period, temporal trends of α- and β-endosulfan could not be established because concentrations were below detection limits in the majority of the samples.

Trends in total endosulfan (sum of α-endosulfan, β-endosulfan and endosulfan sulfate) were determined in ringed seal blubber in the Canadian Arctic starting in 2007 (Figure 2.102). Declining concentrations were observed in seals from Hudson Bay and Lancaster Sound in the Canadian Arctic Archipelago. No significant trends were apparent in samples from East Baffin Island (Cumberland Sound) or the Southeast Beaufort Sea.

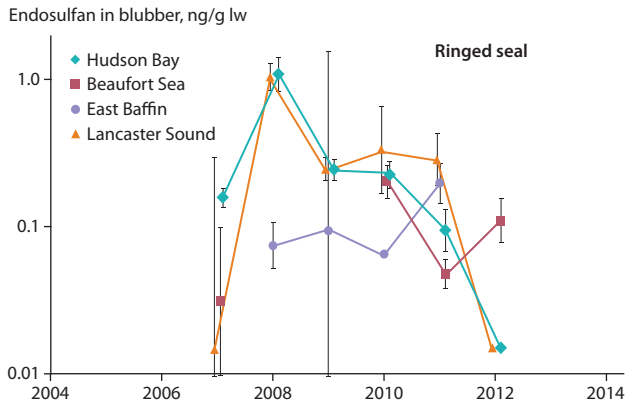


Figure 2.102 Temporal trends in concentration (geometric means ± 95% CI) of total endosulfan (sum of α- endosulfan, β-endosulfan and endosulfan sulfate) in blubber of ringed seals (females and juveniles) from four regional locations in the Canadian Arctic (Muir and Houde, unpubl. data).

2.11.8 Conclusions

Since previous reviews were published (Hoferkamp et al., 2010; Vorkamp and Rigét, 2014), at least seven new pesticides have been measured in Arctic media: MCPA, metribuzin, pendimethalin, phosalone, quizalofop-ethyl, tefluthrin and triallate. However, considering the number of pesticides in current use, the number measured in the Arctic is very limited. For example, modeling efforts have identified other CUPs such as nitrapyrin (Brown and Wania, 2008), picloram (Brown and Wania, 2008; Rayne and Forest, 2010), nitrofen (Brown and Wania, 2008; Zarfl et al., 2012), 2,4,6-trichlorophenol (Brown and Wania, 2008; Rayne and Forest, 2010; Li et al., 2015b) and dinoseb (Brown and Wania, 2008; Rayne and Forest, 2010) as potential Arctic contaminants, although these chemicals have yet to been sought in Arctic media. Future investigations should consider including these potential Arctic pollutants in ongoing monitoring efforts.

Recent studies have added to the information available on spatial and temporal trends of CUPs in the Arctic. In air, concentrations of dacthal and chlorpyrifos appear to be declining. Endosulfan is declining very slowly at Alert but has undergone a more rapid decline at Little Fox Lake in the Yukon (Yu et al., 2015). Data on spatial trends of CUPs in air is lacking because most measurements are restricted to the Canadian Arctic although endosulfan measurements in air have recently been conducted at Pallas and Station Nord. Concentrations of endosulfan at Little Fox Lake in the Yukon were about 2-fold higher than at Alert in the mid-2000s, reflecting closer proximity to Asian and North American sources. Becker et al. (2011) simulated the air, seawater and soil concentrations of endosulfan and its degradation product, endosulfan sulfate, using a global environmental fate model CliMoChem and found that the modeled air concentrations in the Arctic were in good agreement with measured data at Alert. The bimodal seasonality of endosulfan concentrations in air observed at Alert was successfully reproduced by the model. Results for the Arctic ice caps (Svalbard and Devon ice cap) provide some insights into spatial differences. In general, higher deposition of CUPs was observed in Svalbard than in the Canadian Arctic (Ruggirello et al., 2010; Zhang et al., 2013). The differences were particularly striking for chlorpyrifos which was very prominent in the Holtedahlfonna glacier but undetectable in the Devon Ice Cap over the same period (1990s to mid-2000s). Detection limits in both studies were similar. The proximity of the Svalbard glaciers to populated and agricultural regions in northern Eurasia, and prevailing air trajectories, compared with the Canadian High Arctic helps to explain the differences.

Temporal trends of CUPs in Arctic biota are currently limited to measurements of endosulfan in freshwater fish and ringed seal from Canada and Greenland. These studies all show a decline since the mid-2000s. However in fish (burbot and landlocked char) recent increases have been observed in the period 2010–2012. Whether this is a consistent trend reflecting increased deposition or is related to food web or climatic factors is yet to be investigated.

Recent studies have addressed the issue of whether CUPs entering the Arctic via long-range transport are bioaccumulating. Arctic food web studies indicate that CUPs can enter terrestrial and marine food chains and are highest in vegetation and invertebrate animals (Morris et al., 2014, 2016). In general, very low (ng/g lw) concentrations have been detected in terrestrial and marine biota, with the lowest concentrations found in the animals at the greatest trophic levels (ringed seal blubber, polar bear fat, caribou and wolf tissues). Trophic magnification factors indicate significant trophic dilution for all CUPs investigated, probably due to biotransformation and excretion of these compounds (Morris et al., 2014, 2016). This contrasts with the legacy POPs which are present at much higher levels in the same tissues, and several of which undergo trophic magnification (e.g. DDT, chlordane, toxaphene and PCBs) (Kelly and Gobas, 2003; Kelly et al., 2007). However, food web bioaccumulation studies have been conducted on a limited number of CUPs only (PCNB, chlorothalonil, chlorpyrifos, dacthal, endosulfan), although few other non-legacy pesticides are detected at high enough concentrations and frequencies to be included in these types of investigation.

The mix of pesticides used to meet agriculture and public health needs is continuously changing. As new regulations force older pesticides out of the market, new chemicals are taking their place. Changes in climate (Delcour et al., 2015), increasing appearance of pesticide-resistant insects and weeds (Georghiou and Mellon, 1983), and widespread use of genetically-modified crop varieties (Brookes and Barfoot, 2013) will also affect the type and volume of pesticides used in future agricultural practices. Continued monitoring is thus important for ensuring that CUPs and their potential replacement chemicals have minimal impacts on human and environmental health.

2.12 Pentachlorophenol (PCP) and pentachloroanisole (PCA)

Authors: Henrik Kylin, Derek Muir
Contributors: Frank Rigét, Katrin Vorkamp

2.12.1 Introduction

Pentachlorophenol (PCP) was first synthesized for use as a fungicide for wood protection in the 1930s. PCP affects most organisms by decoupling oxidative phosphorylation and other crucial biochemical functions (IPCS, 1987; UNEP, 2013e). As a result it has found a wide range of biocidal and pesticidal uses. Due to adverse environmental and health effects, restrictions on the use of PCP were first imposed in the 1970s with total bans in effect in some countries by the 1980s (UNEP, 2013d). As of 2014, PCP was still in use in India, Canada and the USA (UNEP, 2014a). In May 2015, PCP was included in Annex A of the Stockholm Convention: calling for elimination, with a time-limited exemption for impregnation of utility poles and crossarms (UNEP, 2015a).

A complication concerning the evaluation of PCP is that phenolic compounds are not usually included in analytical protocols for the determination of POPs in environmental samples. However, pentachloroanisole (PCA), the transformation product of PCP is easily included in the standard protocols. This is why PCA has often been used as a proxy measure for PCP. Another complicating factor is that release of native PCP may not be the only source of PCP and PCA to the environment (Kylin et. al., 2017), and not determining both. This makes it difficult to know which of the two chemicals are present in the samples analyzed.

A previous AMAP POPs assessment included early measurements of PCP and PCA in Arctic environmental media (AMAP, 2004). This section focuses on information pertinent to the Arctic and updates environmental measurements of PCP and PCA based on published and unpublished data post-2004 (Table 2.74). For a global perspective and more detailed information on PCP, see IPCS (1987) and UNEP (2013e).

2.12.2 Physical-chemical properties

Phenols are ionizable and their physical-chemical properties are affected by pH. In water at a pH above its pK_a, a phenol is present mainly in its ionized form as phenolate, while at a pH below the pK_a it is mainly in its neutral form. This has profound effects on the environmental behavior of phenolic compounds, because environmental partitioning processes are different for the ionized and neutral forms of the compound. PCP has a pK_a of 4.7, which is within the environmentally relevant range of pH of 4–9 (EC, 2002) and so is affected by the pH of surface waters or precipitation (Appendix 1). Although it may volatilize at a low pH, it is essentially non-volatile at the pH of seawater and many natural surface waters because it will be present as pentachlorophenolate (UNEP, 2013e). The pH of the medium may be the reason why some laboratory experiments do not show any volatilization of PCP (Murthy et al., 1979; UNEP, 2013e). Furthermore, the equilibrium between the phenol and phenolate at a specific pH will determine whether or not PCP is adsorbed to particles (Stapleton et al., 1994). The bioconcentration factor in the aquatic environment will also depend on the relation between the pK_a of PCP and the pH of both the medium and the body fluids involved, as described for other chlorinated phenolic compounds (Söderström et al., 1994). With pH below the pK_a, a phenol will be neutral and partition into a hydrophobic medium, while above the pK_a the partitioning will favor the water phase. Consequently, the ionizable nature of PCP also makes it difficult to interpret water concentrations obtained by some passive samplers, such as semipermeable membrane devices (SPMD) because the uptake characteristics of the sampler will vary with pH.

In contrast to PCP, PCA cannot be ionized. The environmental behavior of PCA is therefore similar to that of classical POPs and so is much easier to predict than that of PCP. However, much less information has been published on the physical-chemical properties and environmental behavior of PCA. For example, the large compilation of physical-chemical data for environmental chemicals undertaken by Mackay et al. (2006) lacks an entry for PCA, and the data for PCA in Appendix 1 are estimates from models. For PCP, there are a few experimental determinations of the physical-chemical properties available. Although PCA will behave similarly to classical POPs, which facilitates modelling, experimentally determined physical-chemical properties of PCA are warranted to evaluate its relevance as a proxy for PCP.

Solving the issue of how well PCA functions as a proxy for PCP is particularly important because much of the data concerning PCP in the Arctic is based not on the occurrence of PCP, but on the occurrence of PCA or PCP+PCA (ΣPCP). Using PCA or ΣPCP as proxies for PCP may mask important information

Table 2.74 Summary of Arctic media for which pentachlorophenol (PCP) and pentachloroanisole (PCA) have been reported. In many cases, the two analytes were not determined separately.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
PCP	×	×	×	×	×	×	×	×	×	×
PCA	×	×	×	×	×	×	×	×	×	×

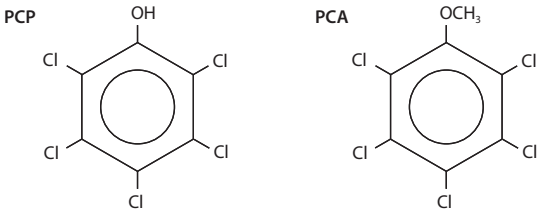


Figure 2.103 Structure of pentachlorophenol (PCP) and pentachloroanisole (PCA).

Table 2.75 CAS numbers for pentachlorophenol (PCP) and pentachloroanisole (PCA).

Compound	Abbreviation	CAS number
Pentachlorophenol	PCP	87-86-5
Pentachloroanisole	PCA	1825-21-4

about environmental pathways and lead to inaccurate conclusions about sources and environmental behavior of both PCP and PCA. See Figure 2.103 and Table 2.75.

2.12.3 Sources, production, use and trends

The background information for PCP in the risk profile prepared for the Stockholm Convention includes a recent inventory of sources, production, and uses (UNEP, 2013d). Historical world production estimates vary. UNEP (1983) estimated a world production of 90 000 tonnes, while a 1981 estimate by the Economist Intelligence Unit based on European Union and North American outputs gave global output estimates of 50 000 to 60 000 tonnes (UNEP, 2013d).

Owing to its wide-ranging biological effects, PCP has had a large number of different uses. Most countries near the Arctic seem to have used PCP mainly as a wood preservative (e.g. against sapstain in sawmills), as an antifungal additive in paints, and as a slimicide in pulp production. Other major uses globally included use as a preservative in textiles and leather, and as a pesticide and defoliant in agricultural practices. PCP was also used as an intermediate for chemical synthesis in the chemical and pharmaceutical industries (UNEP, 2013d). Many countries, as well as the EU, banned or limited the use of PCP during the 1980s and 1990s. PCP is now included in Annex A of the Stockholm Convention; however, with time-limited exemptions for some applications, the current uses in India, Canada and the USA will likely continue for the foreseeable future (UNEP, 2013d, 2014a). It is important to note that release and long-range transport of native PCP may not be the only source of PCP in the Arctic. Degradation (e.g. through reaction with OH radicals) of polychlorinated biphenyl (PCB), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), and pentachloronitrobenzene (PCNB) may also yield PCP (Führer et al., 1997; Führer and Ballschmiter, 1998; UNEP, 2013e), but to date there are few data on which to base firm conclusions on the importance of these indirect sources of PCP to the environment.

No active uses of PCA have been reported (UNEP, 2013d). In the absence of known anthropogenic sources, the presence of PCA is usually seen as an indicator of environmental contamination with PCP. However, although there is much evidence that PCP is converted to PCA via microbial processes (Kitunen et al., 1987; UNEP, 2013e), there does not seem to be any scientific documentation that this is the only source of PCA in the environment. Indeed, Walter and Ballschmiter (1991) suggested that natural chlorination processes were responsible for mono- to trichloro-anisoles found in ocean air. Later, Ballschmiter (2003) indicated that tetra- and pentachloroanisoles were solely of anthropogenic origin. Although there is still no scientific evidence that PCA is a natural product, evidence for the natural production of lower chlorinated phenols and anisoles (i.e. up to three chlorines) has been published (Hodin et al., 1991; Walters and Ballschmiter, 1991; see also Section 2.16). However, recent work indicates that there are unknown sources of PCA (Kylin et al., 2017).

2.12.4 Transformation processes

Several studies on the transformation of PCP are included in the background information collected for the decision to include PCP in the Stockholm Convention (UNEP, 2015a), but few are directly relevant to the Arctic environment.

Both PCP and PCA are hydrolytically stable at pH 4–9, so hydrolysis rates in soil and water under most environmental conditions are expected to be low (UNEP, 2013d). On the other hand, phototransformation of PCP in water exposed to natural sunlight is rapid, with half-lives of 13 to 20 minutes (Wong and Crosby, 1981). However, these experiments were conducted in summer daylight in Davis, California (38.5°N), and photodegradation would be expected to be much slower under Arctic conditions due to lower light intensity during the summer and lack of light during winter. Furthermore, due to reactions with hydroxyl radicals, the estimated atmospheric half-life for PCP is short (12–44 hours), indicating low potential for long-range transport (Slooff et al., 1991; UNEP, 2013e).

A large number of PCP-degrading bacteria have been identified (UNEP, 2013d). Under aerobic conditions, biomethylation of PCP to PCA is well documented, and this is the most common transformation reported in the literature (UNEP, 2013d). Dehalogenation to tetra- and trichlorophenols and production of volatile species have also been observed. On the other hand, if conditions are anaerobic, reductive dehalogenation is likely to be the most common transformation process (UNEP, 2013d), although some formation of PCA (a small percentage of the PCP) has also been observed.

Although PCA is often reported as a transformation product of PCP, it is important to note that the process is reversible (Glickman et al., 1977; Opperhuizen and Voors, 1987; Ikeda et al., 1994; Ikeda and Sapienza, 1995). Thus, depending on the conditions, either PCP or PCA may be the more stable of the two. This adds to the complexity of understanding the environmental fate of these compounds.

Sacco and James (2004) reported on PCP metabolism *in vitro* using a polar bear (*Ursus maritimus*) liver microsomal assay. They found that the sulfonation capacity was lower for PCP

than for other substrates such as 4'-OH-CB79, 4'-OH-CB165 and tris(chlorophenyl)-methanol (TCPM), which all produced detectable sulfate conjugates. Since 2004, when PCP/PCA were reviewed for the AMAP POPs assessment (AMAP, 2004) there appear to have been no other published data reporting on transformation of PCP and PCA in the Arctic environment.

2.12.5 Modeling studies

There are no publications on modelling of the environmental behavior of PCP or PCA in the Arctic.

2.12.6 Environmental concentrations

Environmental concentration data are scarce and information on the occurrence of PCP and PCA, particularly PCP, is scant and patchy. Hoferkamp et al. (2010) summarized available data from the Arctic and UNEP (2013e) summarized global data. As previously mentioned, owing to differences in their analytical chemistry (PCP requires an extra derivatization step before quantification), reports on their environmental occurrence often contain concentration data for PCA or ΣPCP only. Using PCA or ΣPCP concentrations as a proxy for PCP may seem attractive because it saves work, but the assumption behind doing so is that PCP is the only source of PCA to the environment. Recent information (Kylin et al., 2017), however, shows that PCA is a poor proxy for PCP and thus that it is difficult to draw conclusions on their environmental occurrence and fate based on available data.

2.12.6.1 Air and precipitation

There are no data on the atmospheric chemistry of PCP/PCA in the peer-reviewed literature, while grey literature (Slooff et al., 1991; UNEP, 2013e) indicates that PCP should have a low potential for long-range atmospheric transport due to reactions with hydroxyl radicals (photolysis half-life 12–44 hours).

In a study comparing ΣPCP levels in air in southern and northern continental Canada, concentrations were higher in the north than the south (Cessna et al., 1997). But as the samples were only obtained from three locations, it is difficult to draw firm conclusions from this limited material. However, it is notable that the spatial pattern in concentration was similar to that observed in pine needles (Kylin et al., 2017).

PCP and PCA have both been detected in air monitoring programs, with PCA generally found more often and at higher concentrations than PCP. The air monitoring program in Sweden reported PCA concentrations of 7 and 41 pg/m^3 in two air samples collected in 2001 from Pallas, while the concentrations of PCP were <1 pg/m^3 (Palm et al., 2002). Two deposition samples collected at the same time as the air samples had no detectable concentrations of PCP or PCA.

Monitoring of PCA started in 1993 at Alert as part of Canada's National Implementation Plan for AMAP (Fellin et al., 1996; Barrie et al., 1998). Recently compiled data show long-term seasonality for PCA in air samples with a recent decline in air concentration (Figure 2.104) (Su et al., 2008, 2011; Hung et al., 2010). However, the analyses were performed with gas chromatography/electron capture detection (GC/ECD) for samples collected between 1993 and 2010; and it is suspected that PCA may co-elute with 1,2,4,5-tetrachloro-3,6-dimethoxybenzene, a potential transformation product of PCP, PCA or HCHs (Wittlinger and Ballschmiter, 1990; Schreitmueller and Ballschmiter, 1995). Analytical confirmation with Triple Quadrupole GC/MS is currently ongoing to separate the two compounds (Hung, pers. comm., 2016). High concentrations of PCA in a brown snow event suggested long-range atmospheric transport from Asia to Arctic Canada (Welch et al., 1991). Additional studies indicating long-range atmospheric transport of PCP include the presence of PCA in fish in a remote lake on Isle Royale in Lake Superior (Swackhamer and Hites, 1988). However, the premise in all these studies is that PCA is a transformation product of PCP and has no other source.

Führer et al. (1997) and Führer and Ballschmiter (1998) sought PCA and other chloro- and mixed bromochloroanisoles in air along a transect through the Atlantic Ocean from 40°N to 57°S. They suggested that their data showed the chloroanisoles, including PCA, are chiefly transformation products of the respective chlorophenol used in industry, while the bromochloroanisoles are natural products. However, none of the samples are truly representative of Arctic conditions, PCP was not determined, and the total number of samples is

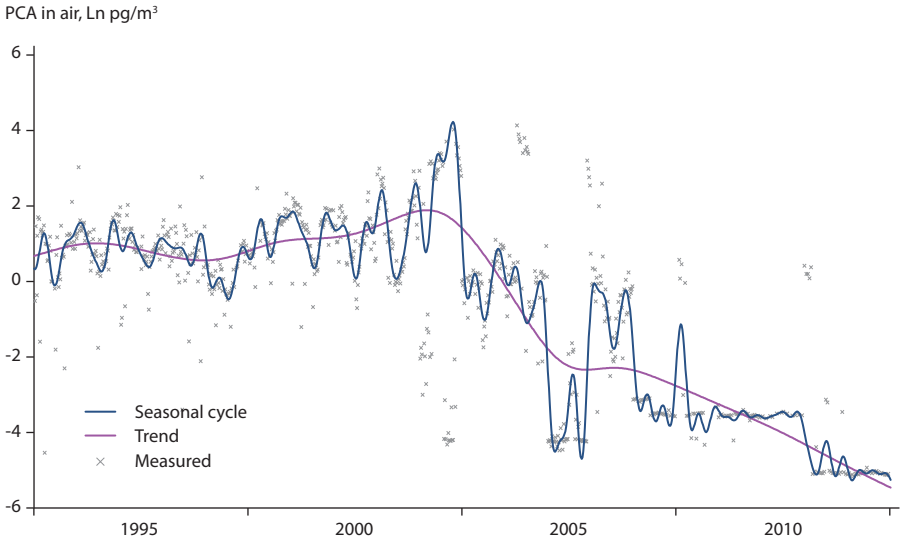


Figure 2.104 Measured air concentrations of PCA in air at Alert, Canada 1993–2012.

low (only two from 'background' conditions in the northern hemisphere). Hence, it is difficult to draw any conclusion from this material as to the source of PCA or the relation between PCP and PCA in the environment in general, and even more difficult to draw conclusions relevant to the Arctic.

2.12.6.2 Terrestrial environment

Published data from terrestrial environments are few. Vorkamp et al. (2004b) reported PCA in several terrestrial organisms (hare, muskox *Ovibos moschatus*, ptarmigan *Lagopus lagopus*, caribou *Rangifer tarandus*, lamb) collected at various sites in Greenland in the period 1998–2001. Mean PCA concentrations ranged from <MDL–0.28 ng/g lw in muscle of ptarmigan (re-calculated from Table 3 in Vorkamp et al., 2004b). PCP concentrations were below the detection limit in a study of bank voles (*Myodes glareolus*) collected in 2001 from Ammarnäs (northwestern alpine Sweden), Vålådalen (southern alpine region) and Vindeln (Lappland) (Lind and Odsjö, 2010).

Data from a long-term study of various POPs in pine needles in transects from southern to northern Europe in the late 1980s and early 1990s have been published in part (Eriksson et al., 1989; Jensen et al., 1992; Kylin, 1996; Strachan et al., 1994). Generally, concentrations of ΣPCP were higher in the north, where PCP was banned, than in the south where it was still in use. This pattern was attributed to long-range atmospheric transport and either formation of PCP from various precursors (Jensen et al., 1992) or, possibly, an effect of global distillation (Kylin, 1996). However, owing to the choice of analytical protocol (determining ΣPCP), it is impossible to know how much of the regional distribution pattern over Europe was due to PCP and how much to PCA.

To gain a better understanding, pine needle samples from Europe and Canada were analyzed determining PCP and PCA separately, and these data were recently compiled (Kylin et al., 2017). The dataset comprised results from more than 1200 samples from over 350 locations in Europe and Canada sampled between 1986 and 1997. There was no correlation between PCP and PCA concentrations in these samples which showed the data did not support methylation of anthropogenic PCP as the main source of PCA in the Arctic (Figure 2.105). On the continental scale, PCP is distributed as expected with higher concentrations in areas where PCP was used at the time of sampling, namely highest in the south and close to PCP production facilities. Concentrations of PCA, on the other hand, show a more northerly distribution with marine influence. On a smaller regional scale there is a slight elevation in PCA concentrations near PCP hotspots, such as former production facilities, but at the continental scale these locally elevated levels do not influence the general pattern.

Although it cannot be ruled out entirely, it is difficult to reconcile known source areas of PCP and the observed distribution of PCP/PCA in the pine needles with long-range transport processes. If the transport is atmospheric, the dominance of PCA in needles along the west coasts of the continents dominated by westerly winds would require transoceanic sources. However, as the expected atmospheric half-life of PCP is relatively short (12–44 hours in air; from Slooff et al., 1991 cited in UNEP, 2013d), such transport is unlikely. In contrast, PCA is predicted to have a much longer atmospheric half-life (117 hours; using EPISuite 4.1 AOPWIN program; US EPA, 2011c). Another possibility is that ocean currents along the coasts transport PCP northward where it may be transformed to PCA, which can be volatilized and deposited to the terrestrial environment. Using the OECD LRT tool (Klasmeier et al., 2006) with physical-chemical property data provided in the risk profile (UNEP, 2013d) and in EPISuite (US EPA, 2011c), yields Characteristic Travel Distances of 740 km versus 2300 km for PCP and PCA, respectively.

Also, as noted in the risk profile (UNEP, 2013d) the degradation of other POPs including PCB, HCB, HCH, and the pesticide PCNB could influence the PCP/PCA ratio at remote locations,

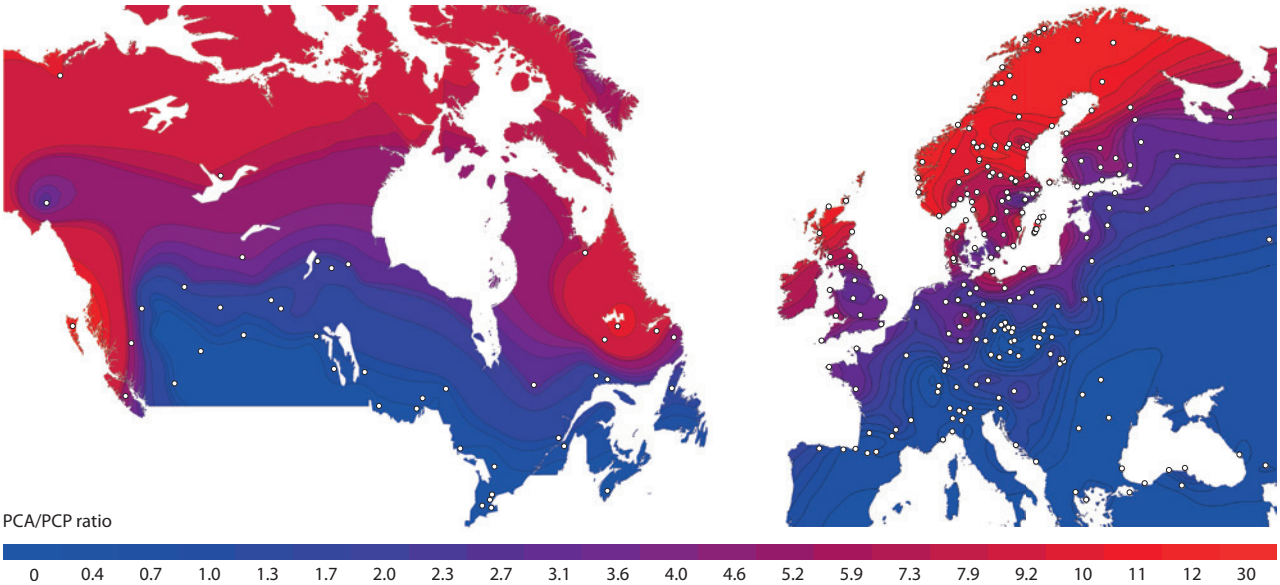


Figure 2.105 PCP/PCA ratios in pine needles collected in Canada (n=42) and Europe (n=283) for the period 1986–1994. Blue indicates predominance of PCP and red indicates predominance of PCA. Note that at the time of sampling, PCP was still used in Finland and much of continental Europe, but prohibited in Norway and Sweden. Despite the use in Finland, the PCA predominance is stronger in Norway and Sweden than in Finland, a pattern that is difficult to explain by long-range atmospheric transport of PCP from continental Europe. Maps courtesy of Hindrik Bouwman (North-West University, Potchefstroom, South Africa).

given that they all undergo long-range atmospheric transport. HCHs, in particular, undergo marine transport and this source has been shown to influence nearshore air measurements (Shen et al., 2004). Thus, it seems that although PCA is formed by the methylation of PCP, there could be other sources combined with differences in long-range transport of PCA and PCP to the Arctic that could partly explain the spatial pattern in Figure 2.105.

An alternative hitherto unrecognized source of PCA could be natural production. The number of known natural halogenated organic compounds is ever increasing (Gribble, 2003, 2010), but other than the pine needle data mentioned here, there is to date no published evidence that suggests PCA may be of natural origin. So whether PCA is actually produced naturally remains to be shown. Furthermore, it is not presently possible to confirm whether the observed PCA signal is truly marine. The observed PCA distribution pattern is consistent with either production in the marine environment or production in the boreal terrestrial environment. Chlorination of natural organic material is more efficient in boreal forest soils than in other soils (Gustavsson et al., 2012; Redon et al., 2013), and these processes produce chlorinated phenols and anisoles with up to at least three chlorines (Hodin et al., 1991) (see also Section 2.16). If the deposition of chloride into the northern maritime boreal forest soils were to promote production of additional chlorinated phenols, this might help explain the northern maritime signal for PCA. However, much of the chlorination in boreal forest soils occurs extracellularly by chloroperoxidases excreted from microorganisms (Gustavsson et al., 2012). These chlorination processes are unspecific as to which aromatic structures are chlorinated, and it is presently difficult to accept that a highly chlorinated compound such as PCA could be produced by random chlorination in nature.

Similar to what is seen in Europe, the ΣPCP concentrations in pine needles in Canada increase northward and along the coasts, except near PCP point sources. This is in agreement with the ΣPCP concentrations in air in continental Canada (Cessna et al., 1997) although as mentioned previously the air data are very limited.

A suggestion that follows from the re-analyzed pine needle data, is that if natural production of PCA does occur this production is promoted by cooler conditions. However, this is not supported by an altitudinal gradient study in the Taurus Mountains (Turgut et al., 2012) where no correlation with altitude/temperature or any soil parameter was found for PCA concentrations.

2.12.6.3 Freshwater environment

Evidence that speaks against natural formation of PCA comes from a sediment core from the High Arctic from Lake Hazen, Nunavut, Canada. In this core, encompassing a time series from 1898 to 2005, PCA concentrations (<MDL–0.52 ng/g dw) were higher in the younger layers (1991–2005) than the older layers (Figure 2.106) (UNEP, 2013d). However, the conclusion that the higher PCA concentration in the recent sediment compared to older sediment reflects increased deposition is based on the premise that PCA does not degrade in sediment. This premise

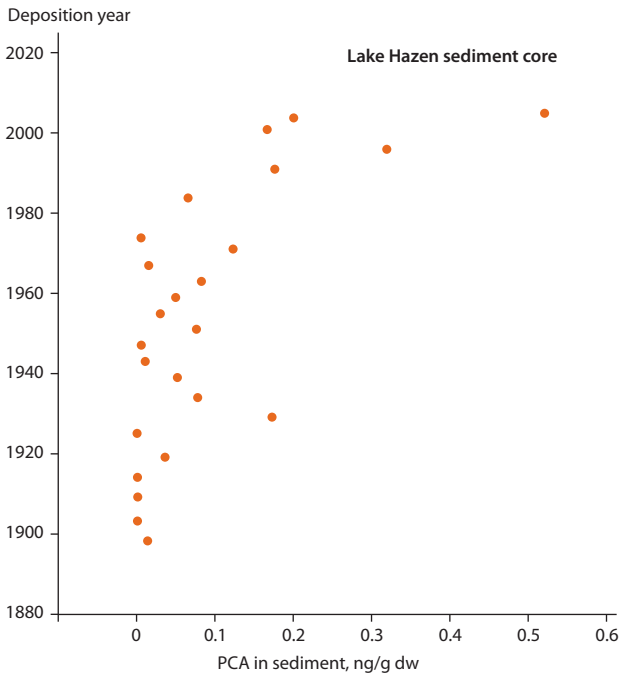


Figure 2.106 Concentrations of PCA in a sediment core from Lake Hazen, Nunavut, Canada (UNEP, 2013d).

may not be correct as several studies have shown demethylation of PCA to PCP in moist soils under both aerobic and anaerobic conditions (UNEP, 2013d). The concentration profile in the Lake Hazen sediment core could, therefore, be a reflection of degradation of PCA in the older sediment layers rather than a consequence of increased deposition in the younger layers.

In northern Sweden, surface water samples collected in 2006 from Lake Abiskojaure (background) and from a mining area along River Kalixälven (point source) had no detectable PCP concentrations (SWECO VIAK, 2007). Törneman et al. (2009b) studied Water Framework Directive priority substances, mostly in water but also in some sediment samples from Lake Abiskojaure. PCP was not detectable in either water or sediment samples. However, in both studies the water samples were obtained by passive samplers (SPMD) and PCA was not determined. The uptake of PCP to these triolein-based samplers will be pH dependent, and PCP was ionized at the prevailing pH.

Freshwater fish collected between 2000 and 2009 from various lakes throughout the Canadian Arctic were found with measurable concentrations of PCA. Mean concentrations of 0.13 ng/g lw (<MDL–1.8) were found for landlocked char (*Salvelinus alpinus*), 0.07 ng/g lw (<MDL–0.35) for lake trout (*Salvelinus namaycush*) and 1.2 ng/g lw (<MDL–3.85) for burbot (*Lota lota*) (UNEP, 2013d).

2.12.6.4 Marine environment

There are some published data on PCP and PCA in Arctic biota (Tables 2.76 and 2.77). In some of these studies, the phenolic fraction was methylated before analysis, which means no differentiation was made between PCP and PCA and that the PCP is actually ΣPCP. In other studies, PCA alone was analyzed as a proxy for PCP. As a result, it is difficult to compare the data from different studies.

Table 2.76 PCP concentrations in Arctic marine biota.

Species	Location	Tissue	n	Mean ± SE (range), ng/g ww	Reference
Glaucous gull	Svalbard, Norway	Plasma	87	(<0.03–0.48)	Verreault et al., 2005b
		Eggs	30	(≤0.01)	
Harbor seal	Svalbard, Norway	Plasma	12	(0.22–0.67)	Routti et al., 2014
Ringed seal	East Greenland	Blubber	15	1.0±0.4[a]	Letcher et al., 2009
	Svalbard, Norway	Plasma	19	0.42 (0.28–0.63)	Routti et al., 2009b
Bowhead whale	Barrow, Alaska	Plasma	19	1.6±0.19 (0.16–3.5)	Hoekstra et al., 2003
Polar bear	East Greenland	Brain	17	0.22±0.03	Gebbink et al., 2008a
		Blood	20	0.10±0.02	
		Adipose	18	1.3±0.5	
		Liver	20	3.6±0.6	
		Whole blood	19	0.3±0.3[b] (0.1–1.4)	Sandala et al., 2004

[a] ng/g lw; [b] SD.

Table 2.77 PCA concentrations in Arctic marine biota.

Species	Location	Tissue	n	Mean ± SD (range), ng/g lw	Reference
Snow crab	West Greenland	Muscle	5	1.1±0.82 (<MDL–2.2)	Vorkamp et al., 2004b
		Liver	5	0.44±0.35 (<MDL–0.93)	
Shrimp	West Greenland	Muscle	11	0.53±0.42 (<MDL–1.8)	Vorkamp et al., 2004b
Atlantic cod	West Greenland	Muscle	9	4.4±4.7 (<MDL–17)	Vorkamp et al., 2004b
		Liver	3	1.5±1.3 (<MDL–2.4)	
Capelin	West Greenland	Muscle	10	1.7±1.5 (<MDL–3.3)	Vorkamp et al., 2004b
Atlantic salmon	West Greenland	Muscle	7	1.2±1.5 (<MDL–3.2)	Vorkamp et al., 2004b
Redfish	West Greenland	Muscle	5	0.08±0.18 (<MDL–0.40)	Vorkamp et al., 2004b
Greenland halibut	West Greenland	Muscle	6	0.02±0.05 (<MDL–0.12)	Vorkamp et al., 2004b
		Liver	5	0.11±0.14 (<MDL–0.34)	
Wolffish	West Greenland	Muscle	5	0.52±0.22 (0.26–0.75)	Vorkamp et al., 2004b
		Liver	5	0.07±0.10 (<MDL–0.18)	
Arctic char	Canada	Muscle	94	0.05±0.02 (<MDL–0.10)	UNEP, 2013d
King eider	West Greenland	Muscle	10	0.03±0.09 (<MDL–0.30)	Vorkamp et al., 2004b
		Liver	5	0.24±0.20 (0.02–0.41)	
Brünnich's guillemot	West Greenland	Liver	5	0.26±0.07 (0.18–0.35)	Vorkamp et al., 2004b
Harp seal	West Greenland	Muscle	20	0.24±0.34 (0.01–1.0)	Vorkamp et al., 2004b
		Liver	9	0.19±0.47 (<MDL–1.4)	
Ringed seal	Canada	Blubber	271	0.11±0.17 (<MDL–0.82)	UNEP, 2013d
Narwhal	West Greenland	Muscle	8	0.65±0.60 (<MDL–1.7)	Vorkamp et al., 2004b
		Liver	7	0.23±0.12 (<MDL–0.34)	
		Kidney	3	0.52±0.29 (0.28–0.84)	
Beluga	West Greenland	Muscle	20	1.9±4.22 (<MDL–20)	Vorkamp et al., 2004b
		Liver	5	0.37±0.22 (0.07–0.66)	
Minke whale	West Greenland	Muscle	18	0.78±0.81 (0.08–3.0)	Vorkamp et al., 2004b
		Liver	3	0.22±0.22 (<MDL–0.43)	
		Kidney	5	0.58±0.44 (<MDL–1.0)	
Polar bear	Alaska, Beaufort Sea	Adipose	57	11±10 (<0.1–42)	Bentzen et al., 2008

ΣPCP has been measured in glaucous gull (*Larus hyperboreus*) and various marine mammals (Table 2.76). Most notably, PCP was determined in polar bears (adipose, blood, brain, liver) from 1999–2000 and ringed seal (*Pusa hispida*) blubber from 2002, all collected from East Greenland and used to calculate biomagnifcation factors (BMFs) (Gebbink et al., 2008a; Letcher et al., 2009). BMFs from ringed seal blubber to polar bear were 1.5 for adipose, 1.1 for brain and 36 for liver, however, the methodology did not separate PCP from PCA (Letcher et al., 2009). PCP concentrations were below the limits of detection in samples of polar cod (*Boreogadus saida*), capelin (*Mallotus villosus*), seal blubber, black-legged kittiwake (*Rissa tridactyla*) and glaucous gull blood/plasma as well as in eider (*Somateria mollissima*) and common guillemot (*Uria aalge*) eggs, collected from Arctic Norway in 2010–2011 (NIVA, 2012).

PCA has been reported in marine invertebrates, fish, seabirds, and marine mammals; the majority exhibiting concentrations of less than a few ng/g lw (Table 2.77). Vorkamp et al. (2004b) reported median PCA concentrations in muscle, liver and kidney of different organisms collected at West Greenland sites between 1998 and 2001. In order to be comparable to other studies, mean values from the Vorkamp et al. (2004b) study were calculated. Mean concentrations ranged from 0.44 to 1.1 ng/g lw in marine invertebrates (e.g. shrimp; snow crab, *Chionoecetes opilio*) and 0.02 to 4.4 ng/g lw in muscle of marine fish (e.g. salmon, redfish, Atlantic cod *Gadus morhua*, Greenland cod *G. ogac*, Atlantic halibut *Hippoglossus hippoglossus*, capelin, wolffish *Anarhichas minor*) with the highest value for Atlantic cod muscle (Table 2.77). In liver of marine fish, mean PCA concentrations ranged from 0.07 to 1.5 ng/g lw. In seabirds (e.g. Brünnich's guillemot, black-legged kittiwake, eider, king eider) the only mean concentrations above detection limits were found in muscle and liver of king eider (0.03 and 0.24 ng/g lw, respectively) and liver of Brünnich's guillemot (0.26 ng/g lw). In marine mammals (e.g. harp seal *Pagophilus groenlandicus*, hooded seal *Cystophora cristata*; ringed seal, walrus *Odobenus rosmarus*, narwhal *Monodon monoceros*, beluga *Delphinapterus leucas*, minke whale *Balaenoptera acutorostrata*) the mean concentrations in muscle ranged from non-detectable (ringed seal) to 1.9 ng/g lw (beluga). In liver, mean PCA concentrations ranged from non-detectable (ringed seal) to 0.37 ng/g lw (beluga). Concentrations in marine mammals did not exceed those in the marine fish and so did not indicate biomagnification (Vorkamp et al., 2004b). Relatively low PCA concentrations (<1 ng/g ww) have been detected in ringed seal from the Canadian Arctic (UNEP, 2013d) and in ringed seal (Routti et al., 2009b) and harbor seal (*Phoca vitulina*) (Routti et al., 2014) from Svalbard, Norway.

Polar bears appear to be an exception to the low concentrations reported for Arctic biota; a single report detailing PCA levels in Alaskan polar bears noted levels of up to 42 ng/g lw (Bentzen et al., 2008).

2.12.7 Environmental trends

2.12.7.1 Spatial trends

Owing to the limited nature of reported environmental data for PCP/PCA and difficulties in interpreting which specific compounds were actually present in any given sample, it is difficult to draw conclusions about the spatial trends. The exception is the pine needle work (Kylin et al., 2017). This indicates that PCP and PCA may have different sources; the distribution patterns are difficult to reconcile with methylation of PCP emitted from known sources as the only source of PCA.

2.12.7.2 Temporal trends

It is difficult to draw general conclusions about temporal trends based on the data available today. However, air concentrations at Alert (Figure 2.104) indicate a recent decrease in PCA in the Arctic (Hung et al., 2010).

2.12.8 Conclusions

Although PCP has been discussed as a potentially hazardous chemical for decades, there are few relevant studies showing the large-scale environmental behavior of this compound. In particular, too few studies have determined PCP and PCA separately. The absence of large datasets in which PCP and PCA have been determined individually and in parallel makes it very difficult to fully explain sources and spatial/temporal distribution patterns. Although there are environmental measurements from the 1960s through the 1980s, these do not focus on processes relevant for the occurrence of PCP in background areas. The problem is largely that PCP itself is not amenable to determination using standard POP-determination protocols, unlike the transformation product PCA. This has led to a much larger amount of data for PCA than for PCP, or to measurements of the two together (ΣPCP) in Arctic samples, which has created the misconception that PCA is a good proxy for PCP, although the two compounds behave quite differently in the environment.

The uncertainty in using PCA as proxy for PCP was pointed out in the Stockholm Convention's risk profile (UNEP, 2013d) where it was noted that degradation of chlorinated hydrocarbons including PCB, HCB, HCH, and PCNB could yield both PCP and PCA. The recently published pine needle data (Figure 2.105) showing major geographic differences in the PCP/PCA ratio illustrates that the two must be determined separately to understand their environmental occurrence and behavior. More efforts to determine key physical-chemical parameters experimentally, especially for PCA, are also needed to enable proper modelling of the environmental behavior of the two compounds. There are few data for PCP and/or PCA in biota, but in general, the concentrations that have been found were low or below detection limits.

2.13 Organotins

Authors: John Kucklick, Michael Ellisor

2.13.1 Introduction

Organotins are a versatile group of compounds widely used in commercial applications, especially in preventing the fouling of boats and moorings by marine organisms. Their toxicity, in particular tributyltin (TBT), to non-target marine organisms has been well documented and has led to global restrictions on the use of TBT in marine applications to prevent fouling (Hoch, 2001; Kannan and Tanabe, 2007; Frouin et al., 2010; Okoro et al., 2011). The International Maritime Organization (IMO) adopted a treaty to ban the use of TBT-based paints on ships in 2003 with full implementation of the treaty by 2008 (Senda, 2007). Owing to the widespread use of TBT, its release into the marine environment, the potential for TBT accumulation in marine food webs, and its toxicity to gastropods (primarily through imposex) this compound has been included in long-term marine monitoring programs in the United States, Europe, and Asia (Sudaryanto et al., 2002; Kimbrough et al., 2008; OSPAR, 2012; Kim et al., 2014a). In general, restrictions on TBT use in the marine environment have led to declines in concentration both in sediment and biota with concomitant declines in the occurrence of toxic effects in marine organisms (Kimbrough et al., 2008; OSPAR, 2012). Continued use of other tin compounds, for instance the use of dibutyltin (DBT) as a plasticizer suggests there may be other sources of organotins to the Arctic that pose an environmental threat in addition to the observed contamination from the historical use of TBT as a biocide. This section therefore includes information on other organotin compounds, discusses their occurrence (Table 2.78), and makes recommendations for future studies on organotins in the Arctic. This information (Table 2.79) builds on material previously reported by AMAP (1998a).

2.13.2 Physical-chemical properties

Organotins are characterized by the presence of one or more covalent bonds between tin and carbon (Sn-C) with the general chemical formula R_nSnX_{4-n}, where R represents an alkyl or aryl group and X is represented by an anion such as chloride, oxide, hydroxide, acetate, or other functional group (see Figure 2.107). The chemical and physical properties of organotin compounds are largely determined by the number and nature of the organic subunits attached to the tin atom.

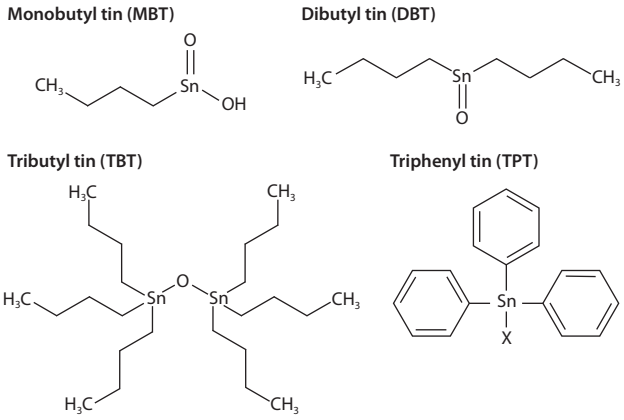


Figure 2.107 Example structures of some organotins.

Table 2.79 Organotin compounds discussed in this chapter.

Compound	Abbreviation	CAS number
Monobutyltin	MBT	1118-46-3
Dibutyltin	DBT	14488-53-0
Tributyltin	TBT	78763-54-9
Trimethylmonobutyltin	TriMeMBT	1527-99-7
Monomethyltin	MMT	–
Dimethyltin	DMT	23120-99-2
Tetramethyltin	TMT	594-27-4
Dimethyldibutyltin	DiMeDBT	1528-00-3
Methyltributyltin	MeTBT	1528-01-04
Monooctyltin	MOT	–
Dioctyltin	DOT	60004-29-7
Monophenyltin	MPT	21707-93-7
Diphenyltin	DPT	6381-06-02
Triphenyltin	TPT	668-34-8

Table 2.78 Summary of Arctic media for which organotin data have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
TBT									×	×
DBT									×	×
MBT									×	×
TPT										×

In general, the degree of substitution of organic moieties reflects the biological activity of organotin compounds where $R_3SnX > R_2SnX_2 > RSnX_3$. The nature of the X moiety has been reported to have little influence on the biological activity of organotins unless the X moiety itself is biologically active or increases the solubility and bioavailability of the compound (Song et al., 2006).

Butyltins in their ionic form are generally not considered to be appreciably transferred to the atmosphere due to their low vapor pressure (Hoch, 2001; Senda, 2007). However, methylated butyltins, for example methylated tributyltin, are volatile and have the potential for atmospheric transport (Amouroux et al., 2000). Amouroux and co-workers found that tetramethyltin (TMT), trimethylmonobutyltin (TriMeMBT), dimethyldibutyltin (DiMeDBT) and methyltributyltin (MeTBT) had total volatile tin flux densities of 20, 90 and 510 nmol/m^2/y from the Gironde estuary (France), Arcachon Harbor (France), and Scheldt estuary (Belgium/Netherlands), respectively. Further research is needed to help understand the ultimate fate of these volatile tin species in the atmosphere and whether they are transported to the Arctic.

2.13.3 Sources, production, use and trends

Except for a few methyltin species, organotin compounds are anthropogenic and owing to their biological and chemical diversity have found widespread use in numerous industrial applications (Table 2.80). The major commercial application of organotin compounds is their use as additives in the manufacturing of plastics in order to prevent thermal and UV decomposition of polyvinyl chloride (PVC). Serving as stabilizers, mono- and dialkyltin species are used to prevent dehydrochlorination, radical decomposition, and atmospheric oxidation of the polymer (Piver, 1973; Hoch, 2001). Although various formulations of organotin stabilizers have been reported, the most utilized compounds are DBT and dioctyltin (DOT) derivatives for their overall utility and low toxicity, respectively. Therefore, DOT derivatives are generally reserved for the production of PVC products that are associated with, or that may come into contact with foodstuffs, such as potable waterlines, food packaging materials, and dinnerware.

In addition to their extensive use as PVC stabilizers, diorganotin compounds are also widely used as catalysts in the production of polyurethane foams and silicones and as precursors for SnO_2 coatings in the glass industry. Due to their high catalytic efficiency and effectiveness for optimizing the rate of chain extension and gas formation during the polymerization process, DBTs and DMTs are commonly used in the production of polyurethane foams (Hoch, 2001). DBTs are also frequently used as a catalyst in the vulcanization of silicones at room temperature in commercial applications where elevated temperatures may be detrimental, such as when making dental impressions and encapsulating electronic equipment (Piver, 1973; Jousseaume et al., 1994). However, dimethyltin (DMT) derivatives, mostly dimethyltindichlorides, are used as precursors for the deposition of SnO_2 films on glass where it is used for solar cells, touch screens, windows, and anti-static layers (van Mol et al., 2006).

The unique biological activity of triorganotin compounds has given rise to a range of agricultural applications and to their extensive use in antifouling paints for reducing the growth of marine organisms on the hulls of marine vessels, which leads to increased drag and higher fuel consumption. The biocidal properties of triorganotin compounds are characteristic of the R-group and have been shown to actuate species-dependent responses depending on the nature of the R-group. For example, trimethyl- and triethyl-organotin derivatives are highly toxic to insects and mammals, respectively, while TBT and triphenyltin (TPT) derivatives have higher toxicities towards fungi, fish, algae, and mollusks (Hoch, 2001; Song et al., 2006). Because of the selective fungicidal and insecticidal properties as well as their acute toxicity for mollusks and other fouling organisms, TBT derivatives have been extensively formulated for use as pesticides, wood preservatives, and antifouling agents (Crowe, 1987a,b; Omae, 2003; Shiryaev and Storozhenko, 2012). The toxicity of alkyl- and phenyltin to aquatic organisms is well documented and has been reviewed elsewhere (Hoch, 2001; Cima et al., 2003; Frouin et al., 2010). The general trend found was that TBT exhibits the highest acute and chronic toxicity to marine organisms at concentrations as low as 1 to 2 ng/L in invertebrates. The acute toxicity declines with DBT, monobutyltin (MBT) and TPT exhibiting lower toxicity to

Table 2.80 Industrial applications of organotin compounds.

Industrial application	Function	General classes of organotin	Reference
PVC stabilizer	Prevents thermal and UV decomposition	R_2SnX_2 and $RSnX_3$ R = methyl, butyl, octyl	Piver, 1973; Hoch, 2001
Antifouling agent	Biocide in antifouling paints	R_3SnX R = butyl, phenyl	Hoch, 2001; Fent, 2006
Wood preservative	Insecticide, fungicide	Bu_3SnX	Hoch, 2001
Catalytic agent	Catalyst in the production of polyurethane foams and curing of silicone	R_2SnX_2 R = methyl, butyl	Piver, 1973; Jousseaume et al., 1994
Glass treatment	Precursor for SnO_2 films on glass	Me_2SnX_2 and $RSnX_3$ R = methyl, butyl	van Mol et al., 2006
Agrochemical	Insecticide, fungicide	R_3SnX R = butyl, phenyl, cyano	Hoch, 2001; Crowe, 1987a,b

marine invertebrates than TBT. Organotin compound toxicity to humans and laboratory animals is summarized elsewhere (Senda, 2007). A complete toxicological review of organotin toxicity is outside the scope of this summary which focuses primarily on reports of organotin compounds in Arctic and subarctic biota.

The primary source of organotins to the marine environment and the Arctic is probably through leaching from ship hulls and through the removal of old organotin paint from ships during maintenance. Antifouling paints maintain activity throughout their lifetime either through the constant erosion of the paint surface thereby exposing active antifouling compounds or through the direct leaching of tin-containing antifoulants from the paint. Ships that were recently painted with TBT-containing paint can leach 600 g or more of organotin per day from the ship hull leading to dissolved concentrations in the surrounding water of several hundred ng/L. This has led to relatively high organotin concentrations in sediment and biota in marine areas associated with high ship traffic and ship maintenance. The input of organotin compounds from other sources is less well understood (Kim et al., 2014a,b). Approximately 70% of the organotin produced to date has been incorporated into plastic, primarily PVC where it functions as a UV stabilizer. For example, DBT is used extensively as a plasticizer in PVC piping and is known to leach into the water supply during water distribution. Leaching of MBT and DBT from piping may continue to act as a potential source to marine waters; however, it has been reported that alkyltin concentrations in wastewater are greatly reduced by sewage treatment plants (Senda, 2007).

2.13.4 Transformation processes

Most information on transformation processes concerns TBT degradation in the environment especially in applications within the marine environment (Hoch, 2001). Photolysis is a major degradation route for TBT leading to dealkylation and formation of DBT and MBT. However, in turbid waters, photolysis of TBT may be hindered leading to its accumulation and preservation in sediments. Studies in Jinhae Bay (South Korea) demonstrated that TBT concentrations in biota and the water column declined after efforts to ban antifouling uses of TBT, while sediment concentrations showed no statistically significant differences ten years after the ban (Kim et al., 2014a). Arp et al. (2014) investigating TBT levels in water and sediments in the Drammensfjord (Norway) over the period 2005–2013 found a substantial drop in average TBT concentrations between 2005 and 2008 and a moderate decrease in the harbor area since 2008. TBT levels in water and particularly sediment away from the major site of legacy TBT release appeared to be declining at a much slower rate (Arp et al., 2014). This suggests that while efforts to restrict TBT use on ships may successfully reduce concentrations in water and biota, sediments may remain a reservoir for future alkyltin contamination.

Detailed studies of organotin cycling in three European estuaries showed that transfer among sediment, air and water media appears fairly complex and to involve several processes other than photolysis (Amouroux et al., 2000; Point et al., 2007b). Dealkylation of TBT in the water column with hydrogen replacing the butyl group may lead to the formation of volatile tin species. Likewise, dealkylation followed by methylation in sediments may also lead to volatile tin species that may be released from the sediment and subject to air-water exchange. However, other work suggests that the solubility of the methylated butyltins in water may be too high for much air-water exchange to occur (Vella and Vassallo, 2002). There is also evidence that TBT can itself directly volatilize from surface water and that this process can be enhanced 1000-fold by the formation of seawater aerosols from bursting bubbles (Saint-Louis and Pelletier, 2004).

2.13.5 Modeling studies

There are no modeling studies on organotins in the Arctic. However, see Arp et al. (2014) for a monitoring and modeling study describing temporal changes in organotins in a southern Norwegian fjord system.

2.13.6 Environmental concentrations

2.13.6.1 Air and precipitation

The transformation of TBT in coastal waters can lead to the formation of volatile tin species (Amouroux et al., 2000). Huang and co-workers (Huang and Klemm, 2004; Huang et al., 2004) investigated the occurrence of organotin species in the gas phase, bulk precipitation and on aerosols in southern Germany. Monomethyltin (MMT), DMT, TMT, MBT, DBT, TBT, DOT and monooctyltin (MOT) were all detected in each of the three matrices. Median gas phase concentrations from two sites ranged from <MDL for MMT to 87.2 pg/m^3 MOT (as tin). MBT was the species present in the highest concentrations in both the aerosol (median up to 71 pg/m^3) and bulk precipitation phases (median up to 11.3 ng/L). While not Arctic locations, the study does show the potential for atmospheric transport of tin species from contaminated locations, which may warrant limited screening for these species within the Arctic region. No studies were found on organotin compounds in air and precipitation for Arctic locations.

2.13.6.2 Terrestrial environment

There are no reports of tin accumulation in the Arctic terrestrial environment. However, there is at least one study of the atmospheric loading of organotins to the terrestrial environment conducted in Germany (Huang et al., 2004). TMT, DMT, MMT, TBT, DBT, MBT, DOT, and MOT were all detected in surface forest soils. MBT and MOT were present in the highest concentrations, generally several thousand milligrams per hectare and were believed to arrive via atmospheric deposition. Further work is needed to determine whether organotins are being delivered to the Arctic via atmospheric deposition.

Tin-based compounds have been used as fungicides in the form of TPT hydroxide (Hoch, 2001). TPT hydroxide is currently registered for use on pecans, sugar beet and potatoes in the United States (US EPA, 1999). There is little if any information on the use of TPT hydroxide in the Arctic; as with the tin species listed above, further work is needed to determine if TPT is reaching the Arctic via use and/or atmospheric deposition.

2.13.6.3 Freshwater environment

Given the use of TBT primarily for prevention of fouling by marine organisms, the vast majority of studies on organotin occurrence have been in marine areas. There are studies on TBT and related tin compounds in river systems (Hoch, 2001), however none appear to cover the Arctic freshwater environment.

SWECO VIAK (2007) investigated organotins in two surface water samples each from Lake Abiskojaure (background) and Kalixälvens gruvsamhälle (old mining village at the Kalixälven River, point source) collected in 2006 in northern Sweden. Despite testing for a range of species – MBT, DBT, TBT, MOT, DOT, monophenyltin (MPT), diphenyltin (DPT) and TPT – only MBT was present in detectable concentrations: 8.3 and 13 ng/L in Lake Abiskojaure and 5.8 and 19 ng/L in Kalixälvens gruvsamhälle.

SWECO Environment (2009) studied EU Water Framework Directive priority substances mostly in water but also in sediment samples from Lake Abiskojaure in northern Sweden. Monthly water analysis for TBT through 2008 detected TBT in two samples: 3 ng/L in April and 2 ng/L in May. TBT was not detected (limit of quantification: 1 ng/g) in sediment samples.

2.13.6.4 Marine environment

There are many reports of organotin contamination in the marine environment particularly from non-Arctic locations. However, there are also several reports describing contamination of the Arctic marine environment by organotins.

Organotins are generally determined in gastropods as these animals are subject to endocrine disruption effects of TBT leading to the development of male characteristics in female gastropods ('imposex'). In Iceland, dogwhelks (*Nucella lapillus*) have been monitored for TBT-induced imposex at selected harbors for more than two decades (Guðmundsdóttir et al., 2011). In general, the incidence of imposex was lower in samples collected in 2008 than in those collected in 1992 and 1993. However, imposex did increase at three harbors between 2003 and 2008 suggesting continued contamination of some harbors despite restrictions on TBT use. Levels of butyltins and phenyltins were also determined in 2009 in dogwhelks and compared to the incidence of imposex (Guðmundsdóttir et al., 2011). Organotins were measurable in all samples, with TBT accounting for 25% to 66% of organotins present. Total organotin levels ranged from 2.07 to 70.4 ng/g dw. TPT and TMT were detected less frequently than butyltins with concentrations ranging from <0.7 to 22.8 ng/g dw. Organotin concentrations were significantly correlated to the occurrence of imposex. The study suggests that although restrictions on organotin use are in place, organotins are still both measureable and affecting the marine environment. However, in 2013, levels of TBT in dogwhelks from Brashavn (Norway) were below the limit of detection (<0.674 ng/g ww) and significant downward trends in TBT concentrations and imposex development were detected in dogwhelks from Lofoten (Norway) (NIVA, 2014).

An earlier study of dogwhelks and blue mussels (*Mytilus edulis*) sampled in Iceland also found detectable concentrations of organotins and that organotin concentrations varied seasonally in biota possibly due to the biological cycles of the organisms (Skarphédinsdóttir et al., 1996).

Elsewhere in the Arctic, TBT was detected in bay mussels (*M. trossulus*) from four of the ten Alaskan harbors investigated and imposex was recorded in dogwinkles (*N. lima*) at all three harbor sites tested whereas none of the control sites exhibited detectable levels of imposex (Tallmon, 2012). Detectable concentrations of TBT ranged from 29 to 54 ng/g ww. In Greenland, butyltins were detected in blue mussels from several harbors sampled in 1999 and 2000 with the highest concentration observed in Nuuk Harbor (254 ng/g ww) (Strand and Asmund, 2003). Sediment samples collected in Nuuk Harbor contained up to 171±32 ng/g dw TBT and 9.6±1.1 ng/g dw DBT. Concentrations of alkyltin in sediments 4 km from the harbor were below the limit of detection (<1 ng/g dw) for all tin species (Jacobsen and Asmund, 2000). DBT and TBT were also detected in blue mussels collected at five locations in nearby Nuuk at concentrations of about 1 ng/g ww per tin species. Organotins have also been detected in walleye pollock (*Theragra chalcogramma*) from the Gulf of Alaska and the Bering Sea collected in 1991 and 1992 (de Brito et al., 2002) in the form of TBT. MBT and DBT were below the detection limits (3.0 and 2.5 ng/g ww). However, TBT concentrations in muscle of walleye pollock ranged from 0.5 to 6.9 ng/g ww.

Organotins have also been detected in other marine fauna, including marine mammals from several Arctic locations. Data for butyltins are available for harbor porpoise (*Phocoena phocoena*), Dall's porpoise (*Phocoenoides dalli*), beluga (*Delphinapterus leucas*), ringed seal (*Pusa hispida*), glaucous gull (*Larus hyperboreus*) and polar bear (*Ursus maritimus*) (Tanabe et al., 1998; Yang et al., 1998; St-Louis et al., 2000; Berge et al., 2004; Strand et al., 2005; Point et al., 2007a) (Table 2.81). Total butyltin (sum of MBT, DBT and TBT) concentrations in harbor porpoise liver were lowest for individuals from near Greenland (average 12 ng/g ww; range 2–20 ng/g ww), followed by western and northern Norway at 263 ng/g (range 63–408 ng/g ww) compared to the more polluted Baltic Sea near Denmark with concentrations of 1092 ng/g ww (range 266–4621 ng/g ww) (Table 2.81). DBT averaged 54% of ΣBT in liver followed by TBT (36%) and MBT (10%). Concentrations were highest in liver, followed by kidney and muscle. ΣBT concentrations were also higher in more southern locations relative to Arctic regions for Dall's porpoise where levels were 757 ng/g ww (range 340–1040 ng/g ww) off the Sanriku coast of Japan versus 99 ng/g ww (range 44–170 ng/g ww) in animals from the Bering Sea (Table 2.81). As with harbor porpoise, DBT was the major butyltin species present.

Butyltin concentrations in liver of beluga collected from the Arctic sites of Point Hope (Alaska) and the Hudson Strait in Canada (St-Louis et al., 2000) can be compared to those from animals from the more polluted St. Lawrence River. Mean ΣBT concentrations in beluga from Point Hope (northern Bering Sea) were 19.8 ng/g ww (range 16.5–23.3 ng/g ww) and below the limit of detection for animals collected from the Hudson Strait. Mean concentrations in beluga from the St. Lawrence River were higher with a mean of 54 ng/g ww (range 8.7–117 ng/g ww) in samples collected

Table 2.81 Mean and range of butyltin concentrations (ng/g ww) in marine mammal liver from Arctic, subarctic and non-Arctic regions (the latter provided for comparison).

Species	Location	Year(s)	n	MBT	DBT	TBT	ΣBT	Reference
Harbour porpoise	Northern Norway	1988	4	34.5 (6–59)	285 (9–969)	98 (4.2–156)	417.5	Berge et al., 2004
		1999	8	10.7 (4.2–20)	66.5 (38–120)	34.4 (19–52)	111.6	Berge et al., 2004
	West Greenland	1999	3	0.5 (<MDL–0.6)	8.3 (2–13)	3.6 <MDL–6.5)	12.4	Strand et al., 2005
	West Norway	1999	4	18.9 (7.6–39)	122 (65–247)	39.6 (22–62)	180.3	Berge et al., 2004
	Inner Danish Waters	1998–1999	20	17 (2.5–61)	817 (205–3689)	258 (58–871)	1092	Strand et al., 2005
	Danish North Sea	1998–1999	15	24 (1.3–102)	732 (41–2328)	196 (26–521)	952	Strand et al., 2005
Beluga	St. Lawrence Estuary, Canada	1995–1998	21	2.4[a] (0.1–32)	22.1[a] (3.6–129)	5.5[a] (<MDL–37)	30[a]	St-Louis et al., 2000
		1988	5	29[a] (8.5–67.7)	19[a] (<MDL–41.2)	5.5[a] (0.2–8.1)	54[a]	Yang et al., 1998
	Hudson Strait, Canada	1998	5	<MDL	<MDL	<MDL	<MDL	St-Louis et al., 2000
	Point Hope, Alaska	1989	3	3.3 (2.2–4.8)	15.4 (13.3–17.2)	1.14 (1.0–1.34)	19.8	Point et al., 2007a
Dall's porpoise	Aleutian Chain, Alaska	1979	1	33	59	26	118	Tanabe et al., 1998
	Bering Sea	1981	2	27 (22–32)	42 (29–55)	16 (12–19)	85	Tanabe et al., 1998
	NW North Pacific	1984	3	37 (17–58)	44 (15–93)	16 (12–19)	97	Tanabe et al., 1998
	Sanriku Coast, Japan	1995	3	97 (50–120)	430 (180–600)	230 (110–310)	757	Tanabe et al., 1998
Ringed seal	Spitsbergen, Norway	2000	6	1	1.6	<1	2.6	Berge et al., 2004
Polar bear	Barrow, Alaska	1999	3	0.544	0.287	0.160	0.99	Point et al., 2007a

[a]Estimated conversion of 92% moisture.

in 1988 (Yang et al., 1998) and 30 ng/g ww in samples from 1995–1998 (St-Louis et al., 2000) (Table 2.81). As with harbor porpoise and Dall's porpoise, DBT tended to dominate the butyltin profile although MBT was the major butyltin in beluga collected in 1988 by Yang et al. (1998).

Data for butyltins in liver of ringed seals and polar bears are presented in Table 2.81. In general, the butyltin concentrations in all these species were very low with non-detectable levels in ringed seals to low ng/g ww or sub ng/g ww levels in polar bear.

Levels of MPT, DPT, and TPT were measured in harbor porpoise from the same locations as discussed above. Total phenyltins were approximately 10-fold lower than for ΣBT. The relative proportions of phenyltins in tissues differed from the distribution of alkyltins with MPT and DPT having roughly equal proportions in liver. Unlike the butyltins, TPT was the only phenyltin detected in kidney samples. This was also true for a sample of one set of muscle samples from harbor porpoise from northern Norway but not for a separate sample set where MPT was the predominant phenyltin (Berge et al., 2004).

Butyltins and phenyltins are both bioaccumulative and so can be subject to trophic transfer. Strand and Jacobsen (2005) undertook an extensive survey of levels in a Danish food web and found biomagnification factors (BMF: wet weight predator/prey concentration ratios) for butyltins to be generally 1 or less except for harbor porpoise where the BMF was 4.4. Harbor seals on the other hand had a BMF of only 0.2 suggesting a greater metabolic elimination capacity for seals relative to cetaceans. Another possibility is that organotin compounds are lost through shedding of hair in seals because organotin compounds are primarily associated with protein and not lipid (Strand and Jacobsen, 2005). The greater BMF observed in harbor porpoise is consistent with relatively high butyltin levels observed in Dall's porpoise (Table 2.81; Tanabe et al., 1998; Tanabe, 1999). Phenyltins appeared to bioaccumulate and biomagnify to a lesser extent than butyltins in the Danish food web study. Low butyltin concentrations in polar bears suggest a low biomagnification potential for butyltins or a high ability for polar bears to metabolize butyltins, as suggested by Strand and Jacobsen (2005).

2.13.7 Environmental trends

2.13.7.1 Spatial trends

Organotin concentrations generally follow population and shipping density. Of the locations where organotin data are available, Greenland and Alaska tend to have the lowest concentrations in both mussels and marine mammals. The highest organotin concentrations in the Arctic appear to occur in harbors in Iceland. More information is needed to establish a more complete picture of spatial trends in organotin concentrations given that their use has been curtailed and that there are declining numbers of studies on organotins.

2.13.7.2 Temporal trends

Berge et al. (2004) analyzed harbor porpoise samples from two time points; 1988 and 1998. Levels of ΣBT were lower in the 1998 samples than the 1988 samples suggesting that restrictions on TBT usage were being reflected in lower levels in the biota. TBT use as an antifoulant in Europe and the United States was curtailed in the late 1980s and early 1990s (Senda, 2007; Hoch, 2001). However, TPT concentrations were higher in harbor porpoise samples collected in 1999 relative to 1988, suggesting increased use of phenyltins during this period.

2.13.8 Conclusions

There are few organotin data for biota from the AMAP region in comparison with lower latitudes, although the reported presence of organotin compounds and their observed environmental effects vindicate the environmental threat of these compounds within the Arctic. Consistent with other summaries, organotin concentrations are higher in areas with higher human population densities, particularly in more southern latitudes such as the Baltic Sea and the St. Lawrence Estuary where shipping activity is also high. Organotin compounds are generally not thought to biomagnify except in cetaceans, which is consistent with the relatively low levels observed in Arctic polar bears and seals. In general, levels of organotin are very low in Arctic biota and may be declining for butyltins. However, substantial environmental effects have been observed through exposure to concentrations of butyltins below the detection limit of current analytical methodologies. In addition, the increase in phenyltins from 1988 and 1998 observed in harbour porpoise (Berge et al., 2004) would argue for continued monitoring of organotin compounds especially phenyltins. Published temporal trend data for organotins in Arctic marine mammals are not available. An unpublished study (D. Point, Laboratoire Geosciences Environnement Toulouse, University of Toulouse, France, pers. comm.) did show a temporal increase in butyltins in ringed seals from Alaska between 1987 and 2005 indicating increased butyltin exposure in this region. Further work is required to determine whether methylated butyltins are transported to the Arctic via the atmosphere, as the study by Amouroux et al. (2000) indicates evasion of methylated butyltins from water where butyltins were heavily used as antifoulants. Continued monitoring of Arctic abiotic matrices and biota, such as that ongoing at lower latitudes (Arp et al., 2014; Langston et al., 2015) is needed to establish whether organotin concentrations are declining as a result of reduced use as antifoulants on ships. Data suggesting that volatile organotin compounds are generated in contaminated regions at lower latitudes, supports the need for studies measuring volatile tin species in the Arctic.

2.14 Polycyclic aromatic hydrocarbons (PAHs)

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2.14.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large class of hydrophobic, semi-volatile organic contaminants comprising at least two fused aromatic rings (Figure 2.108). Both natural and anthropogenic activities, including coal and petroleum use, vehicle emissions, forest fires and volcanic eruptions are responsible for their widespread environmental occurrence (Lima et al., 2005; Dalsøren et al., 2007). Once released to the atmosphere, PAHs disperse via long-range transport and subsequently deposit in surface waters, soils and sediments of remote regions, including the Arctic (Table 2.82) (Wang et al., 2010c; Friedman and Selin, 2012).

Anthropogenic releases prompted the designation of PAHs as persistent organic pollutants (POPs) by the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) and the listing of PAHs by the OSPAR and UNECE conventions (UNECE, 1998; OSPAR, 2000). While there are several hundred individual PAHs, 16 were selected in the mid-1970s as priority pollutants by the United States Environmental Protection Agency (USEPA) based on their toxicity, ability to be analyzed, and environmental occurrence at the time (Keith, 2015). These 16 PAHs (Table 2.83) are frequently targeted for monitoring and have become a *de facto* standard globally (Andersson and Achten, 2015).

The USEPA priority PAHs belong to the group of polycyclic aromatic compounds that tend to predominate in environmental mixtures from pyrogenic sources, i.e. those arising from the incomplete combustion of fossil fuels and organic matter (Lima et al., 2005; Keyte et al., 2013; Achten and Andersson, 2015; Lammel, 2015). Whereas non-combusted fossil fuels contain a high abundance of alkyl-substituted PAHs, the high temperatures of combustion eliminate alkyl side chains, resulting in a higher prevalence of unsubstituted or 'parent' PAHs. Source attribution ratios, which relate the concentration of alkylated-to-parent PAHs, are frequently used to attribute PAHs in environmental samples to either a petrogenic or pyrogenic source (Lima et al., 2005). In general, those from pyrogenic sources are dominated by parent PAHs and also contain more of the high-molecular weight parent PAHs. Heterocyclic compounds – such as those with sulfur (thiophenes), nitrogen (azarenes) or oxygen (furans) in the

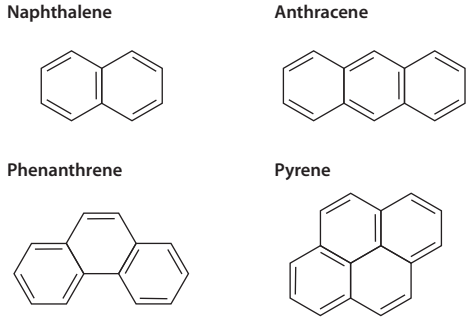

Figure 2.108 Four representative polycyclic aromatic hydrocarbons (PAHs).

Table 2.83 The 16 PAHs defined as priority pollutants by the US Environmental Protection Agency.

Name	CAS#	Rings	MW
Naphthalene	91-20-3	2	128.17
Acenaphthylene	208-96-8	3	152.19
Acenaphthene	83-32-9	3	154.21
Fluorene	86-73-7	3	166.22
Phenanthrene	85-01-8	3	178.23
Anthracene	120-12-7	3	178.23
Fluoranthene	206-44-0	4	202.26
Pyrene	129-00-0	4	202.26
Benzo[*a*]anthracene	56-55-3	4	228.29
Chrysene	218-01-9	4	228.29
Benzo[*b*]fluoranthene	205-99-2	5	253.32
Benzo[*k*]fluoranthene	207-08-9	5	253.32
Benzo[*a*]pyrene	50-32-8	5	253.32
Dibenzo[*a,h*]anthracene	215-58-7	6	278.35
Benzo[*g,h,i*]perylene	191-24-2	6	276.34
Indeno[1,2,3-*cd*]pyrene	193-39-5	6	276.34

Table 2.82 Summary of Arctic media for which combustion-derived PAH concentrations have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine[a]		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
PAHs	×	×	×	×	×	×	×	×	×	×

[a]It is difficult to distinguish between pyrogenic and petrogenic PAHs with certainty in marine samples given the presence of natural underwater hydrocarbon seeps.

ring – are generally present to a lesser degree in pyrogenic materials compared to crude oil and coal-derived materials. Alkylated PAH patterns vary according to origin, with pyrogenic sources typically showing a sloped distribution of $C_0>C_1>C_2>C_3>C_4$ and petrogenic sources showing a bell-shape distribution of C_1–C_4-alkylated PAHs (Andersson and Achten, 2015).

As discussed in Section 2.14.4, the degradation products of nitro-, oxy-, and hydroxy-PAHs may account for a significant fraction of atmospheric PAHs.

PAHs differ from many other POPs and chemicals of emerging concern in that they are unintentional by-products of fossil fuel use and biomass burning and emissions are ongoing. Furthermore, PAHs are readily metabolized by vertebrates and do not undergo biomagnification (Wan et al., 2007). Recent modeling studies have suggested that while concentrations of many of the original 12 POPs have declined in Arctic biota over the past 25 years, concentrations of PAHs have risen by as much as 30-fold in fish and mussels, initiating concern over their emerging role in the Arctic ecosystems (De Laender et al., 2011).

This section of Chapter 2 summarizes the Arctic data available for combustion-derived PAHs between 2004 and early 2015. Because PAHs may originate from sources other than combustion, including natural petroleum seeps and oil and gas activities (the latter addressed in a previous AMAP assessment; Klungsøyr et al., 2010), to distinguish the environmental combustion-derived PAHs from PAHs from other sources, much of the information used here is taken from reports from remote, unexploited Arctic regions and from studies that provide some evidence of a pyrogenic origin.

2.14.2 Physical-chemical properties

The general characteristics common among PAHs are high melting and boiling points, low vapor pressures, and very low water solubility which tends to decrease with increasing molecular mass (Table 2.83; Appendix 1). With low vapor pressures, the majority of PAHs, and especially those with three or four rings, are semi-volatile and readily undergo long-range transport via the atmosphere, where they adsorb to particles such as black carbon, mineral dust and sea salt, or remain in the gas phase (Lammel et al., 2009).

Atmospheric PAHs may be subject to wet and dry deposition to surface waters and soils, where they have longer lifetimes; models suggest that atmospheric half-lives of 3–5 ring PAHs are of the order of hours or days, whereas their persistence in soils can be on the order of decades (Keyte et al., 2013). However, a semi-volatile nature allows many PAHs to re-volatilize from ground compartments and re-enter the atmosphere to undergo enhanced long-range transport potential via multi-hopping (Semeena and Lammel, 2005; Lammel et al., 2009).

Although PAHs are sufficiently lipophilic to bioaccumulate in organisms, they are also subject to biotransformation processes and so do not appear to biomagnify through food chains (Wan et al., 2007), including those in the Arctic (De Laender et al., 2011).

2.14.3 Sources, production, use and trends

Anthropogenic sources of PAHs within the Arctic are isolated and although they may be important on a local scale (Rose et al., 2004) they are generally negligible compared to the deposition of PAH originating from the burning of fossil fuels and biomass at lower latitudes (Law and Stohl, 2007; Wang et al., 2010c; Friedman and Selin, 2012). At the high latitudes and low temperatures of the Arctic, deposition processes become more significant than evaporation (Sharpe, 2008) and atmospheric PAHs may undergo net deposition to surface water, soils and sediments. However, semi-volatile PAHs may also re-volatilize from ground surfaces, resulting in secondary emissions of some PAHs to the Arctic atmosphere (Keyte et al., 2013).

Given the widespread and ongoing emission of PAHs globally, the source(s) of Arctic contamination are difficult to derive empirically. Therefore, modeling approaches have been used to determine the predominant regions, activities and global transport processes influencing PAH concentrations in the Arctic (see Section 2.14.5).

Pyrogenic PAHs are by-products of incomplete combustion and are predominantly emitted to the atmosphere via burning of fossil fuels (coal, petroleum, wood) and via natural sources such as volcanoes and forest fires (Lima et al., 2005). Quantifying emissions is therefore one way to estimate the extent and source of environmental PAH releases.

The most recently published global atmospheric emissions inventories for PAHs are for 2004 and 2007 (Zhang and Tao, 2009; Shen et al., 2013). Both studies estimated global emissions based on the 16 USEPA priority PAHs. The estimated global emission of PAHs for 2004 was 520 000 tonnes (Zhang and Tao, 2009). In 2007, the annual global atmospheric emission was lower at 504 000 tonnes, the primary sources being biomass fuels, including firewood and crop residues (60.5%), open-field biomass burning (agricultural waste burning, deforestation, and wildfires, 13.6%), and petroleum consumption by on-road motor vehicles (12.8%) (Shen et al., 2013). Asian countries contributed half (53.3%) of the global PAH emissions, with the largest emissions in 2007 coming from China (106 000 tonnes) and India (67 000 tonnes), followed by Brazil, Indonesia, Nigeria, Ethiopia, Pakistan, Congo Democratic Republic, Vietnam, and Russia (Shen et al., 2013).

Emissions of the 16 USEPA priority PAHs in circumpolar and neighboring countries in 2007 based on estimates from Shen et al. (2013) are shown in Figure 2.109. These countries (including a category showing the combined northern European countries except for Norway, Sweden, Denmark and Finland) emitted 150 000 tonnes of PAHs in 2007 or about 30% of global emissions.

Source profile estimates for Russia and the USA, the two largest PAH emitters among the circumpolar countries are shown in Figure 2.110. Motor vehicles and wildfire sources were important in both countries although indoor firewood burning was estimated to be much more important in the USA than in Russia.

Shen et al. (2013) also calculated historical global PAH emissions from 1960 to 2008 and projected future emissions through 2030. According to their analysis, total PAH emissions peaked globally in 1995 at 592 000 tonnes and then declined reaching 499 000 in 2008. Future global emissions are projected to continue declining, by 46–71% by 2030.

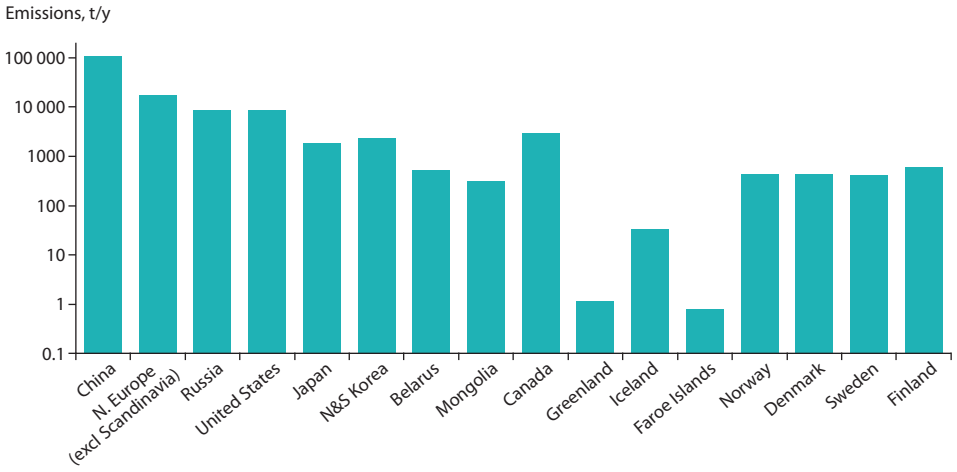

Figure 2.109 Emissions of the 16 USEPA priority PAHs in circumpolar and neighboring countries in 2007 based on estimates from Shen et al. (2013).

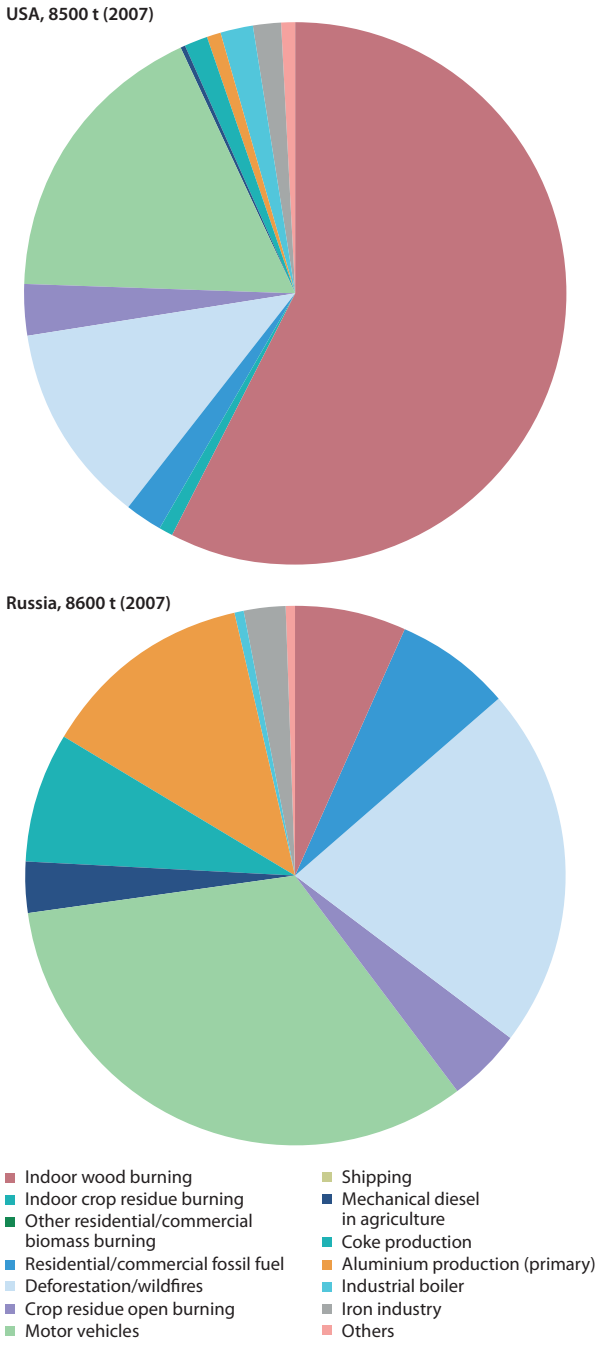

Figure 2.110 Source profiles of PAHs for the USA and Russia (Shen et al., 2013).

2.14.4 Transformation processes

PAHs are readily metabolized by living organisms and thus are not always present in the environment as parent compounds (Xue and Warshawsky, 2005; Haritash and Kaushik, 2009). Microbial activity in soil and sediments alters PAH profiles in the abiotic Arctic environment. Dong et al. (2015) reported PAH concentrations in sediment samples collected from four sites on the Chukchi Plateau to the Makarov Basin in summer 2010. Concentrations of the 16 USEPA priority PAHs varied from 2.0 to 41.6 ng/g dw, and decreased with sediment depth and movement from the southern to the northern sites. Dong et al. (2015) also identified several bacteria involved in PAH degradation *in situ*. The potential degraders include *Cycloclasticus*, *Pseudomonas*, *Halomonas, Pseudoalteromonas*, *Marinomonas, Bacillus, Dietzia, Colwellia, Acinetobacter, Alcanivorax, Salinisphaera and Shewanella*, with *Dietzia* the most abundant and present in all sediment samples. *Cycloclasticus* and *Pseudomonas* showed the best PAH degradation capability under low temperatures. They concluded that PAHs and PAH-degrading bacteria were widespread in the deep-sea sediments of the Arctic Ocean. Bagi et al. (2014) reported on the biodegradation of the PAH, naphthalene, found in abundance in crude oil, and determined the biodegradation rate, temperature response and bacterial community composition of seawaters from two climatically different areas (North Sea and Arctic Ocean). Three-fold higher naphthalene degradation rates were observed in Arctic seawater samples compared to those from the North Sea, suggesting that the biodegradation capacity in cold seawater is not necessarily lower than that of temperate seawater, as is often assumed.

PAHs are actively biotransformed by vertebrates and other organisms, quantifying PAH metabolites is thus a generally accepted method for estimating biotic exposure (Beyer et al., 2010). Specifically, the CYP1A1 phase I hydroxylated PAH metabolites (OH-PAHs) are considered adequate markers of exposure to parent PAHs, and have been measured in several Arctic fish species (see Section 2.14.6.4).

PAHs undergo photochemical reactions in the atmosphere to yield nitro-, oxy- and OH-PAHs as well as many other oxygenated species such as aldehydes and quinones. The topic has been thoroughly reviewed by Keyte et al. (2013) and Atkinson and Arey (2007). Parent PAH atmospheric residence times are generally hours or days at most, due to reaction with

the hydroxyl radical in the gas-phase. OH–PAHs are formed through hydroxyl radical addition to the PAH. Nitro-PAHs can be produced by reaction of nitrate radical as well as from the reaction of OH-PAHs with nitrogen dioxide and loss of a water molecule. Nitro-PAHs can also be formed via HNO_3-catalyzed NO_2 reaction in the particulate phase. Oxy-PAHs are formed through initial OH attack in the gas-phase or ozone reaction in the particulate phase. For the relatively volatile two- and three-ring PAHs, reactions in the gas phase are likely to dominate, while for compounds with four or more aromatic rings, reactions in both phases are important (Lammel, 2015). Nitro- and OH-PAHs may account for up to 20% and 10%, respectively, of the 16 USEPA PAH concentrations in air, and oxy-PAHs for even more (Lammel, 2015). However, nitro-PAHs are mainly associated with urban NO_X sites and are present at near detection limits (<0.01 ng/m^3) at remote alpine locations (Albinet et al., 2008). The levels and spatial extent of nitro-PAHs and other degradation products in the Arctic atmosphere are unknown.

Photodegradation of PAHs also occurs in water by direct photolysis (de Bruyn et al., 2012) or indirect photosensitization processes with transient excited species such as singlet oxygen ($^1O_2$), hydroxyl radical (·OH), and other reactive species formed in sunlit natural waters (Fasnacht and Blough, 2002). Dissolved organic carbon can accelerate the photodegradation of small PAHs such as phenanthrene by enhancing the formation of reactive intermediates and inhibiting the photodegradation of large PAHs such as benzo[*a*]pyrene by binding the PAH molecules (Shang et al., 2015). OH-PAHs are one of the main photochemical transformation products of PAHs in water (Itoh et al., 2006; Kinani et al., 2016) and ice (Dolinová et al., 2006).

2.14.5 Modeling studies

The spatial/temporal distribution and long-range transport of atmospheric PAHs has been studied using measurements and models. Lammel et al. (2009) used a multi-compartment chemistry-atmospheric transport model to investigate the influence of chemical transformation and gas/particle partitioning on the global distribution of PAHs in the atmosphere. The model is based on a general circulation model (GCM) with simplified atmospheric chemistry and an aerosol module that accounts for the aerosol components sulfate, black carbon, organic carbon, mineral dust and seasalt. Three PAHs (anthracene, fluoranthene, benzo[*a*]pyrene) were used in model simulations and tested with several parameterizations of gas/particle partitioning and degradation assumptions. Model results indicated that in all scenarios, the mass fraction of the total environmental PAH burden in air is <4%; most of the global burden is stored in soils and on vegetation surfaces. Globally, PAHs are mostly distributed in and around source regions but do reach the Arctic through long-range atmospheric transport. The fraction of the total environmental burden stored in the Arctic varied by scenario, but ranged from 0.5% to 12.8% for the three compounds tested. Overall, the simulations demonstrated that gas-particle partitioning in air has a substantial effect on the transport and environmental fate of PAHs, with a scenario that assumes adsorption onto organic matter and black carbon (soot) agreeing best with observations in Arctic regions.

Wang et al. (2010c) used a probabilistic model based on backward air mass trajectory calculations to track the sources and atmospheric pathways of PAHs to the Canadian High Arctic. An integrated source contribution function (ISCF) that included air mass movements, emission intensities at sources, and the processes of partitioning, indirect photolysis, and deposition, was used to predict the contributions of various source regions for a total of 15 PAHs. Model results were further validated using air concentrations measured at the Alert air monitoring station in northern Ellesmere Island, Nunavut, throughout 2004. According to the model results, almost all PAHs detected in air at Alert originated from the northern hemisphere, with the three major source areas of eastern Russia/Asia, northern Europe/Russia, and North America accounting for 25%, 45%, and 27% of atmospheric concentrations, respectively. Northeast China accounted for only 2% of the total. The most important emission activities that result in PAH transport to the Canadian High Arctic are biofuel combustion (24%), followed by aluminum electrolysis (22%), and domestic coal burning (21%).

PAH concentrations and source regions also vary seasonally according to the model; in the summer, PAH concentrations are orders of magnitude lower than in the winter and spring when long-range atmospheric transport events occur more frequently. The majority of atmospheric PAHs in the summer and autumn are from northern Canada and North American sources, respectively; however in winter and spring, Russia and Europe are the major sources, with PAHs arriving in conjunction with the well-known Arctic haze events.

Friedman and Selin (2012) gave additional evidence for the seasonality of PAH transport to the Arctic using a chemical transport model (GEOS-Chem) that includes parameters for uncertain PAH properties, such as oxidation, gas-particle partitioning and deposition, Using a model driven by assimilated meteorology from the NASA Goddard Earth Observing System (GEOS), the global transport of three representative PAHs (phenanthrene, pyrene and benzo[*a*]pyrene) was simulated for the period 2004–2009. Model results show PAH concentrations over both non-urban mid-latitude sites and the Arctic are significantly higher in winter than in summer. However, the Arctic experiences stronger seasonal variations, possibly reflecting increased seasonal variation in oxidation or transport, or the effect of springtime Arctic haze. Simulations based in Spitsbergen, Norway were also used to attribute atmospheric PAH concentrations in the Arctic to different source regions. Model results showed European emissions contributed the most (47–70% for the three compounds investigated), followed by emissions from Russia (13–29%) and North America (9–15%). East and South Asian emissions combined contributed just 1–8%. Overall, European and Russian emissions combined accounted for more than 80% of episodic high-concentration events at Spitsbergen.

The same GEOS-Chem model was used to evaluate the effects of future changes in climate and emissions (separately and together) on atmospheric PAH concentrations in the Arctic (Friedman et al., 2013). Model simulations compared the global transport of the same three representative PAHs (phenanthrene, pyrene, benzo[a]pyrene) under present-day climate and emissions, and those projected for 2050. Model

results showed future changes in simulated atmospheric PAH concentrations will be driven by declining anthropogenic emissions, with declining concentrations projected for each PAH simulated. However, the declines projected are greater in the northern hemisphere mid-latitudes (up to 38%) than for the Arctic (up to 8%). Differences in PAH volatility will influence how individual compounds respond to future climate scenarios, as behavior is controlled primarily by competition between increasing deposition and increasing re-emission. Concentrations of volatile PAHs may increase in response to climate change because re-emission increases are projected to outweigh deposition increases, while the opposite is the case for particle-bound PAHs. Overall, the model results suggest the High Arctic is a priority area for resolving the influence of a changing climate versus anthropogenic activities on atmospheric PAHs and emphasize the importance of improving long-term measurements in this region.

2.14.6 Environmental concentrations

2.14.6.1 Air and precipitation

Air and aerosol

PAHs have been monitored in air at the AMAP stations of Alert (82°30'N, 62°20'W), Zeppelin (78°54'N, 11°53'E) and Pallas (68°00'N, 24°15'E) since 1992, 1994, and 1996, respectively (Yu et al., in prep). Figure 2.111 shows the range in air concentration for four PAHs (phenanthrene, pyrene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene) measured at each station. The median concentrations measured at Pallas were generally higher than those measured at the other two sites, which is probably due to its more southerly location and proximity to human activities in northern Europe.

At Zeppelin, the mean annual total PAH concentration (sum of 16 USEPA priority PAHs, ΣPAH_{16}) ranged from 0.50 ng/m^3 (2012) to 3.53 ng/m^3 (1994) (NILU, 2014). In 2013, the mean total PAH concentration was 1.25 ng/m^3, the highest concentration observed since 2001 (NILU, 2014). In 2014, the mean PAH concentration was even higher, at 1.43 ng/m^3 (NILU, 2015). At Alert, the sum of 17 PAHs ranged from 0.003 ng/m^3 (1996) to 3.0 ng/m^3 (1992) (Aas et al., 2013). At Pallas, the sum of 12 PAHs ranged from 0.054 ng/m^3 (1998) to 3.9 ng/m^3 (2006) (Aas et al., 2013).

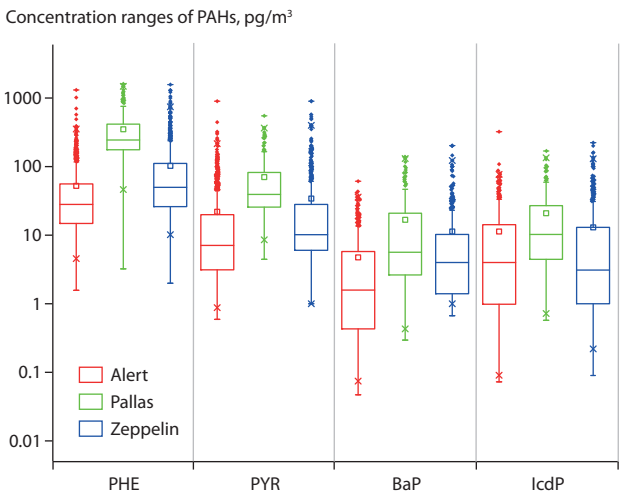

Figure 2.111 Box-and-whisker plots of phenanthrene (PHE), pyrene (PYR), benzo[*a*]pyrene (BaP) and indeno[1,2,3-*c,d*]pyrene (IcdP) measured in air at Alert (1992–2012), Pallas (1996–2013) and Zeppelin (1994–2014). The boxes represent the 25th and 75th percentiles. The lines in the boxes and square symbols represent the median and the mean, respectively. All the outliers beyond the whiskers are shown individually. Yu et al. (in prep).

Figure 2.112 summarizes the time series for phenanthrene and benzo[*a*]pyrene concentrations measured in air at Alert, Pallas and Zeppelin (Yu et al., in prep). At Alert, concentrations of both compounds declined between 1992 and 1999 (statistically significant for phenanthrene, $p<0.05$; but not for benzo[*a*]pyrene, $p=0.078$) and then rose again to peak in 2004. This was followed by a statistically significant decline ($p<0.05$) to the end of 2012. A similar pattern was observed for phenanthrene at Pallas but the decline was not significant ($p>0.05$). Benzo[*a*]pyrene appeared to decline in the early 2000s (statistically non-significant, $p>0.05$) but concentrations have since increased and became more variable after 2010. At Zeppelin, a continuous and statistically significant ($p<0.05$) decline in concentration was observed for phenanthrene, but no change was observed for benzo[*a*]pyrene in the last two decades.

Several studies have reported PAH concentrations in Arctic air collected during research cruises departing from the North Pacific. Ding et al. (2007) reported concentrations of 15 PAHs in gas and particle phase samples collected during a 2003 expedition from Bohai Sea (37.78°N, 123.12°E) to the Arctic (80.22°N, 146.75°W) between July and September, 2003. Total PAHs in air from Arctic sites were 928–6310 pg/m^3 in the gas phase and 23.2–2640 pg/m^3 in the particle phase. A decreasing latitudinal trend was observed for gas-phase PAHs, but not for particulate-phase PAHs. Source attribution ratios indicated that coal burning is likely to be the predominant source of PAHs observed over the Arctic region in summer (Ding et al., 2007).

Wang et al. (2013e) measured gas- and particle-phase PAHs in air from the North Pacific (38°30'N) to the Arctic Ocean (87°11'N) during July through September, 2012. Total concentrations of the nine PAHs measured from the North Pacific to the Arctic Ocean showed little variability; the lowest concentration was recorded near Greenland (41.3 pg/m^3) and the highest near Hokkaido, Japan (112 pg/m^3). On average, gas-phase PAHs accounted for 79.5% of the total atmospheric PAH concentrations and significant linear correlations were observed between the gaseous concentrations of nine PAHs and latitude ($r^2 = 0.69$), indicating that the concentrations of gas-phase PAHs decreased with increasing latitude.

Ma et al. (2013) measured 18 PAHs in marine boundary layer air collected during an Arctic expedition from the East China Sea to the High Arctic between June and September 2010. Atmospheric concentrations were highest in East Asia (30°–48°N, 4000 pg/m^3), followed by the Arctic Ocean (>70°N, 3400 pg/m^3) and the North Pacific Ocean (50°–66°N, 2400 pg/m^3). Source attribution ratios showed atmospheric PAHs originated from the combustion of biomass or coal. Proximity to primary sources, such as continental regions like East Asia, where high PAH concentrations were observed, and the influence of seasonal and regional sources (i.e., forest fires) appear to be the factors broadly controlling atmospheric PAH concentrations in the Arctic.

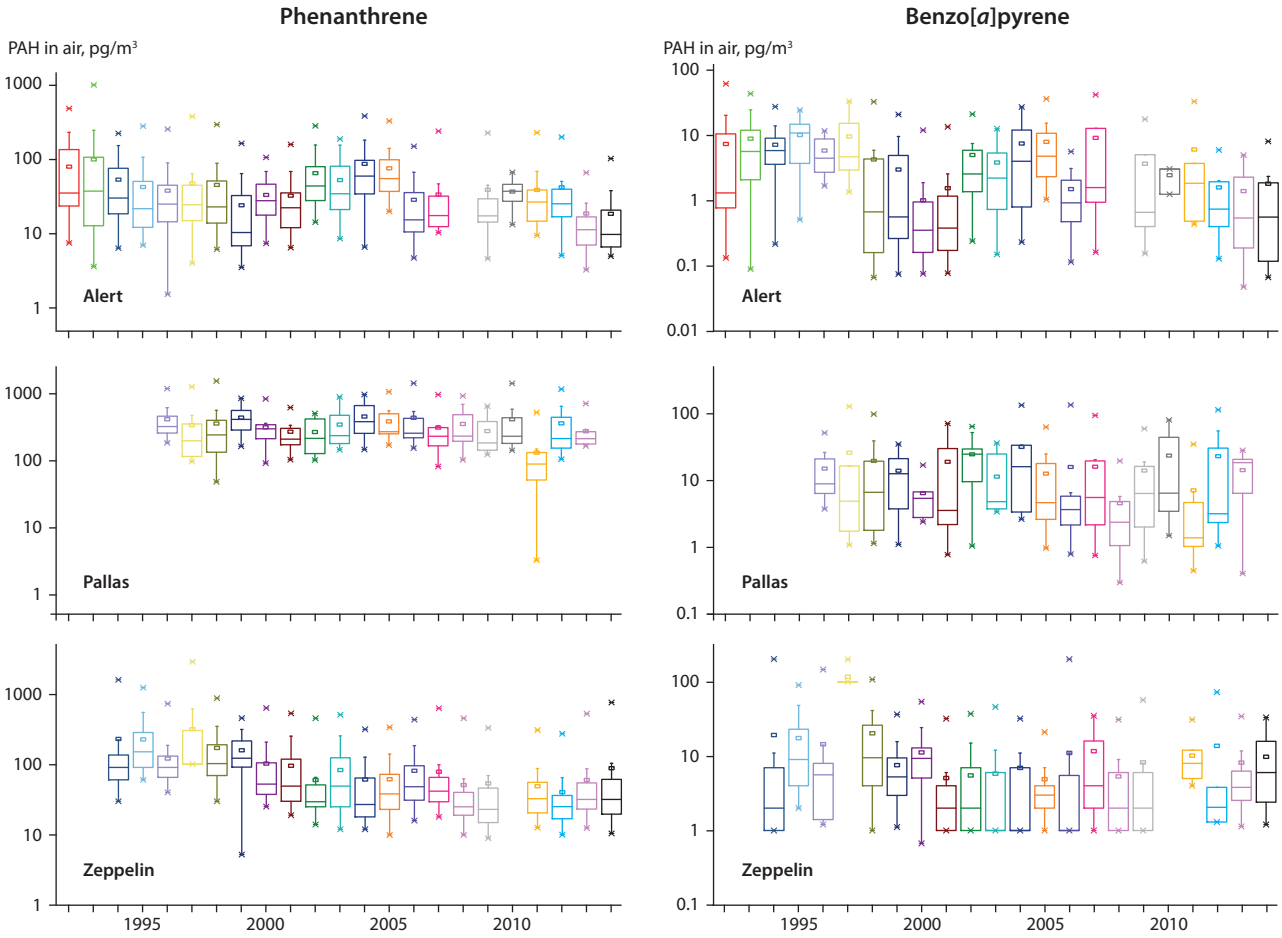

Figure 2.112 Time series of phenanthrene and benzo[*a*]pyrene observed in air at Alert, Pallas and Zeppelin. The boxes represent the 25th and 75th percentiles annually. The lines in the boxes and square symbols represent the annual median and annual mean, respectively. All outliers beyond the whiskers are shown individually. Yu et al. (in prep).

Fu et al. (2008) reported temporal variations in organic compound classes in Arctic aerosol from Alert (82.5°N, 62.3°W) in the Canadian High Arctic, both before and after polar sunrise in 1991. Total suspended particulate matter was collected on a weekly basis between 19 February and 10 June 1991 and screened for PAHs among other organic components. Seventeen PAHs, ranging from three- to seven-rings, were detected in the samples as minor components, but the predominant compounds were fluoranthene, phenanthrene, and pyrene. Total PAH concentrations ranged from 1 to 1031 pg/m^3 (average 160 pg/m^3) and were more abundant during the dark winter than during the sunlit spring.

Arctic maritime air samples were collected in August/September 2008 during a six-week expedition departing from Longyearbyen, Svalbard and heading northward through the marginal ice zone and pack ice zone before reaching 87°30'N, roughly 150 nautical miles south of the North Pole. Concentrations of the 15 PAHs measured were very low and in many cases below detection limits, ranging from 7 to 240 pg/m^3 for total PAH and 0.1 to 100 pg/m^3 for single components (Paatero et al., 2009).

In 2011 and 2012, atmospheric PAHs were measured in the vicinity of two coal-fired power plants in Longyearbyen and Barentsburg (Svalbard), Norway (Schütze et al., 2015). The highest PAH concentrations in air were found near Longyearbyen power plant (62 000 000 pg/m^3 total PAH), with benzo[*a*]pyrene and benzo[*a*]fluoranthene being the major contributors to the total PAHs. The PAH profile directly emitted by the plant was dominated by indeno[1,2,3-*c*,*d*]pyrene, benzo[*g*,*h*,*i*]fluoranthene, benzo[*b*,*j*,*k*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene. However, air samples collected at different distances from the power plant appeared to only partially reflect this PAH profile and varied widely between sites (Schütze et al., 2015).

Passive air sampling of PAHs in Alaska using XAD resin samplers was conducted as part of the Western Airborne Contaminants Assessment Project (WACAP) (Landers et al., 2008; Schrlau et al., 2011). Samplers were deployed for one year (2005–2006) at five locations within national parks in Alaska and the western US lower 48 states. Seventeen PAHs (the 16 USEPA priority PAHs except for naphthalene and including benzo[*e*]pyrene) and retene, an indicator for biomass burning, were determined. Almost all PAHs were below method detection limits (<MDL) (approximately <10 pg or 0.2 pg/g in dry XAD) at all sites. Phenanthrene and pyrene were elevated at the Noatak National Preserve on the Alaska North Slope (Annex Table A2.14/1). Overall, PAH concentrations were lower than in samples from national parks in the western US States but difficult to compare with high volume air sampling because they were not reported on an air volume basis. The samplers were also designed to sample gaseous PAHs and at prevailing temperatures most of the 3- to 5-ring PAHs would have been particulate bound.

Nitrogen-, sulfur- and oxygen-containing polycyclic compounds have rarely been measured in Arctic air. However, dibenzofuran was found to be the most prominent species and accounted for 20–25% of the total PAH monitored at Andøya in northern Norway (<0.3–1.94 ng/m^3) in 2010, sometimes exceeding the sum of the 16 USEPA PAHs (NILU, 2011).

Snow

A suite of organic compounds was measured in snow from the Greenland ice sheet at Summit, Greenland (72°N, 38°W, 3200 m elevation) in summer 2005. A 3-m snow pit was sampled at 20-cm increments to generate a profile of PAHs spanning from 2002 to 2005. Three PAHs known to originate from combustion sources – phenanthrene, fluoranthene, and retene were detected at low concentrations. Total PAHs were highest in the surface layer (1.9 ng/kg), representative of 2005 (von Schneidemesser et al., 2008).

As part of WACAP, PAHs were analyzed in snow from Denali NP, Gates of the Arctic National Park (GAAR), and Noatak National Preserve (NOAT) in Alaska, as well as in snow from more southerly Alaskan and western US national parks from 2003 to 2005 (Landers et al., 2008; Usenko et al., 2010) (Figure 2.113). Total PAH concentrations were low, ranging from 0.3 to 17 ng/L at all six locations in Alaska north of 60°N (Annex Table A2.14/2). Fluoranthene and pyrene predominated in snow from the Denali NP catchments while benzo[*b*]fluoranthene and phenanthrene predominated in snow at the more northerly NOAT and GAAR sites. Annual fluxes of ΣPAH_{16} at Wonder Lake catchment (0.005 µg/m^2) and McLeod Lake (0.03 µg/m^2) in the Denali NP in 2003 were more than 10-fold lower than in western US parks and the Lake Matcharak catchment in GAAR (0.1 µg/m^2). However, snow in Burial Lake catchment (Noatak NP), the most northwesterly site, had 40-fold higher ΣPAH_{16} fluxes than at Lake Matcharak and were maybe affected to a greater extent by long-range atmospheric transport from Asia in winter (Usenko et al., 2010).

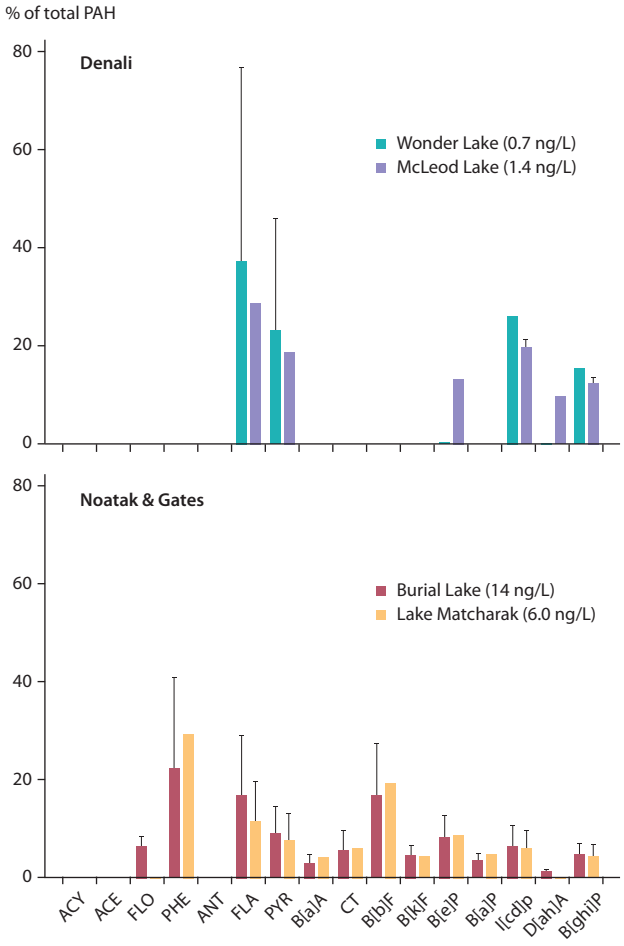

Figure 2.113 PAH profiles measured in the seasonal snowpack from four lake catchments in Alaska national parks (Usenko et al., 2010). Bars represent the average percentage of total PAH concentration and error bars are relative standard deviation. Total PAH concentration for each lake catchment is provided in parentheses.

2.14.6.2 Terrestrial environment

Surface soil, moss, and reindeer dung were collected simultaneously in July and August 2007 from 12 sites at Ny-Ålesund, Svalbard and analyzed for 16 standard unsubstituted PAHs (Wang et al., 2009). Total PAH concentrations were 37–324 ng/g dw in soil, 158–244 ng/g dw in moss, and 49–340 ng/g dw in reindeer dung. Of the three compartments, soil was enriched with the more high molecular weight PAHs (4–6 rings), and had less of the low molecular weight PAHs (2–3 rings) than moss and reindeer dung. The difference in distribution between the three compartments is probably related to the physical-chemical properties of individual PAHs and their different accumulation routes; whereas soil accumulates PAHs mainly through dry/wet particle deposition, moss sequesters PAHs mainly from the gas phase. Interestingly, the PAH profiles of reindeer dung and moss, the main food source for reindeer, were not significantly different (Wang et al., 2009). In addition, the overall proportions of 2- and 3-ring PAHs relative to total PAHs at Ny-Ålesund were higher than published values from non-Arctic sites, which is consistent with a long-range atmospheric transport origin of low molecular weight compounds. A long-term (1987–2006) study of reindeer from Abisko, Sweden reported that PAHs were below the detection limit in muscle (Danielsson et al., 2008).

As part of WACAP, PAHs were analyzed in conifer needles and lichen from samples from four Alaskan national parks north of 60°N, as well as at more southerly Alaskan and western US national parks (Landers et al., 2008; Schrlau et al., 2011). Most of the 16 PAHs were at concentrations below MDLs (Annex Table A2.14/3). Fluoranthene, fluorene and phenanthrene were detectable especially in samples from Katmai NP and Wrangel-St Elias NP, both in southern Alaska. Retene was detected at five of six sampling locations at average concentrations of 1.5–7.6 ng/g dw. Concentrations of retene were highest in national parks in forested areas of southern Alaska and lowest in GAAR on the Alaskan North Slope (Annex Table A2.14/3). Given that sampling occurred in August, the retene was probably from forest fires in the region.

Muscle samples from moose harvested in Denali NP were analyzed as part of WACAP (Annex Table A2.14/4). Eight of the 16 PAHs were detectable at low ng/g ww concentrations. Acenaphthene was the predominant PAH averaging 9.3 ng/g ww (in four of six samples) while the second most common PAH was indeno[1,2,3-*c*,*d*]pyrene at 1.25 ng/g ww (in two of six samples).

2.14.6.3 Freshwater environment

Surface water

Surface waters were sampled from 25 streams in the remote Fuglebekken basin in southern Spitsbergen, Svalbard during July 2009. Total concentrations of 12 PAHs were 4–600 ng/L, with the highest levels detected at the base of the mountain that seasonally receives snow and ice meltwater. Indicator ratios suggest that long-range transport of combustion-related PAHs was the predominant source of PAHs to the basin's surface waters (Polkowska et al., 2011).

A suite of PAHs (phenanthrene, anthracene, fluoranthene, fluorene, pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[1,2,3-*c,d*]pyrene) were investigated in surface water from Lake Abiskojaure in northern Sweden (SWECO VIAK, 2007). Four PAHs were detected: phenanthrene (370 pg/L), fluoranthene (99 pg/L), fluorene (180 pg/L) and benzo[*g,h,i*]perylene (23 pg/L). At Kalixälvens gruvsamhälle (an old mining village at the Kalixälv river in Lapland, point source) six PAHs were detected in surface water: phenanthrene (290 pg/L), fluoranthene (140 pg/L), fluorine (180 pg/L), pyrene (71 pg/L), benzo[*b*]fluoranthene (8 pg/L) and benzo[*g,h,i*]perylene (15 pg/L).

Törneman et al. (2009b) studied EU Water Framework Directive priority substances mostly in water samples from Lake Abiskojaure in northern Sweden. Eight PAHs (indeno[1,2,3-*c,d*]pyrene, naphthalene, anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*k*]fluoranthene, fluoranthene) were investigated in water samples every month in 2008. Only one sample contained detectable concentrations of one PAH, naphthalene (12 ng/L).

As part of WACAP, PAHs were analyzed in lake water from four lakes within national parks north of 60°N as well as in as more southerly Alaskan and western US national parks. Samples were collected in 2004 using filter/modified SpeedDisk systems (Usenko et al., 2005; Landers et al., 2008). Despite good detection limits due to large volume samples (25–50 L), all 16 USEPA PAHs were below MDLs (~0.4–9 pg/L) in almost all samples. The exception was phenanthrene which was detected in McLeod Lake (86 pg/L) and Wonder Lake (2400 pg/L) in Denali NP. Those concentrations are comparable to those detected in Lake Abiskojaure in northern Sweden.

Sediment

Sediment cores from four lakes within national parks north of 60°N in Alaska were analyzed for the 16 USEPA PAHs and retene (Landers et al., 2008; Usenko et al., 2010). Most of the 16 USEPA PAHs were below the MDL (typically <0.5 ng/g dw). Fluoranthene, benzo[*b*]fluoranthene, and phenanthrene predominated in three of the four lakes (Annex Table A2.14/5) similar to the pattern in snow from the same catchments. McLeod Lake in Denali NP had the lowest ΣPAH concentrations with only acenaphthene detected. Lake Matcharak surficial sediment had ~17-fold higher ΣPAH fluxes than Burial Lake, mainly due to 10-fold higher phenanthrene concentrations (Annex Table A2.14/5). This trend is the opposite of the snowpack ΣPAH flux measurements and suggests that the snowpack ΣPAH flux may vary significantly from year-to-year at these Alaskan sites.

Surficial sediments were collected from six remote lakes from Ny-Ålesund, Svalbard in 2005 (Jiao et al., 2009). Total PAH concentrations in lake sediments varied 100-fold, ranging from 11 to 1100 ng/g dw. Although Jiao et al. (2009) cautioned that the exceptionally high PAH concentrations observed in two of the six lakes could be due to proximity to a coal mining operation, PAH indicator ratios suggested the majority of the PAHs were derived from pyrogenic sources.

Eide et al. (2011) measured 22 PAHs in freshwater (and marine) sediment cores from southwestern and northern Norway covering the periods 1950–2002 and 1800–2004. Total PAH concentrations in surface lake sediments ranged from 217 to 7045 ng/g dw and were generally three to four times higher than at the marine sites. Source attribution ratios indicated that pyrogenic sources prevailed at most locations, with the exception of Svalbard which exhibited high concentrations and patterns reflecting the area's active coal mining and combustion activities. The elevated PAH concentrations observed in Svalbard relative to other Norwegian locations have also been described elsewhere, but are not discussed here given their likely petrogenic source (Dahle et al., 2006; Sapota et al., 2009; Konovalov et al., 2010; Jiao et al., 2014).

PAH measurements were obtained from freshwater sediments collected from the seven largest Arctic rivers to assess the role of fluvial transport of black carbon to the Arctic (Elmquist et al., 2008). The samples were collected from the river deltas of the western Siberian lowlands (Ob and Yenisey Rivers), central Siberian uplands (Lena River), East Siberian highlands (Indigirka and Kolyma Rivers) and North America (Yukon and Mackenzie Rivers) in 2004 and 2005. Total concentrations of 18 PAHs were lowest in the Ob River (23 ng/g ww) and highest in the Mackenzie River (454 ng/g ww). Source attribution ratios indicated PAHs from the two North American rivers are likely to have originated from a petrogenic source, whereas those detected in the Russian Arctic rivers are likely to have originated from vehicle emissions (Lena River), wood combustion (Indigirka and Kolyma Rivers) and the combustion of grass, wood and coal (Ob and Yenisey Rivers) (Elmquist et al., 2008).

Biota

The 16 USEPA PAHs and retene were analyzed in whole fish samples from four lakes in Alaska (Landers et al., 2008). Six of the 16 USEPA PAHs were detectable at low ng/g ww concentrations with lake trout (*Salvelinus namaycush*) from Wonder Lake in Denali NP having highest detection frequencies (Annex Table A2.14/6). Lake trout from Lake Matcharak had 6-fold lower concentrations of ΣPAH than in Wonder Lake despite nearly 3-fold higher concentrations in sediment (Annex Table A2.14/5).

2.14.6.4 Marine environment

Seawater

Surface seawater samples were collected during the Fourth Chinese National Arctic Research Expedition from the East China Sea to the High Arctic (33.23–84.5°N) between

June and September 2010 (Ma et al., 2013) and analyzed for 18 PAHs. Generally, seawater PAH concentrations decreased with increasing latitude. Mean concentrations of total PAHs were 150±270 pg/L in East Asia (35–48°N), 76±46 pg/L in the North Pacific Ocean (50–68°N), and 37±18 pg/L in the Arctic Ocean (>70°N). Source attribution ratios suggest that the PAHs in seawater originated from a mixture of petrogenic sources, biomass combustion, and coal and liquid fossil fuel sources (Ma et al., 2013). PAHs were less frequently detected in seawater than in air. Seawater PAH source profiles showed some similarity with those in air, which may be indicative of air-sea gas exchange and deposition of certain PAHs.

Lohmann et al. (2009) analyzed surface seawater samples from 22 stations during a cruise across the North Atlantic and European Arctic. The highest PAH concentrations were detected in the southernmost sample (off Europe) and the two northernmost samples (around 82–84°N). Overall, highest concentrations were determined for phenanthrene (10–180 pg/L), fluoranthene (10–130 pg/L), and fluorene (16–66 pg/L). Concentrations of anthracene, pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene and indeno[*g,h.i*]perylene were mostly <1 pg/L. For all PAHs, source attribution ratios indicated a combustion-derived origin for the PAHs detected. Marine boundary layer air was also collected for analysis, but samples were considered to be cross-contaminated by ship exhaust and concentrations were not reported (Lohmann et al., 2009).

Marine sediment

Sediment PAH data published prior to 2004 were extensively reviewed in a previous AMAP report (Klungsøyr et al., 2010). The majority of reports thereafter come from the Norwegian Arctic and Barents Sea regions (Boitsov et al., 2009a, 2013; Dahle et al., 2009; Jiao et al., 2009; Eide et al., 2011; Zaborska et al., 2011). Although the regions under study overlap, detailed comparisons are difficult given differences in the number of compounds measured.

Measurements made throughout the Barents Sea suggest that anthropogenic inputs of PAHs are likely to be limited. Analyses of surface sediments and sediment cores collected in 2003 and 2004 from the western Barents Sea averaged 400–500 ng PAH/g dw (Boitsov et al., 2009a). In 2006, sediment cores collected from the southwestern Barents Sea in 2006 exhibited similarly low PAH concentrations, averaging 200 ng/g dw (Boitsov et al., 2009b). In both studies, source attribution ratios indicated PAHs were of a natural, mostly petrogenic origin, probably from natural seeps of oil-related hydrocarbons in the area (Boitsov et al., 2009a,b). Another study of sediment cores from the western Barents Sea detected similarly low concentrations of 12 PAHs (range 35±18 to 132±66 ng/g dw). Based on concentrations detected in the deepest layers of the sediment cores, corresponding to the period prior to 1850, natural background PAH concentrations have remained fairly constant throughout the western Barents Sea over time (Zaborska et al., 2011). However, in contrast to previous studies, a predominance of compounds indicative of atmospheric releases from aluminum smelters, coal and wood burning were detected (Zaborska et al., 2011).

Anthropogenic inputs of PAHs are becoming increasingly evident in Norwegian coastal sediments. In a study of the southwestern Barents Sea, Boitsov et al. (2009b) noted that samples collected near Norwegian fjords had PAH attribution ratios indicative of a pyrogenic origin, suggestive that coastal areas may be experiencing low inputs from human activities. Eide et al. (2011) measured 22 PAHs in coastal sediments from Svalbard, Troms and Finnmark counties, Norway, covering the periods 1950–2002 and 1800–2004. Overall, total PAH concentrations in marine sediments ranged from 82 to 3076 ng/g dw, with the highest concentrations detected in Svalbard. Source attribution ratios indicated the PAHs originated from multiple sources, but were predominantly combustion related. Similarly, Boitsov et al. (2013) measured PAH concentrations ranging from 9.5 to 1799 ng/g dw in surface sediments from the northern Norwegian coast (above 68°N) from 1992–1996 and found indications of predominantly pyrogenic sources. However, coastal sediments from two sites along the west coast of Spitsbergen, Svalbard from 2005 exhibited source attribution ratios solely indicative of a petrogenic source, and given the low PAH concentrations detected (25–38 ng/g dw), were attributed to natural processes such as seabed crude oil seeps (Jiao et al., 2009).

New analyses are beginning to provide insight into the extent of PAH deposition to marine sediments across the Arctic. Deep-sea sediments were collected at four sites across the Arctic Ocean, including the Chukchi Plateau, Canada Basin, Alpha Ridge, and Makarov Basin (Dong et al., 2015). Total concentrations of the 16 USEPA priority PAHs ranged from 2.0 to 41.6 ng/g dw and generally decreased with sediment depth. Concentrations also tended to decrease with increasing latitude, from the southernmost site (Chukchi Plateau; 41.6 ng/g dw) to the northernmost site (Makarov Basin, 2.0 ng/g dw).

Marine invertebrates

PAH data for marine biota prior to 2004 were extensively reviewed in a previous AMAP assessment report (Klungsøyr et al., 2010). In 2011, Jörundsdóttir et al. (2014) conducted a survey of PAH concentrations in blue mussel (*Mytilus edulis*) from remote sites in Greenland, Iceland, the Faroe Islands, Norway and Sweden and included urban sites for comparison. Overall, total concentrations of the 16 USEPA priority PAHs ranged from 28 to 480 ng/g dw, with the highest concentration detected in Ísafjörður harbor, a polluted site in northwestern Iceland. However, remote sites in eastern Iceland and western Greenland also had inexplicably high concentrations; 370 and 280 ng/g dw, respectively. Source attribution ratios and the predominance of pyrene in a large proportion of the samples is strongly indicative of a combustion source and atmospheric input (Jörundsdóttir et al., 2014).

In 2010, blue mussels and Iceland scallops (*Chlamys islandica*) were sampled from the Barents Sea near northern Norway (70°N) (Nahrgang et al., 2013). Concentrations of the 16 USEPA priority PAHs ranged from <MDL to 22 ng/g ww in blue mussel, and from 5.7 to 17 ng/g ww in scallops. Corresponding concentrations of 2-3 ringed PAHs, including naphthalene, anthracene/phenanthrene, dibenzothiophene and their alkylated homologues were generally higher at <MDL to 99 ng/g ww in mussels and <MDL to 65 ng/g ww in scallops.

Fish

PAHs are rapidly metabolized in fish, so quantifying PAH metabolites is considered the conventional method for estimating exposure in these species (Beyer et al., 2010). Specifically, the CYP1A1 phase I hydroxylated PAH metabolites (OH-PAHs) are considered excellent chemical markers for exposure to the parent PAHs.

Hydroxylated PAH metabolites were measured in 60 liver samples of Arctic cod (*Boreogadus saida*) collected from offshore regions of the Canadian Beaufort Sea in 2012 (Tomy et al., 2014). Four-ring OH-PAHs were detected in 90% of samples with a mean concentration of 1829.2±159.2 ng/g ww, while mean concentrations of 5/6- ring OH-PAHs in liver were lower (931.6±104.3 ng/g ww) and detected less frequently (75%). The 2/3-ring metabolites were not detected. Because fish were sampled prior to any anthropogenic activity in the region, exposure to the parent PAHs is hypothesized to have originated from natural sources.

Baseline concentrations of nine PAH metabolites were measured in Arctic cod from pristine waters surrounding Svalbard in September 2001 and August 2002 (Jonsson et al., 2010). All nine metabolites were detectable in cod bile with total concentrations averaging 1899 ng/g bile and 1940 ng/g bile for the two sites, Hinlopen Strait and Isfjorden, respectively. Of the nine metabolites analyzed, C2-phenanthrene, C1–OH-naphthalene, C2–OH-naphthalene and C3–OH-naphthalene were present at the highest concentrations, exceeding concentrations of 1-OH-pyrene by an order of magnitude.

Jörundsdóttir et al. (2014) also measured hydroxylated PAH metabolites in Atlantic cod (*Gadus morhua*) caught north of Iceland and along the Norwegian coast. Of the two metabolites measured, 1-OH-pyrene and 3-OH-benzo[*a*]pyrene, only 1-OH-pyrene was found above the limit of quantification, and only in samples from the Norwegian coast, ranging from 44 to 140 ng/mL bile. 1-OH-pyrene was detectable, but not quantifiable in Atlantic cod bile from Iceland. The higher concentrations observed in Norwegian cod are probably due to a known point source of pollution near where they were caught. In contrast, the Icelandic cod were caught in the open sea where exposure to point sources of PAHs is limited (Jörundsdóttir et al., 2014).

In 2010, Atlantic cod from the Barents Sea near northern Norway (70°N) was analyzed for four hydroxylated PAH metabolites, of which only two (1-hydroxypyrene and 1-hydroxyphenanthrene) were present in bile. The metabolites 3-hydroxybenzo[*a*]pyrene and 2-hydroxynaphthalene were not detected (Nahrgang et al., 2013).

Seabirds

Eggs from common eider (*Somateria mollisima*), European shag (*Phalacrocorax aristotelis aristotelis*) and herring gull (*Larus argentatus*) were collected from two remote islands, Sklinna and Røst on the Norwegian coast in 2012 and analyzed for the 16 USEPA priority PAHs (Huber et al., 2015). Of these, five (naphthalene, anthracene, fluoranthene, pyrene, chrysene) were detected at concentrations above the limit of detection. Seabird eggs from Røst, located north of the Arctic Circle, had total PAH concentrations ranging from non-detectable to 29.6 ng/g ww. PAHs were not detectable in eggs of the European shag. In common eider and herring gull eggs, geometric mean PAH concentrations were 0.11 and 7.63 ng/g ww, respectively.

Marine mammals

No PAH data for marine mammals are available. However, concentrations in apex predators are generally low given that PAH concentrations tend to decrease with trophic level owing to biotransformation processes (Wan et al., 2007; De Laender et al., 2011).

2.14.7 Environmental trends

2.14.7.1 Spatial trends

Broad-scale spatial analyses for PAHs in the Arctic are scarce. Yunker et al. (2011) reported the first comprehensive analysis of persistent hydrocarbon tracers in sediment throughout the Arctic Ocean. A large suite of hydrocarbons, including parent and alkyl PAHs, were measured in suspended particulates, sediment cores and surface sediments across the region. Spatial patterns in PAH distribution throughout the Arctic Ocean were investigated using multivariate analyses. Biomarker patterns revealed that central Arctic Ocean basin sediments are compositionally distinct from those of the Beaufort Sea and Barents Sea, but similar to those of the Laptev Sea. Source attribution ratios indicative of a combustion origin were detected in PAHs from suspended particulates in the Chukchi and Lincoln Seas and the central Arctic Basin. However, overall, Arctic sediments were overwhelmingly dominated by natural PAH inputs such that anthropogenic PAHs originating from combustion sources and atmospheric transport were deemed insignificant (Yunker et al., 2011).

Similar results were found by Harvey et al. (2014) and Foster et al. (2015) who analyzed surface sediments from the Chukchi Sea (Alaska) and Baffin Bay (eastern Canada) respectively. Sediments from both locations exhibited PAH profiles overwhelmingly dominated by alkyl-substituted PAHs, indicating a predominance of petrogenic sources over combustion sources and that long-range atmospheric transport may be less important than natural inputs in unexploited regions (Harvey et al., 2014; Foster et al., 2015).

2.14.7.2 Temporal trends

A long-term monitoring project for atmospheric PAHs and other POPs at the High Arctic air monitoring station Alert in Nunavut, Canada has been ongoing since 1992 (Hung et al., 2005). Between 1992 and 2002, PAH gas-phase concentrations of the 16 USEPA priority PAHs ranged from 113 to 516 pg/m^3 and particle-phase concentrations ranged from 38 to 392 pg/m^3. Although strong seasonal fluctuations obscured the detection of reliable temporal trends, general decreases in PAH concentrations were noted between 1993 and 1996, which strongly agrees with declines measured in atmospheric samples from mid-latitudes during the same period (Cortes and Hites, 2000). In a later study, Becker et al. (2016) were able to resolve long-term temporal trends in PAH

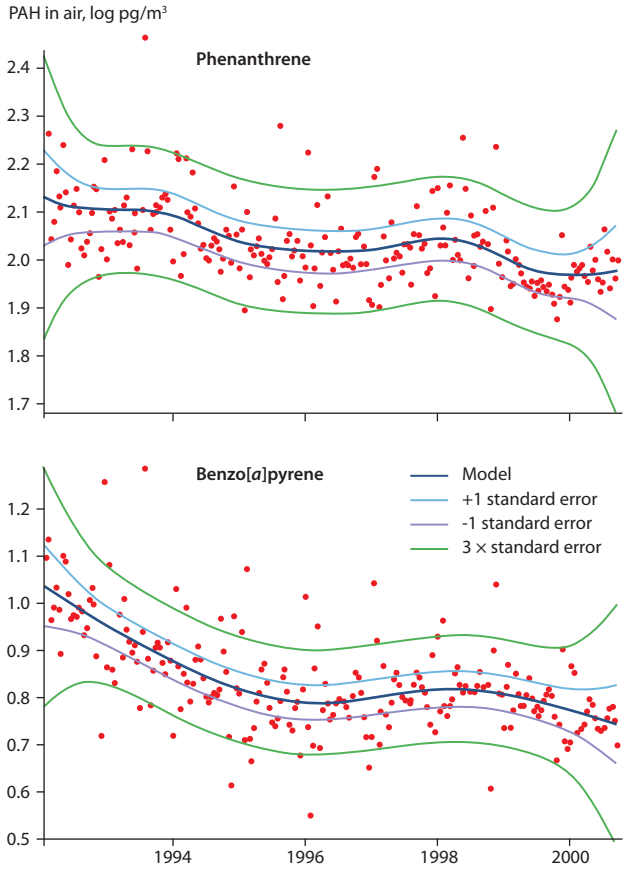

Figure 2.114 Seasonally adjusted data and underlying long-term trends in two PAHs – phenanthrene and benzo[*a*]pyrene – in air at Alert as identified by dynamic harmonic regression. (Becker et al., 2006).

concentration at Alert using dynamic harmonic regression, a statistical time-series tool that identifies and removes seasonal components in the data (Figure 2.114). Applying this technique to the analysis of atmospheric PAH data collected at Alert between 1992 and 2000 identified seasonal patterns in PAH concentration with a consistent summer increase in many of the low-molecular weight (two- to three-ringed) PAHs. Furthermore, removing seasonal trends revealed a decline in PAH concentration over the period 1992–2000. While lighter PAHs exhibited linear declines throughout the study period, many of the higher molecular weight PAHs demonstrated early declines followed by a leveling off of concentration by the mid/late 1990s (Becker et al., 2006).

De Laender et al. (2011) reconstructed temporal trends for PAHs and other legacy POP classes in the Barents Sea and Norwegian Sea using a food web bioaccumulation model to derive complete data sets. Monitoring data for 21 species occupying various trophic levels (from mussels to polar bears) was extracted from the International Council for the Exploration of the Sea (ICES) database and used to infer temporal trends for POPs in seawater and biota between 1985 and 2010. However, temporal trends for PAHs were based on concentrations in mussels only, since trend data were not available for other species. The analysis indicated that concentrations of legacy POPs in the Barents/Norwegian Sea fauna decreased 10-fold over the past 25 years, while concentrations of fossil fuel-derived PAHs increased 10- to 30-fold in seawater and lower trophic level biota (mussels and fish). The trend analysis also indicated that in the last five years of the time range considered (2005–2010), PAH concentrations stabilized, potentially indicating a recent moderation in global fossil fuel emissions (De Laender et al., 2011).

Eide et al. (2011) measured 22 PAHs in freshwater and marine sediment cores from southwestern and northern Norway covering the periods 1950–2002 and 1800–2004. The PAH concentrations in lake sediments of northern Norway have increased in recent decades, although concentrations are still much lower than those from the south. In contrast, in southwestern Norway, total PAHs increased from 1800 to 1950, but then decreased by a factor of four. Eide et al. (2011) attributed the increase in sediment PAH concentrations to the growth in global industrialization over this period. The decrease in sediment PAH from the 1950s onward coincides with the reduction in heath burning and reduced long-range transport of pollutants from Europe. In comparison to freshwater sediments, marine sediments exhibit less pronounced temporal trends, probably due to the greater influence of perturbation by ocean currents, ship traffic, and oil spills.

Similar trends were found by Boitsov et al. (2009b) who measured PAHs in sediment cores from the southwestern Barents Sea in 2006. An almost 10-fold increase in concentration was observed in upper sediment layers, representing the 1910–1940s period. Thereafter, concentrations level off and, from about the 1980s onward, decrease slightly in surface sediments.

Another study investigated PAH concentrations and profiles in Barents Sea sediments from the last 10 years (Dahle et al., 2009). Surface sediment samples were collected from the Barents Sea in the period 2001–2005 and compared with data previously obtained from sediments collected in 1992–1998. Five unique areas were identified within the Barents Sea with regard to their PAH concentrations and profiles, but for most of the regions no significant differences were found between the two periods studied. However, in the southeastern Barents Sea, pyrogenic PAH concentrations and source attribution ratios were significantly higher in the 2000s, suggesting the input of combustion and/or anthropogenic PAHs has increased over time in this region.

Foster et al. (2015) analyzed the composition and concentrations of hydrocarbons in surface and historical sediments from 11 sites across northern Baffin Bay in eastern Canada prior to oil and gas developments in the area. These provide an assessment of whether recently accumulated sediment (post-1900) differs from older (pre-1900) sediment in this regard. Surficial sediments from northern Baffin Bay that reflected present-day concentrations were found to have hydrocarbon concentrations within a factor of 10 of historic, pre-industrial sediments, indicating that post-industrial anthropogenic sources contribute less than 10% to the natural background levels of PAHs.

Recent (post-2000) studies of temporal trends in PAHs in dated lake sediment cores are limited. Earlier work based on cores collected in the 1990s in Norway and Canada was reviewed by Muir and Rose (2004) and is briefly summarized here. Fernández et al. (1999, 2000) measured concentrations and fluxes of 23 PAHs for Lake Arresjøen on northwestern Svalbard (79°40'N) and Øvre Neådalsvatn (62°46'N) in the Caledonian mountain range of central Norway and found that the major

PAHs were primarily pyrogenic in origin. Pyrogenic PAH inputs to Arresjøen showed a steady increase from the 1800s with a maximum in top slices (Fernández et al., 2000). However, Arresjøen had the lowest PAH fluxes of any of the ten European mountain lakes studied. Fernández et al. (1999) concluded that the PAH deposition pattern in high altitude mountain lakes, including Arresjøen, paralleled sulfate deposition, pointing to combustion particles as the main input pathway. Rose et al. (2004) determined 15 PAHs in surface and pre-historical slices of sediment cores from four lakes on Svalbard. Highest fluxes were found in Lake Tenndammen (360 µg/m²/y, Rose, N.L., University College London, unpubl. data), a lake within 20 km of the coal mining towns of Barentsburg and Longyearbyen. PAH fluxes in the four Svalbard lakes appeared to decline with distance from the Barentsburg/Longyearbyen area.

PAHs (the same 23 PAHs as analyzed by Fernández et al. 1999, excluding perylene and retene) were also reported in a series of dated sediment core studies from the Canadian Arctic (Muir and Lockhart, 1994; Lockhart, 1996, 1997; Lockhart et al., 1993, 1994, 1997). Total PAH fluxes in southern Yukon lakes ranged from 9.1 µg/m²/y in remote Kusawa Lake to 174 µg/m²/y in Little Atlin Lake (Lockhart et al., 1997). Two remote lakes in the Mackenzie River basin, Lac St Therese and Yaya Lake, had much higher PAH fluxes (68 and 140 µg/m²/y, respectively) (Lockhart, 1997). The PAH source for the core from Yaya Lake was thought to be annual inputs from the Mackenzie River during spring floods, with the PAHs themselves probably of natural/petrogenic origin due to crude oil seeps upstream (Yunker and Macdonald, 1995). The historical profiles of 3- and 4-ring pyrogenic PAHs (e.g. fluoranthene, pyrene, retene, benzo[*a*]pyrene) reported for eight Arctic and subarctic lakes increased in concentration from the mid-19th century onward (Muir and Lockhart, 1994; Lockhart, 1996, 1997; Lockhart et al., 1993, 1994, 1997).

Fluxes of PAHs were determined in dated sediment cores from four lakes in northern Alaska (Usenko et al., 2010) as part of WACAP (Landers et al., 2008). The two lakes on the Alaska north slope, Burial Lake and Lake Matcharak, both showed increasing ΣPAH, but different rates of increase (Figure 2.115).

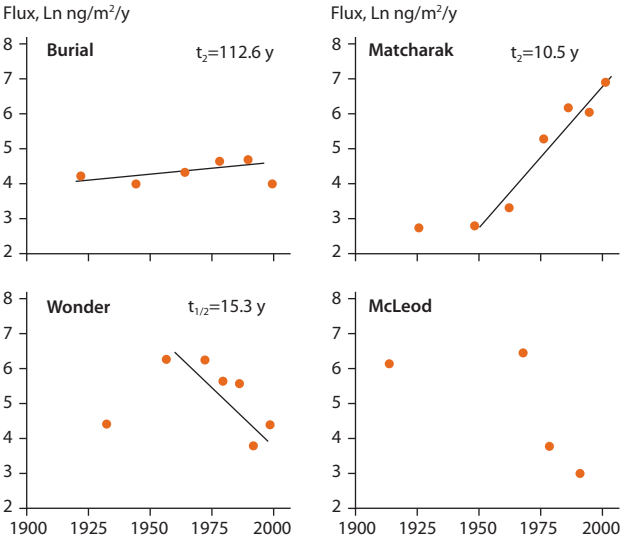

Figure 2.115 Focus-corrected flux profiles of PAHs in WACAP sediment cores. Doubling times (t_2) and half-lives ($t_{1/2}$) are given where least squares regressions were statistically significant ($p<0.05$) (Usenko et al., 2010).

Lake Matcharak had the highest ΣPAH doubling time (10.5 y) of all sites in the western and northern US lakes studied by Usenko et al. (2010). In contrast, the ΣPAH flux in Wonder Lake in Denali NP, a mountainous region in central Alaska, had a half-life of 15.3 y and a decline was also found in nearby McLeod Lake. As noted previously (Figure 2.113), the Alaskan Arctic catchments (Burial Lake and Lake Matcharak) and the Denali catchments (Wonder Lake and McLeod Lake) had significantly different PAH profiles in the sediment suggesting different sources. Using air mass back trajectories, Usenko et al. (2010) suggested the PAH sources for Burial Lake and Lake Matcharak could be the Prudhoe Bay oil fields to the northeast. The Prudhoe Bay oil fields are the largest oil fields in North America and began production in 1977. The rise in concentrations in the core from Matcharak appears to fit the increase in crude oil production (Figure 2.115).

2.14.8 Conclusions

Pyrogenic PAH measurements associated mainly with atmospheric sources have been monitored since the 1990s at three Arctic stations (Alert, Zeppelin, Pallas) and the time series at these locations represent a strong dataset for assessing future PAH emissions. However, generally only the 16 USEPA priority PAHs have been measured and so little is known about nitro-, oxy-, and hydroxy-PAH atmospheric degradation products of the unsubstituted and alkylated PAHs. Also there have been no measurements of heterocyclic PAHs (e.g. thiophenes, azaarenes) in air samples. Recent reviews have noted that the set of 16 USEPA priority PAHs excludes many toxicologically and environmentally relevant PAHs (Andersson and Achten, 2015; Stout et al., 2015).

Environmental PAHs arise from many natural and anthropogenic sources making it difficult to attribute trends in their occurrence to specific activities. Recent use of attribution ratios and models has improved predictions of PAH sources and pathways to the Arctic region.

Several studies suggest that PAHs measured in Arctic marine waters and sediments predominantly originate from natural underwater hydrocarbon seeps (Yunker et al., 2011; Harvey et al., 2014; Foster et al., 2015), while those measured in air and remote terrestrial and freshwater environments originate from pyrogenic, atmospherically-derived sources. Modeling efforts based in the Canadian Arctic (Wang et al., 2010c) and Norwegian Arctic (Friedman and Selin, 2012) also suggest that the atmospheric PAHs in these regions originate from the northern hemisphere – predominantly Russia, northern Europe, and North America. Although Asian countries such as China and India contribute to more than 50% of global PAH emissions (Shen et al., 2013), models suggest Asia is a minor source of PAHs to the Arctic (Wang et al., 2010c; Friedman and Selin, 2012).

Although atmospheric PAHs have been forecast to decline on a global scale as a result of reduced emissions, the significance of this change to the Arctic is less certain.

Models suggest the Arctic will experience less of a decline in PAH levels than northern hemisphere mid-latitude regions; furthermore, that changes in climate will enable PAHs to

re-volatize from ground surfaces, resulting in secondary emissions to the Arctic atmosphere (Friedman et al., 2013). Continued monitoring will be important for understanding the impacts of changing emissions and re-emissions on PAHs levels in the Arctic.

There is also a need for additional studies of Arctic terrestrial and freshwater environments, for which reports of PAHs are scarce. Pyrogenic and biomass combustion sources may be particularly important in terms of PAH concentrations in terrestrial and freshwater environments. However, in some river and lake locations, coal and natural oil and bitumen seeps could also confound interpretation. Determination of a larger suite of PAHs in Arctic air, snow, water, and freshwater sediment samples would provide much needed additional information on sources.

Section 2.14 Annex Contents

Section 2.14 Annex

Table A2.14/1 PAHs in XAD passive air samplers from five sites within national parks in Alaska (north of 60°N) deployed for one year from 2005–2006. See Landers et al. (2008) and Schrlau et al. (2011) for further details.

Location	Latitude/longitude	Phenanthrene		Pyrene		Benzo[*g,h,i*]perylene		ΣPAH_{16} not including retene	
		PASD	dry XAD	PASD	dry XAD	PASD	dry XAD	PASD	dry XAD
		ng	ng/g	ng	ng/g	ng	ng/g	ng	ng/g
Denali NP	63.54°N, -150.98°W 63.45°N, -150.88°W	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Gates of the Arctic NP	67.75°N, -156.23°W	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Katmai NP	58.57°N, -155.80°W	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Noatak NP	68.41°N, -159.22°W	14.48	0.45	2.92	0.09	<MDL	<MDL	17.4	0.54
Wrangell-St. Elias NP&P	61.38°N, -143.60°W	<MDL	<MDL	<MDL	<MDL	3.84	0.12	3.84	0.12

Table A2.14/2 PAHs in snow (pg/L) from national parks in Alaska from the WACAP study (2003–2005). See Landers et al. (2008) for further details.

Sampling site	Parameter	ACE	ACY	ANT	B[a]A	B[a]P	B[b]F	B[e]P	B[ghi]P
Anisak, Noatak NP	n	1	1	1	1	1	1	1	1
	Average	0.01	0.02	0.02	0.53	0.60	3.50	1.60	0.87
Burial, Noatak NP	n	1	1	1	1	1	1	1	1
	Average	0.01	0.02	0.02	0.12	0.20	1.20	0.62	0.35
Kahiltna, Denali NP&P	n	1	1	1	1	1	1	1	1
	Average	5.70	0.02	0.02	0.02	0.01	0.01	0.01	0.13
Kangilipak, Noatak NP	n	1	1	1	1	1	1	1	1
	Average	0.01	0.02	0.02	0.12	0.11	0.70	0.28	0.23
McLeod, Denali NP&P	n	3	3	3	3	3	3	3	3
	Min	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.08
	Max	0.01	0.02	0.02	0.02	0.01	0.01	0.18	0.18
	Average	0.01	0.02	0.02	0.02	0.01	0.01	0.07	0.14
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.05
Wonder, Denali NP&P	n	5	5	5	5	5	5	5	5
	Min	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.02
	Max	0.01	0.02	0.02	0.02	0.13	0.43	0.21	0.22
	Average	0.01	0.02	0.02	0.02	0.06	0.17	0.11	0.14
	SD	0.00	0.00	0.00	0.00	0.07	0.22	0.10	0.08

ACE: acenaphthene, ACY: acenaphthylene, ANT: anthracene, B[a]A: benzo[*a*]anthracene, B[a]P: benzo[*a*]pyrene, B[b]F: benzo[*b*]fluoranthene, B[e]P: benzo[*e*]pyrene, B[ghi]P: benzo[*g,h,i*]perylene, B[k]F: benzo[*k*]fluoranthene, CHR/TRI: chrysene+triphenylene, D[ah]A: dibenzo[*a,h*]anthracene, FLA: fluoranthene, FLO: fluorene, I[123-cd]p: indeno[1,2,3-*c,d*]pyrene, PHE: phenanthrene, PYR: pyrene,. ΣPAH: sum of 16 PAHs not including retene.

Table A2.14/3 Detectable PAHs (ng/g dw) and % lipid in vegetation from national parks in Alaska from the WACAP study (2004). See Landers et al. (2008) for further details.

Site	Sample type	% Lipid				Anthracene		Chrysene+Triphenylene	
		n	Average	max	min	n	Average	n	Average
Denali NP	Conifer needles	14	7.2	9.0	5.5	1	1.9		<MDL[a]
	Lichen	34	18.4	26.1	4.0		<MDL		<MDL
Gates of the Arctic NP	Lichen	4	17.5	19.3	15.6		<MDL	2	0.13
Katmai NP	Lichen	6	5.8	7.1	4.3		<MDL		<MDL
	Conifer needles	5	3.8	4.1	3.2		<MDL		<MDL
Wrangell-St. Elias NP	Conifer needles	7	4.9	5.9	3.6		<MDL		<MDL
	Lichen	6	3.5	5.7	0.9		<MDL		<MDL

Conifers (*Picea mariana*), Lichen (*Flavocetraria cucullata* and *Masonhalea richardsonii*; results combined); [a]All values <MDL assumed to be zero as in Usenko et al. (2010).

Table A2.14/2 cont.

B[k]F	CHR/TRI	D[ah]A	FLA	FLO	I[123-cd]p	PHE	PYR	Retene	ΣPAH
1	1	1	1	1	1	1	1	1	1
0.84	1.20	0.15	3.70	1.10	1.30	0.01	1.80	0.81	17.3
1	1	1	1	1	1	1	1	1	1
0.32	0.28	0.08	1.10	0.58	0.45	1.20	0.63	0.25	7.18
1	1	1	1	1	1	1	1	1	1
0.01	0.01	0.03	0.21	0.01	0.14	0.01	0.17	0.38	6.48
1	1	1	1	1	1	1	1	1	1
0.15	0.26	0.06	0.77	0.16	0.37	0.95	0.39	0.14	4.60
3	3	3	3	3	3	3	3	3	3
0.01	0.01	0.03	0.00	0.01	0.14	0.01	0.01	0.01	0.38
0.01	0.01	0.13	0.40	0.01	0.29	0.01	0.26	1.00	1.38
0.01	0.01	0.06	0.14	0.01	0.23	0.01	0.09	0.44	0.83
0.00	0.00	0.06	0.23	0.00	0.08	0.00	0.15	0.51	0.51
5	5	5	5	5	5	5	5	5	5
0.01	0.01	0.03	0.07	0.01	0.03	0.01	0.04	0.01	0.30
0.10	0.01	0.03	0.58	0.01	0.37	0.97	0.32	0.39	3.22
0.04	0.01	0.03	0.41	0.01	0.22	0.20	0.22	0.18	1.68
0.05	0.00	0.00	0.21	0.00	0.13	0.43	0.11	0.19	1.16

Table A2.14/3 cont.

Fluorene		Fluoranthene		Phenanthrene		Pyrene		Retene	
n	Average	n	Average	n	Average	n	Average	n	Average
	<MDL		<MDL		<MDL		<MDL	10	4.2
3	0.4	9	0.68		<MDL	1	0.27	13	6.6
	<MDL		<MDL		<MDL		<MDL	1	1.5
7	1.17	7	1.3	7	8.53		<MDL	7	3.9
	<MDL		<MDL		<MDL		<MDL		
	<MDL		<MDL		<MDL		<MDL	2	7.6
3	1.48	6	1.36	2	0.69		<MDL	4	2.7

Table A2.14/4 Detectable PAHs (ng/g ww) and % lipid in moose muscle from Denali NP (Alaska), N=6 samples. See Landers et al. (2008) for further details.

	% lipid	Acenaphthene	Acenaphthylene	Benzo[*a*]anthracene	Benzo[*b*]fluoranthene
n	6	4	2	2	2
average	12.9	9.28	0.38	0.43	0.31
min	0.8	6.90	0.36	0.38	0.26
max	26.0	12.0	0.40	0.47	0.36

Table A2.14/5 PAHs (ng/g dw) averaged over 2-cm depth (four 0.5-cm horizons) in sediment cores collected from four lakes in Alaska north of 60°N. See Landers et al. (2008) for further details.

Lake		ACE	ACY	B[a]A	B[b]F	B[e]P	B[ghi]P
Burial, Noatak NP	n	4	4	4	4	4	4
	Average	0.35	0.093	0.022	0.22	0.13	0.10
	Max	0.93	0.13	0.027	0.29	0.17	0.14
	Min	0.065	0.032	0.018	0.13	0.076	0.043
	SD	0.40	0.043	0.004	0.068	0.039	0.041
Matcharak, Gates of the Arctic NP	n						
	Average	<MDL[a]	<MDL	<MDL	<MDL	<MDL	<MDL
	Max						
	Min						
	SD						
McLeod, Denali NP	n	1					
	Average	0.82	<MDL	<MDL	<MDL	<MDL	<MDL
Wonder, Denali NP	n			4	2	4	4
	Average	<MDL	<MDL	0.54	1.40	0.88	0.91
	Max			0.58	1.50	0.99	1.10
	Min			0.50	1.30	0.74	0.76
	SD			0.034	0.14	0.12	0.15

ACE: acenaphthene, ACY: acenaphthylene, B[a]A: benzo[*a*]anthracene, B[b]F: benzo[*b*]fluoranthene, B[e]P: benzo[*e*]pyrene, B[ghi]P: benzo[*g,h,i*]perylene, CHR/TRI: chrysene+triphenylene, D[ah]A: dibenzo[*a,h*]anthracene, FLA: fluoranthene, FLO: fluorene, I[123-cd]p: indeno[1,2,3-*c,d*]pyrene, PHE: phenanthrene, PYR: pyrene,. ΣPAH: sum of 16 PAHs not including retene. [a]All values <MDL assumed to be zero as in Usenko et al. (2010).

Table A2.14/4 cont.

Chrysene+Triphenylene	Fluoranthene	Fluorene	Indeno[1,2,3-*c*,*d*]pyrene	Pyrene
2	2	2	2	2
0.16	0.06	0.54	1.25	0.33
0.12	0.06	0.51	1.10	0.32
0.19	0.07	0.57	1.40	0.34

Table A2.14/5 cont.

CHR/TRI	D[ah]A	FLA	FLO	I[123-cd]p	PHE	PYR	Retene	ΣPAH
4	4	3	3	3	4	4	4	4
0.10	0.025	0.057	0.12	0.039	0.60	0.086	0.032	1.87
0.13	0.030	0.084	0.14	0.042	0.83	0.12	0.036	2.34
0.056	0.017	0.035	0.10	0.035	0.37	0.054	0.023	1.18
0.032	0.006	0.025	0.021	0.004	0.20	0.028	0.006	0.49
				4	4	1	1	4
<MDL	<MDL	<MDL	<MDL	1.8	13.1	2.3	10	23
				3.3	26	2.3	10	36
				1.1	6.4	2.3	10	11
				1.0	8.8			4.7
								1
<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.82
4		2						4
2.05	<MDL	11.0	<MDL	<MDL	<MDL	<MDL	<MDL	8.73
2.40		11.0						14.9
1.60		11.0						2.16
0.37								6.26

Table A2.14/6 Concentrations of PAHs (ng/g ww) in whole fish samples from four lakes in Alaska north of 60°N. See Landers et al. (2008) for further details.

Lake	Species		% Lipid	Fluorene	Phenanthrene	Anthracene	Fluoranthene
Matcharak, Gates of the Arctic NP	Lake trout *Salvelinus namaycush*	n	10				
		Average	3.64	<MDL	<MDL	<MDL	<MDL
		Max	5.88				
		Min	1.88				
		sd	1.40				
Burial, Noatak NP	Lake trout *Salvelinus namaycush*	n	10				
		Average	3.43	<MDL	<MDL	<MDL	<MDL
		Max	5.22				
		Min	0.95				
		sd	1.43				
McLeod, Denali NP	Round whitefish *Prosopium cylindraceum*	n	2				
		Average	5.15	<MDL	<MDL	<MDL	<MDL
		Max	5.57				
		Min	4.73				
		sd	0.59				
	Burbot *Lota lota*	n	4				
		Average	1.38	<MDL	<MDL	<MDL	<MDL
		Max	1.51				
		Min	1.15				
		sd	0.165				
Wonder, Denali NP	Lake trout *Salvelinus namaycush*	n	10	4	5	2	1
		Average	4.86	0.42	2.32	1.35	0.31
		Max	8.15	0.49	2.90	1.37	0.31
		Min	1.21	0.30	1.30	1.32	0.31
		sd	2.516	0.087	0.76	0.035	

[a]All values <MDL assumed to be zero as in Usenko et al. (2010).

Table A2.14/6 cont.

Benzo[*g,h,i*] perylene	Phenanthrene	Retene	Sum of 16 PAHs not including retene[a]
6	2	3	10
0.06	0.87	0.69	0.19
0.17	0.87	1.30	0.93
0.025	0.87	0.38	0.00
0.054		0.53	0.36
6	1	2	10
0.04	1.10	0.46	0.088
0.05	1.10	0.46	1.10
0.03	1.10	0.46	0.00
0.01			0.28
		1	2
<MDL	<MDL	0.60	0.23
		0.60	0.45
		0.60	0.00
			0.32
2	1	2	4
0.083	0.81	0.36	0.24
0.10	0.81	0.40	0.91
0.065	0.81	0.31	0.00
0.025		0.06	0.45
2		2	10
0.019	<MDL	2.70	1.17
0.022		2.70	3.39
0.016		2.70	0.00
0.004			1.37

2.15 'New' unintentionally generated PCBs

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2.15.1 Introduction

While contamination of the Arctic by legacy intentionally manufactured polychlorinated biphenyls (PCBs) is well documented (AMAP, 2010b), the recent discovery of unintentionally generated PCBs in the environment, including the polar region is cause for concern. Legacy PCBs are covered by existing international conventions and regular monitoring, but while the 'new' unintentionally generated PCB congeners are covered by Annex C of the Stockholm Convention (UNEP, 2015e,f) and the U.S. Toxic Substances Control Act (Rodenburg et al., 2015), systematic monitoring and regulatory enforcement are lacking.

Unintentionally generated PCBs are those 93 congeners that have not been intentionally produced as a commercial mixture, for example as 'Aroclor' (by Monsanto in the USA). Frame et al. (1996) referred to unintentionally generated PCB by this definition 'non-Aroclor PCB'. The U.S. Federal Register and Rodenburg et al. (2015) used a different definition for non-Aroclor PCB to more broadly include any PCB that is produced as an unintentionally generated byproduct. This inconsistent use of terminology causes some confusion in the published literature. The former definition by Frame is often preferred because practically, it is difficult to determine whether the origin of a PCB congener such as PCB209 detected in the environment is from unintentional generation of PCB or an intentionally generated PCB mixture, unless it is in close proximity to a known source (e.g. pigment manufacture, Du et al., 2008; Aroclor 1270 and 1271 manufacture, Hermanson et al., 2016).

PCB mixtures were intentionally manufactured for use as dielectric fluids, flame retardants, and other applications due to their advantageous physical properties for these purposes. Manufacturer trade names for these PCB mixtures include Aroclor, Clophen, Phenochlor, Kanechlor, Pyralene, Fenclor and Delor, among others (IARC, 2015). These PCB mixtures are referred to as legacy Aroclor PCB in this chapter. After the manufacture and use of 1325 810 tonnes (Breivik et al., 2007), PCBs were found to be persistent in the environment and to be human carcinogens, endocrine disruptors, and neurotoxins (Simon et al., 2007; Crinnion, 2011; Boas et al., 2012; Lauby-Secretan et al., 2013). PCBs have been included as a persistent organic pollutant (POP) in the regional UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) and the global UN Stockholm Convention on Persistent Organic Pollutants, which ban intentional production of PCBs and include measures to reduce or eliminate releases from unintentional production (UNEP, 2015e,f).

PCBs are often considered 'legacy POPs'. Most PCB analytical methods targeted the predominant PCB congeners in the intentionally manufactured Aroclor PCB mixtures. As a result, unintentionally produced non-Aroclor PCBs were not typically monitored or measured. However, it was long known by the US Environmental Protection Agency (EPA) that PCBs were unintentionally generated during pigment manufacture, and were therefore regulated by the U.S. Toxic Substances Control Act (TSCA). Through the 1979 Code of Federal Regulations, the US EPA capped PCB impurities in pigments at an average of 25 ppm, and not to exceed 50 ppm at any time, with discounting for mono- and di- congeners. But regulatory enforcement is not systematic and ambient monitoring has only recently begun as improvements in analytical methodology have made it possible to measure all 209 PCB congeners (Litten et al., 2002), and as required in certain contexts within the United States, such as heavily contaminated spills designated as Superfund sites for intense review and mitigation (Frame, 1997; Litten et al., 2002; Hu et al., 2008, 2010; US EPA, 2017b). Europeans are generally required to measure only seven congeners, so data from European researchers are lacking. The unintentionally produced PCBs are also indirectly included in the U.S. Clean Water Act through the Water Quality Standards which limit the sum of all PCBs in water to 64 pg/L (parts per quadrillion) (Rodenburg et al., 2015).

PCBs have been measured in emissions of thermal processes, in particular the burning of hazardous waste, but distinguishing between their origin in the waste stream and synthesis in the combustion process is not well studied. Understanding of the dioxin-like biological effects of some PCB congeners led to a focus on measuring a particular subset of 'dioxin-like PCBs' (PCB77, PCB81, PCB126, PCB169, PCB114, PCB118, PCB123, PCB156, PCB157, PCB167 and PCB189) as well as measuring toxic polychlorinated dioxin/furan congeners in thermal processes. The full set of PCB congeners was not determined in those investigations.

The non-Aroclor PCB11 (Figure 2.116) was discovered in ambient air and other media in proportions that cannot be attributed to legacy Aroclor PCB production, and has instead been attributed to pigment and dye manufacture and use (Choi et al., 2008; Hu et al., 2008, 2010; Stone, 2014).

PCB11 has been detected in the Arctic (Choi et al., 2008; Baek et al., 2011; Li et al., 2012; Garmash et al., 2013) (see also Table 2.84) and Antarctic (Baek et al., 2011; Li et al., 2012). PCB209 and other unintentionally generated PCBs in pigment manufacture were also detected in the Arctic (Choi et al., 2008; Baek et al., 2011; Li et al., 2012; Garmash et al., 2013), but as they are congeners of Aroclor mixtures their source and origin cannot yet be definitively determined.

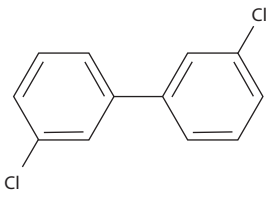

Figure 2.116 The chemical structure of PCB11.

Table 2.84 Summary of Arctic media for which PCB11 and PCB209 data have been reported.

	Air		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
PCB11	×	×	×	×						
PCB209[a]	×	×	×	×						

[a]Whether the source of PCB209 observed in Arctic media is an unintentionally generated PCB or is intentionally produced in PCB mixture or both, cannot be distinguished at this time.

PCB is considered as a class to be toxic, but the relative toxicities of non-Aroclor PCB congeners are not well known and are only beginning to be studied (Boas et al., 2012; Lauby-Secretan et al., 2013; Hu et al., 2014). PCB11, PCB14, PCB35 and PCB209 have recently been found to be the predominant congeners in human blood serum (Koh et al., 2015). PCB11-OH, a metabolite of PCB11 has been found in the same media as PCB11 and is also likely to be toxic.

2.15.2 Physical-chemical properties

PCB11 or 3,3'-dichlorobiphenyl (CAS registry number 002050-67-1) is a PCB congener with chlorines in the 3, 3' positions ($C_{12}H_8C_{l2}$). It has a log K_{OW} of 5.27, and based on its physical-chemical properties (Appendix 1) is expected to be found in the gas phase in air and to bioaccumulate. The focus of discussion on unintentionally generated non-Aroclor PCB in this section is on the PCB11 congener, which has been detected in greatest amounts in the Arctic and unlike PCB209 cannot be sourced to legacy PCB use.

2.15.3 Sources, production, use and trends

PCB11 is one of ten PCB congeners found in the Dry Color Manufacturer's Association Mixture (DCMA), the others being PCB1, PCB29, PCB47, PCB121, PCB136, PCB185, PCB194, PCB206 and PCB209. Of these, PCB11, PCB29, PCB121 and PCB185 should be considered non-Aroclor congeners according to Frame et al. (1996) and based on Monsanto production data from the 1930s and 1940s. The U.S. Federal Register and Rodenburg et al. (2015) used a different definition of non-Aroclor PCB to more broadly include any PCB that is unintentionally generated as a byproduct of pigment manufacture.

The DCMA mixture was used as an analytical standard in a study to quantify/identify PCB congeners in ash samples from two different municipal waste incinerators (Alarie et al., 1989). All PCB congeners were found except for PCB206 and PCB209 which were found in one ash sample but not the other. Jansson et al. (2011) found PCB11 in flue gas from a waste incineration plant at various temperatures (200–450°C) and in two ash samples. PCB11 was the predominant congener in one ash sample. Kim et al. (2004) detected PCB11 in all nine flue gas samples from waste incinerators, ranging from 0.7 to 20 ng/m^3 with a mean of 5.1 ng/m^3. Takasuga et al. (2015) reported PCB11 in thermal processes, cement kiln flue gas and fly ash in Japan.

These results suggest thermal systems to be possible sources of *de novo* synthesis of PCB11 (a process that Baek et al. (2010) claim does not occur) or lack of thermal destruction during incineration. PCB formed by thermal processes are in the category of unintentionally generated PCB.

Non-legacy PCB congeners in the environment can occur by degradation processes in the environment. Hu et al. (2008) and Rodenburg et al. (2015) found the relative concentrations of PCB11 to be too high to have originated from environmental degradation processes.

PCBs were intentionally added to paints, caulking and other products as a flame retardant, but were then banned and replaced by other chemicals with flame retardants properties.

Rodenburg estimated that 1.5 t of PCB11 was unintentionally generated as a byproduct of diarylide yellow pigment in 2006 (Rodenburg et al., 2009; Rodenburg, 2012). The Washington State Department of Ecology analyzed pigments, and products with pigments and dyes, for PCB11, PCB206, PCB208, and PCB209 (Stone, 2014). They found PCBs in yellow, blue and white titanium dioxide with PCB11 concentrations in consumer products ranging from non-detectable to 48.5 ppb (ng/g), with an average of 5.2 ppb (ng/g). They also found non-Aroclor PCBs in tinted caulking, suggesting it is present in a pigment added to the caulking. Guo et al. (2014) detected PCBs in samples of consumer goods from 26 countries in five continents at concentrations ranging from 0.27 to 86 ppb (ng/g). More comprehensive estimates of the source quantity, distribution, and emission are needed. Rodenburg et al. (2015) proposed developing alternative methods of pigment manufacture to reduce unintentional generation of PCB.

2.15.4 Transformation processes

PCB11 is readily inhaled and hydroxylated into a phase one metabolite PCB11-OH. Phase II metabolites result after conjugation to polar functional groups such as sulfate and glucuronide (Hu et al., 2014). PCB11-OH and PCB11 phase II metabolites have been measured in greater concentrations in human blood and organ tissues than PCB11. This indicates that the metabolites are more persistent and may bioaccumulate, and can also be used as tracers for PCB11 exposure (Herrick et al., 2007; Simon et al., 2007; Crinnion, 2011; Hu et al., 2013, 2014; Zhu et al., 2013; Gregoris et al., 2014; Ampleman et al., 2015). The toxicity of PCB11 and its metabolites is currently under investigation (Boas et al., 2012; Lauby-Secretan et al., 2013; Hu et al., 2014).

2.15.5 Modeling studies

There are no published modeling studies for non-Aroclor PCBs in or to the Arctic.

Modeling may be potentially useful to ascertain the efficiency of long-range atmospheric transport of non-Aroclor PCB and to better understand the relative strengths of local Arctic sources versus regional and long-range sources, as has been estimated by modeling other PCB congeners and semi-volatile

polychlorinated dioxins and furans (Commoner et al., 2000; Dutchak et al., 2002; Zuber and Keating, 2011; Gusev et al., 2015). PCB11 is likely to have a similar environmental fate to other dichloro-PCBs in the Arctic, and modeling can make use of its known and estimated chemical-physical properties. A simple regional environmental fate model was employed by Guo et al. (2014) for PCB11 in the Delaware River Basin and statistical methods were used to estimate source apportionment by Du et al. (2008) in the Delaware River for PCB209. These techniques and others can be used in the Arctic if source emissions are estimated.

Source emission estimates, currently lacking, would make it possible to model the global circulation of PCB11, transport pathways to the Arctic, and environmental fate and persistence over time. Modeling and statistical methods could also be used to begin to distinguish the source and origin of congeners such as PCB209 observed in the Arctic which are unintentionally generated in pigment manufacture and intentionally produced in PCB mixtures.

2.15.6 Environmental concentrations

2.15.6.1 Air and precipitation

PCB11 has been found in the atmosphere in both polar regions, usually in high concentrations relative to most other PCB compounds (Choi et al., 2008; Baek et al., 2011; Li et al., 2012). Between 2005 and 2006, Choi et al. (2008) measured PCBs and organochlorines in air at three locations over 12 consecutive months at Ny-Ålesund, Svalbard, using XAD 2-resin passive air samplers. They reported field-blank-corrected time-averaged air concentrations at the three sites of 11.39, 5.19 and 11.26 pg/m^3 PCB11 with a mean of ~9 pg/m^3 PCB11. This mean concentration is much lower than those measured in urban environments. For example, 15–244 pg/m^3 (mean ~56 pg/m^3) in air at an urban site in South Korea (Kim and Song, 2003). Their ubiquitous presence worldwide may be due to unidentified global sources of PCB11 according to Kim and Song (2003).

Baek et al. (2011) deployed XAD-2 resin-based passive air samplers and reported measurements for three one-year periods at Ny-Ålesund (2005–2009). They found an average concentration of 5.44 pg/m^3 PCB11. PCB11 levels in air from one-year passive air samples between 2005 and 2007 were much higher at King George Island in the Antarctic (22.8–87.1 pg/m^3, mean ~60.3 pg/m^3). PCB11 accounted for 74% of the total PCB concentration in their samples (Baek et al., 2011).

Garmash et al. (2013) collected a 37-m deep ice core representing the period 1957–2009 and snow representing the period 2009–2010, from the Lomonosovfonna glacier on Svalbard. Samples were analyzed for all 209 PCB congeners. The snow sample had PCB11 as one of the four predominant PCB congeners, and PCB11 represented 4.5% of the total PCBs found. Garmash et al. (2013) noted that the surface snow sample had a congener profile more similar to the air sample concentrations at Zeppelin station to the south (Aas and Breivik, 2012) than the ice core samples, which had lower proportions of the mono-, di- and tri- chlorinated PCBs (PCB11 was not included in the Zeppelin measurements). Garmash et al. (2013) hypothesized that the surface snow samples measured in the spring are likely to re-emit the lower chlorinated congeners during the summer when temperatures are higher, accounting for the difference between PCB profiles in the surface snow samples compared to the ice core samples. These data are also discussed in Section 2.15.7.2.

2.15.6.2 Terrestrial environment

Zhu et al. (2015) collected soil, reindeer dung, and plant samples at Ny-Ålesund and London Island, Svalbard, and found PCB11 to be the predominant PCB congener. Soil samples contained 69.5 to 167 pg/g dw ΣPCB_{25}, with PCB11 accounting for approximately 8.5% of ΣPCB_{25}. Vegetation samples comprising Knieff's hook moss, tufted saxifrage, mountain avens, Alpine hair grass, sooty sedge, and Arctic bell-heather had concentrations of 11.2–191 pg/g dw PCB11, representing 5.6–25% of ΣPCB_{25}. Reindeer dung contained 107–313 pg/g dw PCB11, representing 26.2±8.4% of ΣPCB_{25}. These findings showing PCB11 as the predominant congener were difficult to explain and Zhu et al. (2015) concluded that the global sources need identifying.

2.15.6.3 Freshwater environment

No data were available for new unintentionally generated PCBs in the Arctic freshwater environment.

2.15.6.4 Marine environment

PCB11 has been detected in marine mussels (0.7–9.1 ng/g), and grey seals (maternal blubber 9.25±7.94 pg/g lipid, maternal blood 3590±1920 pg/g lipid, maternal milk 2.15±0.58 pg/g lipid, pup blubber 7.53±6.05 pg/g lipid) in Nova Scotia, Canada (Addison et al., 1999; King et al., 2002), but measurements for the Arctic marine environment are not available.

2.15.7 Environmental trends

2.15.7.1 Spatial trends

Svalbard is the only location where PCB11 has been sought and measured in the Arctic, so spatial trends in the Arctic environment cannot be made. To date, the Svalbard observations show lower air concentrations of PCB11 in the Arctic than at Antarctic sites. However, the geographical spread of sample sites within the Arctic is not enough for conclusions to be drawn regarding differences between the two polar regions.

Baek et al. (2011) suggested that the southern polar areas may be closer to stronger sources than the northern polar region. Guo et al. (2014) detected PCB11 in consumer goods from 26 countries on five continents, which is an indication that PCB11 emissions are global, but the spatial variation and emission rates are not yet well characterized.

2.15.7.2 Temporal trends

Ice core samples have the potential to provide a record of PCB deposition in the period before atmospheric measurements. Garmash et al. (2013) measured PCB11 in a 37-m ice core

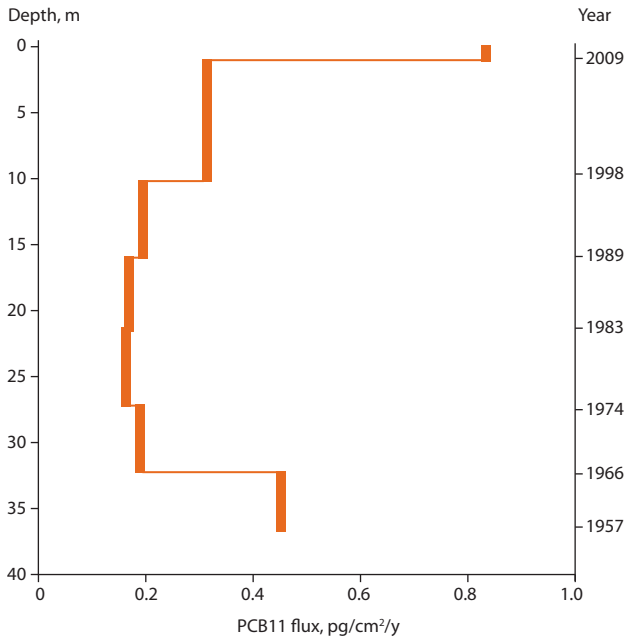

Figure 2.117 Flux of PCB11 congener in Lomonosovfonna ice core (1957–2009) and surface snow (2009–2010) (Garmash et al., 2013).

from the Lomonosovfonna glacier on Svalbard and calculated fluxes over the period 1957–2009 (Figure 2.117). Snow samples representing 2009 to 2010 were also included. The highest deposition fluxes occurred in the earliest period (0.45 pg/cm per year, 1957–1966), followed by two decades of lower fluxes (0.18 pg/cm per year, 1966–1988) and then another increase (0.31 pg/cm per year, 1998–2009). The snow sample showed the highest deposition flux (0.83 pg/cm per year, 2009–2010). Garmash et al. (2013) concluded that this could be explained as evaporative loss to the atmosphere due to higher air temperatures in summer. Garmash et al. (2013) concluded that PCB11 has been emitted since at least 1957, but due to confounding factors, it was not possible to discern any temporal trend.

The Lomonosovfonna glacier is at a relatively high elevation on Svalbard, above the Arctic boundary layer, and PCBs are likely to be delivered by long-range atmospheric transport from sources that are hundreds of kilometers or more away. Weather patterns and air mass transport routes from PCB source regions can be different for each period represented by the ice core, confounding a more general temporal trend. Air mass origin seemed to be important because the highest fluxes were found when air mass back trajectories showed the arrival of air masses from southerly latitudes in the North Sea and as far south as the UK. The likely re-emission of PCB11 and other di-chloro PCB makes it more difficult to establish a trend for these homologues. Garmash et al. (2013) further hypothesized that there may be an additional confounding factor of migration of the more volatile lower chlorinated PCBs between ice and firn layers and possibly to the surface and then reemited to the atmosphere. Nevertheless, the Garmash et al. (2013) findings show PCB11 has been a predominant di-chloro PCB in the Arctic (Svalbard) since at least 1957.

2.15.8 Conclusions

PCB11 and other unintentionally generated PCB congeners have generally not been subject to systematic monitoring in the environment nor subject to sustained actions by regulatory agencies on production and use. Research is currently focused on PCB11, but other unintentionally generated PCB congeners may also present problems to the Arctic environment. Complete congener analysis needs to become standard environmental monitoring and research practice before unintentionally generated PCB congener distribution and importance can be adequately characterized. Unintentionally generated PCB congeners (manufacture and thermal) that are in common with legacy PCB are present in some Arctic measurements at higher levels than expected (notably PCB209), but the relative attribution by type of source is unknown.

The toxicity of PCB11 and its metabolites is only now beginning to be investigated, and other unintentionally generated PCBs even less so. Where measurements have been made in the polar regions, PCB11 has been detected and has accounted for a significant proportion of total PCB congener concentrations. The presence of PCB11 in the Arctic, even in remote areas, shows it is likely to be a global pollutant, persistent in the environment and capable of long-range atmospheric transport. There are too few measurements of PCB11 in the Arctic to draw conclusions about its environmental distribution or its uptake in biological systems. More air monitoring data and measurements of all 209 PCB congeners in environmental media (marine and terrestrial) are required before a comprehensive assessment will be possible. PCB11 is readily metabolized, so its health risk may ultimately be associated more with its metabolites, which have greater persistence in blood and tissue. Thus, its metabolites should also be measured in Arctic wildlife samples. Considering that PCB11 was a known contaminant at the time that PCB Aroclor manufacture was banned and international conventions came into effect, one can only conclude that it was the focus on commercial legacy PCB and the lack of environmental monitoring of PCB11 that has allowed its production, emission, and contamination to rival the other banned legacy Aroclor PCB congeners. Other unintentionally generated PCBs in manufacture and thermal processes are even less understood than PCB11, and although found less in proportion than PCB11 in the Arctic, some may have higher toxicity and impact. Rodenburg et al. (2015) proposed that the pigment manufacturers should pursue alternative methods of manufacture that do not unintentionally generate PCB. The high levels and proportions of PCB11 found in the Arctic warrants efforts towards source mitigation.

2.16 Halogenated natural products

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2.16.1 Introduction

Halogenated natural products (HNPs) are organic compounds containing bromine, chlorine, iodine, and sometimes fluorine. This section distinguishes between light halomethanes and haloethanes, often referred to as 'halocarbons' by the atmospheric community (WMO, 2014), and higher molecular weight HNPs. The latter often contain oxygen and/or nitrogen atoms in addition to halogens (Gribble, 2003). Many, if not most, HNPs are biosynthesized by marine bacteria, macroalgae, phytoplankton, tunicates, corals, worms, sponges and other organisms (Ballschmiter, 2003; Gribble, 2003, 2010; Vetter, 2006; Vetter and Gribble, 2007; Guitart et al., 2011; Agarwal et al., 2014, 2015). Terrestrial plants, lichens, bacteria and fungi also produce HNPs (Gribble, 2003). Altogether, over 4000 HNP compounds have been discovered (Gribble, 2003, 2010; Vetter and Gribble, 2007).

Natural and anthropogenic halocarbons have received much attention as regulators of ozone in the atmosphere and a detailed assessment has recently been published (WMO, 2014). Bioaccumulating compounds with higher molecular weights such as bromophenols and bromoanisoles (BPs, BAs), hydroxylated and methoxylated polybrominated diphenyl ethers (OH-BDEs and MeO-BDEs), brominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), and other HNPs with heterocyclic ring structures have been reported in marine biota and less frequently in sediment, water and air. In marine biota, levels of HNPs often exceed those of polybrominated diphenyl ether (PBDE) flame retardants (Marsh et al., 2005; Rotander et al., 2012a; Alonso et al., 2014) or in some cases even exceed the concentration of recalcitrant polychlorinated biphenyl (PCB) 153 (Hauler et al., 2014).

This section summarizes the occurrence and fate of HNPs in the Arctic physical environment and in Arctic biota. Except for halocarbons, there have been few investigations of HNPs in polar environments. Discussions of HNP formation processes and occurrence in temperate and Antarctic ecosystems are occasionally included to provide context. Information on HNPs is presented by compound class and generally in order of increasing molecular weight, as most information on lower molecular halocarbons relates to air/water media while higher molecular weight compounds are generally reported in biota. An overview of reported HNP occurrences in Arctic-subarctic media is shown in Table 2.85.

2.16.2 Halocarbons

Atmospheric halogens and ozone in the stratosphere are controlled by long-lived species such as halons (e.g. $CBrClF_2$, CBr_2F_2), hydrochlorofluorocarbons (HCFCs), CH_3Cl, CH_3Br, CCl_4 and CH_3CCl_3, which have anthropogenic or mixed anthropogenic and natural sources (WMO, 2014). Important also are a group of mostly natural 'very short-lived substances' (VSLS) which typically have atmospheric lifetimes of <0.5 y (WMO, 2014). VSLS include compounds such as CH_2Cl_2, CH_2Br_2, $CHBr_3$, CH_2BrCl, $CHBrCl_2$, $CHBr_2Cl$, C_2H_5Br, CH_3I, CH_2I_2, CHI_3, CH_2ICl and C_2H_5I (WMO, 2014) (Table 2.86). The extensive literature for atmospheric $CHBr_3$ was reviewed by Quack and Wallace (2003) and for iodocarbons by Carpenter (2003). Mechanisms for production and release of inorganic and organic halogen species at the sea surface were reviewed by Carpenter and Nightingale (2015). Recent updates have been made in the context of establishing global emission inventories for VSLS (Hossaini et al., 2010, 2012, 2013; Ziska et al., 2013; WMO, 2014; Sarwar et al., 2015). The oceanic contribution of CH_3I to stratospheric iodine has been estimated from measurements in air at sea level and transport modelling (Tegtmeier et al., 2013), and a trans-Arctic survey of halocarbons in surface and deep water has been conducted (Karlsson et al., 2013).

Table 2.85 Reported occurrence of HNPs in Arctic-subarctic media. See Table 2.86 for abbreviations.

	Atmosphere		Terrestrial		Freshwater			Marine		
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota
Halocarbons	×	×	×		×			×		
Haloacetates		×	×	×	×			×		
BPs	×			×					×	×
BAs	×							×		×
OH-BDEs										×
MeO-BDEs							×			×
PDBPs									×	×
MHC-1										×
PBHDs										×

Table 2.86 Halogenated natural products relevant to the Arctic region.

Compound	Formula or abbreviation	CAS number
methyl chloride (chloromethane)	CH_3Cl	74-87-3
dichloromethane	CH_2Cl_2	75-09-2
methyl bromide (bromomethane)	CH_3Br	74-83-9
dibromomethane	CH_2Br_2	74-95-3
bromoform (tribromomethane)	$CHBr_3$	75-25-2
bromochloromethane	CH_2BrCl	74-97-5
bromodichloromethane	$CHBrCl_2$	75-27-4
dibromochloromethane	$CHBr_2Cl$	124-48-1
ethyl bromide (bromoethane)	C_2H_5Br	74-96-4
methyl iodide (iodomethane)	CH_3I	74-88-4
diiodomethane	CH_2I_2	75-11-6
iodoform (triiodomethane)	CHI_3	75-47-8
iodochloromethane	CH_2ICl	593-71-5
ethyl iodide (iodoethane)	C_2H_5I	75-03-6
trifluoroacetic acid (acetate)	TFA	76-05-1
2,4-dibromophenol	2,4-DiBP	615-58-7
2,6-dibromophenol	2,6-DiBP	608-33-3
2,4,6-tribromophenol	2,4,6-TriBP	118-79-6
2,4-dibromoanisole	2,4-DiBA	21702-84-1
2,6-dibromoanisole	2,6-DiBA	38603-09-7
2,4,6-tribromoanisole	2,4,6-TriBA	607-99-8
methoxylated polybrominated diphenyl ethers	MeO-BDEs	
hydroxylated polybrominated diphenyl ethers	OH-BDEs	
polybrominated dibenzo-*p*-dioxins	PBDDs	
polybrominated dibenzofurans	PBDFs	
polyhalogenated 1'-methyl-1,2'-bipyrroles	PMBPs	
polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles	PDBPs	
polyhalogenated N-methylpyrroles	PMPs	
polyhalogenated N-methylindoles	PMIs	
bromoheptyl- and bromooctyl pyrroles	BHPs, BOPs	
(1R,2S,4R,5R,1'E)-2-bromo-1-bromomethyl-1,4-dichloro-5-(2'-chloroethenyl)-5-methylcyclohexane	MHC-1	
polybrominated hexahydroxanthene derivatives	PBHDs	
bromovinyl phenols	BVPs	
bromocoumarates	BCUs	

2.16.2.1 Physical-chemical properties

Henry's law constants (H, Pa m^3/mol) and dimensionless air-water partition coefficients ($K_{AW} = H/RT$) for halocarbons in seawater are reported in Annex Table A2.16/1, along with parameters of $\ln H = A + B/T$ for the range 0–20°C (Moore et al., 1995). These are the relevant properties for estimating sea-to-air fluxes, and were used in the global flux estimates of Ziska et al. (2013).

2.16.2.2 Sources, production, and use

Marine phytoplankton and sea ice algae produce reactive species such as HOBr, HOCl and HOI from sea salt halides and hydrogen peroxide under catalysis by haloperoxidases, and these react with organic substrates to yield halocarbons (Sturges et al., 1992; Moore et al., 1996; Cota and Sturges, 1997; Abrahamsson et al., 2003; Carpenter, 2003; Karlsson et al., 2008, 2013; Hill and Manley, 2009; Orlikowska and Schulz-Bull, 2009; Liu et al., 2013a). Halocarbons are also formed by the action of bromo- and iodo-peroxidases on marine dissolved organic matter (Hill and Manley, 2009; Lin and Manley, 2012). Elevated concentrations in air and seawater occur in productive and upwelling regions (reviewed by Ziska et al., 2013). Photochemistry involving organic carbon compounds on snow surfaces can yield halocarbons (reviewed by Simpson et al., 2007). Halocarbons are produced by ice algae (Sturges et al., 1992), microorganisms in sea ice and frost flowers on newly formed ice (Granfors et al., 2013a,b, 2014) and are released to the atmosphere.

Mesocosm experiments in Kongsfjord, Svalbard were carried out in June-July 2010 to examine relationships between halocarbons and ocean acidification (as indicated by pCO_2) in an Arctic ecosystem (Hopkins et al., 2013). Production of halocarbons was strongly related to biological parameters (chlorophyll *a*, microbial plankton community, phytoplankton pigments), either positively or negatively. Concentrations of $CHBr_3$ in the mesocosms were negatively correlated with total bacteria, suggesting biotic degradation. Positive correlations were found between concentrations of CH_2I_2, total bacteria and algal pigments. Concentrations, rate of net production and sea-to-air flux of CH_2I_2 were positively related to pCO_2, while no effects of pCO_2 were seen for CH_3I or $CHBr_3$.

CH_3Br and CH_3Cl have both natural and anthropogenic sources, globally totaling 84 and 3658 Gg/y, respectively (WMO, 2014). Approximately 38% of CH_3Br is derived from ocean emissions and 21% from terrestrial sources (mangroves 1.5%, rapeseed 6.1%, fungi 2.6%, salt marshes 8.3%, wetlands 0.7%, rice paddies 0.8%, shrublands 0.8%), leaving 41% as the anthropogenic contribution from gasoline combustion, fumigation and biomass burning. CH_3Br fumigants accounted for 7–10% of global emissions in 2012 compared to 22–40% before phase-out under the Montreal Protocol in 1996–1998. The natural oceanic source of CH_3Br is now comparable to its oceanic sink. For CH_3Cl, 56% is emitted by tropical and subtropical plants, 8% from other terrestrial sources (mangroves 0.3%, fungi 4.0%, salt marshes 2.3%, wetlands 0.7%, rice paddies 0.1%, shrublands 0.4%), 19% from the ocean and 17% from anthropogenic sources (coal combustion, biomass burning) (WMO, 2014).

Approximately 76% of VSLS halocarbons come from naturally produced $CHBr_3$ and CH_2Br_2 (Hossaini et al., 2012). Transport of these compounds and other VSLS to the stratosphere occurs by deep convection, especially in the tropics (Ziska et al., 2013; WMO, 2014). VSLS may account for 10–40% of stratospheric bromine (WMO, 2014), and may be delaying stratospheric ozone hole recovery in Antarctica (Yang et al., 2014). The ocean contributes over 80% of global CH_3I emissions with known production by phytoplankton and photochemical degradation of organic matter in seawater (WMO, 2014). Terrestrial sources include rice paddies, wetlands and biomass burning (Carpenter, 2003). CH_3I is registered as a pesticide (replacing CH_3Br) in the United States, Japan, and Mexico. However it has been withdrawn from the U.S. market (WMO, 2014). CH_3I is important for the tropospheric ozone budget, but only small quantities enter the stratosphere due to its short atmospheric lifetime (Tegtmeier et al., 2013).

Global emission inventories have been drawn up for $CHBr_3$, CH_2Br_2 and CHI_3 (Hossaini et al., 2013; Ziska et al., 2013). The inventories were based on 'top-down' aircraft observations of halocarbons in the atmosphere, while a 'bottom-up' approach used gas exchange calculations from surface air and ocean water concentrations and the Henry's law constants of Moore et al. (1995) (Annex Table A2.16/1). Sea-to-air flux estimates in the Arctic are based on few surface water data (Section 2.16.2.5, *Marine environment*). Emission source strengths from three top-down and one bottom-up chemical transport models for $CHBr_3$ and CH_2Br_2 are compared in Figure 2.118. Latitudinal variations in emissions of the two halocarbons agree qualitatively among the three top-down models, with fluxes in the order: tropics > subtropics and temperate > subpolar and polar. The one bottom-up model differs greatly in estimating higher fluxes of $CHBr_3$ (but not CH_2Br_2) north of 50°N and higher fluxes of CH_2Br_2 (but not $CHBr_3$) in the southern hemisphere between 40° and 70°S (Figure 2.118). Emission estimates also differ quantitatively; for example, for $CHBr_3$ in the tropics between 0.25–0.9×10^{-13} kg/m²/s for top-down models versus 0.1–0.35×10^{-13} kg/m²/s for the bottom-up model (Figure 2.118). A similar comparison for regions north of 50°N showed 0–0.15 × 10^{-13} kg/m²/s (top-down) versus 0.1–0.6 × 10^{-13} kg/m²/s (bottom-up) (Figure 2.118). Estimated global emissions of VSLS in Gg/y were summarized by Sarwar et al. (2015) and WMO (2014) and are presented in Annex Table A2.16/2.

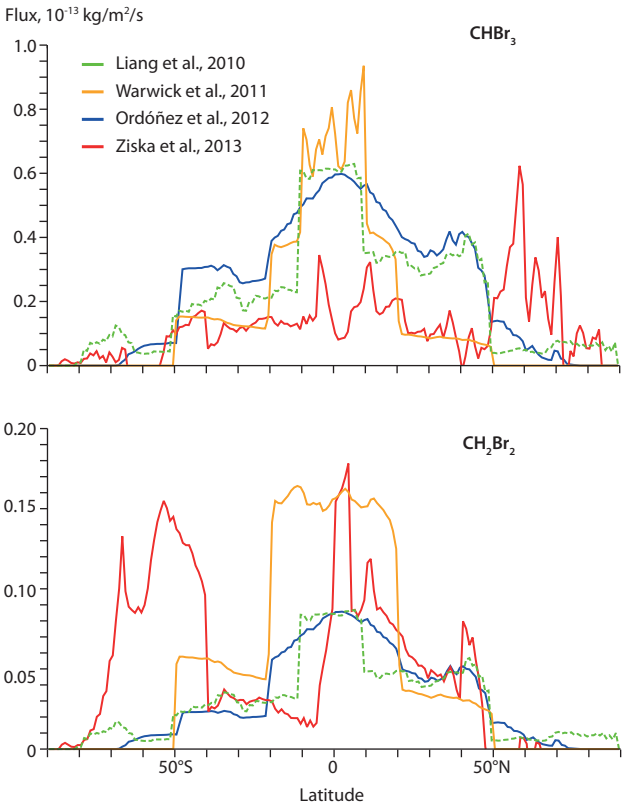

Figure 2.118 Zonally averaged global emission source strengths for $CHBr_3$ and CH_2Br_2, estimated from three top-down models (Warwick et al., 2011 = Pyle et al., 2011 update of Warwick et al., 2006; Liang et al., 2010; Ordóñez et al., 2012) and one bottom-up model (Ziska et al., 2013). Graphic from Hossaini et al. (2013).

Haloacetic acids (acetic acid in which fluorine, chlorine and/or bromine replace one or more hydrogens) are a group of compounds having anthropogenic and natural origins. Since these compounds have pK_A values <3 (Health Canada, 2008), they will exist as acetates at the pH of most environmental media. Higher concentrations of haloacetates were found in the northern hemisphere, suggesting human impact but substantial concentrations also occur in the less industrialized southern hemisphere (Scott et al., 2005a). Anthropogenic sources are atmospheric oxidation of halocarbons (Kotamarthi et al., 1998; Wang et al., 2014c), water chlorination, waste and biomass combustion and herbicide use (Health Canada, 2008). Chloroacetic acids are produced naturally in soils (Hoekstra et al., 1999; Fahimi et al., 2003; Laturnus et al., 2005); however, the overall role of forest soils as sources/sinks for these compounds is unclear (Laturnus et al., 2005). Higher concentrations of mono- and dibromoacetates in fog samples collected in Germany were measured when winds came off the ocean, suggesting a marine source (Römpp et al., 2001). Trifluoroacetate, monochloroacetate and monobromoacetate also appear to have natural sources based on findings in Antarctic firn layers that were formed during the 19th century (Von Sydow et al., 2000a,b) and occurrence of trifluoroacetate in deep ocean water (Frank et al., 2002; Scott et al., 2005b). Sources could include deep ocean vents, although estimated vent emissions are too low to account for the trifluoroacetate burden in the oceans (Scott et al., 2005b).

2.16.2.3 Transformation processes

Lifetimes of VSLS in the mid-latitude marine boundary layer due to photolysis and OH radical reaction are 97–750 d (CH_3Cl), 80–620 d (CH_2Br_2), 14–86 d ($CHBr_3$), 38–45 d ($CHBrCl_2$), 32–225 d ($CHBr_2Cl$) and 4.1–19 d (CH_3I), with the shorter and longer times in summer and winter (WMO, 2014). Reaction with OH radicals accounts for 64% and 46% of total sinks for CH_3Cl and CH_3Br, with the remaining loss processes due to uptake by the ocean and soils and transport to the stratosphere (WMO, 2014). Photolysis of VSLS yields halogen atoms and oxides which are responsible for ozone destruction (Simpson et al., 2007; WMO, 2014). Degradation of VSLS results in 'product gases' with the general formulae CX_2O, CHXO, CHX_2OOH and $CHX_2O_2NO_2$, which may also be transported to the stratosphere (WMO, 2014). Atmospheric oxidation of halocarbons is a source of haloacetates (Section 2.16.2.2).

Halocarbons in ocean water are subject to a number of removal processes, including hydrolysis, reductive dechlorination, halogen substitution, photolysis, microbial degradation and volatilization (Hopkins et al., 2013). Photolysis is generally considered the main loss process for $CHBr_3$, but was minor in Svalbard mesocosm experiments because of screening by a partially transparent cover. Biological processes in the mesocosms were suggested to account for observed losses of bromine and iodine compounds (Hopkins et al., 2013). Chlorine substitution and volatilization account for loss of CH_3I at comparable rates, whereas photolysis and hydrolysis are minor (Carpenter, 2003). Concentrations of $CHBr_3$ decrease with depth in the Arctic Ocean; the reduced levels in deep and intermediate waters are consistent with a halide substitution half-life of 74 y (Karlsson et al., 2013). No ocean sinks have been identified for trifluoroacetate (Scott et al., 2005b).

2.16.2.4 Modeling studies

Modeling is extensively used to estimate surface-air exchange of halocarbons, transport through the troposphere and into the stratosphere, and to derive emission source strengths. Other models consider atmospheric reactions involved in the production and destruction of ozone, the role of halocarbons in ozone regulation, and past and future trends in ozone levels. Discussion of these models is beyond the scope of this report and readers are referred to the recent WMO report (2014) and references therein.

2.16.2.5 Environmental concentrations

Air and precipitation

Much research has been done to quantify sea-to-air fluxes of long-lived and VSLS halocarbons. Most measurements have been in temperate and tropical regions and in the Southern Ocean, with relatively few measurements in the Arctic. Global data have been compiled from many sources (e.g. WMO, 2014) and used for global modeling by Ziska et al. (2013), Hossaini et al. (2012, 2013) and Warwick et al. (2006). Tropospheric average concentrations in 2012 were estimated as mixing ratios (parts-per-trillion by volume, pptv): 7.0±0.1 pptv (CH_3Br), 540±5 pptv (CH_3Cl), and 72-125 pptv (total VSLS) (WMO, 2014). Conversion from pptv to ng/m^3 at standard temperature and pressure can be made using the conversion: molecular weight divided by 22.4. Thus, one pptv = 4.2 ng/m^3 for CH_3Br and 2.3 ng/m^3 for CH_3Cl.

Ground and aircraft observations of $CHBr_3$ and CH_2Br_2 used for estimating emission inventories in the Arctic have been made at Alert (Canada) Summit (Greenland) and Point Barrow (Alaska, USA) (Hossaini et al., 2013). Mixing ratios of $CHBr_3$ at the Arctic ground stations were about 1.5–4.5 pptv in winter and 0.5–1 pptv in summer. Winter mixing ratios were higher in the Arctic relative to tropical stations (e.g. 0.3–1 pptv at Hawaii and Samoa) and winter/summer differences were more pronounced, probably because of the reduced and seasonal photochemical activity at high latitudes. The global range for $CHBr_3$ in the marine boundary layer was 0.4–4.0 pptv (WMO, 2014). Mixing ratios of CH_2Br_2 were 0.8–1.2 pptv at the Arctic stations and showed depletion in summer at Alert and Summit (although less than for $CHBr_3$) (Hossaini et al., 2013) but not at Point Barrow. The global range for CH_2Br_2 in the marine boundary layer was 0.6–1.7 pptv (WMO, 2014). Mixing ratios of CH_3Br at Alert and Point Barrow were 8–10 pptv, also higher in winter-spring than summer (Warwick et al., 2006), compared to a tropospheric average of 7.0 pptv.

Halocarbons were measured in air over the period August–October 2009 along a ship track across the North Pacific between Japan and Canada, across the Canadian Arctic from the Bering Strait to 79°W, and at Alert during September–October (Yokouchi et al., 2013). Mean mixing ratios on the Arctic cruise legs were: 472 pptv (CH_3Cl), 7.6 pptv (CH_3Br), 0.52 pptv (CH_3I), 1.9 pptv ($CHBr_3$) and 1.2 pptv (CH_2Br_2), and were similar to those at Alert. The spatial distributions of CH_3I, $CHBr_3$, and CH_2Br_2 differed from those of CH_3Cl and CH_3Br. Mixing ratios of the former group were highest near perennial sea ice and influenced by air masses that had originated over the Alaskan coast, suggesting the role of macroalgae and ice algae which produce these compounds. They were lowest at the northernmost sites in air masses that had traveled over the polar ice cap. The opposite pattern was seen for the monohalomethanes. This difference can be explained by the Arctic Ocean being a source of CH_3I, $CHBr_3$, and CH_2Br_2, but a sink for CH_3Cl and CH_3Br.

Tropospheric ozone-depletion events (ODEs) in the Arctic occur mainly from March to May when the ocean is frozen, the ground is covered by snow and sunlight returns after the winter darkness. The ODEs are triggered by reactive bromine produced from inorganic bromide in sea salts by 'bromine explosion' reactions (Simpson et al., 2007). Organobromine compounds are thought not to directly result in ODEs, but may be involved in ODE initiation or termination, and reactive iodocarbons such as CH_2I_2 could play a more important role (Simpson et al., 2007). Peaks in inorganic and organic bromine correspond to ODEs at polar sunrise (Li et al., 1994).

Snow-air and sea ice-air interfaces are important sites for production and release of gaseous inorganic and organic halogen species. High events of iodine oxide (IO), probably produced from iodocarbons, were associated with air passing over open water polynyas in Hudson Bay (Mahajan et al., 2010). The halocarbons CH_2I_2, CH_2IBr, and CH_2ICl were found in air over Hudson Bay at Kuujjuarapik during spring when the bay was frozen (Carpenter et al., 2005). The sum of these halocarbons reached 5 pptv, the highest concentrations reported in Arctic air. Strong diurnal variations were observed with higher levels corresponding to daytime winds off the bay. A proposed mechanism of production was by reaction of inorganic halooxide species with organic material in sea ice, snowpack and frost flowers. Concentrations of C_2H_5I, 2-C_3H_7I and CH_2Br_2 in sea ice brine were enriched 1.7, 1.4 and 2.5 times above seawater levels in the Norwegian Sea and Greenland Sea, and supersaturation in both brine and seawater resulted in net sea-to-air fluxes (Atkinson et al., 2014). The enrichment may be due to production by diatoms in brine channels (connected pore spaces within ice through which concentrated sea salt solution can pass, Krembs et al., 2002; Pućko et al., 2010). Highest air concentrations occurred when trajectories passed over porous summer ice. Transition within this century to thinner and more porous ice in the Arctic would increase the potential for brine iodocarbons to be released to the atmosphere, thereby increasing levels of ozone-depleting iodine radicals in the troposphere (Atkinson et al.,

2014). Measurements in the Weddell Sea (Antarctica) showed concentrations of halocarbons in brine > ice > seawater; however when normalized for salinity the order was ice > brine > seawater (Granfors et al., 2014). Correlations with chlorophyll *a* suggested algal production of CHI_3, while both biotic and abiotic processes were hypothesized to produce other halocarbons. Halocarbon levels in winter frost flowers were low, possibly due to evaporation losses. Halocarbons were measured in air and snow as part of the suite of volatile organics sampled at Alert in 2006 and Point Barrow in 2009 (Kos et al., 2014). Halocarbon concentration ranges in surface snow at Alert were 350–34 000 ng/L ($CHBr_3$), 140–1500 ng/L ($CHBr_2Cl$) and <170–5070 ng/L (CH_2Br_2). $CHBr_3$ was quantified at 190±42 ng/L in frost flowers in one sampling event during the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) campaign, but was <120 ng/L in seven other sampling events.

Halocarbons were measured in air within the firn on the Devon Island Ice Cap and at two Antarctic sites in 1998 (Sturges et al., 2001). Concentrations of CH_3Br increased with depth from about 10 pptv at the surface and 10 m, to 300 pptv at 50–60 m. CH_3Br was strongly correlated with CH_3I, which also increased from near zero at the surface to about 60 pptv over the same depth. Other halocarbons (CH_2Br_2, $CHBr_2Cl$, $CHBrCl_2$, $CHBr_3$) in firn air were in the range 0.5–3 pptv and showed slight increases with depth. Higher concentrations in deeper firn layers may indicate production through biotic or abiotic pathways. CH_3Br concentrations in Antarctic firn layers were much lower and declined from 8 pptv at the surface to 6–7 pptv at depth.

Haloacetates are a group of compounds which have both natural and anthropogenic origins (Scott et al., 2005a,b). Haloacetates were measured in precipitation at six sites across southern Canada in 1997–1998, at sampling sites on the Laurentian Great Lakes, and at one northern site, Snare Rapids (Scott et al., 2000). Volume-weighted mean concentrations at Snare Rapids were 0.4 ng/L (trifluoroacetate), 13 ng/L (monochloroacetate), 19 ng/L (dichloroacetate) and 0.6 ng/L (trichloroacetate). Air parcel back trajectories point to urban areas as sources. Trifluoroacetate and Σchloroacetate concentrations were 65–210 and 5–74 times higher at the southern sites.

Background levels of trifluoroacetate were determined in snow, glacial ice and firn from remote locations between 1994 and 1997 (Von Sydow et al., 2000a). Sites of snow sampling were Östergötland (Sweden), Tod Mountain and Resolute Bay (Canada), Mount Cook (New Zealand) and Queen Maud Land (Antarctica). Trifluoroacetate concentrations in these locations ranged from 1–32 ng/L with one high sample of 110 ng/L from Antarctica. Ice from the Mårma glacier (Sweden) with an age of 500 y contained 5 ng/L of trifluoroacetate. Firn core samples from Antarctica were collected from the surface to 19 m. Trifluoroacetate was present at 6–56 ng/L with an average of 25 ng/L and showed no trend with depth. The deepest firn layer was formed about 190 y before sampling. In a related study (Von Sydow et al., 2000b), chloro- and bromoacetates were determined in Antarctic snow and firn samples. Concentrations in surface snow from six sites were in the range: 6–106 ng/L (monochloroacetate), nd–21 ng/L (dichloroacetate), 58–348 ng/L (trichloroacetate), 3–36 ng/L (monobromoacetate), and 1–11 ng/L (dibromoacetate). The chloroacetates and dibromoacetate were also present in the firn depths dated to the pre-industrial period, but monobromoacetate was only found in surface snow.

Terrestrial environment

Concentrations of halocarbons are generally not reported in terrestrial compartments *per se* (soil, vegetation etc.), but rather as fluxes into or from the atmosphere. Global emissions of CH_3Cl and CH_3Br from anthropogenic, terrestrial and oceanic sources were summarized by WMO (2014) (Section 2.16.2.2), but not broken down by geographical distribution. Peatlands are sources of CH_3Cl, CH_3Br, CH_3I, $CHBr_3$ and $CHCl_3$ (Dimmer et al., 2001; Carpenter et al., 2005), and it is suggested that production might occur through elevated levels of bromide in coastal peatlands and soils (Carpenter et al., 2005). Boreal forest soils and the Arctic tundra were net sinks for CH_3Cl and CH_3Br (Rhew et al., 2003) and the latter only a trivial source of CH_3I (Rhew et al., 2007; Teh et al., 2009). The Alaska tundra was a net source of $CHCl_3$ to the atmosphere (Rhew et al., 2008). Measurements at a subarctic wetland in Sweden indicated small net sinks and sources for CH_3Br and CH_3Cl, respectively (Hardacre et al., 2009), while wetlands in Scotland were net sources of these gases (Hardacre and Heal, 2013).

The median concentration for trichloroacetate in 130 samples of pine needles from subarctic Finland was 23 ng/g ww, with 90% of values between 5 and 70 ng/g. Trichloroacetate was also found in arboreal lichens (Juuti et al., 1996).

Freshwater environment

Haloacetates were measured in the Laurentian Great Lakes and small lakes across Canada in 1997–1998, including Great Slave Lake in the north (Muir et al., 2000a). Trifluoroacetate was <0.5 ng/L in Loon Lake, 12–28 ng/L in Lake Kejimkujik, <0.5–10 ng/L in Great Slave Lake and 100–360 ng/L in Lake Winnipeg, possibly due to urban influences from upstream sources. Monochloro- and dichloroacetates were also high in Lake Winnipeg (95–250 and 86–799 ng/L) and lower in the other small lakes (<1–55 ng/L). Trichloroacetate was <2 ng/L except for two samples from Lake Winnipeg (11 and 37 ng/L). In comparison, concentrations of trifluoroacetate were low in Lake Superior (<0.5–2 ng/L) but much higher in the other Great Lakes (74–159 ng/L). The monochloro- and dichloroacetates were found in Lake Superior (<0.5–18 and 21–450 ng/L) and in the other Great Lakes (67–120 and 460–1500 ng/L), while monobromoacetate was not detected in any of the Great Lakes (<30 ng/L). Trichloroacetate was <2 ng/L in all lakes except for one sample in Lake Superior (3 ng/L).

Marine environment

Measurements of $CHBr_3$, CH_2Br_2 and CHI_3 in seawater north of 60°N were reported by Ziska et al. (2013: Supplement S3, data sets 16 and 30). Data are more numerous for 50–59°N in the North Atlantic, North Pacific, North Sea and Baltic Sea (Ziska et al., 2013: Supplement S3, data sets 2, 3, 8, 10, 11, 18, 19, 23, 24, 33, 35, 38, 39, 40 and 41).

Measurements of halocarbons in the surface and deep Arctic Ocean were made in 2005 on an expedition from Point Barrow (Alaska) to Svalbard (Karlsson et al., 2013). Mean concentrations of halocarbons in the polar mixed layer (PML) of the ocean basins were in the range 13–29 pmol/kg ($CHBr_3$), 7–22 pmol/kg (CH_2Br_2), 1.4–3.7 pmol/kg ($CHBr_2Cl$) and 1–2.6 pmol/kg (CH_2ClI), and are summarized in Annex Table A2.16/3. High

levels of $CHBr_3$, up to 160 pmol/kg were found in sea-ice brine. Concentrations were about one third to half of PML values in the warm Atlantic Layer at 200–800 m, and one-fifth of PML values below the sill depth of the Lomonosov Ridge (88°N, 140°W, 1870 m depth), which stretches between the New Siberian Islands over the central part of the ocean to Ellesmere Island in the Canadian Arctic Archipelago. A summary of spatial and depth distributions for $CHBr_3$ and other halocarbons in meltponds, brine and the upper 320 m of the water column is shown in Figure 2.119. The authors proposed that halocarbons are produced in the shelf areas of the Chukchi and Siberian seas, and that bromocarbons are also formed in sea ice over the Lomonosov and Makarov ridges during transport of riverine dissolved organic matter in the Transpolar Drift. Cycles of freezing and thawing enhance their transfer to seawater.

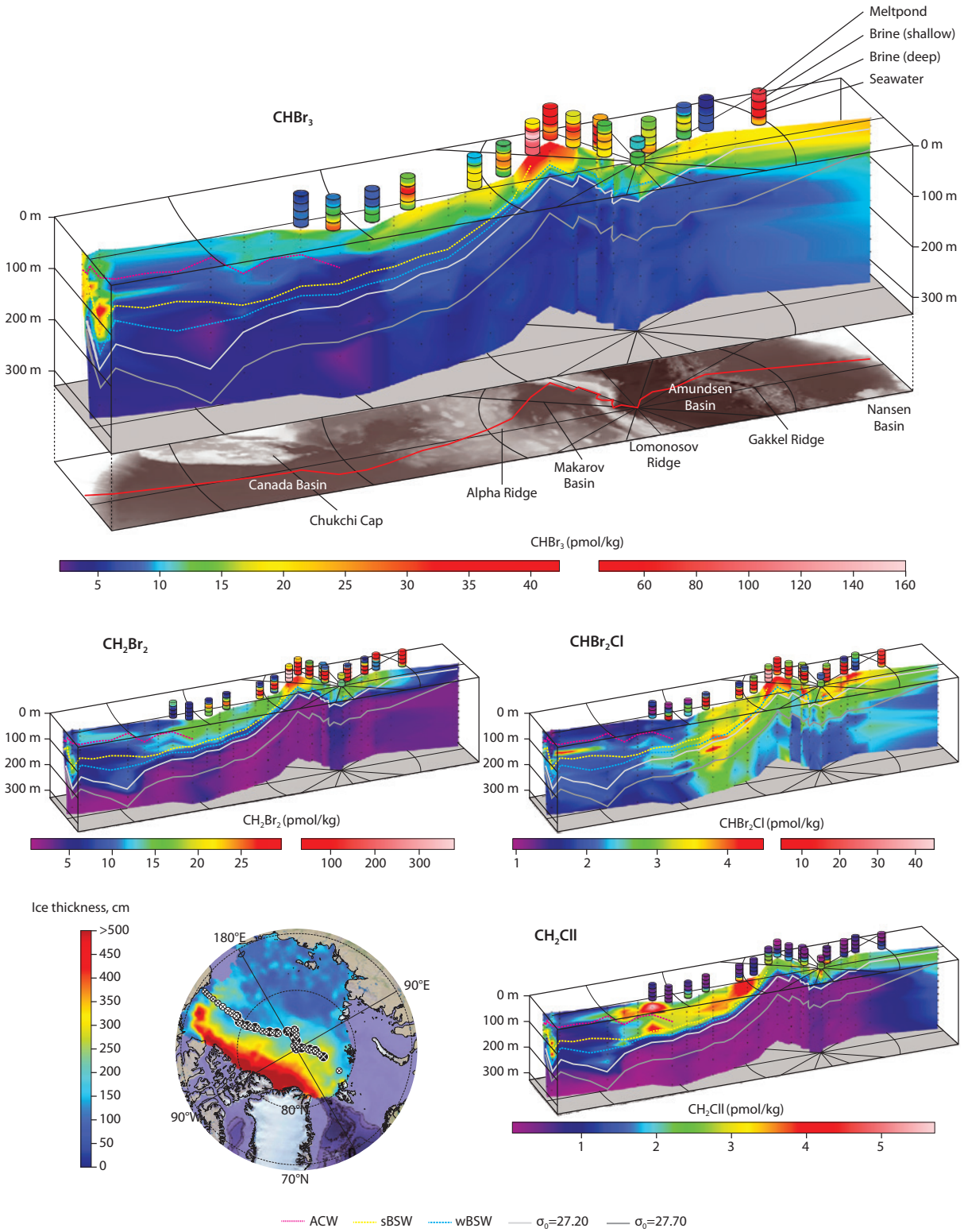

Figure 2.119 Vertical distribution of $CHBr_3$, CH_2Br_2, $CHBr_2Cl$, and CH_2ClI in the upper 320 m. Concentrations in melt ponds, sea-ice brine (two ice depths) and seawater just below the sea ice are also shown. Where identified, Alaskan Coastal Water (ACW), summer Bering Strait Water (sBSW), and winter Bering Strait Water (wBSW) are noted. (Karlsson et al., 2013).

Halocarbons in Norwegian Sea and Greenland Sea seawater averaged: 14.1±45.2 pmol/L ($CHBr_3$), 0.98±0.83 pmol/L (CH_2Br_2) and 0.54±0.31 pmol/L (CHI_3) (3550±11 400, 170±144 and 213±122 pg/L, respectively) (Ziska et al., 2013: Supplement S3 data sets 16 from 2002 and 30 from 1998). Especially high concentrations of $CHBr_3$, up to 358 pmol/L, have been found in Svalbard fjords (Hopkins et al., 2013; Ziska et al., 2013).

$CHBr_3$ was measured in seawater, ice and snow at Resolute Bay (Canada) in 1992 (Cota and Sturges, 1997). Elevated concentrations were found in seawater and ice at the interface, associated with emission by ice algae. Concentrations in sea ice at the snow-ice interface were in the range 336–367 ng/L, and 462–1260 ng/L in the snowpack over sea ice, declining toward the snow surface. $CHBr_3$ concentrations in recent snow were two orders of magnitude lower. Elevated $CHBr_3$ in the snowpack may have diffused from the sea ice layer. Concentrations of $CHBr_3$ in bottom ice algae and kelp (*Agarum cribosum*) in Resolute Bay were 679±355 ng/g dw and 1806±1037 ng/g dw, respectively (Cota and Sturges, 1997). Further discussion of halocarbons in the air-ice-seawater system is found in Section 2.16.2.5, *Air and precipitation*.

Halocarbon distribution and production experiments were conducted at Svalbard (Granfors et al., 2013a). Concentrations in seawater, under-ice seawater, ice, ice brine and frost flowers are summarized in Annex Table A2.16/4; mean abundances were in the order $CHBr_3$ ~ $CHBr_2Cl$ > CH_2Br_2 > $CHBrCl_2$ > CH_2ICl ~ CH_2IBr > CH_2I_2 and brine ~ ice > under-ice seawater > seawater. Two samplings of frost flowers showed $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ concentrations similar to those in brine and ice in one, and much lower concentrations in the other. The net production of $CHBr_3$ in newly formed sea ice was 14 pmol/L/d. Bacterial production of halocarbons in ice and a role of frost flowers in transferring halocarbons to the atmosphere were suggested.

Trifluoroacetate is widespread in the aquatic environment, and has been determined in surface and deep waters of the Arctic, North and South Atlantic and Pacific Oceans (Frank et al., 2002; Scott et al., 2005b). Concentrations in the Arctic were in the range 8–170 ng/L (Nares Strait, eastern Canadian Arctic) and 34–181 ng/L (Canada Basin, western Arctic). Deep ocean concentrations were often as high, or higher than those in the upper water column; for example, 160–181 ng/L (1800–3000 m, Canada Basin), 160 ng/L (3800 m, North Atlantic), and 80–150 ng/L (4800–5200 m, South Atlantic) (Scott et al., 2005b). The deep waters have ^{14}C ages exceeding 1000 years. Profiles were constant in the Mid-Atlantic (190–210 ng/L, 0–4100 m) and Southern Ocean (195–220 ng/L, 10–2000 m) (Frank et al., 2002). Concentrations were lower in the South Pacific (generally 1–10 ng/L) (Scott et al., 2005b). Such uniformity suggests natural production and long lifetimes, but sources have not been identified. Deep profiles in the Mediterranean Sea and Pacific Ocean suggested the presence of ocean vents, although the estimated release was far too low to account for observed inventories (Scott et al., 2005b).

2.16.2.6 Environmental trends

Spatial trends

Spatial variation in tropospheric mixing ratios are large for $CHBr_3$ and CH_2Br_2, although the latitudinal profile and magnitude of estimated emissions is dependent on the model. All models agree on peak levels in the tropics, but the Ziska 'bottom up' model (Ziska et al., 2013) predicts secondary maxima for $CHBr_3$ from 50–70°N and for CH_2Br_2 from 40–70°S (Hossaini et al., 2013) (Figure 2.118). Ratios of CH_2Br_2 : $CHBr_3$ are also variable, and elevated mixing ratios of both VSLS are found in coastal regions close to macroalgae and around islands, and in oceanic upwelling areas (as summarized by Hossaini et al., 2013 and Ziska et al., 2013). Short OH radical lifetimes contribute to spatial and temporal inhomogeneity (Hossaini et al., 2013). Thus, global average mixing ratios are known with better precision for long-lived species than VSLS. For example, mixing ratios of 7.0±0.1 pptv (CH_3Br) and 540±5 pptv (CH_3Cl) versus 0.4-4.0 pptv ($CHBr_3$) and 0.6-1.7 pptv (CH_2Br_2) (WMO, 2014).

Spatial trends in halocarbon concentrations in ground-level air in the Canadian Arctic (Yokouchi et al., 2013) were discussed in connection with their atmospheric concentrations in Section 2.16.2.5.

The spatial and vertical distribution of halocarbons in the Arctic Ocean was reported in detail by Karlsson et al. (2013) and a summary for the upper 320 m of the water column is shown in Figure 2.119. Other graphics in the paper show the vertical distribution to the bottom of the Arctic Ocean, horizontal variation in the lower halocline and Atlantic Layer, and depth profiles at selected stations off Barrow (Alaska) and over the Lomonosov Ridge.

Temporal trends

The following trends in tropospheric halocarbon concentrations were reported by WMO (2014). Total organic bromine declined from a peak of 17 pptv in 1998 to 15 pptv in 2012, largely due to a decrease in CH_3Br, from 9.2 pptv in the mid-1990s to 7.1 pptv in 2012. This decrease was achieved through control of most fumigant uses of CH_3Br under the Montreal Protocol. CH_3Br fumigants accounted for 7–10% of global emissions in 2012 compared to 22–40% before 1996–1998. The natural oceanic source of CH_3Br is now comparable to its oceanic sink. CH_3I concentrations increased by several tens of percent from 2003–2004 to 2009–2010. CH_3Cl concentrations showed a slight decline from 544 pptv in 2008 to 537 pptv in 2012. Total chlorinated VSLS increased from 84 pptv (70–117 pptv) in 2008 to 91 pptv (76–125 pptv) in 2012. CH_2Cl_2 accounted for the majority of this change, with an increase of ~60% over the last decade.

Seasonal variations in mixing ratios of VSLS, namely $CHBr_3$ and CH_2Br_2, were found at Arctic stations (Alert and Summit), high in winter and low in summer, due to lower photochemical activity in winter. In comparison, less seasonality is displayed at tropical and temperate stations (Section 2.16.2.5). Similar seasonal variations have been found for CH_3I (Yokouchi et al., 2012).

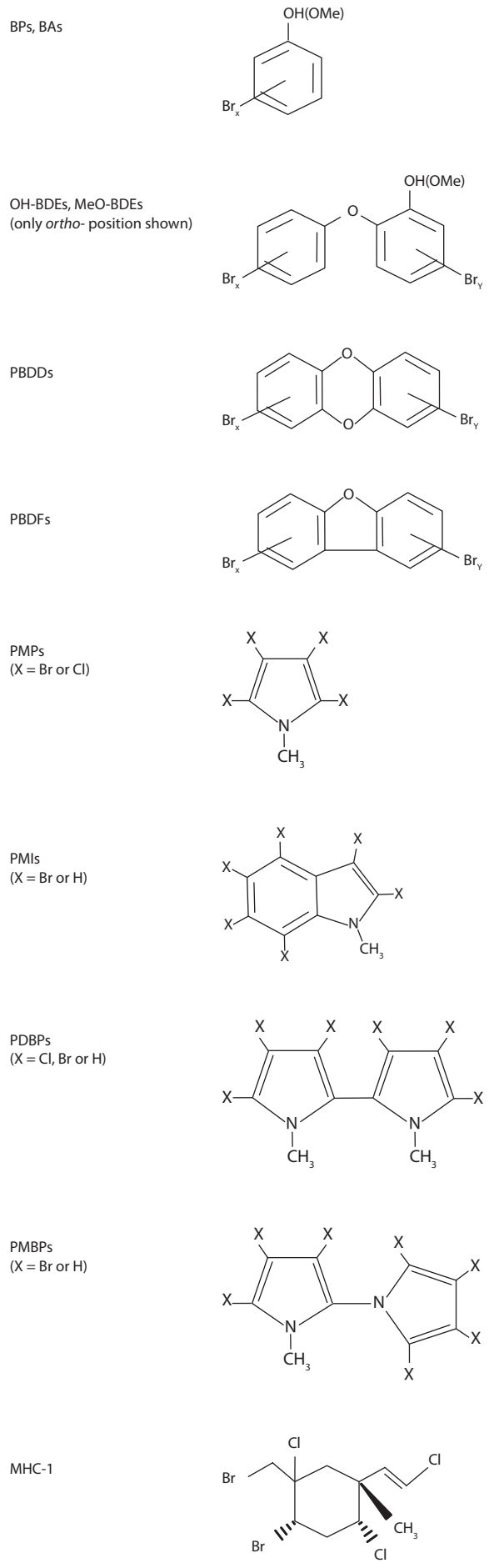

Figure 2.120 Structures of some high molecular weight HNPs.

Long-term trends in CHI_3 have been examined since the late 1990s at remote sites between 82.5°N–40.4°S and over the western and northern Pacific Ocean (Yokouchi et al., 2012). CH_3I concentrations declined until 2003, then rose by several tens of percent until 2009/2010. The interannual variation was approximated by a sine curve with a period of 11 y and showed good correlation with the Pacific Decadal Oscillation, suggesting that CH_3I emissions are affected by global-scale sea-surface temperature.

Concentrations of halocarbons in Arctic Ocean surface waters do not appear to have changed much over the last two decades (Karlsson et al., 2013).

2.16.3 Higher molecular weight HNPs

The higher molecular weight HNPs are very diverse (Figure 2.120). The number of compounds identified in sponge extracts and/or dolphin blubber by non-target screening was over 400 in one report (Hauler and Vetter, 2015) and over 300 in another (Shaul et al., 2015). This section covers bromophenolic compounds, which include simple bromophenols (BPs) and compounds derived from them: bromoanisoles (BAs), hydroxylated polybromodiphenyl ethers (OH-BDEs), methoxylated polybromodiphenyl ethers (MeO-BDEs), and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs). Other compound classes included are polyhalogenated 1'-methyl-1,2'-bipyrroles (PMBPs), polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles (PDBPs), polyhalogenated N-methylpyrroles (PMPs), polyhalogenated N-methylindoles (PMIs), bromoheptyl- and bromooctyl pyrroles, (1R,2S,4R,5R,1'E)-2-bromo-1-bromomethyl-1,4-dichloro-5-(2'-chloroethenyl)-5-methylcyclohexane (mixed halogen compound MHC-1), polybrominated hexahydroxanthene derivatives (PBHDs), bromobenzyl alcohols, bromovinyl phenols and bromocoumarates.

2.16.3.1 Physical-chemical properties

Properties of high molecular weight HNPs are given in Annex Table A2.16/5, and include the ionization constant (for BPs, as pK_A) octanol-water partition coefficient (log K_{OW}), air-water partition coefficient (log K_{AW}), octanol-air partition coefficient (log K_{OA}), liquid-phase vapor pressure (log p_L/Pa) and liquid-phase water solubility (log s_L/(mol/m^3)).

2.16.3.2 Sources, production, use and trends

Like halocarbons, the higher molecular weight HNPs are synthesized by a variety of marine organisms (Fielman et al., 1999, 2001; Whitfield et al., 1999; Ballschmiter, 2003; Gribble, 2003, 2010; Lincoln et al., 2005; Vetter, 2006; Malmvarn et al., 2008; Löfstrand et al., 2010; Unger et al., 2010; Guitart et al., 2011; Haraguchi et al., 2011; Agarwal et al., 2015). A recently discovered pathway is production by marine bacteria (Agarwal et al., 2014). Production processes for natural organohalogens in freshwater and marine sediment were reviewed by Müller et al. (1996) and for total organically bound bromine in terrestrial ecosystems by Leri and Myneni (2012). Organically bound chlorine is common in soils (Redon et al., 2013) and is produced in boreal soils by chlorination of organic matter (Gustavsson et al., 2012).

Biosynthesis of BPs by macroalgae occurs from the substrates phenol, 4-hydroxybenzoic acid and 4-hydroxybenzyl alcohol under bromoperoxidase catalysis (Flodin et al., 1999; Flodin and Whitfield, 1999, 2000). Several pathways have been reported for generating OH-BDEs and MeO-BDEs from BPs, namely bromoperoxidase-catalyzed dimerization (Lin et al., 2014a), photolysis (Liu et al., 2011) and coupling on the surface of δ-MnO_2 (Lin et al., 2014b). PBDDs are produced from BPs by bromoperoxidase-catalyzed coupling (Arnoldsson et al., 2012a), and by photolysis of MeO-BDEs (Arnoldsson et al., 2012b) and OH-BDEs (Bastos et al., 2009; Erickson et al., 2012). Marine bacteria also produce OH-BDEs and MeO-BDEs (Agarwal et al., 2014). Marine sponges contain these and more complex PBDEs substituted with multiple OH groups and mixed halogens (Agarwal et al., 2015).

Evidence of natural origin has been obtained by radiocarbon (^{14}C) analysis of 6-OH-BDE47, 2'-OH-BDE68, 2',6-diOH-BDE159, and 2'-MeO-6-OH-BDE120 (Teuten et al., 2005; Guitart et al., 2011), and for 1,1'-dimethyl-3,3',4,4'-tetrabromo-5,5'-dichloro-2,2'-bipyrrole (Reddy et al., 2004). Other studies have noted the presence of 6-MeO-BDE47 and 2'-MeO-BDE68 in environmental samples that pre-dated the advent of PBDEs; namely a whale oil sample archived since 1921 (Teuten and Reddy, 2007), sediment layers deposited since the late 1800s to early 1900s in the southern Yellow Sea and East China Sea (Fan et al., 2014a,b) and in an archived white-tailed sea eagle (*Haliaeetus albicilla*) egg laid in 1941 (Nordlöf et al., 2012).

Phenols and anisoles containing bromine, chlorine, or both also have anthropogenic sources; for example, water chlorination (Corbi et al., 2007; Sim et al., 2009; Pan and Zhang, 2013), industrial use and hazardous waste incineration (Howe et al., 2005), and metabolism or abiotic degradation of brominated flame retardants (Byer et al., 2014). The world production volume of 2,4,6-TriBP was estimated at 9500 tonnes in 2001 (Howe et al., 2005). 1,2,4,5-tetrachloro-3,6-dimethoxybenzene (also known as 2,3,5,6-tetrachloro-1,4-dimethoxybenzene), ubiquitous in marine air, may be a natural product or a metabolite of anthropogenic organochlorines (Wittlinger and Ballschmiter, 1990; Schreitmüller and Ballschmiter, 1995). MeO-BDEs and OH-BDEs are produced by metabolism of PBDE flame retardants (Stapleton et al., 2009).

Other high molecular weight HNPs have sources in marine bacteria, algae and sponges. MHC-1 was first detected in seafood and isolated and fully characterized from a red algae extract (Vetter et al., 2001, 2008). 2,3,4,5-tetrabromo-1-methylpyrrole was identified in the seagrass *Halophila ovalis* (Gaul et al., 2011) and many PDBP congeners were found in sea cucumber (*Holothuria* sp.) (Hauler et al., 2013). The PMBPs, like the PDBPs, are a diverse set of compounds of which the first discovered in the late 1990s was the 2,3,3',4,4',5,5'-heptachloro-1'-methyl-1,2'-bipyrrole, or Q1 (Vetter et al., 1999). Q1 and mixed Cl- and Br-PMBP congeners have subsequently been reported in many species of marine biota (Vetter et al., 1999, 2001, 2003; Teuten et al., 2006; Pangallo and Reddy, 2008; Hauler et al., 2014) particularly from the Pacific Ocean. Recent work points to a microbial source of these compounds based on compound-specific stable nitrogen determination (Pangallo et al., 2012).

2.16.3.3 Transformation processes

Abiotic and biotic degradation pathways for BPs were summarized by Howe et al. (2005). OH radical reaction half-lives in air were estimated as 13.2 h (4-BP), 44.6 h (2,4-DiBP), 22.5 d (2,4,6-TriBP), and 23 d (PeBP). The EPISUITE program predicts OH radical half-lives in air of 4.1 d (2,4-DiBA) and 8.5 d (2,4,6-TriBA). It has been suggested that the ubiquitous presence of OH-BDEs in precipitation is due to OH radical reaction with PBDEs (Ueno et al., 2008).

Bromophenols and OH-BDEs are O-methylated to form BAs and MeO-BDEs. MeO-BDEs and OH-BDEs in sediment are interconverted by O-methylation-demethylation reactions (Zhang et al., 2012; Fan et al., 2014a). MeO-BDEs (Arnoldsson et al., 2012b) and OH-BDEs (Bastos et al., 2009; Erickson et al., 2012) can be photochemically converted to PBDDs. Metabolism also produces OH-BDEs from MeO-BDEs (Wan et al., 2009; Wiseman et al., 2011; Liu et al., 2012; Wang et al., 2012), and it has been suggested that OH-BDEs in wildlife from remote areas arise from demethylation of accumulated MeO-BDEs (Wan et al., 2009). Evidence of this demethylation was not seen in harbor porpoise (*Phocoena phocoena*) (Weijs et al., 2014) nor in ringed seal (*Phoca hispida*) (Kelly et al., 2008), while no conclusions could be drawn for harbor seal (*P. vitulina*) (Weijs et al., 2014). The opposite, conversion of 6-OH-BDE47 to 6-MeO-BDE47 has been shown to occur in the fish Japanese medaka (*Oryzias latipes*) (Wan et al., 2010). Positive correlations among OH-BDEs, MeO-BDEs and 2,4,6-TriBP in cetaceans suggest that they may share common sources or metabolic pathways (Nomiyama et al., 2011, 2014). A strong correlation was found in polar bear (*Ursus maritimus*) adipose tissue between log-transformed 6-OH-BDE47 and 6-MeO-BDE47 ($p<0.001$), ΣOH-BDEs and ΣMeO-BDEs ($p<0.001$), and (ΣOH-BDEs + ΣBPs) and ΣMeO-BDEs ($p<0.001$) (Wan et al., 2009). The ΣOH-BDEs were correlated to ΣPBDEs in plasma of bald eagle (*Haliaeetus leucocephalus*) from British Columbia (Canada) and California (USA) (Cesh et al., 2010).

Significant correlations have been found between 6-MeO-BDE47 and PBDE-47, a possible precursor, in Greenland shark (*Somniosus microcephalus*) (Strid et al., 2010), glaucous gull (*Larus hyperboreus*) (Verreault et al., 2005a), beluga (*Delphinapterus leucas*), ringed seal and seaduck species (Kelly et al., 2008). Jaspers et al. (2013) found significant correlations between 6-MeO-BDE47 or 2'-MeO-BDE68 and all seven monitored PBDE congeners in muscle tissue of white-tailed sea eagle. Rotander et al. (2012a) found such a correlation was significant but weak in the marine mammals they studied.

Many reports indicate that biotransformation of PBDEs produces OH-BDEs with the OH-group *meta-* or *para-* to the diphenyl ether bond, whereas *ortho*-positioning is favored for the naturally produced compounds (reviewed by Wiseman et al., 2011). This interpretation was criticized by Ren et al. (2013), who found hydroxy groups in the *ortho*-position in some OH-BDEs from an e-waste recycling plant. PBDEs substituted with a single OH- in the *para* position are rare in marine species; however, PBDEs containing one *ortho*-MeO- and two OH- (*meta-* and *para-*) have been identified in marine sponges (Agarwal et al., 2015). By analogy, natural

versus PBDE-derived MeO-BDEs might also be distinguished by *ortho-* versus *meta-/para-* substitution of the MeO- group (Marsh et al., 2004). However, since MeO-BDEs have not been identified in PBDE exposure studies, their source remains unclear and the possibility of naturally-produced MeO-BDEs with *meta-/para-* substitution should be considered (Wiseman et al., 2011).

Haglund et al. (2010) examined congener profiles of MeO-BDEs and PBDDs in Baltic perch (*Perca fluviatilis*) and flounder (*Platichthys flesus*) in relation to lower organisms collected in the same area. MeO-BDEs without adjacent substituents (6-MeO-BDE47) or with two adjacent substituents (2'-MeO-BDE68 and 6-MeO-BDE90) were retained in the fish more than MeO-BDEs with three adjacent substituents (6-MeO-BDE85 and 6-MeO-BDE99). For PBDDs, 1,3,6,8-tetraBDD and 1,3,7,9-tetraBDD were retained more than other PBDDs which have vicinal hydrogens. Debromination of 6-MeO-PBDE85 and 6-MeO-BDE99, and cytochrome P-450 mediated oxidation of PBDDs containing vicinal hydrogens were suggested to explain their limited retention.

2.16.3.4 Modeling studies

No modeling studies of higher molecular weight HNPs for the Arctic were available.

2.16.3.5 Environmental concentrations

Air and precipitation

Halophenolic compounds have been identified in air, at concentrations two to three orders of magnitude below the halocarbons (Section 2.16.2.5). BAs have been found in marine air worldwide, but there are few reports. Quantitative measurements in Arctic air were made in 2007–2008 during expeditions to the Labrador Sea, Hudson Bay and the southern Beaufort Sea. Mean (± standard deviation) concentrations of BAs in surface water and air were as shown in Figure 2.121. Earlier, 2,4,6-TriBA had been identified, but not quantified, in air at Zeppelin Mountain (Svalbard) (Vetter et al., 2002). Later, starting in 2007, TriBA was monitored in air at Birkenes in southern Norway and at Zeppelin (Svalbard), and monitoring was started at another Norwegian Arctic station (Andøya) in 2010 (Bohlin-Nizzetto et al., 2015). In 2014, TriBA levels at Zeppelin were among the lowest observed since the start of monitoring (see Figure 2.124 in Section 2.16.3.6), with weekly concentrations of 0.44–12.4 pg/m^3 and an annual mean of 5.37 pg/m^3. Monthly monitoring indicated a seasonal trend in TriBA air concentrations with the lowest levels observed in spring. Concentrations increased in summer and early autumn; a likely consequence of increased algal blooms during the summer months (Bohlin-Nizzetto et al., 2015).

For comparison, BA concentrations measured in air over the northern Baltic (63°48'N; 20°50'E) during 2011–2015 averaged 21±16 pg/m^3 (2,4-DiBA), ≥4 pg/m^3 (2,6-DiBA) and 43±34 pg/m^3 (2,4,6-TriBA) (Bidleman et al., 2016). These concentrations can be compared to mean air concentrations at Lista (southern Norway) in 2003, which were 19±12 pg/m^3 (2,4-DiBA) and 13±9 pg/m^3 (2,4,6-TriBA), with higher concentrations from May–December than January–April (Melcher et al., 2008).

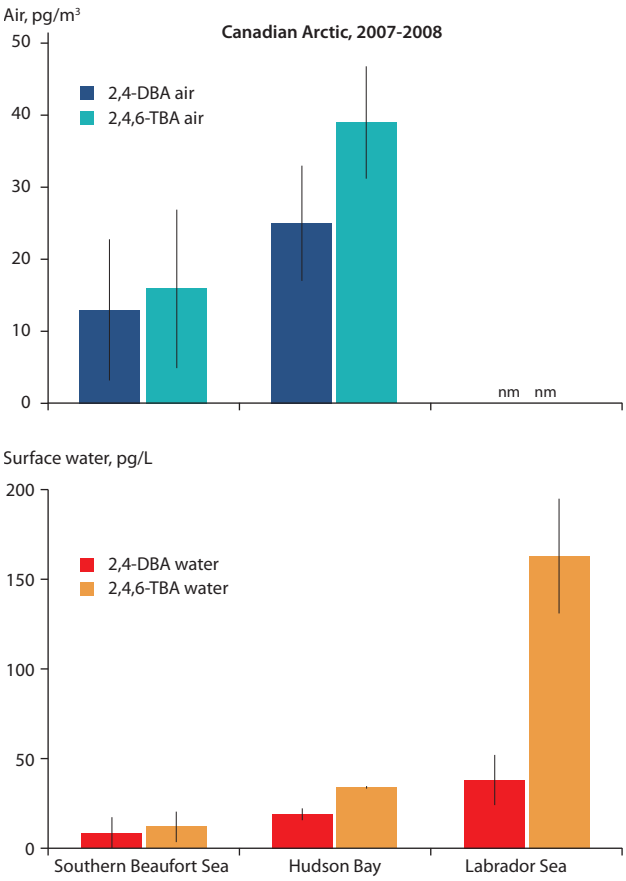

Figure 2.121 Bromoanisoles in surface water and air of the Canadian Arctic, 2007–2008 (mean±SD, nm: air not measured). Data from Wong et al. (2011).

BAs in air and atmospheric deposition (rain, snow, particle fallout) were measured in archived samples collected along a temperate to Arctic gradient in Fennoscandia between 2002 and 2015 (Bidleman et al., 2017). Geometric mean air concentrations were 18–36 pg/m^3 (2,4-DiBA) and 38–65 pg/m^3 (2,4,6-TriBA) at the most southern station Råö on the Swedish west coast (57.39°N, 11.91°E) to 1.9–11 pg/m^3 (2,4-DiBA) and 2.7–11 pg/m^3 (2,4,6-TriBA) at the Arctic station Pallas, Finland (68.00°N, 24.23°E). Intermediate air concentrations were measured in the northern Baltic region (Geometric means 14–30 pg/m^3 for 2,4-DiBA and 15–34 pg/m^3 for 2,4,6-TriBA). Geometric mean deposition fluxes in 2012–2015 were 50–73 pg/m^2/day (2,4-DiBA) and 43–79 pg/m^2/day (2,4,6-TriBA) at Råö; 33–48 pg/m^2/day (2,4-DiBA) and 30–35 pg/m^2/day (2,4,6-TriBA) at Pallas. Deposition fluxes were similar at Råö and Pallas despite lower air concentrations at Pallas, due to greater precipitation scavenging at lower temperatures.

BAs ranging from monobromo- through pentabromo- were previously found on expeditions in the northern and southern hemispheres in 1987, 1993–1994 and 1999–2000. Concentration ranges were: <0.1–2.2 pg/m^3 (2-BA); ≤0.1 pg/m^3 (3-BA); <0.1–3.6 pg/m^3 (4-BA); <0.1–17 pg/m^3 (2,4-DiBA); <0.1–6.2 pg/m^3 (2,6-DiBA); 0.5–69 pg/m^3 (2,4,6-TriBA); <0.1–0.8 pg/m^3 (2,3,4,5-TeBA); <0.1–1.2 pg/m^3 (2,3,4,6-TeBA); <0.1–1.1 pg/m^3 (2,3,5,6-TeBA) and <0.1–5.7 pg/m^3 (PeBA) (Wittlinger and Ballschmiter, 1990; Führer and Ballschmiter,

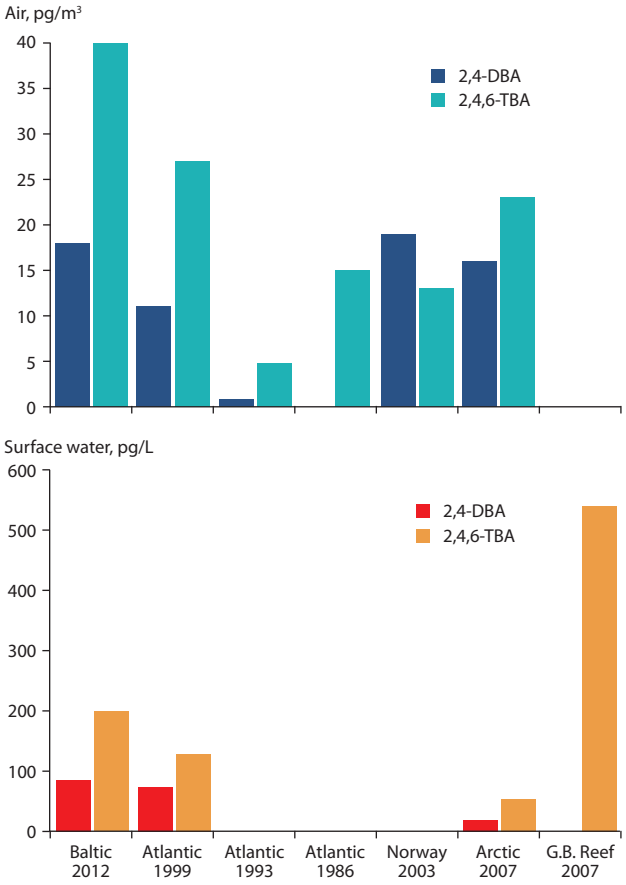

Figure 2.122 Bromoanisoles in ocean surface water and air. Data sources as follows: Baltic-2012 (Bidleman et al., 2014, 2015, 2016), Atlantic-1999 (Pfeifer and Ballschmiter, 2002), Atlantic-1993 (Führer and Ballschmiter, 1998), Atlantic-1986 (Wittlinger and Ballschmiter, 1990), Norway-2003 (Melcher et al., 2008), Arctic-2007 (Wong et al., 2011), Arctic-2007-2014 (Bohlin-Nizzetto et al., 2015), Great Barrier Reef-2007 (Vetter et al., 2009).

1998; Pfeifer and Ballschmiter, 2002). So although data are limited, concentrations of BAs in Arctic air appear comparable to levels seen at lower latitudes (Figure 2.122).

BPs have occasionally been reported in ambient air and deposition in the Arctic. Concentrations of 2,4,6-TriBP in air samples from 2001–2002 were <1 pg/m^3 at Pallas (Finland) as well as the background station of Rörvik on the Swedish west coast (Remberger et al., 2002). These levels can be compared to urban areas of southern Sweden where concentrations were 8–30 pg/m^3. Concentrations of 2,4-DiBP were <10 pg/m^3 at Pallas and Rörvik (Remberger et al., 2002). Atmospheric fluxes (rain, snow, dry particle deposition) at Rörvik were 0.8–4.4 ng/m^2/d (2,4-DiBP) and 1.8–6.6 ng/m^2/d (2,4,6-TriBP); with corresponding fluxes at Pallas of <0.3 ng/m^2/d (2,4-DiBP) and 0.6 ng/m^2/d (2,4,6-TriBP) (Remberger et al., 2002).

BPs were measured in 2014 in air at Pallas and Råö, an Environmental Monitoring and Evaluation Program (EMEP) station not far from Rörvik, as part of a screening study of alternative brominated flame retardants in air (Haglund, 2015). The ranges in air concentration at Råö and Pallas were 1.1–13 and 0.21–3.6 pg/m^3 (2,4-DiBP), 0.050–0.070 and 0.031–0.27 pg/m^3 (2,6-DiBP), 0.48–1.6 and 0.14–1.3 pg/m^3 (2,4,6-TriBP), respectively. MonoBPs were measured at 0.54–4.1 pg/m^3 at Råö and 0.21–9.3 pg/m^3 at Pallas for individual species.

Sea-air exchange of BAs has been estimated using concentrations in surface seawater and air, employing the Henry's law constants reported by Pfeifer et al. (2001) (Annex Table A2.16/5). BAs in Hudson Bay and the southern Beaufort Sea were close to air-water equilibrium or showed net volatilization. Net fluxes (deposition minus volatilization) estimated by the Whitman two-film model were small: -1.2±0.69 (2,4-DiBA) and -0.46±1.1 ng/m^2/d (2,4,6-TriBA) (Wong et al., 2011). A larger departure from equilibrium was found in the northern Baltic Sea, where net volatilization fluxes between May and September were -12 to -44 ng/m^2/d (2,4-DiBA) and -54 to -310 ng/m^2/d (2,4,6-TriBA) using the Pfeifer et al. (2001) Henry's law constants (Bidleman et al., 2014, 2015). By comparison, estimated net fluxes of $CHBr_3$ for 50–80°N were about -860 to -5200 ng/m^2/d by the two-film model (see Figure 2.118).

Recently, experimental measurements of Henry's law constants for 2,4-DiBA and 2,4,6-TriBA were made as functions of temperature (Bidleman et al., 2016) (Annex Table A2.16/5). These are lower than the Pfeifer et al. (2001) values. BA volatilization fluxes from the northern Baltic were lowered to about half the previous estimates using these new Henry's law constants (Bidleman et al., 2016). The new Henry's law constants were also used to reassess the gas exchange of BAs in Hudson Bay and the southern Beaufort Sea, based on the 2007–2008 air and water data (Wong et al., 2011), with the result that 2,4,6-DiBA was near air-water equilibrium, while 2,4-DiBA was near equilibrium or undergoing net deposition (F. Wong, Environment and Climate Change Canada, unpubl.). Outgassing of BAs from the temperate and tropical Atlantic Ocean has also been reported, but fluxes were not quantified (Pfeifer and Ballschmiter, 2002).

Two chlorinated phenolic compounds routinely monitored in Arctic air at the Canadian station Alert are pentachloroanisole (PCA, annual means 1–12 pg/m^3) and tetrachloroveratrole (1,2,3,4-tetrachloro-5,6-dimethoxybenzene) (annual means 0.67–2.0 pg/m^3) (Hung et al., 2005). Chloroanisoles (CAs) including PCA and bromochloroanisoles have also been identified over oceans in the northern and southern hemispheres (Atlas et al., 1986; Wittlinger and Ballschmiter, 1990; Schreitmüller and Ballschmiter, 1995; Führer and Ballschmiter, 1998; Pfeifer and Ballschmiter, 2002). Concentration ranges were: <0.1–16 pg/m^3 (2,6-DiCA); <0.1–243 pg/m^3 (2,4,6-TriCA); <0.1–0.7 pg/m^3 (2,3,4,5-TeCA); <0.1–11 pg/m^3 (2,3,4,6-TeCA); 0.2–40 pg/m^3 (PCA); 1.6–5.7 pg/m^3 (2,4-dibromo-6-chloroanisole) and 0.6–2.5 pg/m^3 (2,6-dibromo-4-chloroanisole) (Wittlinger and Ballschmiter, 1990; Führer and Ballschmiter, 1998; Pfeifer and Ballschmiter, 2002). Another chlorophenolic compound found in marine air is 1,2,4,5-tetrachloro-3,6-dimethoxybenzene (also known as 2,3,5,6-tetrachloro-1,4-dimethoxybenzene), not to be confused with the tetrachloroveratrole mentioned above. Concentrations of 1,2,4,5-tetrachloro-3,6-dimethoxybenzene in marine air were 2–96 pg/m^3 over the North and South Atlantic oceans (Schreitmüller and Ballschmiter, 1995) and 20–280 pg/m^3 at Réunion (Wittlinger and Ballschmiter, 1990). There is concern that this compound may coelute with PCA, a common organochlorine found in Arctic air, on some gas chromatography columns. This may lead to inflation of PCA levels when using electron capture detection, including those measured at Alert up to 2012.

It is not known whether the CAs and related compounds are natural, formed from anthropogenic phenols, or both (see discussion in Section 2.12 for PCP and PCA). Higher concentrations were found in the northern hemisphere than the southern hemisphere, suggesting anthropogenic origins (Schreitmüller and Ballschmiter, 1995; Führer and Ballschmiter, 1998). In contrast, BAs were highest near upwelling zones off the coast of Africa (Führer and Ballschmiter, 1998; Pfeifer and Ballschmiter, 2002). The tetrachloroveratrole found in air at Alert may have origins in the chlorine bleaching process used for pulp and paper (Brownlee et al., 1993).

No data on MeO-BDEs in Arctic air are available but mean concentrations of 0.017±0.016 pg/m^3 (2'-MeO-BDE68) and 0.014±0.014 pg/m^3 (6-MeO-BDE47) were found in air over the northern Baltic Sea in 2011–2013 (Bidleman et al., 2016). These levels are much lower than those reported for the Σtribromo- and Σtetrabromo-MeO-BDEs in air (gas phase) of Busan (South Korea) in 2010–2011 (means 2.1±1.8 and 6.9±8.7 pg/m^3, respectively) (Kim et al., 2014c, 2015).

Terrestrial environment

Organically bound bromine is widespread in the terrestrial environment. X-ray absorption near edge structure (XANES) spectroscopic studies show that all the bromine in isolated humic substances, decaying plant material, and the organic fraction of soils is covalently bonded to carbon (Leri and Myneni, 2012). Organically bound chlorine in soils is discussed in Section 2.16.3.2.

No reports were found for most high molecular weight HNPs in Arctic soils or plants (PCP and PCA are discussed below and in Section 2.12). BPs were determined in moss around two incinerator facilities on the subarctic Faroe Islands (62°N, 7°W) in 2009. Levels at one site were 0.53 ng/g dw (2,4-DiBP) and 0.46 ng/g dw (2,4,6-TriBP) and <0.3 ng/g dw (2,4-DiBP) and <0.1 ng/g dw (2,4,6-TriBP) at the other (Schlabach et al., 2011). In comparison, two soil samples from Gårdsjön research forest in southern Sweden contained higher concentrations: <3–15 ng/g dw (2,4-DiBP) and 2–5 ng/g dw (2,4,6-TriBP) (Remberger et al., 2002).

Although biogenic MeO-BDEs are mainly associated with the marine environment, there may be terrestrial sources which have not yet been identified. There are no published studies of MeO-BDEs or OH-BDEs in Arctic soils. However, MeO-BDEs and OH-BDEs have been found in soils and pine needles near Busan (South Korea) sampled in 2010–2011 at pg/g levels (Kim et al., 2014c, 2015).

PCA has been extensively investigated in air and vegetation and was thought to be primarily a metabolite of the PCP wood preservative. However, a recent study casts doubt on this (Section 2.12). The two compounds are poorly correlated in conifer needles, with PCP dominating in temperate North America and Europe, and PCA dominating in the Arctic (see Figure 2.12/1). Anthropogenic versus natural origins of PCA are still unclear.

Freshwater environment

Pike (*Esox lucius*) from subarctic Lake Storvindeln (collected 1993) in the north and Lakes Bolmen (collected 1967–2000) and Roxen (collected 1972) in southern Sweden were analyzed for PBDEs and MeO-BDEs (Kierkegaard et al., 2004b). 2'-MeO-BDE68 and 6-MeO-BDE47, two congeners shown to have biogenic origins in the marine environment (Section 2.16.3.2), were found in all years. Highest concentrations of 6-MeO-BDE47 and 2'-MeO-BDE68 were found in muscle of pike from Lake Bolmen (290–3600 and 110–1800 pg/g ww) > Lake Storvindeln (35 and 110 pg/g ww) > Lake Roxen (1.9 and 1.4 pg/g ww). MeO-BDE levels in pike were equal to or greater than PBDE concentrations, but did not correlate with PBDEs nor did they show relationships with eutrophication, location or sampling season. Concentrations of 2'-MeO-BDE68 and 6-MeO-BDE47 in Arctic char (*Salvelinus alpinus*) collected from the Arctic Lake Abiskojaure in 2005 were 15 and 4 ng/g lw (Nordlöf et al., 2010).

Geometric mean concentrations of ΣMeO-BDEs (2'-MeO-BDE68 + 6-MeO-BDE47 + 5-Cl-6-MeO-BDE47) in eggs of white-tailed sea eagle from freshwater lakes in Sweden were 86 ng/g lw in the Arctic region (collected 1994–2005) and 39 ng/g lw in central and southern inland habitats (1992–2005). Geometric mean ΣPBDE concentrations in these birds were 720 and 1500 ng/g lw, respectively (Nordlöf et al., 2010).

Marine environment: bromophenolic HNPs

Seawater and sediment

BAs in seawater were measured on expeditions across the Canadian Arctic Archipelago and the southern Beaufort Sea in 2007–2008 (Wong et al., 2011). Mean concentrations in surface water of the southern Beaufort Sea off Banks Island were 8.8±7.7 pg/L (2,4-DiBA) and 10.2±8.1 pg/L (2,4,6-TriBA). Higher concentrations of the two BAs were found in Hudson Bay and Hudson Strait (19±3.3 and 34±0.7 pg/L) and the Labrador Sea (38±14 and 163±32 pg/L) (see Figure 2.121). It is possible that BAs in surface seawater may have arrived via air or ocean current transport from lower latitudes, but the wide variation in concentrations and differing compound proportions suggests local production, as for halocarbons (Section 2.16.2.5). Concentrations of BAs in Arctic seawater are lower than those reported for the Baltic Sea, Atlantic Ocean and on the Great Barrier Reef (Figure 2.122).

No data are available for BPs in seawater in the Arctic, but they have been identified in surface water and sediment of the North Sea and southern Baltic Sea (Weigel et al., 2005; Reineke et al., 2006).

No reports of other high molecular weight HNPs in Arctic seawater were found. Mean concentrations in northern Baltic Sea seawater in 2011–2013 were 25±17 pg/L (6-MeO-BDE47) and 8.2±5.9 pg/L (2'-MeO-BDE68) (Bidleman et al., 2016).

Concentrations in sediment at harbor sites in the Faroe Islands were 0.79–2.9 ng/g dw (2,4-DiBP) and 0.47–7.8 ng/g dw (2,4,6-TriBP), while ranges for other areas in Scandinavia were <0.07–1.7 ng/g dw (2,4-DiBP) and <0.02–4.8 ng/g dw (2,4,6-TriBP) (Schlabach et al., 2011). BPs are widespread in temperate marine sediments, especially if they contain infauna which produce them (Fielman et al., 2001; Lincoln et al., 2005).

MeO-BDEs or OH-BDEs were not found in sediment of eastern Hudson Bay or Hudson Strait in the Canadian Arctic Archipelago, sampled 1999–2003, at detection limits of 1–4 pg/g dw (Kelly et al., 2008). PBDDs have not been

reported in sediment from the Arctic. MeO-BDEs and OH-BDEs (Zhang et al., 2012; Fan et al., 2014a,b) and PBDDs (Terauchi et al., 2009; Haglund et al., 2010) have been reported in temperate marine sediments.

Marine vegetation

The bromophenolic compound 2,3-dibromo-4,5-dihydroxybenzyl alcohol was identified in the red alga *Polysiphonia arctica*, collected from Kongsfjorden, Spitzbergen (Dummermuth et al., 2003). Neither OH-BDEs nor MeO-BDEs were found in macroalgae from eastern Hudson Bay at detection limits of 0.06–0.2 ng/g lw (Kelly et al., 2008). No other reports from the Arctic were found. Production of higher molecular weight HNPs by macroalgae and phytoplankton in temperate and tropical ecosystems is well documented (Section 2.16.3.2).

Invertebrates

Low bioaccumulation of BPs is expected because of their low log K_{OW} values: 2.56–3.48 (2,4-DiBP), 3.74–4.24 (2,4,6-TriBP) (Howe et al., 2005) and dissociation at seawater pH. BAs are neutral and have higher log K_{OW} – 3.75 (DiBA) and 4.44 (2,4,6-TriBA) – and therefore higher bioaccumulation potential (Pfeifer et al., 2001). Nonetheless, concentrations of BPs were similar or higher than those of BAs in blue mussel (*Mytilus edulis*) from three sites on the Baltic or Swedish west coast, sampled in 2008. Mean concentrations were in the range 2.4–16 ng/g eom (extractable organic matter) (2,4-DiBP), 11–28 ng/g eom (2,4,6-TriBP), nd–3.5 ng/g eom (2,4-DiBA), and 1.9–46 ng/g eom (2,4,6-TriBA) (Löfstrand et al., 2010). Pooled samples of blue mussel collected from 10 stations in the Baltic Proper in 2011–2012 contained 0.56–44 ng/g lw (2,4-DiBP), 17–240 ng/g lw (2,4,6-TriBP), 0.33–5.3 ng/g lw (2,4-DiBA), and 5.2–66 ng/g lw (2,4,6-TriBA) (Dahlberg et al., 2016a). Hauler et al. (2014) found 2,4,6-TriBA in the majority of blue mussels, collected from the Baltic Sea and North Sea between 2007 and 2012, at concentrations of <0.1–19 ng/g lw.

2,4,6-TriBA was found in invertebrates sampled in 2003 along the Norwegian coast (Vetter et al., 2007). Periwinkle (*Littorina littorea*) from Sklinna contained 0.50 ng/g ww, and the range in blue mussel from the Trondheim Fjord at Munkholmen and Ekne was 1.6–9.8 ng/g ww. 2,6-DiBA was found at Ekne at 0.49 ng/g ww. BPs or BAs have not been reported in other Arctic/subarctic invertebrates. Concentrations of 2,4,6-TriBA in Antarctic krill (*Euphausia superba*) were 57–398 pg/g lw (Bengtson-Nash et al., 2008). Several species of Antarctic sponge contained 2,4-DiBP, 2,4,6-TriBP and their corresponding BAs (Vetter and Janussen, 2005).

OH-BDEs were not found in blue mussel from eastern Hudson Bay at detection limits of 0.06–0.2 ng/g lw. However, the geometric mean concentrations of ΣMeO-BDEs and ΣPBDEs were 14 and 5.4 ng/g lw, respectively (Kelly et al., 2008). Concentrations of the predominant congeners were 2.3–34 ng/g lw (6-MeO-BDE47) and 0.8–10 ng/g lw (2'-MeO-BDE68). Other MeO-BDEs found were 2'-MeO-BDE28, 6'-MeO-BDE49 and 6'-MeO-BDE66. Blue mussel from Munkholmen contained 0.15–0.48 ng/g ww of 2'-MeO-BDE68 while 6-MeO-BDE47 was found only at Ekne at 0.28 ng/g ww. Periwinkle from Sklinna contained 0.042 ng/g ww of each MeO-BDE (Vetter et al., 2007).

PBDDs have not been reported in Arctic invertebrates.

Fish, seabirds and marine mammals

Most studies of bromophenolic HNPs in Arctic/subarctic regions have concerned fish, seabirds and marine mammals. Reports are summarized in three Annex tables (Tables A2.16/6, A2.16/7, A2.16/8) as ranges, means (arithmetic or geometric) or medians of 2,4,6-TriBP, 2,4,6-TriBA, two abundant MeO-BDE congeners (6-MeO-BDE47 and 2'-MeO-BDE68) and their OH-analogs, and ΣMeO-BDEs and ΣOH-BDEs. The ΣPBDEs and BDE-47 are also listed where available. PBDDs appear not to have been investigated in the Arctic in these organisms. 6-MeO-BDE47 concentrations generally exceed those for 2'-MeO-BDE68. The following discussions include some reports from the Baltic region and southern-central Norway for comparison with Arctic/subarctic regions.

Fish

2,4,6-TriBA, MeO-BDEs and PBDEs were measured in 20 Greenland shark muscle and liver samples collected in 2001–2003 from Icelandic waters (Strid et al., 2010). Median concentrations of 2,4,6-TriBA in muscle and liver were 0.37 and 0.38 ng/g lw, respectively. Median concentrations of ΣMeO-BDEs for muscle and liver were both 100 ng/g lw, which was higher than for the ΣPBDEs (35 and 41 ng/g lw, respectively). The predominant congeners were 6-MeO-BDE47 and 2'-MeO-BDE68. A significant correlation was found between log-transformed concentrations of 6-MeO-BDE47 and BDE-47 in Greenland shark muscle, but not liver. Concentrations of the two OH-BDE analogs of these were much lower at <0.01–0.11 ng/g lw.

Geometric mean concentrations of ΣMeO-BDEs in muscle of fish from Hudson Bay (collected 1999–2003) were 9.9 ng/g lw (polar cod, *Boreogadus saida*), 3.0 ng/g lw (sculpin, *Myoxocephalus scorpioides*) and 42 ng/g lw (salmon, *Salmo* sp.). The geometric mean concentrations of ΣPBDEs were 9.8, 73 and 9.3 ng/g lw, respectively. OH-BDEs were not detected (Kelly et al., 2008).

Cod liver from Vestertana Fjord (Finland) collected between 1987 and 1998 contained two structurally unidentified tetraMeO-BDEs with total concentrations 0.32–17.3 ng/g lw (Sinkkonen et al., 2004). In the same study, whole-body homogenates of 40 pooled Atlantic salmon (*Salmo salar*) collected from Hraunsfjördur (Iceland) in 1998 contained 3.0 ng/g lw (ΣMeO-BDEs) and 12 ng/g lw (ΣPBDEs).

Cod liver from Trondheim Fjord contained 6.3–6.4 ng/g ww 2,4,6-TriBA, 0.75 ng/g ww 2,6-DiBA, 2.5–3.3 ng/g ww (Σ2'-MeO-BDE68 + 6-MeO-BDE47) and 19-22 ng/g ww Σ_6PBDEs. Saithe (*Pollachius virens*) liver from Sklinna contained 54.7 ng/g ww 2,4,6-TriBA, 1.7 ng/g ww 2,6-DiBA, 1.4 ng/g ww (Σ2'-MeO-BDE68 + 6-MeO-BDE47) and 14 ng/g ww Σ_6PBDEs (Vetter et al., 2007).

A few reports from the Baltic Sea are available for comparison. MeO-BDEs and similar compounds with both bromine and chlorine substitution were identified in Baltic salmon, but levels were not quantified (Marsh et al., 2004). Salmon muscle, sampled in 1991 contained ng/g lw ΣMeO-BDE (structures not identified) of 40, while the ΣPBDE concentrations was 300 ng/g lw (Haglund et al., 1997). ΣMeO-BDE concentrations in perch muscle collected between 1990 and 2005 averaged 34 ng/g lw (Haglund et al., 2010), which is similar to the

salmon concentrations. ΣMeO-BDE concentrations in liver of Baltic cod caught in 2013 averaged 5.4±2.9 ng/g lw, which is of the same order of magnitude as concentrations for cod in Trondheim Fjord. The mean ΣOH-BDE concentration in these cod liver samples was 2.8±1.3 ng/g lw, while Σ_{36}PBDEs was 58±31 ng/g lw (Roszko et al., 2015). Baltic herring (*Clupea harengus*) collected in 1993 contained 0.38 ng/g ww 6-MeO-BDE47 and 0.11 ng/g ww 2'-MeO-BDE68 (Kierkegaard et al., 2004b). Herring collected in 2012 from two Baltic Proper sites contained 9.3–420 ng/g lw 6-MeO-BDE47 and 1.5–73 ng/g lw 2'-MeO-BDE68 (Dahlberg et al., 2016b).

Seabirds

White-tailed sea eagles from Greenland were sampled in 2007–2009 (Jaspers et al., 2013). Median ΣMeO-BDE concentrations were 41, 16, 29, 26, 22, and 8.8 ng/g lw in muscle, preen oil, liver, kidney, blood and adipose tissue, respectively, and consisted of 56–75% 6-MeO-BDE47. Median ΣPBDE concentrations in these tissues were 420, 190, 180, 150, 150 and 150 ng/g lw, respectively. Significant correlations were found between individual BDE congeners and the MeO-BDEs, which suggests similar bioaccumulation pathways.

For comparison, geometric mean concentrations of ΣMeO-BDEs in egg of white-tailed sea eagle from the southern Bothnian Sea (collected 1992–2004) and Baltic Proper (1994–2001) were 350 and 230 and ng/g lw, and the ΣPBDEs averaged 4200 ng/g lw. These Baltic ΣMeO-BDEs concentrations were 4–6 times higher than in white-tailed sea eagle egg from northern and southern inland locations in Sweden, while the Baltic/inland ratios for ΣPBDEs were 3–6 (Nordlöf et al., 2010). Geometric mean concentrations in five white-tailed sea eagle eggs from 1996–2001 collections on the southern Baltic coast were 23 ng/g lw 2'-MeO-BDE68, 90 ng/g lw 6-MeO-BDE47 and 3120 ng/g lw ΣPBDEs (Nordlöf et al., 2012).

HNPs and PBDEs were measured in blood, plasma, liver, egg yolk and whole body (with and without feathers) of glaucous gull collected in the Norwegian Arctic between 2002 and 2006 (Verreault et al., 2005a, 2007a,b,c) (Annex Table A2.16/7). Concentrations (mean±SD) in blood of glaucous gull from Svalbard in 2002 were 3.54±0.97 ng/g ww (ΣOH-BDEs), 2.78±0.80 ng/g ww (ΣMeO-BDEs) and 51.5±15.9 ng/g ww (ΣPBDEs). Concentrations in liver were 3.57±2.83 ng/g ww (ΣOH-BDEs), 32.2±12.4 ng/g ww (ΣMeO-BDEs) and 522±154 ng/g ww (ΣPBDEs). Whole-body homogenate samples (without feathers) had concentrations of 0.27±0.07 ng/g ww (ΣOH-BDEs), 19.4±4.3 ng/g ww (ΣMeO-BDEs) and 202±20 ng/g ww (ΣPBDEs) (Verreault et al., 2007c). Means in plasma of male and female glaucous gull from Bjørnøya in 2004 and 2006 ranged from 0.37±0.07 to 2.7±1.3 ng/g ww (ΣOH-BDEs), 0.67±0.10 to 2.1±0.4 ng/g ww (ΣMeO-BDEs), and 8.6±1.1 to 21.3±5.4 ng/g ww (ΣPBDEs) (Verreault et al., 2007a,b). Concentrations in egg yolk were 20.2±2.7 ng/g ww (ΣMeO-BDEs) and 163±14 ng/g ww (ΣPBDEs). OH-BDEs were not determined in the egg yolk (Verreault et al., 2007b).

Eggs of guillemot (*Uria aalge*) were collected between 2002 and 2005 from Vestmannaeyjar (Iceland), Sandøy (Faroe Islands), and Hjelmsøya, Bjørnøya and Sklinna (Norway), with comparative sampling at Stora Karlsö in the Baltic Proper. The range of geometric mean concentrations of BDE-47 in Arctic/subarctic birds was 5.9–38 ng/g lw. MeO-BDEs were only detected at the Baltic site: geometric means of 9.8 ng/g lw 2'-MeO-BDE68, 5.1 ng/g lw 6-MeO-BDE47 and 2.9 ng/g lw 6-MeO-BDE90, and the Baltic guillemots had a geometric mean BDE-47 concentration of 120 ng/g lw. Concentration ranges of 6-OH-BDE47 and 2'-OH-BDE68 in Arctic/subarctic birds were 0.44–17 and ND–0.53 ng/g lw, respectively (Jörundsdóttir et al., 2009). A whole-body homogenate of guillemot from the Baltic Proper, collected in 1998, contained 2.0 ng/g lw of Σtetrabrominated MeO-BDEs with unidentified structures, but no MeO-BDEs were found in guillemot from the Norwegian west coast. The ΣPBDEs in the Baltic versus Norwegian coastal guillemot were 231–332 and 76–118 ng/g lw, respectively (Sinkkonen et al., 2004).

Eggs of common eider (*Somateria mollisima*) were collected in 2012 from the Norwegian coastal sites of Sklinna and Røst (Huber et al., 2015). The ΣBP concentrations were 0.29–23 ng/g ww in two egg pools from Sklinna. Lower variation in concentrations was seen in three egg pools from Røst (0.29–1.1 ng/g ww). 2,4,6-TriBP and 2,4,6-TriBA concentrations in eggs were 0.29–21 and 0.55–1.1 ng/g ww, respectively, at Sklinna and 0.29–0.67 and 0.25–0.61 ng/g ww, respectively at Røst. The ΣPBDE concentrations in eggs from Sklinna and Røst were 0.77–1.39 and 0.55–1.40 ng/g ww, respectively. Geometric mean concentrations of ΣMeO-BDE in livers of common eider collected between 1999 and 2003 in Hudson Bay (Canada) were 1.3 and 2.1 ng/g lw, while the ΣPBDE concentrations were 20 and 71 ng/g lw (Kelly et al., 2008).

Long-tailed duck (*Clangula hyemalis*) which breeds in freshwaters of Siberia and northern Europe were collected in the Baltic Proper between 2000 and 2009 and their livers analyzed for BPs, BAs, OH-BDEs and MeO-BDEs (Dahlberg et al., 2016a). Concentration ranges were 0.22–3.1 ng/g lw (ΣBP), 0.63–1.2 ng/g lw (ΣBA), 3.4–8.0 ng/g lw (ΣOH-BDE) and 2.3–6.9 ng/g lw (ΣMeO-BDE). The latter two classes were dominated by 6-OH-BDE47, 6-OH-BDE99, 6-MeO-BDE47 and 6-MeO-BDE99.

Two studies have examined bromophenolic HNPs in egg and liver samples from European shag (*Phalacrocorax aristotelis aristotelis*) from coastal Norway, at Sklinna (Vetter et al., 2007; Huber et al., 2015) and Røst (Huber et al., 2015). 2,4,6-TriBA concentrations in shag egg samples collected in 2012 were 0.45–1.02 ng/g ww (Sklinna) and 1.45–1.76 ng/g ww (Røst) (Huber et al., 2015). In comparison, 2,4,6-TriBA concentrations in egg and liver samples from Sklinna collected in 2003 were 0.35–11.4 and 0.61–3.3 ng/g ww, respectively (Vetter et al., 2007). 2'-MeO-BDE28 and 6-MeO-BDE47 concentrations in the 2003 egg samples from Sklinna were 0.023–0.09 and 0.059–0.36 ng/g ww, while liver samples contained only 2'-MeO-BDE68 at 0.18–12.8 ng/g ww. ΣPBDE concentrations in the 2012 shag egg samples were 2.0–3.9 ng/g ww (Huber et al., 2015), while ΣPBDE concentrations in shag egg and liver samples collected in 2003 were 0.8–4.9 and 0.13–0.43, respectively (Vetter et al., 2007).

Herring gull (*Larus argentatus*) egg samples from Sklinna and Røst collected in 2012 contained 2,4,6-TriBA concentrations of 0.10–0.13 and 0.10–0.57 ng/g ww, respectively, 2,4,6-TriBP concentrations of 0.12–0.17 and 0.26–0.50 ng/g ww, respectively and ΣPBDE concentrations of 9.8–13 and ND–6.8 ng/g ww, respectively (Huber et al., 2015).

Geometric mean concentrations of ΣMeO-BDEs and ΣPBDEs in liver of white-winged scoter (*Melanitta fusca*) from eastern Hudson Bay were 1.3 and 71 ng/g lw; OH-BDEs were not determined (Kelly et al., 2008).

2,4,5-TriBA concentrations in liver of northern fulmar from Bjørnøya averaged 0.6±0.1 4 ng/g lw (Knudsen et al., 2007).

PBDDs have not been reported in Arctic seabirds.

Marine mammals

Rotander et al. (2012a) determined MeO-BDEs and PBDEs in pooled blubber samples of pilot whale (*Globicephala melas*), ringed seal, minke whale (*Balaenoptera acutorostrata*), fin whale (*B. physalus*), harbor porpoise, hooded seal (*Cystophora cristata*), and Atlantic white-sided dolphin (*Lagenorhynchus acutus*), collected from Arctic and subarctic locations off the Faroe Islands, Norway, Greenland and Iceland, over a period of more than 20 years (1986–2009). The ranges of concentration for 2'-MeO-BDE68, 6-MeO-BDE47, BDE-47 and Σ_{10}PBDEs in each species and year are given in Annex Table A2.16/8. The overall concentration ranges for all marine mammal species were 0.2–23 ng/g lw (2'-MeO-BDE68), 0.3–653 ng/g lw (6-MeO-BDE47), 2.4–1389 ng/g lw (BDE-47) and 18–2792 ng/g lw (ΣPBDEs). Highest MeO-BDE levels were found in the toothed whales (pilot whale and white-sided dolphin), and these often exceeded concentrations of BDE-47. Levels were lower in the baleen whale species (minke whale and fin whale), and lowest in hooded seal and ringed seal. Strong correlations were found between the log-transformed concentrations of 2'-MeO-BDE68 and 6-MeO-BDE47 in seven marine mammal species from the North Atlantic and western Greenland. Out of 14 OH-BDEs sought in pilot whale plasma (sampled 2010–2011), only 4'-OH-BDE was found in 10 animals at 1.77±0.40 ng/g ww, and 6-OH-BDE was found in one whale at 0.8 ng/g ww (Hoydal et al., 2015).

Liver samples from two beluga from Hudson Bay (collected 2002–2003) contained 2'-MeO-BDE68 and 6-MeO-BDE47, whereas two beluga liver samples collected from the St. Lawrence estuary (2000–2003) in southern Canada contained 4'-MeO-BDE17 and 6-MeO-BDE47. The sum concentration of these two congeners in both locations was 43–100 ng/g lw in Hudson Bay and 20–25 ng/g lw in the St. Lawrence estuary (McKinney et al., 2006). Hudson Bay beluga blubber samples collected between 1999 and 2003 contained geometric mean ΣMeO-BDE concentrations of 310 ng/g lw (calves), 62 (females) and 300 ng/g lw (males). The predominant congeners were 6-MeO-BDE47 and 2'-MeO-BDE68. Other compounds found at lower levels were 6'-MeO-BDE17, 2'-MeO-BDE28, 4-MeO-BDE42, 5-MeO-BDE47, 6'-MeO-BDE49, 6'-MeO-BDE66, 6-MeO-BDE90 and 6-MeO-BDE99. Geometric mean concentrations of ΣOH-BDEs were 0.23 ng/g lw (calves), 0.06 ng/g lw (females) and 0.1 ng/g lw (males), whereas ΣPBDE concentrations averaged 27 ng/g lw (calves), 16 ng/g lw (females) and 34 ng/g lw (males). MeO-BDEs and PBDEs were also reported in beluga milk (females), whole blood (males and females) and liver (males) (Annex Table A2.16/8) (Kelly et al., 2008).

The geometric mean ΣMeO-BDE concentration in blubber samples of male ringed seal collected from Hudson Bay was 6.7 ng/g lw and consisted almost entirely of 6-MeO-BDE47 (67%) and 2'-MeO-BDE68 (27%). The geometric mean concentration of Σ_{15}PBDEs was 11 ng/g lw. OH-BDE congeners were below 0.007 ng/g lw (Kelly et al., 2008). OH-BDEs and PBDEs were reported in plasma of ringed seals from Svalbard and the Baltic Sea (Routti et al., 2009a). For the Svalbard animals, the mean concentrations of ΣOH-BDEs and Σ_{10}PBDEs were 0.019 (consisting of only 6-OH-BDE47) and 1.1 ng/g ww, respectively. Levels were higher in Baltic seals, averaging 0.36 ng/g ww ΣOH-BDEs and 7.1 ng/g ww ΣPBDEs. A greater variety of OH-BDEs was found in Baltic seals, consisting of 2'-OH-BDE68, 6-OH-BDE67, 3-OH-BDE47, 6-OH-BDE90 all at 0.066–0.079 ng/g ww and 4'-OH-BDE49 at 0.026 ng/g ww.

Blubber of ringed seals sampled in East Greenland in 1986, 2000 and 2006 were analyzed for 6-MeO-BDE47, 2'-MeO-BDE68 and Σ_{10}PBDEs. In 1986, concentrations were 1.6–2.8 ng/g lw 6-MeO-BDE47, 0.5–0.8 ng/g lw 2'-MeO-BDE68) and 27–38 ng/g lw (Σ_{10}PBDEs. Corresponding concentrations in 2000 were 1.4–2.2 ng/g lw, 0.4–0.9 ng/g lw and 34–72 ng/g lw, and in 2006 were 0.3–2.1 ng/g lw, 0.2–0.4 ng/g lw and 23–34 ng/g lw (Rotander et al., 2012a). Out of 15 MeO-BDEs and 14 OH-BDEs sought in ringed seal blubber from East Greenland in 2010–2011, only 6-MeO-BDE47, 2'-MeO-BDE68, 6-MeO-BDE85, and 6-OH-BDE47 were found. Concentrations were 4.6±0.4 ng/g lw (ΣMeO-BDEs) and 0.7±0.5 ng/g lw (6-OH-BDE47), while the ΣPBDE concentration was 149±87 ng/g lw (Letcher et al., 2009). Biomagnification factors from ringed seal to polar bear (adipose tissue) were 1.0 (Σ_3MeO-BDEs), 1.3 (6-OH-BDE47), and 0.64 (ΣPBDEs).

Only two OH-BDE congeners were detected among the 14 congeners monitored in polar bears from East Greenland (collected 1999–2001) (Gebbink et al., 2008b). There were tissue-specific differences. 6-OH-BDE-47 was found only in adipose tissue, while 3-OH-BDE-47 was found mainly in blood but also in adipose tissue. These tissues were also screened for 15 MeO-BDE congeners (4'-MeO-BDE17, 6'-MeO-BDE17, 2'-MeO-BDE28, 4-MeO-BDE42, 3-MeO-BDE47, 5-MeO-BDE47, 6-MeO-BDE47, 4'-MeO-BDE49, 6'-MeO-BDE49, 2'-MeO-BDE68, 6-MeO-BDE85, 6-MeO-BDE90, 6-MeO-BDE99, 2-MeO-BDE123, 6-MeO-BDE137). Only three MeO-BDE congeners were detected in the adipose tissue and blood and none in liver or brain. ΣOH-BDE concentrations were 0.9±0.5 ng/g ww (adipose tissue) and 2.9±1.0 ng/g ww (blood), while ΣMeO-BDE concentrations were <0.1–25 (adipose tissue) and <0.19–0.78 ng/g ww (blood). Concentrations of ΣPBDEs were 83±19 ng/g ww (adipose tissue), 1.2±0.1 ng/g ww (blood), 2.9±0.4 ng/g ww (brain), and 40±4 ng/g ww (liver). In a study of Svalbard polar bears sampled in 2002, concentration ranges were <0.01–0.17 ng/g ww (ΣMeO-BDEs) and <0.08–0.54 ng/g ww (ΣOH-BDEs), while the range of ΣPBDEs was 2.65–9.72 ng/g ww (Verreault et al., 2005a).

The ΣBP, ΣOH-BDE, ΣMeO-BDE and ΣPBDE concentrations in liver of polar bear, collected in Alaska, between 1993 and 2002, averaged 0.15±0.19, 0.023±0.015, 0.012±0.009 and 0.74±0.23 ng/g ww, respectively (Wan et al., 2009). There were strong correlations between log-transformed concentrations of 6-OH-BDE47 and 6-MeO-BDE47 (p<0.001), between ΣOH-BDEs and ΣMeO-BDEs (p<0.001), and between Σ_7OH-BDEs + ΣBPs and ΣMeO-BDEs (p<0.001).

Kelly et al. (2008) performed a detailed study of MeO-BDE biomagnification in the food web of east Hudson Bay (Canadian Arctic) with samples collected between 1999 and 2003. MeO-BDEs were not detected in sediment or macroalgae but measurable concentrations were found in blue mussel (14 ng/g lw), Arctic cod muscle (9.9 ng/g lw), sculpin muscle (3.0 ng/g lw), salmon muscle (42 ng/g lw), eider duck liver (1.3 ng/g lw), white-winged scoter liver (2.1 ng/g lw), male ringed seal blubber (6.7 ng/g lw), and beluga blubber (310, 62, 300 ng/g lw in calves, females, males, respectively). The predominant congeners were 2'-MeO-BDE68 and 6-MeO-BDE47. Trophic magnification factors (TMFs) for 2'-MeO-BDE68 and 6-MeO-BDE47 were 2.3 and 2.6, respectively. These were lower than TMFs of 3–11 for recalcitrant PCBs, but higher than TMFs of 0.1–1.6 for PBDEs. The ΣMeO-BDE concentrations exceeded those of ΣPBDEs in beluga, salmon and blue mussel while the opposite was the case for other members of the food web. ΣMeO-BDE concentrations were generally lower than for ΣPCBs and ΣDDTs, but were comparable to concentrations of other legacy organochlorines such as chlorobenzenes, hexachlorocyclohexanes (HCHs), and chlorinated cyclodienes. Compared to the MeO-BDEs, OH-BDEs in the Hudson Bay food web were orders of magnitude lower or not detected (Kelly et al., 2008).

The Hudson Bay TMFs are similar to those for ΣMeO-BDEs (2'-MeO-BDE68 + 6-MeO-BDE47) and ΣPBDEs of 2.9 and 3.9, respectively, in a Sydney Harbour (Australia) food web comprising squid, crustaceans and fish (Losada et al., 2009). Biomagnification factors in a North Sea fish to harbor seal or harbor porpoise food web for 2'-MeO-BDE68 and 6-MeO-BDE47 ranged from 0.1–1.9 and 0.4–23.3, respectively (Weijs et al., 2009b). The transformation capacity appears to be higher for harbor seal than porpoise (Weijs et al., 2009a,b).

Median concentration ranges for 2'-MeO-BDE68 + 6-MeO-BDE47 in blubber of humpback whale (*Megaptera novaeangliae*) from three sites on the Antarctic Peninsula, biopsied in 2000–2003, were 0.25–0.4 ng/g lw (males) and 0.11–0.18 ng/g lw (females). The ΣMeO-BDEs accounted for about 5–20% of organobromines (the remainder was PBDEs) in both males and females at two sites, but 60% in males versus 15% in females from the third (Dorneles et al., 2015).

PBDD/Fs have not been reported in Arctic marine mammals.

Marine environment: other HNPs

Compared to bromophenolic compounds, there have been few reports of other high molecular weight HNPs in the Arctic environment. These are discussed along with more numerous reports in temperate and tropical ecosystems to guide research into the types of compounds which could be sought in future Arctic investigations.

Other HNP classes reported in biota include polyhalogenated 1'-methyl-1,2'-bipyrroles (PMBPs), polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles (PDBPs), polyhalogenated N-methylpyrroles (PMPs), polyhalogenated N'methylindoles (PMIs), bromoheptyl- and bromooctyl pyrroles (BHPs, BOPs), 1R,2S,4R,5R,1E)-2-bromo-1-bromomethyl-1,4-dichloro-5-(2-chloroethenyl)-5-methylcyclohexane (mixed halogen compound MHC-1), polybrominated hexahydroxanthene derivatives (PBHDs), bromovinylphenols (BVPs) and bromocoumarates (BCUs) (Vetter et al., 1999, 2001, 2007, 2008; Fielman et al., 2001; Tittlemier et al., 2002a,b; Lincoln et al., 2005; Vetter and Janussen, 2005; Vetter, 2006; Melcher et al., 2007; Vetter and Gribble, 2007; Gaul et al., 2011; Hauler et al., 2013, 2014; Barón et al., 2015; Hauler and Vetter, 2015; Shaul et al., 2015).

PDBPs are a structurally diverse group of compounds comprising many potential congeners. Early studies were able to confirm the presence of several PDBP congeners in Arctic fauna as well as to describe their bioaccumulation in the Arctic food web of the Northwater Polynya (northern Baffin Bay) in 1988 (Tittlemier et al., 2002b). Samples analyzed included sediment, zooplankton, whole Arctic cod, liver of the seabirds, dovekie (*Alle alle*), black guillemot (*Cepphus grylle*), black-legged kittiwake (*Rissa tridactyla*), glaucous gull, as well as ringed seal blubber. DBP-Br_4Cl_2 (BC-10) and DBP-Br_6 compounds were found in sediment at 0.0020±0.0002 and 0.028±0.028 ng/g dw. Mean concentrations of ΣPDBPs (DBP-Br_3Cl_3, DBP-Br_4Cl_2, DBP-Br_5Cl, DBP-Br_6) in the three zooplankton species were 0.021 ng/g lw (*Calanus*), 0.057 ng/g lw (*Sagitta*; only DBP-Br_4Cl_2 detected) and 0.93 ng/g lw (*Mysis*; all four congeners found). The four congeners were also found in all bird species, with $\Sigma PDBP_4$ concentrations in the order glaucous gull (68 ng/g lw) > black-legged kittiwake (32 ng/g lw) > black guillemot (9.6 ng/g lw) > dovekie (3.2 ng/g lw), and Arctic cod (1.1 ng/g lw). The ΣPDBP concentration in ringed seal was 0.14 ng/g lw and only three congeners were present. TMFs (excluding the seal data) were 14.6 (DBP-Br_4Cl_2) > 7.0 (DBP-Br_6) = 6.9 (DBP-Br_5Cl) > 5.2 (DBP-Br_3Cl_3). These were comparable to the TMF of 9.8 for CB-153 observed in the same food web (Fisk et al., 2001), indicating that PDBPs are highly bioaccumulative. The very low concentrations observed in ringed seal relative to other organisms at a similar trophic level strongly suggest metabolism of the PDBPs by seals (Tittlemier et al., 2002b).

A comparative study was made of PDBPs in blubber of marine mammals from the eastern and western Arctic with those worldwide (Tittlemier et al., 2002a). The ranges in geometric mean for ΣPDBPs in Arctic species were 0.4–1.2 ng/g lw (ringed seal), 0.6 ng/g lw (bowhead whale, *Balaena mysticetus*), 2.0–17.8 ng/g lw (beluga), 4.3–8.3 ng/g lw (harbor seal) and 234 ng/g lw (Steller sea lion, *Eumetopias jubatus*) from Alaska. Similar concentrations were found in Steller sea lion from Japan and California (331 and 177 ng/g lw, respectively). However, far higher geometric mean concentrations (range: 14.3–2540 ng/g lw) were generally found in other marine mammals (pinnipeds, cetaceans) from temperate and tropical latitudes (Tittlemier et al., 2002b).

Higher concentrations of PDBPs and different patterns of congeners were observed in samples from Pacific Ocean influenced environments relative to non-Pacific Ocean influenced environments. DBP-Br_4Cl_2 dominated the congener profile in Pacific seals (excluding ringed seals), whereas DPB-$BrCl_3$ and DBP-Br_5Cl were more prominent in seals from coastal Europe and Svalbard. Congener patterns also differed in beluga from different Arctic regions, with DBP-Br_4Cl_2 predominating in Alaskan animals and DBP-Br_6 in beluga from the Canadian Arctic Archipelago, Svalbard and the St. Lawrence River. It was suggested that PDBPs undergo

extensive transport from a source located primarily in the Pacific Ocean. Evidence from congener patterns indicates that both ocean currents and atmospheric transport are likely to play a role in the movement of PDBPs. The occurrence of ΣPDBPs at 0.35 ng/g lw in the Baikal seal (*Pusa sibirica*) also suggests air transport (Tittlemier et al., 2002a).

Several PDBP congeners were detected in blubber from juvenile male northern fur seals (*Callorhinus ursinus*) collected from St. Paul Island, Alaska (N. Rosenfelder, pers. comm.). The congeners detected included DBP-Br_2Cl_4 (BC-10), Br_3Cl_3 (two congeners), Br_5Cl and Br_6. Confirming the observation made previously, BC-10 was the most abundant of the PDBPs found in the northern fur seal samples.

As for the PDBPs, PMBPs are a diverse set of compounds of which the first to be discovered was the perchlorinated PMBP-Cl_7, or Q1 (2,3,3',4,4',5,5'-heptachloro-1'-methyl-1,2'-bipyrrole). This compound was first described in the late 1990s and has subsequently been reported in many species of marine biota particularly from the Pacific Ocean along with PMBPs with mixed bromo- and chloro- substitution (Vetter et al., 1999, 2001, 2003; Teuten et al., 2006; Pangallo and Reddy, 2008; Hauler et al., 2014). Q1 was measured in waters from the Great Barrier Reef (Australia) at a mean concentration of 25 pg/L (Vetter et al., 2009), and in Antarctic air at 0.007–0.009 pg/m^3 (Vetter et al., 2000).

Q1 was sought, but not found, in air samples from Svalbard (Vetter et al., 2002). In contrast, Q1 concentrations of 0.004–0.069 pg/m^3 were found in 32 of 49 samples collected at Lista (Norway) in 2003 (Melcher et al., 2008). Q1 was also quantified at 0.004–0.092 pg/m^3 in air at Lista (Melcher et al., 2008), but was <0.00006 pg/m^3 in air at Svalbard (Vetter et al., 2000).

Recent work points to a microbial source for these compounds based on compound-specific stable nitrogen determination (Pangallo et al., 2012). Approximately 70 mixed bromo- and bromo- chloro- PMBP congeners have now been reported in marine mammal blubber and liver collected from the Pacific and Atlantic Oceans (Teuten et al., 2006; Vetter et al., 2007; Pangallo et al., 2008). PMBP concentration profiles, with concentrations increasing with trophic level strongly suggests that these compounds biomagnify similarly to persistent organic pollutants (POPs) (Pangallo and Reddy, 2008). Concentrations of several PMBP congeners, in particular MBP-Br_6Cl, in cetaceans and seals from the temperate North Atlantic Ocean, were equal to or near concentrations of CB153 (about 1 ng/g lw). While there are no published data for PMBPs in Arctic fauna, their presence is suggested by their occurrence in marine mammals from adjacent latitudes.

MHC-1 was first detected in seafood from northern European waters and isolated and fully characterized from a red algae extract (Vetter et al., 2001, 2008) MHC-1 concentrations from Arctic and subarctic fauna were 84 and 140 ng/g lw respectively, in blubber of Greenland harp seal (*Pagophilus groenlandicus*) and hooded seal (*Cystophora cristata*) from Jan Mayen (sampled 1991) (Vetter et al., 2008). For Norwegian coastal fauna collected between 1992 and 2003, concentrations were 14–20 ng/g lw (egg of white-tailed sea eagle), 1.8–25 ng/g ww (shag), 0.24–0.17 ng/g ww (blue mussel), and 2.9–13 ng/g ww (liver of cod and saithe). The MHC-1 concentration was 2250 ng/g lw in salmon from the Faroe Islands (Vetter et al., 2008). Tribrominated and tetrabrominated PBHDs were found in cod liver from Ekne in the Trondheim Fjord, Norway at 0.50 and 0.39 ng/g lw. Tetrabrominated PBHD was found in saithe liver from Sklinna, Norway at 0.89 ng/g lw (Vetter et al., 2007).

2.16.3.6 Environmental trends

Spatial trends

Based on a recent review of PBDE and MeO-BDE concentrations in marine mammals globally, ΣPBDEs exceeded ΣMeO-BDEs by about a factor of 9 in the northern hemisphere, whereas MeO-BDEs in southern hemisphere marine mammals were about 100 times higher than those in the northern hemisphere. Highest concentrations in cetaceans are found in the tropical southern hemisphere, where specimens were collected near coral reef areas that were subject to upwelling. In comparison, cetaceans collected in the northern hemisphere were from temperate and polar regions (Alonso et al., 2014). It is probable that MeO-BDE concentrations exceed those of legacy POPs in the southern hemisphere while in the northern hemisphere, including the Arctic, MeO-BDE concentrations are generally a small fraction compared to total legacy POPs.

Although many HNPs are produced in the ocean, they are also found in wildlife from inland areas. Whether they are atmospherically transported or produced locally is unclear. MeO-BDE and PBDE concentrations in white-tailed sea eagle eggs from freshwater lakes in Sweden were lower than in eggs from white-tailed sea eagles living on the Baltic Sea coast (Section 2.16.3.5, *Freshwater environment*) (Nordlöf et al., 2010).

OH-BDE and PBDE concentrations were similar in eggs of guillemot from Iceland, the Faroe Islands and coastal Norway, whereas levels in eggs of guillemot from Stora Karlsö in the Baltic Proper were many times higher. MeO-BDEs were only detected in the Baltic eggs (Jörundsdóttir et al., 2009).

PDBP congener profiles in seal species (excluding ringed seals, where levels were low) suggest Pacific versus non-Pacific influence. This also extends to the Arctic, where the congener profile in beluga from Pt. Lay (Alaska) differs from the Canadian Arctic Archipelago and Svalbard profiles (Figure 2.123).

Temporal trends

A time series of measurements for HNPs in air exists for a non-Arctic coastal station at Lista (Norway), where BAs, Q1 and anthropogenic HCHs were measured throughout 2003 (Melcher et al., 2008). Concentrations of 2,4-DiBA and 2,4,6-TriBA were low in January–April, increased rapidly during May and were relatively stable through December. Q1 showed lower levels from February–August and higher levels from September–January. In comparison, HCHs showed a typical POPs concentration cycle of higher concentrations in summer–autumn and lower concentrations in winter–spring.

TriBA has been monitored in air at Zeppelin (Svalbard) and Birkenes in southern Norway since 2007, and since 2010 at Andøya in Arctic Norway (Bohlin-Nizzetto et al., 2015).

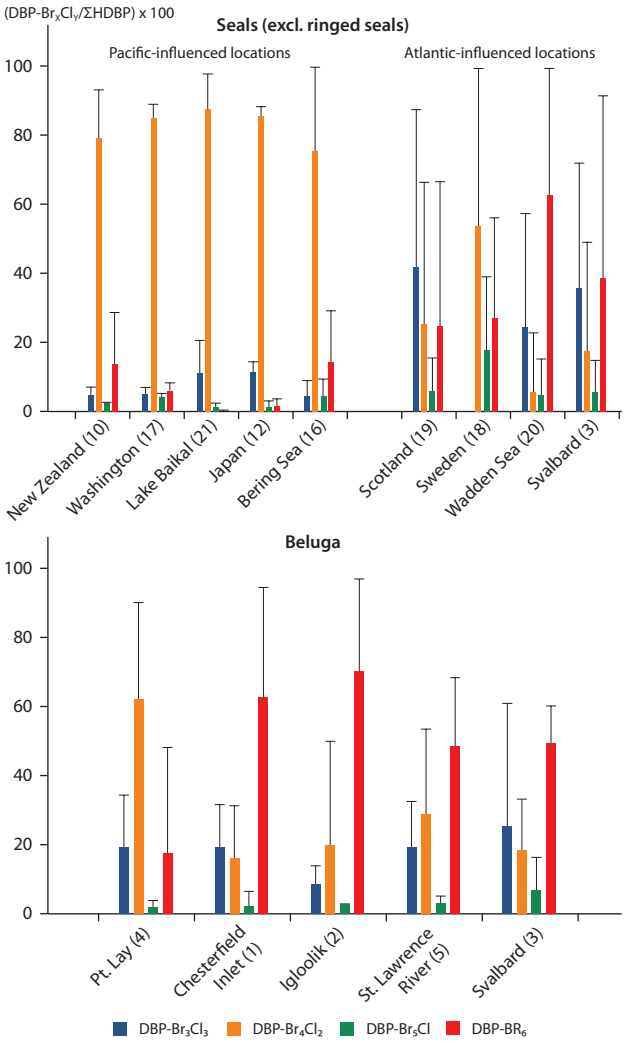

Figure 2.123 PDBP congener profiles (expressed as percentages of Σ_4PDBPs) in marine mammals living in waters influenced by Pacific versus Atlantic Ocean transport. From Tittlemier et al. (2002a). Numbers in parentheses refer to locations specified in that paper. Note: PDBPs are called HDBPs by Tittlemier et al. (2002a).

Svalbard concentrations are higher than at the other sites, but no temporal trend in annual concentrations is apparent (Figure 2.124). As in southern Norway (Melcher et al., 2007), 2,4,6-TriBA concentrations in Svalbard air increased in early summer and remained stable through late autumn, declining in winter-spring (Bohlin-Nizzetto et al., 2015).

BAs in air were measured at station Råö in southern Sweden between 2004–2015 and at station Pallas in Arctic Finland between 2002–2015. No temporal trends were found at Råö. A significant increase was found at Pallas for 2,4-DiBA (p<0.05), but not for 2,4,6-TriBA (Bidleman et al., 2017).

Changes in MeO-BDE concentration that show no trend over time or are different from those of classical POPs such as PCBs and PBDEs are frequently invoked as an indication of their natural origin. In the marine mammals studied by Rotander et al. (2012a), there was no clear relationship between the 20-y trends of PBDEs and MeO-BDEs.

Concentrations of individual congeners relative to the sum of PDBPs were not significantly correlated to year of collection (1987 to 2007) in juvenile male northern fur seals collected from St. Paul Island, Alaska (N. Rosenfelder, pers. comm.). Likewise

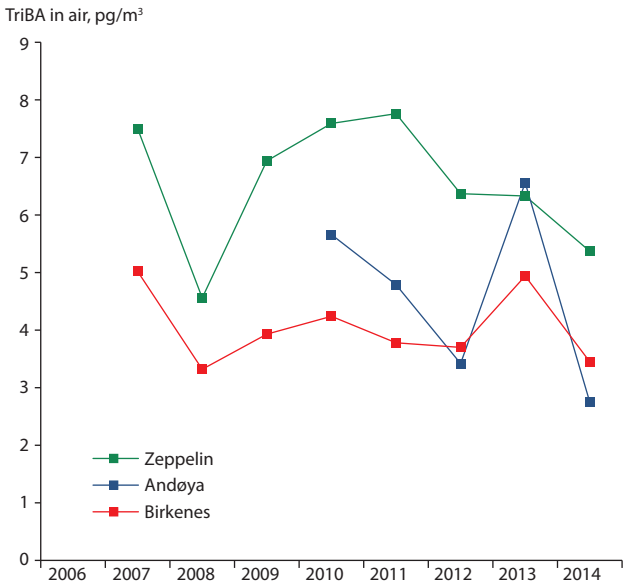

Figure 2.124 Annual mean concentrations of TriBA in air. Adapted from Bohlin-Nizzetto et al. (2015).

the relative proportion of the five PDBP isomers was identical in a seal collected in 1987 compared to a seal collected in 2007. These observations support a natural source of the PDBPs because strong temporal trends were generally observed for anthropogenic POPs in these samples while there was no trend for the PDBPs.

No other temporal trends for HNPs in the Arctic were available.

PBDE congeners in eggs of white-tailed sea eagles on the Baltic Sea coast, collected between 1992 and 2004, decreased between the early and late 1990s, then increased in the early 2000s. MeO-BDEs displayed no trends over this period (Nordlöf et al., 2010). POPs in five white-tailed sea eagle eggs from 1996–2001 collections on the southern Baltic coast were compared with an archived egg laid in 1941, also on the southern Baltic Sea coast (Nordlöf et al., 2012). 2'- MeO-BDE68 and 6-MeO-BDE47 concentrations were virtually the same in the 1996–2001 egg (geometric means 23 and 90 ng/g lw) and the single 1941 egg (30 and 86 ng/g lw). By contrast, the geometric mean of ΣPBDEs in the recent egg was 3120 ng/g lw, while PBDE congeners were <2 ng/g lw in the 1941 egg.

2.16.4 Conclusions

Halogenated natural products existed before industrial production of anthropogenic organohalogens and the roles of these compounds in ecosystem functioning are still being investigated and debated. The diversity of HNPs is immense – over 4000 compounds have so far been identified (Vetter and Gribble, 2007). These range in complexity from simple, low molecular weight halocarbons (e.g. $CHBr_3$) to large compounds with molecular weights in the same range as those of POPs or higher (e.g. MeO-BDEs, PDBPs).

Halocarbons contribute to the bromine cycle and ozone regulation. The role of largely natural VSLS halocarbons has come into prominence in recent years. A recent development is the detailed mapping of halocarbon concentrations in the Arctic Ocean and possible links to dissolved organic matter

(Karlsson et al., 2013). Concentrations of halocarbons in surface water do not appear to have changed much over the last two decades (Karlsson et al., 2013). This could change in the future, with changes in river runoff, precipitation and loss of ice cover affecting primary production, species composition, circulation patterns, formation of halocline water and air-sea exchange (Karlsson et al., 2013). A decline in the extent of summer sea ice in the Arctic is expected to result in an increase in photosynthetically active radiation at the sea surface and thus primary production (Zhang et al., 2010). It has been suggested that the role of halocarbons in Arctic atmospheric chemistry may increase with a loss of ice cover (Hopkins et al., 2013). Freshening of the polar mixed layer is an unknown factor which might affect bromocarbon production by limiting the availability of bromide.

Higher molecular weight HNPs are found at all levels of Arctic/subarctic ecosystems. The bulk of research has focused on MeO-BDEs and OH-BDEs with less attention given to BPs, BAs, PBDDs and HNPs with heterocyclic ring structures. There are only a few, unpublished, measurements of PDBPs since the studies of Tittlemier et al. (2002a,b) were published, and only one investigation of MHC-1 in Arctic/subarctic biota (Vetter et al., 2008). PBDDs, PMBPs and PDHPs have not been reported in Arctic biota, but their presence can be inferred from their occurrence in oceans at southern latitudes.

Measurements of bromophenolic HNPs have mainly been carried out on seabird and marine mammal species. Investigations of HNPs in algae, fish and invertebrates are sparse. Only one study has examined macroalgae and sediments for MeO-BDEs and OH-BDEs, with negative results (Kelly et al., 2008). It seems likely that Arctic macroalgae and phytoplankton would produce these compounds, as well as BPs and BAs, given their widespread occurrence in the Baltic Sea and other marine areas. Trophic magnification of HNPs in the Arctic has been reported only by Kelly et al. (2008) and Tittlemier et al. (2002b). Temporal/spatial trends are poorly known relative to anthropogenic POPs. There have been some studies of metabolic transformations, such as for MeO-BDEs, OH-BDEs and PBDEs, but not for other compounds.

Many biosynthetic pathways and subsequent transformation mechanisms have been identified for higher molecular weight HNPs. Work in this area has been largely confined to temperate and tropical environments, with little attention paid to the polar regions, even though it is apparent that HNPs are found there. Measurements of HNPs in abiotic samples are lacking. Very little is known about production of higher molecular weight HNPs in Arctic ecosystems, but relevant factors are likely to be similar to those for halocarbons (Section 2.16.2.2). It is not known if these compounds are produced or occur in snow and ice. As for the halocarbons, air-sea exchange of higher molecular weight HNPs would be enhanced by a loss of ice cover.

The relative importance of higher molecular weight HNP biosynthesis within the Arctic versus delivery by atmospheric and oceanic currents is unknown. If these external processes are important, levels of HNPs in the Arctic may also respond to changes in temperate and tropical oceans. Atmospheric transport is suggested by the presence of MeO-BDEs and/or OH-BDEs in precipitation and biota from inland lakes and rivers (Section 2.16.3.5), although biosynthesis from available bromine in terrestrial and lentic ecosystems cannot be ruled out. The possibility of delivery by ocean currents is suggested by different congener profiles of PDBPs in beluga from Alaska versus the Canadian Arctic Archipelago and Svalbard (Tittlemier et al., 2002b).

Section 2.16 Annex Contents

Section 2.16 Annex

Table A2.16/1 Henry's law constants and dimensionless K_{AW} of volatile halocarbons at salinity 30.4‰ (Moore et al., 1995).

		Intercept[a]	Slope[a]	
	K_{AW}, 20°C	A	B	Range, °C
CH_3Cl	0.37	9.17	-2982	0–6
$CHCl_3$	0.15	11.17	-3840	0–20
CH_2Br_2	0.034	11.70	-4418	0–20
$CHBr_3$	0.022	13.16	-4973	0–20
$CHBr_2Cl$	0.043	13.62	-4914	0–20
$CHBrCl_2$	0.080	13.43	-4678	0–20
CH_3I	0.23	13.32	-4338	0–20
CH_2I_2	0.013	12.77	-5006	0–20
CH_2ClI	0.036	11.37	-4305	0–20

[a]Parameters of $\ln K_{AW} = A + B/T$.

Table A2.16/2 Global annual estimates of VSLS release.

Compound	Global release, gigagrams[1]	Reference
$CHBr_3$	120–820	(1,2)
CH_2Br_2	57–280	(1,2)
$CHBr_2Cl$	19.7–26	(1)
$CHBrCl_2$	17–22.6	(1)
CH_2BrCl	10–11	(1)
CH_3I	157–550	(1,2)
CH_2I_2	116–128	1
CH_2ICl	234–258	1
CH_2IBr	87.3–96	1

(1) Ordóñez et al. (2012), Sarwar et al. (2015); (2)WMO (2014).

Table A2.16/3 Halocarbons in the polar mixed layer of the Arctic Ocean (pmol/kg) (Karlsson et al., 2013).

	Alaskan shelf/slope	Canada Basin	Makarov Basin	Eurasian Basin
$CHBr_3$	13±3	14±3	29±11	18±3
CH_2Br_2	7±3	12±3	22±7.3	15±4
$CHBr_2Cl$	1.4±0.4	2.2±0.8	3.7±0.7	3.3±0.5
CH_2ClI	1±0.6	2.2±0.9	3.3±0.8	2.6±0.6

Table A2.16/4 Halocarbons in seawater and ice at Svalbard, mean and range (pmol/L). Summarized from Granfors et al. (2013a).

	Brine	Ice	Under-ice seawater	Seawater	Frost flowers
$CHBr_3$	86 (47–120)	65 (13–270)	18 (11–59)	13 (3.3–25)	2.1–66
CH_2Br_2	28 (27– <120)	35 (8.7–150)	14 (4.3–19)	11 (2.6–25)	0.71–5.2
$CHBr_2Cl$	68 (29–150)	53 (4.7–200)	18 (4.6–29)	9.6 (2.7–21)	0.66–56
$CHBrCl_2$	10 (4.0–21)	10 (0.71–40)	2.8 (0.38–7.0)	3.1 (0.23–30)	0.13–6.7
CH_2I_2	0.72 (0.44–1.9)	2.5 (0.29–11)	0.70 (0.17–3.0)	0.55 (0.19–1.2)	
CH_2ICl	3.0 (1.2–5.1)	4.1 (0.60–9.2)	1.1 (0.63–2.0)	0.81 (0.47–1.0)	0.062–0.75
CH_2IBr	1.8 (0.46–7.0)	2.8 (0.25–8.5)	1.5 (0.84–3.0)	1.0 (0.37–1.8)	0.019–0.53
Salinity, psu	120 (91–140)	120 (49–200)	35 (30–39)	34 (34–35)	51–53

Table A2.16/5 Physicochemical properties of higher molecular weight HNPs. References given in parentheses. Properties are at 25°C unless stated otherwise (see Ref. [5]).

	pK_A	log K_{OW}	log K_{AW}	log K_{OA}	log p_L, Pa	log s_L, mol/m
Bromophenols [1,2]						
2.4-DiBP	7.79	2.56 to 3.48	-4.83		-0.41	1.02
2,6-DiBP		2.37				
2,4,6-TriBP	6.08	3.74 to 4.24	-5.84 to -4.90		-1.54 to -1.38	-0.04
PeBP	4.4	5.30 to 5.96	-6.50 to -5.32		-4.3	-1.83
Bromoanisoles						
2.4-DiBA		3.75 [3]	-2.29 [3], -2.71 [4]	6.04 [3]	0.64 [3]	-0.46 [3]
2,6-DiBA		3.42 [3]	-1.95 [3]	5.37 [3]	1.03 [3]	-0.42 [3]
2,4,6-TriBA		4.44 [3]	-1.52 [3], -2.46 [4]	5.96 [3]	-0.09 [3]	-1.96 [3]
PeBA		5.43 [3]	-3.44 [3]	8.87 [3]	-3.52 [3]	-3.47 [3]
OH-BDEs[a]						
6'-OH-BDE17		5.18, 5.33 [5,6]				
2'-OH-BDE28		5.50, 5.50 [5,6]				
5-OH-BDE47				10.82 [7], 11.23 to 11.26 [8]		
6-OH-BDE47		6.59, 6.02 [5,6]	-4.98 to -4.24 [9]	10.83 [7], 10.89 to 11.00 [8]		
4'-MeO-BDE49		6.09, 5.98 [5,6]	-5.27 to -4.91 [9]	11.00 [7], 11.25 [8]		
2'-OH-BDE68		6.17, 6.00 [5,6]	-4.68 to -4.51 [9]	10.68 [7]		
6-OH-BDE90		6.60, 6.57 [5,6]				
6'-Cl-2'-OH-BDE68		6.22, 6.35 [5,6]				
5-Cl-6-OH-BDE47		6.54, 6.34 [5,6]				
MeO-BDEs[a]						
6'-MeO-BDE17		5.74, 6.03 [5,6]				
2'-MeO-BDE28		6.06, 6.13 [5,6]	-4.10 to -3.80 [9]	10.16 [7], 9.93 to 10.12 [8]		
5-MeO-BDE47		6.72, 6.72 [5,6]				
6-MeO-BDE47		7.17, 6.73 [5,6]	-4.11 to -3.43 [9]	10.84 [7], 10.60 to 10.71 [8]		
4'-MeO-BDE49		6.68, 6.70 [5,6]				
2'-MeO-BDE68		6.91, 6.78 [5,6]	-3.95 to -3.72 [9]	10.64 [7], 10.63 to 10.73 [8]		
6-MeO-BDE90		7.36, 7.26 [5,6]				
6'-Cl-2'-MeO-BDE68		7.33, 7.06 [5,6]				
5-Cl-6-MeO-BDE47		7.34, 7.05 [5,6]				
PBDDs [10]						
MoBDD		5.23	-3.72	8.95	-2.17	-3.70
DiBDD		6.12	-4.12	10.24	-3.35	-5.02
TriBDD		7.01	-4.52	11.53	-4.24	-6.37
TeBDD		7.90	-4.92	12.82	-5.21	-7.70
PDMPs[b] [11]						
DBP-Br_3Cl_3		6.5	-4.25		-3.72	-2.87
DBP-Br_3Cl_3		6.4	-4.92		-4.03	-2.50
DBP-Br_4Cl_2		6.5	-4.84		-4.37	-2.93
DBP-Br_5Cl		6.6	-5.56		-4.77	-2.60
DBP-Br_6		6.7	-6.09		-5.12	-2.43
Q1[c] [12,13]		6.3 to 6.4			-2.61 to -2.81	

[1] Howe et al. (2005); [2] Kuramochi et al. (2004a); [3] Pfeifer et al. (2001), experimental; [4] Bidleman et al. (2016), experimental log H/(Pa/m³/mol), 2,4-DiBA = 8.79-2418/T, 2,4,6-TriBA = 7.88-1980/T; K_{AW} = H/RT; [5] Yu et al. (2008a), experimental, 30°C; [6] Zhai et al. (2014), predicted; [7] Zhao et al. (2010), experimental; [8] Liu et al. (2013b), predicted; [9] calculated from log K_{AW} = log K_{OW} - log K_{OA}; [10] Arnoldsson (2012), predicted; [11] Tittlemier et al. (2004), experimental; [12] Vetter et al. (2004), experimental; [13] Hackenberg et al. (2003), experimental. [a]References [6], [8] and [8] include log K_{OW} and K_{OA} values for additional OH-BDE and MeO-BDE compounds, and Reference 7 includes parameters for log K_{OA} = A + B/T; [b]polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles; [c]Q1 = 2,3,3',4,4',5,5'-heptachloro-1'-methyl-1,2'-bipyrrole.

Table A2.16/6 Bromophenolic HNPs and PBDEs in Arctic and subarctic marine fish (ng/g)[a,b].

Species	Location	Year	Tissue	Lipid (L) or wet (W) weight
Salmon (*Salmo* spp.)	Hudson Bay, Canada	1999–2003	Muscle	L
Sculpin (*Myoxocephalus scorpioides*)	Hudson Bay, Canada	1999–2003	Muscle	L
Arctic cod (*Boreogadus saida*)	Hudson Bay, Canada	1999–2003	Muscle	L
Cod (*Gadus morhua callarias*)	Vestertana Fjord, Finland	1987–1998	Liver	L
Atlantic cod (*Gadus morhua*)	Trondheim Fjord Norway	2003	Liver	W
Saithe (*Pollachius virens*)	Sklinna, Norway	2003	Liver	W
Atlantic salmon (*Salmo salar*)	Hraunsfjord, Iceland	1998	Whole body	L
Greenland shark (*Somniosus microcephalus*)	Iceland	2001–2003	Muscle	L
			Liver	L

[a] PBDEs are only reported for studies which also include HNPs; [b] single numbers are arithmetic means, geometric means or medians; [c] see references for number of congeners sought and found. (1) Kelly et al. (2008); (2) Sinkkonen et al. (2004); (3) Vetter et al. (2007); (4) Strid et al. (2010).

Table A2.16/7 Bromophenolic HNPs and PBDEs in Arctic and subarctic seabirds (ng/g)[a,b].

Species	Location	Year	Tissue	Lipid (L) or wet (W) weight	PBDEs	
					PBDE-47	ΣPBDEs[c]
White winged scoter (*Melanitta fusca*)	Hudson Bay, Canada		Liver	L		71
Eider duck (*Somateria mollissima*)	Hudson Bay, Canada	1999–2003	Liver	L		20
	Coastal Norway	2012	Egg	W	<0.01	0.55-1.4
White-tailed sea eagle (*Haliaeetus albicilla*)	East Greenland	1999–2009	Liver	L	98	180
			Muscle	L	213	420
	Swedish Arctic	1994–2005	Egg	L	280	720
	Bothnian Sea	1992–2004	Egg	L	2500	4100
	Inland, southern Sweden	1994–1995	Egg	L	830	1500
	Baltic Proper	1994–2001	Egg	L	2600	4300
		1996–2001	Egg	L	1830	3120
		1941	Egg	L	<2	
Glaucous gull (*Larus hyperboreus*)	Svalbard	2002	Liver	W		522±154
			Blood	W		51.5±15.9
			Whole body	W		202±20
		2004	Plasma, M	W	8.8±1.6	20.2±5.1
			Plasma, F	W	10.6±1.1	19.8±2.1
	Bjørnøya	2006	Plasma, M	W		18.8±3.1
			Plasma, F	W		8.6±1.1
			Egg yolk	W		163±14
Guillemot (*Uria aalge*)	Iceland	2002	Egg	L	38	
	Norwegian Arctic	2005	Egg	L	5.9-12	
	Faroe Islands	2003	Egg	L	21	
	Norwegian west coast	1998	Whole body	L	57-82	76-118
Northern fulmar (*Fulmarus glacialis*)	Bjørnøya		Liver	L		
Shag (*Phalacrocorax aristotelis*)	Coastal Norway	2003	Egg	W	0.23-1.3	0.8-4.9
			Liver	W	0.09-0.43	0.13-0.43
		2012	Egg	W		2.0-3.9
Herring gull (*Larus argentatus*)	Coastal Norway	2012	Egg	W	0.32-0.52	

[a] PBDEs are only reported for studies which also include HNPs; [b] single numbers are arithmetic means, geometric means or medians; [c] see references for number of congeners sought and found. (1) Kelly et al. (2008), (2) Huber et al. (2015); (3) Jaspers et al. (2013); (4) Nordlöf et al. (2010); (5) Nordlöf et al. (2012); (6) Verreault et al. (2007c); (7) Verreault et al. (2005a); (8) Verreault et al. (2007b); (9) Jorundsdottir et al. (2009); (10) Sinkkonen et al. (2004); (11) Knudsen et al. (2007); (12) Vetter et al. (2007).

PBDEs		2,4,6-TriBP	2,4,6-TriBA	MeO-BDEs			OH-BDEs			Reference
PBDE-47	ΣPBDEs[c]			6-47	2'-68	ΣMeO-BDEs[c]	6-47	2'-68	ΣOH-BDEs[c]	
	9.3			34	6.1	42		nd		(1)
	73			1.4	0.63	3.0		nd		(1)
	9.8			4.9	2.3	9.9		nd		(1)
						0.32-17				(2)
13-16	18-22		6.3-6.4			2.5-3.3				(3)
8.7	12		54.7			1.4				(3)
7.3-7.9	11-13					1.9-4.1				(2)
24	35		0.37	74	15	100	<0.01	0.03		(4)
24	41		0.28	79	12	100	0.02	0.11		

2,4,6-TriBP	2,4,6-TriBA	MeO-BDEs			OH-BDEs			Reference
		6-47	2'-68	ΣMeO-BDEs[c]	6-47	2'-68	ΣOH-BDEs[c]	
		2.0	0.22	2.1		nd		(1)
		0.86	0.29	1.3		nd		(1)
0.29-21	0.25-1.1							(2)
		20	8.7	29				(3)
		23	18	41				(3)
		40	40	86				(4)
		270	50	340				(4)
		20	12	39				(4)
		180	40	230				(4)
		90	23					(5)
		83	30					(5)
				32.2±12.4			3.57±2.83	(6)
				2.78±0.80			3.54±0.97	(6)
				19.4±4.3			0.27±0.07	(6)
		0.05±0.01		0.95±0.32	0.14±0.02	<0.07	0.43±0.07	(7)
		0.04±0.01		0.69±0.10	0.14±0.02	<0.07-0.19	0.37±0.07	(7)
				2.10±0.40			2.71±1.29	(8)
				0.92±0.12			2.21±0.75	(8)
				20.2±2.7			na[d]	(8)
		nd	nd		2.7-8.1	0.23-0.53		(9)
		nd	nd		0.44-17	ND-0.51		(9)
		nd	nd		1.0-4.5	0.077-0.50		(9)
				nd				(10)
0.6±0.1								(11)
	0.35-11.4	0.059-0.36	0.023-0.09					(12)
	0.61-3.3		0.18-12.8					(12)
0.14-0.72	0.45-1.9							(2)
0.12-0.32	0.10-0.57							(2)

Table A2.16/8 Bromophenolic HNPs and PBDEs in Arctic and subarctic marine mammals[a,b] (ng/g).

Species	Location	Year	Tissue	lipid (L) or wet (W) weight	PBDEs	
					PBDE-47	ΣPBDEs[c]
Beluga whale (*Delphinapterus leucas*)	Hudson Bay, Canada					
calves		1999-2003	Blubber	L		27
adult F		1999-2003	Blubber	L		16
adult F		1999-2003	Milk	L		9.6
adult F		1999-2003	Blood	L		3.9
adult M		1999-2003	Blubber	L		34
adult M		1999-2003	Blood	L		6.8
adult M		1999-2003	Liver	L		18
adult MF		2002-2003	Liver	L		2-193
Pilot whale, M (*Globicephala melas*)	Faroe Islands	2006-2007[c]	Blubber	L	489-711	1081-1565
		1997	Blubber	L	304-1389	708-2792
		1986	Blubber	L	11-37	470-704
		2010-2011	Plasma	W		
Minke whale, M (*Balaenoptera acutorostrata*)	W. Iceland	2003-2006	Blubber	L	41-68	125-210
	Greenland	1998	Blubber	L	29-69	86-228
	Norway	1993, 1999	Blubber	L	54-212	86-412
Fin whale, MF (*Balaenoptera physalus*)	W. Iceland	2006-2009	Blubber	L	7.6-13	41-82
	W. Iceland	1986-1989	Blubber	L	2.4-5.1	18-62
Ringed seal, M (*Phoca hispida*)	Hudson Bay, Canada	1999-2003	Blubber	L		11
MF	E. Greenland	2006	Blubber	L	16-28	23-34
MF		2000	Blubber	L	23-55	34-72
MF		1986	Blubber	L	18-28	27-38
MF		2001-2002	Blubber	L		149±87
MF	Svalbard	2007	Plasma	W		1.1
Hooded seal, F (*Cystophora cristata*)	W. Iceland	2007	Blubber	L	19-21	46-69
		1997	Blubber	L	25-47	86-161
		1990	Blubber	L	15-90	53-87
Harbour porpoise, M (*Phocoena phocoena*)	Norway	2000	Blubber	L	53-301	171-605
	W. Iceland	1997	Blubber	L	43-59	106-207
		1992	Blubber	L	38-52	140-174
White-sided dolphin, M (*Lagenorhynchus acutus*)	Faroe Islands	2006	Blubber	L	94-112	508-545
		2001-2002	Blubber	L	204-221	906-1021
		1997	Blubber	L	70-110	333-425
Polar bear, MF (*Ursus maritimus*)	E. Greenland	1999-2001	Adipose	W		83±19
MF		1999-2001	Blood	W		1.2±0.1
MF		1999-2001	Brain	W		2.9±0.4
MF		1999-2001	Liver	W		40±4
F	Norwegian Arctic	2002	Plasma	W	5.0±0.5	5.4±0.5
MF	Alaska, USA	1993-2002	Liver	W		0.74±0.23

[a] PBDEs are only reported for studies which also include HNPs; [b] single numbers are arithmetic means, geometric means or medians; [c] see references for number of congeners sought and found. (1) Kelly et al. (2008); (2) McKinney et al. (2006); (3) Rotander et al. (2012a); (4) Hoydal et al. (2015); (5) Letcher et al. (2009); (6) Routti et al. (2009a); (7) Gebbink et al. (2008b); (8) Verreault et al. (2005a); (9) Wan et al. (2009).

2,4,6-TriBP	2,4,6-TriBA	MeO-BDEs			OH-BDEs			References
		6-47	2'-68	ΣMeO-BDEs[c]	6-47	2'-68	ΣOH-BDEs[c]	
		250	53	310		0.12	0.23	(1)
		48	12	62		0.02	0.06	(1)
		50	12	63		0.02	0.05	(1)
		8.7	2.4			nd	nd	(1)
		240	58	300		0.04	0.1	(1)
		25	4.8	31		nd	nd	(1)
		250	52	310		nd	nd	(1)
				43-100			<0.5	(2)
		228-307	11-18					(3)
		90-461	4.3-18					(3)
		416-653	12-23					(3)
							1.77±1.40	(4)
		52-86	6.8-13					(3)
		29-56	6.7-11					(3)
		2.9-18	0.9-3.3					(3)
		17-55	4.0-8.1					(3)
		11-48	1.4-6.8					(3)
		4.5	1.8	6.7	<0.007	<0.007		(1)
		0.3-2.1	0.2-0.4					(3)
		1.4-2.2	0.4-0.9					(3)
		1.6-2.8	0.5-0.8					(3)
				4.6±0.4	0.7±0.5			(5)
					0.019		0.019	(6)
		6.4-6.7	1.3-1.6					(3)
		6.8-11	1.2-2.3					(3)
		8.3-14	1.2-2.3					(3)
		56-95	3.3-4.9					(3)
		36-107	3.3-4.8					(3)
		43-110	3.2-4.4					(3)
		225-249	9.3-13					(3)
		220-438	13-14					(3)
		5.6-195	1.6-8.4					(3)
				<0.1-25			0.9±0.5	(7)
				≤0.78			2.9±1.0	(7)
				<0.5			<0.2	(7)
				<0.5			<0.5	(7)
				≤0.17			≤0.54	(8)
				0.023±0.015			0.012±0.009	(9)

2.17 Marine plastics and microplastics

Authors: Claudia Halsband, Dorte Herzke

2.17.1 Introduction

This section reviews the state of knowledge to late-2015 concerning microplastic in the Arctic. Marine litter and especially plastic debris in the oceans has emerged as a major environmental concern worldwide and is recognized as a threat to marine ecosystems due to the vast amounts involved (Jambeck et al., 2015). Plastics are man-made materials comprising a wide range of organic polymers. They are semi-persistent and known to break down from macroplastic particles (>5 mm in size) to smaller plastic particles through exposure to ultraviolet (UV) light and physical abrasion, but total degradation is slow (Gewert et al., 2015). Most of the plastic material floating in the world's oceans is microplastic debris (<5 mm) (Cózar et al., 2014; Law et al., 2014b). Plastics are released into the environment during industrial activities such as commercial fishing, use of plastic abrasives, and spillage of plastic pellets, but also from domestic applications such as washing of plastic microfiber clothes, use of personal care products containing microplastics (e.g. toothpaste and exfoliators) and municipal wastewater.

Owing to the great connectivity between the Arctic Ocean and adjacent seas through Fram Strait and the Bering Strait, the problem of plastic litter is likely to extend into the Arctic Ocean. However, there are few studies in this region. To understand the distribution of plastic litter in the Arctic Ocean, knowledge of local sources is as important as an understanding of transport pathways from the more densely populated areas further south. As well as the five known 'great garbage patches' of the world oceans, a sixth is predicted for the Barents Sea based on calculations from drifter buoy data (van Sebille et al., 2012) but has still to be seen. Many coastal areas and inland waters also have high levels of plastic pollution, including some in the Arctic (Strand et al., 2015). Although marine plastic has been observed globally and in the Arctic for decades, only recently have national and international scientific efforts begun to understand the sources, occurrence and fate of marine plastics in the Arctic.

There is growing evidence of the broad impact of marine plastics on the marine ecosystem (Rochman et al., 2016 and references therein). Marine plastics affect marine organisms in several interlinked ways; through mechanical interactions such as entanglement, ingestion, blockage of intestines and/or hindering limb movements (Laist, 1987) or through toxicological effects of harmful plastic-related chemicals (Koelmans et al., 2014). Although the entire marine foodweb, from plankton to large organisms such as sea turtles, seals and whales, is known to be affected by marine plastic, the complex interactions of physical-chemical and biological processes are not well known (Figure 2.125). How the extreme environmental conditions of the Arctic might affect plastic transport and degradation processes is not yet known. Emerging knowledge from lower latitudes may not be transferable to the Arctic environment, so studies specific to Arctic conditions are needed. Increased human activity, a changing climate and shifting migration routes of marine organisms also have the potential to increase marine plastic pollution in the Arctic in the future.

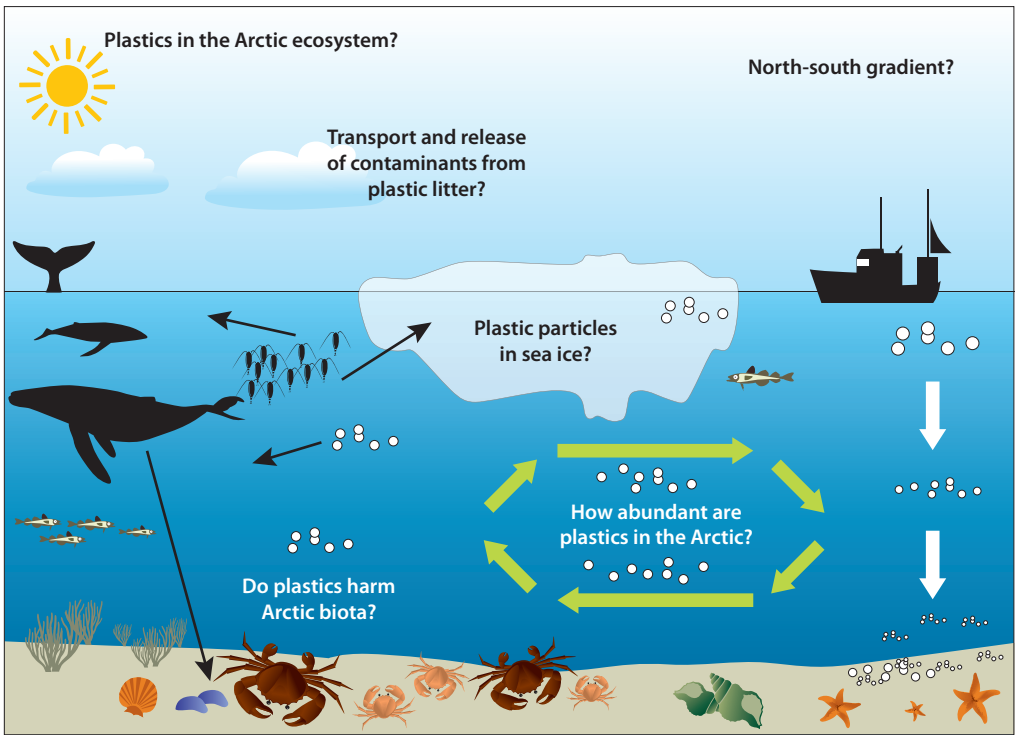

Figure 2.125 Examples of knowledge gaps on the impact of plastic litter in the Arctic (Herzke and Bjørklid, NILU, Norway; Halsband Akvaplan-niva, Norway).

2.17.2 Physical-chemical properties

Marine litter and especially plastic debris, comprises many different compounds and complex polymer materials. Depending on their composition, density and shape they may be found throughout the water column and in or on sediments and beaches. Most polymers in use, such as polypropylene (PP) and polyethylene (PE) exhibit a density lower than water, causing them to float at the sea surface. Higher density polymers such as polyvinylchloride (PVC) and polyethylene terephthalate (PET) are prone to sink to the seafloor (Woodall, 2015). However, the situation becomes more complex in relation to moving water masses and marine microorganisms. Low-density materials are found in the sea surface microlayer, although wave action and wind velocity can affect mixing patterns and temporarily submerge low density materials. In estuarine habitats, low density plastics may become submerged where fronts converge. As well as altering the ecology of litter-associated species assemblages, the fouling of debris, accumulation of biofilms and colonization by algae and invertebrates may also affect the density of the litter, causing it to sink. Marine litter can also act as a vector for hydrophobic chemicals (Rios et al., 2010). Organic pollutants, such as polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs) present in seawater can adsorb onto the plastic surface during its residence in the water. Sorption increases as the plastic weathers due to the increase in available surface area (Mato et al., 2001). Certain polymers, such as polypropylene and polyethylene have been shown to adsorb a broad variety of organic pollutants as polycyclic aromatic hydrocarbons (PAHs) and PCBs (Teuten et al., 2009; Bakir et al., 2012; Rochman et al., 2013). Conversely, polymers can also act as a source of pollutants, leaching chemicals used as additives (e.g. UV stabilizers, softeners, flame retardants) (Hirai et al., 2011).

2.17.3 Sources, production, use and trends

The quantities of plastics produced each year are enormous, increasing from the onset of plastic mass production (1.7 million t/y in 1950) to today (288 million t/y in 2012) (PlasticsEurope, 2014). Between 4.8 and 12.7 million tonnes were estimated to have entered the oceans in 2010 alone (Jambeck et al., 2015).

Locating the sources of plastic litter is often difficult, especially for microplastics, because the nature of the original plastic items can only be inferred from polymer identity and – where analyzed – the composition of additives such as plasticizers and colors. Summaries of current knowledge on the distribution, composition and abundance of marine litter and plastics, as well as on the sources and pathways of microplastics (Bergmann et al., 2015; GESAMP, 2015) indicate that plastics are the most common type of marine litter (representing up to 95%) and ubiquitous in all world oceans, originating from numerous sources. A major input comes from land, but also from ships and other installations at sea. There are both point sources and diffuse sources, and once at sea this debris can travel long distances before being deposited on beaches or on the seafloor, or degraded to form microplastics with their own set of pathways, including the marine food web. The amount of human plastic waste production is enormous, but varies between countries. How much of this enters the environment depends on local and regional development and on the implementation of appropriate disposal and recycling measures – or the lack thereof. Despite standardized monitoring methods now beginning to emerge, there is large spatial and temporal variability in marine plastic occurrence and this hampers quantitative assessments of the extent of the problem. Terrestrial plastic occurrence is even less well studied, although point sources do exist and may represent a source of marine microplastics through runoff from land to sea. There are several hypothetical pathways of marine plastics and microplastics into the Arctic. First, transport via ocean currents from populated areas further south is highly likely (Lusher et al., 2015). Large amounts of Atlantic water enter the Arctic Ocean through Fram Strait containing variable amounts of plastic items and microplastics, as is also the case for other pollutants such as POPs and metals (Bergmann et al., 2015). Second, local sources will add to the overall flux of marine plastic entering the Arctic by municipal and commercial activities on land or at sea. Trevail et al. (2015a) summarized the state of marine microplastic pollution in the Arctic, distinguishing between primary and secondary sources of microplastics. Lusher et al. (2015) found mainly synthetic fibers (95%) between mainland Norway and Svalbard. These were hypothesized to be breakdown products from larger plastic items derived from sea-based activities (shipping, fishing, recreation, offshore industries). Fiber input from households (from washing textiles such as plastic-based fleece) in waste water is likely to be another source (Browne et al., 2015). However, it is challenging to distinguish inputs generated by the few Arctic human settlements (directly through coastal littering and wastewater discharge and indirectly through runoff from land via Arctic catchment areas) from those originating from sources outside the Arctic.

Merrell (1980) observed marine plastic on ten 1-km beaches at Amchitka Island, an Aleutian Island in the Bering Sea back in the 1970s. Most of this litter had originated from fishing vessels, but some items were from the Asian coast, at least 1150 km away. In 1974, 345 kg of plastic litter were found per kilometer of beach. The same author reported that in 1972, an estimated 1664 tonnes of plastic litter had been lost or dumped from fishing vessels in the Bering Sea and North Pacific Ocean. Only a few years later, Lucas (1992) observed marine plastic litter on beaches of Sable Island, Nova Scotia, Canada. The litter came from the ocean, and had not originated from the island itself, confirming that marine plastic was also present in the North Atlantic Ocean. Plastic ingestion by marine biota has also been observed since the 1970s. Bourne (1976) found 1 to 2 particles per stomach in North Sea fulmars (*Fulmarus glacialis*) in the early 1970s. In the 1970s and 1980s, several studies showed the global oceanic presence of virgin industrial pellets (Colton et al., 1974; Wong et al., 1974; Gregory, 1978; Shiber, 1979, 1982; Morris, 1980) and their ingestion by a wide range of marine wildlife (e.g. Bourne and Imber, 1982; Connors and Smith, 1982; Laist, 1987).

2.17.4 Transformation processes

Transformation or rather decomposition of marine plastic can happen along three, often parallel, routes. First, larger plastic parts are quickly broken down into smaller particles caused by mechanical forces of waves and photo-degradation. However, when plastic litter starts to sink, decomposition is reduced dramatically due to the lack of light and the low temperatures leading to half-lives of plastic litter of up to several hundred years. Second, chemical degradation by UV and/or hydrolysis

can result in a rapidly growing number of chemicals released into the marine environment. Third, biofouling of the plastic by bacteria, algae and other organisms might lead to breakdown by mechanically eroding the surface. Fotopoulou and Karapanagioti (2015) found weathered high density polyethylene (HDPE) had an uneven surface, was yellow, and occasionally, colonized by microbes. Pathways for degradation of marine plastic were recently reviewed by Gewert et al. (2015). They concluded that biodegradation and photo-initiated oxidization led to chemical attack of the carbon-carbon backbone of the polymer (polyethylene, polypropylene, polyvinylchloride). Hydrolysis is another breakdown mechanism and affects polymers with additional elements in their main structure (polyethylene terephthalate, polyurethane). As a consequence, oxygen-containing functional groups are added to the molecular structure, speeding up the degradation process to form many different molecules. All processes start on the surface, causing the surface to become brittle and porous (Gewert et al., 2015). Biological transformation may originate from organisms that bore into the material and through colonization by rafting organisms. Only a small proportion of plastic fragments north of 60°N are colonized (Barnes and Milner, 2005), for example by barnacles (Barnes and Milner, 2005) or bryozoans (Winston et al., 1997).

2.17.5 Modeling studies

Few modeling studies have considered the distribution and transport of plastic debris to the Arctic. Van Sebille et al. (2012) used observational data from the Global Drifter Program in a particle-trajectory tracer approach to model the fate of debris from coastal sources on time-scales of years to centuries. Their model predicted six major garbage patches, one in each of the five subtropical basins and one so-far unreported patch in the Barents Sea. They concluded that the connectivity between the ocean basins is higher than expected at centennial scales and as a result a significant amount of marine debris could eventually accumulate in the North Pacific patch.

Zarfl and Matthies (2010) attempted to estimate the influx of organic pollutants adsorbed to plastic debris to the Arctic. Estimates ranged from 62 000 to 105 000 t/y, subject to spatial and temporal variability and sampling bias. They then estimated the mass fluxes of PCBs, polybrominated diphenyl ethers (PBDEs), and perfluorooctanoic acid (PFOA) in plastics transported into the Arctic via the main ocean currents and compared these fluxes with those in the dissolved state and in air. The calculated mass fluxes of the chemicals studied were several orders of magnitude higher in air than in seawater, suggesting that plastic plays a minor role in transporting these compounds northward. High uncertainty in the field data (i.e. plastic concentrations in the pelagic realm) results in large variation in the estimated mass fluxes.

2.17.6 Environmental concentrations

2.17.6.1 Air and precipitation

There are no published data on plastics and microplastics in air and precipitation in the Arctic region.

2.17.6.2 Terrestrial environment

There are no published data on plastics and microplastics in the terrestrial Arctic.

2.17.6.3 Freshwater environment

Current knowledge of microplastics distribution and impacts in freshwater systems was reviewed by Wagner et al. (2014) and Eerkes-Medrano et al. (2015), who highlighted the lack of data on distribution, transport and effects on biota. No data from Arctic freshwater systems exist to date and methods for detection, enumeration and identification remain to be developed. However, some similarities with the marine environment may be expected in terms of particle transport by currents, ubiquity of plastic particles within the system, and impacts on biota. A major difference could be the typically smaller size of freshwater systems, which could result in different spatial and temporal patterns in the transport and mixing of plastic particles within the water column (Eerkes-Medrano et al., 2015). For benthic systems, Corcoran (2015) described the pathways of plastic litter from land to marine and brackish/freshwater environments and concluded that the controlling parameters are similar in both, i.e. proximity to human point sources, river input, geomorphology of the basin, and the behavior of water circulation. Nevertheless this is an important knowledge gap in the Arctic (Table 2.87).

2.17.6.4 Marine environment

Little information is available on plastic debris concentrations in the Arctic marine environment (Trevail et al., 2015a). Most monitoring efforts in the Scandinavian countries have excluded inaccessible Arctic regions, such as the coasts of Svalbard and Greenland and the open Arctic Ocean. A collaboration between Norway and Russia documented marine litter, including macroplastics, in the Barents Sea (Prokhorova and Krivosheya, 2014). This showed the highest plastic litter concentrations to occur along the major ocean currents in areas of intensive fishery and shipping activity. Plastic debris was recorded on the surface, in the water column, and at the seafloor, with the number of items being highest in the pelagic trawls. In the Arctic Pacific, the only information on marine plastic litter distribution is available from dietary studies of seabirds. The northernmost survey of pelagic microplastic distributions

Table 2.87 Summary of Arctic media for which marine plastics and microplastics data have been reported.

	Air		Terrestrial		Freshwater			Marine			Sea ice
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	
Macroplastics (>5 mm)								×	×	×	
Microplastics (<5 mm)								×	×	×	×

was conducted in the Bering Sea (Doyle et al., 2011), looking at plastic concentrations in zooplankton net samples. These were collected in Northeast Pacific ecosystems during research cruises in the southeastern Bering Sea in spring and autumn 2006. Plastic particles (items ≥0.5 mm in size) occurred at both shallow and deep water stations along the Alaska Peninsula in the Bering Sea, but not at the shallowest stations furthest to the east along the Alaska Peninsula. Plastics were found in 9–84% of the surface samples, while microplastics were only found in sub-surface layers in one winter survey. Concentrations were estimated at 0.004–0.19 particles/m^3 and 0.014–0.209 mg dry mass m^3, and were comparable to the levels recorded for regions along the Californian coast with a mean of 0.045 pieces/m^3. Macroplastics were observed floating on the sea surface in Fram Strait and were counted by visual observation during helicopter surveys (Bergmann et al., 2016a). Observation of the deep Arctic seafloor (Bergmann and Klages, 2012) showed plastic debris at densities of 7710 items/km^2, comparable to densities observed in the deep northern Gulf of Mexico (Wei et al., 2012) and even higher than those for marine canyons near Lisbon (Portugal) (6600 items/km^2), which were classified as moderately high (Oliveira et al., 2015).

Systematic sampling of the water column was conducted in June 2014 between Tromsø (Norway) and Svalbard to 78.08°N (Lusher et al., 2015). Two particle sampling methods yielded different results for the 200–500 µm size class. The average concentration of microplastics sampled with a Manta net (mesh size 333 µm), which filters large volumes of water (and plankton) in a small geographic area in the upper few centimeters of the water column, was 0.34 particles/m^3. In comparison, subsurface sampling with the ship's pump, which collects small volumes of water over long distances at 6 m depth gave an average particle count of 2.68/m^3 (after sieving over a 250 µm sieve). Almost all samples contained microplastics, 95% and 93% respectively. The results are comparable to those from other studies around the world and slightly higher (but not statistically significant) than counts using the same methodology in the North Atlantic (Lusher et al., 2014).

The speed of horizontal transport of macro- and microplastics in open water differs: large buoyant debris is exposed to wind stress, while most microplastics are completely submerged. Transport of submerged marine debris from the Tohoku Tsunami was predicted to reach the International Dateline after six months and then to slow and require another 2.5 years to reach 130°W, the latter equivalent to the speed of the north Pacific current (Lebreton et al., 2012). Also important when assessing environmental fate are the physical-chemical properties of the monomers and additive chemicals (boiling point, vapor pressure, water solubility, octanol-water partitioning) as well as the properties of the polymers themselves (size, shape, pore size) (Teuten et al., 2009; Lithner et al., 2011).

The current lack of QA/QC tools and standardized methodology for sampling and identification, means distribution and transport data from different studies cannot be compared. This remains a major challenge worldwide, not only in the Arctic.

Another important matrix for microplastics in polar regions is sea ice. High concentrations of microplastics in Arctic sea ice were found in a study on multi-year ice. Obbard et al. (2014) found up to 250 particles/m^3 in sea ice cores collected at several sites across the Arctic Ocean. The polymers found in various shapes and colors were rayon (a man-made semisynthetic, 54%), polyester (21%), nylon (16%), polypropylene (3%), polystyrene (2%), acrylic (2%), and polyethylene (2%). More recent studies showed even higher concentrations of microplastics in ice cores from the Fram Strait, exceeding the values of Obbard et al. (2014) a hundred-fold (Bergmann et al., 2016b). The sources are difficult to determine, but two pathways are probable: entrapment of marine microplastics during ice crystal formation and atmospheric deposition with snowfall. However, declining sea ice will eventually release these particles into the water column, potentially presenting a major source of plastic pollution for pelagic organisms. Beyer (2015) suggested a procedure to prepare ice cores for microplastics analysis. Standardized methods for the extraction of microplastics from sea ice and other ice environments (e.g. glaciers) are needed.

Indirect evidence for plastic transport into the Arctic is available from seabirds. Seabirds appear particularly vulnerable to marine plastic ingestion (Robards et al., 1995). The northern fulmar (*Fulmarus glacialis*) is a surface feeding seabird with an extensive foraging range over offshore areas throughout its entire lifecycle. This makes it an ideal monitoring sentinel for marine plastic litter (van Franeker et al., 2011; Avery-Gomm et al., 2012; Kühn and van Franeker, 2012; Bond and Lavers, 2013; Rebolledo et al., 2013). The ingested plastic particle load in beached dead fulmars is monitored annually as a contribution to the monitoring of OSPAR's Ecological Quality Objectives (EcoQOs) (OSPAR, 2009a; van Franeker et al., 2011). Ingestion behavior of northern fulmars has been reported from a number of Arctic regions by van Franeker and Law (2015), where plastic items weighing more than 0.1 g were found to decline in number along a south-north gradient. Plastic has also been found in the stomachs of other seabirds, for example thick-billed murre (*Uria lomvia*) in the eastern Canadian Arctic (Provencher et al., 2010). Blais et al. (2005) showed that Arctic seabirds transport marine-derived contaminants into the Arctic and Kühn et al. (2015) hypothesized that much of that may come from plastic. Dietary studies of birds from the Canadian and European Arctic have reported ingested plastics (Mallory, 2008; Provencher et al., 2010). Trevail et al. (2015b) investigated fulmars from Svalbard and found that 88% of the 40 birds examined had ingested plastic, averaging 0.08 g or 15.3 pieces per individual, and 22.5% exceeded OSPAR's EcoQO. Herzke et al. (2016) reported ingested plastic in fulmars caught slightly further south, in the Norwegian Arctic (Finnmark). In this study, 36% exceeded the EcoQO threshold (n=75) and 81% of all investigated individuals contained ingested plastic. Particle size varied from 1.8 to 9.1 mm (mean 5.0 mm) in addition to some longer threads. Of 20 subsampled individuals, an average of 0.2 g or 24 plastic pieces were found with a maximum of 106 plastic pieces.

Plastic ingestion by other Arctic marine biota

Owing to their resemblance and overlap in size range with food items, plastic litter is ingested by marine organisms of all sizes and trophic positions. Together with the high plastic loads in the world's oceans, plastic items have been found in the gut of a wide range of marine species, from small plankton to top predators

(Colabuono et al., 2009; Law et al., 2010; Collignon et al., 2012; Fossi et al., 2012; Desforges et al., 2015). The largest of these animals may help transport microplastics into, around and/or out of the Arctic region independent of the major physical transport mechanisms, such as ocean currents and prevailing winds. The consequences of plastic ingestion for health and fitness parameters such as growth, survival, performance and reproduction are largely unknown, although several studies have investigated such effects in various organisms (reviewed by Cole et al., 2011; Wright et al., 2013). Particles of plastic may be retained in the digestive system causing a decrease in feelings of hunger and thus a reduced intake of food (do Sul and Costa, 2014). Plastics can be transferred to seabird offspring if they are fed by regurgitation (Henry et al., 2011). Plastic consumption can also occur by consuming plastic-contaminated food items. Pollutants can be released from ingested plastic and transferred into tissues, causing potential toxicological effects.

Coastal environment (beaches)

Monitoring data for plastic litter on beaches in Europe has been collected under the OSPAR Convention since 2001. Beaches in the Arctic were included in 2011, located in northern Norway and Svalbard (Figure 2.126). In the latest OSPAR assessment of marine litter in the North-East Atlantic region (OSPAR, 2009b), Contracting Parties provided qualitative data only for Arctic waters. Several types of plastic litter were found on the Norwegian coast (bags, boxes, buckets, helmets, nets, trawls) and Icelandic coast (including plastic bags). Tourism and recreational activities are a significant land-based litter source on the Norwegian coastline. There has been no research on land-based sources of marine litter in the Faroe Islands, but an estimate based on the litter landed as part of the project *Fishing for Litter* in port Tofta Havn indicates that municipal waste management, rivers, tourism and recreational activities could be direct input sources. Fishing boats and the fishing industry in general as well as other types of marine transport sea are the main sea-based sources of plastic litter in the European Arctic seas, including offshore oil/gas installations. In Norway, the aquaculture industry makes a significant contribution at the local scale, and in some areas contributes ~30% of the total quantity in the Norwegian Arctic (OSPAR, 2009b).

Marine litter observed on beaches varies from place-to-place and year-to-year depending on changes in ocean currents, weather conditions and incidents on vessels and offshore installations that result in the loss of materials to the sea. For example, on a 100-m section of beach in Rekvika (Troms, Norway) the number of plastic items collected varied between 2670 (1 October 2011) and 12 928 (1 May 2012). For comparison, the average number of all plastic items found on 100-m sections of beaches on Svalbard and the Norwegian Arctic mainland in 2013 were between 300 and 12 000 items, respectively. Figure 2.126 illustrates the average composition

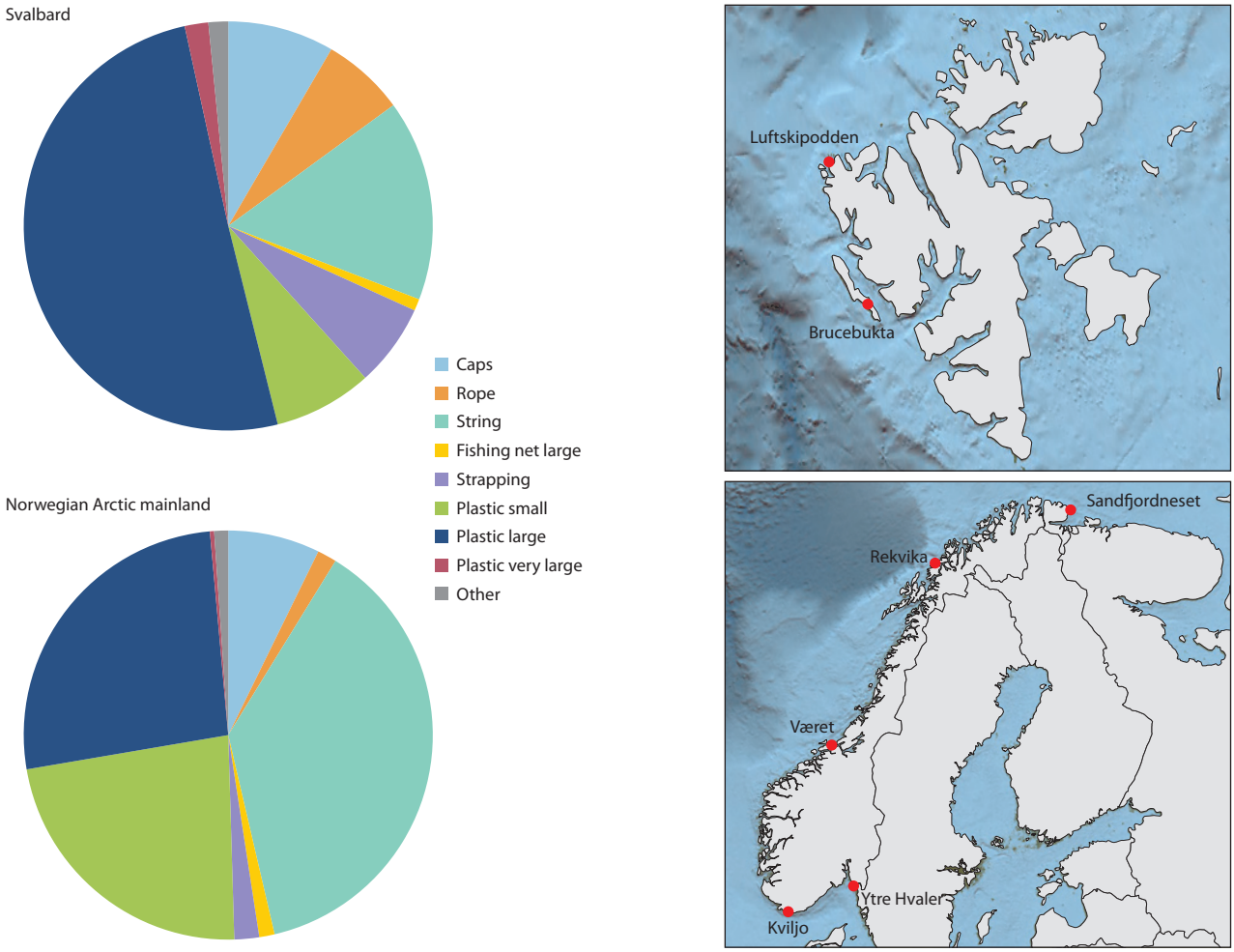

Figure 2.126 Composition of main plastic items found on a 100-m section of beach located on Svalbard and the Norwegian Arctic mainland coast (OSPAR, 2009b), and locations of the beach monitoring sites.

of plastic items collected in both regions on a 100-m length of beach. The composition of plastic beach litter found on Svalbard seems more diverse (which suggests a wider range of sources) compared to the items found on the Arctic mainland of Norway.

2.17.7 Environmental trends

Methods for defining debris, sampling, and interpreting patterns in space or time vary considerably among studies, making it difficult to draw conclusions about trends.

2.17.7.1 Spatial trends

Cózar et al. (2014) described global accumulation zones for plastic debris in the convergence zones of each of the five subtropical gyres. They hypothesized that the majority of particles were not recorded in their synthesis of surface water estimates for plastic concentrations due to fragmentation, sinking, food web processes, and unknown processes.

Lusher et al. (2014, 2015) found higher concentrations of microplastics in the northern North Atlantic (between mainland Norway and Svalbard's southwest coast) than in the northeast Atlantic off Ireland. Whether this represents a latitudinal gradient is still to be confirmed, but several mechanisms could explain this difference. The Arctic may act as a sink for marine plastics, with debris transported northward via the Gulf Stream and then into the Arctic Ocean. Plastics may accumulate in these currents along the way and receive inputs from mainland Europe and Scandinavia, and perhaps even further afield. Plastic particles trapped in multi-year sea ice for long periods (decades) may be released into the water column through ice melt, which is expected to increase as the climate continues to warm (Obbard et al., 2014). Information on the distribution of marine plastics and microplastics in the North Pacific is limited to the band between 20° and 52°N (Goldstein et al., 2013; Desforges et al., 2014; Law et al., 2014b). For the Arctic, there are only indirect estimates based on seabird (northern fulmar) ingestion (Avery-Gomm et al., 2012). However, there are no regional trends available, probably owing to small sample sizes, long retention times for plastics in intestines, and long migration routes from the subarctic North Pacific along the continental shelf to Baja California.

At smaller geographical scales, Browne et al. (2010) studied the distribution of macro- and microplastics along an estuary on the UK south coast, and found distinct patterns of debris accumulation in downwind habitats. Such patterns can also be assumed for Arctic estuaries and coastal runoff sites into fjords.

2.17.7.2 Temporal trends

Rising sea levels, altered rainfall patterns, and changes in solar radiation, wind speed, waves, and oceanic currents associated with climate change are all likely to increase the transfer of debris from coastal cities to marine and coastal habitats, including those in the Arctic (Browne et al., 2015). Few studies have investigated temporal trends in marine litter, especially in the Arctic.

According to the most recent OSPAR data, the amount of plastic beach litter at Svalbard showed little change between 2011 and 2014, but declined over this period on the Norwegian

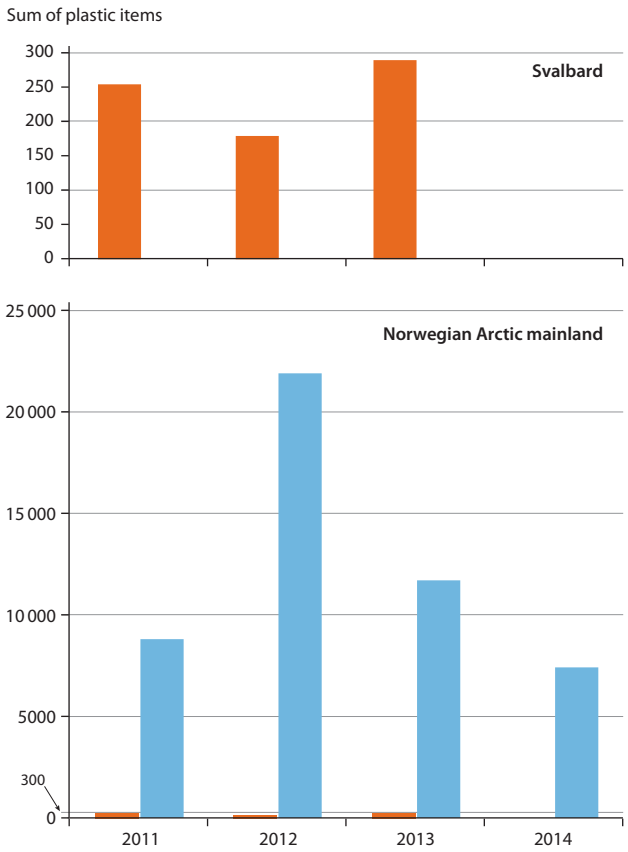

Figure 2.127 Total number of plastic litter items collected on a 100-m section of beach on Svalbard and on the Norwegian Arctic mainland (data from www.mcsuk.org/ospar/survey/export).

Arctic mainland. However, abundance is generally much higher along the Norwegian Arctic mainland coast than on Svalbard (Figure 2.127). Available data cover only 3-4 years and changes over time can not yet be estimated.

The Alfred Wegener Institute for Marine and Polar Research established the deep-sea observatory HAUSGARTEN in eastern Fram Strait west of Svalbard. This comprises nine stations along a bathymetric gradient crossed by a latitudinal transect of eight stations at the central HAUSGARTEN station. Bergmann and Klages (2012) analyzed photographs taken at a set camera transect at the HAUSGARTEN observatory in 2002, 2004, 2007, 2008 and 2011 to study the quality and quantity of macro litter in the deep Arctic sea. This involved 2878 images or an area of 8570 km^2 (excluding 741 images from 2008). Between 2002 and 2008 the number of images with litter decreased followed by a period of strong increase; from 0.54% of images showing litter in 2008 to 2.87% in 2011. When grouping litter into size categories, most items were of medium size (10–50 cm; 67%), followed by small (<10 cm; 30%) and large items (>50 cm; 3%). Litter items per km^2 over the study period as a whole varied between ~1000 (2007) and ~7500 (2011) (Bergmann and Klages, 2012).

Three bottom trawl surveys in inlet and offshore locations of Kodiak Island (Alaska) between 1994 and 1996 gave some information on the composition and abundance of benthic marine debris in that region (Hess et al., 1999). The surveys comprised benthic tows roughly 1.85 km long. The number of plastic items collected varied little between years at 77 (1994), 115 (1995) and 74 (1996).

Obbard et al. (2014), who identified plastic particles in sea ice cores at several sites across the Arctic Ocean, suggested that sea ice cores may provide a valuable retrospective record of the historical deposition of plastic litter in the Arctic.

2.17.8 Conclusions

Despite the exponential increase in available data on marine plastic debris globally, including the Arctic, status reports are limited by a lack of standardization in methodology and reporting consistency. This makes it difficult to draw general conclusions about temporal and spatial trends. Harmonized methodology is required for sampling, identifying and quantifying plastic items across the full size range. How Arctic conditions influence plastic transport, sedimentation and breakdown is not well known. The few reports of *in situ* measurements in Arctic and subarctic regions, together with experimental evidence for temperate organisms and reports of high amounts of plastics in Arctic seabirds, show marine biota are exposed to plastic pollution and experience negative effects. Marine litter floating in surface waters provides an artificial substrate/habitat, potentially accumulating persistent organic pollutants that are then accessible to marine life (Hirai et al., 2011; Tanaka, 2013; Herzke et al., 2016). Because macro- and microplastics cannot be effectively removed from the ocean, research is needed to understand how biological systems, such as fish and seabirds and their associated food webs are affected by ingestion, accumulation, chemical leakage and further breakdown of microplastics, particularly in a warming climate. To enable better understanding of the fate of plastic waste in the Arctic environment and to assess changes over time, current 'benchmarks' must be established against which changes can be compared. This requires a strengthening of research efforts in the Arctic regions.

Research topics that will improve understanding of marine plastic pollution and effects in the Arctic include: the identification and quantification of sources of marine plastic pollution in the Arctic; the occurrence, characteristics and distribution of marine plastic in the Arctic marine, freshwater and terrestrial ecosystems; the identification of hot-spots and local sources; the role of Arctic conditions on the fate and transport of marine plastic in water, ice and air; the potential changes in plastic distribution and transport to and within the Arctic under climate change; the impact of plastic pollution on Arctic food webs; and the remediation and avoidance of plastic pollution in the Arctic.

3. Biological and toxicological effects of chemicals of emerging concern

Author: Robert Letcher

Prior to 2010, numerous studies had been published on the (potential) biological effects of organohalogen compounds in Arctic biota as summarized by Letcher et al. (2010). Over the past six years, biological effects studies on Arctic biota have remained mainly focused on legacy persistent organic pollutants (POPs) and mercury (Hg), but have included polybrominated diphenyl ethers (PBDEs) and perfluoroalkyl carboxylic and sulfonic acids (PFASs). This chapter summarizes information on the chemical complexity and recent levels of organohalogen compounds and Hg and/or associated effects in key Arctic marine and terrestrial mammal, bird and fish species and populations, based on a concurrent AMAP assessment (AMAP, 2018).

Effects studies continue to be based on correlative relationships between biomarker/effect endpoints and measurements of organohalogen compounds in body tissues, for example liver, fat and/or muscle, as well as in blood plasma samples. Thus, an indication of effects is based on a weight of correlative evidence rather than being characterized as cause-effect. Current knowledge of the combined effects of legacy and emerging POPs (PBDEs and PFASs) and Hg is also reported because several individual or congener contaminants can affect similar pathways and effect outcomes. Furthermore, consideration of combined or 'complex mixture' effects (which includes targeted and as yet unidentified chemicals of emerging concern) will advance understanding of the impacts of contaminants as a consequence of using these more environmentally realistic exposure scenarios for Arctic biota. Depending on ecological factors such as species and population as well as the organohalogen or metal contaminants detected, tissue levels in highly exposed Arctic animals can be high enough to exceed putative risk threshold levels previously estimated for non-target and non-Arctic species (Fisk et al., 2005). In non-Arctic species studies, exposure to specific organohalogen compounds and Hg results in deleterious and observable effects via mode(s) of action and mechanisms (endocrine, immunological, neurological) that are a function of the contaminant type and level of exposure. Such effect levels are either derived from laboratory studies, semi-field studies or observations of affected animals in the wild. However, as described in a very recent Arctic effects assessment (AMAP, 2018), new approaches make use of techniques such as risk quotient calculations to summarize the cumulative effects of environmental contaminants from which critical body burdens can be estimated. The ultimate goal is to better predict or estimate the effects of contaminants in Arctic wildlife at the individual, population and ecosystem level.

Extensive knowledge gaps exist on the biological and toxicological effects of POPs in Arctic biota (AMAP, 2018). These include the establishment of concentration thresholds of biologically relevant (and not statistically determined) health effects, the use of toxic threshold endpoints (e.g. risk quotients), assessments of combined effects of contaminant exposure with natural stressors (e.g. infectious and zoonotic diseases), integration of wildlife and human health assessments, and assessment of how multiple stressors are directly and indirectly impacted by a changing Arctic due to global climate change (Letcher et al., 2010; McKinney et al., 2015). The need for new methods and approaches has been identified, including expansion of *in vitro* experimental approaches, and individual and combined effects of both specific chemicals and chemical mixtures. Advances in approaches and techniques to assess toxicology and biological effects are also needed for Arctic biota at different levels of biological organization. As reviewed by Bahamonde et al. (2016), a major advance in the past five years has been the result of the 'omics' revolution, which has generated unprecedented amounts of data on molecular changes that can occur in a cell, tissue, or whole organism as a function of chemical stress. For ecotoxicology, these approaches have been used to annotate adverse outcome pathways for environmental contaminants; to characterize chemical modes of action; to investigate mechanisms of organismal adaptation; and to identify candidate biomarkers of exposure. There are numerous examples of studies that have applied 'omics' technologies to study environmental contaminants, and these have often included gene expression analysis using microarrays and next-generation sequencing (Mehinto et al., 2012; Wiseman et al., 2013). Furthermore, because they can address post-transcriptional changes associated with contamination, proteomic and metabolomic studies have become more prevalent. *In silico* modeling has also expanded in the Arctic context to extrapolate biological effects at the individual level to the population and ecosystem level. Nevertheless, to date, there appear to have been no published studies as yet reporting the use of 'omics' approaches for Arctic wildlife and fish and in relation to POP or organohalogen exposure.

More specifically for chemicals of emerging Arctic concern (CEACs), up until the present there is essentially a total knowledge gap with respect to biological or toxicological effects in Arctic biota. For example, there appear to have been no new effects studies on polychlorinated naphthalenes (PCNs) in Arctic biota since the last AMAP assessment in 2010 (Bidleman et al., 2010). However, there have been important reviews published recently on the (environmental) toxicology of several classes of compound, such as PFASs, brominated flame retardants (BFRs), chlorinated flame retardants (CFRs), phosphate flame retardants (PFRs; including organophosphate esters), phthalates, siloxanes, pharmaceuticals and personal care products (PPCPs), organotins, polycyclic aromatic hydrocarbons (PAHs) and microplastics, that are of established and/or increasing importance with respect to exposure in non-Arctic biota. These reviews are listed in Table 3.1 and outcome highlights and knowledge deficiencies are noted and discussed in the following sections. This non-Arctic species information is revealing and suggestive of mechanisms and modes of action and adverse outcome pathways of ecotoxicological effect and impacts for Arctic biota, especially wildlife and fish.

Table 3.1 Summary of reviews on the biological effects and toxicology of chemicals of emerging concern (CECs) in non-Arctic biota, and knowledge highlights and deficiencies of potential relevance to Arctic biota.

Class	Review and references therein	Examples of biological effects and toxicology, and knowledge highlights and deficiencies
PFASs	de Witt, 2015	• PFASs are more protein associated than lipid associated, and so PFAS protein binding is important to understand toxicological effects in exposed organisms. • Use of physiologically-based pharmacokinetic (PBPK) models is effective in predicting and understanding the toxicokinetics of PFASs in biological systems. • The metabolic effects of PFASs have various connections with other systemic toxicities induced by PFAS. • Human and rodent studies remain incomplete and show that more information is needed about mechanism(s) of immunotoxicity to reduce PFAS-associated health effects and to improve regulatory exposure limits.
BFRs	Hendriks and Westerink, 2015; Koch et al., 2015	• Thyroid, immune and reproductive development effects have been reported for various wildlife (e.g. birds and mammals) as a result of BFR exposure. • Besides conventional neurotoxicity tests like determining *in vivo* (neuro)behavioral effects, and *in vitro* cytotoxicity and Ca^{2+}-homeostasis, an increasing number of studies rely on tests in alternative species, such as the tropical species zebrafish as a representative for fish in general. • Some neurological studies on BFRs and halogenated organophosphate esters (OPEs) already exist (e.g. for fish) and the number of studies is steadily growing. • Combined epidemiological and toxicological studies for PBDEs underline the need for similar studies for replacement BFRs. • Although HBCDD is an established POP, knowledge of its toxicodynamics and effects in mammals, birds and other wildlife is limited.
CFRs	Crump et al., 2011; Feo et al., 2012; Wang et al., 2016	• Few studies have reported on Dechlorane Plus (DDC-CO) effects and toxicity. • Toxicological effects of DDC-CO and related compounds have mainly been observed at the transcriptome and metabolome levels. • Experiments in laboratory animals show effects only at high doses, with no effects seen at environmentally relevant doses.
OPEs and plasticizers	Wei et al., 2015	• More short-term and long-term toxicological data are needed on antagonistic, or even synergistic effects of OPEs and mixtures in the aquatic environment to achieve more reliable risk assessments. • There is a lack of detailed information on the potential toxicological effects of organismal exposure to OPEs. • The health impacts of exposure cannot be evaluated against the proposed reference-dose-response (RfD) values; thus, establishing RfDs based on a solid toxicological background and adequate toxicity end points is an urgent research priority.
Phthalates	Net et al., 2015	• Many laboratory-based studies have focused on the ecotoxicology of phthalates in biota including aquatic organisms and rodents. • Phthalates elicit endocrine-disrupting effects, such as in relation to reproductive physiology in fish and mammals. • Estrogenic effects are an important biological impact of phthalates on wildlife, and appear to act by interfering with the functioning of hormone systems. • Phthalates, as well as various abiotic and biotic degradation products (via hydrolysis, photolysis, photo-oxidation, and biodegradation) can affect fertility and cause developmental toxicity in humans and many aquatic and terrestrial animal species.
Siloxanes	Dekant and Klaunig, 2016	• Rapid elimination by exhalation, means bioaccumulation of the major environmental siloxane, decamethylcyclopentasiloxane (D5), in lipid-rich tissues is not expected. • Laboratory studies on rodents showed D5 exposure caused a limited number of potentially adverse effects and no reproductive or developmental toxicity.
PPCPs	Arpin-Pont et al., 2016	• More studies on temporal trends, regional, and global monitoring of PPCPs are needed to understand their environmental profiles and potential risks to wildlife and other biota. • There are few accurate data on the fate of PPCPs in the marine ecosystem and effects on marine organisms is greatly lacking. • As an example, a model fish species exposed to the anxiolytic drug benzodiazepine (oxazepam) in water exhibited increased activity, reduced sociality, and higher feeding rates. • The lack of assessments of potential risk of PPCP exposure to marine species is a major knowledge gap. Long-term ecotoxicological tests on sensitive species at environmental levels are required. • There is still (as of 2013) a lack of knowledge on the ecological effects of pharmaceuticals in the environment.
Organotins	Graceli et al., 2013	• Organotins can induce impairments in immunological, reproductive and metabolic function *in vivo* and *in vitro*. They are potent, endocrine-disrupting chemicals that act against marine invertebrates, mainly (but not exclusively) mollusks. They are also suspected to cause imbalances in the endocrine systems of mammals, including humans and rodents. • Organotins are obesogenic chemicals and tributyltin (TBT) is an example of an environmental endocrine-disruptor that promotes adipogenesis through RXR and PPARγ activation *in vitro* and *in vitro*. • Improved studies on absorption, distribution, metabolism and elimination are required in different animal models.
PAHs	Andersen et al., 2015	• PAHs are the primary toxic constituents in crude oil, and cytotoxic, immunotoxic, mutagenic and carcinogenic effects have been reported in many fish species including Arctic polar cod.
Microplastics	Lönnstedt and Eklöv, 2016	• As of 2016, global plastic production is estimated at about 300 million tonnes annually and rising. • Plastic breaks down into smaller pieces in the environment through degradation by ultraviolet radiation, physical forces, and hydrolysis, among others. • Plastic debris can affect marine biota physically and chemically where the latter contributes leached chemical pollutants that are part of the plastics or that have been absorbed by the plastic. • European perch larvae exposed to environmentally relevant concentrations of microplastic polystyrene particles showed inhibited hatching, decreased growth rates, and altered feeding preferences and innate behaviors.

3.1 Per- and polyfluoroalkyl substances

Perfluorooctane sulfonate (PFOS) is the dominant and most frequently detected PFAS in wildlife from around the world including the Arctic (see Section 2.1). The general toxicological features of PFASs include major species and sex differences in pharmacokinetic disposition depending on carbon-chain length and functional groups, and differential potencies based on their primary mechanism of action, that is, activation of the nuclear receptor PPARα (de Witt, 2015 and references therein). Current understanding of adverse effects associated with PFAS exposure based on laboratory animal models include hepatotoxicity, tumor induction, developmental toxicity, immunotoxicity, neurotoxicity and endocrine disruption. Associations and probable links between exposure to some PFASs and adverse health outcomes in humans have been suggested by recent epidemiological reports. Ecological and human health risk assessments of most PFASs are still in their infancy. A new generation of PFASs has emerged in commerce, with little information regarding their environmental fate and distribution as well as potential environmental health effects.

Known PFAS toxicological effects and important knowledge gaps were summarized by de Witt (2015 and references therein). For example, transplacental and lactational transport are considered important exposure routes for biota, because developmental toxicity is thought to be one of the primary toxic outcomes of PFAS exposure. Renal elimination is a key determinant of biological half-life for PFASs. However, it is not clear how the renal tubular secretion system contributes to net transfer across renal tubular cells. More information on the mechanistic representation of renal tubular transfer, estimation of albumin-binding properties, and human data is required to improve physiologically-based pharmacokinetic (PBPK) models for the prediction and understanding of PFAS kinetics in biological systems. Metabolic effects have various connections with other systemic toxicities known to be elicited by PFASs, and may serve as the fundamental basis for other observed toxicities. Developmental effects of PFAS exposure have been shown in postnatal laboratory rats or mice, where typically there is increased mortality in the first hours or days after birth. Also, effects have been reported that may persist beyond weaning, including delayed eye opening, potential for delayed puberty, abnormal mammary gland development, and liver hypertrophy. With regard to neurological effects, PFASs affect molecular targets in the brain of test animals after gestational exposure and in the newborn period, and the cholinergic system may be a possible target for the PFAS. PFAS-induced disturbance in the processes of synaptogenesis, dendritic outgrowth and ontogeny of neurotransmitter systems all seem plausible mechanisms, and apoptosis, specific proteins, signaling molecules, calcium homeostasis and oxidative stress can be the molecular reasons behind the disturbances of these processes.

From rodent model studies on immunological effects, both PFOS and perfluorooctanoic acid (PFOA) are known to induce a dose responsive suppression on adaptive immunity in mice, and the mechanism(s) involved is likely to be linked with altered cytokine signaling that arises from interaction of PFASs with PPARα, but may also be related to the interaction of PFASs with other signaling molecules. Human and rodent studies remain incomplete and more study is necessary on the mechanism(s) of immunotoxicity to reduce PFAS-associated health effects and improve regulatory exposure limits. Considerable research has been done to elucidate the potential carcinogenic effects of PFASs. There is evidence that the liver is the main target of PFOA exposure due to activation of PPARα. This mechanism contributes to the induction of liver tumors in rats. There is limited evidence that Leydig cell tumors may be induced by a hormonal mechanism mediated by PPARα activation.

3.2 Brominated flame retardants

Brominated flame retardants have spread globally via air and water, are found in abiotic and biotic samples from the polar regions, and bioaccumulate in aquatic and terrestrial food chains including in the Arctic (see Section 2.2). Some BFRs also appear to biomagnify. Along with potential thyroid, immune and reproductive effects, as summarized recently by Hendriks and Westerink (2015 and references therein), research shows that the nervous system is a sensitive target organ, with neurotoxicological effects occurring via some common neurotoxic mechanisms. In recent years, there have been more studies on the newer, replacement flame retardants. Besides conventional neurotoxicity tests, such as determining *in vivo* (neuro)behavioral effects and *in vitro* cytotoxicity and Ca^{2+}-homeostasis, an increasing number of studies have relied on alternative/surrogate species, such as zebrafish (*Danio rerio*) (as representative of fish in general). Zebrafish studies with some BFRs and halogenated organophosphate esters already exist and the number of studies has steadily increased. Hendriks and Westerink (2015) concluded that the combined epidemiological and neurotoxicological study results for PBDEs clearly underline the need for more study on replacement and emerging BFRs.

Proper risk assessments are hampered by an overall scarcity of data for non-PBDE flame retardants, particularly regarding environmental persistence, human exposure levels, and the formation of breakdown products and possible metabolites as well as their toxicity. The lessons learned from the significant adverse health effects of PBDEs and to a lesser extent recently established BFRs such as hexabromocyclododecane (HBCDD), clearly show the need for a full (eco)toxicological risk assessment before new flame retardants are commercially introduced on the market and used on a large scale.

Another recent review, by Koch et al. (2015 and references therein), focused on HBCDD and the known biological effects were summarized. It was concluded that knowledge on the toxicodynamics of HBCDD remains limited even with HBCDD considered an established environmental contaminant. Studies reported thus far indicate a considerable toxicological potential in exposed animals. For example, recent studies show increased transcription of the catalase gene in the gills of clams after exposure to HBCDD. Catalase is important because of its ability to protect cells against H_2O_2-mediated oxidative stress, which is a result of the increased ROS (reactive oxygen species) concentrations following exposure to HBCDD. In human Hep G2 cells, HBCDD induces the expression of different cell surface molecules (TCR, MHC class II, CD11c, CD80 and CD86) and the production of cytokines (interleukin-4), hence

HBCDD may accelerate the immune system and cause allergic reactions. The maturation and function of bone marrow derived dendritic cells (BMDC), which show an increased expression of surface molecules after exposure to HBCDD, are regulated by thyroid hormones. HBCDD is well known for its ability to alter the composition of these hormones, which may lead to an accelerated maturation of BMDCs. Hepatic CYP2B and CYP3A were induced by HBCDD especially in female rats. The pregnane-X receptor (PXR) and/or the constitutive androstane receptor (CAR) are responsible for this induction.

Some studies addressed potential effects of HBCDD, usually in combination with other contaminants. For white-tailed sea eagle (*Haliaeetus albicilla*), potential associations were studied between HBCDD (in combination with PBDEs and bromobiphenyl-153) and female productivity but none were found (Nordlöf et al., 2010). No association was found either when HBCDD and intestinal parasites were studied in glaucous gulls (*Larus hyperboreus*) found dead or dying on Bjørnøya (Sagerup et al., 2009).

3.3 Chlorinated flame retardants

Concern for chlorinated flame retardants in the Arctic is largely focused on Dechlorane Plus (DDC-CO) and related compounds (see Section 2.3). DDC-CO, dechlorane 602, dechlorane 603 and dechlorane 604 are flame retardants that have been used for a long time as a substitute for Mirex. As summarized in a review by Feo et al. (2012), DDC-CO and related compounds have been detected in different aquatic and terrestrial species, supporting their bioaccumulation and biomagnification. However, until 2011, toxicity data for DDC-CO were essentially non-existent and effectively all information was from a US EPA HPV Test Challenge report (EHSI, 2004). This showed that at the highest administered dose of 25 000 mg/kg body weight, DDC-CO had no effect on Sherman–Wistar rats in an acute oral toxicity study and that the No-Observable-Adverse-Effect-Level (NOAEL) after 90 days in a repeated dose (sub-chronic) study was 100 000 ppm. A 28-day dermal exposure with rabbits was the only toxicity study to report any adverse effects of DDC-CO; female rabbits showed a significant dose-related decrease in liver and ovary weight compared to control animals at concentrations of 2000 mg/kg body weight (treated for 5 days within a week-long period). In the first known toxicology study in an avian species, Crump et al. (2011) reported on toxicological and molecular responses to DDC-CO exposure in a combined *in vitro*/*in ovo* study in chicken embryonic hepatocytes and in chicken embryos following injection of DDC-CO into the air cell of eggs prior to incubation. In egg injections and embryo development, there were no effects on pipping success up to a dose of 500 ng DDC-CO/g egg. Also, none of the mRNA transcripts changed as a result of *in vitro* or *in ovo* exposure to DDC-CO. It was concluded that at current environmental exposure levels, no adverse effects of DDC-CO on avian embryonic viability or pathways associated with the genes assessed were predicted. Two recent studies indicate DDC-CO may possess subtle toxicological effects at the transcriptomic, metabolomic, and proteomic levels in mice (Wu et al., 2012) and sturgeon (Liang et al., 2014). Mice exposed to DDC-CO via oral gavage for 10 days exhibited altered expression of genes involved in carbohydrate, lipid, nucleotide, and energy metabolism, as well as signal transduction processes (Wu et al., 2012). Juvenile Chinese sturgeon (*Acipenser sinensis*) exposed to DDC-CO via intraperitoneal injection showed altered protein expression, with changes being observed in proteins associated with stress response, metabolism, signaling pathways, and apoptosis (Liang et al., 2014). These observations are supported by a recent review by Wang et al. (2016), which concluded that the toxicological effects of DDC-CO and related compounds are mainly observed at the transcriptome and metabolome levels. There do not appear to be any other reports of DDC-CO effects in the published literature. Similarly, Wang et al. (2016) concluded that there do not appear to be any published data on the toxicological effects of DDC-CO analogs.

3.4 Organophosphate ester-based flame retardants and plasticizers

Prior to 2010, organophosphate esters (OPEs) were not even known to be a CEC in the Arctic (de Wit et al., 2010) and so biological effects were completely unknown and unstudied for Arctic biota. As reported by Wei et al. (2015 and references therein; see also Section 2.4), increasing use of these compounds worldwide (due in part to the phase-out and regulation of BFRs such as PBDEs) has increased the emissions of OPEs from consumer products and traffic as the predominant sources in the environment. OPEs are now ubiquitously detected in non-source areas throughout the world, including the Antarctic and Arctic. Significant variations in global levels and distribution patterns can be attributed to the factors including differences in their applications, sources, and environmental transformation. A major deficiency regarding exposure effects is that more short-term and long-term toxicological data are needed concerning antagonistic, or perhaps synergistic effects of OPE mixtures in the aquatic environment to achieve more reliable risk assessments. There is a current lack of detailed information on the potential toxicological effects from organismal exposure via dermal contact, dust ingestion, inhalation and dietary intake. Further studies are required to associate the potential health effects with long-term and chronic exposure to OPEs. The health impacts of exposure cannot be evaluated against the proposed reference-dose-response (RfD) values; so, establishing RfDs based on a solid toxicological background and on adequate toxicity end points is an urgent research priority before any conclusions regarding the potential health effects of OPEs can be drawn.

3.5 Phthalates

As summarized in a review by Net et al. (2015 and references therein), some phthalates are endocrine-disrupting chemicals, and their environmental behavior has attracted considerable attention due to their potential impact on ecosystem functioning and public health. Many studies have focused on the ecotoxicology of phthalates in biota including aquatic organisms and rodents. Compilation data of the major environmental phthalates, di-n-butyl phthalate (DnBP) and di (2-ethylhexyl) phthalate (DEHP) showed aquatic organisms can accumulate high levels. Phthalates are involved in endocrine disrupting-effects that can affect reproductive physiology, as has been shown in different species of fish and mammals. For example, a study reported that exposure

to DEHP from hatching to adulthood accelerated the start of spawning and decreased egg production in exposed marine medaka (*Oryzias latipes*) females, whereas exposure to both DEHP and mono (2-ethylhexyl) phthalate (MEHP) reduced the fertilization rate of oocytes spawned by untreated females paired with treated males. The estrogenic effect is one of the important biological impacts of phthalates on wildlife and appears to act by interfering with the functioning of various hormone systems. Dimethyl phthalate (DMP), butylbenzyl phthalate (BBP), DnBP, and DEHP affect reproduction in annelids (aquatic and terrestrial), mollusks, crustaceans, insects, fish and amphibians, impair development in crustaceans and amphibians, and induce genetic aberrations. Net et al. (2015) concluded that phthalates, as well as various abiotic and biotic degradation products (via hydrolysis, photolysis, photo-oxidation, and biodegradation) can cause toxic effects on fertility and the development of humans as well as on many aquatic and terrestrial species. Chronic exposure of phthalates to aquatic organisms and humans thus raises many toxicological questions.

3.6 Siloxanes

Internal reports from Dow Corning Corporation have reported inhalation toxicity for the linear siloxanes L2 (hexamethyldisiloxane), L3 (octamethyltrisiloxane) and L4 (decamethyltetrasiloxane) within rats. Effects ranged from respiratory distress, neurological dysfunction, hepatic toxicity and increased liver weight (Meyers et al., 2013). However, concentrations producing effects (>400 ppm) were much higher than the highest summed lVMS (L2, L3, L4, L5) indoor air concentrations (37 parts per trillion) (Pieri et al., 2013).

Dekant and Klaunig (2016 and references therein) reviewed the toxicology of the major environmental cyclic siloxane, decamethylcyclopentasiloxane (D5). D5 is a highly lipophilic and volatile compound with a particular kinetic behavior after oral administration (see Section 2.7). In rodents exposed via the diet, D5 concentrations were shown to be rapidly reduced due to evaporation, and feeding studies were therefore extremely difficult to conduct. In this same study, after inhalation D5 was absorbed into the lungs and thus showed inhalation is the only reasonable route of exposure and thus an important contribution to the systemic bioavailability of D5. Due to this rapid elimination by inhalation, bioaccumulation of D5 in lipid-rich tissues is not expected. Data from repeated dose inhalation studies showed D5 exposure of experimental animals results in only a small number of potentially adverse effects and does not result in reproductive or developmental toxicity. In repeated chronic exposure inhalation studies, the effects observed were limited to local effects in the nasal cavity and the lungs, reversible liver weight increases without histopathological changes, and a small increase in the incidence of uterine adenocarcinoma in female rats after two-year inhalation exposure. D5 was shown not to be genotoxic. Due to the absence of both genotoxicity and estrogenicity of D5 in a variety of rodent model systems, it was concluded that neither genotoxicity nor a direct estrogen effect was responsible for the slight increase observed in uterine tumors. While D5 does not appear to be a direct dopamine agonist, experimental data with lab rodents are indicative of an indirect interaction of D5 on the dopamine system and the alteration of the pituitary control of the estrus cycle. Like other dopamine receptor agonists, D5 decreases pituitary lactotroph release of prolactin *in vitro* and decreases circulating prolactin levels *in vivo*. Further studies *in vitro* suggest D5 may interfere with one or more downstream components of the dopamine signal transduction pathway. The observed effects of D5 on mammalian (rat) estrus cyclicity are consistent with a dopamine-like effect, and further suggest that D5 may be accelerating the aging of the reproductive endocrine axis.

After D5, the second major environmental siloxane is octamethylcyclotetrasiloxane (D4). The toxicity of D4 has been investigated in several aquatic species. No adverse effects were observed in midges exposed to dissolved concentrations in water between 0.5–15 µg/L (Kent et al., 1994). However, 50% mortality occurred in juvenile rainbow trout (*Oncorhynchus mykiss*; body mass <1 g) at 10 µg/L in water and after 14 days of exposure (Sousa et al., 1995), indicating a toxicological risk to fish at early life stages. In rats, D4 has displayed weak estrogenic activity (McKim et al., 2001) as well as impaired fertility at high inhalation exposures (Meeks et al., 2007; Quinn et al., 2007; Siddiqui et al., 2007a).

Fairbrother et al. (2015) also reviewed toxicology of D5 in the literature and concluded that D5 poses no toxicity risk in the environment. Aquatic toxicity has been observed experimentally in the amphipod crustacean *Hyalella azteca* exposed to natural sediment spiked with D5 (Norwood et al., 2013). Over a 28-day exposure, chronic LC50 was observed at 191 and 857 µg/g dw concentrations in sediment containing 0.5% and 11% organic carbon, respectively. However, toxicity risk to the environment is considered low as concentrations observed near point sources (0.8–1.4 µg/g dw sediment; Humber Estuary, Inner Oslofjord) (Powell et al., 2010; Sparham et al., 2010) were well below those shown to induce effects. This is supported by tissue-based risk assessments with summed cVMS (D4, D5 and D6 (dodecamethylcyclohexasiloxane)) concentrations in biota reported in the literature (0.2 nmol/g lipid to 0.1 µmol/g lipid) are below estimated critical target lipid body burdens that cause both acute (115 µmol/g lipid) and chronic (25 µmol/g lipid) affects for all cVMS (Redman et al., 2012). Inhalation exposure to D5 was found to cause increases in liver weight and respiratory tract irritation at 160 ppm after a 28-day exposure (Burns-Naas et al., 1998). In chronic inhalation exposures, increased incidences of endometrial adenocarcinoma were reported at concentrations between 10 and 160 ppm after 1 year (Dekant and Klaunig, 2016).

3.7 Pharmaceuticals and personal care products

Pharmaceuticals and personal care products (PPCPs) are a large class of different chemicals and are used in a variety of ways, for example drugs used in human and veterinary medicine, fragrances, sunscreen agents, and cosmetics ingredients (see Section 2.8). PPCPs presently include over 3000 substances with new ones entering the market every year. Arpin-Pont et al. (2016 and references therein) reviewed current knowledge on PPCP contamination of the marine environment. At the time this review was written they had found that 196 pharmaceuticals and 37 personal care products had been reported for more than

50 marine sites. Despite the scarcity of quantitative PPCP data, contamination of the marine ecosystem is a new reality, with data available in the literature confirming the risk of exposure for marine wildlife species. Arpin-Pont et al. (2016) concluded that it is essential to acquire more accurate data on the fate of PPCPs in the marine ecosystem and the effects of PPCPs on marine organisms. A major knowledge gap is the lack of assessments of potential risk of PPCP exposure to marine species. Also, there is a need for long-term ecotoxicological tests on sensitive species at environmental levels. As summarized by Brodin et al. (2013), several ecotoxicological studies have been reported for pharmaceutical compounds, but there is still a general lack of knowledge about the ecological effects of pharmaceuticals present in the environment. In the same paper it was shown that the anxiolytic drug benzodiazepine (oxazepam) altered the behavior and feeding rate of wild European perch (*Perca fluviatilis*) when exposed to water with concentrations typical of levels in surface waters influenced by effluents from wastewater treatment plants. More specifically the exposed fish exhibited increased activity, reduced sociality, and higher feeding rates. It was concluded that anxiolytic drugs in surface waters could thus alter animal behaviors that are known to have ecological and evolutionary consequences.

3.8 Organotins

Organotins belong to an organometallic class of pollutants, and are used mainly as biocides in antifouling boat paints (see Section 2.13). Antifouling paints are used to reduce encrustations by barnacles, algae, mussels, and other marine invertebrates. Antifouling solutions are based on two main triorganotins, tributyltin (TBT) and triphenyltin (TPT), which are known to be the most toxic of the organotins. Organotins commonly break down in the environment. For instance, TBT degrades to dibutyltin and monobutyltin, and TPT degrades to diphenyltin and monophenyltin. As reviewed by Graceli et al. (2013 and references therein), the toxicity of organotins is a controversial issue. Exposure to triorganotins, especially TBT, has been shown to induce impairments in immunological, reproductive and metabolic function *in vivo* and *in vitro*, particularly in gastropods. Organotins are potent, endocrine-disrupting chemicals that act against marine invertebrates, mainly (but not exclusively) mollusks. TBT can cause disorders in the mammalian reproductive system, such as impairment of the modulation of the hypothalamic-pituitary-gonadal axis (ovary and testis). Moreover, TBTs can cross the maternal-fetal-placental unit, inducing physiological and morphological changes, which lead to abnormal fetal and postnatal development. In addition, recent investigations suggest that organotins are obesogenic chemicals and that TBT is an example of an environmental endocrine disruptor that promotes adipogenesis through RXR and PPARγ activation *in vitro* and *in vitro*. This compound is correlated with changes in the immune system because it modulates the release of cytokines. Organotins can alter homeostatic metabolic set-points, disrupt appetite controls, perturb lipid homeostasis to promote adipocyte hypertrophy, and stimulate adipogenic pathways that enhance adipocyte hyperplasia. Graceli et al. (2013) concluded that more study is required on the absorption, distribution, metabolism and elimination of organotins in different animal models.

3.9 Polycyclic aromatic hydrocarbons

It is well known that the Arctic contains some of the world's largest reserves of petroleum resources and the region is becoming increasingly accessible due to declining sea ice and technological advances. Oil spills from operational or accidental discharges represent a major threat to Arctic marine organisms and therefore studies on the effects of oil pollution are given high priority. As summarized by Andersen et al. (2015 and references therein), PAHs are the primary toxic constituents of crude oil, and cytotoxic, immunotoxic, mutagenic and carcinogenic effects have been reported in many fish species. Exposure of embryos and fry to crude oil-derived polycyclic aromatic hydrocarbons (PAHs) causes cardiac dysfunction and abnormalities in the neural system, spinal curvature and craniofacial structures. In one example, analyses of the liver transcriptome of polar cod from Svalbard revealed rapid and specific responses to crude oil, but with a relatively small effect of temperature. It was concluded that although polar cod seems able to cope with acute oil exposure and temperature changes over relatively short periods, long-lasting phenotypic effects such as epigenetic changes warrant further study.

3.10 Microplastics

As reported by Lönnstedt and Eklöv (2016 and references therein), annual global plastic production is currently around 300 million tonnes, and rising by 20 million tonnes a year. In and around urbanized areas in particular, much of the waste plastic enters waterways and is then transported into the ocean, ultimately reaching more remote regions such as the Arctic. Degradation (for example by ultraviolet radiation, physical forces, and hydrolysis) causes the breakdown of plastics in the environment into much smaller pieces. Plastic debris can affect marine biota physically and chemically in cases where the latter contributes leached chemical pollutants that are part of the plastics or that have been absorbed by the plastic. As of 2016, Lönnstedt and Eklöv (2016) concluded that although passive ingestion of plastic microdebris by filter feeders (such as fish) is known to occur, the ecological significance of ingestion is poorly understood. To better understand potential effects of microplastic waste on the vulnerable younger life stages of fish, Lönnstedt and Eklöv (2016) examined how natural levels of microplastic particles affected the development, behavior, and survival of European perch (*Perca fluviatilis*). European perch larvae that were exposed to environmentally relevant concentrations of microplastic polystyrene particles (90 μm in diameter) showed inhibited hatching, decreased growth rates, and altered feeding preferences and innate behaviors. Also, individual fish exposed to microplastics did not respond to olfactory threat cues, which can increase predator-induced mortality rates. Overall, it was concluded that the results demonstrated that microplastic particles operated both chemically and physically on larval fish performance and development.

4. Further contaminants of potential Arctic concern

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Data for environmental measurements of more than 150 individual chemicals and groups of substances in the Arctic were presented in Chapter 2. However, these data represent just a tiny fraction the roughly 150 000 substances that have been registered for use in Europe or the USA over the past 30 years, or the more than 124 million that have been assigned Chemical Abstracts Service (CAS) Registry Numbers (see www.cas.org/content/chemical-substances). So are there additional chemicals with Arctic accumulation potential? This chapter examines several approaches to answering this question: computer-based or '*in silico*' screening, chemical analysis for target chemicals, and non-target analytical screening.

4.1 Identifying further chemicals of emerging (Arctic) concern

4.1.1 *In silico* screening of chemical inventories

Over the past 10 years, various studies have addressed the question of how many of the tens of thousands of chemicals in commerce globally constitute additional persistent organic pollutants (POPs), i.e. contaminants that would meet the Stockholm Convention criteria for classification as POPs. These studies can be described as *in silico* screening because they have been carried out by estimating environmentally relevant physical-chemical properties using Quantitative Structure Property Relationship (QSPR) models for thousands of individual compounds with known molecular structures and then screening the lists to identify those with predicted persistence, bioaccumulation and/or long-range transport potential (LRTP) that exceed various regulatory guidelines.

The screening studies have focused on identifying and prioritizing chemicals that are persistent (P), bioaccumulative (B) and toxic (T) based on whether they exceed threshold values for each property (Muir and Howard, 2006; Öberg, 2006; Brown and Wania, 2008; Stenberg et al., 2009; Brooke and Burns, 2010; Howard and Muir, 2010; Papa and Gramatica, 2010; Rorije et al., 2011; Öberg and Iqbal, 2012; Strempel et al., 2012; Bänsch-Baltruschat et al., 2015; Gramatica et al., 2015). The starting point for all of these studies are lists of chemicals with known molecular structure in various publically available databases developed by chemical regulators. For example, the European Inventory of Existing Chemical Substances (EINECS); the European List of Notified Chemical Substances (ELINCS); the US Toxic Substances Control Act Inventory Update Rule (TSCA-IUR); the Canadian Domestic Substances List (DSL); and the European Chemicals Agency (ECHA) list of pre-registered substances under REACH; as well as the database (SMILECAS) that is included with the US EPA EPISuite program (Table 4.1). To be on the TSCA, EINECS, ELINCS or REACH inventories, these substances must be produced or imported in quantities of over 1 t/y (Europe) or 4.5–11.6 t/y (USA). The number of substances included in the studies is limited mainly to neutral organic chemicals for which existing QSPR models for predicting P, B and T are most applicable, and so omits most organometallics, and all inorganics, salts, polymers and surfactants.

As part of this assessment, data on properties of a number of chemicals of Arctic concern have been compiled in an online AMAP database. The database serves as an 'electronic' Annex (Appendix 1) to this assessment report that can also be used for other purposes such as informing the design of future monitoring studies and sampling campaigns as well as the development of exposure assessment models.

Table 4.1 Recent screening studies for chemicals on European or US/Canadian chemical inventory lists with persistence (P), bioaccumulation (B), and long-range transport potential (LRTP).

Study	Databases/lists used	Total chemicals initially screened	Final list for which parameters estimated	P and B	P, B and LRTP
Muir and Howard (2006)	Environment Canada DSL organics	11 317	11 317	30	28
Howard and Muir (2010)	DSL, TSCA-IUR	22 263	22 263	610	105
Strempel et al. (2012)	EINECS, ELINCS & SMILECAS	127 281	94 483	1202	nd
Scheringer et al. (2012)	EINECS & SMILECAS	122 000	93 144	nd	510
Rorije et al. (2011)	EINECS, pesticides (US/EU), pharmaceuticals (EU/WHO)	107 337	64 721	1986	1171
Öberg and Iqbal, (2012)	ECHA pre-registration	118 285	48 782	829	125
Gramatica et al. (2015)	Reassess results of above studies	4412	3567	1313	nd
	Total (duplicates removed)			3743	

nd: Not determined; DSL: Canadian Domestic Substances List; TSCA-IUR: US Toxic Substances Control Act Inventory Update Rule; EINECS: European Inventory of Existing Chemical Substances; ELINCS: European List of Notified Chemical Substances; SMILECAS: (a database); ECHA: European Chemicals Agency; US: United States; EU: European Union; WHO: World Health Organization.

Many screening studies have included consideration of LRTP and whether substances might undergo deposition and accumulate in remote regions (Muir and Howard, 2006; Brown and Wania, 2008; Howard and Muir, 2010; Rorije et al., 2011; Öberg and Iqbal, 2012; Scheringer et al., 2012; Strempel et al., 2012; Bänsch-Baltruschat et al., 2015). Results of recent screening studies are summarized in Table 4.1. The criteria used for screening varied with each study but generally followed Stockholm Convention, US EPA and/or REACH guidance (see Chapter 5 for more information on these criteria).

Muir and Howard (2006) used a database of 11 317 organic chemicals for which physical-chemical properties had been estimated as part of the categorization of the Canadian DSL (Environment Canada, 2004). They identified 28 substances with POP-like characteristics, i.e. with modeled LRTP and bioconcentration factor (BCF) characteristics exceeding the Stockholm Convention criteria (BCF >5000, atmospheric oxidation half-life (AO t½) ≥2 days). Of this group, 18 were listed in the EINECS or TSCA databases (i.e. with production volumes >4.5 t/y). Howard and Muir (2010) assembled a database of 22 263 chemicals based on the DSL and TSCA-IUR. This list represented chemicals in commerce in North America, with production generally >4.5 t/y during one or more inventory updates between 1992 and 2006. Using more conservative criteria than Muir and Howard (2006), they identified 105 chemicals with modeled P, B and LRTP characteristics based on log K_{OW} >3, AO t½ >2 days, and log K_{AW} > -5 and < -1.

Brown and Wania (2008) screened a list of chemicals derived from the SMILESCAS database for chemicals with high Arctic accumulation potential and POP-like properties (log K_{OA} ≥6, log K_{AW} <0.5/≥ -7, log K_{OW} ≥3.5) in combination with a novel approach, based on a structural profile of known Arctic contaminants defined by halogenation, internal connectivity, and molecular size. They identified 2025 chemicals with elevated Arctic bioaccumulation potential and persistence in air. Of these, 822 matched the structural profile of known Arctic contaminants with 120 of these also found on chemical registry lists (i.e. having high production). Harju et al. (2009) applied a similar methodology to examine the Arctic accumulation potential of 21 'new' brominated flame retardants (BFRs), i.e. BFRs already commercially available as replacements for polybrominated diphenyl ethers (PBDEs). They identified 12 of the 21 as potentially relevant for further investigation and monitoring in the Norwegian environment.

Strempel et al. (2012) identified 1202 substances that were potentially very persistent and very bioaccumulative (vPvB). Although they did not estimate LRTP, their list is useful because most of the chemicals were at one time in commerce in Europe (i.e. on EINECS which included chemicals with >10 t/y production as of 1981). Of the 1202 substances, 130 were also identified by Brown and Wania (2008). In a related study, Scheringer et al. (2012) screened a group of 94 483 substances and identified 510 chemicals with potential POP-like properties that have not been evaluated as potential POPs under the Stockholm Convention. Many of the compounds are well-known halogenated aromatics (polychlorinated naphthalenes, PCNs; PBDEs; chlorobenzenes) however other groups with possible POP-like characteristics included triazines with fluorinated or chlorinated substituents; perfluorinated alkanes and perfluorinated alkyl ethers (linear, branched, and cyclic) and 1,3-dichloro-6-(trifluoromethyl)-phenanthrene-9-carbonyl chloride (CAS 94133-67-2). Ten of the 510 substances were high production volume chemicals (HPVCs), with production or use in Europe of >1000 t/y and so more likely to be detectable in remote locations.

Rorije et al. (2011) identified 1171 substances with POP-like P and B characteristics (BCF >5000, half-life in water >1440 h, AO t½ ≥2 d). Almost all substances currently on the Stockholm Convention list were among the 1171 except for hexabromobiphenyl. Candidate POPs (as of 2015) dicofol, PCNs, and short-chain chlorinated paraffin (SCCPs), were also among the identified substances. Top-ranked, in terms of LRTP, were a series of per- or polyfluorinated chemicals, due to their volatility and persistence. Number one ranked for P and B criteria combined was N,N-*bis*(2-hydroxyethyl)-4-((4,4,5,5,5-pentafluoro-3-(pentafluoroethyl)-1,2,3-*tris*(trifluoromethyl)-pent-1-enyl)oxy)benzenesulphonamide which could degrade to a perfluorinated alkyl acid. The most bioaccumulative was 1,4-dibutoxy-2,5-dichlorobenzene.

A study for the Norwegian Environment Agency identified 15 chemicals as potential POPs with Arctic accumulation potential (Lambert et al., 2011). The chemicals were selected through a scoring system and use of the list of 250 most persistent and bioaccumulative chemicals reported by Rorije et al. (2011). All 15 have been included in lists of analytical targets and are discussed in Section 4.2.

Öberg and Iqbal (2012) screened chemicals on the ECHA pre-registration list for REACH. They selected 48 782 neutral organic chemicals for detailed screening based on the applicability domain of QSPR estimation models. Their approach differed from other studies by use of overall persistence (P_{OV}) and LRTP calculated with the OECD P_{OV} and LRTP Tool (Wegmann et al., 2009). They used threshold values of 195 days for P_{OV} and characteristic travel distance (CTD) >5097 km, which is the CTD of 2,4,4'-trichlorobiphenyl (CB-28). They identified 68 neutral organic chemicals on the REACH preregistration list as potential POPs, many of which were known or candidate POPs, for example PCNs, polychlorinated biphenyls (PCBs), or identified in studies by Scheringer et al. (2012), Strempel et al. (2012) and Rorije et al. (2011) because the substances were also in EINECS. Seven chemicals that were unique to their study are listed in Table 4.2.

Gramatica et al. (2015) used a PBT Index, that was originally derived from a Principal Component Analysis of available experimental data of half-lives, bioconcentration, and aquatic toxicity data for 180 representative non-PBT and PBT chemicals, and modeled by four simple molecular descriptors, to assess the results from most of the above studies (Muir and Howard, 2006; Howard and Muir, 2010; Rorije et al., 2011; Öberg and Iqbal, 2012; Strempel et al., 2012). The combined list was 4412 substances. After screening with the PBT Index model they identified 1313 substances meeting PBT criteria.

Table 4.2 Chemicals in commerce (>1 t/y Europe or 4.5 t/y USA) identified with P, B and LRTP characteristics that have not been determined in Arctic environmental media as of January 2016.

Based on listing in the European (REACH registered as of 2015) and US (TSCA) chemical inventory update (IUR). Cells with 'PR' indicate the chemical was pre-registered under REACH (>1 t/y) in 2008 but may not be in commercial use in Europe or North America as of 2015. Quantity in use in metric tonnes per year (range in t/y) based on values reported in the REACH registered chemical list, REACH pre-registration (>1 t/y), and TSCA IUR (>4.5 t/y in 2002 and 2006).

	CAS number	REACH, t/y	IUR 2006, t/y	IUR2002, t/y	REACH Pre-reg 2008	Reference
Bis (4-chlorophenyl) sulfone	80079	10 000–100 000	4500–23 000	4500–23 000	PR	Howard and Muir (2010)
1,2,3,4,5-Pentabromo-6-chlorocyclohexane	87843	>1	<4.5	4.5–227	PR	Muir and Howard (2006)
Pyrene, 1,3,6,8-tetrabromo-	128632	>1	4.5–227	227–454	PR	Scheringer et al. (2012)
3,5-Bis(trifluoromethyl) bromobenzene	328701	>1			PR	Öberg and Iqbal (2012)
Perfluorotripropylamine	338830	100–1000			PR	Scheringer et al. (2012)
Perfluoroperhydrophenanthrene	306912	>1	<4.5	<4.5	PR	Howard and Muir (2010); Scheringer et al. (2012)
Tris(perfluorobutyl)amine	311897	>1	<10	<10	PR	Scheringer et al. (2012)
Bromopentafluorobenzene	344047	>1	<10	<10	PR	Howard and Muir (2010)
Undecafluoro(nonafluorobutyl) cyclohexane	374607	>1			PR	Rorije et al. (2011)
1,2,3,4-Tetrachlorohexafluorobutane	375451	>1			PR	Scheringer et al. (2012)
1,1,1,2,2,3,4,5,5,6,6,6-Dodecafluoro-3,4--bis(trifluoromethyl)hexane	1735484	>1			PR	Rorije et al. (2011)
Pyridine, 3,5-dichloro-2,4,6-trifluoro-	1737935	>1	<4.5	454–4550	PR	Howard and Muir (2010)
Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, 1,4,5,6,7,7-hexachloro, dibutyl ester	1770805	>1	<4.5	4.5–227	PR	Howard and Muir (2010)
Cyclotrisiloxane, 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)-	2374143	100–1000	4.5–227	454–4550	PR	Howard and Muir (2010)
Cyclotetrasiloxane, 2,4,6,8-tetraethenyl-2,4,6,8-tetramethyl-	2554065	100–1000	<4.5	4.5–227		Howard and Muir (2010)
Propanoyl fluoride, 2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]-	2641341	>1	4.5–227	<4.5	PR	Öberg and Iqbal (2012)
1,1,1,2,2,3,4,5,5,5-Decafluoro-3-(1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl)-4-	5028518	>1			PR	Rorije et al. (2011)
N,N'-Bis(4-(tert-butyl)phenyl)benzene-1,4-diamine	5432995	>1			PR	Rorije et al. (2011)
Heptamethylphenylcyclotetrasiloxane	10448096	>1	<4.5	<4.5	PR	Howard and Muir (2010)
Octadecafluoro-9--(trifluoromethyl) decanoylfluoride	15720986	>1			PR	Rorije et al. (2011)
1H-Isoindole-1,3(2H)-dione, 2,2'-(1,2-ethanediyl)bis[4,5,6,7-tetrabromo-	32588764	100–1000	454–4550	454–4550	PR	Howard and Muir (2010)
3-[2-Chloro-4-(trifluoromethyl)phenoxy] phenyl acetate	50594779	>1	<4.5	454–4550	PR	Howard and Muir (2010)
6-[(2-Nitrophenyl)azo]-2,4-di-tert-pentylphenol	52184197	>1	454–4550	<4.5	PR	Scheringer et al. (2012)
2,2,3,5,6-Pentafluoro-5-(pentafluoroethoxy)-3,6-bis(trifluoromethyl)-1,4-dioxane	84041667	>1			PR	Öberg and Iqbal (2012)
1,2-Dichloro-3-(trichloromethyl)benzene	84613978	>1			PR	Öberg and Iqbal (2012)

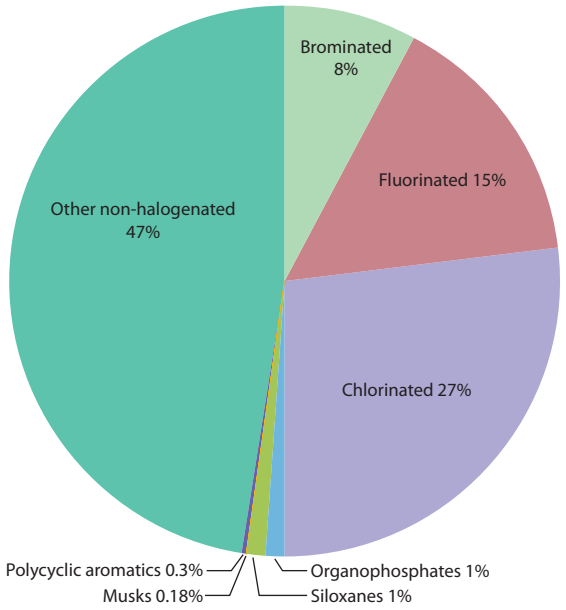

Figure 4.1 Broad classes of the 3743 chemicals with POP-like properties identified by the six PBT and LRT screening studies listed in Table 4.1.

The combined list of chemicals identified by all studies in Table 4.1 contains 3743 substances. Depending on the study, 1.3–3.1% of chemicals that were screened were P and B under REACH criteria and 0.1–1.8% were P, B and LRTP by Stockholm Convention criteria. The substances can be roughly categorized into eight classes; brominated, chlorinated, fluorinated, organophosphate esters, siloxanes, musks, polycyclic aromatics, and a broad class of non-halogenated organics (Figure 4.1). The substances include some already regulated chemicals such as PBDEs because they were on older lists, for example, TSCA inventory updates. However, 606 of the 3743 substances were also on the REACH inventory so had been subject to recent evaluation and registration.

In addition to developing a list of chemicals with POP-like properties, Scheringer et al. (2012) also reviewed the lists of Öberg and Iqbal, Rorije and co-workers, and Muir and Howard. Their comparison was used as the starting point for the list in Table 4.2 which presents 25 chemicals with P, B and LRTP characteristics and that are known to have been registered in European or US/Canadian inventories. As of January 2016, these chemicals had not been included in Arctic monitoring programs although measurements of bis (4-chlorophenyl) sulfone have been made in guillemot (*Uria aalge*) eggs from the Faroe Islands, Iceland, Norway and Sweden (Jörundsdóttir et al., 2009) as well as in glaucous gull (*Larus hyperboreus*) plasma from Bjørnøya (Arctic Norway) (Verreault et al., 2005b). Most (23/25) are halogenated with fluorinated compounds predominating (15/23). These 25 are a subset of the 3743 substances generated from the combined lists of Scheringer et al. (2012), Howard and Muir (2010), Rorije et al. (2011), and Muir and Howard (2006). They were selected from combined lists after searching the inventory lists for information on production and use. Priority was given to chemicals with production volume information. Chemicals reported to be used as intermediates (i.e. within a manufacturing process) were excluded, on the assumption that releases would be small although this assumption may not be correct. Table 4.2 is not a priority list, but is intended to show that chemical inventories contain many substances with POP-like characteristics.

4.1.2 Long-range transport potential in oceans

Identifying P and B chemicals that may undergo long-range transport via oceans is challenging because screening criteria are influenced by the selection of water flow velocities in rivers and ocean currents. Some POPs are known to be preferentially transported in ocean waters and this has been confirmed for perfluorooctane sulfonate (PFOS) (Yamashita et al., 2008; Armitage et al., 2009c) and β-hexachlorocyclohexane (β-HCH) (Li et al., 2002). Modelling ocean transport of PFOS, chlordecone and lindane, showed a significantly higher mass fraction in water at steady-state than in air (Zarfl et al., 2011). However, partitioning into water is not sufficient by itself to make transport in the water compartment the dominant route. Semi-volatile chemicals such as HCH isomers can be transported in oceans and in air.

Zarfl et al. (2011) applied the ELPOS model[7] to calculate the CTD for water transport. This model is a simplified version of the regional-scale model of EUSES-SimpleBox which is legally accepted for chemical assessment in the European Union. The results revealed that, among the Stockholm Convention list of POPs, only the highly soluble PFOS has a higher CTD in water (CTD_W) than in air. Zarfl et al. (2011) also suggested the use of the ratio of the CTD in air (CTD_A) to CTD_W to compare chemicals according to their LRTP properties, since the results obtained for the CTD are independent of emission rates. They applied their model to the Canadian DSL list of neutral organic chemicals (11 317 substances) and found that 38% of compounds had a higher CTD_W than CTD_A.

In addition to transport of chemicals dissolved in water, the possibility of transport on microplastic particles has been discussed (Zarfl and Matthies, 2010). Zarfl and Matthies (2010) noted that, besides sorption of hydrophobic chemicals from seawater, plastic polymers contain additives that might otherwise not undergo ocean or atmospheric transport, such as colorants, UV-stabilizers and matting agents, flame retardants, phthalates, bisphenol-A and anti-microbial agents (Thompson et al., 2009). Zarfl and Matthies (2010) concluded that on a mass basis, transport on plastics would be four to six orders of magnitude smaller than atmospheric or seawater currents (see also Section 2.17).

4.1.3 Uncertainties in identifying additional chemicals of emerging concern

The list in Table 4.2 is not intended to set priorities for future monitoring in the Arctic. It is meant to show that chemical inventories in Europe and North America contain many substances that have POP-like characteristics. Strempel et al. (2012) found that 5.2% of chemicals registered between 1982

[7] https://www.usf.uni-osnabrueck.de/forschung/projekte_in_der_umweltsystemmodellierung/projekt_elpos.html

and 2007 in the ELINCS had PBT characteristics (they did not include LRTP characteristics). It also indicates that when substances are banned or phased out by national or global regulation there are typically many potential replacements among lists of existing, registered, chemicals. This is the case for PBDEs which have been substituted by many brominated and phosphorus flame retardants with highly varied molecular structures which were in existing chemical inventory lists (Covaci et al., 2011; van der Veen and de Boer, 2012). A good working methodology that takes into account the potential POP-like properties of replacement chemicals is not yet in place. In POPRC (Persistent Organic Pollutants Review Committee) work, replacement chemicals are briefly discussed during the Annex F phase, when the Risk Management Evaluation is being done, but not exhaustively. Additional processes and documents are often put in place for the analysis of alternatives. A better and more consistent process is required.

In silico screening studies for chemicals with POP-like characteristics have mainly focused on registered chemicals rather than on degradation products. Yet degradation or transformation products may be more persistent and bioaccumulative. The anisoles, for example pentachloroanisole, are one such example. These degradation products of phenols (that also have possible natural sources – see Section 2.12) have no commercial applications, so are absent on any of the lists. Chemicals with perfluorinated alkyl chains, such as the fluorotelomer alcohols or halo-perfluoroalkanes predominate on some lists of chemicals that have LRTP in the atmosphere (Rorije et al., 2011; Scheringer et al., 2012). However, most are likely to degrade to perfluorocarboxylates (Young and Mabury, 2010). Thus, monitoring of the degradation products in the Arctic may be more important for many fluorinated substances.

Owing to uncertainties in estimating P, B and AO t½ there is considerable uncertainty in the number of chemicals that could have Arctic accumulation potential. Strempel et al. (2012) estimated uncertainty factors: 4 for half-lives, 4 for BCF, and 3.5 for K_{OW}. Thus their initial estimate of 2930 actually ranged from 153 to 12 493 chemicals classified as potential PBTs. Similar uncertainties apply to the other studies; Scheringer et al. (2012) estimated a range of 190 to 1200 for chemicals with POP-like characteristics.

Another problem is the 'street-light effect' whereby only chemicals that are similar to well-characterized existing substances are identified due to the use of QSPR models that are 'trained' with (incomplete, possibly non-representative) measurements of physical-chemical properties. Most studies to date have relied on the same suite of models based on the USEPA EPISuite software (US EPA, 2011c), although other approaches using molecular descriptors have also been employed, especially for identifying PBT chemicals (Papa and Gramatica, 2010; Gramatica et al., 2015). These approaches are best suited for identifying neutral organics. Thus while substances with phenolic, sulfonic and carboxylic acid moieties have been included in most studies, most inorganics and organometallic compounds have been left out. Although substances that are ionized at environmentally relevant pH are unlikely to be transported in the atmosphere, except on particles, they could undergo transport via ocean currents. It has been estimated that 50% of the chemicals on the REACH preregistration list are acids, bases, or zwitterionics, i.e. ionogenic (Franco et al., 2010). Similarly the categorization of the Canadian DSL showed that 10%, or about 2300 of 23 000, were inorganic, organometallics and organic-metal salts (Robinson et al., 2004). Future assessments should consider ionogenic compounds more thoroughly and especially their potential for transport in ocean currents or on particles due to particular use patterns and persistence.

UVCBs (Unknown and Variable composition, Complex reaction products and Biologicals) represent another challenge for assessments of chemicals in commerce with Arctic accumulation potential. The DSL categorization identified 20% of substances as UVCBs (Robinson et al., 2004). Included in this group are well-known substances such as the chlorinated paraffins, which are characterized by chain length and chlorine content, but generally not by individual congeners. Representative components can often be used for UVCB assessment (US EPA, 2015c).

To date, peer reviewed studies related to screening of lists of chemicals in commerce for POP-like characteristics have used the chemical inventories of the USA, Canada and Europe. Chemical inventories exist for many other countries[8]. For example, the Chinese Inventory of Existing Chemical Substances (IECSC) has 45 600 substances, and the Japanese Existing and New Chemical Substances Inventory (ENCS) has about 26 000. A recent report of a chlorinated polyfluorinated ether sulfonic acid, 6:2-Cl-PFAES, in Arctic biota (Gebbink et al., 2016) is an illustration of the need for knowledge about chemical use in Asian countries that are major producers of synthetic organic chemicals. China is apparently the only country with documented usage of PFAESs (Wang et al., 2013a).

4.2 Analytical screening studies

While the screening of lists of chemicals in commerce is a good starting point, the decision on which chemicals to include in monitoring programs and/or analytical screening studies is still very challenging given limited information on uses and physical-chemical properties, as well as the lack of analytical standards with which to validate methods. Targeted and non-targeted approaches specific to measurements in the Arctic environment are now briefly discussed.

4.2.1 Targeted approaches

Targeted screening (Figure 4.2) refers to studies that identify chemicals of emerging concern (CECs) using reference standards as well as 'suspect' screening for substances of known molecular weight, but without a standard, that may have been identified by *in silico* screening approaches. A series of reports by the Nordic Council of Ministers have reported on a wide range of chemicals in consumer products

[8] www.cas.org/content/regulated-chemicals

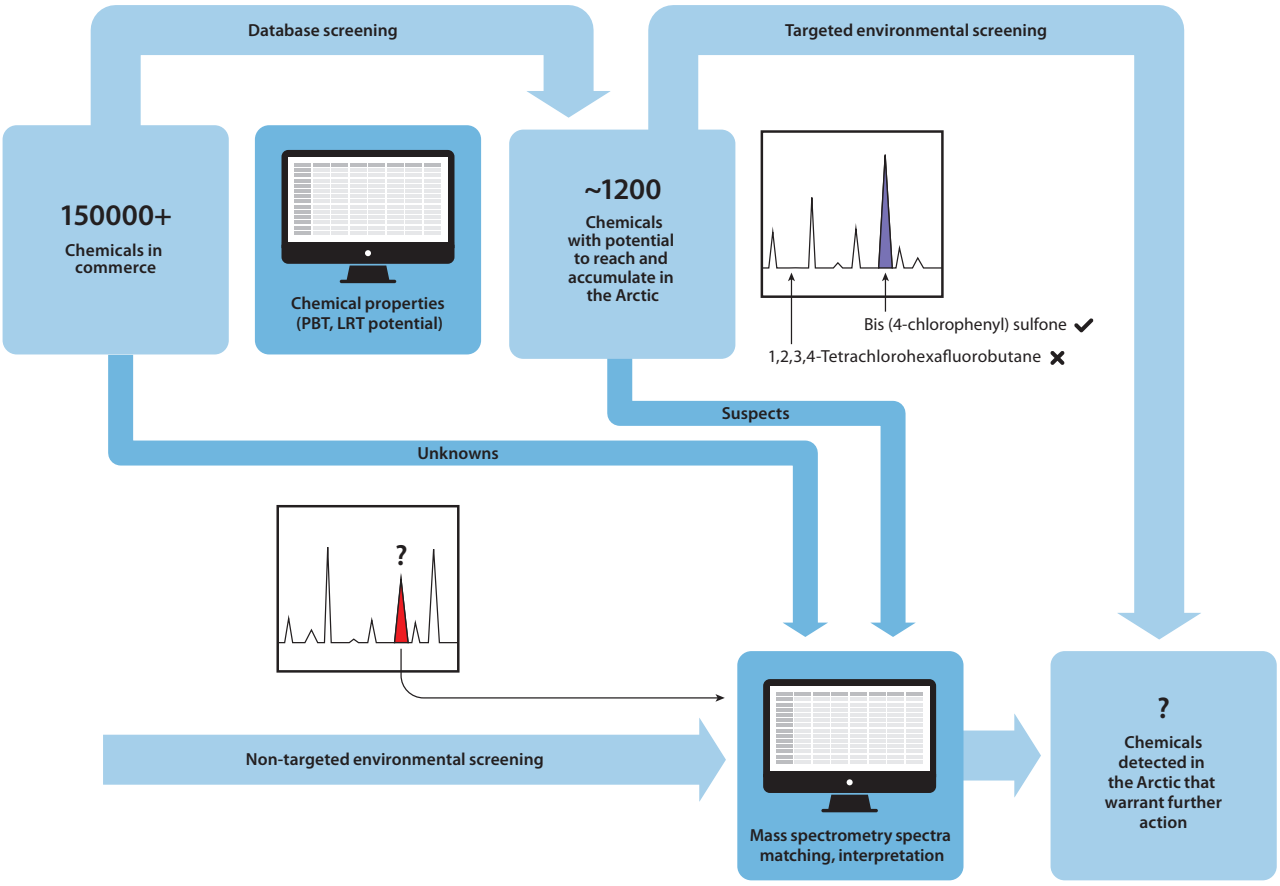

Figure 4.2 Tiered approach to early identification of chemicals of potential Arctic concern. Screening of large chemical databases and non-target analyses of environmental samples can be used as an initial step to identify a smaller number of substances with potential to be Arctic pollutants. In a subsequent step, the smaller pool of suspect chemicals of concern are then sought in environmental samples via targeted analysis, to confirm their actual presence in the Arctic. Those detected at consistent and elevated levels are then identified as candidates for further action.

in Scandinavian countries including the Faroe Islands, Iceland and Greenland[9]. Priority is generally given to substances used in high volumes or that are likely to be environmentally persistent and hazardous to humans and other organisms. Results from these studies, which included measurements of poly- and per-fluoroalkyl substances (PFASs), BFRs, phosphorus flame retardants (PFRs), phthalates and siloxanes are cited in Chapter 2. The Norwegian Environment Agency has also supported a series of targeted screening studies to determine CECs in the Arctic environment (Green et al., 2008; Evenset et al., 2009; Sagerup et al., 2010; Norwegian Environment Agency, 2013). Several of these have used a list of priority chemicals established by Harju et al. (2009) as well as expert judgement to establish targets. Gebbink et al. (2016) took a similar targeted approach to determine previously unidentified PFASs in marine mammals from Greenland. The contaminant monitoring program in Greenland (AMAP Core Program) includes a sub-program on 'new contaminants', which addresses less-studied compounds (Vorkamp et al., 2015; Rigét et al., 2016). Shen et al. (2012) used a 'suspect' screening approach to identify two novel dechlorination products of Dechlorane 602 in beluga (*Delphinapterus leucas*) blubber using gas chromatography (GC) and very high resolution mass spectrometry (MS). However, to date 'suspect' screening using information from lists of priority substances has not been widely applied in Arctic environmental samples.

4.2.2 Non-targeted approaches

A relatively new approach is non-target screening (see Figure 4.2) that uses accurate mass high resolution mass spectrometry (HR-MS) coupled to 1- or 2-dimensional gas chromatography (GC or GC×GC) or liquid chromatography (LC) to search for chemicals in environmental extracts (Schlabach, 2013; Schymanski et al., 2015). It involves processing of instrumental data to search for complete unknowns starting from the exact mass, isotope, adduct, and fragmentation information. Schlabach (2013) analyzed air samples from a remote site in Norway (Birkenes) and identified 'suspect' unknowns using GC×GC-MS, GC-HRMS and LC-HRMS. The non-target analysis detected many polymer additives including phthalates and one adipate, and three organophosphates, polymer antioxidants, fungicides, pharmaceuticals, and unknown fluorinated compounds. While there are few studies using this approach for Arctic environmental samples, this is certain to change in the near future given the rapid developments in the non-target analysis field. The lists of chemicals with Arctic accumulation potential in Section 4.1 provide analysts with plenty of 'suspects' to try to identify.

[9] http://nordicscreening.org

4.3 Conclusions and recommendations

Screening for chemical inventories in Europe and North America has shown them to contain many chemicals in commerce with POP-like characteristics. Exact numbers are difficult to estimate due to uncertainties in the information on physical-chemical properties. The combined total from recent studies was 3743 including all identified as PBT. Scheringer et al. (2012) estimated the range for substances with a combination of POP-like characteristics for persistence, bioaccumulation and long-range transport potential to be from 190 to 1200 chemicals.

Further screening of inventories particularly those for China and Japan would be useful to provide a global picture of the production of chemicals with POP-like characteristics.

Screening studies for chemicals with POP-like characteristics have mainly focused on registered chemicals rather than on degradation products.

Further screening for degradation products of chemicals in commerce for POP-like characteristics would be worthwhile given the many examples of degradation products detected in Arctic environmental media.

Some POPs are known to be preferentially transported in ocean waters and screening of a large list of neutral organic chemicals (11 317 substances) showed that 38% of the compounds had a higher CTD_W than CTD_A.

Further screening for chemicals with POP-like characteristics and potential for ocean transport would be worthwhile given the high proportion of chemicals identified in initial screening.

Non-target screening for chemicals in Arctic samples has revealed some previously unidentified chemicals and has potential, especially when combined with lists of substances identified by *in silico* screening to widen the number of CECs identified in the Arctic.

Further non-target screening for chemicals with POP-like characteristics should be conducted using priority lists developed by recent peer-reviewed studies.

5. Conclusions and recommendations

Authors: Jennifer Balmer, Derek Muir, Cynthia de Wit, Katrin Vorkamp, Simon Wilson

This chapter comprises four main sections: general conclusions from this assessment of chemicals of emerging Arctic concern (Section 5.1), summary conclusions drawn from the reviews of chemical groups presented in Chapter 2 (Section 5.2), conclusions relating to monitoring and assessment (Section 5.3), and conclusions of relevance to policy options and implications (Section 5.4). The chapter concludes with a summary of the main key findings of this assessment (Section 5.5). Recommendations arising from this assessment are interspersed throughout this chapter in italics.

5.1 General conclusions

This assessment confirms that a broad range of new chemicals of emerging concern (CECs), not previously studied in the Arctic, are in fact present in the Arctic environment. Examples include pharmaceuticals and personal care products (PPCPs), a large number of per- and polyfluoroalkyl substances (PFASs), new brominated, organophosphorus-based and chlorinated flame retardants (BFRs, PFRs, CFRs), hexachlorobutadiene (HCBD), siloxanes, byproduct polychlorinated biphenyls (PCBs, e.g. PCB11), phthalates, halogenated natural products (HNPs), seven new current use pesticides (CUPs) and macro/microplastics. Several CECs identified in previous AMAP assessments of persistent organic pollutants (POPs) (AMAP, 2004, 2010b) continue to be prominent and concentrations of some are increasing in Arctic air and wildlife. These include some PFASs, decabromodiphenyl ether (BDE-209), hexabromocyclododecane (HBCDD), other BFRs, polychlorinated naphthalenes (PCNs), short-chain chlorinated paraffins (SCCPs), pentachloroanisole (PCA) and pentachlorophenol (PCP), and several CUPs. Some of these chemicals are now included in the Stockholm Convention on POPs or are under consideration for inclusion, but the majority are not. This report does not cover all possible chemicals that could be reaching the Arctic. There are likely to be CECs that have been found in other parts of the world that may be relevant to screen for in terms of the Arctic. Modelling and *in silico* screening exercises using generated physical-chemical properties indicate that there are several possible candidate chemicals in current use that have potential to reach the Arctic (see Chapter 4) (Muir and Howard, 2006; Howard and Muir, 2010; Scheringer et al., 2012).

> *New chemicals identified in remote sites in other parts of the world should be included in future screening programs in the Arctic. Additional chemicals with Arctic accumulation potential, as compiled in Chapter 4 should also be screened for in future studies in the Arctic. In addition, there is a need to determine physical-chemical properties of CECs experimentally to verify modelled data.*

Fewer data are available on CECs in the Arctic compared with legacy POPs. Most data for CECs in the Arctic come from air monitoring programs, with some data in marine biota coming from Nordic and national screening programs. These monitoring data are complemented by research data published in the scientific literature. There are far fewer data from terrestrial or freshwater environments. For biota in particular, most data are from the marine environment. The presence of many CECs in air samples from the High Arctic provides evidence of long-range transport from source regions.

Few spatial trends were available due to lack of data from large parts of the Arctic. Essentially no data were available from Russia. Only a few data sets were available from Alaska (USA), Sweden, Finland and Iceland. For Canada, most data were available from Nunavut and with relatively few from the Northwest Territories or Yukon. Larger data sets were available from Greenland (Denmark), Faroe Islands, Svalbard and northern Norway. Lack of data from many Arctic regions has thus hindered understanding of spatial trends for CECs.

Very few temporal trend studies exist for CECs in the Arctic. Those that do exist are primarily for air, although most data series are still likely to be too short to determine trends. Some studies on ice cores (i.e. deposition samples) are also available for BDE-209, new BFRs, PCB11, PFASs and CUPs, however temporal resolution is limited. Long-term (>6 y) temporal trends of CECs in biota are limited to PFAS (C_9–C_{14} perfluorinated carboxylic acids; PFCAs) and some BFRs. For example HBCDD is shown to have increased in concentration in seals, beluga (*Delphinapterus leucas*) and polar bears (*Ursus maritimus*) in the mid-2000s with more recent leveling off, declines or non-detects. Few trends for CECs are statistically significant due to the limited number of sampling years.

> *More data are required on concentrations of CECs in different environmental media, in different ecosystems and over wider geographical areas to enable a better understanding of the fate of these compounds in the Arctic. Temporal trends in biota for CECs are also needed, for example to follow trends for those CECs that are listed under or are being considered for listing under the Stockholm Convention. Temporal trends for CECs not under consideration for regulation will be helpful to monitor for new chemicals that may need to be considered for listing in the future. The design of temporal trend studies should take into account that many CECs occur in lower concentrations than legacy POPs.*

The presence of many CECs in biota indicate their potential for bioaccumulation. Such chemicals include long-chain PFCAs, several BFRs (such as 2,4,6-tribromophenyl 2,3-dibromopropyl ether, TBP-DBPE; 1,2-bis(2,4,6-tribromophenoxy)ethane, BTBPE; decabromodiphenyl ethane, DBDPE; hexabromobenzene, HBBz; bis(2-ethylhexyl)tetrabromophthalate, BEH-TEBP; 2-ethylhexyl-2,3,4,5-tetrabromobenzoate, EH-TBB), dechlorane plus (DDC-CO), PFRs, phthalates, SCCPs, siloxanes (decamethylcylopentasiloxane, D5), some PPCPs, PCNs, HCBD, several CUPs, organotins, and some HNPs. In the few studies where data were available for food webs, there are indications that some CECs have the potential to biomagnify (long-chain PFCAs,

α-HBCDD, DBDPE, SCCPs, PCNs). On the other hand, BDE-209 and a limited number of CUPs that have been studied were found to undergo metabolism and/or trophic dilution. For many CECs, the data sets were either too limited or data were only available for abiotic matrices so it was not possible to study bioaccumulation and biomagnification.

Studies of Arctic food webs are needed to determine the bioaccumulation and biomagnification potential of many CECs, in particular for top predators. Based on evidence of long-range atmospheric transport, persistence and bioaccumulation potential, several CECs may be potential POPs and these chemicals represent priorities for further monitoring and toxicity studies.

For some CECs, concentrations were found to be higher near settlements and urban sites. This was especially evident for several CECs that are used in consumer products, such as siloxanes, PPCPs, and phthalates. For example, siloxanes and PPCPs were found locally in receiving waters impacted by sewage effluents (often untreated) from Arctic communities. Their persistence is likely to be enhanced by the cold conditions and long periods of darkness, which slow microbial and photo-degradation. Thus, some CECs differ from POPs in that localized point sources of pollutants in the Arctic may be important. However, the magnitude of their contribution to concentrations of many CECs in the Arctic (i.e. via transport in products, versus long-range transport via winds and ocean transport), has not been assessed.

Such studies should be carried out for CECs in order to understand the most important sources and transport routes for their entry to the Arctic and to be able to prioritize actions to reduce discharges and emissions.

For most CECs, production volumes are considered proprietary information and production sites, and spatial and temporal patterns of consumer or industrial use and emission, are generally unknown. Thus it is not possible to estimate global or regional emissions which could be used to model long-range atmospheric or oceanic transport. An exception is chlorinated paraffins (including SCCPs but also medium-chain CPs), which are known to be produced in China in volumes each year that are comparable to all PCBs ever produced. Nevertheless, current data for SCCPs are too limited, spatially and temporally, to point to East Asia as a source region for chlorinated paraffins in the Arctic.

The lack of production, use and emission data hinders understanding of the environmental fate of many CECs, and chemical producers and users are encouraged to be more forthcoming with such data. Where production and emission data do exist, environmental inventories should be compiled and validated with spatial and temporal trend data.

Many of the chemicals addressed in this assessment have been analyzed using previously established methods for other, similar classes of persistent chemicals and the methods may not yet have been fully validated. For most CECs, there has been a general lack of inter-laboratory comparison exercises, and where these have been performed, they have only included a few chemical classes. Thirteen laboratories participated in the last AMAP inter-laboratory study, and some new BFRs, CFRs, PFRs, PFASs, PCNs, and SCCPs were included. For SCCPs and PFRs, up to four laboratories for each CEC group took part. For other analytes, the results were satisfactory for around half of the laboratories, while for many legacy POPs (polybrominated diphenyl ethers, PBDEs; PCBs; organochlorine pesticides) results were satisfactory for most laboratories. Thus, there is potential for improvement in the analyses of CECs. For most of the CECs, there are no standard reference materials with certified concentrations available to validate methods. Because many CECs are used in consumer products and building materials, there is considerable risk of contamination of low level samples during sampling and lab processing.

Harmonized methods for sampling, identification and quantification of groups of CECs are needed. Best practice for the analysis of specific CECs should be identified, and recommended methods should be added to the AMAP monitoring guidelines when such methods are available. Inter-laboratory comparison exercises for CECs should be continued and laboratories producing results from the Arctic for use in AMAP assessments are encouraged to participate. Several suitable certified reference materials (CRMs) exist but concentrations of new chemicals in these need to be certified or if this is not possible, new CRMs for CECs need to be developed.

As clearly shown in Chapter 3, for many CECs there is a general lack of toxicological data. Such data are needed to better understand environmental and health issues related to these compounds and for risk assessments.

Toxicity studies of CECs should be encouraged.

5.2 Levels and trends

5.2.1 Per- and polyfluoroalkyl substances

New data are available for a wider range of PFASs in the Arctic since the previous detailed review (AMAP, 2010b). New PFASs detected include perfluoro-4-ethylcyclohexane sulfonate (PFECHS) an analog of perfluorooctane sulfonate (PFOS), perfluorobutane sulfonamide (FBSA) a precursor of perfluorobutane sulfonate (PFBS), and 6:2-chloro-polyfluorinated ether sulfonic acid (6:2-Cl-PFAES or F-53B), a chlorinated polyfluorinated ether sulfonic acid.

New PFASs, which may be replacement compounds for PFOS and other long-chain (C_8–C_{16}) PFASs, precursors or degradation products of precursors of various PFAS-containing products, require additional measurements in the Arctic environment.

New measurements have shown that very long-chain (C_{13}–C_{15}) PFCAs, which had been reported previously in Arctic marine biota, especially seabirds, are present in freshwater fish, seals, polar bear and reindeer (*Rangifer tarandus*). The relative proportions or pattern of the PFCA isomers also differ between the European Arctic, Greenland and Canada. There is evidence that these C_{13}–C_{15} PFCAs are more prominent in fatty tissues than shorter-chain PFCAs.

More data are needed on C_{13}–C_{15} PFCAs to determine their spatial trends and especially temporal trends in Arctic biota.

Few spatial trend data are available for PFASs. Extensive datasets exist for long-term trends of long-chain (C_8–C_{12}) PFCAs in Arctic biota with some datasets including archived samples from the 1970s and 1980s. With the exception of air, results are mainly from Canada and Greenland. The trends in PFCAs over time vary across the North American Arctic and Greenland, with increasing levels of some PFCAs observed especially in East Greenland (seals, polar bears). Another temporal pattern that has emerged since 2010 has been increasing PFCAs in biota following previous declines from higher concentrations in the early 2000s, which has not been observed for atmospheric sampling of volatile precursors (fluorotelomer alcohols; FTOHs) or perfluorooctanoate (PFOA) on filters. These trends may be explained by continuing emissions of long-chain PFCAs and/or their precursors in Asia (including India and Russia) despite reductions in the emission of these compounds in Europe and North America.

Spatial and temporal trend monitoring for PFASs should continue, particularly for PFOA and long-chain (C_8–C_{15}) PFCAs given their known propensity for biomagnification and ubiquitous presence in Arctic biota. In particular, data for Russia and northern Europe are needed. Annual biological sampling would help to detect the relatively fast changing concentrations in biota. Further information on global uses and production would be useful to help interpret the trend data.

There are an increasing number of measurements of perfluorobutanoate (PFBA) in freshwater, seawater, snow and air samples which indicate that it is the most prominent PFCA in these abiotic media. PFBA has multiple sources. It is an atmospheric degradation product of chlorofluorocarbon replacements HFC-329 ($CF_3(CF_2)_3H$), HFE-7100162 ($C_4F_9OCH_3$), and HFE-7200 ($C_4F_9OC_2H_5$), as well as of FTOHs. Although it is expected to be eliminated by vertebrates quickly due to its high solubility, the predominance of PFBA in abiotic samples suggests that it could be present, particularly in fish and invertebrates that are continuously exposed via gill respiration.

Further measurements of PFBA are needed to understand its levels and trends in Arctic biota.

While the effectiveness of biological sampling for temporal trends in long-chain PFCAs has been demonstrated this does not apply to the C_4–C_7 PFCAs or PFBS, which are generally present at low concentrations in biota.

In addition to air sampling, analysis of abiotic media such as ice cores, as well as annual sampling of lake waters and seawater appear to be the best approaches for these less bioaccumulative PFASs.

5.2.2 Brominated flame retardants

This assessment has addressed BDE-209, HBCDD, tetrabromobisphenol A (TBBPA) and a diverse group of 'novel' (i.e. newly studied) brominated flame retardants (BFRs) which have presumably been used in parallel to or as replacements for those BFRs that are now banned. In addition to BDE-209 and HBCDD, the following compounds have been detected in Arctic media: TBP-DBPE, 2,4,6-tribromophenyl allyl ether (TBP-AE), 2,4,6-tribromophenyl 2-bromoallyl ether (TBP-BAE), BTBPE, DBDPE, EH-TBB, BEH-TEBP, HBBz, pentabromobenzene (PBBz), 1,3,5-tribromobenzene (1,3,5-TBBz), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), 2,3,5,6-tetrabromo-*p*-xylene (TBX) and 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane (tetrabromoethylcyclohexane; DBE-DBCH). TBBPA, tetrabromo-*o*-chlorotoluene (TBCT), pentabromobenzyl acrylate (PBB-Acr) and octabromotrimethylphenylindane (OBTMPI) were included in air analyses, but detected infrequently. The detection of these compounds in the Arctic provides evidence of their long-range transport potential.

In abiotic media such as air and ice, concentrations of BDE-209 and HBCDD usually exceeded those of the novel BFRs. Concentrations of BDE-209 were often higher than for any other PBDE congener in particulate air samples and sediment. Compared with lower brominated PBDEs in abiotic media, the novel BFRs appear to fall into two categories: those with concentrations similar to PBDEs (TBP-DBPE, HBBz, PBBz, 1,3,5-TBBz, EH-TBB, BEH-TEBP, PBT) and those with concentrations lower than PBDEs (BTBPE, PBEB, TBX, DBE-DBCH, TBCT, PBB-Acr, OBTMPI). DBDPE was found to be comparable to BDE-209.

More data are needed to consolidate these initial observations and to assess the environmental concentrations of these novel BFRs. Knowledge of gas phase and particle partitioning is sparse and needs to be enhanced for understanding and assessing long-range atmospheric transport.

In biota, BDE-209 and TBBPA were barely detectable, while α-HBCDD was widely present. The novel BFRs were generally detected at low concentrations in biota, namely close to detection limits and at lower concentrations than for α-HBCDD and PBDEs. Exceptions include a concentration of TBP-DBPE of several hundred ng/g in harp seal (*Pagophilus groenlandicus*) blubber and brain and DBDPE concentrations exceeding those for BDE-47 in biota from Svalbard.

The findings of high concentrations of TBP-DBPE and DBDPE in some Arctic species warrant verification. Analytical methods need to be capable of detecting low concentrations of novel BFRs in complex samples such as animal tissues.

Spatial trend analyses are incomplete because most of the data available are from Canada, Norway and Greenland, with some additional data from Finland, Sweden, Iceland and the Faroe Islands. BDE-209 concentrations in air were higher in the Bering/Chukchi Sea region than near Greenland, possibly due to production sites in Asia. HBCDD concentrations in biota followed the spatial trend of many legacy POPs, with concentrations highest in the European Arctic.

Geographical trends should be established for the novel BFRs, to enable a better understanding of transport processes and local exposure. Data from Russia and Alaska are needed in particular. Given the low environmental concentrations of these compounds, the development of suitable and comparable analytical methods will be important.

Temporal trend analyses in air and deposition indicate decreasing concentrations of BDE-209. For HBCDD, most temporal trends indicate increasing concentrations, although the opposite trend has also been found. Increasing concentrations

have also been found for BTBPE in biota and EH-TBB/BEH-TEBP in air. Multi-year air measurements are also available for TBP-AE, BTBPE, HBBz, PBBz, PBT and PBEB, but more data are required before it will be possible to establish a trend.

Temporal trend monitoring should be continued where currently established. Given the recent regulation of HBCDD, effectiveness monitoring of the regulations should be pursued. Temporal trends (including retrospective trends) of the novel BFRs will be relevant if screening studies indicate high or changing concentrations.

BDE-209 does not appear to biomagnify in marine mammals. The data presently available on Arctic biota do not indicate bioaccumulation of TBBPA. For HBCDD, enrichment of the α-isomer through the food web has been found. Biomagnification has also been suggested for DBDPE. Higher concentrations in high trophic level animals were shown for HBBz, but the studies were usually not designed to focus on biomagnification.

The findings for DBDPE warrant verification. Dedicated biomagnification studies would greatly enhance the current knowledge of the novel BFRs provided that suitable analytical methods are available.

Little is known about production sites and volumes of novel BFRs. Toxicological knowledge is sparse.

5.2.3 Chlorinated flame retardants

This assessment has addressed several chlorinated flame retardants (CFRs): dechlorane plus (DDC-CO) and some of its analogs and derivatives (Dechlorane 602, DDC-DBF; Dechlorane 603, DDC-Ant; Dechlorane 604, HCTBPH; undecachloropentacyclooctadecadiene, $aCl_{11}DP$; decachloropentacyclooctadecadiene, $aCl_{10}DP$; dechlorane plus monoadducts, DPMA). Short-chain chlorinated paraffins (SCCPs), also used as flame retardants were assessed separately (see Section 5.2.6).

The detection of DDC-CO in Arctic air confirms its potential for long-range transport. Concentrations were similar to those for the main PBDE congeners and, in some studies, comparable to those in urban air. The DDC-CO derivatives were detected to some extent, but generally close to detection limits.

The air data should be consolidated, including verification of some high concentrations of DDC-CO. The air measurements have the potential to develop into temporal trends.

Studies from air and seawater confirm that DDC-CO is mainly attached to particles.

Compared with the abiotic media, few studies exist on DDC-CO in biota. Concentrations are generally lower than for PBDEs, or were below detection levels. DDC-CO was also detected in terrestrial biota. Some studies detected DDC-CO analogs and derivatives, but not DDC-CO itself.

The current database needs to be extended to assess the potential bioaccumulation of DDC-CO and associated compounds. No information is yet available on DDC-CO and associated compounds in freshwater biota.

The majority of studies, including biota studies, found *anti/syn* ratios for DDC-CO isomers similar to that of the technical product (3:1), indicating lack of isomer-specific degradation processes. However, deviations in the ratio have also been reported. Inconclusive observations exist as to whether the *anti/syn* ratio changes with distance from potential sources of DDC-CO.

Studies addressing potentially isomer-specific processes should be pursued.

Although DDC-CO has been on the market for decades, little information is available on production and use. For the DDC-CO analogs and derivatives in particular, more background information about production and use would be useful.

Understanding of targeted industrial products vs. byproducts vs. degradation products needs to be improved.

5.2.4 Organophosphate-based flame retardants and plasticizers

While there are about 20 high production volume organophosphate-based flame retardants and plasticizers (PFRs) only about ten have been detected in the Arctic environment, mainly in air samples. Data indicate that PFRs are widely present in Arctic air and possibly in seawater at much higher concentrations than halogenated flame retardants such as PBDEs. However, there is currently a dearth of information on PFRs in terrestrial and freshwater abiotic and biotic media in the Arctic, as well as a total lack of knowledge on spatial or temporal trends.

Further measurements of PFRs are needed to assess exposure of Arctic wildlife, their spatial or temporal trends, and sources (long-range transport and local).

PFRs have been reported in Arctic air samples in high volume sampling in Svalbard, northern Sweden and Finland, in passive sampling within the Global Atmospheric Passive Sampling (GAPS) network, and on oceanographic cruises in the Canadian Arctic and the Chukchi/Bering Sea. High volume sampling has shown PFRs are mainly associated with particles in Arctic air. The major PFRs in Arctic air are tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), triphenyl phosphate (TPHP), 2-ethylhexyl-diphenyl phosphate (EHDPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), with TCEP predominating in all studies. Air concentrations of chlorinated PFRs are generally higher than for BFRs or CFRs in the same samples, sometimes 100-fold higher.

Air measurements of PFRs need to be expanded to the North American Arctic and Russia in order to assess spatial trends in sources. Both high volume and passive sampling of air could be used.

Limited data for seawater indicate that PFRs are widespread in marine waters within the Canadian Arctic, at concentrations of up to 13 000 pg/L for TCIPP. However the preliminary results reported to date may be confounded by shipboard contamination.

Seawater measurements of PFRs need to be expanded across the Arctic. The apparent high levels being reported need to be confirmed.

In biota, PFRs have been detected in Hudson Bay polar bears, in lake trout (*Salvelinus namaycush*) and plasma, feathers and eggs from birds in northern Norway, and in fish, seabirds, seals, Arctic fox (*Alopex lagopus*) and polar bear from Svalbard. Concentrations of PFRs in biota are typically lower than for BFRs and legacy POPs, and are being reported at the low part-per-billion levels. TCEP, TPHP and tris(2-butoxyethyl) phosphate (TBOEP) are the major PFRs detected in Arctic biota.

Preliminary data on PFRs are too limited to assess overall exposure of fish and wildlife in the Arctic. Further measurements should be given high priority considering the relatively elevated levels (compared to BFRs) reported in air and water.

Measurements of PFRs remain challenging due to contamination issues owing to the wide use of PFRs and their presence in laboratory air and media used for extraction and isolation.

Analytical methodology and quality assurance issues need to be addressed as part of the effort to obtain reliable measurements of PFRs in Arctic environmental samples. Further inter-laboratory comparisons are needed.

5.2.5 Phthalates

Screening studies have confirmed the presence of phthalates in both populated and remote areas of the Arctic, however there continues to be a general lack of monitoring data for this class of compounds. There is no temporal monitoring program for phthalates in the Arctic or Nordic countries, thus environmental trend data are non-existent. Furthermore, monitoring data for regions outside the European Arctic are scarce.

Environmental concentrations are generally highest near populated areas of the Arctic, but phthalates have also been detected in remote regions, away from human activity. Local wastewater treatment plants and atmospheric transport appear to be the main pathways for phthalates to enter the Arctic region. Phthalates have been detected in various Arctic media – including air, water, sediment and biota, however, data for terrestrial systems are completely lacking.

More data are needed from all Arctic countries in order to assess the environmental distribution, temporal trends and toxicological consequences of the presence of phthalates in the Arctic region.

The varying physical-chemical properties of the individual phthalate esters affect their transport and behavior in the environment. Di(2-ethylhexyl) phthalate (DEHP) is the most frequently measured phthalate ester, although others have also been detected in Arctic media. In addition, there has been a recent change in the usage patterns of phthalates in Nordic countries, with a substantial decline in DEHP usage due to substitution with other phthalate esters and plasticizers.

Future monitoring efforts should include a wider range of phthalate esters in analyses and should take into account changes in usage and substitutions.

5.2.6 Short-chain chlorinated paraffins

Short-chain chlorinated paraffins (SCCPs) are C_{10}–C_{13} chlorinated alkanes (paraffins) with a strong similarity to established chlorinated POPs in terms of their ability to undergo long-range atmospheric transport and to bioaccumulate. Although the manufacture of SCCPs has declined in North America and Europe, since the 1990s it has increased in China and India. Although data on the occurrence of SCCPs in the Arctic remain scarce, a growing body of evidence indicates that SCCPs can be found in a wide range of Arctic media, including biota.

Further measurements of SCCPs are needed to fully assess exposure of fish and wildlife. Measurements should be extended to MCCPs and LCCPs, which may be replacing SCCPs for some uses.

No spatial trend data are available for the Arctic. Air monitoring and a sediment core study indicate increases in SCCP concentrations since the 1990s. This trend is not paralleled by SCCPs in beluga from the Canadian Arctic. However, no systematic temporal trend analysis yet exists for SCCPs in the Arctic.

Spatial and temporal trend information should be high priorities as part of future measurements of SCCPs. Given the recent regulation of SCCPs, effectiveness monitoring of the regulations should be pursued. Measurements of spatial and temporal trends should be extended to include MCCPs and LCCPs where appropriate, starting with atmospheric measurements.

SCCPs have been detected in Hudson Bay and East Greenland polar bears, the top predator of the Arctic marine food web. Studies involving several prey species in the polar bear food chain indicate biomagnification of SCCPs.

Further studies are needed to assess exposure of top predators and biomagnification in Arctic marine food webs including seabirds and marine mammals, with a focus on SCCPs and MCCPs.

SCCP concentrations are often similar to or even higher than those for PCBs and other chlorinated POPs. However, analytical challenges associated with the complexity of CP mixtures have limited the reliability and comparability of environmental SCCP measurements.

Current and future understanding of the environmental fate and significance of CP mixtures in the Arctic would be greatly enhanced by improved analytical capabilities and strategic sampling of remote Arctic regions representative of background concentrations.

5.2.7 Siloxanes

Volatile methylsiloxanes (VMS) have a wide range of commercial applications and have been reported in various environmental media from Arctic regions. Although releases of both linear VMS (lVMS) and cyclic VMS (cVMS) occur, only cVMS have been found in Arctic media, indicating greater emissions and/or greater environmental persistence compared to lVMS.

Further study is needed on lVMS as well as on other siloxanes with similar physical-chemical properties that are in current use.

Long-range atmospheric transport of cVMS to the Arctic has been demonstrated and monitoring data show that annual concentrations have remained stable in recent years. Higher atmospheric concentrations occur during winter months due to lower atmospheric concentration of hydroxyl radicals resulting in lower photo-degradation during winter. However, even under Arctic conditions, atmospheric deposition is not expected to occur due to the inherent volatility of cVMS.

Further study is needed on temporal trends in cVMS in the atmosphere and on possible transformation products (from reactions with hydroxyl radicals) that could be more susceptible to deposition in the Arctic environment.

Exposure of aquatic organisms to cVMS in the Arctic occurs primarily from local sources such as human settlements. Due to limited wastewater treatment in such communities, wastewater discharges are considerable sources of cVMS to aquatic environments. High inputs translate into high exposure, with tissue concentrations in biota in the µg/g lipid weight range and at similar or greater levels compared to legacy POPs.

To date, measurements of VMS in Arctic seawater, freshwater, and biota have been limited to the European Arctic (mainly Svalbard and northern Norway). Given the ubiquitous use of VMS in consumer products that enter wastewater systems, additional measurements are needed to determine the levels and spatial spread of contamination near other major Arctic communities, including those in North America, Greenland, and Russia and to be able to prioritize actions to reduce these discharges.

Exposure and accumulation of cVMS will also be influenced by the characteristics of the environment into which they are released. Taking into consideration that degradation mechanisms (i.e. hydrolysis) will decrease at lower temperatures, cVMS may exhibit longer environmental residence times in Arctic regions.

Considering the wide range of applications for VMS and the potential for increased use with new applications, continued monitoring of this class of compounds is needed. Monitoring data are also crucial for assessing changes in environmental concentrations as a result of potential future restrictions.

5.2.8 Pharmaceuticals and personal care products

Pharmaceuticals are substances used in the diagnosis, treatment, or prevention of disease and for restoring, correcting, or modifying organic functions in veterinary and/or human medical therapeutic treatments. Personal care products are non-medicinal consumable products that are used in the topical care and grooming of the body. Over the past decade, several national and international research and screening studies have confirmed the presence of pharmaceuticals and personal care products (PPCPs) in the Arctic environment. Although pharmaceutical use in the Arctic is low compared to densely populated regions of the globe, the lack of modern wastewater treatment plants, even in larger settlements in the North, in addition to low ambient temperatures, slow microbiological transformation and no photochemical degradation during winter, results in surprisingly high rates of release of selected pharmaceuticals into the Arctic environment.

Medium and long-term monitoring data are needed for PPCPs in the Arctic environment to determine temporal and spatial trends, as well as bioaccumulation in species exploited for human consumption. PPCP transformation products should be included as part of an integrated fate assessment.

Pharmaceuticals are designed to express a specific biochemical function at low concentrations as part of an integrated therapeutic procedure. This biochemical effect, desirable during therapy, may cause unwanted toxicological effects on non-target organisms when the compound is released into the environment. In the Arctic, pharmaceutical residues are released into low- to very low ambient temperatures in receiving aqueous environments. Low biodegradability and thus prolonged residence time should be expected for most of the pharmaceuticals entering the aquatic system. This is especially critical when significant amounts of antibiotic/antimicrobial agents are released in a low temperature environment and as a result enhance the potential for resistance against these substances in local microbial communities. However, the scientific results so far available through published papers and reports must be considered indicative only.

Comprehensive environmental studies on the fate, environmental toxicology and distribution profiles of pharmaceuticals applied in high volumes and released under cold Northern climate conditions should be given high priority by national and international authorities. This is also necessary to ensure that local food sources can continue to be harvested by future generations of indigenous populations without any concern for health and well-being.

The environmental-toxicological consequences of continuous releases in the Arctic are therefore expected to differ compared to temperate regions of the globe. An impact on human populations consuming contaminated local fish and invertebrates or exposed to resistant microbial communities, cannot be excluded.

Reliable information is needed on environmental toxicology of PPCPs for selected Arctic species.

Scientific information confirms that PPCPs were found in high concentrations in the aquatic environment near wastewater treatment plants as primary sources. Some of the substances measured exhibit considerable mobility and are found in samples far from the primary sources.

Available analytical methods may need to be further developed and validated to enable continuous and regular monitoring. This includes harmonizing methodology, use of quality control criteria, and continuous inter-comparison of methodology.

Fate and transport models for PPCPs need to be developed for Arctic conditions.

The environmental effects of PPCPs in combination with non-chemical stressors as well as ongoing Arctic climate change, need to be studied.

5.2.9 Polychlorinated naphthalenes

Polychlorinated naphthalanes (PCNs) had applications similar to polychlorinated biphenyls (PCBs) and were added to the Stockholm Convention in 2015. Few new data have become available since the previous AMAP assessment of PCNs and those that do exist do not change the findings of the previous assessment: PCNs undergo long-range atmospheric transport to the Arctic, the dataset for PCNs in biota is small, spatial trends are poorly defined, few temporal trends are available, few data are available for high trophic level predators, certain PCN congeners biomagnify in Arctic seabirds, and there are no PCN data for Arctic marine food webs.

Biota studies published since the previous AMAP assessment have included seabirds, pinnipeds, cetaceans and polar bears. No new data have become available on terrestrial and freshwater biota, nor have lower trophic levels been studied.

Some concentrations for seals and polar bears were higher in more recent samples than in those analyzed prior to the previous assessment. However, methodological differences could not be ruled out. Temporal trends in biota from Canada and from waters around Greenland indicate decreasing trends, but also considerable interannual variability.

Given the regulation of PCNs through the Stockholm Convention, temporal trends in the Arctic will be relevant for effectiveness monitoring.

Biomagnification of PCNs has been confirmed, but only from one study. Few efforts have been made to assess PCN congener patterns, for example with a view to studying sources or biotransformation in the food chain.

Research into PCN congener profiles may contribute to a better understanding of the environmental fate of PCNs in the Arctic.

Spatial trend assessments are limited to Canada and Greenland and data comparability is not certain.

Increased geographical coverage, including Alaska, Russia and northern Europe, and a more systematic approach to PCN monitoring would help assess PCN levels in the Arctic.

For monitoring purposes, AMAP should consider proposing a standard set of congeners (analogous to the seven indicator PCBs) as a minimum to be included in analyses.

5.2.10 Hexachlorobutadiene

Hexachlorobutadiene (HCBD) has been measured consistently in Arctic air, however data on its occurrence in other Arctic media and biota are scarce. Measurements in abiotic media such as ice cores, seawater, freshwaters, soils and sediments are particularly lacking.

Additional measurements of HCBD in Arctic media, especially abiotic matrices, are needed to understand its environmental transport, fate, and persistence.

Field and laboratory studies suggest that HCBD has the potential to bioaccumulate, but not biomagnify, due to relatively fast biotransformation and elimination processes. Data available for Arctic biota suggest that HCBD concentrations are measurable in a range of species.

Future monitoring efforts and toxicological studies of HCBD in Arctic biota should include terrestrial, freshwater and marine biota.

Spatial and temporal trends in HCBD within the Arctic are lacking and are needed to identify sources and transport pathways. Recently adopted as a POP under the Stockholm Convention, continued monitoring of HCBD will be important to monitor the effectiveness of these regulations. HCBD is primarily generated as an unintended by-product in the production of other industrial solvents. HBCD is now regulated under both Annex A and Annex C of the Stockholm Convention.

Long-term monitoring and expanded spatial monitoring of HCBD in the Arctic will be important for assessing the impact of newly-imposed regulations.

5.2.11 Current use pesticides

Over the past five years at least seven new current use pesticides (CUPs) have been measured in Arctic media: 2-methyl-4-chlorophenoxyacetic acid (MCPA), metribuzin, pendimethalin, phosalone, quizalofop-ethyl, tefluthrin and triallate. However, considering the number of pesticides in current use, the number measured in the Arctic is very limited.

Future investigations should consider including more pesticides with predicted Arctic accumulation potential in ongoing chemical surveillance efforts.

Recent studies have added to the information available on spatial and temporal trends of CUPs in the Arctic. In air, concentrations of dacthal and chlorpyrifos appear to be declining. In the Canadian Arctic, endosulfan is declining very slowly at Alert but has undergone a more rapid decline at Little Fox Lake in the Yukon although levels were about 2-fold higher than at Alert in the mid-2000s, reflecting closer proximity to Asian and North American sources. Data on spatial trends in CUPs in air are lacking because most measurements are restricted to the Canadian Arctic although endosulfan measurements in air have recently been conducted at Pallas (Finland) and Villum Research Station, Station Nord (Greenland).

Studies of temporal trends in CUPs in the Arctic atmosphere should continue and be extended to the European Arctic, where there are measurements for only a few CUPs.

Results for CUPs from the Arctic ice caps (Svalbard and Devon Ice Caps) have provided some insight into geographic differences. In general, higher deposition of CUPs was observed in Svalbard than in the Canadian Arctic. The proximity of the Svalbard glaciers to populated and agricultural regions in northern Eurasia, and prevailing air trajectories, compared with the Canadian High Arctic, helps to explain the differences.

Analyses of ice cores and firn from Arctic ice caps have proved useful for assessing current and past deposition of CUPs and should be expanded to include more chemicals.

Temporal trends in CUPs for Arctic biota are currently limited to measurements of endosulfan in freshwater fish and ringed seal (*Pusa hispida*) from Canada and Greenland. The studies all show concentrations of endosulfan declining from the higher levels of the mid-2000s. However in fish (burbot *Lota lota* and landlocked char *Salvelinus alpinus*) recent increases have been

observed in the period 2010–2012. Whether this is a consistent trend reflecting increased deposition or related to food web or climatic factors has yet to been investigated.

Temporal trend data for CUPs in Arctic biota are particularly useful for risk assessment. The list of CUPs measured in ongoing temporal trend studies should be expanded to more fully assess trends of CUPs and their degradation products with Arctic accumulation potential.

Recent studies have addressed the issue of bioaccumulation/biomagnification for CUPs entering the Arctic via long-range transport. In general, very low ng/g (lipid weight) concentrations have been detected in both terrestrial and marine biota. Highest concentrations are found in vegetation (terrestrial ecosystem) and plankton and fish (marine ecosystem). Lowest concentrations have been found in ringed seal blubber and polar bear adipose as well as in caribou and wolves, and trophic dilution was found for pentachloro-nitrobenzene (PCNB), chlorothalonil, chlorpyrifos, dacthal, and endosulfan in polar bear-ringed seal food web studies from Canada. However it should be noted that the food web biomagnification studies have been conducted on only these five CUPs.

Food web bioaccumulation studies should be expanded to include a broader suite of CUPs with Arctic accumulation potential.

The wide range of pesticides used to support agriculture and public health needs is continuously changing. Changes in climate, the increasing appearance of pesticide-resistant insects and weeds, and wide-scale use of genetically-modified crop varieties will also affect the type and volume of pesticides used in agricultural practices.

Continued monitoring and surveillance of CUPs will be important for ensuring that replacement chemicals are not accumulating in the Arctic due to increased use in northern agricultural regions.

5.2.12 Pentachlorophenol (PCP) and pentachloroanisole (PCA)

Several studies have measured pentachloroanisole (PCA) and considered this to be a proxy for pentachlorophenol (PCP). It is questionable whether this approach is sufficiently accurate to determine the environmental fate of PCP. Owing to the phenolic structure of PCP and its related physical-chemical properties, the environmental fate of PCP is likely to differ from that for non-ionic POPs.

There are indications of other sources of PCA, in addition to transformation from PCP. For example, natural formation could play a role although this needs to be confirmed.

PCP can also be a degradation product (such as from PCBs or hexachlorobenzene; HCB), but little information is available about the significance of such degradation for Arctic observations.

As far as possible, PCP and PCA should be analyzed separately to allow separate environmental assessments of each. Potential interference in the analysis of PCA from 2,3,5,6-tetrachlorodimethoxy-benzene should be investigated.

Research into the natural formation of PCA or other currently unknown sources would help elucidate the importance of keeping PCA and PCP apart, in analyses and assessments. In addition, more solid knowledge of the degradation of legacy POPs to PCP would help in assessing PCP in the Arctic.

Both compounds are widely detected in Arctic air, with higher detection frequency and higher concentrations for PCA. One study traced the occurrence of PCA in snow in Arctic Canada to transport from Asia.

A long-term sediment core trend starting from the late 19th century documented the increase in PCA. Air studies have indicated decreasing trends in the past ten years.

Given the regulation of PCP and PCA through the Stockholm Convention, temporal trends in the Arctic will be relevant for effectiveness monitoring.

Both PCA and PCP (sometimes meaning PCA+PCP) were present in marine biota, while only PCA was detected in freshwater fish and terrestrial biota. Most concentrations were relatively low (<1 ng/g lw), but concentrations of 5–12 ng/g lw were also found in Atlantic cod (*Gadus morhua*), landlocked char, lake trout, and polar bear.

Systematic Arctic bioaccumulation and biomagnification studies should be carried out for PCP and PCA.

5.2.13 Organotins

The toxicity of organotins, especially tributyl tin (TBT), to non-target marine organisms led to global restrictions on their use for marine applications in the mid-2000s. While TBT has been included in long-term marine monitoring programs in the USA, Europe, and Asia, data for organotins in the Arctic are scarce and outdated. The few studies that are available were undertaken prior to 2000.

Data collected pre-2000 show organotin concentrations in Arctic biota were generally very low and followed geographical trends in population density and shipping activity, with the lowest levels found in Greenland and Alaska and the highest measured in harbors in Iceland. With the exception of several small, outdated and/or unpublished studies, temporal trends in organotin concentrations in the Arctic are non-existent.

New data are needed to assess the current status of organotin concentrations in the Arctic environment, including spatial and temporal trends to determine the impact of global use restrictions on TBT and possible new sources of organotins.

Given the primary use of organotins as antifoulants on ships, the majority of the Arctic data available are for seawater, marine sediments and marine biota. However, recent studies indicate that volatile organotin species may be formed at lower latitudes, indicating the potential for atmospheric transport of tin species to the Arctic from contaminated locations. Moreover, atmospheric deposition of organotins to the terrestrial environment has recently been documented in temperate locations, suggesting that atmospheric loading could also serve as a pathway for organotins to the terrestrial Arctic.

Given the documented potential for volatilization and deposition of organotins, screening of Arctic air, terrestrial and freshwater matrices for organotins appears warranted and is thus recommended.

The majority of organotin data for Arctic biota is for gastropod species, however, there are also some data for marine mammals. Of these studies, cetaceans, such as harbor porpoise (*Phocoena phocoena*) and beluga, were generally found to have higher organotin levels than seals or polar bears.

Additional studies of organotins in marine mammals, especially cetaceans, are needed for risk assessments.

Although TBT use has been curtailed due to global restrictions, the continued use of other tin compounds, such as dibutyl tin (DBT) as a plasticizer, suggests there may be ongoing sources of organotins to the Arctic.

Continued monitoring of organotins is warranted. Studies should include measurements of TBT as well as other current-use organotins, such as DBT.

5.2.14 Polyaromatic hydrocarbons

Polyaromatic hydrocarbons (PAHs) may enter the environment from either natural or anthropogenic sources, and the application of new models has improved understanding of PAH sources and pathways to the Arctic. Modelling efforts indicate that atmospheric PAHs in the Canadian and Norwegian Arctic are likely to have originated in the northern hemisphere – predominantly Russia, northern Europe, and North America – while Asia is a minor source, despite contributing more than 50% of global PAH emissions. Models indicate that concentrations and source regions of PAHs in Arctic air can vary seasonally, with the higher concentrations in winter and spring likely to have originated in Russia and Europe.

Continued refinement of geospatial models supported by environmental measurements will aid efforts to identify sources and pathways of PAHs to the Arctic.

Attribution ratios suggest PAHs found in Arctic marine waters and sediment predominantly originate from natural underwater seeps, while those measured in air, freshwater, and terrestrial environments are likely to have originated from atmospheric and combustion-derived sources. Although data for PAHs in Arctic air are numerous, data for PAHs in terrestrial and freshwater environments remain scarce.

There is a need for additional data on PAHs in Arctic terrestrial and freshwater abiotic environments and biota.

PAHs are readily metabolized by living organisms – from soil microbes to vertebrates – and thus are not always present in the environment as parent compounds.

Studies of PAHs in Arctic biota should consider including parent PAHs and metabolites for accurate estimates of exposure and toxicity.

Inputs of PAH to the Arctic from local sources are considered to be negligible compared to PAH atmospherically deposited from the burning of fossil fuels and biomass at lower latitudes. Globally, PAH emissions are expected to decline in the future, however models suggest the Arctic may not experience the same magnitude of decline projected for other world regions. Furthermore, future changes in climate may contribute to a re-volatilization of environmental PAHs, providing a source of secondary emissions to the Arctic atmosphere. Continued monitoring of these chemicals is therefore warranted.

Future environmental monitoring will be important for understanding the impacts of changing emissions and re-emissions of PAHs in the Arctic.

5.2.15 'New' unintentionally generated PCBs

Sources of PCB11 and other non-Aroclor PCB congeners (PCB29, PCB121, PCB185) have not been specifically addressed by regulatory agencies and international conventions on POPs. PCB11 has been detected in Arctic ice caps and in air, soil and vegetation, and represents a significant proportion of total PCB congener concentrations. The presence of PCB11 in the Arctic, even in remote areas, demonstrates that it is likely to be a global pollutant, persistent in the environment and capable of long-range atmospheric transport.

Ongoing temporal trend monitoring programs for POPs in Arctic biota do not currently include PCB11 or most of the non-Aroclor PCB congeners.

Further measurements of the geographic and environmental media distribution of PCB11 in the Arctic are needed given its continued emission as a by-product in, for example, pigments and dyes. More air monitoring and measurements of PCB11 in marine and terrestrial biota including temporal trends, are necessary for a comprehensive assessment.

PCB11 is readily metabolized, so health risk may come more from its metabolites, which have a greater persistence in blood and tissue. The toxicity of PCB11 and its metabolites are only beginning to be studied.

The metabolites of PCB11 and other non-Aroclor PCBs should be measured in Arctic wildlife.

5.2.16 Halogenated natural products

Halogenated natural products (HNPs) have been around for a long time yet their role in ecosystem functioning is still being debated. Most HNPs are produced by marine organisms but some also have anthropogenic sources. HNPs are an enormously diverse group, ranging in complexity from simple, low molecular weight halocarbons (e.g. $CHBr_3$) to large compounds with molecular weights in the same range as POPs or higher (e.g. methoxylated polybrominated diphenyl ethers, MeO-BDEs; polyhalogenated 1,1'-dimethyl-2,2'-bipyrroles, PDBPs). Except for halocarbons, there have been few studies on HNPs in the Arctic.

Halocarbons contribute to the bromine cycle and ozone regulation, and the role of largely natural, very short-lived substance (VSLS) halocarbons has come to prominence in recent years. Halocarbon concentrations in marine surface waters appear to have changed little over the past two decades, but this may change with future changes in river runoff, precipitation and loss of ice cover. These may lead to increased primary production, and to changes in species composition, circulation patterns, formation of halocline water and air-sea exchange. The role of halocarbons in Arctic

atmospheric chemistry may also increase with the loss of sea-ice cover. Freshening of the polar mixed layer is an unknown factor which might affect bromocarbon production by limiting the availability of bromide.

Further work is needed to improve models of air-water gas exchange for halocarbons in the Arctic and to quantify their production/release at air-snow-ice interfaces and in melt ponds. Participation of marine and terrestrial dissolved organic matter, and bacteria in the synthesis of halocarbons in the Arctic Ocean should be investigated.

Higher molecular weight HNPs are found at all levels of Arctic-subarctic ecosystems. Most research has focused on MeO-BDEs and hydroxylated polybrominated diphenyl ethers (OH-BDEs) with less attention given to bromophenols (BPs), bromoanisoles (BAs), polybrominated dibenzodioxins (PBDDs) and HNPs with heterocyclic ring structures. There are only a few, unpublished, measurements of PDBPs since studies published in 2002, and only one investigation of MHC-1 in Arctic-subarctic biota is available. PBDDs, polyhalogenated 1'-methyl-1,2'-bipyrroles (PMBPs) and PDBPs have not been reported in Arctic biota, but their presence can be inferred from their measurement in southern latitude oceans.

The scope of studies in the Arctic should be broadened to include more classes of HNPs.

Measurements of bromophenolic HNPs have mainly been carried out in seabirds and marine mammals but some data are also available for air and precipitation. Investigations of HNPs in algae, fish and invertebrates are sparse and MeO-BDEs and OH-BDEs were not found in the only available study of macroalgae and sediments. It seems likely that Arctic macroalgae and phytoplankton would produce these compounds, as well as BPs and BAs, given their widespread occurrence in the Baltic Sea and other marine areas. Trophic magnification of HNPs in the Arctic has been reported in two studies. Temporal/spatial trends are poorly known compared to anthropogenic POPs. There have been some studies on metabolic transformations, such as for MeO-BDEs, OH-BDEs and PBDEs, but not for other compounds.

HNPs should be included in monitoring programs to track their trends relative to anthropogenic compounds. Further work is needed to identify metabolic processes and relationships between MeO-BDEs, OH-BDEs and PBDEs, as well as metabolites of other HNPs. There is also a need for trend monitoring and trophic transfer studies in the Arctic.

Many biosynthetic pathways and subsequent transformation mechanisms have been identified for higher molecular weight HNPs. Work in this area has been largely confined to temperate and tropical environments, with little attention given to polar regions, despite HNPs being found there. Measurements of HNPs in abiotic samples are lacking. Very little is known about natural production of higher molecular weight HNPs in Arctic ecosystems, but relevant factors are likely to be similar to those for halocarbons. It is not known whether these compounds are produced or occur in snow and ice. As for halocarbons, air-sea exchange of higher molecular weight HNPs would be enhanced by loss of sea-ice cover.

Studies are needed on the production of higher molecular weight HNPs, factors controlling production and transformation, and exchange pathways (air-sea-snow-ice). It would be beneficial to conduct these studies together with halocarbons.

The relative importance of higher molecular weight HNP biosynthesis within the Arctic versus delivery by long-range transport processes is unknown. If external processes are important, levels of HNPs in the Arctic may also respond to changes in temperate and tropical oceans. Atmospheric transport is suggested by the presence of MeO-BDEs and/or OH-BDEs in precipitation and in biota from inland lakes and rivers, although biosynthesis from available bromine in terrestrial and lentic ecosystems cannot be ruled out. The possibility of delivery by ocean currents is suggested by different congener profiles of PDBPs in beluga from Alaska versus the Canadian Archipelago and Svalbard.

Studies should be conducted to address the issue of long-range transport versus local production of higher molecular weight HNPs.

5.2.17 Plastics

Although reports of marine plastic in the Arctic region are increasing, the methods used to monitor plastic debris lack standardization, making it difficult to draw conclusions about temporal and spatial trends in distribution.

Harmonized methods for sampling, identification, and quantification of plastic particles, from macro- to nano-sizes, are needed.

Plastics are among the most common types of marine litter and are ubiquitous in all oceans. Plastic debris may originate from land, ship, or other sea installations, and may travel long distances before being broken down to microplastic particles or being deposited on beaches or the seafloor. Currently, the sources, transport, and degradation pathways for marine plastics in the Arctic are poorly understood.

More research is needed to understand the environmental sources and fate of plastic debris in the Arctic.

Mounting evidence suggests that Arctic biota are exposed to plastic debris and may suffer negative effects as a result. Compounding the direct impacts of plastic exposure, marine litter can also concentrate POPs from the water, and serve as another source of these pollutants to marine organisms.

Further research is needed to understand how Arctic biota are affected by ingestion, accumulation, breakdown and possible leakage of POPs and other chemicals from microplastics.

The effects of climate change are expected to alter the amount of plastic debris present in the Arctic. Changing weather patterns, increased human activity, and declining sea ice are likely to strengthen the release and transport of plastic debris to the region. However, without a current understanding of the magnitude and spatial distribution of marine plastics in the Arctic, temporal changes are difficult to identify.

Benchmarks documenting the magnitude and distribution of marine plastics are needed now to provide a baseline for assessing the probable changes that will occur in future as a result of the changing climate and other environmental changes.

5.3 General monitoring and assessment

5.3.1 Monitoring

For most of the chemicals and groups of substances covered in this assessment, 'environmental monitoring data' are scarce and typically only available for a limited range of environmental media. Most recent studies have focused on air and marine biota at relatively few Arctic locations (Annex Table A5.1). While many species of marine biota have been analyzed, there is a general lack of information about the extent to which some CECs may be taken up and accumulated by Arctic biota and biomagnified through food webs.

Several of the substances discussed have been found in 'screening monitoring' studies. These studies generally target 'presence' (at measureable concentrations) and are limited in the number of samples analyzed. Screening studies organized by the Nordic Council of Ministers (http://nordicscreening.org/) as well as national screening studies have provided information on a range of CECs in the Arctic region. While Nordic 'screening monitoring', for example for PPCPs and plasticizers (Huber et al., 2013; Remberger et al., 2013) has focused on situations where local contamination (and measurable concentrations) is most likely (e.g. areas close to wastewater discharges, harbor areas, etc.), some national screening studies have focused on providing evidence of long-range transport (e.g. Vorkamp et al., 2015).

Notwithstanding the limitations of screening studies, the current assessment demonstrates the value of such studies for identifying new chemicals of potential concern (under different environmental situations). Supported by *in silico* screening (as discussed in Chapter 4), this can help establish priorities with regard to contaminants that may warrant inclusion in more routine monitoring work. With over 160 individual and groups of substances listed in Annex Table A5.1, this is challenging. There are several pre-requisites to the introduction of new substances into routine monitoring activities:

- QA/QC – sufficiently robust analytical methodology, laboratory comparability (and in the case of temporal studies consistency over time), availability of standards and reference materials, and availability of guidelines and protocols
- Evidence of sufficiently high (i.e. detectable and quantifiable) concentrations in relevant media to warrant inclusion in routine monitoring
- Balancing resources to expanding monitoring work while at the same time sustaining existing monitoring (especially important in relation to long-term temporal trend studies).

In many cases, existing monitoring guidelines that relate to legacy POPs can also apply to many CECs; for other substances however, including microplastics, new guidelines and QA systems will need to be developed.

Table 5.1 provides an overview of chemicals/chemical groups reviewed in Chapter 2 with the aim of identifying those with the most potential for moving from screening status into targets for routine monitoring. Several chemicals/chemical groups appear to meet the above criteria because they are already extensively analyzed (e.g. PFASs, PAHs) or can be added relatively easily to target lists (HBCDD, selected novel BFRs and CFRs, PCNs, alkylated PAHs, selected CUPs, PCB11). Several others should be included since they are listed under the Stockholm Convention or other international agreements, but available information suggests concentrations will be very low (HCBD, PCA, organotins). SCCPs were recently added to the Stockholm Convention and are relevant to monitor, but accurate and comparable analytical methods are still a challenge.

Temporal trend studies use a number of different methodological approaches, with associated differences in respect to their suitability for monitoring trends in CECs. Air monitoring programs using high-volume sampling techniques are expensive to maintain, but have the potential to monitor levels of CECs over time in air at a limited number of important Arctic background sites. Passive air sampling offers the potential for much greater spatial coverage and if conducted repeatedly at the same locations, reasonable temporal trend information as well (Hung et al., 2013b). However, the calibration of passive samplers remains challenging, usually with the consequence of lower accuracy than achieved by high-volume sampling. Air samples are a required matrix for effectiveness evaluation in the General Monitoring Plan of the Stockholm Convention. Archived extracts from air monitoring programs have also been valuable for retrospective analysis of new contaminants.

Passive water sampling has recently started in the Arctic (Carlsson et al., 2012b; Muir et al., 2015c) although not specifically focused on CECs and usually targeting compounds of a specific log K_{OW} range. As with air sampling, this approach offers potential for much broader geographic coverage as well as temporal trend information (Booij et al., 2016). However, deployment of passive samples in Arctic seawater has unique challenges due to ice and remote conditions.

In addition to air monitoring, temporal trend monitoring studies based on biota are becoming increasingly powerful with respect to detecting trends in legacy POPs (in particular a number of Stockholm Convention POPs for which trend information is critically important for 'effectiveness evaluation') (AMAP, 2014a, 2015). AMAP POP assessments (AMAP, 1998b, 2004; de Wit and Muir, 2010) have repeatedly stressed the need to maintain existing long-term trend studies and that redirection of monitoring resources to address new substances should not be at the expense of disrupting other key monitoring activities. Recent studies have also indicated changes in the generally decreasing temporal trends for legacy POPs in the Arctic, possibly induced by climate change phenomena (Rigét et al., 2016). Notwithstanding this, it has also been noted that several legacy POPs are now approaching low enough levels that it may be possible to conserve resources, either by sampling at less frequent intervals (e.g. every second year rather than every year) or by making more use of sample archiving (which retains the potential to fill temporal gaps). Both the Canadian and Danish (Greenland) Arctic contaminants programs have moved to a 2-year cycle for some legacy POPs (NCP, 2015b; Rigét et al., 2016). This allows additional priority substances (e.g. chemicals newly listed under the Stockholm Convention or potential candidates for listing) to be included in screening studies, retrospective temporal trend studies, or (annual) biota trend monitoring activities. However, it should be recognized that temporal trend studies initiated now based on annual sampling of

Table 5.1 Status of CECs with respect to requirements for their inclusion in routine monitoring programs in the Arctic.

	Analytical methods and quality assurance measures in place or feasible	Are concentrations detectable and quantifiable? (optimal media for study)
PFASs	Limitations on methods for short-chain (C_4–C_6) and 'new' PFASs such as PFECHS and 6:2-Cl-PFAES	Yes. Large datasets available for C_8-C_{14}-PFCAs in biota and for volatile PFASs in air
BDE-209	Intercomparison studies/proficiency testing schemes available	Yes (abiotic media)
HBCDD	Intercomparison studies/proficiency testing schemes available. Lack of certified values in reference materials	Yes (air, snow, biota)
'novel' BFRs	Diverse group of compounds. Lack of certified values in reference materials and lack of intercomparison studies	Yes (air, snow, biota), but analytical detection limits will be challenging for some compounds
CFRs	Lack of certified values in reference materials, lack of intercomparison studies	Yes (air, biota), but analytical detection limits will be challenging
PFRs	Limited number of mass labelled standards. Lack of certified values in reference materials; few intercomparison studies	Yes (water, air and abiotic archives - ice cores, sediment may be best media for temporal trends). Very limited data for biota
Phthalates	Limited number of mass labelled standards. Lack of certified values in reference materials. Not addressed in current intercomparison studies	Yes, but sporadic detection (very limited data for biota)
SCCPs	Methods available but many challenges due to complex mixture of chlorinated n-alkanes in environmental samples, with the consequence of limited comparability. Intercomparison studies available. Lack of certified reference materials	Yes (air, biota)
Siloxanes	Lack of certified reference materials; not addressed in any current intercomparison studies	Yes (air, biota). Biota sampling near communities. Background levels poorly defined
PPCPs	Diverse group of compounds. Validated methods available for ~150 PPCPs using LC-MS/MS. Mainly wastewater focused. Lack of reference materials; not addressed in any current laboratory performance studies	Yes (local: community wastewater and harbors). Very limited data for Arctic biota
PCNs	Validated methods available. Lack of certified values in reference materials. Not addressed in current inter-laboratory studies	Yes (biota), but concentrations are low compared with legacy POPs
HCBD	Validated methods available. Lack of certified values in reference materials. Intercomparison studies/proficiency testing schemes available	Yes (biota), but concentrations are low compared with legacy POPs
CUPs	Validated methods available for multi-pesticide analysis	Yes (air, snow, biota). Very limited number studied in Arctic compared to >1000 in commerce
PCP/PCA	Validated methods available. Lack of certified values in reference materials. Not addressed in current inter-laboratory studies	Yes for PCA (air, biota), but concentrations are low compared with legacy POPs. Very limited data for PCP (air, biota)
Organotins	Validated methods available for tributyl tin. Intercomparison studies/ proficiency testing schemes available. Less established for other organotins	Yes (biota). Large dataset for TBT in marine gastropods. Limited Arctic data for other butyl and phenyl tins
PAHs	Validated methods available for unsubstituted PAHs but more limited validation for alkylated PAHs. Certified reference materials and intercomparison studies/proficiency testing schemes available	Yes (air, sediment, low trophic level biota). Overlap with oil-gas industry monitoring
'New' unintentionally generated PCBs	Validated methods available, but usually not addressed in intercomparison studies	Yes (air), unknown for biota because of limited data due to focus on bioaccumulative congeners found in commercial PCBs
Microplastics	Guidelines needed, taking into consideration guidelines recently published by other organizations (e.g. OSPAR, 2010; EC JRC, 2013; ICES, 2015)	Yes (water, fish, seabirds) but low occurrence relative to non-Arctic regions

biota or air monitoring may take many years before time series are available that are suitable for reliable trend assessment, and that frequency of sampling is an important consideration with respect to the power of the monitoring program to reliably detect trends (AMAP, 2014a, 2015). Some chemicals that should be considered a priority for temporal trend studies are also indicated in Table 5.1.

Retrospective temporal trend studies based on archived samples are becoming an increasingly relevant source of information on trends in CECs. In an Arctic monitoring context, the costs associated with sample collection are often as great as (if not greater than) the costs associated with laboratory analysis and for this reason more attention should be paid to sample archives as a solution to studying temporal trends in CECs.

Status in monitoring programs and resource implications	Temporal trends in the Arctic and use of specimen bank or other archives
Included in some national programs	Temporal trends available for air and biota, including use of archived biota samples if stored appropriately
Included in some national monitoring programs. Can be combined with analysis of lower brominated PBDEs, but usually requires its own instrumental analysis	Temporal trends available for air and biota. Archived samples can be used if stored appropriately
Included in some national monitoring programs; can be combined with other analyses, but requires LS-MS/MS for isomer-specific analyses	Temporal trends available for air and biota, including use of archived biota samples if stored appropriately
Included in some national monitoring programs. The analytical method can be combined with other POP or CEC analyses	Very limited to date due to few sampling years. Archived samples can presumably be used if stored appropriately
The analytical method can be combined with other POP or CEC analyses	No temporal trend available as yet. Archived samples can presumably be used if stored appropriately
Some national monitoring (e.g. wastewaters) underway	No temporal trend available as yet. Potential contamination from wide use of PFRs in consumer products limits use of archived samples
Some national monitoring e.g. wastewaters and sediments (Nordic Countries), particular efforts required to avoid contamination	Potential contamination from wide use of phthalates in consumer products limits use of archived samples
Use of high-resolution mass spectrometry preferred but limited analytical capacity globally. Time consuming analysis because of its complexity	Good potential to use archived samples
Included in some national monitoring programs, particular efforts required to avoid contamination	Very limited to date due to few sampling years. Potential contamination from wide siloxane use in consumer products limits use of archived samples
Sampling close to communities. Analysis by LC-MS/MS	No temporal trend available as yet. Continuous emissions anticipated due to human and veterinary therapeutic uses. Quantities in use are generally known by national authorities
The analytical method can be combined with other POP analyses, however, potential interferences from PCBs should be considered	Few temporal trends available. Good potential to use archived samples
The analytical method can be combined with other POP analyses	No temporal trend available as yet. Good potential to use archived samples
Included in some national monitoring programs	Temporal trends available for air, water, ice cores and biota. Quantities in use are generally known by national authorities
PCA already included in some national monitoring programs	No temporal trend available as yet. Good potential to use archived samples
TBT already included in some national programs	Few temporal trends available
Already included in some national monitoring programs	Temporal trends available for air, sediment and biota. Limited historical data for sediment cores in lakes, ice cores. Good potential to use archived samples
Requires expanding current PCB congener lists	Temporal trend available for ice cores. Good potential to use archived samples
Low cost compared to POPs analyses. Uses widely available technologies (microscopy, Fourier transform infrared stereoscopy), particular efforts required to avoid contamination	Should be initiated. Potential contamination limits use of archived samples

This assessment has not addressed exposure of humans in the Arctic to CECs. The AMAP Human Health Assessments (AMAP, 2009, 2015) have included information on human exposure to several groups of substances including BFRs (BDE-209, TBBPA, HBCDD), PFASs, phthalates (including phthalate metabolites), and PPCPs (parabens). Recent national level studies have also investigated other halogenated organics and phthalates in Arctic human blood serum (Ayotte et al., 2015; Lenters et al., 2015; Long et al., 2015). However, compared to the numbers of chemicals analyzed in environmental media, the number determined in human biomonitoring studies is very limited. Given the broader suite of CECs showing up in Arctic biota which are consumed as traditional/local food items, a broader screening for CECs in Arctic human populations is warranted.

Core AMAP monitoring at present focusses on long-range transported pollutants. This assessment has also identified chemicals of emerging Arctic concern that may have local sources; these chemicals include most PPCPs, siloxanes, phthalates and organotins. The extent (geographical and frequency) of monitoring for these chemicals is limited, compared to that for halogenated organic compounds such as PFASs, BFRs, and CFRs. Some may be candidates for broader geographic surveys and for temporal trends studies, as outlined in Table 5.1.

Monitoring recommendations

Monitoring programs should be expanded to extend spatial trends for CECs, in particular to cover additional areas in Russia, Alaska, Sweden, Finland and Iceland

Baselines should be established for temporal trends, with a view to implementing well-designed temporal trend monitoring for priority CECs; specimen archiving should also be undertaken to allow the possibility for retrospective temporal trend studies of CECs as methods and QA/QC advances allow

Such monitoring should include POPs added or under review for listing under the Stockholm Convention in existing temporal trend monitoring studies (air and biota)

Monitoring supported by research studies is needed to provide greater knowledge on the presence of microplastics in the Arctic and potential to act as 'carrier' of other chemicals, including a route of dietary exposure to animals, and associated effects

(AMAP) monitoring strategies should be adjusted to make it possible to examine the presence in the Arctic of contaminants with local sources as well as long-range transported substances

Wider application of (target and non-target) analytical screening is needed for additional CECs, different media, and additional geographical locations (including areas with potential influence of local sources)

Broader screening is needed for CECs in Arctic human biomonitoring studies.

5.3.2 Assessment of chemicals of emerging Arctic concern

According to AMAP's Strategic Framework Document 2010+ (AMAP, 2010a), AMAP has a mandate from the Arctic Council "to monitor and assess the status of the Arctic region with respect to pollution (e.g. persistent organic pollutants, heavy metals, radionuclides, acidification, and petroleum hydrocarbons) and climate change issues by documenting levels and trends, pathways and processes, and effects on ecosystems and humans, and by proposing actions to reduce associated threats for consideration by governments". Furthermore, "AMAP's primary function is to provide sound science-based information to inform policy and decision-making processes in relation to issues covered by its mandate. AMAP aims to make effective use of up-to-date information and results from monitoring and research activities, and to promote and harmonize activities under relevant national and international programs that can support AMAP assessments". A primary objective of the AMAP work on POPs is to provide the Arctic Council with up-to-date scientific assessment reports on the state of the Arctic environment. These, in turn, support the work of regional, national and international agreements such as the Stockholm Convention and other similar initiatives (such as the POPs Protocol of the Convention on Long-range Transboundary Air Pollution) as well as local, regional and national authorities in their chemical regulations and emissions reduction work. With respect to CECs, an important recipient of this information is the Stockholm Convention POPs Review Committee (POPRC) that is responsible for reviewing chemicals that may be relevant for regulation under the Stockholm Convention and compiling evaluating dossiers on chemicals proposed for listing under the annexes of the Convention. Of particular relevance in this context is the fact that the Convention recognizes that "Arctic ecosystems and indigenous communities are particularly at risk because of the biomagnification of POPs, and that contamination of their traditional foods is a public health issue". POPRC's reviewing criteria take Arctic data into account when evaluating the potential for long-range environmental transport, persistence and bioaccumulation of proposed chemicals (see Section 5.4.1.1).

In the current assessment, several new chemicals have been found in the Arctic, some of which fulfill the Stockholm Convention POPs criteria, whereas for others, lack of data prevents classification or the chemicals do not fulfill all the criteria. For some compounds, this is the first review of environmental data and a clearer picture of their environmental fate emerges. For chemicals that do not fulfill Stockholm Convention POPs criteria, it is important that data are provided to national authorities in Arctic Council countries so that they can take action. It is also essential that AMAP information on CECs is routinely updated and that the mechanisms for timely delivery of this information to groups such as POPRC are improved. At present, AMAP information is made available on a largely *ad hoc* basis, taking advantage of the fact that some AMAP experts are also members of, or observers to POPRC. Better planning of AMAP CEC information and deliverables with respect to the timing for handling of chemicals under POPRC should be implemented (see also Section 5.4), as a supplement or possible replacement for the current strategy of updating information at about five year intervals.

Assessment recommendations

Consideration should be given to how best to optimize the delivery of AMAP information to groups such as the Stockholm Convention POPRC. It may also be necessary to re-evaluate mechanisms available for protecting Arctic ecosystems from hazardous chemicals, in light of the information concerning new CECs that may not be suitable for addressing under initiatives such as the Stockholm Convention (e.g. microplastics and chemicals that do not meet POPs criteria such as pharmaceuticals that impact local nearshore environments, etc.)

The impacts of climate change on the transport and fate of chemicals of emerging Arctic concern as well as POPs need to be addressed. An AMAP assessment on this topic is planned to start in early 2018.

5.4 Policy options and implications

5.4.1 The 'chemical regulation' landscape

5.4.1.1 Global agreements

The information and documentation provided by AMAP in its 1998 and 2002 POPs assessments (AMAP, 1998b, 2004) was used very effectively in the processes that led to the adoption and entry into force of the POPs Protocol to the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP), and shortly thereafter the UNEP Stockholm Convention on POPs (Stone, 2015).

By supplementing national regulations that existed at that time, these hemispheric/global agreements were seen by the Arctic countries and others as key to regulating several chemicals that were widely recognized as harmful to ecosystems and humans, but which arrived in the Arctic following releases in areas far from the Arctic via (global) long-range transport. This included industrial chemicals such as PCBs, and various organochlorine pesticides such as DDT and toxaphene (Box 5.1). However, as discussed in the AMAP 2009 POPs assessment (AMAP, 2010b) and this assessment, new chemicals continue to enter commercial use including chemicals introduced as replacements for banned or phased-out substances. In this respect, and also in the context of protecting the Arctic, the existence of global or regional Conventions alone does not imply that pollution from hazardous chemicals is a 'solved problem'.

The screening criteria applied in the UNECE POP Protocol and the Stockholm Convention are listed in Table 5.2. Annex E of the Stockholm Convention specifies that POPRC should decide on the basis of available information in the risk profile if "the chemical is likely as a result of its long-range environmental transport to lead to significant adverse human health and/or environmental effects such that global action is warranted".

The procedures for listing chemicals under the CLRTAP and Stockholm Conventions are essentially reactive. Looking back at the timeline from discovery of PCBs and the identification of DDT in Arctic wildlife to their global regulation it clearly took decades for action at the international level. After a chemical has been formally added to the Stockholm Convention annexes, it can take a number of years for parties that ratified that chemical for inclusion to follow the regulations, if the party had asked for exemptions. For chemicals listed in Annex B (Restriction) (such as DDT and PFOS), there are allowed uses. Not all countries that ratified the 12 initial POPs also ratified the subsequently added POPs (i.e. there are 'opt-in' and 'opt-out' countries).

The process from nomination to a final decision by the Conference of the Parties on their inclusion has in many cases moved more quickly since 2004, with 14 chemicals added between 2009 and 2015[10]. However, the fact remains that the Stockholm Convention essentially addresses only a small fraction of the chemicals that have been in commerce (sometimes for decades) and which have already been released to the environment, and can only address those that undergo long-range environmental transport. At the same time, there are (practical) limitations on the number of chemicals that can be added to the Convention listings, including the time it takes to review the Dossier (three years minimum). Some substances (e.g. microplastics, pharmaceuticals) – simply due to their composition or characteristics – may not qualify for inclusion under the existing global Conventions. This has led to calls for more proactive approaches to chemical regulation, much of which is currently based on a screening of chemicals based on their physical-chemical properties prior to their approval for use. However, these approaches also have limitations, not least with respect to the availability

Box 5.1 Current status for POPs listed under CLRTAP and the Stockholm Convention

The Stockholm Convention entered into force in 2004. As of 2016, the POPs list comprises 26 chemicals with four under consideration for inclusion (http://chm.pops.int/TheConvention/ThePOPs/ListingofPOPs/tabid/2509/Default.aspx).[10]

The United Nations Economic Commission for Europe (UNECE) Aarhus Protocol on Persistent Organic Pollutants (POPs) entered into force in 2003. As of 2010, when it was last amended, the Protocol included 23 substances. The substances are the same as listed under the Stockholm Convention, except for PAHs (www.unece.org/env/lrtap/pops_h1.html).

Table 5.2. Overview of screening criteria in the UNECE POPs Protocol and the Stockholm Convention (summarized from Van Wijk et al., 2009).

Definition	Persistence	Bioaccumulation	Long-range transport potential	Toxicity
UN-ECE POPs Protocol	Half-life in water >2 months or in sediment >6 months or in soils >6 months	BCF or BAF >5000 or log K_{ow} >5	Vapor pressure <1000 Pa and half-life in air >2 days or monitoring data in remote area	Potential to adversely affect human health or environment
Stockholm Convention on POPs	Half-life in water >2 months or in sediment >6 months or in soils >6 months; evidence that the chemical is otherwise sufficiently persistent	BCF or BAF >5000 or log K_{ow} >5 or monitoring data in biota	Measured levels far from source or monitoring data in remote area or multimedia modeling evidence and half-life in air >2 days	Evidence of adverse effects on human health or the environment or toxicity characteristics indicating potential damage to human health or environment

BCF: bioconcentration factor; BAF: bioaccumulation factor.

[10] At the most recent Conference of the Parties in 2017, three more substances (DecaBDE, dicofol, SCCPs) were listed.

and reliability of the information on chemical properties (and possible biological effects).

Another global UN initiative is the Strategic Approach to International Chemicals Management (SAICM), a policy framework to foster sound management of chemicals. As of early 2017, SAICM has several emerging policy issues of relevance to emerging chemicals including environmentally persistent pharmaceutical pollutants, endocrine-disrupting chemicals, and perfluorinated chemicals (SAICM, 2017).

5.4.1.2 National and regional initiatives

National and regional approaches to addressing POPs and PBT substances were reviewed in detail by van Wijk et al. (2009). The main criteria used to identify industrial chemicals of concern in Europe, the USA and Canada are listed in Table 5.3. Pharmaceuticals, cosmetic and personal care products, food additives, and pesticides are regulated under separate Food and Drug and pesticide legislation and so are not discussed here. However, it should be noted that there is some overlap, especially between industrial chemicals and personal care product additives.

Europe

The European Regulation for Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) entered into force in 2007 to regulate the production, import and use of industrial chemicals. Within the REACH framework (its Annex XIII), special consideration is given to chemicals with persistent, bioaccumulative or toxic (PBT) properties or very persistent and very bioaccumulative (vPvB) properties, although not specifically to long-range transport (Table 5.3). The amount of data required under REACH depends on the annual production or imported volume. For chemicals with >10 t/y, registrants need to assess the risks for human health and the environment, including possible PBT or vPvB properties, within a Chemical Safety Report. For chemicals at the <10 t/y level, only information about 'ready biodegradation' and lipophilicity (log K_{OW}) is required unless there are indications that the substance may have PBT properties based on modelling. Currently the REACH chemical inventory contains about 20 000 substances representing chemicals with production or import of >1 t/y. Chemicals are added continuously from the pre-registered list of about 143 000 existing substances as well as from newly developed chemicals. As noted in Chapter 4, about 3% (Strempel et al., 2012) of the chemicals registered under REACH have been identified as possibly having P, B or POP-like criteria using existing quantitative structure-property relationship (QSPR) models. The screening has been mainly for neutral organic compounds and omits most organometallic compounds, and all inorganic compounds, salts, polymers and surfactants.

USA/Canada

In the USA, chemicals produced or imported at >25 000 lbs (11 360 kg/y) are subject to review and regulation under the Toxic Substances Control Act (TSCA). The TSCA inventory update rule has required manufacturers and importers to update registrations every four years since 1986. Until 2002, the threshold was 10 000 lbs/y. The current estimates are that

Table 5.3. Overview of main PBT criteria in Europe, the USA and Canada (summarized from Van Wijk et al., 2009).

Definition	Persistence	Bioaccumulation	Long-range transport potential	Toxicity
EU PBT Criteria	Half-life >60 days in marine water or >40 days in freshwater or >180 days in marine sediment or >120 days in freshwater sediment or >120 days in soil	BCF >2000	Not applicable	Chronic NOEC <0.01 mg/L or CMR or endocrine-disrupting effects
EU vPvB Criteria	Half-life > 60 days in marine or freshwater or >180 days in marine or freshwater sediment or soil	BCF >5000	Not applicable	Not applicable
USEPA Toxics Release Inventory Reporting	Half-life ≥2 months in soil, sediment, or water or half-life ≥2 days in air	BAF or BCF ≥1000	Not applicable	
USEPA New Chemicals Program	Transformation half-life >2 months	BCF >1000	Not applicable	Develop toxicity data where necessary based on various factors, including concerns for persistence, bioaccumulation, other physicochemical factors, and toxicity based on existing data
Canada[a]	Half-life in air ≥2 days, water ≥6 months, sediment ≥12 months, soil ≥6 months	BAF ≥5000 or BCF ≥5000 or log K_{ow} ≥5	Subject to transport to remote areas	Not set in policy or regulations, set as 1 mg/L (acute aquatic) or 0.1 mg/L (chronic aquatic) as part of categorization of substances on Domestic Substances List

vPvB: Very persistent and very bioaccumulative; BAF: bioaccumulation factor; BCF: bioconcentration factor; NOEC: no observable effective concentration; CMR: carcinogenic, mutagenic or toxic to reproduction. [a]As provided in the Canadian Toxic Substances Management Policy (1995) and in the Canadian Environmental Protection Act 1999 Persistence and Bioaccumulation Regulations (2000).

around 88 000 industrial chemicals have been registered and used in U.S. commerce since 1976. Of these, roughly 30 000 are polymers that are considered to present little health risk although perspective on this may be changing as macro- and microplastics gain more attention. About 17 000 substances in TSCA are Confidential Business Information (i.e. no CAS# provided) and thus their identities are unknown. New chemical notifications since the 1980s have added about 25 000 substances to the list. However, the most recent inventory update (2012) lists only 7670 at >25 000 lbs/y actually in use or imported because previously registered chemicals may be produced in volumes below that threshold or are no longer in production. The US EPA's new chemical evaluation criteria (Table 5.3) are designed to identify potential PBT chemicals but do not specifically consider long-range transport. No systematic review of existing chemicals is required under TSCA (unlike under REACH) and this has led to the substitution of banned or phased-out chemicals (e.g. flame retardants and plasticizers) with others having similar properties because they are already registered. TSCA has recently been updated by the US Congress (Chemical Watch, 2016). The new legislation requires the U.S. EPA to assess the risk of existing chemicals under 'judicially enforceable deadlines'. This process will include identification of substances on the market, designation of low and high priorities, risk evaluation of high-priority substances, and restrictions (Chemical Watch, 2016). Thresholds for reporting chemical manufacture or import and for criteria for evaluation of PBT characteristics remain unchanged.

Canada also has environmental legislation and regulations which identify P and B substances and provides for the virtual elimination of chemicals that meet the criteria for persistence and bioaccumulation. It is the only country to specifically consider atmospheric half-life and transport to remote areas (Table 5.3). Combining the Canadian Domestic Substances list and TSCA inventory updates yields some 23 000 chemicals that have been produced, imported or used in significant volumes (>10 000 or >25 000 lbs/y) in the USA and Canada since the 1980s. Howard and Muir (2010) identified 310 chemicals with predicted atmospheric half-lives of >2 days or about 1.3% of substances, not including current use pesticides, in commerce in USA/Canada.

Other regions

It is worth noting that the major sources of release for many chemicals entering the market today are in the heavily industrialized/populated regions of Asia, as opposed to Europe and North America as was the case when AMAP's original (1998b) assessment was prepared. In this context, besides global agreements, the lists of substances in the national chemical regulatory systems in these regions are becoming increasingly relevant to understand possible sources of chemical contamination of the Arctic via long-range transport. One example is a chlorinated polyfluorinated ether sulfonic acid (PFOS replacement) that is apparently manufactured and used only in China, and which was detected in biota in Greenland. India and Russia are reported to be major centers for production of fluoropolymers with manufacturers that have not signed on to stewardship programs to reduce long-chain PFASs (e.g. PFOA) in products (Bock, 2015).

As discussed in Chapter 4, chemical regulatory legislation and requirements to register chemicals exist for many other countries (see www.cas.org/content/regulated-chemicals). For example, the Chinese Chemical Inventory of Existing Chemical Substances (IECSC) has 45 600 substances, the Japanese Existing and New Chemical Substances Inventory (ENCS) has about 26 000, and the South Korean inventory has 40 500. Japan has regulated industrial chemicals since the 1970s under its Chemical Substances Control Law, which includes criteria for identifying persistent, hazardous, and bioaccumulative substances (www.meti.go.jp/policy/chemical_management/english/cscl/about.html). South Korea and China have developed chemical management legislation designed to mirror REACH so that their chemical products can be imported into Europe.

In 2014, the Eurasian Economic Commission (EEC), comprising Russia, Kazakhstan and Belarus, announced an agreement to adopt a technical regulation on the safety of chemical products by 2017 (Chemical Watch, 2014). An inventory of 33 000 substances based on the Russian Safety Passport (RSP), used voluntarily in Russia would become mandatory once the technical regulation enters into force. The RSP is the equivalent of the EU safety data sheet. The Russian Register of Potentially Hazardous Chemical and Biological Substances (RBEPH) (www.rpohv.ru/lang/en) maintains a database on potentially hazardous chemical substances produced or imported starting in 1992. Data requirements for substance registration are similar to those for REACH. As of 2010, this database contained about 18 400 substances, although 15 000 investigated prior to 1992 were included (Reihlen and Ruut, 2010). The chemical inventory is not publically available via the RBEPH website.

As is the case for Russia, India also has a major chemical manufacturing industry which is export-oriented. India has regulations for import and export, manufacturing, transportation, consumer use of chemicals and protection of human health and the environment. However, no comprehensive chemical database or registry exists (CHEManager, 2012). In 2013, India's chemicals exports agency announced that it was preparing an inventory of several thousand chemicals that are exported, as an initial step towards compiling the country's first comprehensive inventory of all the chemicals in commerce (Chemical Watch, 2013).

5.4.2 CECs in relation to regulatory criteria

5.4.2.1 Bioaccumulation/biomagnification

With important exceptions (such as long-chain PFASs), most of the CECs addressed in this assessment are detected at lower concentrations in Arctic biota than legacy POPs, such as PCBs, chlorobenzenes, hexachlorocyclohexanes (HCHs) or PBDEs in the pentaBDE product. In the absence of temporal trends and more systematic food web studies for many CECs, these biota concentrations are snapshots. However, concentrations of several CECs (e.g. PFAS and PFRs) are higher in water than many neutral chlorinated or brominated POPs. Thus fish and wildlife exposure may still be occurring for these compounds, even with bioaccumulation factors staying below national guidelines or Stockholm Convention guidance (e.g. BCF=5000).

Assessments of bioaccumulation need to consider accumulation in several tissues, for example proteinaceous tissues, such as liver and blood for PFASs, as well as the presence of transformation and metabolic products.

5.4.2.2 Persistence

The presence of many CECs at remote locations in the Arctic not influenced by northern communities, is an indication of their persistence under conditions of long-range environmental transport in the atmosphere or by oceans. Current guidance under the Stockholm Convention, as well as national criteria for identifying PBT chemicals, appears to have failed to identify many of these compounds. Examples include most PFRs, which are regarded as readily degradable, as well as many CUPs (e.g. chlorpyrifos and dacthal). To some extent this may simply reflect the large volumes used. However, it also points to the need for information on persistence in the atmosphere or ocean under realistic temperature and sunlight conditions. Continuous emissions from local sources, such as wastewater discharge, may result in a situation of 'pseudo-persistence' as degraded molecules are continuously replaced.

5.4.2.3 Ecological toxicity

As noted in Chapter 3, there is a substantial knowledge gap with respect to biological or toxicological effects of the CECs discussed in Chapter 2, in the context of impacts on Arctic biota. Important reviews have been published on the (environmental) toxicology of several classes of CEC compounds, including PFASs, BFRs, CFRs, PFRs, phthalates, siloxanes, PPCPs, OTs, PAHs and microplastics (see Table 3.1). However, a key challenge is to assess possible CEC effects against the background of elevated exposure to legacy POPs and methylmercury (which are elevated in many top predator species in the Arctic), as well as additional stressors such as climate change and periods of starvation. The forthcoming AMAP update assessment of biological effects of POPs and mercury (expected 2018) will be addressing these issues.

5.5 Key findings

Chemicals of emerging concern identified in the Arctic

- This assessment documents evidence of the occurrence of 16 major groups of chemicals of emerging concern as well as microplastics, in the Arctic.
- Targeted analytical screening studies found many chemicals not previously included in comprehensive assessments, and increased our knowledge of some previously assessed chemicals. New chemicals assessed included: PPCPs, PFASs, BFRs, CFRs, PFRs, HCBD, siloxanes, SCCPs, seven CUPs, PCB11 (non-Aroclor PCB), phthalates, HNPs, PAHs, organotins, PCA/PCP and macro- and microplastics. Some of these findings such as the presence of SCCPs in the Arctic, supported the data needs for recent deliberations of global regulations. Previously assessed chemicals where more data have become available include several PFASs, BDE-209, HBCDD, some other BFRs, PCNs and other CUPs.
- In addition to their presence as a result of long-range transport in air and ocean currents, local sources, in particular linked to wastewater discharges, for some CECs used in consumer products (such as phthalates, and siloxanes) may be important but the extent of this impact is not known. For PPCPs, local sources seem to be particularly relevant.
- Generally, levels of most new chemicals identified in the Arctic are lower than for the legacy POPs previously considered in AMAP assessments; nevertheless, high concentrations of PFRs were found in Arctic air, much higher than for BFRs. Air concentrations of SCCPs also exceeded those of legacy POPs, but SCCP quantification is more uncertain.
- Information on temporal trends of new chemicals is sparse, but where available often shows stable or increasing levels, as is the case for some PFCAs, novel BFRs and cVMS. Data for BDE-209, PCNs and some CUPs suggest decreases, but inconsistencies exist.
- Few spatial trends were available and those that were available mainly covered northern Europe, the Canadian Arctic, Greenland and parts of the Arctic Ocean.
- Most CECs found in the Arctic were identified in air samples. Some CECs were found in biota, indicating bioaccumulation: long-chain PFCAs, several BFRs (HBCDD, TBP-AE, BTBPE, DBDPE, HBBz, BEH-TEBP, EH-TBB), dechlorane plus, PFRs, phthalates, SCCPs, siloxanes (D5), some PPCPs, PCNs, HCBD, several CUPs, OTs, and some HNPs. Several of the CECs found in biota appear to biomagnify: long-chain PFCAs, α-HBCDD, DBDPE, SCCPs, and PCNs.
- Owing to regulation and shifts in production, Asia is now an important source region for some chemicals of emerging concern, such as PFASs, SCCPs, and some BFRs.

Other chemicals of potential concern

- Screening for some 150 000 chemicals in commerce in Europe and North America based on their physical-chemical properties and databases of production and use, identified around 1200 substances that have potential for long-range transport to the Arctic; of these 25 are identified in this assessment as priority for consideration in Arctic analytical screening/monitoring studies.

Gaps and how to fill them

Few spatial trends were available, as data for CECs are limited or not available from large parts of the Arctic, especially Russia, Alaska, Sweden, Finland and Iceland.

Temporal trend data were also lacking for the majority of compounds. Thus baseline data for spatial and temporal trends are needed.

Lack of information on effects of many identified CECs means that it is not possible to evaluate potential impacts on Arctic wildlife and/or human health, other than from simple comparisons with more studied chemicals based on similarity of structure and properties.

The examination of microplastics is considered a first order review of available information; consideration of these substances should be extended both with respect to their presence, potential to act as a 'carrier' for other chemicals, and as a route of dietary exposure to animals, and associated effects.

Consideration should be given to the need to adjust (AMAP) monitoring strategies to examine the presence in the Arctic of contaminants with local sources as well as those with distant sources carried to the Arctic via long-range transport.

Target and non-target analytical screening needs to be more widely applied, and consideration should be given to including additional POPs (and CECs that are found to be widely present in the Arctic) in routine (AMAP) monitoring programs – especially POPs that are listed, under review or that may have potential to be listed under the Stockholm Convention.

Broader screening needs to be applied for CECs in Arctic human biomonitoring studies.

Consideration should be given to how to optimize the delivery of AMAP information to initiatives such as the Stockholm Convention; it may also be necessary to re-evaluate the mechanisms available for protecting Arctic ecosystems from hazardous chemicals in the light of the information concerning new CECs that may not be suitable for the Stockholm Convention (e.g. microplastics and chemicals that do not meet POPs criteria such as pharmaceuticals that impact local nearshore environments, etc.).

The impacts of climate change on the transport and fate of chemicals of emerging Arctic concern as well as POPs need to be addressed. An AMAP assessment on this topic is planned to start in 2018.

Almost all of the 'new' CECs (i.e. those not previously covered in AMAP assessments) are included in inventories of chemicals in commerce. For example, the European INventory of Existing Commercial chemical Substances (EINECS) in Europe or TSCA in the USA. This underlines the importance of screening and evaluating existing inventories which list chemicals in commerce having relatively high production volumes, i.e. >1 t/y. Current screening of these lists by most regulatory authorities has not specifically considered long-range transport potential to the Arctic or accumulation potential in Arctic food webs.

The large chemical manufacturing and consumer product industries in East Asia, Russia and India could be adding additional chemicals to the global environment that are not produced or imported in Europe or North America. Further work is needed to apply the same quality and scope to chemical inventories from these countries as for North America and Europe and to develop a global inventory of commercial chemicals.

Chemicals management needs to move from assessing the presence of chemicals in the Arctic as an identification tool for chemicals possibly needing regulation (reactive approach), to a system where chemicals with predicted properties likely to lead to their transport to the Arctic and to bioaccumulation in biota are not allowed in commerce (proactive approach).

Unintentional byproducts or impurities in commercial chemicals are the other major group of CECs in this assessment (e.g. byproduct PCBs, HCBD, PCNs, PCA, PAHs, FTOHs, perfluoroalkyl sulfonamides) and others covered in previous AMAP assessments (such as chlorinated diphenyl ethers, chlorinated styrenes, chlorinated veratroles). Current regulations may not be sufficient to identify these byproducts, as illustrated by the discovery of PCB11 in yellow pigments. On the basis that a high proportion of commercial chemicals have some halogen moieties as part of their molecular structure, there is potential for other undocumented halogenated chemical byproducts or impurities, which may be more persistent and bioaccumulative than the parent chemicals.

HNPs represent a particularly challenging issue. Background levels of HNPs are needed in order to help assess effects of anthropogenic halogenated compounds, especially BFRs and CFRs.

Regulations and assessment guidance for pharmaceuticals and some personal care products needs to consider the potential for slower degradation in the wastewater systems of Arctic communities or their release into cold Arctic aquatic environments.

Regulations and assessment guidance for current use pesticides need to include evaluation for long-range transport potential and the potential for accumulation within the Arctic food web.

Section 5 Annex Contents

Section 5 Annex

Table A5.1 Overview of Arctic media for which chemicals of emerging Arctic concern have been reported.

	Atmosphere		Terrestrial		Freshwater			Marine				Waste
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	Sea ice	Sewage
Per- and polyfluoroalkyl substances												
PFBA	×	×			×		×	×	×	×		
PFPeA	×	×			×		×					
PFHxA	×	×		×	×		×	×		×		
PFHpA	×	×		×	×				×	×		
PFOA	×	×		×	×	×				×		
PFNA	×	×		×	×	×	×			×		
PFDA	×	×		×	×	×		×		×		
PFUnDA	×	×		×	×	×	×			×		
PFDoDA		×		×	×	×				×		
PFTrDA				×						×		
PFTeDA										×		
PFPeDA										×		
PFHxDA										×		
6:2-Cl-PFAES		×								×		
PFBS	×	×		×	×					×		
PFHxS	×	×		×	×	×				×		
PFHpS	×			×	×					×		
PFOS	×	×	×	×	×	×	×	×	×	×		
PFDS	×			×						×		
PFDoS										×		
4:2 FTS					×							
6:2 FTS					×					×		
FBSA										×		
PFOSA	×	×	×	×	×	×	×	×	×	×		
N-EtFOSA	×											
N-EtFOSE	×											
N-MeFOSE	×											
N-MeFOSEA	×											
PFECHS		×			×			×		×		
6:2 FTOH	×											
8:2 FTOH	×											
10:2 FTOH	×											
8:2 FTUCA										×		
10:2 FTUCA										×		
7:3 FTCA												
8:2 FTCA												
10:2 FTCA												
Brominated flame retardants (BFRs)[a]												
BDE-209	×	×		(×)	(×)			×	×	×		
BEH-TEBP	×			(×)			×			×		
BTBPE	×	×		×			×	×		×		

Table A5.1 cont.

	Atmosphere		Terrestrial		Freshwater			Marine				Waste
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	Sea ice	Sewage
DBDPE	×	×		(×)		(×)	(×)		×	×		
DBE-DBCH	×	×					(×)			×		
EH-TBB	×			×			×			×		
HBBz	×	×		(×)			×	×		×		
HBCDD	×	×		(×)	(×)		×			×		
OBTMPI	(×)									(×)		
PBB-Acr	×											
PBBz	×	×						(×)		(×)		
PBEB	×	×		(×)			(×)			×		
PBT	×	×		(×)			×	×		×		
TBBPA	×						(×)			(×)		
TBBz		×										
TBCT	×									(×)		
TBP-AE	×						(×)			×		
TBP-BAE	×						(×)			×		
TBP-DBPE	×						(×)	×		×		
TBX	×									×		
Chlorinated flame retardants (CFRs)[a]												
DDC-CO	×	×	×	×				×	×	×		
DDC-DBF	×		×	×				×	×	×		
DDC-Ant	(×)		×	×				×	×	×		
HCTBPH	×		×	×				×	×	(×)		
$aCl_{11}DP$	×	×										
DPMA												
Organophosphate-based flame retardants and plasticizers												
TCEP	×						×			×		
TCIPP	×						×			×		
TDCIPP	×						×			×		
TPHP	×						×			×		
TBP	×						×			×		
TMPP										×		
EHDPP	×									×		
TBOEP	×						×			×		
TEHP	×									×		
TNBP	×											
TIBP	×									×		
DPhBP										×		

Table A5.1 cont.

	Atmosphere		Terrestrial		Freshwater			Marine				Waste
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	Sea ice	Sewage
Phthalates												
DMP	×							×		×		
DEP	×							×	×	×		
DnBP	×							×	×	×		
DIBP	×							×				
BBP	×							×	×	×		
DEHP	×				×	×	×	×	×	×		
DnOP										×		
DINP									×	×		
DIDP									×	×		
DUP									×			
DnHP									×	×		
Short-chain chlorinated paraffins (SCCPs)												
SCCPs	×		×	×	×	×	×		×	×		
Siloxanes												
L2												
L3												
L4												
D4	×					×	×		×	×		
D5	×					×	×		×	×		
D6	×					×	×		×	×		
Pharmaceuticals and personal care products (PPCPs)[b]												
NSAIDs (11)					×	×		×				×
Antidepressants/ SSRI (10)					×	×		×				×
β(beta)-blockers (5)					×	×						×
Calcium channel blockers (1)						×						×
ACE blockers (3)						×						×
Angiotensin receptor antagonists (3)						×						×
Antiepileptics (1)					×							×
Antimicrobials (4)					×			×				×
Antibiotics (14)					×			×				×
Additives (5)	×		×		×					×		×
Fragrances (5)					×							×
Steroid hormones (5)					×	×						×
Lipid regulators (3)					×							×
Illicit drugs (4)					×							×
Stimulants (2)					×			×				×
Anti-cancer (2)												×
Artificial sweeteners (2)					×							×
Surface tension suppressors (6)					×	×	×					×

Table A5.1 cont.

	Atmosphere		Terrestrial		Freshwater			Marine				Waste
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	Sea ice	Sewage
Hypnotics (1)												×
Antidiabetics (1)												×
Anticoagulants (2)						×						×
Diuretics (4)						×						×
Chelating agents (1)						×						×
UV-filters (3)												×
Bisphenol monomers (5)												×
Polychlorinated naphthalenes (PCNs)[c]												
PCNs	×	+				+ (subarctic)	+			×		
Hexachlorobutadiene (HCBD)												
HCBD	×			×		×	×			×		
Current-use pesticides (CUPs)[d]												
Chlorothalonil	+,×	+		×	+			+, ×				
Chlorpyrifos	+,×	+		×	+		+	+, ×		+		
Dacthal	+,×	+		+, ×	+	+	+	+, ×		+, ×		
Diazinon		+			+							
Dicofol	+,×							+, ×				
Endosulfan	+,×	+		+, ×	+		+	+, ×	×	+, ×		
MCPA	×											
Methoxychlor	+	+		+	+		+	×		+		
Metribuzin	×											
Pendimethalin	×											
Pentachloro-nitrobenzene (PCNB)	×	+,×		×	+			×		×		
Phosalone	×											
Quizalofop ethyl	×											
Tefluthrin	×											
Triallate	×											
Trifluralin	+,×	+			+	+		+, ×	×			
Pentachlorophenol (PCP) and pentachloroanisole (PCA)[e]												
PCP	×	×	×	×	×	×	×	×	×	×		
PCA	×	×	×	×	×	×	×	×	×	×		
Organotins												
TBT									×	×		
DBT									×	×		
MBT									×	×		
TPT										×		
Polycyclic aromatic hydrocarbons (PAHs)[f]												
PAHs	×	×	×	×	×	×	×	×	×	×		

Table A5.1 cont.

	Atmosphere		Terrestrial		Freshwater			Marine				Waste
	Air	Snow	Soil	Biota	Water	Sediment	Biota	Water	Sediment	Biota	Sea ice	Sewage
'New' unintentionally generated PCBs												
PCB11	×	×	×	×								
PCB209[g]	×	×	×	×								
Halogenated natural products												
Halocarbons	×	×	×		×			×				
Haloacetates		×	×	×	×			×				
BPs	×			×					×	×		
BAs	×							×		×		
OH-BDEs										×		
MeO-BDEs							×			×		
PDBPs									×	×		
MHC-1										×		
PBHDs										×		
Marine plastics and microplastics												
Macroplastics (>5 mm)								×	×	×		
Microplastics (<5 mm)								×	×	×	×	

[a]Brackets indicate that the compound was sought, but not detected in the respective medium; [b]The number of compounds analyzed for each compound group is given in parentheses; [c] '×' indicates new data (i.e. available since the previous AMAP assessment) and '+' indicates older data (as reviewed by Bidleman et al., 2010). In the case of older and new data, only '×' is used; [d] '×' indicates new data (i.e. available since the previous AMAP assessment) and '+' indicates older data (summarized from Hoferkamp et al., 2010; Weber et al., 2010; Vorkamp and Rigét, 2014); [e] In many cases, the two analytes were not determined separately; [f]It is difficult to distinguish between pyrogenic and petrogenic PAHs with certainty in marine samples given the presence of natural underwater hydrocarbon seeps; [g]Whether the source of PCB209 observed in Arctic media is an unintentionally generated PCB or is intentionally produced in PCB mixture or both, cannot be distinguished at this time.

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Appendix 1 Database of Physical-Chemical Properties of Chemicals of Emerging Arctic Concern

Electronic Annex, see https://chemicals.amap.no

Appendix 2 Species names

Invertebrates	
Bay mussels	*Mytilus trossulus*
Blue mussel	*Mytilus edulis*
Dogwhelk	*Nucella lapillus*
Dogwinkle	*Nucella lima*
Iceland scallop	*Chlamys islandica*
Periwinkle	*Littorina littorea*
Sea cucumber	*Holothuria sp.*
Snow crab	*Chionoecetes opilio*
Fish	
Arctic char	*Salvelinus alpinus*
Arctic cisco	*Coregonus autumnalis*
Arctic cod	*Boreogadus saida*
Atlantic cod	*Gadus morhua*
Atlantic halibut	*Hippoglossus hippoglossus*
Atlantic salmon	*Salmo salar*
Baltic herring	*Clupea harengus*
Brown trout	*Salmo trutta*
Burbot	*Lota lota*
Capelin	*Mallotus villosus*
Chinese sturgeon	*Acipenser sinensis*
European perch	*Perca fluviatilis*
Fathead minnow	*Pimephales promelas rafinesque*
Flounder	*Platichthys flesus*
Greenland cod	*Gadus ogac*
Greenland halibut	*Reinhardtius hippoglossoides*
Greenland shark	*Somniosus microcephalus*
Halibut	*Hippoglossus hippoglossus*
Lake trout	*Salvelinus namaycush*
Landlocked char	*Salvelinus alpinus*
Medaka	*Oryzias latipes*
Ninespine stickleback	*Pungitius pungitius*
Pacific herring	*Clupea pallasi*
Perch	*Perca fluviatilis*
Polar cod	*Boreogadus saida*
Rainbow trout	*Oncorhynchus mykiss*
Saithe	*Pollachius virens*
Sculpin	*Myoxocephalus scorpioides*
Sheefish	*Stenodus leucicthys*
Shorthorn sculpin	*Myoxocephalus scorpius*
Smelt	*Osmerus eperlanus*
Walleye	*Theragra chalcogramma*
Whitefish	*Coregonus sp.*
Wolfish	*Anarichas minor*
Zebrafish	*Danio rerio*
Birds	
American herring gull	*Larus smithsonianus*
Arctic tern	*Sterna paradisaea*
Atlantic puffin	*Fratercula arctica*
Black guillemot	*Cepphus grylle*
Black-legged kittiwake	*Rissa tridactyla*
Brünnich's guillemot/ Thick billed murre	*Uria lomvia*
Common eider	*Somateria mollissima*
Common guillemot	*Uria aalge*
Dovekie	*Alle alle*
European shag	*Phalacrocorax aristotelis*
Glaucous gull	*Larus hyperboreus*
Great black-backed gull	*Larus marinus*
Great skua	*Stercorarius skua*
Guillemot	*Uria aalge*
Herring gull	*Larus argentatus*
Ivory gull	*Pagophila eburnea*
King eider	*Somateria spectabilis*
Kittiwake	*Rissa tridactyla*
Lesser black-backed gull	*Larus fuscus*
Little auk	*Alle alle*
Long-tailed duck	*Clangula hyemalis*
Northern fulmar	*Fulmarus glacialis*
Peregrine falcon	*Falco peregrinus*
Ptarmigan	*Lagopus muta*
Shag	*Phalacrocorax aristotelis*
Thick billed murre / Brünnich's guillemot	*Uria lomvia*
White-tailed sea eagle	*Haliaeetus albicilla*
White-winged scoter	*Melanitta fusca*
Marine mammals	
Atlantic white-sided dolphin	*Lagenorhynchus acutus*
Baikal seal	*Pusa sibirica*
Bearded seal	*Erignathus barbatus*
Beluga	*Delphinapterus leucas*
Bowhead whale	*Balaena mysticetus*
Dall's porpoise	*Phocoenoides dalli*
Fin whale	*Balaenoptera physalus*
Greenland harp seal	*Pagophilus groenlandicus*
Grey seal	*Halichoerus grypus*
Harbor porpoise	*Phocoena phocoena*
Harbor seal	*Phoca vitulina*
Harp seal	*Pagophilus groenlandicus*
Hooded seal	*Cystophora cristata*
Humpback whale	*Megaptera novaeangliae*
Killer whale	*Orcinus orca*
Long-finned pilot whale	*Globicephala melas*
Minke whale	*Balaenoptera acutorostrata*
Narwhal	*Monodon monoceros*
Northern fur seal	*Callorhinus ursinus*
Pilot whale	*Globicephala melas*
Ringed seal	*Pusa hispida*
Spotted seal	*Phoca largha*
Steller sea lion	*Eumetopias jubatus*
Walrus	*Odobenus rosmarus*
White-beaked dolphin	*Lagenorhynchus albirostris*
White-sided dolphin	*Lagenorhynchus acutus*
Land mammals	
Arctic fox	*Vulpes lagopus*
Arctic hare	*Lepus arcticus*
Bank vole	*Myodes glareolus*
Caribou/Reindeer	*Rangifer tarandus*
Eurasian lynx	*Lynx lynx*
Moose	*Alces alces*
Mountain goat	*Oreamnos americanus*
Muskox	*Ovibos moschatus*
Polar bear	*Ursus maritimus*
Reindeer/Caribou	*Rangifer tarandus*
Wolf	*Canis lupus*
Wood mouse	*Apodemus sp.*

Appendix 3 Acronyms and abbreviations

β-HCH	Beta-hexachlorocyclohexane
AMAP	Arctic Monitoring and Assessment Programme
AO t½	Atmospheric oxidation half-life
BA	Bromoanisole
BCF	Bioconcentration factor
BFR	Brominated flame retardant
BMF	Biomagnification factor
BP	Bromophenol
CA	Chloroanisole
CAS	Chemical Abstracts Service (registry)
CEAC	Chemical of emerging Arctic concern
CEC	Chemical of emerging concern
CFR	Chlorinated flame retardant
CLRTAP	Convention on Long-range Transboundary Air Pollution
CTD	Characteristic travel distance
CTD_A	Characteristic travel distance in air
CTD_W	Characteristic travel distance in water
CUP	Current use pesticide
DBT	Dibutyltin
DSL	Domestic Substances List (Canada)
dw	Dry weight
ECF	Electrochemical fluorination
ECHA	European Chemicals Agency
EINECS	European Inventory of Existing Chemical Substances
ELINCS	European List of Notified Chemical Substances
FOSA	Fluorinated sulfonamide
FTOH	Fluorotelemer alcohol
GAPS	Global Atmospheric Passive Sampling network
HBCDD	Hexabromocyclododecane
HCH	Hexachlorocyclohexane
Hg	Mercury
HNP	Halogenated natural product
HPVC	High production volume chemical
K_{aw}	Air-water partition coefficient
K_{oc}	Organic carbon partition coefficient
K_{ow}	Octanol-water partition coefficient
LCCP	Long-chain chlorinated paraffin
Ln	Natural logarithm
log	Logarithm to the base 10
LRTP	Long-range transport potential
lw	Lipid weight
MBT	Monobutyltin
MCCP	Medium-chain chlorinated paraffin
MDL	Minimum detection limit
OCP	Organochlorine pesticide
OPE	Organophosphate ester
PAH	Polycyclic aromatic hydrocarbon
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PBT	Persistent (P), Bioaccumulative (B), Toxic (T)
PCB	Polychlorinated biphenyl
PCN	Polychlorinated naphthalene
PE	Polyethylene
PET	Polyethylene terephthalate
PFAS	Perfluoroalkyl carboxylic and sulfonic acid
PFCA	Perfluorocarboxylic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFSA	Perfluoroalkane sulfonic acid
PFR	Phosphorus flame retardant
pK_A	Acid dissociation constant
POP	Persistent organic pollutant
POPRC	Persistent Organic Pollutants Review Committee
PP	Polypropylene
PPCPs	Pharmaceuticals and personal care products
PUF	Polyurethane foam
PVC	Polyvinylchloride
QA/QC	Quality assurance/quality control
QSAR	Quantitative structure-activity relationship
QSPR	Quantitative structure-property relationship
RPF	Relative potency factor
SCCP	Short-chain chlorinated paraffin
SIP	Sorbent-impregnated polyurethane foam
TBBPA	Tetrabromobisphenol A
TBT	Tributyltin
TCDD	2,3,7,8-Tetrachlorodibenzo-*p*-dioxin
TEF	Toxic equivalency factor
TEQ	TCDD toxic equivalents
TMF	Trophic magnification factor
TSCA	Toxic Substances Control Act (US)
TSCA-IUR	US Toxic Substances Control Act Inventory Update Rule
UNECE	United Nations Economic Commission for Europe
US EPA	United States Environmental Protection Agency
UV	Ultraviolet radiation
VECAP	Voluntary Emissions Control Action Programme
VMS	Volatile methylsiloxanes
vPvB	Very persistent and very bioaccumulative
VSLS	Very short-lived substances
WACAP	Western Airborne Contaminants Assessment Project
ww	Wet weight
WWTP	Wastewater treatment plant

Arctic Monitoring and Assessment Programme

The Arctic Monitoring and Assessment Programme (AMAP) was established in June 1991 by the eight Arctic countries (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden and the United States) to implement parts of the Arctic Environmental Protection Strategy (AEPS). AMAP is now one of six working groups of the Arctic Council, members of which include the eight Arctic countries, the six Arctic Council Permanent Participants (indigenous peoples' organizations), together with observing countries and organizations.

AMAP's objective is to provide 'reliable and sufficient information on the status of, and threats to, the Arctic environment, and to provide scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions to reduce adverse effects of contaminants and climate change'.

AMAP produces, at regular intervals, assessment reports that address a range of Arctic pollution and climate change issues, including effects on health of Arctic human populations. These are presented to Arctic Council Ministers in 'State of the Arctic Environment' reports that form a basis for necessary steps to be taken to protect the Arctic and its inhabitants.

This report has been subject to a formal and comprehensive peer review process. The results and any views expressed in this series are the responsibility of those scientists and experts engaged in the preparation of the reports.

The AMAP Secretariat is located in Oslo, Norway. For further information regarding AMAP or ordering of reports, please contact the AMAP Secretariat (Gaustadalléen 21, N-0349 Oslo, Norway) or visit the AMAP website at www.amap.no.

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