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Review

Levels and trends of poly- and perfluorinated compounds in the arctic environment ☆

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ABSTRACT

Poly- and perfluorinated organic compounds (PFCs) are ubiquitous in the Arctic environment. Several modeling studies have been conducted in attempt to resolve the dominant transport pathway of PFCs to the arctic—atmospheric transport of precursors versus direct transport via ocean currents. These studies are generally limited by their focus on perfluorooctanoate (PFOA) fluxes to arctic seawater and thus far have only used fluorotelomer alcohols (FTOHs) and sulfonamide alcohols as inputs for volatile precursors. There have been many monitoring studies from the North American and European Arctic, however, almost nothing is known about PFC levels from the Russian Arctic. In general, there are very few measurements of PFCs from the abiotic environment. Atmospheric measurements show the widespread occurrence of PFC precursors, FTOHs and perfluorinated sulfonamide alcohols. Further, PFCAs and PFSAs have been detected on atmospheric particles. The detection of PFCAs and PFSAs in snow deposition is consistent with the volatile precursor transport hypothesis. There are very limited measurements of PFCs in seawater. PFOA is generally detected in the greatest concentrations. Additional seawater measurements are needed to validate existing model predications. The bulk of the monitoring efforts in biological samples have focused on the perfluorinated carboxylates (PFCAs) and sulfonates (PFSAs), although there are very few measurements of PFC precursors. The marine food web has been well studied, particularly the top predators. In contrast, freshwater and terrestrial ecosystems have been poorly studied. Studies show that in wildlife perfluorooctane sulfonate (PFOS) is generally measured in the highest concentration, followed by either perfluorononanoate (PFNA) or perfluoroundecanoate (PFUnA). However, some whale species show relatively high levels of perfluorooctane sulfonamide (PFOSA) and seabirds are typically characterized by high proportions of the C_{11}–C_{15} PFCAs. PFOA is generally infrequently detected and is present in low concentrations in arctic biota. Food web studies show high bioaccumulation in the upper trophic-level animals, although the mechanism of PFC biomagnification is not understood. Spatial trend studies show some differences between populations, although there are inconsistencies between PFC trends. The majority of temporal trend studies are from the Northern American Arctic and Greenland. Studies show generally increasing levels of PFCs from the 1970s, although some studies from the Canadian Arctic show recent declines in PFOS levels. In contrast, ringed seals and polar bears from Greenland continue to show increasing PFOS concentrations. The inconsistent temporal trends between regions may be representative of differences in emissions from source regions.

Contents

☆ This paper is a contribution to the AMAP POPs assessment.

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1. Introduction

The family of poly- and perfluorinated compounds (PFCs) includes a large number of chemicals used in numerous industrial and commercial applications (Kissa, 2001). The C—F bond makes the fluorocarbon chain extremely resistant to heat and chemical attack (e.g. by acids and bases, and reducing and oxidizing agents). PFCs are unique compared to the legacy POPs in that what is used in commercial products (e.g. fluorinated polymers) is generally not what is actually detected in the environment (i.e. the perfluorinated carboxylates, PFCAs, and perfluorinated sulfonates, PFSAs). Environmental monitoring of PFCs has been largely advanced by relatively recent developments in LC-MS/MS technology. Two groups of PFCs, the PFCAs and PFSAs have in the past eight years received attention because of their widespread presence in the environment, humans and wildlife (Houde et al., 2006; Lau et al., 2007). The two most widely known PFCs are perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA), although longer-chain PFCAs may be more prevalent than PFOA in wildlife. PFSAs and PFCAs are environmentally persistent and the longer chain compounds ($>C_6$ for PFSAs and $>C_8$ for PFCAs) have a tendency to bioaccumulate and biomagnify in food webs (Kannan et al., 2005a; Tomy et al., 2004b). The PFCAs and PFSAs are degradation compounds of commercial products (e.g. fluorinated phosphate surfactants) and compounds used in the manufacture of commercial products (e.g. fluorinated alcohols and acrylates). With the exception of PFOA, perfluorononanoate (PFNA), and PFOS, PFCAs and PFSAs were not directly produced in large quantities (Prevedouros et al., 2006). The bioaccumulation potential of PFCAs has been recently discussed and compared to PFSAs in a critical review by Conder et al. (2008).

PFCs are produced via two major synthesis processes: electrochemical fluorination (ECF) and telomerization. The ECF process was used primarily by the 3M Company from the 1950s to 2001 in the perfluorooctane sulfonyl fluoride (PFOSF) chemistry. PFOSF-based chemicals include the perfluorooctanesulfonamide ethanols (FOSEs), perfluorooctane sulfonamide (PFOSA) and PFOS. The FOSEs and PFOSA have been shown to degrade abiotically (D'eon et al., 2006; Martin et al., 2006) to PFOS and PFOA as well as via biotic degradation (Tomy et al., 2004a; Xu et al., 2004, 2006) to PFOS. It is worthwhile to note the degradation of PFOSF-based compounds will only yield PFOA and not other chain-length PFCAs. The ECF process was also used to manufacture PFOA from 1947 to 2002. In 2001, the 3M Company announced the voluntary phase-out of its PFOSF-based chemicals in favour of shorter chain-length compounds. However, it has been reported that PFOS has been directly produced in China since 2003, which may influence global emission patterns (http://chm.pops.int/Portals/0/Repository/comments_draftRME2008/UNEP-POPS-POPRC-DRME-08-CHI-SCCP.English.PDF). In contrast, the telomerization process has been used by various companies since the 1970s for the production of fluorotelomer alcohols (FTOHs), fluorotelomer olefins, fluorotelomer acrylates, fluorotelomer iodides and PFCAs. FTOHs have been shown to degrade via abiotic (Ellis et al., 2004; Hurley et al., 2004) and biotic (Hagen et al., 1981) mechanisms to PFCAs. For example, the 8:2 FTOH has been shown to degrade to PFOA, and perhaps small quantities of PFNA, in biological systems (Martin et al., 2005). More recent research has shown that the

fluorotelomer olefins (Nakayama et al., 2007; Vésine et al., 2000), iodides (Young et al., 2008) and acrylates (Butt et al., 2009) may form PFCAs via atmospheric oxidation. As discussed in detail later in the review, compounds manufactured via the ECF process have been shown to contain both the linear and several branched isomers (Arsenault et al., 2008; Chu and Letcher, 2009; Houde et al., 2008). In contrast, compounds produced by the telomerization process contain only the linear isomer (Kissa, 2001).

The sources of PFCs to the arctic are not well understood and the proposed transport pathways will be discussed in detail in this review. PFCs may be released into the environment by direct discharge ("direct emissions") from the production of fluorochemicals and disposal of products containing fluorochemicals. In addition, the degradation of "precursor compounds" such as FTOHs and PFOSF-based chemicals has been identified as an "indirect source" of PFCs to the environment. The sources of some PFCAs to the environment and emission estimates have been reviewed by Prevedouros et al. (2006). A list of fluorinated compounds that may degrade to PFCAs has been recently compiled by the OECD (2007).

There is clear evidence that many PFSAs and PFCAs are globally distributed. This has prompted regulations on the production and uses of several PFCs by national and international regulatory agencies, such as U.S. EPA (2002, 2006), Environment Canada (Renner, 2005; Canada Gazzette, 2006) and European Union (Directive 2006/122/EC). PFOS has recently been added by the OSPAR Commission to the list of chemicals for priority action (OSPAR Commission, 2006), has been included by the Stockholm Convention (2005) as a candidate persistent organic pollutant (POPs) and is on the list of 'new contaminants' being monitored by the Arctic Monitoring and Assessment Program (AMAP 2004).

The detection of some PFCs in human blood from arctic regions (Dallaire et al., 2009; Weihe et al., 2008) has also raised concerns about their potential toxicity. Several studies have been published on the toxicological effects of PFCs. A recent review by Lau et al. (2007) summarizes the advances in understanding the toxicological mode of action of PFCs.

The potential for long range transport of PFSAs and PFCAs, their tendency to bioaccumulate and to induce toxic effects are characteristics of POPs. Unlike legacy POPs—which accumulate in lipid rich tissues—PFSAs and PFCAs bind to blood proteins and accumulate mainly in the liver, kidneys and bile secretions (Jones et al., 2003b). Similar to legacy POPs, PFSAs and PFCAs are transported to remote regions such as the circumpolar Arctic.

In general, the effects of PFCs on wildlife are not known, in particular for arctic biota. In a recent study, Sonne et al. (2008) investigated the potential impact from exposure to PFSAs and PFCAs on liver lesions in East Greenland polar bears (*Ursus maritimus*). An assessment of the effects of POPs, including PFCs, on Arctic wildlife is presented in this issue (Letcher et al., this issue).

Since 2001 there has been considerable progress in the assessment of the environmental levels and potential transport pathways of PFCs to arctic regions. The intent of this review is to provide a state of the science summary of the PFC monitoring data in the arctic environment. The scope of this review will include the PFCAs and PFSAs, as well as their known precursor compounds (see Table 1 for a list of analytes). Specific areas of discussion include the current understanding of PFC transport pathways, overall levels and, spatial and temporal trends in the biotic and abiotic environments, as well as a discussion of data gaps and future research needs. Fig. 1 shows a map of the circumpolar arctic, whereas Fig. 2 focuses on the North America Arctic, Greenland and Iceland.

Table 1
Acronyms and CAS numbers of PFCs cited.

Compound	Acronym	CAS number
Perfluorocarboxylates		
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	PFUnA	2058-94-8
Perfluorododecanoate	PFDoA	307-55-1
Perfluorotridecanoate	PFTrA	72629-94-8
Perfluorotetradecanoate	PFTA	373-06-7
Perfluoropentadecanoate	PFPA	141074-63-7
Perfluorosulfonates		
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
6:2 fluorotelomer sulfonate	6:2 FtS	27619-97-2
Perfluorosulfonamides and sulfonamide ethanols		
Perfluorooctane sulfonamide	PFOSA	754-91-6
N-ethyl perfluorooctane sulfonamide	*N*-EtFOSA	4151-50-2
N-ethyl perfluorooctane sulfonamide ethanol	*N*-EtFOSE	1691-99-2
N-methyl perfluorooctane sulfonamide ethanol	*N*-MeFOSE	24448-09-7
N-methyl perfluorooctane sulfonamide ethylacrylate	*N*-MeFOSEA	25268-77-3
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

2. Transport pathways

The source of PFCs to the Arctic environment is complex and has been the subject of considerable scientific interest. While two major potential transport mechanisms of PFCs to the arctic have been postulated, the relative contribution of each pathway remains unresolved (Fig. 3). One pathway involves the transport of volatile precursors via the atmosphere, degradation by atmospheric oxidation to PFCAs and PFSAs and subsequent wet and dry deposition. Volatile precursors include the FTOHs which have been shown to degrade to PFCAs (Ellis et al., 2004; Hurley et al., 2004) and the perfluorinated sulfonamide alcohols (FOSEs) which have been shown to degrade to PFCAs and PFSAs (D'eon et al., 2006; Martin et al., 2006). In addition, recent research has shown that the fluorotelomer olefins (Nakayama et al., 2007; Vésine et al., 2000), iodides (Young et al., 2008) and acrylates (Butt et al., 2009) may form PFCAs via atmospheric oxidation. The second pathway involves the transport of directly emitted PFCAs and PFSAs via oceanic currents to the Arctic marine environment (Armitage et al., 2006; Wania, 2007). PFCAs and PFSAs may be emitted during fluorochemical manufacturing processes and as residuals in consumer products. In addition, they have been intentionally added in some products (e.g. aqueous film forming foams, AFFF). Although there is some uncertainty as to the actual pK_a values, PFCAs and PFSAs are expected to be found primarily as anions (Brace, 1962; Goss, 2008; Grondin et al., 1976) in aquatic environments, particularly ocean waters. As such, they will be relatively water soluble and amenable to oceanic transport. In addition, PFCAs and PFSAs are extremely persistent under ambient environmental conditions.

Local inputs may be another important source of PFCs to arctic regions. For example, Stock et al. (2007) detected comparatively elevated levels of perfluorohexane sulfonate (PFHxS), PFOS, perfluoroheptanoate (PFHpA) and PFOA in the water and sediment of Resolute Lake near Resolute Bay on Cornwallis Island, Nunavut, Canada. The authors attributed the elevated PFC levels to AFFF contamination and sewage runoff from the local airport. Although Resolute Lake flows directly into the Barrow Strait, ringed seals (*Phoca*

Fig. 1. Map of the circumpolar arctic region.

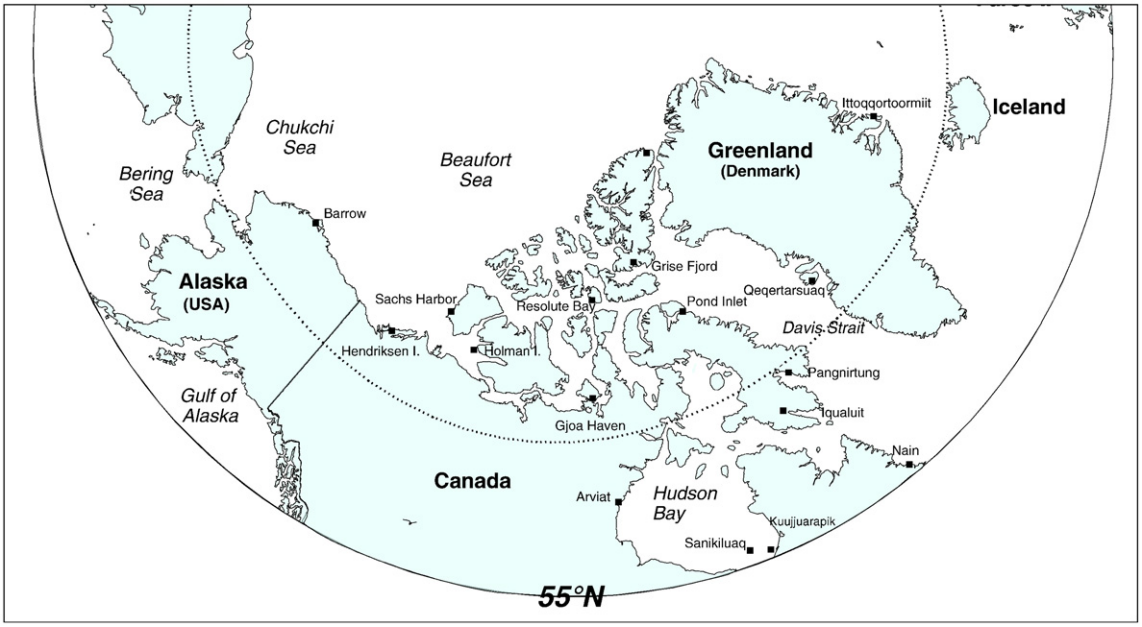

Fig. 2. Map of North American Arctic, Greenland and Iceland.

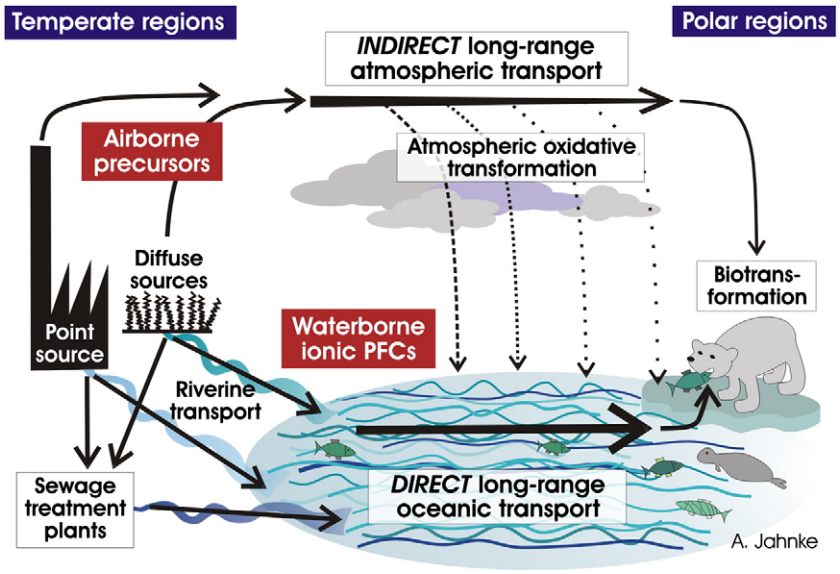

Fig. 3. Major transport pathways of PFCs to the Arctic Schematic by Annika Jahnke.

hispida) from the region did not show comparatively elevated PFC levels (Butt et al., 2008). Therefore, it is unclear if local PFC sources will significantly influence PFC concentrations in the arctic regional marine environment.

Several models have been developed to quantify the relevant contribution of the "indirect" and "direct" transport pathways. A brief description of each model is presented, followed by a discussion of supporting evidence for each pathway.

Wallington et al. (2006) estimated the formation of PFCAs from the atmospheric oxidation of 8:2 FTOH using the IMPACT model. Although the focus of the study was PFOA, the formation of other PFCAs (PFNA and lower chain-length PFCAs) was also investigated. The global emission of 8:2 FTOH was estimated as 1000 tonnes per year, the upper range predicted in order to maintain the observed atmospheric FTOH concentrations (Ellis et al., 2003). The model predicted that 8:2 FTOH would be globally distributed, consistent with the measured half-life of approximately 20 days (Ellis et al., 2003). Arctic air concentrations were predicted to be 5-fold lower than from the southern source regions. PFOA was also predicted to be ubiquitously formed in the atmosphere, but with concentrations frequently higher in remote regions (such as the arctic) due to the presence of low NO_x concentrations. The molar yield of PFOA from 8:2 FTOH degradation was estimated to be 3–6% in the Northern Hemisphere and similar yields of PFNA were also predicted. When integrated over the latitudes of 65–90°N, the estimated PFOA deposition flux from 8:2 FTOH was 0.4 tonnes per year. Young et al. (2007) showed that this deposition flux was similar to that extrapolated from surface snow measurements in the Canadian Arctic.

Armitage et al. (2006) examined the PFOA flux from direct emissions to the Arctic via oceanic currents using the Globo-POP model. PFOA emission estimates between 1950 and 2004 were taken from Prevedouros et al. (2006). In addition, projected PFOA emission estimates (2005–2050) were assumed based on recent emission reductions and from reduction commitments made by industry. The model predicted surface ocean water concentrations to range from 25–90 pg/L in the Northern Polar zone (arctic region) during 2005. The authors noted that these results agreed well with ocean measurements from the Greenland Sea (Theobald et al., 2007). The estimated net flux of PFOA to the Northern Polar zone was 8–23 tonnes per year. The authors note that this flux is 20 to 60-fold greater than that predicted from FTOH degradation by Wallington et al. (2006). It was suggested that these modeling results support the study hypothesis that direct emissions are responsible for the PFOA burden in the arctic surface water. The model predicted doubling times of approximately 7.5–10 years for PFOA surface water concentrations between 1975 and 2004. It was noted that these doubling times agreed well with those observed in arctic wildlife (Smithwick et al., 2006). Despite the estimated downturn in direct PFOA emissions in the early 2000s, arctic seawater levels were predicted to increase until about 2030 and then gradually decline (Fig. 4).

Wania (2007) extended the work of Armitage et al. (2006) by using the Globo-POP model to compare PFOA fluxes to the arctic surface waters (defined as the "Northern Polar zone" in the model) resulting from both the direct transport via ocean currents as well as that generated by the atmospheric oxidation of FTOHs. In addition, the Arctic Contamination Potential (ACP) was calculated as an estimate of the relative efficiency of each transport pathway. FTOH production values from the mid-1970s to 2005 were taken from Prevedouros et al. (2006) and the DuPont Global PFOA Strategy (2005). The model assumed 2% of FTOH production was emitted to the atmosphere. The 2005 FTOH emission rate was 200 tonnes per year which was considerably lower than that used by Wallington et al. (2006). PFCA yields from FTOH atmospheric oxidation were assumed to be between 3 and 10% as estimated from Wallington et al. (2006). Direct emissions of PFOA were taken from Armitage et al. (2006). The

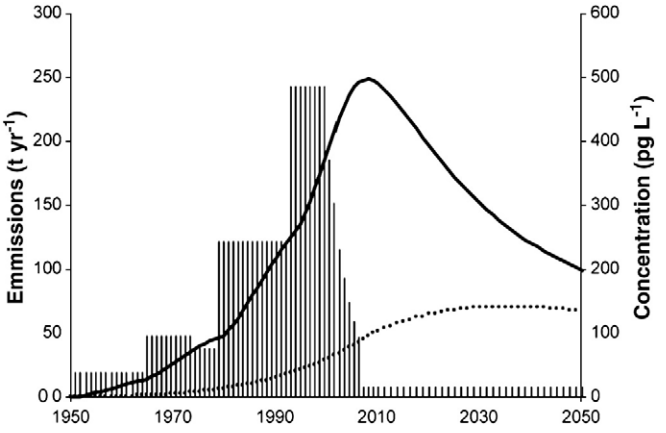

Fig. 4. Modeled PFOA concentrations in ocean water from northern hemisphere for period 1950–2050. Vertical bars represent annual emissions, solid line represents model concentrations in the Northern Temperate zone, dotted line represents model concentrations in the Northern Polar zone (arctic region). Reprinted with permission from Armitage et al. (2006). Copyright 2006 American Chemical Society.

cumulative emission rate for FTOHs was approximately 1500 tonnes from 1974 to 2005, whereas, the cumulative PFOA emission rate from direct releases between 1950 and 2005 was 5000 tonnes. The model predicted that, after 10 years of continuous release, the ACP of directly emitted PFOA is about 16-fold greater than that of PFOA generated by the atmospheric degradation of FTOHs. This suggests that oceanic transport is a more efficient process to deliver PFOA to the arctic surface waters. The difference was largely due to the relatively low yield of PFCAs from FTOH atmospheric oxidation. The model results predicted the flux to the Arctic by directly emitted PFOA to be 9–20 tonnes/year for the years 2000–2005. In comparison, the deposition flux of all PFCAs generated from FTOH atmospheric degradation was predicted to be 110 kg/y in 2005. This suggests that oceanic transport is about 1–2 orders of magnitude more significant than atmospheric deposition for PFOA. Further, it was noted that PFCA flux from FTOH degradation was 5 to 10-fold less than predicted for PFOA deposition alone by Wallington et al. (2006), which is consistent with lower FTOH emission estimates. Similar to Armitage et al. (2006), it was shown that model predictions for arctic seawater concentrations resulting from direct PFOA emissions were consistent with measured levels from the Greenland Sea (Theobald et al., 2007). In contrast, arctic seawater concentrations resulting solely from FTOH degradation were about 2 orders of magnitude lower. It was suggested that this implies the quantity of PFCAs generated from FTOH atmospheric degradation is too low to explain measured seawater levels. Interestingly, the model predicted that the bulk of PFCAs generated from FTOH degradation would be deposited in the mid-latitude Northern hemisphere oceans and subsequently transported to the Arctic via ocean currents. Therefore, a lag in arctic seawater levels was predicted, similar to Armitage et al. (2006), in response to reduced direct PFOA and FTOH emissions.

Schenker et al. (2008) estimated the PFOA deposition to the Arctic derived from the degradation of FTOHs and perfluorooctyl sulfonamide ethanols between 1998 and 2005 using the CliMoChem model. PFOA emission estimates were taken from Prevedouros et al. (2006) whereas precursor emission estimates were derived from information presented by Prevedouros et al. (2006) and Wania (2007). The model explicitly included the volatile precursors as well as intermediates. The model assumed a 5% yield of PFOA from FTOHs, as modeled by Wallington et al. (2006). A similar PFOA yield from PFOSF-based alcohols was assumed based on the similarity in the reaction pathways and recent smog-chamber results (D'eon et al., 2006; Martin et al., 2006). The model predicted similar PFOA deposition fluxes from the degradation of FTOHs and PFOSF-based compounds until 2002 (Fig. 5). After 2000, PFOA deposition from FTOH degradation dominated the overall deposition profile, presumably as a result of the cessation of PFOSF production by the major manufacturer. However, the authors note that recent atmospheric measurements of PFOSF-based compounds were in fact much larger than those predicted by the model. Thus, it is possible that PFOA fluxes derived from PFOSF-based compounds may be under-predicted by the model. Further, the authors note that the actual PFOA yield may be lower than the 5% assumed in the model. It was shown that fluxes from direct PFOA emissions, via the ocean currents, were about 2 orders of magnitude greater than those from precursor degradation. However, it was shown that the deposition fluxes from the model agreed well with those derived by ice core measurements from the Canadian Arctic (Young et al., 2007).

The modelling studies published to date have primarily focused on PFOA fluxes to the arctic seawater. It is important to note that PFOA is generally only infrequently detected, and at low levels, in arctic wildlife. In fact, the PFC profiles in arctic biota are typically dominated by PFOS and the long-chain PFCAs (i.e. PFNA, perfluoroundecanoate (PFUnA) or perfluorotridecanoate (PFTrA)). In contrast to PFOA, no or comparatively little direct production of the long-chain PFCAs (e.g. perfluorodecanoate (PFDA), perfluorododecanoate (PFDoA)) (Prevedouros et al., 2006) has been reported. Therefore, there is an immediate need for models that include PFOS and the long-chain PFCAs. In addition, other volatile PFC precursor compounds have been identified and should be included in future modelling endeavours. Perfluorotelomer-based olefins have been shown to degrade to perfluoroaldehydes, and thus will form PFCAs, via atmospheric oxidation (Nakayama et al., 2007; Vésine et al., 2000). In addition, fluorotelomer-based iodides (Young et al., 2008) and acrylates (Butt et al., 2009) have recently been shown to form PFCAs by atmospheric oxidation. Further, the fluorotelomer-based phosphates (PAPs), which are used in commercial products for paper treatment and floor waxes (Zonyl RP and Masurf FS-115 technical information), are non-volatile precursors that have been shown to metabolise to PFCAs (D'eon and Mabury, 2007). However, considering the labile nature of PAPs and potential for sorption to organic matter, it is unclear whether PAPs would be transported to the Arctic via ocean currents.

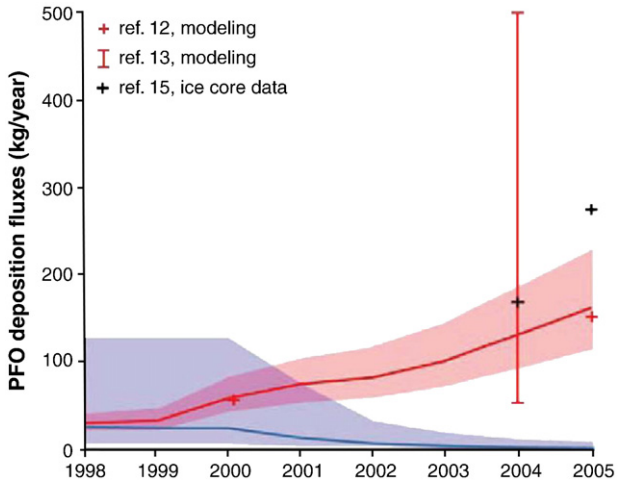

Fig. 5. Modeled PFOA deposition fluxes (solid lines and bands) to the Arctic (65°N to 90°N) resulting from FTOH atmospheric degradation (red) and FOSE atmospheric degradation (blue). Crosses indicate results from other models (red) and fluxes extrapolated from surface snow measurements (black). Reprinted with permission from Schenker et al. (2008). Copyright 2008 American Chemical Society.

There is considerable empirical support for the "indirect" transport pathway. FTOHs, FOSEs and FOSAs have sufficient atmospheric lifetimes to undergo long-range transport (D'eon et al., 2006; Ellis et al., 2003; Martin et al., 2006) and have been detected in the arctic atmosphere (Shoeib et al., 2006; Stock et al., 2007). As well, intermediate (8:2 and 10:2 fluorotelomer unsaturated carboxylate (FTUCA)) and terminal degradation products (PFOA and long-chain PFCAs) have been detected on atmospheric particles in the Arctic (Stock et al., 2007). PFOS and PFCAs have been detected in snow cores from remote ice caps in the Canadian Arctic (Young et al., 2007). Deposition fluxes extrapolated from surface snow measurements (Young et al., 2007) are consistent with those from models (Schenker et al., 2008; Wallington et al., 2006). Further, PFCs have been detected in surface water (Stock et al., 2007), sediment (Stock et al., 2007) and fish (Muir et al., 2008) from arctic lakes that are primarily influenced by atmospheric deposition. It was noteworthy that ratios of PFOA: PFNA and PFDA:PFUnA in the lake water and sediment were consistent with those measured from the ice cap snow (Stock et al., 2007; Young et al., 2007). Further, it has been suggested that the PFC doubling times observed in arctic wildlife, as well as the apparent rapid reduction in PFOS levels in some species (Butt et al., 2007b; Hart et al., 2009), is too short to be explained by oceanic transport (Smithwick et al., 2006) which show long delays (~30 years) in response to emission changes. Finally, the predominance of certain PFCs, in arctic wildlife, that are known to have insignificant levels of

direct production (PFOS and some long-chain PFCAs) is suggestive of volatile precursors as the source of these PFCs. It should be noted that PFC profiles in wildlife are not directly comparable to those measured in sources, such as seawater or industrial emissions. Wildlife profiles are complicated by compound specific bioaccumulation potentials that may vary between species. In addition, various factors such as tissue-specific biotransformation and protein-binding may also be important, however, the relevance of these factors is not currently known.

Support for the "direct" transport pathway largely comes from results obtained from global transport models that indicate the yield of PFOA from FTOH atmospheric degradation is insufficient to account for arctic seawater concentrations. Further, it is noted that predicted arctic seawater levels of PFOA are consistent with measured values. There have been some efforts to characterize the spatial distribution of PFCs in Canadian Arctic and sub-arctic seawater (Rosenberg et al., 2008). This study, in addition to the study of PFCs in the Greenland Sea (Theobald et al., 2007) and Labrador Sea (Yamashita et al., 2008), represent the only measurements on PFCs in Arctic seawaters. Further measurements of Arctic seawater levels, from various regions in the circumpolar Arctic are needed to confirm model predictions. As well, the models are ultimately sensitive to emission levels (Armitage et al., 2006; Wania, 2007) and estimated yields of PFCAs from precursors.

It has recently been suggested that PFCAs may be transported to the Arctic via the gas-phase in their protonated form (McMurdo et al., 2008). The authors noted that while the PFOA anion is known to have a negligible vapour pressure and Henry's Law constant, these properties are appreciable in the protonated PFOA. Also, it was suggested that the formation of marine aerosols, such as during wave breaking, enhances the formation of gas-phase PFOA. Obviously, the fraction of PFCAs that will be in their protonated form, and thus subject to volatilization, under ambient environmental conditions is a function of the pK_a value. The relevance of this transport pathway is unclear since there is uncertainty regarding their pK_a values (Brace, 1962; Goss, 2008; McMurdo et al., 2008). A full discussion regarding the PFCA pK_a values in beyond the scope of this review. However, in a recent study by Cheng et al. (2009) it was shown that in a negative electrospray ionization mass spectrometer, the normalized molecular ion ratios of both PFOS and PFOA were independent of pH under the range studied (pH 1–6). These findings confirm the lack of formation of the protonated species under these pH conditions. Since the pKa of PFOS is not disputed, and is considerably <1, it was concluded that the pKa of PFOA is also <1. The authors note that in ocean water at pH ~8.1, the ratio of protonated-PFOA to unprotonated-PFOA should be well below 10^{-7}. These findings provide support for the hypothesis that PFCAs will predominately be in the anionic form in the aqueous environment.

There are limited empirical reports of gas-phase PFCAs in the atmosphere. Kim and Kannan (2007) reported levels of C_7–C_{12} PFCAs, PFHxS, PFOS and PFOSA in the gas-phase from Albany, New York. In fact, it was shown that the gas-phase levels of some PFCs exceeded that of the particle phase. However, traditional experimental techniques may not be appropriate for the collection of gas-phase PFCAs and PFSAs. Arp and Goss (2008) suggest that gas-phase PFCAs may irreversibility bind to the glass-fiber and quartz-fiber media typically used as particulate filters in high-volume air samplers, thus preventing their collection on gas-phase sorbents. Therefore, the relevance of the atmospheric transport of gas-phase PFCAs as an important pathway to the Arctic remains to be elucidated.

3. Abiotic measurements

3.1. Atmospheric measurements

FTOHs and sulfonamide alcohols were measured in air from the North Atlantic and Canadian Archipelago (Shoeib et al., 2006). The samples ($n=20$) were collected during a cruise in July 2005. FTOHs and sulfonamide alcohols were detected in all Arctic air samples, confirming their extensive occurrence in the Arctic atmospheric environment (Fig. 6). These findings were consistent with models that predict the long-range atmospheric transport and widespread distribution of FTOHs (Wallington et al., 2006) in arctic regions. The 8:2 FTOH was the dominant FTOH measured, representing between 50 and 70% (sum of gas- and particle-phases) of the total FTOH concentration, followed by the 10:2 FTOH and 6:2 FTOH. FTOH concentration ranges (sum of gas- and particle-phases) were: 5.8–26 pg/m^3 for the 8:2 FTOH, 1.9–17 pg/m^3 for the 10:2 FTOH, and <DL (below detection limit) −6.0 pg/m^3 for the 6:2 FTOH. Sulfonamide alcohol concentration ranges (sum of gas- and particle-phases) were: 2.6–31 pg/m^3 for *N*-methyl perfluorooctane sulfonamide ethanol (*N*-MeFOSE), <DL−8.9 pg/m^3 for *N*-EtFOSE. *N*-methyl perfluorooctane sulfonamide ethylacrylate (*N*-MeFOSEA) was below detection limits in all samples. The FTOH and sulfonamide alcohol concentrations measured in the Arctic air samples were approximately one order of magnitude lower than those collected from the more southern, urbanized regions which are suspected source regions. FTOHs and sulfonamide alcohols were mainly found in the gas-phase. The percent found on particles was <DL for 6:2 FTOH, 23% for 8:2 FTOH, 15% for 10:2 FTOH, 32% for *N*-MeFOSE and 22% for *N*-EtFOSE.

Spatial variation in the relative proportion of the volatile fluorinated compounds was observed. Air samples collected in the eastern region of the North Atlantic were dominated by *N*-MeFOSE. Back-trajectory analysis showed that these samples were representative for air originating from the North Atlantic. In contrast, air samples collected between western Greenland and the Canadian Archipelago showed a dominance of 8:2 FTOH. Air from these samples was representative of the Canadian Arctic Archipelago and Beaufort Sea region.

Stock et al. (2007) reported neutral precursors and degradation products (PFCAs, telomer acids & PFSAs) in air from Resolute Bay, Nunavut, Canada. Samples were collected during the 2004 summer. Gas- and particle-phase were analyzed separately for the neutral precursors. FTOHs were detected in 50% of the samples and were almost exclusively in gas-phase. The mean concentration of ΣFTOHs (gas- and particle phase) was 28 pg/m^3 with individual FTOH mean levels ranging from 2.8 pg/m^3 for 10:2 FTOH to 14 pg/m^3 for 8:2 FTOH. The mean ΣPFSAms (FBSEs + FBSAs + FOSEs + FOSAs + PFOSA) level was 112 pg/m^3, 4-fold greater than ΣFTOHs. Mean concentrations of individual PFSAms ranged from 11 pg/m^3 (*N*-EtFOSA) to 29 pg/m^3 (*N*-MeFOSE).

PFCAs, telomer acids and PFSAs were measured in the filter samples only. PFOS (mean = 5.9 pg/m^3) was the major compound with concentrations 1–2 orders of magnitude greater than most PFCAs and PFSAs. PFHxS (0.2 pg/m^3) and perfluorodecane sulfonate (PFDS) (0.2 pg/m^3) were also detected. PFOA (1.4 pg/m^3) was the dominant PFCA. Longer-chain PFCAs were detected less frequently and at comparatively lower levels. Mean concentrations of PFNA and PFDA were both 0.4 pg/m^3 and mean concentrations of PFUnA, PFTrA and perfluorotetradecanoate (PFTA) ranged from 0.02 to 0.06 pg/m^3. PFHpA and PFDoA were not detected. The FTOH intermediate degradation compounds, 8:2 FTUCA (0.06 pg/m^3) and 10:2 FTUCA (0.07 pg/m^3), were detected at levels similar to the longer-chain PFCAs.

PFCs were measured in the particle phase of air samples from Zeppelinstasjonen, Svalbard collected in 2006 and 2007 (Norwegian Institute for Air Research, 2007a,b). PFOS and PFOSA were monitored in 2006 samples collected between late September and early December 2006. PFOS and PFOA were monitored in 2007 samples collected between early August and late December 2007. In the 2006 samples, mean PFOS levels were 0.11 pg/m^3 (range: 0.03–0.50 pg/m^3) and mean PFOSA concentrations were 0.07 pg/m^3 (0.01–0.22 pg/m^3). In the 2007 samples, mean PFOS levels were 0.18 pg/m^3 (range: 0.02–

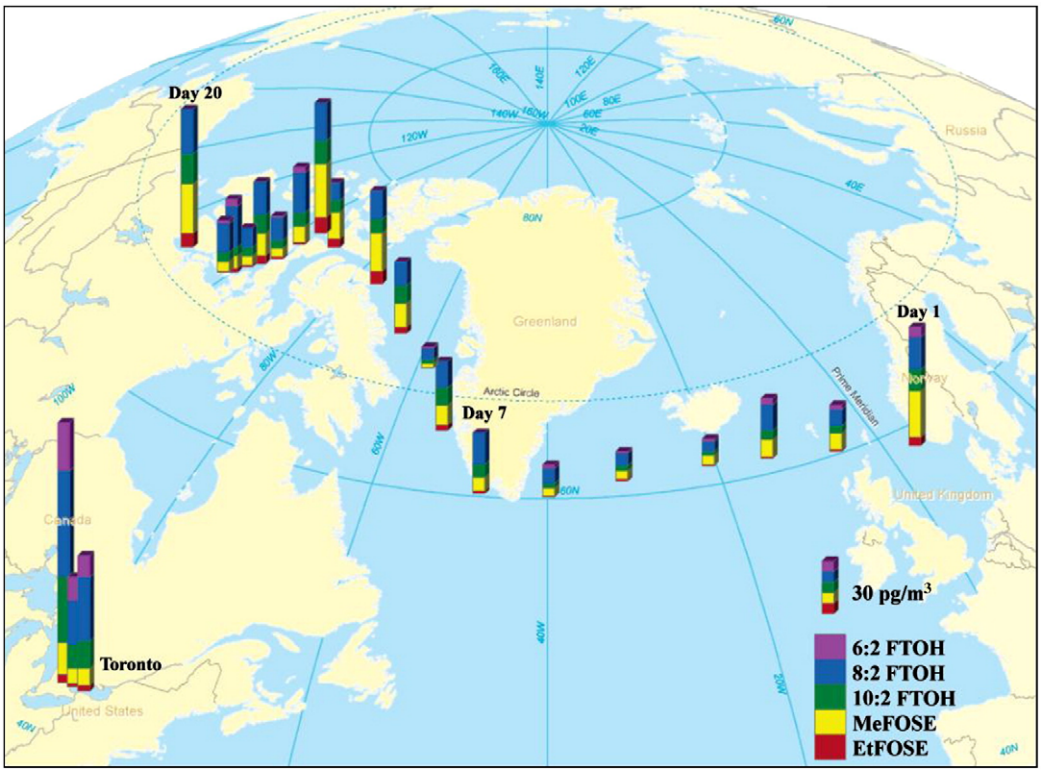

Fig. 6. Total air concentrations (sum of gas-phase and particle-phase) of individual FTOHs and FOSEs from North Atlantic and Canadian Archipelago. Reprinted with permission from Shoeib et al. (2006). Copyright 2006 American Chemical Society.

0.97 pg/m^3) and mean PFOA concentrations were 0.44 pg/m^3 (0.15–1.51 pg/m^3).

3.2. Snow

3.2.1. Canadian Arctic

Perfluorinated carboxylates (C_8–C_{11} PFCAs) and PFOS were analyzed in snow from the Agassiz, Devon, Meighen and Melville ice caps in the Canadian arctic (Young et al., 2007). The sampling locations were located near the summit of the ice caps and were not thought to be significantly influenced by blowing snow. Therefore, due to the physical location of the sampling sites on the ice caps, the snow samples acted as a surrogate for atmospheric deposition. Surface snow samples were collected from the 4 ice caps during the spring of 2005 and 2006, representing deposition from 2004 to 2005. Perfluorinated carboxylates and PFOS were observed in surface snow samples from all ice caps with concentrations in the low pg/L levels. Specifically, surface concentration ranges were: 1.4–4.6 pg/L for PFOS, 13.1–53.7 pg/L for PFOA, 5.0–12.1 pg/L for PFNA, 1.5–4.5 pg/L for PFDA and 1.1–5.1 pg/L for PFUnA. Devon Island ice cap concentrations were approximately one order of magnitude greater than the other locations, possibility due to its relatively more southern latitude. PFC deposition fluxes were calculated by correcting the snow concentrations for density. Fluxes from each ice cap were extrapolated across the entire area north of 65ºN in order to calculate the total PFC deposition to the Arctic. Calculated 2005 Arctic deposition fluxes were 114–587 kg/yr (arithmetic mean = 271 kg/yr) for PFOA, 73–860 kg/yr (295 kg/yr) for PFNA, 16–84 kg/yr (38 kg/yr) for PFDA, 26–62 kg/yr (46 kg/yr) for PFUnA, 250–1593 kg/yr (651 kg/yr) for total PFCAs, and 18–48 kg/yr (33 kg/yr) for PFOS. The PFOA and PFNA deposition fluxes were in good agreement with the 400 kg/yr calculated in a modeling study by Wallington et al. (2006).

In addition, snow depth samples were collected from the Devon ice cap, representing atmospheric deposition from 1996 to 2005. Temporal trends of PFCAs showed overall relatively constant deposition fluxes. In contrast, PFOS deposition fluxes, after increasing from 1996 to 1998, were shown to decrease from 1998 to 2001 with relatively constant fluxes from 2001 onwards. These temporal trends reflect the changes in PFOSF production, although it is noted that the peak deposition flux occurred several years prior to the phase-out reported by industry. These temporal trends are consistent with PFOSF production trends. The source of the PFCAs on the ice caps was inferred to be from the atmospheric oxidation of FTOHs. Ratios of PFC to sodium (marker for seawater) concentrations were not correlated, suggesting that marine aerosols were not a significant source of PFCs to the ice caps. Further, ratios of adjacent PFCAs (e.g. PFOA and PFNA) were approximately unity and significantly correlated. Finally, the detection of PFDA and PFUnA, compounds which are not directly commercially produced, suggests an indirect source such as FTOHs.

3.2.2. Greenland

Surface snow from an ice flow east of Greenland was analyzed for PFC levels (Theobald et al., 2007). The major PFCs measured were PFOS (range: 25.2–137 pg/L), PFOA (50.9–520 pg/L) and PFDA (110–149 pg/L). PFHxS (8.2–40.2 pg/L), PFOSA (24.2–39.4 pg/L), Perfluorohexanoate (PFHxA) (<10–34.8 pg/L), PFHpA (12.1–85.4 pg/L) and PFNA (<30–76.6 pg/L) were measured in comparatively lower concentrations. It was noted that surface snow concentrations were much greater than seawater levels from the region.

3.3. Lake water and sediments

3.3.1. Amituk, Char and Resolute Lakes on Cornwallis Island, Canadian Arctic

Stock et al. (Stock et al., 2007) reported PFC levels in surface water from four lakes (Amituk Lake, Char Lake, Resolute Lake and Meretta Lake) on Cornwallis Island, Nunavut, Canada. Char, Resolute and Meretta Lakes are located nearby the hamlet of Resolute Bay, whereas Amituk Lake is located approximately 40 km north. Samples were collected during 2003 and 2005 with the exception of Amituk Lake

(2003 only). PFC profiles and concentrations were similar in Amituk Lake and Char Lake. Mean PFOS concentrations ranged from 1.2 to 1.8 ng/L while PFHxS and PFDS were not detected. The C_7–C_{12} PFCAs were also detected in water from Amituk Lake and Char Lake. Ranges of mean concentrations were 0.3–0.6 ng/L for PFHpA, 0.9–4.1 ng/L for PFOA, 0.3–1.5 ng/L for PFNA, 1.1–10.1 ng/L for PFDA, 2.5–4.9 ng/L for PFUnA and nd−0.4 ng/L for PFDoA. In contrast, the PFC profiles and concentrations were noticeably different in Resolute Lake and Meretta Lake. PFHxS, PFOS, PFHpA and PFOA levels were up to 60-fold higher as compared to Amituk Lake and Char Lake. For example, mean PFOS concentrations ranged from 23 to 69 ng/L and mean PFOA concentrations ranged from 5.6 to 14 ng/L. Concentrations of the C_9–C_{12} PFCAs were similar to those in Amituk Lake and Char Lake. Meretta Lake serves as the inflow to Resolute Lake and thus both lakes appear to be contaminated by the same source. Intermediate FTOH degradation products, 8:2 FTUCA and 10:2 FTUCA, were also detected in all lakes with mean concentrations ranging from nd−1.9 ng/L for 8:2 FTUCA and nd−6.4 ng/L for 10:2 FTUCA.

As well, PFCs in sediment from Amituk, Char and Resolute Lakes were reported (Stock et al., 2007). Surface and depth samples were analyzed, allowing for temporal trend analysis (Fig. 7). PFCAs greater than PFDA were not detected and levels of 8:2 FTUCA were <LOQ. Consistent with the surface water samples, elevated levels of some PFCs were measured in Resolute Lake. The ΣPFC concentration in the top sediment slice was approximately 5 and 7 ng/g dw in Char and Amituk Lakes as compared to approximately 100 ng/g dw in Resolute Lake. All three lakes showed varying PFC profiles. Amituk Lake sediments were dominated by PFHpA at concentrations up to 3.9 ng/g dw. The C_8–C_{12} PFCAs were detected in comparatively lower levels. PFHxS was the major PFSA in Amituk Lake sediments while perfluorobutane sulfonate (PFBS) and PFOS were also detected. The major PFC in Char Lake sediment was PFOA at concentrations up to 1.7 ng/g dw. PFHpA and the C_9–C_{12} PFCAs were also detected but at generally lower levels. Resolute Lake sediments were dominated by PFOS with concentrations (range: 24–85 ng/g ww) that were 1–2 orders of magnitude greater than other measured PFCs. PFHxS and PFBS were also detected in some slices but at lower concentrations. PFOA and PFHpA were the dominant PFCAs measured with concentrations ranging from 2.3–7.5 ng/g dw to 0.95–6.8 ng/g dw in the first and second slices, respectively. PFNA was detected in levels up to 3.2 ng/g dw. PFDA, PFUnA and PFDoA levels were <LOQ.

The elevated PFHxS, PFOS, PFHpA and PFOA levels measured in the surface water of Meretta and Resolute Lakes, and the sediment of Resolute Lake, was attributed to AFFF contamination from the local airport and sewage runoff. As indicated in an earlier section, arctic char from Resolute Lake also showed elevated levels of some PFCs relative to Char and Amituk Lakes. The authors noted that the long-chain PFCAs (C_{10}–C_{12} PFCAs) were not elevated in the Resolute Lake water or sediment which was suggestive of an atmospheric source of these compounds. It was also noted that the ratios of PFOA:PFNA and PFDA:PFUnA in Amituk and Char Lakes sediment and water were generally consistent with those in Arctic glacial ice caps (Young et al., 2007).

3.3.2. Isomers in Char Lake sediments; surface water from Char Lake and Amituk Lake

De Silva et al. (2009a) reported PFCA isomers in sediment and surface water from Char Lake, and sediment from Amituk Lake on Cornwallis Island, Nunavut, Canada. Both lakes are thought to primarily receive PFCAs from atmospheric deposition (Stock et al., 2007).

PFOA profiles in Char Lake sediment showed a predominance of the linear isomer. The isopropyl (*iso*-) isomer (*iso*-:*n*-ratio = 2–3%) and the 5 m- isomer (1–2%) were also detected in the sediment. In Char Lake and Amituk Lake, the iso- and 5 m-PFOA isomers were detected at very low levels. Branched isomer proportions in Char Lake were 0.3% and 0.6% for the 5 *m*- and *iso*-PFOA isomers, and in Amituk Lake were 0.2% and 0.5% for the 5 *m*- and *iso*-PFOA.

PFNA profiles in Char Lake sediment were dominated by the linear isomer (96–97%). All four branched PFNA isomers (*iso*-, 1-, 3-, 4-) were detected and the *iso*-PFNA (2–3%) was the major branched isomer detected. The linear isomer was also the major isomer detected in the Char Lake and Amituk Lake surface waters. However, the only branched isomer detected was *iso*-PFNA with *iso*-:*n*-PFNA ratios in the two lakes ranging from 0.8–1%.

In the Char sediment, the *iso*-isomer was the only branched isomer detected in the longer-chain PFCA profiles. The *iso*-:*n*-PFCA ratios were 1–4% for PFDA, 1–2% for PFUnA and 4–8% for PFDoA. In contrast,

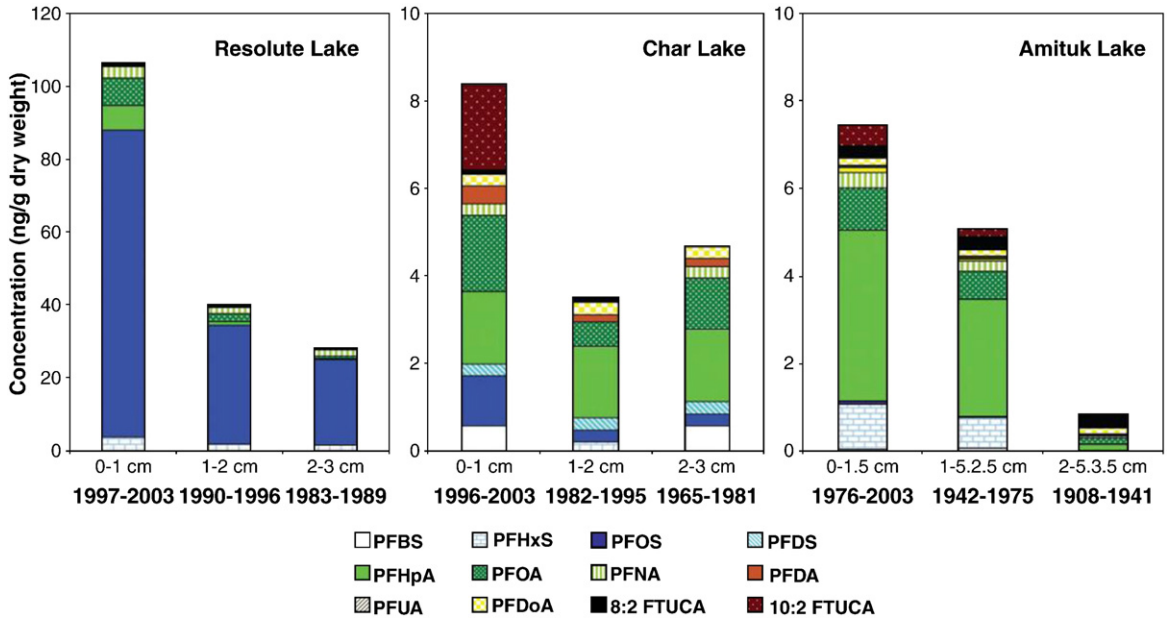

Fig. 7. PFC concentrations (ng/g dry weight) in sediment core slices from Resolute, Char and Amituk Lake on Cornwallis Island, Nunavut, Canada (Stock et al., 2007). Reprinted with permission from Stock et al. (2007). Copyright 2007 American Chemical Society.

branched isomers of PFDA, PFUnA or PFDoA were not detected in the lake surface waters.

3.4. Seawater and marine sediments

3.4.1. Greenland Sea

PFC concentrations in surface seawater samples from the Greenland Sea have been reported (Theobald et al., 2007). Twenty-one samples were collected between eastern Greenland and Tromsö, Norway including locations near Svalbard. The major PFCs detected were PFOA (range: <30–111 pg/L) and PFOS (<10–90 pg/L). PFHxS (<6–19 pg/L), PFHxA (10.2–37.6 pg/L), PFHpA (<12–31 pg/L) and PFNA (<30–55 pg/L) were measured in comparatively lower concentrations. PFOSA was detected at very low levels (<2–3.2 pg/L). PFDA levels were <20 pg/L. PFC concentrations were greatest west of Norway. It was suggested that these samples may have been influenced by the Gulf Stream, although it was noted that the number of samples was too low to make definitive conclusions.

3.4.2. Labrador Sea

Yamashita et al. (2008) reported PFBS, PFOS and PFOA concentrations in seawater from the Labrador Sea in the North Atlantic Ocean. Three surface water samples (0–2 m) and two depth profiles were collected during September 2003 and 2004, respectively. Depth samples were collected from south-western Greenland ("AO1", 11 depth samples between 45 and 3500 m) and from south-eastern Greenland ("AO2", 13 depth samples between 15 and 2750 m). In the "AO1" water column, PFOA was the dominant PFC measured. Surface water concentrations of PFOS and PFOA were 20 pg/L and 55 pg/L, respectively. PFBS, PFOS and PFOA concentrations were relatively constant with depth until 2000 m, after which PFBS and PFOA levels increased. In the "AO2" water column, PFBS was the dominant PFC measured. PFBS, PFOS and PFOA were elevated in the surface waters followed by uniform concentrations down to 2000 m. PFC depth profiles were consistent with temperature and salinity measurements which suggested a well-mixed water column down to 2000 m. Similar to the AO1 column, PFBS and PFOA levels increased below 2000 m. It was suggested that the increase in PFCs below 2000 m in both water columns was due to the influence of a deep water current, specifically the "Denmark Strait Overflow Water".

3.4.3. Canadian Arctic

Rosenberg et al. (2008) assessed the spatial and vertical distribution of PFCs in seawater from arctic and sub-arctic seawater in the Canadian Arctic archipelago. While C_6 to C_{11} PFCAs as well as PFBS, PFHxS and PFOS were detected in almost all samples, PFOA and PFNA were the dominant PFCAs in seawater accounting for 60% of the ΣPFCA concentration while PFOS accounted for over 75% of ΣPFSAs. Mean PFOA concentrations in water from the Labrador Sea at the Makkovik Margin ($n=2$, 182 pg/L) were ~3-fold greater than those measured by Yamashita et al. (2008) for a site (AO1) in the central Labrador Sea but similar to those measured further south off Newfoundland. Concentrations of PFOS in seawater ranged between ~10 pg/L from the McClintock Channel and 424 pg/L from Kuujjuarapik.

3.4.4. Iceland and Faroe Islands

PFCs in seawater from Iceland ($n=1$, 4 replicates) and the Faroe Islands ($n=3$) were reported by Kallenborn et al. (2004). PFOA was the major PFC measured with concentration ranges of 3.53–4.02 ng/L in Iceland and 3.62–7.24 ng/L in the Faroe Islands. PFHxA was the next highest PFC with concentration ranges of 0.63–0.73 ng/L and 0.59–1.85 ng/L in Iceland and the Faroe Islands, respectively. PFBS, PFHxS, PFOS (Faroe Islands only) and PFNA (Iceland only) were also detected at levels generally <1 ng/L. PFOSA levels were <LOQ at both sites.

Kallenborn et al. (2004) reported marine sediment PFC levels from Gufunes Bay, Iceland ($n=1$) and from Torshavn, Vagsbotni and Fjardakanningar in the Faroe Islands ($n=1$ per location). In the Iceland sample, all PFCs measured (PFHxS, PFOS, PFOSA, PFHxA, PFOA, and PFNA) were <LOQ. The Faroe Islands samples also contained very low levels of PFCs. PFHxS, PFOSA and PFOA were <LOQ. PFOS (range: <LOQ−0.11 ng/g), PFHxA (<LOQ−0.09 ng/g) and PFNA (<LOQ −0.03 ng/g) were detected in some Faroe Island sediment samples.

3.4.5. Russian Arctic

PFCs were monitored in ice cores sampled from Baydaratskaya Bay in the Russian Federation during May 2007 (Saez et al., 2008). The samples represent frozen seawater with some snow deposition on the surface. Samples were collected from different depths, ranging from the surface to 300 cm. A pooled sample, comprising samples from various depths was reported. The most abundant analyte was PFOSA (mean ± standard deviation = 824 ± 592 pg/L), followed by PFOA (131 ± 77.2 pg/L). PFHxS was below the limit of detection. The remaining PFCAs (C_4, C_6–C_{12}) and PFSAs (PFBS, PFOS) were measured in comparatively lower levels with mean concentrations ranging from 3.6 ± 5.0 pg/L for PFDoA to 37.4 ± 39.2 pg/L for PFNA.

3.5. Sewage sludge and effluent

PFCs in sewage sludge from Iceland ($n=2$) and the Faroe Islands ($n=1$) were reported by Kallenborn et al. (2004). PFOA was the dominant PFC measured in both the Iceland (range: 0.25–0.40 ng/g ww) and Faroe Island (1.08 ng/g ww) samples. PFHxS and PFOS were detected at comparatively lower levels. PFHxS levels were 0.01–0.02 ng/g ww and 0.02 ng/g ww in the Iceland and Faroe Islands, respectively. PFOS levels were 0.07–0.22 ng/g ww and 0.24 ng/g ww in the Iceland and Faroe Islands samples, respectively. PFHxA was <LOQ in the Iceland samples but was 0.35 ng/g ww in the Faroe Island sample. PFOSA and PFNA levels were <LOQ in both locations.

Sewage effluent from the Faroe Islands ($n=1$) was reported by (Kallenborn et al. (2004). PFC profiles were dominated by PFHxA (1.61 ng/L), PFOA (1.26 ng/L) and PFOS (1.22 ng/L). PFBS (0.20 ng/L), PFHxS (0.26 ng/L) and PFNA (0.44 ng/L) were also detected at comparatively lower levels. PFOSA levels were <LOQ.

The sewage sludge and effluent concentrations are representative of anthropogenic discharges to the Arctic environment and as such may represent point sources of PFCs. The relevance of these sources to the receiving environments is not known. Presumably the levels are representative of PFC consumer products and consumer applications and thus will vary by community.

3.6. Abiotic environment conclusions

In summary, there have been very limited PFC measurements in the abiotic environment. To date, the majority of abiotic measurements are from the Canadian Archipelago and the North Atlantic. There have been some air measurements of neutral precursors (FTOHs, FOSEs and FOSAs) and degradation compounds (telomer acids, PFCAs, and PFSAs), mainly from the Canadian Archipelago and the North Atlantic. Although limited, current studies have shown that FTOHs and sulfonamide alcohols are ubiquitous in the Arctic environment, confirming that these compounds are subject to long range transport. The detection of telomer acids, PFCAs and PFSAs on particulate-associated fractions is supportive of atmospheric oxidation of precursors as the source of these compounds. Spatial variation in the atmospheric profile of neutral precursors may be indicative of continental emission trends, although data is very limited. Snow has been used as a surrogate for atmospheric deposition of PFCs. Deposition fluxes of PFCs are consistent with some model predications. There is also very limited data on PFCs in lake water and sediment. There are limited measurements of PFCs in Arctic seawaters and studies to date have only been from the Canadian Arctic archipelago, the Labrador and Greenland Seas in the North Atlantic,

and the Russian Federation. However, the detection of PFCs in Arctic seawaters confirms that direct transport via ocean currents also occurs. Additional seawater measurements are critical to validate existing model predications, to assess the relative importance of direct versus indirect long-range transport (see Section 2), as well as to elucidate the spatial and temporal trends observed in some wildlife species. Finally, there have been limited temporal trend studies in abiotic media. Present studies either show poor temporal resolution (lake sediment) or extend over only a few years (snow core).

4. Biotic measurements

4.1. Marine ecosystem

4.1.1. Zooplankton and invertebrates

Zooplankton (*Calanus hyperboreus*), shrimp (*Pandalus borealis*, *Hymenodora glacialis*) and clams (*Mya truncata*, *Serripes groenlandica*) were analyzed for PFOS, PFOSA, PFOA and (*N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA) in samples from the eastern Canadian Arctic (Tomy et al., 2004b). Whole body samples were analyzed. PFOS levels were 1.8 ± 0.3 ng/g ww (mean ± standard error), 0.35 ± 0.15 ng/g ww and 0.28 ± 0.09 ng/g ww in the zooplankton, shrimp and clams, respectively. PFOSA was not detected in any sample. Respective PFOA levels were 2.6 ± 0.3 ng/g ww and 0.17 ± 0.06 ng/g ww in zooplankton and shrimp but PFOA was not detected in clams. Interestingly, *N*-EtFOSA was detected in relatively high levels in shrimp (10.4 ± 8.6 ng/g ww) and clams (20.1 ± 16.5 ng/g ww). Levels of *N*-EtFOSA in zooplankton were 0.39 ± 0.07 ng/g ww.

There were few detections of PFCs in three species of zooplankton (*C. hyperboreus*, *Thermisto libellula*, *Chaetognatha*) collected near Sachs Harbor in the western Canadian Arctic during 2004 (whole body, 1 pooled sample analyzed per species) (Powley et al., 2008). PFDA and PFDoA levels were 1.1 ng/g ww and 0.95 ng/g ww in *C. hyperboreus*, respectively, while the remaining PFCs analyzed were not detected. Similarly, the only PFCs detected in *Chaetognatha* were PFDA (0.50 ng/g ww) and PFDoA (0.51 ng/g ww). PFOS (0.2 ng/g ww), PFDA (0.73 ng/g ww) and PFDoA (0.37 ng/g ww) were detected in *T. libellula*.

PFCs were analyzed in the ice amphipod (*Gammarus wilkitzkii*, whole body) from the Barents Sea in 2004 (Haukås et al., 2007). PFOS and PFOA levels were 3.85 ± 1.17 ng/g ww (mean ± standard error) and 3.15 ± 0.34 ng/g ww, respectively. Interestingly, the 6:2 fluorotelomer sulfonate (6:2 FtS) was also detected in the ice amphipod (0.48 ± 0.24 ng/g ww).

4.1.2. Fish

Tomy et al. (2004b) investigated PFOS, PFOSA, PFOA and *N*-EtFOSA levels in arctic cod (*Boreogadus saida*, whole body homogenate) and redfish (*Sebastes mentella*) liver from the eastern Canadian Arctic. PFOS concentrations were 1.3 ± 0.7 ng/g ww (mean ± standard error) and 1.4 ± 0.9 ng/g ww in arctic cod and redfish, respectively. PFOSA was not detected in either species. PFOA concentrations were lower than PFOS in arctic cod (0.16 ± 0.06 ng/g ww) but showed similar levels to PFOS in redfish (1.2 ± 0.8 ng/g ww). Interestingly, *N*-EtFOSA levels were relatively high in arctic cod (92.9 ± 41.9 ng/g ww) but were not detected in redfish.

Arctic cod (whole body homogenate) from the western Canadian Arctic also showed relatively low PFC concentrations (Powley et al., 2008). Concentration ranges were 0.3–0.7 ng/g ww for PFOS, 0.3–0.5 ng/g ww for PFDA, nd−0.6 ng/g for PFUnA, and 0.1–0.2 ng/g ww for PFDoA. PFDS, perfluorododecane sulfonate (PFDoS) and the C_7–C_9 PFCAs were not detected. Arctic cod liver from the Barents Sea showed similar PFC concentrations relative to those from the eastern and western Canadian Arctic (Haukås et al., 2007). For example, mean (± standard error) PFOS and PFNA levels were 2.02 ± 0.13 ng/g ww and 0.20 ± 0.02 ng/g ww, respectively, in the Barents Sea arctic cod. PFOA levels ranged from nd−1.88 ng/g ww and PFDA ranged from nd −0.44 ng/g ww. Also detected were PFHxS (0.04 ± 0.003 ng/g ww) and perfluorohexanoate (PFHxA) (2.22 ± 0.34 ng/g w). The 6:2 FtS was not detected in Barents Sea arctic cod.

PFC levels were reported in long-rough dab (*Hippoglossoides platessoides*), shorthorn sculpin (*Myoxocephalus scorpius*) and dab (*Limanda limanda*) from Iceland, and in shorthorn sculpin, dab and atlantic cod (*Gadus morhua*) from Faroe Islands (Kallenborn et al., 2004). Liver samples were analyzed in all species. PFOS levels were comparatively high in the Icelandic fish: long-rough dab (range: 12–28 ng/g ww), shorthorn sculpin ($n = 1$, 19 ng/g ww) and dab ($n = 1$, 17 ng/g ww), relative to the Faroese fish: shorthorn sculpin (range: 2.0–2.5 ng/g ww), dab (range 1.3–2.1 ng/g ww), atlantic cod ($n = 1$, 0.85 ng/g ww). PFHxS was below the LOQ in all samples. PFHxA, PFHpA, PFOA and PFNA were below LOQ in all fish species except the Icelandic long-rough dab which showed concentration ranges of <0.5–9.6 ng/g ww for PFHxA, <0.3–1.8 for PFHpA and <0.4–1.4 ng/g ww for PFNA.

4.1.3. Seabirds

PFC levels in black guillemot (*Cepphus grylle*) and northern fulmar (*Fulmaris glacialis*) liver samples collected from Prince Leopold Island, Nunavut, Canada in 1993 were reported by Martin et al. (2004). Concentrations of PFOS, PFOSA and C_8–C_{15} PFCAs were either below method detection limits or not detected in all samples with the exception of PFOS in northern fulmars (mean = 1.3 ng/g ww).

Tomy et al. (2004b) reported PFC levels in black-legged kittiwake (*Rissa tridactyla*) and glaucous gull (*Larus hyperboreus*) liver samples from the eastern Canadian Arctic. PFOS levels were 10.0 ± 4.6 ng/g ww (mean ± standard error) and 20.2 ± 3.9 ng/g ww in the black-legged kittiwake and glaucous gull, respectively. By comparison, PFOA levels were much lower. PFOA was not detected in the black-legged kittiwake but was 0.14 ± 0.05 ng/g ww in the glaucous gull.

PFCs were monitored in guillemot (*Uria aalge*) eggs from 4 locations in the north eastern Atlantic: Vestmannaeyjar (Iceland), Sandøy (The Faroe Islands), Sklinna (Norway) and Hjelmsøya (Norway) (Löfstrand et al., 2008). The eggs were collected between 2002 and 2005. PFOS was the predominant PFC measured and mean concentrations were 15 ng/g ww in the Sandøy population, 16 ng/g ww in the Vestmannaeyjar population and 85 ng/g ww in both the Sklinna and Hjelmsøya populations. PFOSA concentrations ranged from non-detect (Hjelmsøya) to 9.9 ng/g ww in Sklinna. PFOA and PFNA were not detected in any population. Mean PFDA levels were 38 ng/g ww and 42 ng/g ww in the Vestmannaeyjar and Sklinna eggs but was not detected in the Sandøy and Hjelmsøya eggs. PFUnA levels ranged from 18 ng/g ww (Hjelmsøya) to 57 ng/g ww (Sandøy), and PFDoA levels ranged from 2.7 ng/g ww (Hjelmsøya) to 28 ng/g ww (Vestmannaeyjar). *N*-EtFOSA concentrations were low and ranged from non-detect (Sklinna) to 2.0 ng/g ww (Hjelmsøya).

Butt et al. (2007a) reported PFC temporal trends in liver samples of thick-billed murres (*Uria lomvia*) and northern fulmars from Prince Leopold Island, Nunavut in the Canadian Arctic. Thick-billed murre samples were from 1975, 1987, 1993 and 2004, whereas northern fulmars were from 1975, 1987, 1993 and 2003. In the most recent samples (2004 thick-billed murres, 2003 northern fulmars), PFC profiles were dominated by the C_{11}–C_{15} PFCAs. Mean concentrations in murres and fulmars, respectively, were 4.6 and 1.4 ng/g ww for PFUnA, 3.7 and 0.9 ng/g ww for PFDoA, 7.1 and 3.8 ng/g ww for PFTrA, 4.5 and 2.9 ng/g ww for PFTA, and 2.0 and 2.3 ng/g ww for perfluoropentadecanoate (PFPA). Comparatively lower concentrations (<1 ng/g ww) of PFHpA, PFOA, PFNA and PFDA were measured in the murre and fulmar samples. PFOS levels were 0.76 and 0.41 ng/g ww in thick-billed murre and northern fulmar, respectively. PFOSA levels were below the method detection limit (2.3 ng/g ww).

PFCs were monitored in liver samples of black guillemot collected from Greenland in 2000 and northern fulmar collected from the Faroe

Islands between 1998 and 1999 (Bossi et al., 2005b). PFOS levels were 3–16 ng/g ww (range) in the black guillemot and 24–29 ng/g ww in the northern fulmar. PFHxS, PFOSA and PFOA were either not detected or below the LOQ in all samples. PFC levels in northern fulmar eggs from the Faroe Islands (Kallenborn et al., 2004) showed similar levels to those reported in livers (Bossi et al., 2005b). PFOS levels in northern fulmar eggs were 31–37.5 ng/g ww (range). PFOSA concentrations were much lower than PFOS (<0.1–0.46 ng/g ww). Similarly, low concentrations of PFHpA (0.4–0.45 ng/g ww) and PFNA (1.0–1.3 ng/g ww) were detected in the northern fulmar eggs. PFHxS, PFDS, PFHxA and PFOA were below the LOQ.

PFCs were reported in the plasma and eggs from glaucous gulls collected from Bear Island and Svalbard in the Norwegian Arctic during 2004 (Verreault et al., 2005). PFOS was the predominant PFCA measured in both tissues and was 104 ± 13.2 ng/g ww (mean ± standard error) and 134 ± 16.6 ng/g ww in egg and plasma, respectively. PFHxS levels were much lower than PFOS in both egg (range: <0.27–1.23 ng/g ww) and plasma (1.12 ± 0.15 ng/g ww). PFOA, PFNA, PFTA and PFPA were below method detection limits in the egg samples. In eggs, the predominant PFCAs were PFUnA (21.4 ± 2.82 ng/g ww) followed by PFTrA (15.1 ± 3.61 ng/g ww); comparatively lower concentrations of PFDA (2.08 ± 0.46 ng/g ww) and PFDoA (3.35 ± 0.62 ng/g ww) were measured. Similar trends were shown in the plasma with the dominant PFCA being PFUnA (74.4 ± 8.06 ng/g ww), followed by much lower levels of PFTrA (11.0 ± 1.29 ng/g ww), PFDoA (7.68 ± 1.04 ng/g ww) and PFDA (6.56 ± 0.82). PFOA, PFNA, PFTA and PFPA were also detected in the plasma, although generally at much lower levels.

Haukås et al. (2007) reported PFC levels in black guillemot and glaucous gull liver samples harvested from the Barents Sea in 2004. PFOS was the dominant PFC measured in both the black guillemot (mean ± standard error: 13.5 ± 2.79 ng/g ww and glaucous gull (65.8 ± 22.4 ng/g ww). PFHxS concentrations were much lower in both species, 0.17 ± 0.02 ng/g ww and 0.26 ± 0.06 ng/g ww in the black guillemot and glaucous gull, respectively. Similarly, PFCA concentrations were much lower than PFOS. PFNA was the most frequently detected PFCA with concentrations of 1.13 ± 0.08 ng/g ww and 1.90 ± 0.42 ng/g ww in the black guillemot and glaucous gull, respectively. PFHxA, PFOA and PFDA were also detected in both species.

PFCs in herring gull (*Larus argentatus*) eggs collected from Hornøya and Røst in the Norwegian Arctic during 1983, 1993 and 2003 were reported by Verreault et al. (2007). In the 2003 samples, PFOS was the dominant PFC measured in both Hornøya (mean ± standard error: 37.0 ± 4.9 ng/g ww) and Røst (42.2 ± 3.5 ng/g ww). PFHxS, PFDS and PFOSA levels were much lower (generally <1 ng/g ww) in both populations. PFBS concentrations were below the LOQ. PFCA profiles were dominated by PFUnA (4.2 ± 0.62 ng/g ww and 2.6 ± 0.36 ng/g ww in Hornøya and Røst, respectively) and PFTrA (2.5 ± 0.47 ng/g ww and 2.0 ± 0.07 ng/g ww in Hornøya and Røst, respectively). PFNA and PFDA levels were 1.1 ± 0.09 ng/g ww and 1.3 ± 0.17 in Hornøya, and were 1.1 ± 0.8 ng/g ww and 0.98 ± 0.10 ng/g ww in Røst. PFOA, PFTA and PFPA were detected at levels <1 ng/g ww. PFHxA and PFHpA were below the LOQ.

4.1.4. Marine mammals

4.1.4.1. Whales. PFCs in narwhal (*Monodon monoceros*) and beluga (*Delphinapterus leucas*) liver samples from the eastern Canadian Arctic were reported by Tomy et al. (2004b). PFOS levels were similar in narwhal (mean ± standard error: 10.9 ± 2.3 ng/g ww) and beluga (12.6 ± 1.1 ng/g ww). Interestingly, PFOSA levels were similar or greater than PFOS levels in the narwhal (6.2 ± 2.3 ng/g ww) and beluga (20.9 ± 7.9 ng/g ww). *N*-EtFOSA levels were 10.9 ± 7.1 ng/g ww and 3.9 ± 2.2 ng/g ww in narwhal and beluga liver. Comparatively low levels of PFOA were measured (narwhal: 0.9 ± 0.1 ng/g ww, beluga: 1.6 ± 0.3 ng/g ww).

Muir et al. (2004) reported PFC levels in beluga liver from east Hudson Bay, Canada, collected between 1999 and 2000. PFOSA concentrations (mean ± standard deviation: 145 ± 53.4 ng/g ww) were nearly 10-fold greater than PFOS (17.3 ± 12.3 ng/g ww). PFHxS was not detected. C_8–C_{15} PFCAs were detected with mean concentrations ranging from 26.9 ± 7.8 ng/g ww for PFUnA to 1.1 ± 0.3 ng/g ww for PFPA.

PFC concentrations in minke whale (*Balaenoptera acutorostrata*) liver samples from Greenland were reported by Bossi et al. (2005b)). The PFOSA concentration (1 pooled sample) was 29 ng/g ww. In contrast, PFOS was below LOQ and PFHxS and PFOA were not detected. PFC levels are also investigated in minke whale liver from Iceland (Kallenborn et al., 2004). PFOS (range: 19–71 ng/g ww) and PFOSA (7.2–19 ng/g ww) were the dominate PFCs measured. PFHxS (<0.4–1.1 ng/g ww), PFDS (3–5 ng/g ww), PFHxA (0.68–0.99 ng/g ww) and PFNA (1.1–2.4 ng/g ww) were also detected in the Icelandic minke whale. PFHpA and PFOA were below LOQ.

Harbour porpoise (*Phoceoena phocoena*) liver samples from Iceland were analyzed by Van de Vijver et al. (2004). Mean PFOS levels were 38 ng/g ww. PFDA, PFUnA and PFDoA were also detected.

Bossi et al. (2005b) reported PFC levels in long-finned pilot whale (*Globicephala melas*) liver from the Faroe Islands collected in 2001. Comparable levels of PFOS (range: 28–65 ng/g ww) and PFOSA (43–62 ng/g ww) were shown. PFHxS and PFOA were not detected. Kallenborn et al. (2004) reported liver PFC levels of Faroese pilot whales collected in 2002. Similar to Bossi et al. (2005b), comparable levels of PFOS (range: 88–336 ng/g ww) and PFOSA (172–364 ng/g ww) were reported. PFHxS (0.39–1.0 ng/g ww) and PFDS (11–30 ng/g ww) levels were much lower than PFOS and PFOSA. PFCA profiles were dominated by PFNA (5.4–20 ng/g ww) followed by lower levels of PFHxA (0.53–1.0 ng/g ww) and PFOA (0.35–1.7 ng/g ww). PFHpA was below the LOQ.

4.1.4.2. Pinnipeds. Kannan et al. (2001) reported PFOS concentrations in various pinniped species from Alaska and the Norwegian Arctic. PFOS ranges in the blood and liver of northern fur seal (*Callorhinus ursinus*) were <6–12 ng/g ww and <10–122 ng/g ww, respectively. PFOS levels in the blood of steller sea lion (*Eumetopias jubatus*) was <6 ng/g ww. Concentrations of PFOS in ringed seal blood were 8.1 ± 2.5 ng/g ww (mean ± standard deviation) and 10.1 ± 2.7 ng/g ww in samples collected from the Norwegian Arctic in 1996 and 1998, respectively.

Giesy and Kannan (2001) also reported PFOS concentrations in pinnipeds from the arctic. PFOS levels in the liver of Alaskan northern fur seal ranged from <35–120 ng/g ww. PFOS concentrations in the plasma of ringed seals from the Canadian Arctic ranged from <3–12 ng/g ww. Plasma in gray seal (*Halichoerus grypus*) from the Canadian Arctic had a mean PFOS concentration of 28 ng/g ww. The mean PFOS concentration in ringed seal plasma from the Norwegian Arctic was 9 ng/g ww.

PFOS and PFOA levels in walrus (*Odobenus rosmarus*) liver samples from the eastern Canadian Arctic were reported by Tomy et al. (2004b). Mean ± standard error concentrations were 2.4 ± 0.4 ng/g ww and 0.34 ± 0.09 ng/g ww for PFOS and PFOA, respectively.

Hart et al. (2009) reported PFOS, PFOSA and PFNA concentrations in liver samples of northern sea otter (*Enhydra lutris kenyoni*) from Alaska between 1992 and 2007. Considering the 2007 samples, mean concentrations (± standard deviation) were 2.8 ± 2.1 ng/g ww for PFOS, <1.7 ng/g ww for PFOSA and 9.4 ± 10.4 ng/g ww for PFNA.

Martin et al. (2004) reported PFC concentrations in liver samples of ringed seal from Holman, Northwest Territories and Grise Fjord, Nunavut in the Canadian Arctic. PFOS was the major PFC measured at concentrations of 16 ng/g ww and 19 ng/g ww in Holman and Grise Fjord, respectively. PFOSA levels were much lower at 0.36 ng/g ww and 2.0 ng/g ww in Holman and Grise Fjord, respectively. PFNA was the dominant PFCA measured (5.9 ng/g ww and 4.9 ng/g ww in Holman and Grise Fjord), followed by PFUnA (3.3 ng/g ww and

3.8 ng/g ww) and PFDA (2.1 ng/g ww and 2.9 ng/g ww). PFDoA and PFTrA were measured at concentrations <1 ng/g ww. PFOA and PFTA (Holman only) were less than method detection limits. PFTA (Grise Fjord only) and PFPA were not detected.

Bossi et al. (2005b) reported PFC levels in ringed seal livers from three locations in Greenland: Qeqertarsuaq (west Greenland), Ittoqqortoormiit (east Greenland) and Avanersuaq (northwest Greenland). Samples were collected in 2002 (Qeqertarsuaq and Ittoqqortoormiit) and 1998 (Avanersuaq). Two pools of 5 individuals each were reported. PFOS levels ranged from 52–67 ng/g ww, <10–10 ng/g ww to 27 ng/g ww in Qeqertarsuaq, Ittoqqortoormiit and Avanersuaq, respectively. PFOSA concentrations were <4 ng/g ww in Qeqertarsuaq and Ittoqqortoormiit seals, and were not detected in Avanersquaq seals. PFOA was not detected or below the quantification limits in all populations. PFHxS was not detected in any population.

Bossi et al. (2005a) reported temporal trends of PFCs in liver samples of ringed seals from Qeqertarsuaq and Ittoqqortoormiit, Greenland. In the most recent samples (2003), PFOS dominated the PFC profiles with a mean concentration of 27.9 ng/g ww and 95.6 ng/g ww in Qeqertarsuaq and Ittoqqortoormiit, respectively. PFHxS (mean = <0.8 ng/g ww and 0.9 ng/g ww in Qeqertarsuaq and Ittoqqortoormiit) and PFOSA (<0.5 ng/g ww and 1.2 ng/g ww) were measured at much lower concentrations. PFUnA was the dominant PFCA measured (3.6 ng/g ww and 9.0 ng/g ww), followed by PFNA (2.0 ng/g ww and 4.1 ng/g ww) and PFDA (1.3 ng/g ww and 3.3 ng/g ww).

PFC concentrations in blubber, blood and liver from ringed seal ($n=5$) and bearded seal (*Eriganthus barbatus*, $n=1$) collected near Sachs Harbour, North West Territories in the Canadian Arctic were reported by Powley et al. (2008). PFC concentrations were generally greatest in the liver followed by the blood and then blubber. Regarding ringed seal concentrations, PFOS was the dominant PFC measured with concentration ranges of 2.5–8.6 ng/g ww and 18–34 ng/g ww in the blood and liver, respectively. PFDS and PFDoS concentrations were either very low or not detected in the ringed seal blood and liver. PFOS (range: 0.4–0.9 ng/g ww) and PFDA (ND −0.2 ng/g ww) were the only PFCs detected in the ringed seal blubber. PFNA, PFDA and PFUnA were the dominant PFCAs measured in the ringed seal blood and liver. Blood and liver concentrations ranges were 0.6–1.6 and 3.6–4.5 ng/g ww for PFNA, 0.4–1.1 and 2.0–3.3 ng/g ww for PFDA, 0.9–2.5 and 4.8–6.9 ng/g ww for PFUnA and, 0.1–0.3 and 0.8–1.0 ng/g ww for PFDoA. PFHxA, PFHpA and PFOA were not detected in the blood and liver. Considering bearded seal samples, PFOS (2.6 ng/g ww) was the dominant PFC measured in liver. PFNA (1.3 ng/g ww) was the dominant PFCA with comparatively smaller concentrations of PFDA, PFUnA and PFDoA measured. PFDS, PFDoS, PFHxA, PFHpA and PFOA were not detected in bearded seal liver. PFCs were not detected in bearded seal blubber. Further, the only PFC detected in bearded seal blood was PFOS (1.3 ng/g ww).

Butt et al. (2007b) reported temporal trends of PFCs in ringed seal liver samples from Resolute Bay (Lancaster Sound) and Arviat (Hudson Bay) in the Canadian Arctic. In the most recent samples (2005), PFOS was the dominant PFC measured with mean concentrations of 19.6 and 8.1 ng/g ww in the Arviat and Resolute Bay population, respectively. PFOSA was measured at comparatively much lower levels, 0.15 ng/g ww in both populations. PFHxS and PFBS were not detected in either population. PFUnA was the major PFCA measured with mean concentrations of 12.0 and 7.5 ng/g ww in Arviat and Resolute Bay seals, respectively. Other predominate PFCAs were PFNA (5.1 and 4.8 ng/g ww in Arviat and Resolute Bay), PFDA (3.8 and 3.4 ng/g ww) and PFTrA (3.3 ng/g in Arviat seals, this analyte was not reported in the Resolute Bay seals). PFTA and PFPA were reported at levels less than 0.40 ng/g ww. PFOA levels were 1.0 ng/g ww in the Arviat seals and were <0.85 ng/g ww in the Resolute Bay seals. PFHpA was not detected in either population.

Spatial trends of PFCs in ringed seal livers from the Canadian Arctic were reported by Butt et al. (2008). Seal livers were collected from 11 locations between 2002 and 2005. PFOS was the dominant PFC measured in all populations with the exception of Gjoa Haven. Mean PFOS levels ranged from 6.5 ng/g ww in Resolute Bay seals to 88.8 ng/g ww in the Inukjuak seals. PFOSA was measured in comparatively much lower levels with mean concentrations ranging from 0.05 ng/g ww (Arviat) to 2.7 ng/g ww (Grise Fjord). PFHxS levels were also comparatively very low. PFDS was detected only in the Resolute Bay (0.02 ng/g ww) and Inukjuak (0.01 ng/g ww) seals. PFBS was not detected in any population. The major PFCAs were PFNA (range of population means: 1.8 ng/ww to 47.5 ng/g ww), PFDA (1.1 ng/g ww to 15.7 ng/g ww) and PFUnA (2.2 to 26.2 ng/g ww). PFDoA (0.32 to 4.9 ng/g ww), PFTrA (0.68 to 5.3 ng/g ww), PFTA (0.11 to 0.65 ng/g ww) and PFPA (0.02 to 0.18 ng/g ww) were detected at low concentrations. PFHpA and PFOA were infrequently detected at levels of approximately 0.10 ng/g ww and 1.0 ng/g ww, respectively.

4.1.4.3. Polar bears. PFCs in polar bears from Alaska have been well studied. Kannan et al. (2001) reported PFOS levels in blood (mean = 34 ng/g ww) and liver (350 ng/g ww) in Alaskan polar bears. Similar PFOS levels in liver were reported in polar bears collected from near the Beaufort Sea (mean ± standard deviation = 793 ± 195 ng/g ww) and Chukchi Sea (537 ± 204 ng/g ww) (Kannan et al., 2005b). The C_8–C_{11} PFCAs were also monitored in these populations. PFNA was the dominant PFCA and levels were 58 ± 30 ng/g ww and 64 ± 41 ng/g ww in the Beaufort Sea and Chukchi Sea, respectively. PFOA, PFDA and PFUnA were much smaller with a concentration ranking of PFUnA>PFDA>PFOA. Levels in the Beaufort Sea population were 3.4 ± 3.9 ng/g ww for PFOA, 6.9 ± 4.2 ng/g ww for PFDA and 8.6 ± 2.8 ng/g ww for PFUnA. Similar levels were measured in the Chukchi Sea bears and were 2.4 ± 1.1 ng/g ww for PFOA, 6.2 ± 6.6 ng/g ww for PFDA and 9.5 ± 12 ng/g for PFUnA. Smithwick et al. (2005) reported PFCs in liver samples collected from the Bering and Chukchi Sea region (samples were grouped together and reported as "Chukchi Sea"). Similar to other reports, PFOS (mean = 729 ng/g ww) was the dominant PFC measured. PFHxS and PFOSA were detected at very low levels. The C_8–C_{15} PFCAs were also detected, and PFNA (214 ng/g ww) was the major PFCA. PFDA and PFUnA levels were 33 ng/g ww and 27 ng/g ww, respectively. The remaining PFCAs (PFOA, C_{12}–C_{15} PFCAs) ranged from <0.6 ng/g ww for PFPA to 2.4 ng/g for PFOA.

There are several reports of PFCs in polar bears from East Greenland. Bossi et al. (2005b) reported PFC concentrations in livers from East Greenland polar bears. The mean PFOS level (2 pools of 5 individuals each) was 1285 ng/g ww. PFHxS and PFOA levels were less than the LOQ (7 and 12 ng/g ww, respectively). PFOSA levels ranged from ND−5 ng/g ww. Smithwick et al. (2005) also reported PFC levels in polar bear liver from East Greenland. PFOS (mean = 2140 ng/g ww) was the predominant PFC measured, and PFHxS (80 ng/g ww) and PFOSA (8.5 ng/g ww) were measured in much lower concentrations. The major PFCAs were PFNA (191 ng/g ww), PFUnA (104 ng/g ww) and PFDA (72 ng/g ww). PFOA and the C_{12}–C_{15} PFCAs were detected in comparatively lower concentrations, ranging from 1.4 ng/g ww for PFOA to 19 ng/g ww for PFTrA. Temporal trends of PFCs from East Greenland polar bear livers collected between 1984 and 2006 were reported by Dietz et al. (2008). Considering the most recent samples (2006), PFC levels and profiles were consistent with other reports (Bossi et al., 2005b; Smithwick et al., 2005). PFOS (median = 2878 ng/g ww) was the major PFC reported and PFOSA levels were comparatively much lower (16.5 ng/g ww). PFCA profiles were dominated by PFNA (216 ng/g ww) followed by PFUnA (91.9 ng/g ww), PFDA (82.5 ng/g ww), PFTrA (65.3 ng/g ww). PFOA (12.9 ng/g ww) and PFDoA (12.3 ng/g ww) were measured in lower concentrations.

Smithwick et al. (2005) reported PFCs in polar bear liver from 7 locations in the circumpolar Arctic (Alaska, Northwest Territories, High Arctic, South Baffin Island, South Hudson Bay, East Greenland and Svalbard). Blood samples measured in the Svalbard population

were converted to a liver-based equivalent. In all populations, PFOS was the major PFC measured, levels ranged between 729 ng/g ww (mean, Chukchi Sea) and 2730 ng/g (South Hudson Bay). PFOSA levels were much lower, ranging from <1.7 ng/g ww (High Arctic and Northwest Territories) to 8.5 ng/g ww (East Greenland). PFHxS concentrations ranged from 36 ng/g ww (High Arctic) to 2940 ng/g ww (Svalbard). PFNA, PFDA and PFUnA were the major PFCAs measured. PFNA ranged from 102 ng/g ww (Svalbard) to 405 ng/g (Northwest Territories), PFDA ranged from 33 ng/g ww (Chukchi Sea) to 103 ng/g (Northwester Territories), and PFUnA ranged from 27 ng/g ww (Chukchi Sea) to 114 (South Hudson Bay). Comparatively lower levels of PFOA and the C_{12}–C_{15} PFCAs were also detected.

4.1.5. Marine ecosystem summary

The marine ecosystem has been well studied with excellent geographical coverage, with the exception of the Russian Arctic, encompassing all trophic levels. In general, it is difficult to make broad conclusions regarding the presence of certain PFCs in biota since not all studies have monitored for the complete set of PFSAs and PFCAs. The few studies of zooplankton and invertebrates generally only show detectable levels of PFOS and PFOA whereas the longer-chain PFCAs are typically not detected. Marine fish species show low levels of PFOS and occasionally detections of PFDS and PFOSA, however, the PFCAs are generally not detected. In seabirds, PFOS is ubiquitously detected and frequently PFOSA is also detected. PFHxA, PFHpA and PFOA are generally not detected in seabirds, however, the suite of longer-chain PFCAs (PFNA–PFPA) is frequently detected. There are many reports of PFCs in pinnipeds. PFOS and PFOSA are universally detected in pinnipeds with infrequent reports of PFHxS levels. PFHxA, PFHpA and PFOA are generally very low or below quantification limits. However, levels of the longer-chain PFCAs (PFNA–PFUnA) are commonly reported and there are occasional reports of the C_{12}–C_{15} PFCAs. In whales, PFOS and PFOSA are ubiquitously reported with PFOSA levels generally higher than PFOS. Most studies have only monitored the lower-chain PFCAs in whales (C_6–C_9 PFCAs), but when monitored the longer-chain PFCAs are detected. Polar bears are also well studied in the arctic environment. Polar bears have been shown to have high levels of PFOS, PFOSA and the C_8–C_{13} PFCAs. There are also occasional reports of PFTA and PFPA levels in polar bears.

4.2. Freshwater ecosystems

4.2.1. Fish

PFCs were investigated in land-locked arctic char (*Salvelinus alpinus*) muscle from Amituk Lake ($n=11$), Char Lake ($n=5$) and Resolute Lake ($n=14$) on Cornwallis Island in the Canadian Arctic (Muir et al., 2008). The major PFCs detected were PFOS, PFOSA and PFNA. Interestingly, concentrations of PFHxS, perfluoroheptane sulfonate (PFHpS) and PFOS were much greater in Resolute Lake char as compared to char from Amituk Lake and Char Lake. Levels of PFNA, PFDA and PFOSA were similar between the lakes. For example, the geometric mean PFOS levels were 0.22 ng/g ww (range: 0.03–2.7 ng/g ww), 0.72 ng/g ww (0.34–3.9 ng/g ww) and 25.4 ng/g ww (13.0–52.6 ng/g ww) for Amituk Lake, Char Lake and Resolute Lake, respectively. In fact, the authors note that PFOS levels in the Resolute Lake char were comparable to those from Lake Ontario (Furdui et al., 2007). The elevated concentrations of some PFCs in char were consistent with elevated PFC levels in water and sediment that has previously been reported for Resolute Lake (Stock et al., 2007). It was suggested that the elevated PFC levels may be the result of direct contamination from aqueous film forming foams at the nearby airport. Amituk Lake and Char Lake are thought to receive PFCs only from atmospheric deposition.

Land-locked arctic char liver ($n=2$) was investigated in Lake á Mýranar on the Faroe Islands (Kallenborn et al., 2004). PFOS (range: 4.7–4.8 ng/g ww) and PFOSA (3.6–4.2 ng/g ww) showed similar levels and were the only PFCs detected.

PFC levels in burbot (*Lota lota*) liver from Fort Good Hope, NWT, Canada were reported by Stern et al. (Stern and Tomy, 2007). Samples were collected in 1986, 1999, 2003 and 2006. In the 2006 samples, PFC profiles were dominated by PFDA (median ± standard deviation: 8.3 ± 9.4 ng/g ww) and PFNA (4.7 ± 4.5 ng/g ww). Comparatively lower levels of PFOS (1.9 ± 0.8 ng/g ww) and PFOA (1.1 ± 1.1 ng/g ww) were also detected. PFUnA levels were below the method detection limit.

Stern et al. (2007) reported PFCs in lake trout (*Salvelinus namaycush*) liver from Kusawa Lake and Lake Laberge in the Yukon Territory, Canada. In the Kusawa Lake samples, the only PFC found above detection limits was PFOA ($n=9$, mean ± standard deviation = 2.93 ± 7.78 ng/g ww). In the Lake Laberge trout only PFOS was detected ($n=1$, 2.18 ng/g ww).

Martin et al. (2004) reported PFC levels in liver samples of freshwater fish from Kuujjuarapik (eastern Hudson Bay) and Lac Minto, Quebec, Canada. Species investigated were arctic sculpin (*Myoxocephalus scorpioides*), brook trout (*Salvelinus fontinalis*), lake whitefish (*Coregonus clupeaformis*), lake trout, northern pike (*Esox lucius*) and white sucker (*Catostomus commersoni*). In general, PFOS and PFOSA dominated the PFC profiles. PFOS concentrations ranged from 5.7 ng/g ww (mean) in white sucker to 39 ng/g ww in brook trout. PFOSA levels ranged from 2.8 ng/g ww in brook trout to 19 ng/g ww in arctic sculpin. PFCA profiles were dominated by the odd number chain-length PFCAs, either PFNA (arctic sculpin and brook trout), PFUnA (lake trout, northern pike, and white sucker) or PFTrA (lake whitefish). PFOA was less than the method detection limit and PFPA was not detected.

Temporal trends (1999, 2000, 2001, 2002, 2004, 2005, 2006) of PFOS, PFNA, ΣPFSAs and ΣPFCAs were reported in lake trout muscle from Lutsel K'e (eastern arm of Great Slave Lake), Northwest Territories, Canada (Evans et al., 2006). PFC profiles were dominated by PFOS, particularly during the earlier time points. PFC concentrations peaked during 2001 (PFOS: 4.7 ng/g ww, PFNA: 1.6 ng/g ww) followed by a decrease to 2006 (PFOS: 0.04 ng/g ww, PFNA: 0.02 ng/g ww).

4.2.2. Freshwater ecosystem summary

There are a few reports of PFCs in freshwater ecosystems and, with one exception, all studies are from the Canadian Arctic. The studies of freshwater biota are limited to fish, however, some of the species covered in the "terrestrial ecosystem" section are closely associated with freshwater. PFOS is ubiquitously detected in freshwater fish but there are very few reports of other PFSAs such as PFHxS and PFHpS. PFNA and PFDA are commonly detected in freshwater fish, whereas, PFOA is generally not detected. There are some reports of higher chain-length PFCAs (PFUnA–PFTA), however, these PFCAs were not commonly monitored.

4.3. Terrestrial ecosystem

4.3.1. Birds

PFC levels were measured in common loon (*Gavia immer*) livers from Kuujjuarapik in northern Quebec, Canada (Martin et al., 2004). Mean PFOS and PFOSA concentrations were 20 ng/g ww and 5.9 ng/g ww, respectively. The only PFCA detected above the limits of quantification was PFUnA (1.3 ng/g ww).

4.3.2. Mammals

PFCs were investigated in liver samples from mink (*Mustela vison*) collected near Watson Lake, Yukon Territory, Canada in 2001 (Martin et al., 2004). Mean PFOS and PFOSA levels were 8.7 ng/g ww and 1.4 ng/g ww, respectively. Interestingly, PFNA concentrations (mean = 16 ng/g ww) were greater than PFOS in the mink livers. Levels of PFDA and PFUnA were 3.7 ng/g ww and 4.3 ng/g ww. PFOA,

PFDoA and PFTrA were below quantification limits, PFTA and PFPA were not detected.

Relatively high PFOS levels (mean: 250 ng/g ww) were found in livers of arctic fox (*Alopex lagopus*) collected near Arviat, Nunavut, Canada (Martin et al., 2004). PFOSA levels were much lower (19 ng/g ww). Similarly, PFCA levels were also much lower than PFOS. Mean concentrations ranged from 1.5 ng/g ww for PFDoA to 22 ng/g ww for PFNA. PFOA and PFTA were below quantification limits and PFPA was not detected.

Liver samples from caribou (*Rangifer tarandus*) harvested in various locations in Nunavut, Canada between 1997 and 1999 were investigated for PFCs (Tittlemier et al., 2005a). Mean PFOS levels ranged from 3.8–24.4 ng/g ww and PFOSA was not detected. PFNA showed the highest PFCA concentration with mean concentrations ranging from ND−26.3 ng/g ww. PFOA, PFDA, PFUnA and PFDoA mean levels ranged from ND−12.2 ng/g ww for PFOA, ND−14.5 for PFDA, 3.9–11.6 ng/g ww for PFUnA and ND−10.8 ng/g ww for PFDoA. *N*-EtFOSA was not detected.

4.3.3. Terrestrial ecosystem summary

There are very few reports of PFCs in terrestrial wildlife and presently only studies from the Canadian Arctic wildlife have been published. Although studies are limited, PFOS and PFOSA were commonly detected as well as the C_9–C_{11} PFCAs. In addition, some species did show levels of some of the longer-chain length PFCAs such as PFDoA and PFTrA.

4.4. Trends

4.4.1. Food web studies

4.4.1.1. Eastern Canadian Arctic. A marine food web from the eastern Canadian Arctic, was analyzed for PFOS, PFOA, PFOSA and *N*-EtFOSA (Tomy et al., 2004b). Samples were collected from various locations from 1996–2002, which may confound trend interpretation due to spatial and temporal variation. Stable isotopes of nitrogen were analyzed to assess relative trophic level. In approximate order of trophic level, the food web consisted of clams (*Mya truncate*, *Serripes groenlandica*), various zooplankton species, shrimp (*Pandalus borealis*, *Hymenodora glacialis*), walrus, arctic cod, redfish, narwhal, beluga whale, black-legged kittiwake and glaucous gull. Whole body homogenate was analyzed in the arctic cod, clams and zooplankton samples, whereas, liver samples were analyzed for the remaining organisms. PFOS and PFOA were detected in low ng/g concentrations with PFOS levels generally greater than PFOA. PFOS was shown to biomagnify through the entire food web (Fig. 8). A significant linear relationship ($p<0.0001$) was found between ln (natural logarithm) PFOS concentration and trophic level and followed the equation ln PFOS (ng/g wet wt) = −3.285 + (1.14 * trophic level). The PFOS trophic magnification factor was calculated as 3.1 and was generally lower than those calculated for persistent organochlorines. In contrast, PFOA did not biomagnify through the food web as a whole, but did biomagnify between certain individual feeding relationships (e.g. cod to beluga). Interestingly, PFOS precursor compounds, *N*-EtFOSA and PFOSA were detected in some food web organisms, sometimes at concentrations much greater than PFOS. The potential metabolism of neutral volatile PFOS precursors likely represents a source of PFOS to marine biota especially at higher trophic levels.

4.4.1.2. Western Canadian Arctic (Banks Island). Powley et al. (2008) investigated PFCs in a marine food web located near Sachs Harbour on Banks Island in the western Canadian Arctic. Samples were collected in June 2004. The food web samples consisted of 3 species of zooplankton (*Calanis hyperboreus*, *Themisto libellula*, *Chaetognatha*), arctic cod, ringed seal and bearded seal. Whole body samples were analyzed for zooplankton ($n=1$ homogenate per species) and arctic cod ($n=5$), whereas liver, blood and blubber were analyzed in the ringed seal ($n=5$) and bearded seal samples ($n=1$). PFC concentrations were dominated by PFOS. PFOS concentrations ranged from ND −0.2 ng/g for zooplankton and 0.3–0.7 ng/g ww for arctic cod. The rank order of PFOS in tissues of ringed seal were liver (18–34 ng/g ww) ≫ blood (2.5–8.6 ng/g ww) > blubber (0.4–0.9 ng/g ww). PFOS ringed seal liver levels were similar to those reported from other arctic regions. Although only 1 individual was analyzed, PFOS levels were much lower in the bearded seal as compared to the ringed seals. Similar trends were observed with the PFCAs. This may represent differences in feeding ecology between these seal species, although nitrogen and carbon stable isotopes were not measured in the study to confirm this hypothesis. PFOS concentrations in the bearded seal tissues were ND in blubber, 1.3 ng/g ww in blood and 2.6 ng/g ww in liver. PFDS was detected only in 1 sample (ringed seal liver) at 0.05 ng/g ww which was near the limits of detection. PFDoS was not detected in any sample. PFCAs with less than eight carbons were not detected in any of the food web samples. PFCA profiles were dominated by PFUnA and the usual "odd-even" pattern was observed in which odd-numbered PFCAs had greater levels than adjacent even-numbered PFCAs. The 7:3 fluorotelomer saturated carboxylate (FTCA), a product from 8:2 FTOH degradation, was only observed in ringed seal liver at low ng/g levels. The detection of the 7:3 FTCA is indicative of 8:2 FTOH degradation, via abiotic or biotic mechanisms, as a source of at least some portion of the PFCA body burden.

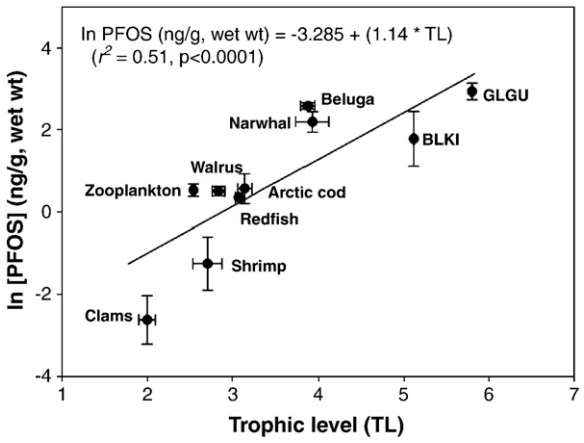

Fig. 8. Mean (±1 SE) PFOS concentrations (ng/g wet wt)—trophic level relationship for the eastern Arctic food web. BLKI = black-legged kittiwakes; GLGU = glaucous gulls. Reprinted with permission from Tomy et al. (2004b). Copyright 2004 American Chemical Society.

The PFC patterns varied between trophic levels with PFOS generally becoming enriched, as compared to the PFCAs, with increasing trophic level. For example, PFOS constituted the lowest proportion of PFCs in the zooplankton, but was found in the greatest proportion in ringed seal liver. Biomagnification factors (BMFs) were calculated for arctic cod/zooplankton and seal blood/arctic cod. BMFs for arctic cod/zooplankton were less than 1 for PFDA and PFUnA, but was 8.7 for PFOS. This suggests biomagnification only for PFOS from zooplankton to arctic cod. For arctic cod to seal blood, BMFs were greater than 1 with the exception of PFDoA.

4.4.1.3. Barents Sea (Norwegian Arctic). PFCs were examined in a marine food web from the Barents Sea, located east of Svalbard (77–79 °N, 30°E) (Haukås et al., 2007). Samples were collected in May–July 2004. The food web consisted of sea ice amphipod ($n=6$ pools), arctic cod ($n=16$ pools, consisting of 50 individuals total), black guillemot ($n=18$) and glaucous gull ($n=9$). Whole body homogenates of the amphipods were analyzed, whereas, liver was analyzed in arctic cod,

black guillemot and glaucous gull. Stable isotopes of nitrogen were determined to assess relative trophic level. Mean trophic levels were 2.0 for ice amphipod, 3.7 for arctic cod, 4.3 for black guillemot and 4.5 for glaucous gull. Trophic level values were statistically different for all species with the exception of black guillemot and glaucous gull. BMFs were calculated based on trophic level and weighted based on the presumed diet. The authors noted that interpretations of PFC trophic transfer may be complicated by the fact that arctic cod are unlikely to consume ice amphipods, as well as the glaucous gull consumes more prey species than just polar cod and black guillemot. In addition, trend interpretations may be complicated by the migration of the glaucous gull to more industrial areas which presumably have higher PFC levels than the Barents Sea.

PFOS was the dominant PFC analyzed and constituted 52%, 41%, 80% and 91% of total PFCs for ice amphipod, polar cod, black guillemot and glaucous gull, respectively. The mean PFOS concentrations generally increased with trophic level, although PFOS concentrations were statistically similar between ice amphipods and arctic cod (Fig. 9). Thus, a non-linear relationship was shown between PFOS concentration and trophic level. The relationship between PFOS and trophic level was significantly linear when ice amphipods were excluded. Within species there was no correlation between PFOS concentration and trophic level.

Interestingly, the 6:2 FtS was only detected in the ice amphipod (3 out of 6 pools) and 1 black guillemot individual. The 6:2 FtS may be a precursor to PFHxA (Key et al., 1998). Further, PFOA contributed about 50% of the ΣPFC concentration in the ice amphipod, much higher than the other species. In fact, PFOA was infrequently detected in other species, but was detected in all 6 ice amphipod pools. It was suggested that the presence of the more hydrophilic PFOA and 6:2 FtS in ice amphipods may be due to partitioning from surrounding water.

Trophic level-corrected biomagnification factors >1 were observed for PFHxS, PFNA, PFOS and ΣPFC in most predator–prey relationships except for polar cod-ice amphipods. The highest BMFs were observed for PFOS.

4.4.1.4. Greenland, various locations. PFOS, PFOSA, PFOA and PFHxS was analyzed in liver samples of polar bear, minke whale, ringed seal, black guillemot and shorthorn sculpin from various locations around coastal Greenland (Bossi et al., 2005b). Two samples (pools of 5 individuals each) were collected from northeast Greenland (Avanersuaq), west Greenland (Qeqertarsuaq) and east Greenland (Ittoqqortoormiit) from 1998 to 2002. Stable isotopes of nitrogen were not measured and thus trophic level was not determined. PFOS was the dominant PFC detected with the exception of the minke whale in which PFOSA levels were greater than PFOS. PFOA, PFHxS and PFOSA were not detected or below the LOQ for all samples with the exception of the minke whale and 1 shorthorn sculpin sample. PFOS levels in the east Greenland species showed trends of shorthorn sculpin<ringed seal<polar bear. These results indicate PFOS biomagnification although trophic level was not determined on these samples. West Greenland polar bears were not analyzed.

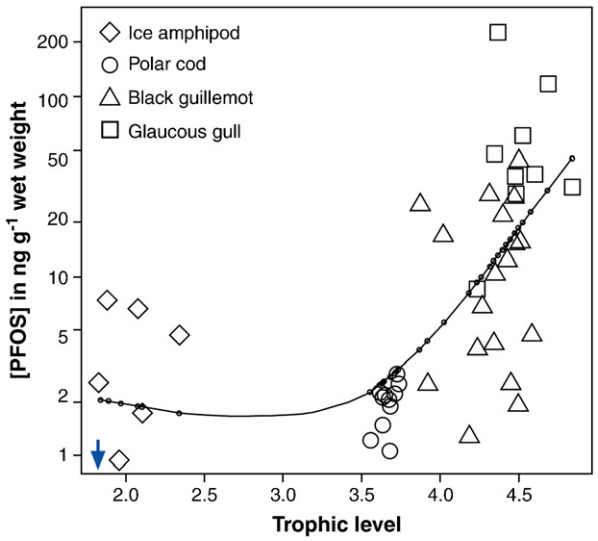

Fig. 9. Relationship between PFOS concentration (ng/g wet wt) and trophic level, as quantified by $\delta^{15}N$ for Barents Sea food web (Haukås et al., 2007). In the figure legend "polar cod" is identified as "arctic cod" in the text. Arrow indicates one ice amphipod sample was below the range displayed in the figure. Reprinted with permission from Haukås et al. (2007). Copyright 2007 Elsevier.

4.4.1.5. Food web studies: conclusions. In conclusion, studies of PFCs in marine ecosystems have generally shown that there can be trophic-level biomagnification within a food web, especially for PFOS and some long-chain PFCAs. However, there have been limited studies of PFCs in arctic food webs. In fact, only marine food webs have thus far been examined. To date, there have been no studies of PFCs in freshwater or terrestrial food webs. This represents a significant knowledge gap in our understanding of the trophic transfer of PFCs in arctic food webs. Further, the food web studies published to date are generally not spatially or temporally integrated but rather may incorporate samples collected over several years and from varying regions.

It should be noted that positive correlation between trophic position and PFC concentration does not necessarily imply that biomagnification is occurring. There are significant uncertainties regarding the mechanism of bioaccumulation and biomagnification for PFCs. Unlike other "legacy" halogenated organic contaminants (e.g. PCBs and PBDEs), PFCs appear to bind to proteins rather than partition into lipid. As such, PFCs are transported in the body through the blood and preferentially accumulate in protein-rich tissues such as the liver and kidney. Therefore, biomagnification may be related to the quantity and composition of proteins in specific tissues and organs, as well as the protein elimination ability of the organism. At present, PFC "protein normalized" biomagnification factors do not exist and thus comparison of PFC levels among tissues and between species is difficult. Calculation of PFC biomagnification factors using a single tissue (e.g. liver) may be erroneous since this may not accurately represent consumption trends (e.g. polar bears primarily consume the skin and blubber tissue of ringed seals). In addition, there is the potential formation of recalcitrant PFCs (i.e. PFSAs and PFCAs) from the metabolism of precursor compounds within the body. This is further complicated by potentially differing metabolic capabilities between species. Additional research is needed to elucidate the mechanisms of PFC biomagnification.

4.4.2. Spatial studies

Bossi et al. (2005b) assessed the geographic distribution of PFOS, PFOA and PFOSA in biota (fish, birds and mammals) from Greenland and the Faroe Islands. Individual species were pooled according to age and sex to obtain representative samples ($n=5$) for each of three sampling locations in Greenland. For PFOS, there was a general overall trend of concentrations being greater in animals from east Greenland (Ittoqqortoormiit) than in west Greenland (Qeqertarsuaq). For ringed seal collected in 2002, PFOS concentrations ranged from 52 to 67 ng/g ww (n=2, all males) from Ittoqqortoormiit, <10–10 ng/g ww ($n=2$, all males) in animals from Qeqertarsaaq and 27 ng/g ww ($n=2$, all females) from Avanersuaq. Similar PFOS concentrations were measured in animals collected from Qeqertarsaaq in 2000 (13 ng/g ww). PFOA and PFOSA concentrations were too small to make any meaningful spatial comparisons. In a more recent study, Bossi et al. (2005a) again examined the spatial distribution of PFOS and PFOSA along with a more expanded suite of PFCAs in juvenile

ringed seals from Qeqertarsaaq and Ittoqqortoormiit collected over a 20 year time-span. Consistent with their previous study, PFOS concentrations were greater (ANOVA, $p<0.0001$) in animals from Ittoqqortoormiit for all the sampling years. A similar trend was shown for PFHxS, PFOSA, PFNA, PFDA and PFUnA in which concentrations were greater in Ittoqqortoormiit animals as compared to Qeqertarsaaq.

In black guillemot collected in 2000 from Ittoqqortoormiit, PFOS concentrations in females (13 ng/g ww) were only slightly smaller than those in males (16 ng/g ww) and similar to females from Qeqertarsauq (14 ng/g ww) (Bossi et al., 2005b). Interestingly, PFOS was not detected in animals collected in 2002. PFOS was also detected in shorthorn sculpin from Ittoqqortoormiit (range: 13–18 ng/g ww, all females) but was undetectable in animals from Qeqertarsauq.

Verreault et al. (2007) reported on the spatial trends of sixteen PFCs in whole eggs of herring gulls from two isolated colonies in northern Norway. Thirty samples of freshly laid eggs were randomly collected in 1983, 1993 and 2003 from Hornøya, situated in the north eastern part of northern Norway and Røst (this site consisted of samples from Røst and Hekkingen which were in close proximity to each other and were therefore considered one colony) in the southern part along the west coast. Both sites were thought to represent two distinct population exposure scenarios. Concentrations of PFHxS, PFOA and PFNA in samples from 1993 were greater in the southernmost colony; no other statistically significant difference in PFC concentration were observed for the other sampling years. The contribution of the individual PFCA to the total PFCA burden in the eggs were compared between colonies and sampling years. PFOA concentrations were greater in eggs from Røst sampled in 1993 and 2003 than those from Hornøya sampled in the same year. The authors suggest that this might be due to proximal sources of PFOA in the coastal region of northern Norway and/or to enhanced contribution of PFOA to this region due to oceanic transport. There were also greater proportions of PFTeA and PFPeA in eggs collected in 1993 from Røst than Hørnøya.

Löfstrand et al. (2008) also used seabird eggs as biomonitors to assess the spatial distribution of PFCs in five locations from West Nordic countries: Vestmannaeyjar (Iceland), Sandøy (the Faroe Islands), Sklinna (Norway), Hjelmsøya (Norway) and Stora Karlsö (Sweden). The site from Sweden was thought to represent a sampling location close to known sources of PFCs but is not actually located in the arctic region as defined by AMAP. In general, different spatial patterns were found for PFOS, PFCAs, PFOSA and *N*-EtFOSA. The greatest concentration of PFOS was detected in eggs from Sweden (mean: 400 ng/g ww) which was statistically different to concentrations from all the other sites. PFOS concentrations were lowest in eggs from Iceland and the Faroe Islands (mean: 16 and 15 ng/g ww). Samples from Norway contained PFOS concentrations (mean of both sites: 85 ng/g ww) that were about 5 times lower than that of the Swedish samples. PFOSA and *N*-EtFOSA were detected less frequently than PFOS and in contrast to PFOS, PFOSA concentrations were greatest in eggs from Sklinna, Norway. *N*-EtFOSA was detected in only ten animals with concentrations ranging from 0.77 ng/g ww in eggs from Iceland to 2 ng/g ww in samples from Hjelmsøya. The PFCA spatial pattern was different to that of PFOS. PFOA was not detected in the samples and PFNA was only detected in eggs from Sweden. PFUnA was the most abundant PFCA detected and the rank order of concentrations were Sweden (mean: 82 ng/g ww)>Faroe Islands (mean: 57 ng/g ww)>Norway (mean of both sites: 30 ng/g ww)> Iceland (mean: 18 ng/g ww).

Smithwick et al. (2005) examined PFC concentrations in polar bear liver tissue from five locations in North America and two in the European Arctic collected between 1999 and 2002. North American samples were from Nunavut ($n=26$) that was subdivided into South Baffin Island (consisting of animals from Pangnirtung, Qikiqtarjuaq, Iqaluit and Kimmirut) and the High Arctic (consisting of animals from Resolute, Grise Fjord and Pond Inlet), Northwest Territory ($n=7$), Northwestern Alaska ($n=10$, consisting of animals from Chukchi Sea and Bering Sea) and South Hudson Bay (Sanikiluaq). European samples were from Eastern Greenland ($n=29$, Scoresby Sound) and Svalbard. (It should be noted that because only blood plasma was available for samples from Svalbard, the authors used a conversion factor to estimate PFC concentrations in liver.) PFOS concentrations were greater than any other PFC examined in the study (Fig. 10). There was a significant geographic trend for PFOS with animals from south Hudson Bay and Greenland having significantly greater concentrations than Svalbard, High Arctic and the Northwest Territory ($p<0.05$). This was attributed to closer proximity of these sites to possible sources in Europe and eastern North America. PFOS concentrations in animals from the Chukchi Sea were smaller than those from any other region.

For the PFCAs, PFDoA, PFTriA and PFPA showed a similar trend to that of PFOS. Other PFCs, namely, PFNA, PFDA, PFUnA, PFTA, PFHxS and PFOSA did not show distinguishable overall geographic trends. Interestingly, PFOS and PFCAs with greater than 11 carbon atoms had similar geographic distributions while PFOA, PFNA, PFDA, PFHxS and PFOSA were more evenly distributed or showed greater concentrations in the western North American Arctic.

For each location, there were some statistically significant correlations found for some of the PFCA homologues (Table 2). The strongest correlation was consistently observed between PFDA and PFUnA. This was attributed to a common source of PFCAs at each location. This was further addressed by calculating ratios of adjacent-chain-length PFC concentrations. Chukchi Sea samples were found to have a much greater proportion of PFNA to PFOS than those in the eastern sampling locations. Similar relationships were also found between PFUnA to PFDA, PFDA to PFNA and PFDoA to PFUnA. Further,

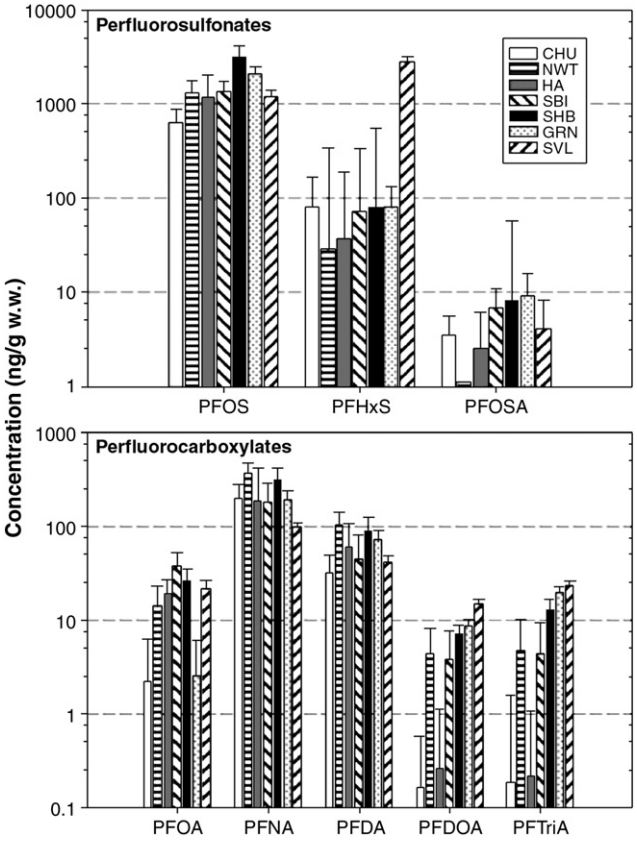

Fig. 10. Geometric mean concentrations (ng/g ww) of PFCs in polar bear liver from the North American and European Arctic. Error bars represent 95% confidence intervals. Reprinted with permission from Smithwick et al. (2005). Copyright 2005 American Chemical Society. "CHU" = Chukchi Sea, "NWT" = Northwest Territory, "HA" = High Arctic, "SBI" = South Baffin Island, "SHB" = South Hudson Bay, "GRN" = Eastern Greenland, "SVL" = Svalbard.

Table 2
Correlation coefficient (r^2) of linear regression between adjacent chain length PFCAs in polar bear liver from the North American and European Arctic. Reprinted with permission from Smithwick et al. (2005). Copyright 2005 American Chemical Society.

	Chain length							
	9:10		10:11		12:13		9:11	
Location	r^2	P	r^2	P	r^2	P	r^2	P
Chukchi Sea	0.65	<0.01	0.78	<0.01	0.38	0.06	0.28	0.12
NWT	0.88	<0.01	0.80	0.01	0.81	0.01	0.57	0.08
High Arctic	0.98	<0.01	0.83	<0.01	0.83	<0.01	0.78	<0.05
South Baffin Island	0.66	<0.01	0.95	<0.01	0.62	0.02	0.57	0.03
South Hudson Bay	0.76	0.03	0.97	<0.01	0.38	0.38	0.72	0.07
Greenland	0.90	<0.01	0.75	<0.01	0.55	<0.01	0.79	<0.01
Svalbard	0.77	<0.01	0.71	<0.01	0.30	0.56	0.37	0.02

the proportion of PFNA was much greater than PFOA in Chukchi Sea samples but smaller in the eastern sampling areas. Differences in the sources of PFCs to the eastern and western locations were suggested to explain the patterns.

Tomy et al. (2006) examined the spatial distribution of PFCs in beluga from the Canadian Arctic. Ten animals were collected from each of the following locations: Arviat (2003), Sanikiluaq (2003), Kimmirut (2003), Pangnirtung (2002) and Hendrickson Island (2005). Although the authors reported on some regional differences in PFC concentrations, there were no broad geographic trends that were discernable. PFCA concentrations were greatest in animals from Kimmirut (216.9± 14.2 ng/g ww, geometric mean ± 1 SE) and the smallest at Pangnirtung (25.6 ± 4.7 ng/g ww). The rank order of PFOS in liver was Sanikiluaq (47.7 ± 8.2 ng/g ww) > Pangnirtung (22.6 ± 2.5 ng/g ww) > Hendrickson Island (11.9± 1.8 ng/g ww) > Arviat (7.9 ± 3.6 ng/g ww) > Kimmirut (5.4 ± 0.7 ng/g ww). ΣPFCA concentrations were significantly different (one-way ANOVA) in Kimmirut animals relative to those from Pangnirtung and Arviat ($p<0.05$); ΣPFCA concentrations in Sanikiluaq animals also differed to those at Arviat and Pangnirtung ($p<0.05$). PFOS concentrations in animals from Sanikiluaq were also different to those from Kimmirut, Hendrickson Island and Arviat; PFOS concentrations in Pangnirtung animals were different to those from Kimmirut ($p<0.05$). Like PFCAs, PFOSA concentrations were greatest in animals from Kimmirut (305.6± 25.3 ng/g ww) followed by Arviat (188.3 ± 36.3 ng/g ww). Spatial trends of PFOSA were different to that of PFOS. PFOSA concentrations were statistically different in animals from Kimmirut compared with those from Pangnitung, Sanikiluaq and Hendrickson Island ($p<0.05$); differences were also evident between animals from Arviat and those from Sanikiluaq and Pangnirtung ($p<0.05$).

Spatial concentrations of PFCs were examined in ringed seals from 11 locations in the Canadian Arctic collected between 2002 and 2005 (Butt et al., 2008) (Fig. 11). Ten individuals were collected from each of the following locations: Sachs Harbour (2005), Gjoa Haven (2004), Resolute Bay (2005), Arviat Bay (2004), Arctic Bay (2004), Grise Fjord (2003), Inukjuak (2002), Pond Inlet (2004), Qikiqtarjuaq (2005), Pangnirtung (2002) and Nain (2005). The authors found statistically significant differences in PFC concentrations among the 11 locations. However, these differences were driven largely by elevated concentrations at Gjoa Haven and Inukjuak, and by smaller concentrations at Pangnirtung. Geometric mean concentrations of PFNA, PFDA and PFOS at Gjoa Haven were about 8, 4 and 2.6-fold greater than those of the other 10 ringed seal populations.

The authors also used stable isotopes of nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) to discern differences in the trophic level and carbon sources, respectively. Mean $\delta^{15}N$ data suggested that all the animals were from the same trophic level. Interestingly, the Gjoa Haven animals had a $\delta^{13}C$ value that was significantly depleted as compared to the other populations suggesting a more carbon-rich terrestrial source. After adjusting their dataset for $\delta^{13}C$ values, concentrations of most PFCs were generally greater in the Grise Fjord, Qikiqtarjuaq, Arviat and Nain populations.

Regional comparisons of PFC concentrations were then explored by grouping the ringed seals into four broad regions (excluding Gjoa Haven and Inukjuak): southeast Beaufort Sea, Hudson Bay, South Baffin Island & Labrador and High Arctic (Fig. 12). With the exception of PFUnA and PFTrA which were statistically greatest in the Hudson Bay population, all the other PFCs analyzed were statistically similar across the regions. The authors caution that temporal variation in the dataset especially for PFOS and PFOSA might confound interpretation of spatial trends.

4.4.2.1. Spatial trend summary. In summary, there is still a paucity of information on the geographic distribution of PFCs in the circumpolar arctic. Thus far, only marine ecosystems have been investigated and no spatial studies exist on freshwater or terrestrial wildlife. The studies done to date in North America do capture wider and more large-scale geographic regions. Results indicate some spatial differences between populations, however, the origins of these trends have generally not been investigated. Further, geographic trends across the regions were not the same for all PFCs, confounding spatial trend interpretation. Overall the selection of biological species used as biomonitors are prudent as they represent an integrated and realistic measure of exposure to PFCs. More conclusive and large-scale datasets exist for other emerging halogenated compounds, such as the brominated diphenyl ethers (BDEs). This is perhaps not too surprising because existing sample extracts from research on more studied halogenated compounds like PCBs are suitable for BDE research. The scenario of course is quite different for the PFCs where different extraction and sometimes tissue compartments are needed.

4.4.3. Temporal trends

4.4.3.1. North American Arctic

4.4.3.1.1. Burbot. PFC temporal trends (1986, 1999, 2003, 2006) were examined in burbot liver ($n=10$ per time point) from Fort Good Hope, Northwest Territories, Canada (Stern and Tomy, 2007). PFOS levels were steady from 1986 to 2003 but a large decrease was shown from 2003 (mean ± standard deviation = 9.88 ± 10.16 ng/g ww) to 2006 (1.93 ± 0.78 ng/g ww). PFOA exhibited somewhat similar trends with steady concentrations from 1985 to 1999 and consistent decreases from 1999–2003 and 2003–2006. In contrast, PFDA levels were steady from 1985 to 1999 with consistent increases from 1999 to 2003 and 2003–2006. PFNA and PFUnA both showed increases from 1985 to 2003 with noticeable decreases from 2003 to 2006.

4.4.3.1.2. Lake trout. Temporal trends (1999, 2000, 2001, 2002, 2004, 2005, 2006) of PFOS, PFNA, ΣPFSAs and ΣPFCAs were reported in lake trout muscle from Lutsel K'e (eastern arm of Great Slave Lake), Northwest Territories, Canada (Evans et al., 2006). PFC concentrations showed increasing concentrations from 1999 to 2001, followed by a marked decrease from 2001 to 2006. For example, PFOS concentrations increased from 1.9 to 4.7 ng/g ww between 1999 and 2001, decreasing to 0.04 ng/g ww in 2006. Similarly, PFNA concentrations increased from 0.4 to 1.6 ng/g ww between 1999 and 2001, decreasing to 0.02 ng/g ww in 2006. Statistical analysis was not reported.

4.4.3.1.3. Northern sea otter. PFC temporal trends were investigated in livers of male northern sea otters from south-central Alaska from 1992 to 2007 (Hart et al., 2009). Samples were collected from Prince William Sound ($n=36$), Resurrection Bay ($n=7$) and Kachemak Bay ($n=34$) but were grouped together for the temporal analysis. Samples were analyzed from every year with the exception of 1995 and the sample size ranged from 1 to 11 individuals per year. For the temporal trends analysis, only adults and sub-adults were included and samples were grouped into three time periods: "1992–1997" ($n=318$), "1998–2001" ($n=324$) and "2002–2007" ($n=26$). PFOS

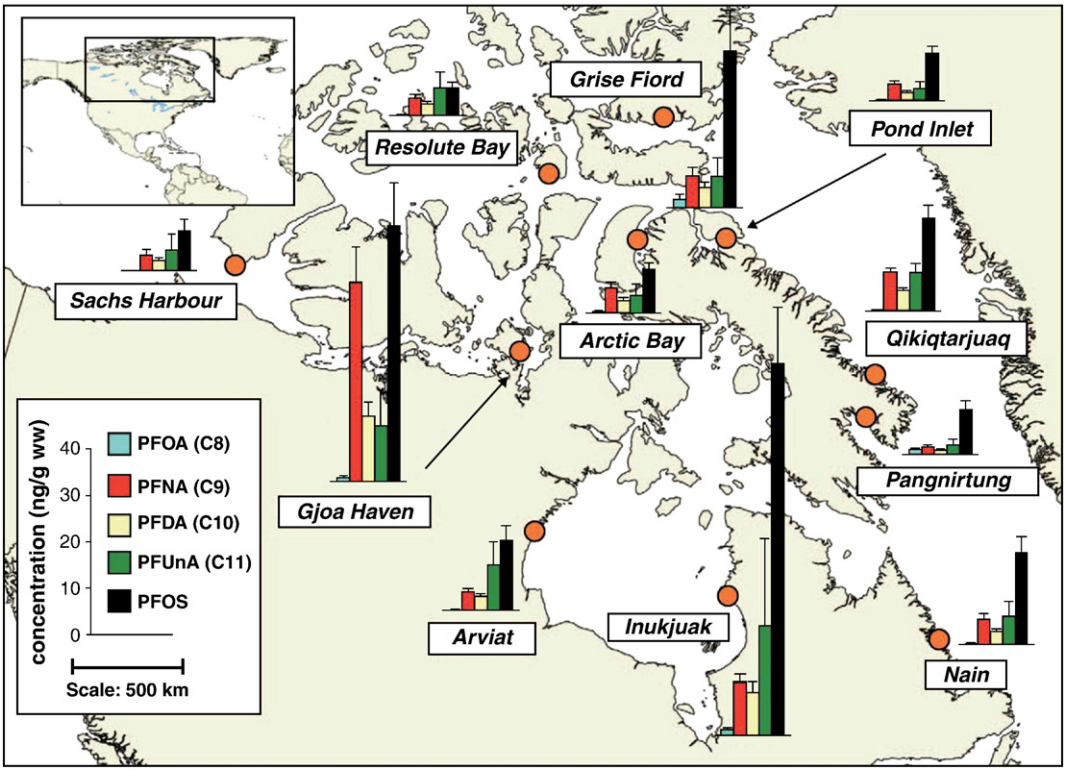

Fig. 11. Geometric mean concentration (ng/g ww) of PFOA, PFNA, PFDA, PFUnA and PFOS in ringed seal liver from Canadian Arctic. Error bars indicate one standard error. Reprinted with permission from Butt et al. (2008). Copyright 2008 Allen Press Publishing Services.

showed an overall decline during the study period with a statistically significant decrease from the 1992–1997 period to the 2002–2007 period. In addition PFOS levels showed a significant decrease from the 1998–2001 period to the 2002–2007 period. Considering individual years, PFOS levels peaked in 2001 at 21.2 ± 22.7 ng/g ww (mean ± standard deviation). PFOS concentrations showed similar levels at the start (1992) and end (2007) of the study period. Similar temporal trends were observed for PFOSA with an approximately 8-fold decrease from the 1998–2001 period to the 2002–2007 period. PFOSA peaked in 1999 at 15.2 ± 8.6 ng/g ww. In contrast to PFOS and PFOSA, PFNA showed increasing levels from the 1998–2001 period to the 2002–2007 period. PFNA concentrations peaked in 2007, increasing from <2 ng/g ww in 2004 to 9.4 ± 10.4 ng/g ww in 2007. In addition, the PFC profiles shifted during the study period. PFOS and PFOSA dominated the earlier time periods, contributing 61% and 71% of the ΣPFC profile in the 1992–1997 and 1998–2001 periods, respectively. The PFOS and PFOSA contribution decreased to 37% of the ΣPFC profile in the 2002–2007 period while the PFCA contribution increased 2-fold to 66%. PFOA, PFDA and PFUnA were below the LOQ.

4.4.3.1.4. Ringed seal. Temporal trends were examined in ringed seal liver from two populations in the Canadian Arctic, Arviat (western Hudson Bay) (1992, 1998, 2004, and 2005) and Resolute Bay (Lancaster Sound) (1972, 1993, 2000, 2004, and 2005) (Butt et al., 2007b). PFCs analyzed included C_7–C_{15} PFCAs, 8:2 FTCA & FTUCA, 10:2 FTCA & FTUCA, C_4, C_6, C_8, C_{10} perfluorinated sulfonates and PFOSA. PFHpA, PFBS, PFHxS and PFDS were not detected in any seal sample. The 8:2 FTCA & FTUCA were detected but were below the method detection limits (defined as the mean blank levels plus three times the standard deviation of the blanks). The 10:2 FTCA was detected but concentrations were not reported due to quantification problems.

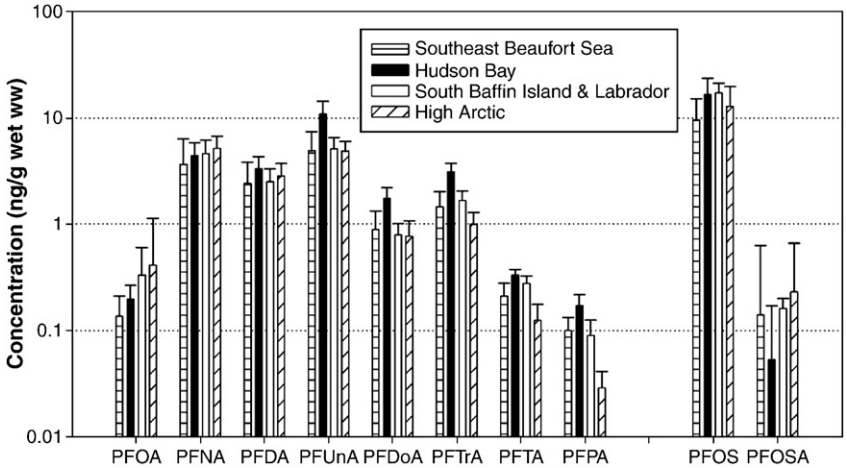

Fig. 12. Geometric mean concentration (ng/g ww) of selected PFCs in ringed seals from the Canadian Arctic. Error bars represent 95% confidence intervals. Reprinted with permission from Butt et al. (2008). Copyright 2008 Allen Press Publishing Services.

PFOA was infrequently detected above the MDL and thus not included in temporal trend analysis.

The C_9–C_{15} PFCAs showed overall increasing levels during the time interval investigated. Calculated doubling times ranged from 19.4 ± 1150 (95% confidence interval) years to 15.8 ± 12.2 years for PFDoA to 10.0 ± 7.2 to 7.7 ± 2.0 years for PFNA in the Arviat and Resolute Bay populations, respectively (Figs. 13 and 14). However, the later time points (1998, 2003 and 2005 for Arviat, and 2000, 2004 and 2005 for Resolute Bay) for the PFCAs were not statistically different from each other, implying the PFCA levels may be levelling off in ringed seals from these locations. In contrast to the PFCA trends, PFOS showed maximum concentrations during 1998 and 2000 at Arviat and Resolute Bay, respectively. Both populations showed statistically significant decreases from their maximum to 2005. In the Arviat population, two consecutive statistically significant decreases were observed, initially 1998 to 2003 and also from 2003 to 2005. In the Resolute Bay population, PFOS levels declined from 2000 to 2004 but were not statistically significant. However, the overall PFOS decline from 2000 to 2005 was significant. Apparent PFOS disappearance half-lives were 3.2 ± 0.9 (95% confidence interval) years and 4.6 ± 9.2 years for Arviat and Resolute Bay, respectively.

4.4.3.1.5. Beluga whale. Temporal trends in PFOS, PFOSA and C_8–C_{12} PFCAs were investigated in beluga whale liver from Hendrickson Island, Northwest Territories (1984, 1993, 1995, 2001, 2005, 2006 and 2007) and Pangnirtung, Baffin Island, Nunavut (1982, 1986, 1992, 1995, 2002, 2005, 2006 and 2007) in the Canadian Arctic (Tomy et al., 2008). Ten individuals were analyzed per time point with the exception of 2006 Pangnirtung samples ($n = 5$). Temporal trends were not consistent between the two populations. For PFOS, an overall statistically significant increase was shown from 1984 to 2005 in the Hendrickson Island population with an apparent levelling off after 2005. In the Pangnirtung population, PFOS levels increased linearly from 1982 to 2002, increasing at a rate of ~0.5 ng/g ww per year, with an apparent decline shown after 2002. However, these latter decreases were not statistically different from the 2002 maximum. PFOSA temporal trends were similar to PFOS. For ΣPFCAs, the Hendrickson Island population showed a linear decrease over the study period, decreasing from a maximum of 157 ± 15 ng/g (geometric mean ± SE) in 1984 to a minimum of 9.7 ± 1.5 ng/g ww in 2006. In contrast, ΣPFCA levels in the Pangnirtung population increased from 1982 (9.5 ± 2.4 ng/g ww) to 2002 (23.2 ± 4.7 ng/g ww) with an apparent levelling off after 2002.

4.4.3.1.6. Seabirds. PFC temporal trends were examined in thick-billed murre (1975, 1993, and 2004) and northern fulmar (1975, 1987, 1993, and 2003) liver samples from Prince Leopold Island (Lancaster Sound) in the Canadian Arctic (Butt et al., 2007a). Between 8 and 10 individuals were analyzed per time point. PFCs analyzed included C_7–C_{15} PFCAs, 8:2 FTCA & FTUCA, 10:2 FTCA & FTUCA, C_6, C_8, C_{10} perfluorinated sulfonates and PFOSA. In general, PFCs showed increasing levels over the entire study period in both species (1975 to 2003/2004 in thick-billed murres and northern fulmars, respectively) (Fig. 15). Considering PFCAs, the concentration increases over both time periods (1975 → 1993 and 1993 → 2004) were significant for thick-billed murres but the trends were not as clear for the northern fulmars. For northern fulmars, PFCAs showed either maximum concentrations in 1993 or statistically similar concentrations in 1987, 1993 and 2003, suggesting a levelling off in PFCA levels beginning in the early 1990s. Doubling times could be calculated for both species since the increase over the entire study period was significant. Doubling times in thick-billed murres ranged from 2.3 yrs for PFPA to 9.9 yrs for PFDoA, and from 2.5 yrs for PFPA to 11.7 yrs for PFDA in northern fulmars. PFOS levels were statistically similar in both populations between 1993 and 2003/2004. The authors caution that the temporal trends should be viewed as representative of long-term trends due to the large interval between sampling periods.

4.4.3.1.7. Polar bear. Temporal trends in PFCs were examined in polar bear livers from eastern and western populations in the North American Arctic between 1972 and 2002 (Smithwick et al., 2006). The "eastern" population comprised samples collected near northern Baffin Island, Canada, with samples collected in 1972, 1975, 1982, 1984, 1993 and 2002. The "western" population comprised samples collected near Barrow, Alaska with samples collected in 1972, 1982 and 2002.

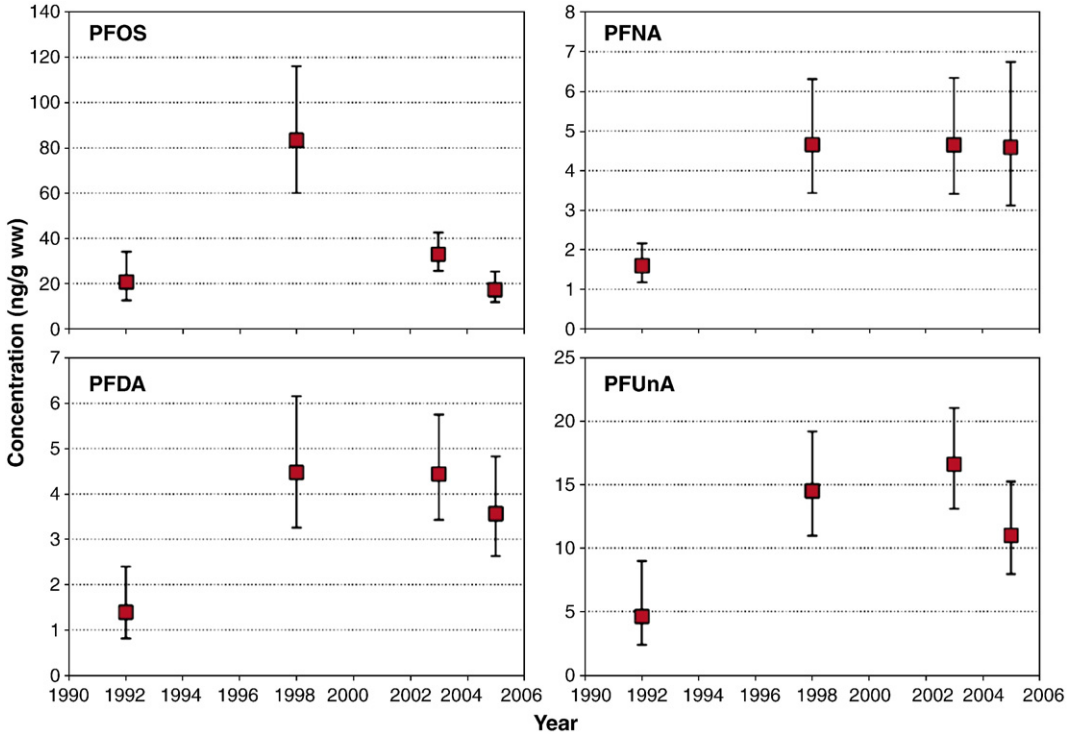

Fig. 13. Geometric mean concentrations (ng/g ww) of PFOS, PFNA, PFDA and PFUnA in ringed seals from Arviat, Nunavut, Canada (1992–2005). Error bars indicate 95% confidence interval. Reprinted with permission from Butt et al. (2007b). Copyright 2007 American Chemical Society.

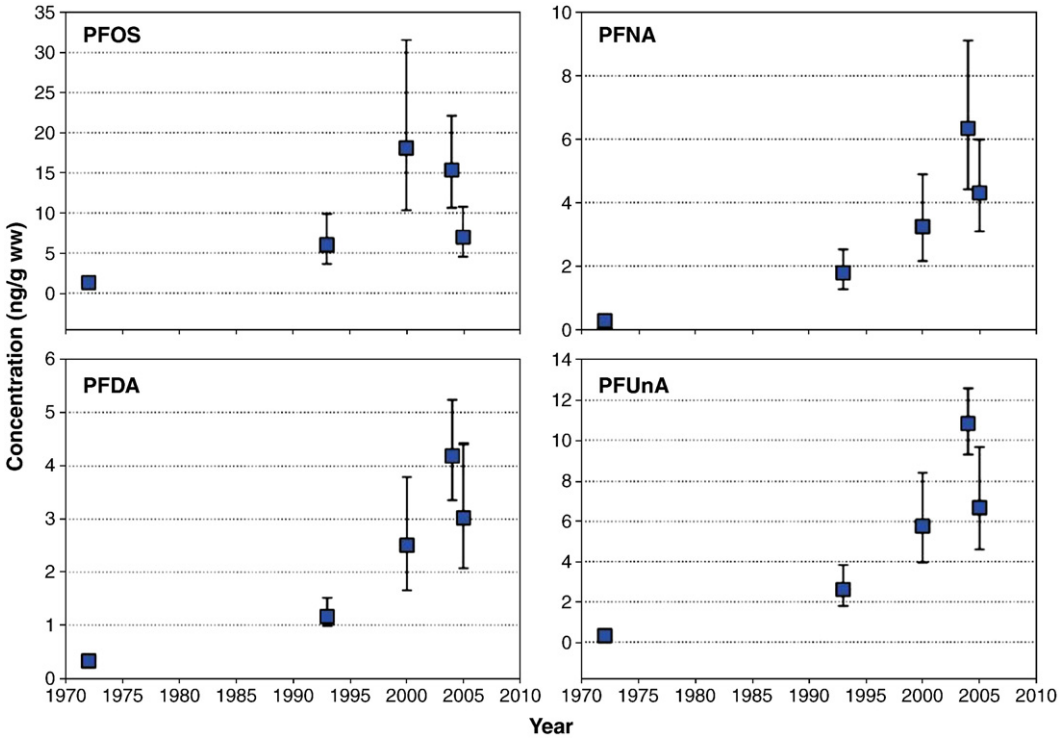

Fig. 14. Geometric mean concentrations (ng/g ww) of PFOS, PFNA, PFDA and PFUnA in ringed seals from Resolute Bay, Nunavut, Canada (1972–2005). Error bars indicate 95% confidence interval. Reprinted with permission from Butt et al. (2007b). Copyright 2007 American Chemical Society.

PFOS, PFNA, PFDA and PFUnA showed significant increases over the study period in both the eastern and western populations (Figs. 16 and 17). Significant increases were also observed for PFHxS in the western group only and for PFOA in the eastern group only. PFOSA showed decreasing temporal trends in both groups, but was statistically significant in the eastern population only. PFDoA levels were near detection limits in all samples. PFTrA and PFTA were only detected in the 2002 samples, and PFPA, 8:2 FTCA & FTUCA, and 10:2 FTCA & FTUCA were not detected in any sample. Doubling times were calculated for C_8–C_{12} PFCAs, PFHxS, PFOS and PFOSA. Doubling times ranged from 3.6 ± 0.9 years for PFNA in the eastern group to 13.1 ± 4.0 years in the western group. The mean doubling times (mean of C_8–C_{11} PFCAs and

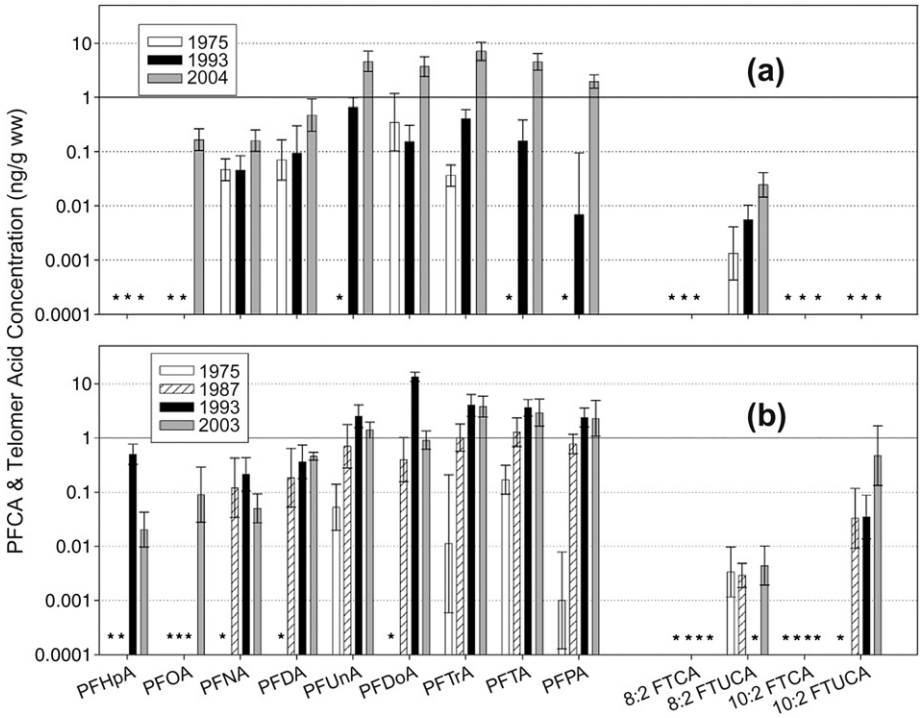

Fig. 15. Geometric mean concentration (ng/g ww) of PFCAs and fluorotelomer acids in (a) thick-billed murres and (b) northern fulmars from Prince Leopold Island, Nunavut, Canada. Errors bars indicate 95% confidence intervals. "*" indicates that all samples were below MDL or were not detected for that time point. Reprinted with permission from Butt et al. (2007a). Copyright 2007 American Chemical Society.

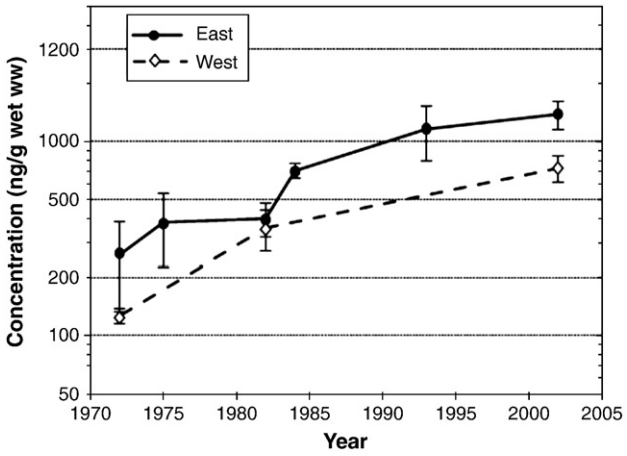

Fig. 16. PFOS temporal trends in polar bear livers from near northern Baffin Island, Canada (east) and near Barrow, Alaska (west) between 1972 and 2002. Vertical bars indicate 95% confidence intervals. Reprinted with permission from Smithwick et al. (2006). Copyright 2006 American Chemical Society.

PFOS) were much shorter in the eastern population (5.8 years) as compared to the western population (9.1 years). Considering individual PFCs, the rate of increase with time was significantly greater for PFNA and PFDA in the eastern population as compared to the western population. The rate of increase was statistically similar for PFOS and PFUnA between both populations. It was shown that the PFOS doubling times in polar bears (9.8 and 13 years for the eastern and western populations, respectively), was in good agreement with the PFOSF production doubling time of about 11 years. It was suggested that the PFOS doubling times observed in the polar bears was too short to account for transport via ocean currents.

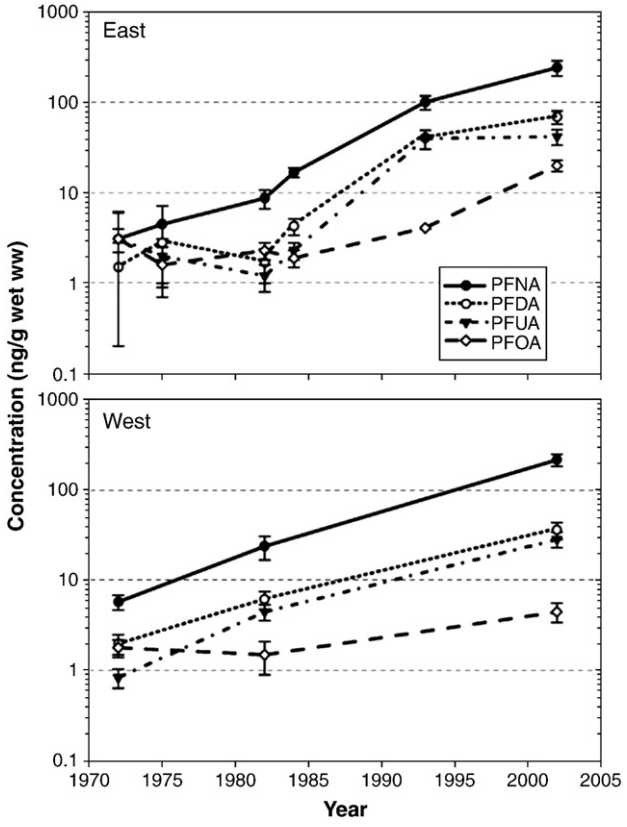

Fig. 17. PFOA, PFNA, PFDA and PFUnA temporal trends in polar bear livers from near northern Baffin Island, Canada (east) and near Barrow, Alaska (west) between 1972 and 2002. Vertical bars indicate 95% confidence intervals. Reprinted with permission from Smithwick et al. (2006). Copyright 2006 American Chemical Society.

4.4.3.2. Greenland

4.4.3.2.1. Ringed seal. Temporal trends of PFC concentrations were investigated in ringed seal livers from two locations in Greenland (Bossi et al., 2005a). Seals were collected from Ittoqqortoormiit (East Greenland) in 1986, 1994, 1999 and 2003, and from Qeqertarsuaq (West Greenland) in 1982, 1994, 1999 and 2003. Increasing PFOS levels over the study period were shown for the Ittoqqortoormiit and Qeqertarsuaq populations, although the regression was not significant for the Ittoqqortoormiit seals. Using a log-linear regression of the median concentration, PFOS annual increases were 8.2% (standard error = 3.9%) for Ittoqqortoormiit and 4.7% (SE = 1.1%) for Qeqertarsuaq. Similarly, PFDA annual increases were 3.3% and 1.7% in Ittoqqortoomiit and Qeqertarsuaq populations respectively; and PFUnA annual increases were 6.8 and 5.9%.

PFC temporal trends in Greenland ringed seals were recently updated with collections in 2006 (Riget, unpublished) (Fig. 18). Levels of PFOS, PFDA and PFUnA in the 2006 samples were greater than in 2003 in both populations. Annual increases over the entire study period (1986–2006 for Ittoqqortoormiit and 1982–2006 for Qeqertarsuaq) were greater than those measured over the 1986/1982–2003 time period. Annual increases in the Qeqertarsuaq seals were 10.7%, 5.7% and 7.6% for PFOS, PFDA and PFUnA, respectively. Similarly, annual increases in the Ittoqqortoormiit seals were 12.1%, 6.4% and 7.8% for PFOS, PFDA and PFUnA, respectively. However, the only significant regression was for PFUnA in both the Ittoqqortoormiit and Qeqertarsuaq populations.

4.4.3.2.2. Polar bear. Temporal trends were investigated in polar bear liver samples from Ittoqqortoormiit in East Greenland between 1984 and 2006 (Dietz et al., 2008) (Fig. 19). Samples were analyzed for 19 out of the 21 years ($n = 128$ subadults). Yearly increases were investigated by a log-linear regression of the median and in some instances a LOESS smoothing equation was applied to obtain a better fit. By using the log-linear model, significant annual increases were shown for all PFCs investigated with the exception of PFOSA, which did not show any significant trend. Yearly annual increases were shown for PFOS (4.7% per year), PFOA (2.5%), PFNA (6.1%), PFDA (4.3%), PFUnA (5.9%) and PFTrA (8.5%). Using a nonlinear LOESS smoother model it was shown that PFOS, PFOSA, PFDA and PFTrA showed steeper linear increases after 1990 or 2000. For PFOSA, annual increases were 9.2%. After 2000, annual yearly increases were 19.7% for PFOS, 18.6% for PFDA and 27.4% for PFTrA. The dramatic increase in recent sampling years warrants further investigation to determine if these trends will continue.

It was suggested that the continued PFOS increase observed in Greenland polar bears and ringed seals may be indicative of other primary sources or different pathways to this region (Dietz et al., 2008). It was further speculated that the temporal trends in Greenland wildlife may be representative of a time lag in PFOS transport to East Greenland.

4.4.3.3. Norway

4.4.3.3.1. Seabirds. Temporal trends (1983, 1993, and 2003) were investigated in herring gull eggs from two colonies located on the northern coast of Norway, Hornøya and Røst ($n = 5$ per colony per time point) (Verreault et al., 2007). PFOS concentrations from both colonies increased nearly 2-fold (statistically significant increase) from 1983 to 1993 (Fig. 20). PFOS levels appeared to level off between 1993 and 2003. PFHxS levels showed similar trends to PFOS in both colonies. In contrast, PFDS showed increasing levels throughout the entire study period (1983 to 2003). PFCA levels showed significant increases between 1983 and 1993 followed by either nonsignificant increases from 1993 to 2003 (C_8–C_{11} PFCAs) or levelling off (C_{12} and

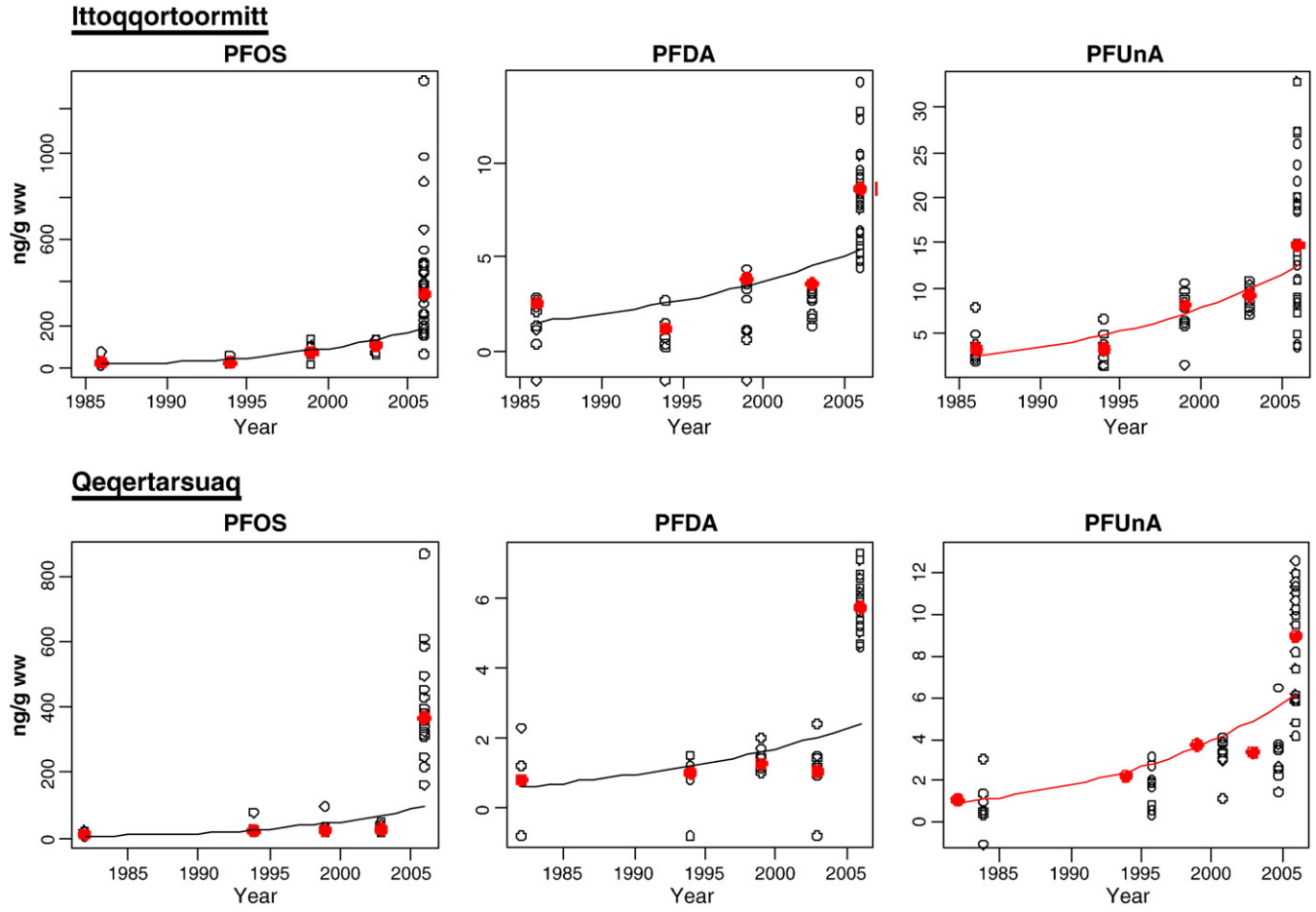

Fig. 18. Temporal trends in PFOS, PFDA and PFUnA in ringed seal liver from Ittoqqortoormiit (East Greenland), 1986–2006, and Qeqertarsuaq (West Greenland), 1982–2006 (Riget, unpublished). Red circles represent median concentrations, red line represents significant log-linear regression, black line represents non-significant log-linear regression.

C_{13} PFCAs). Variation in the PFCA composition was observed between sampling years, suggesting the PFCA sources may have changed over time. For example, eggs from Røst in 1993 and 2003 had significantly higher proportions of PFOA as compared to 1983. Further, Røst eggs collected from 1993 had higher proportions of PFTA and PFPA. Doubling times were not calculated due to the limited time points.

4.4.3.3.2. Temporal trend conclusions. In summary, there are numerous studies examining temporal trends of PFCs in arctic wildlife. Studies thus far have been exclusively from marine ecosystems (marine mammals, seabirds and polar bears) with the exception of burbot and lake trout from the Northwest Territories, Canada. Most temporal trend studies have been from the North American Arctic and Greenland.

Temporal trends between Arctic regions are not consistent. For example, declining PFOS concentrations have been shown in sea otter (Hart et al., 2009), ringed seal (Butt et al., 2007b) and beluga whale (Tomy et al., 2008) from the Canadian Arctic, whereas, ringed seals (Bossi et al., 2005a) and polar bears (Dietz et al., 2008) from Greenland continue to show increasing PFOS levels from the 1980s to 2006. Some temporal studies may be confounded by the relatively large temporal intervals. Further, temporal trends within species from different regions are inconsistent. For example, Tomy et al. (2008) observed declining ΣPFCAs trends in Hendrickson Island beluga but increasing ΣPFCA trends in Pangnirtung beluga. The inconsistencies observed between temporal studies may be due to differences in emissions from source regions, although spatially resolved temporal emission data is not presently known. Disparate regions of the Arctic are influenced by air currents from different regions (Macdonald et al., 2000), and thus could receive unique temporal patterns of volatile precursors. In addition, it has been suggested that the North American and European Arctic are influenced by dissimilar ocean waters (Jones et al., 1998). For example, it has been suggested that surface seawater in the Canadian Archipelago and northern Hudson Bay is entirely of Pacific origin (Jones et al., 2003a). In contrast, the European Arctic is primarily influenced by Atlantic Ocean waters.

4.5. PFC profiles

4.5.1. General

In general, PFOS levels are shown to dominant the PFC profiles in arctic wildlife. Except for some whale species, PFOSA is usually detected at lower levels than PFOS. PFOSA has been to shown to be metabolically labile (Tomy et al., 2004a; Xu et al., 2004). Individual PFCA levels are typically lower than PFOS, although the ΣPFCA levels may be comparable in magnitude to PFOS. The PFCA profiles are usually dominated by either PFNA or PFUnA with a distinctive "odd-even" pattern in which concentrations of odd chain-length PFCAs are greater than adjacent even chain-length PFCAs. It has been suggested that these trends are the result of FTOHs as the dominant source of PFCAs (Martin et al., 2004). For example, it has been shown that the atmospheric oxidation of 8:2 FTOH yields approximately equal proportions of PFOA & PFNA (Ellis et al., 2004). Similar patterns are expected for other FTOHs (i.e. atmospheric oxidation of 10:2 FTOH yields equal amounts of PFDA & PFUnA). Bioaccumulation has been shown to increase with increasing chain-length (Martin et al., 2003a; Martin et al., 2003b), thus it would be expected that PFNA

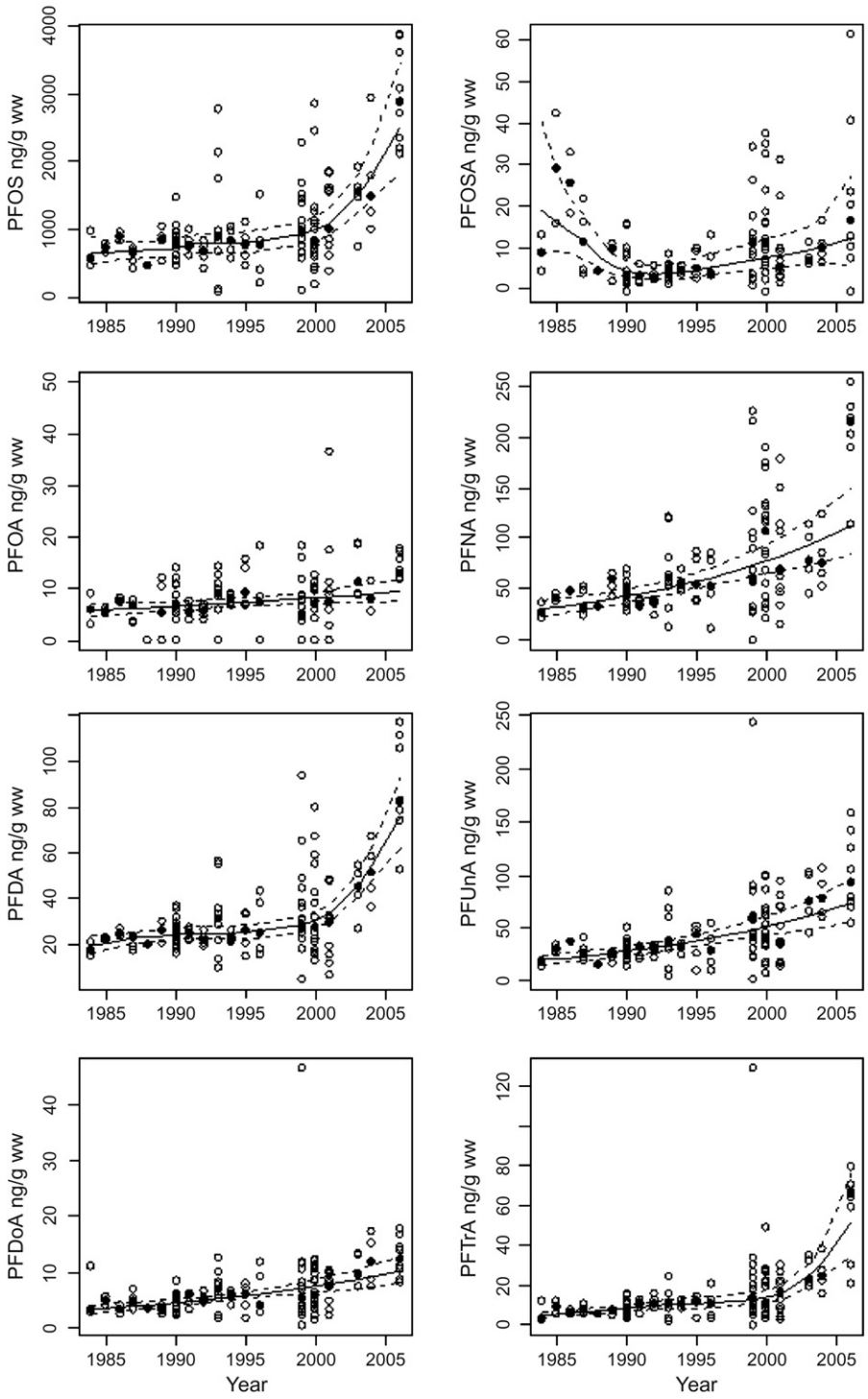

Fig. 19. Temporal of PFCs in East Greenland polar bear liver from 1984 to 2006. Filled points represent log-linear regression lines or LOESS smoother lines. Broken lines represent 95% confidence limits. Reprinted with permission from Dietz et al. (2008). Copyright 2008 American Chemical Society.

concentrations would be greater than PFOA, assuming exposure concentrations at the base of food web are equal. Alternatively, it has been reported that a PFNA commercial product (Surflon S-111) contains significant quantities of PFUnA and PFTrA (Prevedouros et al., 2006). However, the contribution of this commercial product to the observed PFCA patterns is unclear.

PFOA and PFCAs of lower chain lengths are typically not detected, or are in low concentrations. This is despite the fact that global PFOA seawater concentrations are generally similar, or greater than PFOS (Yamashita et al., 2008). These trends are presumably due to the low bioaccumulation potential of PFOA and lower chain-length PFCAs (Martin et al., 2003a,b). These trends are also observed in wildlife from non-Arctic regions.

The mechanisms explaining the apparently greater bioaccumulation potential of PFSAs as compared to PFCAs have not been fully elucidated. Several researchers have investigated structure–activity relationships that demonstrate differences in the behaviour of biological binding between the carboxylates and sulfonates and a

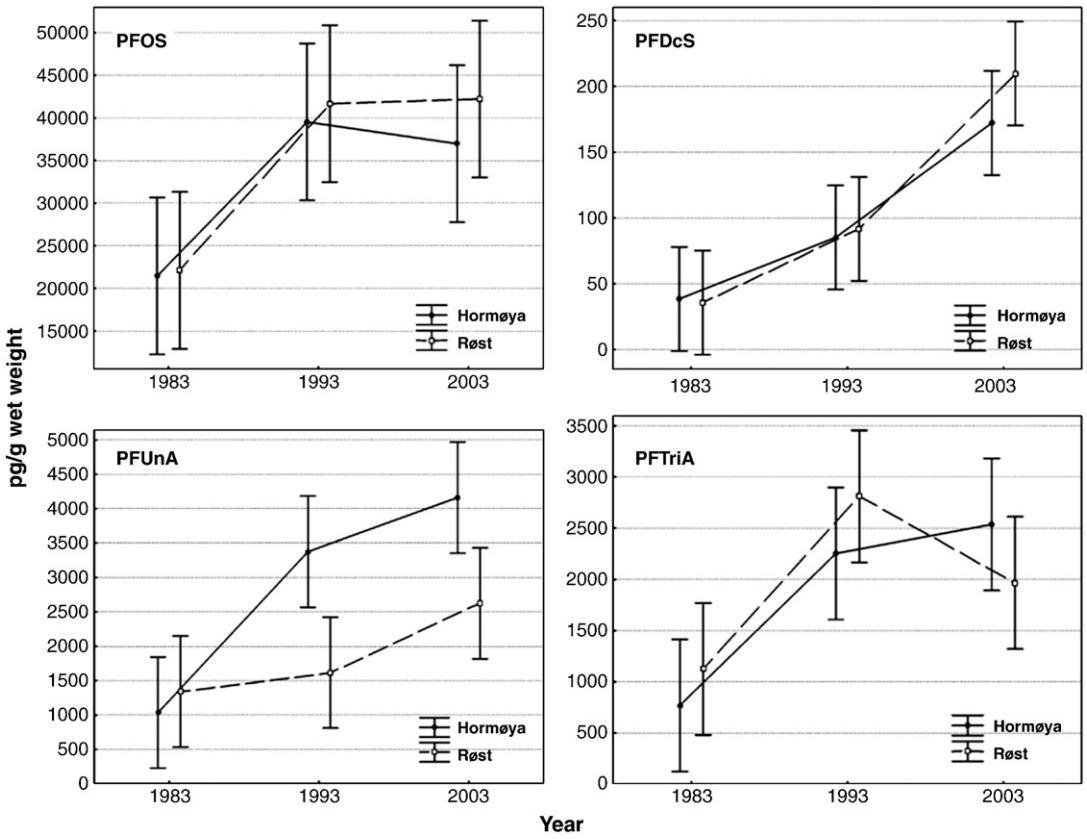

Fig. 20. Temporal trends of PFOS, PFDS, PFUnA and PFTrA in herring gull eggs from the Hornøya and Røst, Norwegian Arctic. PFDcS and PFTriA are identified as PFDS and PFTrA, respectively, in the manuscript. Reprinted with permission from Verreault et al. (2007). Copyright 2007 American Chemical Society.

full discussion of these trends is beyond the scope of this review. Gender differences in elimination rates are observed for PFOA, but generally not for PFOS (Lau et al., 2007) and may represent differences in the mechanism of protein binding. In addition, PFOS has been shown to bind more strongly than PFOA to liver-fatty acid proteins (Luebker et al., 2002). Chen and Guo (2009) showed differences in binding affinity to human serum albumin between various PFCAs and PFSAs. These observed differences in protein binding likely influences overall clearance and accumulation potential.

4.5.2. Seabirds and freshwater birds

Longer-chain PFCAs (i.e. C_{11}–C_{15} PFCAs) have been shown to dominant PFCA profiles in some seabirds (Butt et al., 2007a; Löfstrand et al., 2008; Verreault et al., 2005) as well as the common loon (Martin et al., 2004). In contrast, PFNA and PFUnA are the dominant PFCAs in most wildlife. It is unclear why the long-chain PFCAs dominate seabird profiles.

4.5.3. Whales

Several whale species have been shown to have PFOSA concentrations that are greater than, or approximately equal to, PFOS (Bossi et al., 2005b; Muir et al., 2004; Tomy et al., 2008). Bossi et al. (2005b) noted that cetaceans from the Mediterranean Sea showed PFOSA levels that were 1 to 5-fold greater than PFOS (Kannan et al., 2002). Further, melon-headed whales from the Japanese coast were shown to have comparable levels of PFOS and PFOSA (Hart et al., 2008). These trends are in contrast to the majority of wildlife species that show relatively very low PFOSA levels. It has been shown that PFOSA is a metabolic precursor to PFOS (Tomy et al., 2004a; Xu et al., 2004), and thus the relatively high levels of PFOSA in some cetaceans may be representative of a diminished metabolic capacity.

4.6. Isomer patterns

PFCs are primarily produced either through ECF or telomerization (3M, 1999; Kissa, 2001). The ECF process was used by the 3M Company in the manufacture of its PFOSF chemistry until the voluntary cessation of production in 2001. ECF is known to yield mainly linear alkyl chains as well as branched isomers in minor proportions. Chemicals produced by the PFOSF chemistry include PFOS, PFOSA and perfluorooctane sulfonamide alcohols (FOSEs). The FOSEs and PFOSA have been shown to degrade abiotically to PFOS and PFOA (D'eon et al., 2006; Martin et al., 2006) as well via biotic degradation to PFOS (Tomy et al., 2004a; Xu et al., 2004). PFOS is thought to be produced exclusively by ECF and thus will be found in both linear and branched forms. In addition, PFOA was directly manufactured through electrochemical processes from 1947 to 2002 (Prevedouros et al., 2006). In contrast, the telomer process is known to only yield linear alkyl chains. This chemistry is used by various companies for the production of FTOHs, fluorotelomer olefins, iodides, acrylates and PFCAs (Prevedouros et al., 2006). Various fluorotelomer-based compounds have been shown to degrade abiotically and biotically to PFCAs (Ellis et al., 2004; Hagen et al., 1981; Hurley et al., 2004). Thus, PFCAs originating from ECF sources (i.e. PFOSF based compounds) will contain linear and branched isomers, whereas, PFCAs from telomerization sources will be in exclusively linear isomers. Because both production approaches give rise to different isomer patterns in the end-product, it was initially suggested that PFCA isomer patterns in biota could be correlated to exposure by products derived from the two synthetic approaches.

De Silva and Mabury (2004) investigated isomer patterns of C_8–C_{13} PFCAs in polar bear liver samples from two locations, southeastern Hudson Bay ($n=7$) in the Canadian Arctic and eastern Greenland ($n=8$). Overall, the PFCA profiles were dominated by linear isomers

with the linear isomers comprising at least 90% of the total isomer distribution for each PFCA investigated. Given that ECF sources have been shown to have much higher isomer abundances (Arsenault et al., 2008) than observed in the polar bear livers, these results suggest that both ECF and telomer-based products contributed to the PFCA burden. Specifically, PFNA isomer profiles were nearly entirely linear with branched isomers detected in only 3 out of 15 samples. These results suggest that the source of PFNA in these two locations was not from an ECF source, and thus presumably from a telomerization source. Isomer profiles of PFDA, PFUnA and PFDoA were similarly dominated by the linear isomer (>96%), again suggesting a predominately non-ECF source of these compounds. Also, it was shown that PFOA isomers were a mixture of several branched isomer forms, whereas the longer chain PFCAs had only the isopropyl branched isomer. It was noted that the presence of only the isopropyl branched isomer, and not a mixture of isomers, is not consistent with an ECF source. The branched isomer patterns were found to vary between locations, which may be indicative of varying sources. Greenland polar bears showed the greatest proportion of branched isomers for PFOA, PFUnA and PFTrA. Conversely, the Hudson Bay polar bears had the highest proportion of PFNA, PFDA and PFDoA branched isomers. Greenland may receive air flow from both North America and European sources, whereas, Hudson Bay would primarily receive North American air flows. Thus, differences in emission between these two regions could account for the isomer patterns observed.

De Silva et al. (2009a) followed up their polar bear study by examining C_8–C_{12} PFCA isomers in ringed seal liver from Resolute Bay, Nunavut, Canada (1993, 2000, 2004; $n=2$ individuals per year). The ringed seals were from a larger sample set previously analyzed by Butt et al. (2007b). Similar to the polar bear samples (De Silva and Mabury, 2004), PFCA profiles were dominated by the linear isomer. It was suggested that these trends are indicative of a primarily telomer source of PFCAs. Further, it was shown that all branched isomers of PFOA were <LOD. Only the isopropyl branched isomer was detected in the C_9–C_{12} PFCA profiles. Ranges of *iso*:*n*-isomer were 1–4% for PFDA, 1–2% for PFUnA and 4–8% for PFDoA. It was noted that the PFCA isomer patterns in the Resolute Bay ringed seals closely resembled those in the southeastern Hudson Bay polar bears.

Isomer profiles were also measured in a food web from the western Canadian Arctic (Powley et al., 2008). No branched PFCA isomers were detected, suggesting telomer-based products were the predominate source of PFCAs. PFOS branched isomers were shown to comprise 50% of the total PFOS isomer profile in arctic cod, but only 4% in seals. The authors suggested that these trends represent a preferential elimination of branched PFOS isomers through the food chain. However, differing tissues were analyzed between the arctic cod (whole body) and ringed seal (liver) which may confound the observed trends. In addition, it is unclear if the ringed seal diet consisted primarily of arctic cod.

Chu and Letcher (2009) monitored levels of the linear and 11 branched PFOS isomers in polar bear liver from the Canadian Arctic (Nunavut) and plasma from Svalbard. Canadian polar bear liver samples ($n=8$) were collected in 2007–2008 and Svalbard samples ($n=5$) were collected in 2007. Samples were analyzed by GC–MS using a novel in-port derivatization. Individual isomer standards were purchased from a commercial source, eliminating any potential bias due to differing response factors. In addition to the linear PFOS isomer, 6 mono-substituted branched PFOS isomers were detected in the polar bear samples. The mean percentage composition of the linear PFOS isomer was 92.4% and 82.4% in the polar bear liver and plasma, respectively. Compared to a technical PFOS standard (linear isomer composition = 65.0%), these results indicate an enrichment of linear PFOS isomer through the food chain and is consistent with results from a Lake Ontario food web (Houde et al., 2008).

However, the use of isomers for source identification may be confounded by isomer discrimination during trophic transfer. For example, Houde et al. (2008) showed that branched PFOS isomers were diminished between the surface water and biota in a Lake Ontario food web. In addition, De Silva et al. (2009b), in a dietary exposure study with rainbow trout, showed the preferential elimination of PFOA branched isomers relative to the *n*-isomer. Therefore, further research is needed before isomer patterns in wildlife can be used as markers for electrochemical versus telomer sources.

4.7. Animal body burdens

There are few reports of PFC body burden in arctic wildlife. Liver and blood are the most frequently analyzed tissue in wildlife due to the tendency of PFCs to accumulate in the enterohepatic system (Martin et al., 2003a). However, predator animals may eat either the whole animal (e.g. seals eating fish) or blubber (e.g. polar bears eating seals). Thus, it may be useful to analyze PFC total body burden to achieve a more realistic assessment of biomagnification potential.

PFC concentrations in blubber, blood and liver were investigated in ringed seal ($n=5$) and bearded seal ($n=1$) collected from near Sachs Harbour, North West Territories in the Canadian Arctic (Powley et al., 2008). Total animal body burdens were not calculated. Considering individual PFCs, concentrations were generally greatest in the liver followed by the blood and finally blubber. In fact, only PFOS (range: 0.4–0.9 ng/g ww) and PFDA (ND−0.2 ng/g ww) were detected in the blubber. In comparison, PFOS levels ranged between 2.5–8.6 ng/g ww and 18–34 ng/g ww in the blood and liver, respectively. Similarly, PFDA levels ranged between 0.4–1.1 ng/g ww and 2.0–3.3 ng/g ww in the blood and liver, respectively. PFCs were not detected in the bearded seal blubber. It is unclear whether these trends represent actual partitioning of the PFCs into the seal blubber or PFCs in the blood vessels found within the blubber.

PFCs were investigated in the plasma, liver, brain and eggs of glaucous gulls from the Norwegian Arctic (Verreault et al., 2005). PFOS levels showed plasma>liver~egg>brain. Similarly, ΣPFCA levels showed plasma>egg>liver>brain. There were few PFCAs detected in the brain samples. While the long-chain PFCAs dominated all tissues, specifically PFUnA and PFTrA, the individual dominant PFCA did vary by tissue type. PFUnA was the predominant PFCA in plasma and eggs, whereas, PFTrA was predominant in liver. As well, the ΣPFCA: PFOS ratio varied among tissues, representing variation in the relative distribution of PFOS and ΣPFCA in the body. The ΣPFCA: PFOS ratios were significantly greater in plasma as compared to eggs, liver and brain, which were similar to each other.

4.8. "Neutrals" and precursors

Several polyfluorinated compounds have been shown to form PFSAs and PFCAs through metabolic processes. The presence of metabolically active "precursor" compounds within the animals may represent reservoirs of PFSAs and PFCAs. The production of PFOS from the biotransformation of *N*-ethyl perfluorooctane sulfonamide ethanol (*N*-EtFOSE) (Xu et al., 2004), *N*-EtFOSA (Tomy et al., 2004a) and PFOSA (Xu et al., 2006) has been observed in liver microsomal fractions of several species. Also, numerous studies have shown the formation of PFCAs from the metabolism of FTOHs (Fasano et al., 2006; Hagen et al., 1981; Kudo et al., 2005; Martin et al., 2005; Nabb et al., 2007) in whole animals and microsomes, with FTCAs and FTUCAs as intermediates. The 6:2 FtS may be a precursor to PFHxA (Key et al., 1998). More recently, PFHpA and PFOA were shown as metabolites in the biotransformation of 8:2 analogues of polyfluorinated phosphate surfactants (D'eon and Mabury, 2007). The actual exposure of arctic wildlife to PFSA and PFCA precursors is not known. Many of these compounds possess high Henry's Law constants (Lei et al., 2004) which effectively precludes exposure via water breathing

organisms. With the exception of PFOSA, there are very few reports of PFSA and PFCA precursors in arctic wildlife. As such, to avoid repetition, discussion of precursors levels in this section does not include PFOSA.

Tittlemier et al. (2005b) reported N,N-Et_2FOSA and *N*-EtFOSA levels in beluga and narwhal liver from the Canadian Arctic. Mean N, N-Et_2FOSA and *N*-EtFOSA concentrations were 1.2 and 3.6 ng/g ww and 3.3 and 11 ng/g ww for beluga and narwhal liver, respectively. PFCAs and PFSAs were not reported in these samples.

Tomy et al. (2004b) reported *N*-EtFOSA levels in organisms from an eastern Canadian Arctic food web. Levels of *N*-EtFOSA ranged from 0.39 ± 0.07 ng/g ww (mean ± standard error) for mixed zooplankton to 92.8 ± 41.9 for arctic cod. Interestingly, *N*-EtFOSA levels in some species were greater than PFOS and PFOA. *N*-EtFOSA was not detected in the redfish samples. Walrus, black-legged kittiwake and glaucous gull samples were not analyzed for *N*-EtFOSA.

Levels of *N*-EtFOSA were reported in guillemot eggs from Iceland, Faroe Islands, Norway and Sweden (Löfstrand et al., 2008). Mean *N*-EtFOSA levels were 0.77, 0.98 and 2.0 ng/w ww in the Vestmannaeyjar (Iceland), Sklinna (Norway) and Hjelmsøya (Norway) populations, respectively. *N*-EtFOSA was not detected in the Faroe Island guillemot eggs. In general, *N*-EtFOSA levels were similar in magnitude to PFOSA but much lower than those of PFOS and the C_{10}–C_{12} PFCAs.

Haukås et al. (2007) reported 6:2 FtS concentrations in organisms from a Barents Sea food web. The 6:2 FtS was detected in 3 out of 6 ice amphipod samples (mean ± standard error: 0.48 ng/g ww ± 0.24) and 1 black guillemot sample (3.4 ng/g ww). The 6:2 FtS was not detected in the arctic cod and glaucous gull samples. As well, Verreault et al. (2007)) reported 6:2 FtS levels in herring gull eggs from Hornøya and Røst in Northern Norway. Levels of 6:2 FtS were below the LOQ (0.16 ng/g ww) in samples from both colonies.

Several studies have monitored for but did not detect the 8:2 and 10:2 FTCAs & FTUCAs (Löfstrand et al., 2008; Powley et al., 2008; Verreault et al., 2005). In a survey of 11 ringed seal populations across the Canadian Arctic (Butt et al., 2008), FTCAs and FTUCAs were detected in low levels. The 8:2 and 10:2 FTUCAs were detected in all populations. However, with the exception of Grise Fiord seals (8:2 FTUCA geometric mean = 6.0 n/g ww) and Pond Inlet seals (4.0 ng/g ww), levels were predominantly less than the MDL. Fluorotelomer saturated and unsaturated acids were also detected in temporal ringed seals from Resolute Bay and Arviat in the Canadian Arctic (Butt et al., 2007b). The 8:2 FTCA and FTUCA levels were below method detection limits. The 10:2 FTUCA levels ranged from <0.75 to 9.6 ng/g ww in the Arviat population and from <0.75 to 1.3 ng/g ww in the Resolute Bay population. The 8:2 and 10:2 FTUCAs were also detected in thick-billed murres and northern fulmars from Prince Leopold Island in the Canadian Arctic (Butt et al., 2007a). In the most recent samples, the geometric mean concentrations of 8:2 FTUCA were 0.02 and 0.01 ng/g ww for thick-billed murres and northern fulmars, respectively. The geometric mean 10:2 FTUCA concentrations were <0.20 and 0.48 ng/g ww for thick-billed murres and northern fulmars, respectively.

5. Conclusions and research needs

To date, the bulk of the monitoring efforts in the arctic environment have concentrated on the PFCAs and PFSAs. The PFCAs and PFSAs are unique from the legacy POPs in that they are potential degradation compounds of commercial products (e.g. fluorinated polymers, fluorinated phosphate surfactants) and of compounds used in the manufacture of commercial products (e.g. fluorinated alcohols and acrylates). Furthermore, some PFCAs and PFSAs are also produced and applied directly. However, with the exception of PFOA, PFNA and PFOS, PFCAs and PFSAs were not industrially produced in large quantities.

The sources and transport routes of PFCs to the arctic are not well understood and have recently been the subject of considerable research effort. The two major postulated pathways are: the atmospheric transport and oxidation of volatile precursors, and the direct transport of PFCAs and PFSAs via ocean currents. Local inputs do not appear to significantly influence regional PFC concentrations; however, research is very limited. Several modeling studies have attempted to quantify the relevance of the two major postulated transport pathways. Thus far, models have used FTOHs and sulfonamide alcohols as inputs for volatile precursors. Future modeling studies should include additional precursors such as the fluorinated olefins, iodides and acrylates, as well as, the fluorinated phosphates. Model results are inherently sensitive to emission estimates. For example, Wallington et al. (2006), using an emission rate of 1000 tonnes per year, showed the FTOH degradation could explain environmental levels of PFCAs. In contrast, several others studies, using lower FTOH emissions rates, suggest that direct emissions of PFCAs and subsequent ocean transport is the dominant transport pathway. Modeling studies published to date have primarily focused on PFOA fluxes to arctic seawater, presumably due to the general dominance of PFOA in water samples. However, considering that PFOA is generally only infrequently detected in arctic wildlife, and at low levels, future modeling efforts should also include the PFSAs and longer-chain PFCAs.

Overall, there are few measurements of PFCs in abiotic media from the arctic. The majority of the abiotic measurements are from the Canadian Arctic and the North Atlantic. Atmospheric measurements from the North Atlantic and Canadian Arctic show the presence of PFC precursors, specifically the FTOHs and sulfonamide alcohols. PFC degradation products (PFCAs and PFSAs) and precursor intermediates (fluorotelomer carboxylates) have also been detected on atmospheric particles. Presumably these compounds originate from the atmospheric oxidation of precursor compounds. Spatial variation in the relative fraction of FTOHs and sulfonamide alcohols was observed between the North Atlantic and Canadian Archipelago, and may be representative of continental emission patterns. Expanded atmospheric monitoring is required to confirm these trends. In addition, atmospheric monitoring should include recently identified potential PFCA precursors such as the fluorinated olefins, iodides and acrylates. Finally, temporal analysis of arctic air samples would assist in understanding wildlife temporal trends.

Snow samples act as a surrogate for atmospheric deposition and have been analyzed from the Canadian Arctic and Greenland. The presence of PFOS and PFCAs in the snow samples confirmed that PFCs can be transported to the arctic environment via the atmosphere, presumably as volatile precursors with subsequent atmospheric oxidation and deposition. Depth samples, representing deposition from 1996 to 2005, in a snow pit from the Canadian Arctic showed relatively constant deposition fluxes of PFCAs, but decreasing fluxes of PFOS from 1998 to 2001 followed by constant fluxes thereafter. These trends, taken together with some of the wildlife temporal studies, may indicate that the arctic environment is responding to changes in PFOSF-production, although additional studies in other regions of the arctic are needed.

There are very limited measurements of PFCs in seawater. Studies to date are relatively spatially constrained and are primarily from the Canadian Archipelago, the Labrador and Greenland Seas in the North Atlantic, and the Russian Federation. PFOA is generally detected in the greatest concentrations. Levels of long-chain PFCAs have not been reported. The detection of PFCs in arctic seawater confirms that direct transport via ocean currents occurs. However, it is unclear whether the PFCs in the seawater have originated from direct emissions or from the atmospheric oxidation of precursors and subsequent deposition to the ocean surface. There is an immediate need for additional seawater measurements to validate existing model predications. Such measurements will greatly assist in assessing the relative importance of direct versus indirect long-range transport.

PFCs appear to be ubiquitously detected in arctic biota. The marine food web has been well studied, in particular top predators such as seabirds, ringed seals and polar bears. There have been few reports of PFCs in marine zooplankton and fish. Earlier monitoring efforts generally only reported levels of PFOS, PFOSA, PFOA and occasionally a small set of other PFCAs such as PFNA. However, in recent years there are more frequent reports of the longer-chain PFCAs. The importance of monitoring for longer-chain PFCAs is demonstrated by the fact that these compounds typically dominate PFCA profiles.

The freshwater ecosystem has been poorly examined, and in fact reports are limited to freshwater fish. Similarly, the terrestrial ecosystem has also been poorly investigated. The only reports of PFCs in terrestrial wildlife are from the Canadian Arctic. The limited reports of PFCs in freshwater and terrestrial ecosystems represent significant knowledge gaps in our understanding of PFCs in the arctic. PFCs have been detected in the surface water and sediments of freshwater lakes in the Canadian Arctic. There is a need for additional studies examining lake water and sediment levels in other regions of the arctic. Sediment core analysis shows the general increase in PFC levels over the past 50 years.

Food web studies are limited and have been restricted to the marine environment. As such, there is an immediate need to study freshwater and terrestrial food webs. The marine food web studies published to date have generally shown high bioaccumulation in species at the top of the food web, particularly for PFOS and some long-chain PFCAs. However, the positive correlation between trophic position and PFC concentration is not necessarily indicative of biomagnification since there are significant uncertainties regarding the mechanism of PFC bioaccumulation and biomagnification. For example, biomagnification factors are typically calculated based on single organ concentrations (i.e. liver) that may not accurately represent consumption trends.

Similarly, there are few spatial trend studies and those published to date have only examined marine ecosystems. There is a requirement for spatial trend studies on freshwater and terrestrial wildlife. Further, there is a need for spatial studies that are larger in scale, preferably encompassing the entire circumpolar arctic. In particular, there is almost nothing known about PFC levels in the Russian Arctic. Understanding spatial patterns may assist in our interpretation of emission patterns and transport pathways. The more large-scale geographic studies have generally been from the North American Arctic. Although some studies have reported spatial differences between populations, in general the causes of these discrepancies have not been investigated. In addition, interpretation of PFC spatial patterns is confounded by the fact that trends between PFCs are generally not consistent.

With few exceptions, most temporal trend studies are from marine ecosystems in the North American Arctic and Greenland. There is a need for temporal trend studies from other arctic regions. In addition, temporal trend studies from freshwater and terrestrial ecosystems are needed. To date, temporal studies have shown inconsistent trends between regions, possibly due to differences in emissions from source regions, although spatially resolved temporal emission data is not presently available. Declining PFOS levels have been observed in sea otter, ringed seal and beluga whale from the Canadian Arctic, however, ringed seals and polar bear from Greenland show continued increasing PFOS levels from the 1980s to 2006. Given these inconsistencies, continued monitoring in existing studies is needed to confirm trends.

There are very few measurements of PFC precursors, such as the FOSEs, FOSAs and FTOHs, in wildlife. As such, trends are difficult to interpret. Given that these compounds have been shown to metabolically degrade to form PFSAs and PFCAs, the presence of "precursors" may represent reservoirs of these compounds. Additional measurements of PFC precursors in wildlife are needed. However, given the labile nature of these compounds in wildlife, it is unclear whether wildlife will accumulate significant quantities of PFC precursors.

There are few measurements of the C8 PFOSF-chemistry replacement compounds such as FBSE (butyl sulfonamide alcohol). PFBS and PFBA are expected to be formed from FBSE and derivatives through metabolic and abiotic mechanisms analogous to the FOSEs. However, it is unlikely that PFBS and PFBA will accumulate in arctic wildlife considering their short biological half-life (Chang et al., 2008; Martin et al., 2003b).

There is increasing evidence of recent climate change in the arctic environment. The magnitude of warming is variable across the arctic, but overall it is nearly twice that of the global average (Graversen et al., 2008; Johannessen et al., 2004). A changing climate has been linked to dramatic ecosystem changes in many global regions (Parmesan and Yohe, 2003) including the arctic (Post et al., 2009). Climate change may influence contaminant accumulation through altering transport pathways and changing food web dynamics (Macdonald et al., 2005). These processes are complex and it remains unclear if or how PFC levels will be specifically influenced. Therefore, it is suggested that future research focus on the influence of climate change on PFC levels in the arctic.

In conclusion, PFCs were first reported as contaminants in arctic wildlife by Giesy and Kannan in 2001. Since that time, our understanding of the levels and trends of PFCs in the biotic and abiotic environment of the circumpolar arctic has improved drastically. As with many other persistent organohalogenated compounds, we now appreciate that the arctic environment is ubiquitously contaminated with PFCs, however, many data gaps still exist. The effects of PFCs on arctic wildlife are not yet known. In addition, there is relatively limited understanding of PFCs in the abiotic environment, as well as in terrestrial and freshwater biota. Some PFCs appear to biomagnify in arctic food webs; and in a global context some of the highest known PFC concentrations are measured in polar bears. Further, potential transport pathways have been postulated in the literature, and several models have been developed in attempt to understand the relevance of these pathways.

Additional monitoring efforts should be designed in a deliberate manner to assist in our understanding on the fate and disposition of PFCs in the arctic. As mentioned above, additional seawater samples are needed. In particular, seawater samples should spatially distributed such that the potential influence of the major oceanic currents (and thus related to source region) can be identified. Additional air monitoring of precursors, including newly identified chemicals, and degradation compounds are necessary to understand fluxes to the terrestrial and marine environments. Similar to seawater collection, air monitoring should be spatially distributed to investigate contributions from different source regions. Additional monitoring of temporal trends in biota is needed to confirm observed trends. Archived biota samples should be chosen such that there is a long time course with sufficient temporal resolution to establish trends and distinguish the influence of inter-year variability. Given the observed differences in temporal trends in ringed seals from two arctic regions, spatially variable sample locations are needed. As well, temporal trends in additional wildlife species are needed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2010.03.015.

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