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Endosulfan, a global pesticide: A review of its fate in the environment and occurrence in the Arctic☆

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ABSTRACT

This review investigates the fate and behaviour of endosulfan, a current-use organochlorine pesticide, in temperate environments and the Arctic. Usage data and patterns, physical–chemical properties, environmental partitioning and degradation, environmental levels, global distribution and temporal trends are evaluated and discussed in the context of criteria that designate a substance as a persistent organic pollutant. Endosulfan is one of the most abundant OC pesticides in the global atmosphere and is capable of undergoing long range transport to remote locations such as the Arctic. Degradation of the two isomers, α- and β-endosulfan, does occur in temperate/tropical soil and aquatic systems, both by abiotic and biotic processes, although this is highly dependent on the prevailing environmental conditions. Endosulfan sulfate is the major metabolite and this recalcitrant compound has been detected in air and is present in remote mountain lake sediments, although in comparison to α-endosulfan, data for this compound in the wider environment are lacking.

Temporal trends from ice/snow cores as well as mountain lake sediments reveal a marked increase in endosulfan accumulation from the 1980s onwards. Furthermore, unlike other 'legacy' OC pesticides, levels of α-endosulfan do not show a decline in atmospheric monitoring data, reflecting ongoing use of this pesticide in the northern hemisphere. Endosulfan is present at low concentrations (relative to the pesticide, lindane) in surface Arctic Ocean waters, with the atmosphere likely to be the major contemporary source. Residues of endosulfan have been detected in marine biota for different geographical regions of the Arctic, with higher bioaccumulation factors ($>10^3$–10^7) for zooplankton and various species of fish, compared to studies in warmer/temperate systems. Endosulfan is present in marine mammals, although there is uncertainty in the various Arctic biota datasets due to differences in analytical techniques. For some biota, biomagnification factors for α-endosulfan are >1, notably from fish to seal, although there is a wide variability in values between the same species for different regions of the Arctic. There is little if any evidence of trophic magnification of α-endosulfan in well-defined marine foodwebs, with some evidence of bio-dilution at higher trophic levels, presumably due to increased metabolism. Endosulfan does fulfil several of the criteria under the UNEP Stockholm Convention for designation as a persistent organic pollutant. The α- and β-isomer have similar physical–chemical properties and environmental behaviour to some of the obsolete organochlorine pesticides, although an assessment of their persistence and toxicity should be viewed alongside endosulfan sulfate, as 'Σendosulfan'. Persistence of 'Σendosulfan' coupled to ongoing use of endosulfan pesticides, will ensure continued long-range transport and contamination of remote environments.

1. Introduction

Endosulfan is an organochlorine (OC) pesticide that has widespread use in many parts of the world, including for example, the European Union, India, Indonesia, Australia, Canada, United States, Mexico and central America, Brazil and China (Ayres and Ayres, 2000; Botello et al., 2000; Herrmann, 2002; Laabs et al., 2002a,b; OSPAR, 2002; Shen et al., 2005). Endosulfan has been in use for ~5 decades and is effective against a broad number of insect pests and mites (Maier-Bode, 1968; Douthwaite, 1982; Herrmann, 2002; OSPAR, 2002; Roberts et al., 2003). As a result, this pesticide is applied to a wide number of crop types including cotton, cereals, fruit trees and plantation crops such as tea and coffee. However, due to its semi-volatility and relative persistence, endosulfan is a ubiquitous environmental contaminant

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☆ This paper is a contribution to the AMAP POPs assessment.
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occurring in many environmental compartments. Concentrations of endosulfan in air, soil, water and vegetation, have now been reported in a wide number of different environments, often well removed from the locations of direct application (e.g., Gregor, 1990; Gregor and Gummer, 1989; Bidleman et al., 1990, 1992; Simonich and Hites, 1995; Hargrave et al., 1997; Halsall et al., 1998; Braune et al., 1999; Garbarino et al., 2002; Carrera et al., 2002; Pozo et al., 2006; Usenko et al., 2007). Endosulfan is one of the most commonly detected pesticides in surface waters of the U.S. (38 states) (Siddique et al., 2003) and is one of the most abundant OC pesticides in air (Shen et al., 2005). Unlike other OC pesticides, long term monitoring of air around the Laurentian Great Lakes throughout the 1990s and 2000s did not reveal a declining trend in concentrations of endosulfan, presumably due to ongoing use of this pesticide (Buehler et al., 2004; Sun et al., 2006). Concern arises due to the ubiquitous occurrence of endosulfan, and the physical–chemical properties, which are analogous to those of the 'legacy' OC pesticides (e.g., Shen and Wania, 2005) now included in the Stockholm Convention on Persistent Organic Pollutants (POPs) (http://chm.pops.int/). Indeed, endosulfan is present in remote locations and therefore has a propensity to undergo long range transport, and is routinely detected in arctic air, being one of the most abundant pesticides after α- and γ-HCH in this environment (Halsall, 2004; Halsall et al., 1998).

Here we review the environmental occurrence, chemistry and fate of endosulfan and examine its environmental behaviour in relation to other OC pesticides with a focus on the Arctic. We also examine the propensity of this chemical and its major degradate, endosulfan sulfate, to undergo uptake in biota and review evidence for bioconcentration/bioaccumulation in Arctic marine foodwebs; suggesting areas where further research is needed and whether endosulfan meets criteria for designation as a persistent organic pollutant under the UNECE and UNEP Stockholm Convention.

2. Technical endosulfan

Technical grade endosulfan is commercially available as a mixture typically containing >95% of two diastereoisomers, known as α-endosulfan (or I) and β-endosulfan (or II) in ratios from 2:1 to 7:3 depending on the technical mixture (Herrmann, 2002). Market names include *Thiodan*®, *Endox*®, *Thiomul*®, *Beosit*®, *Endocell*®, *Malix*®, *Thionex*®, *Insecto*®, and *Tiovel*®. Fig. 1 displays the chemical structures of the two isomers and endosulfan sulfate. Endosulfan formulations include emulsifiable concentrate, wettable powder, smoke tablets and ultra-low volume liquid formulations, the latter often used under subtropical conditions to minimise volatilisation losses (Extoxnet, 1996). In temperate regions, the pesticide is typically applied to crops using air-blast or ground boom sprayers (e.g., see US-EPA, 2007a).

3. Consumption and use

Since its introduction as a broad spectrum insecticide in 1954 by Farbwerke Hoechst, Germany (Maier-Bode, 1968), endosulfan has become an important agrochemical and pest control agent resulting in its global use to control a range of insect pests for a number of diverse applications. Examples include endosulfan use in tropical countries for control of tsetse fly (Douthwaite, 1982; Fox and Matthiessen, 1982) and as an agent used in wood treatment (Extoxnet, 1996). Li and Macdonald (2005) have calculated the annual global production volume of endosulfan to be 12,800 tonnes (t), with India estimated to be the largest producer with six plants producing about 5400 tonnes/year (t/y) (Ayres and Ayres, 2000) with a total use of 113,000 t from 1958 to 2000, followed by the United States with 26,000 t from 1954 to 2000 (Li and Macdonald, 2005). In China, annual use is estimated to average 2800 t/y during the period 1998 to 2004 (Jia et al., 2009). The cumulative global use of endosulfan in agriculture was estimated to be 308,000 t (1950 to 2000) (Li and Macdonald, 2005). European consumption (based on sales data) decreased over the period 1995 to 1999, from 1028 t/y (1995) to 469 t/y (1999); a reduction of 54% (Ayres and Ayres, 2000). As a comparison, consumption of lindane (γ-HCH)—an OC pesticide with recent use in both Europe and North America—was >2000 t/y for Europe, in the period 1994–1996 (Breivik et al., 1999). Global use of endosulfan for the period 1996–2004 is displayed in Fig. 2. While endosulfan use appears to have declined in the northern hemisphere over this period, use in the southern hemisphere has increased (e.g., South America, Australia), maintaining an annual average global use of 12,450 t over the period 2000 to 2004 (Mackay and Arnold, 2005).

4. Physical–chemical properties of endosulfan

Table 1 summarises key physical–chemical properties for the two endosulfan isomers and endosulfan sulfate. The isomers of endosulfan are semi-volatile, with similar vapour pressures to other chlorinated pesticides, making them susceptible to volatilization to the atmosphere with subsequent atmospheric transport and deposition (e.g., Gregor and Gummer, 1989; Bidleman et al., 1992; Hoff et al., 1992; Burgoyne and Hites, 1993; Simonich and Hites, 1995; Halsall et al., 1998; Unsworth et al., 1999; Muir et al., 2004; Shen et al., 2005). For example, *p*,*p*′-DDE, the main metabolite of *p*,*p*′-DDT, and *cis*-chlordane have sub-cooled liquid vapour pressures (P_L) of 0.0034 Pa and 0.0073 Pa respectively at 25 °C (Shen and Wania, 2005). Where possible, the regression equations have been included in Table 1 to allow derivation of the respective property over a range of environmentally relevant temperatures. Parameters to allow calculations of temperature-dependent P_L values have been derived by Hinckley et al. (1990) for α- and β-endosulfan, endosulfan sulfate (as well as endosulfan ether and lactone). The vapour pressures of the α- and β-isomers are similar, while endosulfan sulfate is ~4-fold lower. Interestingly, the aqueous solubility of the β-isomer is markedly higher than the α-isomer (~10-fold) and as a result the β-isomer has a lower Henry's Law constants (H) and will therefore partition to aqueous phases more readily. A similarly low H could be considered for endosulfan sulfate, assuming this compound has an aqueous solubility akin to the β-isomer (see Table 1). Both the β-isomer and the sulfate are likely to experience relatively higher vapour scavenging from the atmosphere by precipitation than the α-isomer, and be more susceptible to vapour dissolution to surface waters (e.g., marine

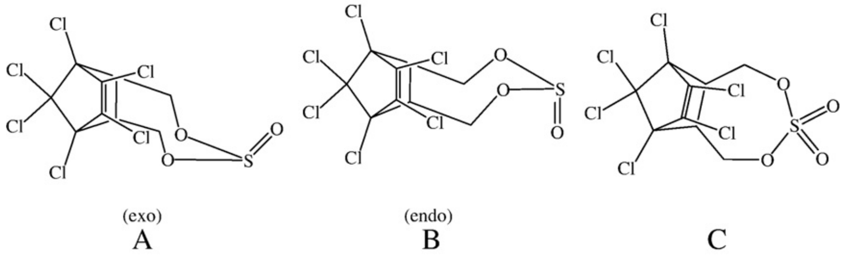

Fig. 1. Chemical structures of α-endosulfan (or I) (CAS: 959-98-8), (A); β-endosulfan (or II) (CAS: 33213-65-9) (B) and endosulfan sulfate (CAS: 1031-07-8) (C). CAS nomenclature for endosulfan: 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide.

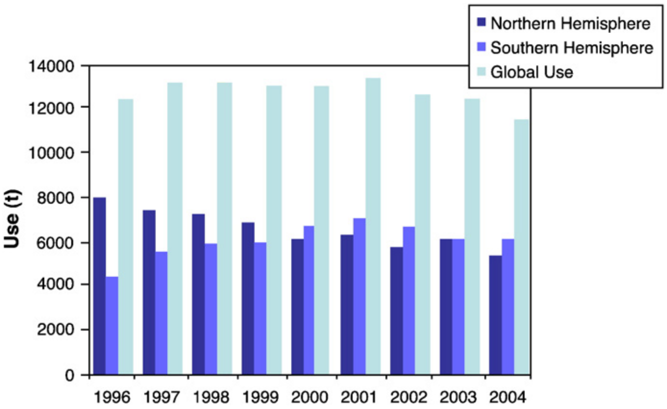

Fig. 2. Summary of global endosulfan use (Mackay and Arnold, 2005).

surface waters) during long range transport. Evidence of this for the β-isomer is available from precipitation samples collected in the Great Lakes region of Canada, where the average concentration of the β-isomer, for samples collected over the 1995–1999 period, was higher than the α-isomer. For example, at a site near Lake Erie (within a region of intensive agriculture) the average concentration of the β-isomer was 2.8 ng/L compared to 0.89 ng/L for the α-isomer. Near Lake Superior (the most remote site) the average concentrations were lower (0.39 (α) and 1.10 (β) ng/L), but still dominated by the β-isomer (Chan et al., 1994, 2003).

Empirically-derived Henry's law constants (H) were determined by Rice et al. (1997a,b) and more recently the temperature-dependent regressions have been derived by Cetin et al. (2006). Rice et al. (1997a,b) found a temperature dependency for α-endosulfan but could not establish a similar relationship for β-endosulfan. This was later confirmed by Cetin et al. (2006), who derived temperature-dependent regression parameters for H for both α- and β-endosulfan in pure water and saline solutions, respectively. In general, physical–chemical property data for endosulfan sulfate are lacking or have a high degree of uncertainty.

One of the criteria for designation of a chemical as a POP is that it has log $K_{OW} > 5$ (UNEP, 2001). Both endosulfan isomers do not exceed this value, but are close to it (Table 1), suggesting a potential for bioaccumulation. Evidence of bioconcentration and bioaccumulation is available from both laboratory and field studies (e.g., Douthwaite, 1982; Toledo and Jonsson, 1992; Jonsson and Toledo, 1993a; Aguilera-del Real et al., 1997; Harris et al., 2000; Pérez-Ruzafa et al., 2000; Amaraneni, 2002; Kelly and Gobas, 2003; Herrmann, 2002; OSPAR, 2002; Vidal et al., 2002; Wenzel et al., 2002; Hobbs et al., 2003; Klemens et al., 2003; de Mora et al., 2004; Miglioranza et al., 2004 (see Section 7.3)). The relatively high K_{OC} values indicate a propensity for partitioning to the organic carbon fraction in soils and sediments for both endosulfan isomers and the sulfate (Wan et al., 1995; Kathpal et al., 1997; Antonious et al., 1998; Leung et al., 1998; Guerin, 1999; Kammerbauer and Moncada, 1998; Kaur et al., 1998; Robinson and Mansingh, 1999; Ghadiri and Rose, 2001; Castro et al., 2002; González-Farias et al., 2002; Ismail et al., 2002; Laabs et al., 2002a; Lee et al., 2003), although wide ranges in empirical values make it difficult to choose an appropriate value for fate modelling. Shen and Wania (2005) derived physical–chemical property data for a set of OC compounds, including the endosulfan isomers. The authors evaluated and adjusted empirically-derived literature values to ensure internal thermodynamic consistency and their *final adjusted values* for P_L, S_L, H, K_{OW} and K_{OA} at 25 °C are provided in Table 1.

5. Behaviour and fate of endosulfan in the environment

5.1. Partitioning behaviour in the environment

In the atmosphere, endosulfan is found predominantly (>95%) in the gas phase (Burgoyne and Hites, 1993; Van Drooge et al., 2004; Sofuoglu et al., 2004), even at the colder temperatures encountered in the Arctic (Halsall et al., 1998; Hung et al., 2005). Once in the atmosphere, either through agricultural application or subsequent temperature-induced volatilisation, endosulfan is subject to atmospheric transport and deposition. To the authors' knowledge there are no published data on the gas phase degradation of endosulfan in the atmosphere (e.g., photochemical oxidation) but the range of half-lives through reaction with OH-radicals can be calculated as 3.5–1.3 days, assuming OH-radical concentration range of $0.5–1.5 \times 10^6$ molecules/cm^3 (AOPWIN v3.20, US-EPA, 2007b). In other words, endosulfan is relatively stable in the atmosphere with wet and dry deposition playing an important role in its removal. Wet deposition measurements for endosulfan, as part of current use pesticide (CUP) monitoring programmes across Canada, have been summarised by Tuduri et al. (2006) and more recently, endosulfan has been reported from a long-term record of CUP deposition measurements (1988–1999) across eastern Canada. In this extensive dataset, endosulfan was the most frequently detected compound alongside α- and γ-HCH, pentachlorophenol and atrazine.

Studies investigating air–water exchange of endosulfan are relatively few; although vapour dissolution and wet deposition is likely to be a significant source of endosulfan to large, fresh water

Table 1
Key physical–chemical properties for α-, β-endosulfan and endosulfan sulfate.

	α-endosulfan	β-endosulfan	endosulfan sulfate
MW (g/mol)	406.9	406.9	422.9
P_L (Pa)	0.0044[a]	0.0040[a]	0.0013 [b]
	$\log P = -4201/T + 11.87$[b]	$log\ P = -4306/T + 12.08$[b]	$log\ P = -4470/T + 12.11$[b]
S_L (mol/m^3)	0.0063 [a]	0.089 [a]	≈ 0.089 (as β-isomer)
H (Pa m^3/mol)	0.70 [a]	0.045 [a]	≈ 0.015
	$\mathrm{Ln}\ H = -4157/T + 13.7$[c]	$\mathrm{Ln}\ H = -3737/T + 9.6$[c]	$(H = P_L/S_L)$
Log K_{OW}	4.94 [a]	4.78 [a]	3.64 [d]
Log K_{OC}	3.6 [e] (4.48 [f])	4.3 [e] (4.32 [f])	3.18 [f]
Log K_{OA}	8.49 [a]	9.53 [a]	–
	Log $K_{OA} = 4333/T – 5.90$[g]	.	

[a] Shen and Wania (2005).
[b] Hinckley et al. (1990).
[c] Cetin et al. (2006) (H for saltwater also available).
[d] Estimated using KOWWIN V1.67 (US-EPA (2007b)).
[e] Peterson and Batley (1993).
[f] $K_{OC} = 0.35\ K_{OW}$ (see Seth et al. (1999)).
[g] Shoeib and Harner (2002).

lakes and ocean surfaces. Recently, air–water gas exchange of OC pesticides in Lake Taihu, China revealed that endosulfan is undergoing net deposition to the lake surface, in contrast to several of the 'legacy' OC pesticides which are undergoing net volatilisation from the lake surface either due to declining levels in the overlying atmosphere or from waste discharges into the lake from pesticide manufacturing plants (Qiu et al, 2008). Air–water exchange in marine environments has been examined in the Arctic (Hargrave et al., 1997; Weber et al., 2006—(see Section 7.2) and, more recently, in coastal waters of the eastern Mediterranean (Odabasi et al., 2008). In all cases endosulfan appears to be undergoing net deposition presumably due to the ongoing use and atmospheric transport of this chemical. However, derived fluxes, particularly for earlier studies, should be viewed with caution due to the uncertainty in the temperature-adjusted values of H. In the most recent study, the summer time deposition flux for Σendosulfan (Σ = α, β, -sulfate) in Izmir Bay, Turkey in the eastern Mediterranean, was 919 ± 624 ng/m^2/day, compared to an earlier (1993) derived flux of 0.5–1.3 ng/m^2/day in the ice-free waters of the Canadian Arctic Archipelago. An investigation of OC pesticides in the Lake Malawi area in southern Africa (Malawi) during 1997/98 (Karlsson et al., 2000) revealed concentrations of α-endosulfan in air to be much lower than those measured in southern Ontario (North American Great Lakes region) (factor of ~20), with concentrations in Lake Malawi ranging between <1 and 13 pg/L, even though endosulfan is used in this region. A net deposition flux to the lake surface was derived as 0.89 ng/m^2/day. The low levels measured in lake water and the correspondingly low fluxes probably reflect conditions in the tropics, where warmer temperatures promote chemical transformation (thereby removing α/β-endosulfan from the water column) as well as altering chemical dynamics in general, relative to temperate and polar regions. It is plausible that the tropics serve as both a source (e.g., higher temperatures promoting pesticide volatilisation) and regional sink for endosulfan (e.g., chemical degradation) (Karlsson et al., 2000). Emission sensitivity maps for endosulfan and other CUPs and POPs measured in air at Bjørnøya in the Norwegian arctic show source regions in northwestern Europe and eastern North America (Kallenborn et al., 2007) while Alert in northern Ellesmere Island has been shown to be almost equally affected by air from northern Canada, the Pacific region, eastern Russia, and the North Atlantic/Greenland (Hung et al., 2002).

Endosulfan appears to be mainly associated with sediments in freshwater systems. Peterson and Batley (1993) conducted partitioning and aquatic fate studies for endosulfan and demonstrated that a major proportion of endosulfan would associate with sediments over time, reflecting the relatively high K_{OC} values (log $K_{OC\alpha}$ 3.6; log $K_{OC\beta}$ 4.3, see Table 1), with a relatively higher enrichment in the sediment for the β-isomer. Zhang et al. (2003) reported similar partitioning for both isomers in the Minjiang river estuary (China), observing elevated concentrations of organochlorine pesticides (including endosulfan) in sediment pore water relative to the overlying water column. Several studies report an enrichment of β-endosulfan in sediment pore water compared to the α-isomer (González-Farias et al., 2002; Witter et al., 1999; Walse et al., 2002; Zhang et al., 2003), implying that the α-isomer has greater potential for aquatic transport. Remobilisation experiments conducted by Peterson and Batley (1993) indicated that α-endosulfan was more readily desorbed from sediments than the β-isomer with significant colloidal association for endosulfan sulfate (Peterson and Batley, 1993). Sorption to sediments, where α-isomer concentrations in the sediment were greater than the β-isomer, was reported by Mansingh et al. (2000) in several Jamaican rivers. However, the ratio of the two isomers in the sediments ('α/β') reflected technical-endosulfan and was probably related to recent use of the pesticide, rather than sediment–water partitioning over the longer term. It is useful to note that the α-isomer has a slightly higher K_{OW} value than the β-isomer (based on the final adjusted values derived by Shen and Wania (2005)—see Table 1), resulting in a higher K_{OC} value, if calculated directly from K_{OW}. However, the literature derived values for K_{OW}, before adjustment, were log 4.74 (α-) and log 4.78 (β-) (Shen and Wania, 2005), which would result in calculated K_{OC} values as $K_{OC\beta} > K_{OC\alpha}$.

A study conducted on the Namoi River, NSW Australia, revealed endosulfan sorption to bottom sediment to be higher on the larger size particle fractions (>63 µm diameter) compared to the finer size fractions (<24 µm), with implications for particle-bound transport as well as desorption following sediment re-suspension (Leonard et al., 2001). The authors noted that the larger size particle fraction may have different organic carbon and mineral composition than the finer particles, and possibly comprise an aggregate of finer particles accounting for the higher endosulfan concentrations. In a static laboratory test utilizing both spiked and 'native' sediments, a higher rate of desorption was found for the α-isomer, enhancing its bioavailability and resulting in the formation of endosulfan sulfate in the water column. It is plausible that significant partitioning to sediments may increase the aquatic lifetime of certain pesticides by suppressing the rate of hydrolysis and photochemical degradation (e.g. Macalady and Wolfe, 1985) This has been demonstrated for endosulfan in a seawater/sediment microcosom, where the half-lives of both isomers were significantly extended (α>β) compared to those observed in seawater (non-sterile) alone (Cotham and Bidleman, 1989).

Studies on air–soil and air–vegetation exchange have revealed a strong potential for re-volatilisation of endosulfan. For example, under sub-tropical conditions, volatilisation was found to be the main route of loss from surface soil (Kathpal et al., 1997) and volatilisation from temperate soil was found to be ~2-fold higher for α-endosulfan compared to β-endosulfan (Rice et al., 2002). In addition, it was found that laboratory tests can greatly underestimate the dissipation half-life in the field by a factor of up to 30 (Laabs et al., 2002b). Volatilisation of the technical endosulfan mix from plant surfaces has been found to be five times higher compared to volatilisation from soil, which implies that volatilisation from plant surfaces is likely to be an important source of endosulfan to the atmosphere following pesticide application (Ruedel, 1997). Overall, the α-isomer volatilises to a greater extent from both solid and aqueous surfaces compared to the β-isomer (Antonious et al., 1998). This, coupled to its predominance in the technical mixtures, and the possibility of β- to α-conversion in the environment (see next section), is likely to explain the dominance of the α-isomer in the background atmosphere.

5.2. Beta–alpha conversion

Significant conversion of the β-isomer to the α-isomer has been reported from a number of studies (Rice et al., 1997a; Schmidt et al., 2001, 1997; Walse et al., 2002) and the physical basis for irreversible conversion of the β-isomer to the α-isomer has been established (Schmidt et al., 2001), whereby physical-state transitions, such as volatilisation cause asymmetry in the β-isomer, increasing the potential for transformation to the α-isomer. Isomeric conversion (β- to α-) has been demonstrated to occur at the solid–water interface (Walse et al., 2002) as well as at the air–water interface (Rice et al., 1997a,b). Walse et al. (2003) report isomerisation from β-endosulfan to α-endosulfan to be favoured by a factor of three compared to the reverse process. A solely α to β conversion has been reported under field/crop conditions (Mukherjee and Gopal, 1994), but needs further confirmation as the α-isomer was converted in only minor quantities (~1% conversion). Rice et al. (1997a) found evidence of a positive correlation between the β to α conversion and temperature, with implications for a temporal and spatial effect on the conversion process in the wider environment. Moreover, the conversion process has to be taken into consideration when discussing the spatial distribution of the endosulfan isomers and additional work will be required before the environmental implications of isomer conversion are realised. The average ratio of environmental (air, water, soil, sediment, and vegetation) α- and β-endosulfan is 2.4, but with a range from ~1.5 to 27 (e.g., Bidleman et al., 1992; Simonich and Hites, 1995; Jantunen and Bidleman, 1998; Leung et al., 1998; McConnell et al., 1998; Robinson and Mansingh, 1999; Witter et al., 1999; Donald et al., 1999; Castillo et al., 2000; Mansingh et al., 2000; Pérez-Ruzafa et al., 2000; Menone et al., 2001; Vilanova et al., 2001; Carrera et al., 2002; Herrmann, 2002; Laabs et al., 2002a; Zhang et al., 2003; Weber et al., 2006). This wide range in ratios is likely to reflect: a) variations in the technical formulations of endosulfan; b) differing rates of isomer degradation; c) preferential sorption/partitioning and, possibly, d) β- to α-isomer conversion.

5.3. Degradation and formation of endosulfan sulfate

Endosulfan is subject to both biotic and abiotic degradation in the environment that may result in oxidation to the corresponding sulfate or hydrolysis in aquatic systems to endosulfan diol. In turn the diol may degrade further to endosulfan ether, endosulfan α-hydroxyether, or endosulfan lactone (Walse et al., 2003). The degradation of α- and β-endosulfan is shown schematically in Fig. 3 along with the transformation products arising from abiotic and biotic processes (Walse et al., 2002, 2003). Both endosulfan isomers were found to degrade twice as quickly in non-sterile sediments compared to sterile conditions indicating the importance of biotic degradation with endosulfan sulfate the only detectable metabolite (Navarro et al., 2000). Indeed, endosulfan sulfate represents the predominant residue in a variety of environmental media (e.g., Kathpal et al., 1997; Antonious et al., 1998; Navarro et al., 2000; Guerin, 2001; Laabs et al., 2002b; Walse et al., 2003). In aquatic systems, the α-isomer is converted more readily to endosulfan sulfate than the β-isomer (Leonard et al., 2001; Mukherjee and Gopal, 1994; Walse et al., 2003). For example, the stereo-selective oxidation of aqueous endosulfan results in a yield of endosulfan sulfate that is approximately 3-fold higher for α-endosulfan, indicating preferential metabolism over β-endosulfan (Walse et al., 2003), although oxidation of either α- or β-endosulfan to endosulfan sulfate was not observed under controlled sterile conditions (Walse et al., 2002). There are relatively few studies that have examined the persistence of endosulfan in soil under field conditions. Degradation rates strongly depend on the soil conditions (particularly soil water content and ambient temperature). For example, Ghadiri and Rose (2001) studying endosulfan degradation in an agricultural clay soil in western Queensland, Australia, found that degradation was greatly reduced at lower temperatures (20 °C, compared to 40 °C) and lower soil water content (15% compared to 40% or fully submerged). β-Endosulfan was observed to degrade more slowly than the α-isomer with the range of half-lives reported as: α-isomer 7–75 days; β-isomer 33–376 days. Similarly, endosulfan was found to have a long half-life of >200 days in a sub-tropical agricultural soil in northern India (Kathpal et al., 1997). Endosulfan sulfate has been identified as the main metabolite of endosulfan degradation in soil and sediments (Antonious and Byers, 1997; Ghadiri and Rose, 2001; Laabs et al., 2002b; Wan et al., 2005) and has also been observed on plant surfaces (Antonious et al., 1998). Endosulfan sulfate degrades at a slower rate, and hence is more persistent than the parent isomers, although it has been observed to have lower acute aquatic toxicity on select aquatic biota. For example, toxicity studies conducted on goldfish (*Carassius auratus*) and carp (*Leuciscus idus melanotus*) revealed 48-h LC_{50} values up to 100 µg/L for endosulfan sulfate, compared to values <10 µg/L for α-endosulfan (US-EPA, 2007c). In an assessment of endosulfan toxicity to a range of freshwater organisms representing various trophic levels in farm ditches in the Lower Fraser Valley of BC, Canada, Wan et al. (2005) found α-endosulfan to be the most toxic of the two isomers. However, more importantly, a combination of the α- and β-isomers and endosulfan sulfate appeared to be more potent than any single endosulfan isomer. The study concluded that the upper concentration ranges of endosulfan observed in Lower Fraser Valley farm ditches that drain into salmon streams often exceed the 96-h LC_{50} values of juvenile salmon and that concentrations measured in ditch sediments are likely to negatively affect the development and survival of benthic organisms.

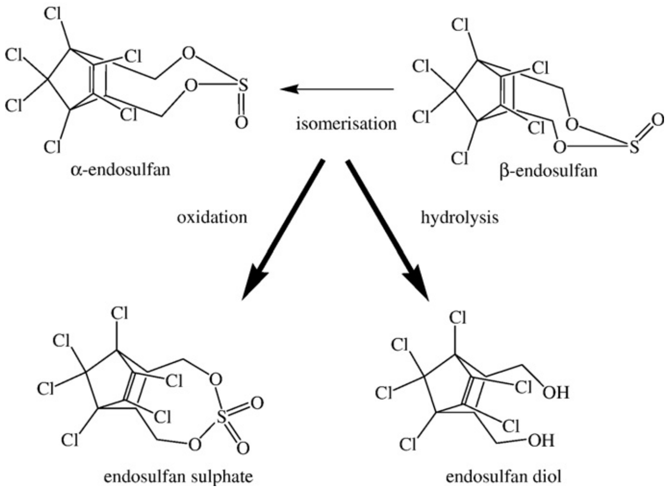

Fig. 3. Transformation pathways of α- and β-endosulfan in the environment.

Various studies that have observed the degradation of endosulfan in aqueous phases identified hydrolysis as the dominating abiotic degradation process (Peterson and Batley, 1993; Kaur et al., 1998; Guerin, 1999; Guerin, 2001; OSPAR, 2002; Walse et al., 2002), resulting in the formation of endosulfan diol as shown in Fig. 3. Kaur et al. (1998) found a positive correlation between hydrolysis rate (k_{hydro}) and pH, with base-driven hydrolysis a predominant degradation process in slightly alkaline waters. For example, Navarro et al. (2000), reported a higher rate of disappearance of endosulfan residues in seawater (pH 8.1) compared to pure water (pH 5.5–7), and found that endosulfan sulfate was the major degradate detected over time with its concentration in sediment higher than in water. In addition, Walse et al. (2002) found aqueous endosulfan sulfate to be stable compared to the α- and β-isomers. The same authors investigated the surface-catalysed transformation of aqueous (HCO_3^- buffered) endosulfan and found the rate constants to be higher for β-endosulfan compared to α-endosulfan, proposing that hydrolysis of endosulfan sorbed on surfaces differs from those in solution. Interestingly, Walse et al. (2002) also reported that photolysis with environmentally relevant UV-A light had no statistically significant effect on endosulfan degradation compared to duplicate experiments performed in the dark, indicating that direct photolysis is of little importance on the environmental fate of aqueous endosulfan. These studies, conducted under controlled conditions, do not necessarily mirror environmental conditions as the persistence of both isomers increases in the presence of humic acid and other dissolved constituents (Kaur et al., 1998). Furthermore, hydrolysis of endosulfan sulfate to endosulfan diol is markedly slower compared to the hydrolysis of α-endosulfan (OSPAR, 2002) (see Fig. 3).

For biotic (microbial) degradation, Guerin (1999) found extensive degradation of endosulfan (>85%) by indigenously mixed microbial populations under anaerobic conditions, but did not find significant enhancement of degradation from enriched inocula. These results demonstrate the biodegradation potential of α-endosulfan in low-oxygen containing environments such as sediments and this may have implications for interpreting historic accumulation trends of the α-isomer in freshwater sediments. Guerin (2001) revealed that degradation in aquatic systems also occurred at neutral pH in the absence of biological material or chemical catalysts, although endosulfan sulfate was not formed in aerated waters in the absence of microbial activity or strong chemical oxidants, suggesting that formation of sulfate was primarily due to biological oxidation. In a natural aerobic aquatic environment, endosulfan sulfate is likely to represent the predominant residue of technical-grade endosulfan over time (Guerin, 2001). Aquatic half-lives have been reported to be 23–27 h and 22–27 h for the α- and the β-isomer respectively, depending on the initial nominal concentration (Jonsson and Toledo, 1993b). These values are much lower than the persistence criteria designated for a POP (UNEP, 2001), (i.e. aqueous $t_{1/2}$ >2 months), although in the colder marine waters at high latitudes (i.e. Arctic Ocean) base-driven hydrolysis half-lives for endosulfan are likely to be greatly extended (e.g., several months), compared to warmer waters in temperate or tropical regions (e.g., hours to days).

6. Global distribution

Endosulfan is ubiquitous, and has been detected in a variety of environmental media across the globe, with the abundance of reported data on the order of α->β->-sulfate. Reviewing the global occurrence of endosulfan, data are categorised according to the following: *source*, where either production or direct application occurs; *regional*, with short to medium range transport as a transfer pathway; and *remote*, areas such as the Polar Regions requiring long-range transport processes. Here, the focus of this review is on the occurrence of endosulfan in regional and remote environments.

Prior to the large scale deployment of passive air samplers in the 2000s, endosulfan has been shown to exhibit widespread distribution in vegetation; displaying relatively high concentrations in tree bark samples collected from a large number of countries, with concentrations akin to the hexachlorocyclohexanes (HCHs) and *p,p′*-DDE (Simonich and Hites, 1995). The authors concluded that endosulfan (notably β-endosulfan) was, however, unlikely to undergo 'global distillation'—the preferential transfer and enrichment of more volatile compounds to higher latitudes—with levels observed in tree bark generally reflecting local or regional use of this pesticide (Simonich and Hites, 1995). Nonetheless, endosulfan (particularly the α-isomer) is susceptible to long-range atmospheric transport with detectable quantities (similar to other organochlorine pesticides) in air and water in remote regions. For example, endosulfan has been reported in remote mountainous regions (McConnell et al., 1998; Blais et al., 1998; Donald et al., 1999; LeNoir et al., 1999; Vilanova et al., 2001; Carrera et al., 2002; Van Drooge et al., 2004; Wilkinson et al., 2004) and in the Arctic (Gregor and Gummer, 1989; Gregor, 1990; Bidleman et al., 1990; Welch et al., 1991; Hargrave et al., 1997; Jantunen and Bidleman, 1998; Halsall et al., 1998; Braune et al., 1999; Garbarino et al., 2002; Hung et al., 2002; Weber et al., 2006).

Data for endosulfan in the southern hemisphere are limited to a smaller number of studies compared to the northern hemisphere, with a review of existing literature up to 1999 conducted by Connell et al. (1999). In essence, endosulfan concentrations in biota and freshwater sediments were reported to be lower than those of the DDTs and PCBs, with concentrations in biota found in the range of 10–1000 ng/g_{lipid} for 'background' locations, with higher concentrations in selected biota close to urbanized areas of Australia, South Africa and South America. More recently, passive air sampling conducted across a latitudinal transect in Chile has revealed α- and β-endosulfan concentrations in air that range from 4 to 101 pg/m^3 with the highest concentrations observed towards the north of the country (Pozo et al., 2004). Air mass back trajectories (i.e. the analysis conducted to determine the direction of air parcels) reveal that the northern regions may be a source of endosulfan to other parts of Chile. Endosulfan has contemporary use in Chile as well as in other parts of Central and South America, with the α-isomer detected in air sampled in western Antarctica, as part of a global passive air monitoring network (Pozo et al., 2006) (see next section).

6.1. Spatial and temporal distributions

As endosulfan is a CUP, it is one of the most abundant OC compounds in the atmosphere of continental North America (Shen and Wania, 2005), as well as in high mountain areas in North America (Blais et al., 1998; Shen et al., 2005) and central Europe (Carrera et al., 2002; Vilanova et al., 2001). The widespread deployment of passive air sampling devices in the 2000s (e.g. Global Atmospheric Passive Sampling (GAPS)) has confirmed the presence of endosulfan (principally the α-isomer) across the globe, with a wide range in reported concentrations (10 s to100s pg/m^3) (Pozo et al, 2006). Fig. 4 summarises the concentrations of endosulfan in air, alongside other OC pesticides measured during the same campaign. Very high concentrations (>1 ng/m^3) of endosulfan were observed at several sites in the Canary Isles and Argentina, presumably due to local pesticide use. In a separate survey, also using passive air samplers, Shen et al. (2005) reported a number of organochlorine pesticides, including α- and β-endosulfan, across the North American continent. Samplers were deployed along east–west and north–south transects with a number of sample sites located in Arctic Canada. The concentrations of the endosulfan isomers as well DDTs are presented in Fig. 5, and arise through the year-long deployment of the PAS devices during 2000/01. The time-integrated air concentrations (akin to the GAPS data above) provide useful geographical trends, and allow concentrations observed at remote sites (e.g., the Arctic) to be placed in context with temperate regions. From Fig. 5 the lowest endosulfan concentrations clearly occur at the Arctic sites, with much higher concentrations evident in Mexico and the western (British Columbia) and eastern (Prince Edward Island) fringes of Canada reflecting the agricultural use of endosulfan in these regions.

The occurrence and fate of OC pesticides in pristine mountain environments is of growing interest, due to their proximity to regions of intensive pesticide use (see Daly and Wania, 2005). Endosulfan has been detected in mountain air, snow/ice and aquatic systems (see above). Deposition measurements at high altitude remote lakes in the Pyrenees, Alps and Caledonian mountains, Norway, revealed the abundance of endosulfan at high altitude locations, with depositional fluxes ranging between 190 and 340 ng/m^2/month (similar to γ-HCH) at two of the sites in the Pyrenees and Alps, with a significant contribution by the β-isomer (Carrera et al., 2002). A correlation was evident between the isomer ratio and the degree of remoteness of the various upland lakes, marked by a relative rise in β-endosulfan with increasing distance to possible application sites. For the Norwegian site, the fluxes of α- and β-endosulfan were approximately three orders of magnitude lower, with only the more recalcitrant endosulfan sulfate present at this site. This spatial variation probably reflects the agricultural activities and use of endosulfan in southern Europe. A temporal pattern was also observed in this study with the highest fluxes measured during the summer months of June to August. This reflects the time of year when endosulfan is in use, but also when warmer summer temperatures promote volatilization of endosulfan from soils, vegetation and other surfaces (e.g., Burgoyne and Hites, 1993). Systematic air measurements conducted in earlier studies in southern Canada (Hoff et al., 1992) and the mid-west U.S. (Burgoyne and Hites, 1993) have revealed a notable summertime increase in vapour concentrations of α-endosulfan in air, and these studies have been confirmed by the regular summertime increases in endosulfan concentrations observed within the multi-year atmospheric datasets of the North American Great Lakes Integrated Atmospheric Deposition Network (IADN) (Sun et al., 2006). In sub-tropical regions seasonal weather patterns combined with regional endosulfan use can strongly affect concentrations of endosulfan in air. High concentrations of α-endosulfan were observed in Hong Kong and Guangzhou in southern China during the Asian winter monsoon, when air flow was predominantly from eastern China and regions where endosulfan is used on cotton fields (Li et al., 2007).

Donald et al. (1999) revealed historical accumulation of endosulfan within ice in a temperate glacier (Snow Dome Glacier) in the Canadian Rocky Mountains. Endosulfan was present in ice dated to the late 1950s, with a steep increase in concentrations from 1980

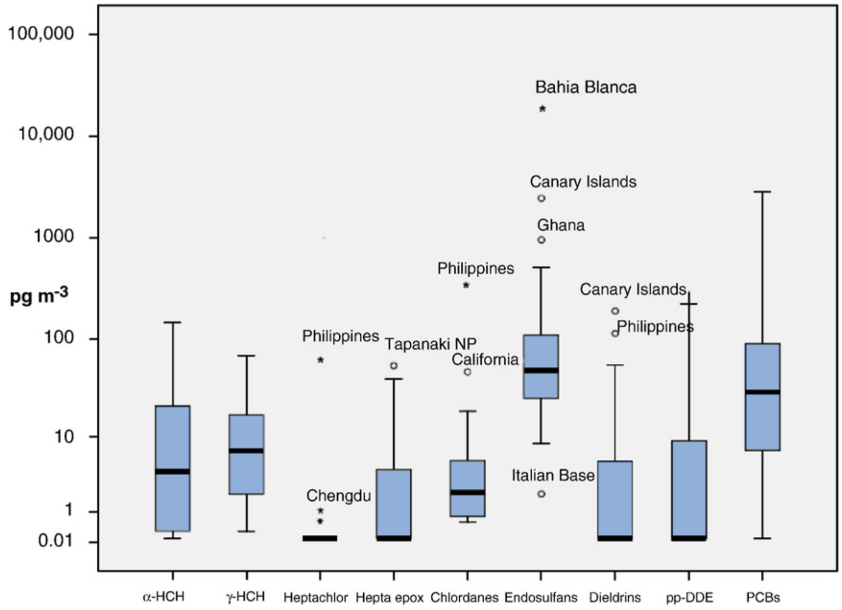

Fig. 4. Concentrations of Σendosulfan and other semi-volatile OC pesticides and PCBs in the global atmosphere, determined from the deployment of PUF-disk passive samplers in a global atmospheric passive sampler (GAPS) network (Pozo et al., 2006). Reproduced with kind permission of the American Chemical Society.

onwards to the early 1990s; the uppermost ice layer at the time of this study was dated as 1995. Endosulfan has also been measured in the snow pack and lake sediments at high altitude sites in several national parks in the western US (LeNoir et al., 1999; McConnell et al., 1998; Hageman et al., 2006, Usenko et al., 2007). Interestingly, Hageman et al. (2006) found that endosulfan concentrations in snow were strongly positively correlated to regional cropland intensity within 150 km of the parks (correlation coefficient >0.8), with regional atmospheric transport likely to account for the majority of endosulfan (>60%) present in the high altitude snowpack for those parks located closer to regions of high cropland intensity. The occurrence of endosulfan, particularly endosulfan sulfate, in lake sediments within Rocky Mountain National Park in the western US, has shown a steady increase in concentrations since the mid-1950s, reaching a maxima in surfacial sediments dated to 2003 (Usenko et al., 2007). Blais et al. (2001) estimated that seasonal glacial melt was a major source of OC pesticides to a subalpine lake in Alberta, Canada. For endosulfan, the contribution from glacial meltwater (in June) was approximately equivalent to the amount delivered by precipitation directly to the lake surface. Blais et al. (2001) suggest that warming associated with climate change will enhance the release of accumulated deposits of OC pesticides in glacial ice and this will further increase the loading of endosulfan to glacial-fed systems.

7. Occurrence in the Arctic

The Arctic has been subject to numerous studies on persistent organic pollutants and can be regarded as a 'sentinel' region with which to assess the persistence of chemical contaminants and their ability to undergo long-range transport. Furthermore, where systematic measurements have been conducted, datasets can be used to assess baseline trends of key contaminants and examine bioaccumulation in remote foodwebs. The following sections focus on the occurrence of endosulfan in different environmental compartments of the Arctic and examine evidence for its accumulation in several geographically-distinct marine foodwebs.

7.1. Air, snow and ice

α-endosulfan is one of the most abundant OC pesticide in the Arctic atmosphere after HCB and α/ γ-HCH, and is therefore susceptible to long-range atmospheric transport from source regions. Concentrations of α-endosulfan in the Arctic atmosphere average ~3–6 pg/m^3 (annual averages 1993–2005) compared to γ-HCH (lindane) which averaged ~4–16 pg/m^3 in the 1990s and 1.4–10 pg/m^3 in the 2000s (Hung et al., 2010—this issue). The highest averages were measured in the Yukon Territory, Canada at 8.3 pg/m^3. Table 2 provides a summary of average concentrations observed at nine Arctic sites (three of which are in Siberia) operated as part of the Canadian Northern Contaminants Program (NCP). Large spatial differences across the Arctic in endosulfan concentrations are not evident. β-endosulfan is only reported at Alert after 2002 with average concentrations of 0.10 to 0.17 pg/m^3 from 2002 to 2005. These values are lower than those reported from the Bering–Chukchi sea region during August/September 1993 which ranged between <0.27 and 1 pg/m^3 (Chernyak et al., 1996). The low levels of β-endosulfan in air are likely to be related to its higher aqueous solubility and lower *H* relative to the α-isomer (see Section 4 and Table 1) and hence the β-isomer is more likely to be removed from the atmosphere (through vapour dissolution into seawater and wet deposition). A seasonal pattern of α-endosulfan in the atmosphere, marked by elevated concentrations during the spring months of April/May and a later peak in October/November, has been observed at a number of stations including Alert and Dunai (located >70°N) and to a lesser extent Amderma and Tagish (<70°N). This seasonality termed the 'spring maximum event' (SME) is also apparent for other organochlorine pesticides, notably γ-HCH (Hung et al., 2005) and differs from temperate North American regions where the highest endosulfan concentrations occur during the summer months of July and August (see above). The seasonal pattern of α-endosulfan in Arctic air may be affected by enhanced transport from air to seawater during summertime when sea-ice coverage is reduced as Weber et al. (2006) have shown net deposition from air to the Arctic Ocean predominates (see Section 7.2 below). A comparison of α-endosulfan air concentrations measured at five Arctic stations, namely Alert, Kinngait, Little Fox Lake, Barrow and Valkarkai, between 2000 and 2003 have shown similar concentrations across the stations in November–May, but large spatial divergence in June–October. This reflects that the Arctic stations are affected by different source regions during the application season (S et al., 2008). Data from Alert (Canadian High Arctic) have been used to reveal longer term temporal trends of OC pesticides (e.g., Hung et al., 2002, 2010—this issue; Becker et al., 2008). The long-term trend of endosulfan—derived using Digital Filtration, a statistical time-

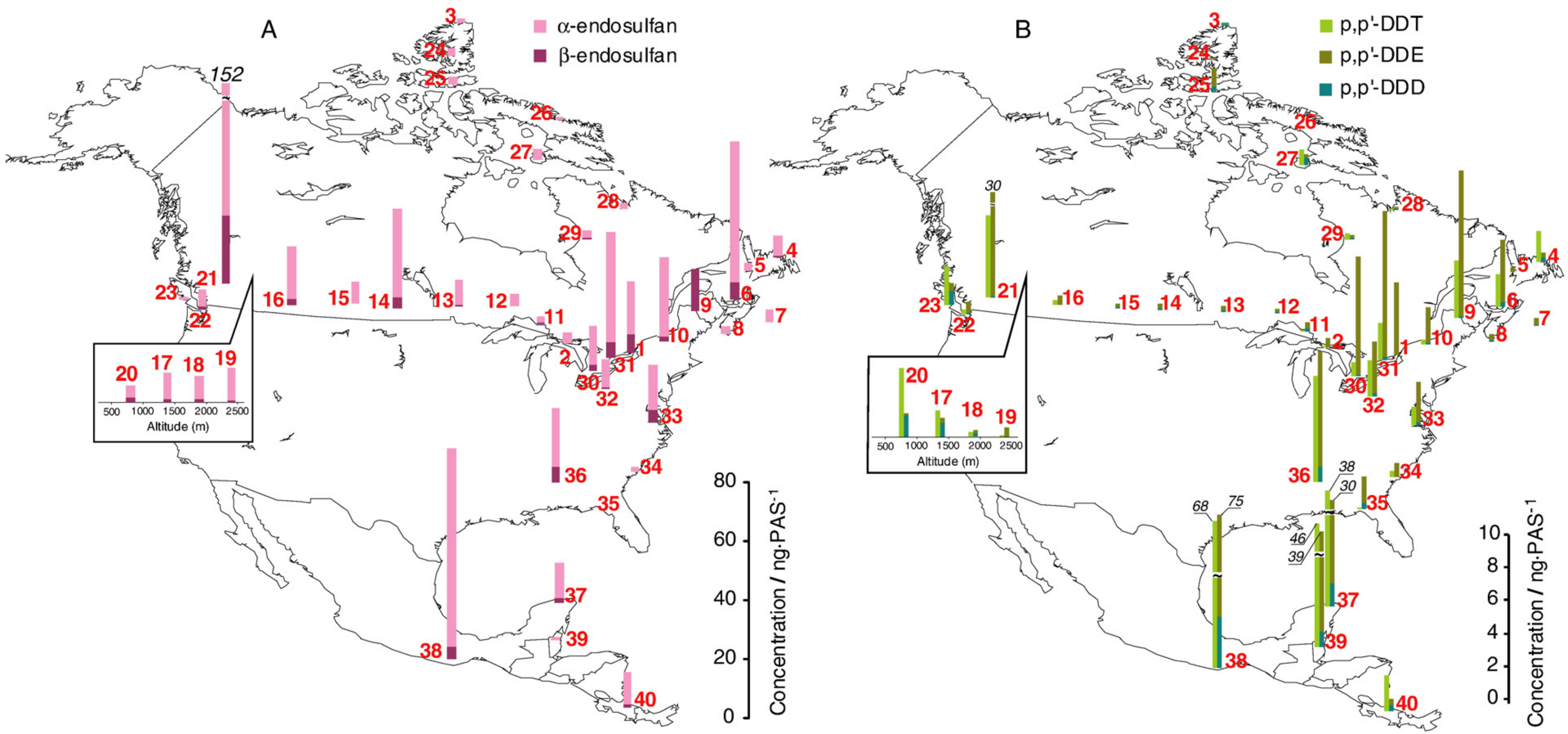

Fig. 5. Concentrations of α- and β-endosulfan (A) and DDTs (B) in XAD passive air samplers (PAS) across North America in 2000/01 (Shen et al., 2005). Reproduced with kind permission of the American Chemical Society.

Table 2
A summary of α-endosulfan and γ-HCH concentrations in air (pg/m^3) measured at the Canadian Northern Contaminant Program (NCP) monitoring stations in the Arctic (see Hung et al. (2009) review in this issue).

Sampling location	Sample years	α-endosulfan arith. mean (range)	γ-HCH arith. mean (range)
Alert, Nunavut, Canada	1993–05	4.49 (<0.01–16.5)	6.00 (0.14–59.2)
Tagish, Yukon, Canada	1993–95	5.82 (<0.06–15.3)	12.1 (0.18–138)
Dunai, E.Siberia	1993–94	2.99 (<0.05–7.18)	9.83 (3.68–22.7)
Amderma, W. Siberia	1999–00	3.66 (<0.03–13.2)	7.79 (0.78–24.24)

series model that filters out regular seasonal fluctuations to reveal the underlying trend—does not show a decline from 1993 to 2005, unlike other OC pesticides (e.g., γ-HCH and *p*,*p*′-DDT), presumably due to continued use of endosulfan in source regions (Hung et al., 2010—this issue).

There are only a limited number of published studies that report organochlorine pesticide concentrations in arctic snow and ice and these have been summarised by Herbert et al. (2006). In general, pesticide concentrations in snow (reported as mass of chemical per volume of snow meltwater) display a wide range which is attributable to a number of factors discussed by Herbert et al. (2006). A notable study, conducted in 1986, reported OC pesticides in snow, including γ-HCH and α-endosulfan, for 12 sample sites located across the Canadian Arctic Archipelago (Gregor and Gummer, 1989). Concentrations in snow for γ-HCH and α-endosulfan ranged from 0.22–4.46 to 0.09–1.09 ng/L respectively, with mean values across all the sites of 1.35 and 0.42 ng/L for γ-HCH and α-endosulfan respectively. More recent studies also report a wide range in concentrations, but there are fewer data available for endosulfan. Garbarino et al. (2002) detected α-endosulfan in snow sampled from coastal areas in northwest Alaska, although concentrations were below the limits of quantification (2 ng/L) due to the low volumes of extracted meltwater (2 L of meltwater compared to 10–50 L typically reported in other studies). To date, the majority of endosulfan snow data exist for northern Canada, where fresh snow samples were collected systematically (every two to four weeks) for several locations through the winter months of 1992–1995 (Strachan et al., unpublished data). A summary of concentrations for the endosulfan isomers and γ-HCH are presented in Table 3 for six Canadian sites sampled in 1994 and 1995 that cover a wide geographical area. In addition, concentrations are also included from recent studies conducted in the Norwegian Arctic, where surface glacial snow was sampled on Svalbard (Hermanson et al., 2005), and fresh snow was sampled near Tromsø on the Norwegian mainland (Herbert et al., 2005). In the latter study, snow extracts were re-analysed by GC-MS (NCI) for α- and β-endosulfan which had not been reported in the original study. Extracts were also bulked (by combining 5 separate snow sample extracts) and screened for endosulfan sulfate using an authentic standard. This compound was not detected in any of the snow samples or field blanks, although this may, in part, be due to loss of the sulfate during the sample clean-up steps of the analytical procedures.

Table 3
Arithmetic mean (SD) concentrations in snow (ng/L meltwater) measured at different locations within Arctic Canada and Norway.

Location	γ-HCH	α-endosulfan	β-endosulfan
Canada 1994/5[a]			
Alert	2.35 (2.02)	1.59 (1.33)	0.007 (0.007)[b]
Eureka	5.61 (1.75)	0.680 (0.378)	<0.001
Cape Dorset	0.675 (0.731)	0.503 (0.416)	0.009 (0.008)
Fraser River	0.258 (0.201)	0.310 (0.208)	0.009[c]
Snare River	0.371 (0.249)	0.252 (0.177)	0.011 (0.015)
Tagish	0.165 (0.120)	0.326 (0.154)	0.022 (0.042)
Norway 2000/03			
Svalbard[d]	0.169	0.136	0.037
Tromsø[e]	1.50 (0.335)	0.830[f]	<MDL[g]
Canada 2005/06			
Devon Island ice cap[h]	ND	0.040	ND

[a] Strachan et al. (unpublished data).

[b] Detected in only 5 samples ($n=5$).

[c] $n=2$.

[d] Hermanson (unpublished data), values for a surface snow layer.

[e] Re-analysis of surface snow extracts (for details see Herbert et al. (2005)).

[f] $n=3$ (relatively high method detection limits (MDL = 0.410 ng/L) resulted in the exclusion of most samples).

[g] β-isomer was below the method detection limits (MDL = 0.060 ng/L) for all samples.

[h] Muir and Zheng (2007); Muir et al. (2007).

In general, levels of α-endosulfan in surface snow are comparable to γ-HCH, which is in contrast to levels observed in arctic seawater, where α-endosulfan has much lower concentrations than those of γ-HCH This reflects the efficiency by which falling snow will remove semi-volatile contaminants from the atmosphere. Levels of α-endosulfan in arctic air are a factor of ~2 lower than γ-HCH; however, due to its lower vapour pressure, the tendency of α-endosulfan to partition to snow surfaces will be greater (see Lei and Wania, 2004) and is likely to account for the similar concentrations observed in fresh snow. It is worth noting however, that the studies selected in Table 3 represent relatively fresh snow, whereas the earlier Canadian study conducted by Gregor and Gummer (1989) (which reported higher concentrations of γ-HCH on average) sampled composite snow comprising older snow layers taken towards the end of the winter season. The presence of β-endosulfan in both Canadian and Norwegian surface snow confirms that the atmosphere is a potential source of this chemical to the Arctic, a noteworthy point in light of the scarcity of air measurements for this isomer.

Fig. 6 illustrates the range of concentrations of α-endosulfan and γ-HCH in snow for a selection of the Canadian studies taken from Table 3. The sites were chosen to reflect different latitudes, where Alert is the most northerly (82°N) and the Fraser River site as the most southerly (60°N). Fraser River, located in British Columbia, is the only site not located within the Canadian Arctic archipelago. The largest range in concentrations for both compounds was observed at the more

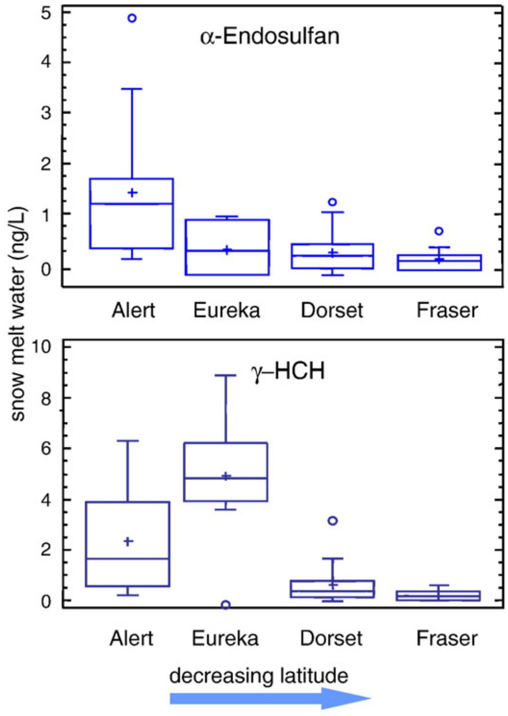

Fig. 6. Concentrations of α-endosulfan and γ-HCH measured systematically in surface snow collected at sites across northern Canada during the winter months of 1994/95 (Strachan et al., unpublished data).

northerly sites of Alert and Eureka. These sites experience the coldest annual air temperatures and yet displayed some of the highest concentrations. As wintertime concentrations in air do not vary significantly over the Canadian Arctic for both compounds, then temperature differences amongst these sites (where colder temperatures result in enhanced vapour scavenging by snow) is likely to account for the high concentrations at the two most northerly sites relative to the southerly sites that experience warmer air temperatures.

The relative loading of γ-HCH and α-endosulfan between these sites is dependent on the amount of snowfall. Alert has the lowest annual precipitation rate out of all of the sample sites (~150 mm water/year), and taking the average concentration of α-endosulfan in snow as 1.59 ng/L (Table 3), yields a flux of 239 ng/m^2/year. Cape Dorset, on the other hand, had an average concentration in snow some 3-fold lower at 0.503 ng/L; however, the precipitation rate is ~300 mm water/year, resulting in a flux of 151 ng/m^2/year, which is a factor of only 1.6 less than Alert.

The occurrence of endosulfan in glacial firn and ice has been observed in the Devon ice cap in the Canadian Arctic (Muir and Zheng, 2007) and a temperate glacier located in the Canadian Rockies (Donald et al., 1999) (see Section 6.1). In both studies, the concentrations of α-endosulfan were lower than in fresh snow and ranged between 0.01–0.09 ng/L. Muir and Zheng (2007) also found higher concentrations in fresh snow (0.04 ng/L; 2004–05) compared to a subsurface horizon representing the previous annual deposition (2003–04). The increase in concentrations in the most recent layers should not be interpreted as an upward trend in endosulfan deposition. This is because the concentrations do not take into account the difference between the rates of precipitation between the years; secondly, the concentrations are likely to decrease as further compaction takes place due to subsequent snow burial and conversion of snow to firn, whereby endosulfan loss may occur due to re-volatilisation An increasing trend for Σendosulfan in the Devon ice cap (based on samples from a dated snow pit) appears to be in keeping with the increased deposition observed in a temperate mountain glacier in the mid-1990s by Donald et al. (1999).

While there are a limited number of studies that report organochlorine pesticides in arctic snow, there are even fewer studies that have examined their subsequent release and transport in melt water during periods of seasonal thaw. A field study conducted in the Canadian Arctic (Amituk Lake, Cornwallis Island, Nunavut) provided snow and meltwater data that were utilised to develop a chemical snow model to simulate the behaviour of organic contaminants with snow ageing and melting (Wania et al., 1999). During snow melt, chemicals were found to follow an elution order, whereby those with relatively higher water solubility were released from the snowpack first. In the model simulation, this resulted in the release of α- and γ-HCH, followed by α-endosulfan and then other chemicals with progressively lower solubilities. While detailed field and laboratory investigations are required to verify model results, there is some evidence from combined field measurements and modelling that demonstrate that α-endosulfan input to Arctic freshwater lakes is strongly influenced by seasonal snowmelt. For example, a marked increase in α-endosulfan concentrations has been observed in Amituk Lake; coinciding with periods of meltwater input during early summer (Helm et al., 2002).

Muir et al. (2007) determined α-endosulfan and endosulfan sulfate in lake water and snow melt tributary water from Lake Hazen in northern Ellesmere Island and in Char Lake on Cornwallis Island in the Canadian Arctic. The results for α-endosulfan were compared to Amituk Lake in the 1990s reported by Helm et al. (2002) and presented in Table 4. Concentrations of α-endosulfan and endosulfan sulfate in open lake waters of Hazen and Char lakes were similar and in the sub-ng/L range. Endosulfan sulfate was found to be the major (detectable) endosulfan-related residue with concentrations about ten-fold higher than α-endosulfan. Tributary inputs for Lake Hazen, based on samples taken in early June 2004 and 2005 during the beginning of summer snow melt had 30-fold higher concentrations of α-endosulfan and 5-fold higher concentrations of endosulfan sulfate than lake waters.

Table 4
Endosulfan concentrations (ng/L) in Arctic lake waters [a] and tributaries (Helm et al., 2002; Muir et al., 2007).

Lake	Analyte	Year	Open lake	SD	Tributary	SD
Hazen[b]	α-endosulfan	2005	0.001	0.001	0.046	0.020
	Endosulfan sulfate	2005	0.019	0.006	0.091	0.065
	α-endosulfan	2004	0.001	0.001	0.027	0.006
Char[c]	α-endosulfan	2006	0.003	0.001		
	endosulfan sulfate	2006	0.032	0.006		
Amituk[d]	α-endosulfan	1993	0.045		0.137	
		1994	0.043		0.087	

[a] All analyses by GC-NIMS except for results reported by Helm et al. (2002).
[b] Samples collected in June 2004 and 2005 from open lake water (under ice) and from two tributaries (Muir et al., 2007).
[c] Samples collected in July 2006 from open lake waters.
[d] Results from Helm et al., 2002.

7.2. Endosulfan in arctic lake sediments

Endosulfan has been detected in sediments of remote, high-evation lakes (3024–3030 masl) in the western USA, mainly in the form of endosulfan sulfate (Usenko et al., 2007; Mast et al., 2007). Given the relatively high concentrations of endosulfan entering Arctic lakes (Table 4), the presence of endosulfan in sediments might be expected, however, only limited information is available. Stern et al. (2005a) observed only α-endosulfan in a dated sediment core from Lake DV09 on Devon Island in the Canadian Arctic Archipelago. The maximum concentration (0.04 ng/g dw) and flux (6.2 $\text{ng m}^{-2}\text{ yr}^{-1}$) were observed in the surface horizon and endosulfan was undetectable below horizons dated to 1988. The trend of increasing concentration in the 1990s observed by Stern et al. (2005a) is in general agreement with those from mountain lake sediments (Usenko et al., 2007).

7.3. Endosulfan in Arctic seawater and air–water exchange

Recently Weber et al. (2006) provided a review of existing data of endosulfan in surface waters of the Arctic Ocean. The data were obtained from seven, mainly ship-based, sampling campaigns conducted throughout the 1990s and early 2000s. Concentrations in both coastal seas and the open ocean were summarised and are illustrated in Fig. 7 along with γ-HCH to serve as a useful comparison. Surface seawater concentrations for α- and β-endosulfan ranged from <0.1–8.8 (mean 2.3) pg/L to 0.1–7.8 (mean 1.5) pg/L, while γ-HCH concentrations were ~100-fold higher than α-endosulfan, ranging between <0.70 and 894 (mean 250) pg/L. From these studies, both isomers of endosulfan were present in surface seawater largely in the dissolved phase, with the β-isomer showing a higher proportion in seawater relative to the atmosphere. Geographical distributions for α-endosulfan revealed the highest concentrations in the western Arctic, specifically in the Bering and Chukchi Seas with lowest levels towards the central Arctic Ocean. In contrast, γ-HCH revealed higher concentrations towards the central Arctic Ocean, as well as in the coastal regions near Barrow, Alaska and the White Sea in northwest Russia, respectively. A fugacity approach was taken to assess the net direction of air–water transfer of these two pesticides, using coupled concentrations in surface seawater and air. The air concentrations were selected from the closest Canadian NCP air monitoring sites to the relevant seawater study site and also for the relevant time period. For α-endosulfan, water–air fugacity ratios were all <1 indicating net deposition to all regions of the Arctic Ocean, with the lowest values (0.1–0.2) evident in the Canadian Archipelago. Given the uncertainty

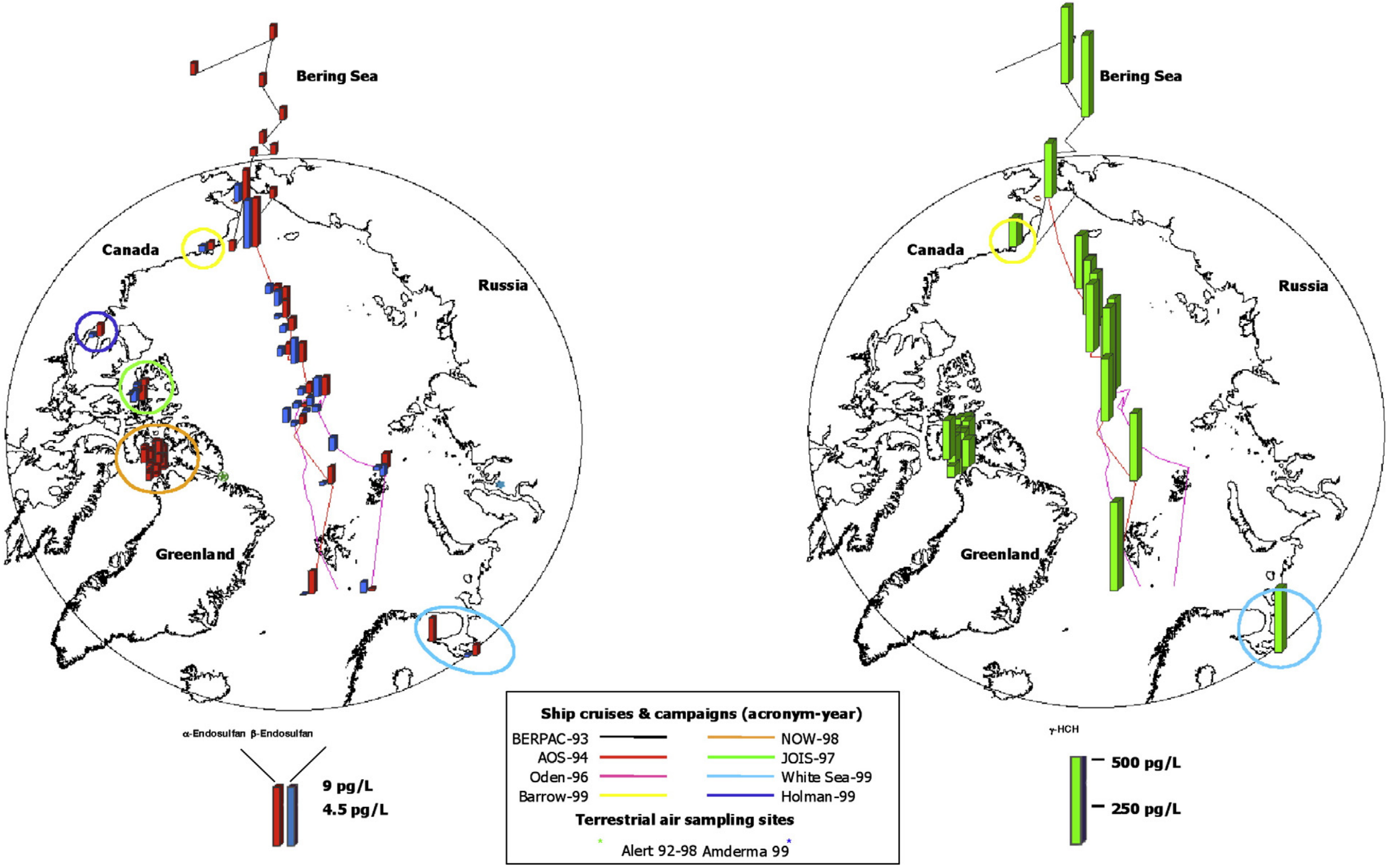

Fig. 7. Concentrations of α- and β-endosulfan and γ-HCH (pg/L) in surface waters of the Arctic Ocean obtained from mainly ship-based campaigns (legend) during the 1990s and 2000 (Weber et al., 2006). Reproduced with kind permission of the American Chemical Society.

in temperature adjusted *H* (factor ~10) utilised by Weber et al. (2006), it is plausible that equilibrium may have been reached for this compound in the western fringes of the Arctic Ocean where the highest concentrations in water were observed. Similarly, fugacity ratios for γ-HCH were generally <1 and in agreement with other separate studies, although like α-endosulfan, net deposition predominated over the Canadian Archipelago. In the central and eastern regions of the Arctic Ocean, as well as in the two coastal areas of this study, the fugacity ratios for γ-HCH where ~1 indicating equilibrium. The elevated concentrations in water and higher *FR*s in these coastal areas support the assessment that riverine/coastal sources are important for this chemical, but less so for α-endosulfan for which air to water transfer during the ice-free summer months is likely to be the major source to the Arctic Ocean. Given that levels of α-endosulfan were not declining in the Arctic atmosphere by the mid-2000s (based on the air monitoring data from Alert (Hung et al., 2010—this issue; S et al., 2008)), then it is likely that endosulfan is continuing to load into ice-free surface waters of the Arctic Ocean, with the atmosphere serving as the predominant contemporary source to the marine environment. Carroll et al. (2008) estimated that the major Russian rivers of the Ob and Yenisei provide ~8 kg/y of α-endosulfan into the Arctic Ocean. Assuming a similar discharge from rivers in the North American Arctic, then atmospheric deposition is likely to account for >85% of the α-endosulfan in the surface waters (10 m depth) of the entire Arctic Ocean. More recent studies of endosulfan in Arctic Ocean waters have confirmed earlier measurements and extended the times series for measurements in the Canadian Arctic Archipelago (Morris et al., 2008). Morris et al. (2008) reported α-endosulfan and endosulfan sulfate in Barrow Strait during icemelt in mid-June averaging 1.4 and 4.6 pg/L at 2 m depth and 0.2 and 1.9 pg/L at 10 m depth.

7.4. Biological uptake and occurrence in Arctic food webs

Unlike the systematic air sampling programmes for persistent organic pollutants (including OC pesticides) operated in Arctic Canada and Norway, the data for endosulfan in biota are derived from specific field campaigns from a number of different geographical regions, with limited data with which to assess temporal trends. Furthermore, unlike most of the abiotic data on endosulfan, the analytical methods vary among studies with the utilisation of both GC-ECD and GC-MS techniques for the analysis of biological samples. Use of the former, without confirmation mass spectrometry, has led to uncertainties in data quality through the possible mis-identification of chromatographic peaks with other, closely eluting analytes, such as the chlordanes. As part of larger contaminants databases with a focus on PCBs and other OC pesticides, endosulfan has been measured within a number of marine biota studies or data reviews conducted in Canada (Muir and Small, 2005; Kelly, 2005; Kelly et al., 2007; Stern and Ikonomou, 2003), Alaska (Bentzen et al., 2008), Greenland (Johansen et al., 2004a,b) and the Russian Arctic (Muir et al., 2003a). Data are available primarily for α- and β-endosulfan, and, to a much lesser extent, for endosulfan sulfate.

7.4.1. Measurement challenges for endosulfan in biota

The results in Table 5 illustrate the challenges of determining low levels of endosulfan isomers in fish and mammals. To assemble the information for the table, arctic char, ringed seal, and beluga sample extracts from studies described in Muir et al. (2003a,b) and Kwan et al. (2003) were analysed for α- and β-endosulfan by GC-ECD and by GC low-resolution negative chemical ionization MS (GC-NIMS) (Muir and Small, 2005). The GC-NIMS conditions for α- and β-endosulfan and endosulfan sulfate involved monitoring of ions, m/z 406 and 408, as well as m/z 372 and 374. These are the major fragment ions for endosulfan-related compounds under NIMS conditions. The arctic char, ringed seal and beluga extracts were prepared as described in detail in Johansen et al. (2004a). The results show that both isomers are subject to interference in the analysis by GC-ECD.

While GC-NIMS gave consistently lower concentrations than ECD in all three Arctic species which have α-endosulfan close to the method detection limit (MDL). Thus there is uncertainty for α-endosulfan in both methods although agreement between the two quantification methods is adequate for qualitative assessments. In the case of β-endosulfan there appear to be interferences particularly in the arctic char samples which yield false positives for this isomer by GC-ECD. Procedural blanks showed no inferring peaks. Because the interference occurs at m/z 406 under GC-NIMS conditions it is likely due to co-eluting chlordane or toxaphene components. Both total toxaphene and total chlordane related compounds are present in arctic char muscle samples at concentrations that are at least 10-fold higher than total endosulfan (Muir et al., 2006, 2008). Chlordane and toxaphene are also major contaminants in ringed seal and beluga blubber. Cis-chlordane co-elutes or partially co-elutes with α-endosulfan using a 30 m DB-5 column, typically used for GC separations of organochlorine compounds.

Kelly (2005) and Kelly et al. (2007) determined α-, β-endosulfan and endosulfan sulfate (Table 5) in ringed seal and beluga blubber samples by GC-high resolution MS (GC-HRMS) using the method of Rayne and Ikonomou (2003). The method detection limits for α-, β-endosulfan and -sulfate were 0.34, 0.30, and 0.085 ng/g wet weight for blubber by this method (Kelly, Fisheries and Oceans Canada, Sidney BC, pers. comm.). Procedural blanks had no endosulfan traces. Using GC-ECD, Kwan et al. (2003) determined α-, β-endosulfan in selected beluga blubber and Muir et al. (2000b) analysed endosulfan in ringed seal blubber samples from the same sample collections as those used by Kelly (2005). Thus it was possible to compare GC-ECD and GC-HRMS results for α- and β-endosulfan for a subset of the individual animals analysed by Kelly (2005) and Kelly et al. (2007).

The GC-HRMS results confirm the presence of all three endosulfan species in beluga and ringed seal (Tables 5 and 6). Agreement between GC-ECD and GC-HRMS for α-endosulfan in ringed seals was good (0.37 ± 0.38 ng/g vs. 0.45 ± 0.48 ng/g wet weight) and mean concentrations were similar to those for the central Canadian arctic (Table 5). On the other hand, β-endosulfan was higher by GC-HRMS than GC-ECD and also much higher than results found for central Canadian arctic ringed seals by GC-NIMS. Kelly (pers. comm.) noted that α- and β-endosulfan were quantified with GC-HRMS using a response factor for ^{13}C-trans-nonachlor because of interference from deuterated endosulfan. Thus it is possible that the β-endosulfan results are overestimated by this method.

Agreement between GC-ECD and GC-HRMS for endosulfan in beluga blubber was poor with much lower results for α-endosulfan by high-res MS (12 of 13 samples < MDL of 0.34 ng/g). This is in general agreement with the discrepancy of results for α-endosulfan by GC-ECD versus those by GC-NIMS in central Canadian Arctic ringed seals. As noted for seals, the GC-HRMS results for β-endosulfan in beluga were much higher than by GC-ECD and also higher than found in a sub-set of the same eastern Hudson Bay beluga samples that were analysed by GC-NIMS.

Endosulfan sulfate was consistently detectable in all samples, however, it represented a minor proportion of total endosulfan in ringed seal and beluga blubber samples (Table 6). Agreement between GC-HRMS and GC-NIMS for endosulfan sulfate in beluga blubber was poor with about 25-fold higher concentrations estimated by the HRMS method.

In summary, the analysis of samples by NIMS and HRMS shows that, while α-, β-endosulfan and -sulfate are present in Arctic biota, the use of GC-ECD significantly overestimated actual concentrations. The deviation between ECD and MS for α-endosulfan in ringed seals was last with ECD/MS ratio of 0.8 for eight Northern Quebec samples analysed by HRMS to a factor of 4 for twenty two central Arctic samples analysed by NIMS (Table 6). The deviation among 22 arctic char samples was 2-fold. While HRMS might be assumed to give the

Table 5
Analysis of arctic char (muscle), ringed seal and beluga samples for α- (α-ES) and β-endosulfan (β-ES) by GC-ECD and GC-MS.

Species location		N	α-ES	α-ES	β-ES	β-ES	Error or disagreement (ECD/MS[c])	
Instrumental method >>>			GC-ECD[a]	GC-NIMS[b]	GC-ECD[a]	GC-NIMS[b]	α-ES	β-ES
Arctic char	Resolute and Char Lakes	22	0.12 ± 0.09	0.06 ± 0.03	0.46 ± 0.55	0.003 ± 0.003	2	153
Ringed seal	Central Canadian arctic (Arctic Bay, Resolute, Gjoa Haven)	22	2.0 ± 3.2	0.47 ± 0.22	1.7 ± 2.1	0.21 ± 0.19	4	8
Beluga	Eastern Hudson Bay	4	4.0 ± 5.9	0.33 ± 0.14	6.5 ± 2.8	0.21 ± 0.14	12	31
Instrumental method >>>			GC-ECD[a]	GC-HRMS[d]	GC-ECD[a]	GC-HRMS[d]		
Ringed seal	Northern Quebec	8	0.37 ± 0.38	0.45 ± 0.48	0.88 ± 0.78	2.2 ± 3.3	0.8	0.4
Beluga	Eastern Hudson Bay	13	16.9 ± 12.3	<0.34	10.5 ± 11.0	8.0 ± 6.3	50	1.3

Concentrations are ng/g wet weight.

[a] GC-ECD—Gas Chromatography–Electron Capture Detection.

[b] GC-NIMS (Gas Chromatography–Negative Ion Mass Spectrometry) results for arctic char quantified using m/z 406 and 408 for α-and β-endosulfan and m/z 386/388 for endosulfan sulfate. Results for seal and beluga blubber using m/z 372 and 374. GC-ECD results from Muir et al. (2003a,b).

[c] ECD/MS—(Gas Chromatography)–Electron Capture Detector/Mass Spectrometry.

[d] GC-HRMS (Gas Chromatography/High Resolution Mass Spectrometry (electron impact (EI) mode)) results for seal and beluga from Kelly (2005) following methodology of Rayne and Ikonomou (2003). α- and β-endosulfan were quantified using response factor for trans-nonachlor because of interference from deuterated endosulfan. GC-ECD results from Muir et al. (2000b) and Kwan et al. (2003) for the same samples.

most accurate results because of millimass resolution, higher MDLs and interference from deuterated internal standards may have compromised some of these data particularly for β-endosulfan. As a result of these apparent inaccuracies we have focused mainly on results that have been confirmed by GC-MS in discussions of bioaccumulation and biomagnificaiton.

7.4.2. Evidence of bioaccumulation and biomagnification

In view of the uncertainties with endosulfan measurements in biota the estimation of bioaccumulation factors (BAFs) and biomagnification factors (BMFs) was limited to endosulfan results determined by GC-MS. BAFs for α-endosulfan were estimated using concentrations measured by GC-MS in Arctic char, salmon, arctic cod, ringed seals and beluga (Table 5) coupled with concentrations measured in seawater or lake water (char). These are presented in Table 7 on wet weight and lipid weight ($\mathrm{BAF}_{\mathrm{lw}}$) basis. $\mathrm{BAF}_{\mathrm{lw}}$ values for total (©) endosulfan ranged from 2.21×10^4 to 6.76×10^5 with the highest values for the marine mammals. Wet weight BAF (ww) values for Σendosulfan in char, cod, and salmon ranged from 1690 to 7280. Given the uncertainty of endosulfan measurements at low levels in biota discussed above and the possible spatial and temporal variation in water concentrations of endosulfan species, these BAFs should be viewed with caution. A previous study (Muir and Small, 2005) focused only on $\mathrm{BAF}_{\mathrm{ww}}$s for α-endosulfan which are generally higher than the POPs criteria of 5000 for bioconcentration factor (BCF) or $\mathrm{BAF}_{\mathrm{ww}}$ in aquatic species (UNEP, 2001), by 10 to 100-fold. However, it is more appropriate to evaluate the BAFs based on the Σendosulfan concentrations since some of the body burden could be due to biotransformation to endosulfan sulfate. The average $\mathrm{BAF}_{\mathrm{ww}}$s for Σendosulfan in 3 species of fish (4080) do not exceed the 5000 criteria, however, BAFs for Σendosulfan based on concentrations in beluga and ringed seal blubber (where $\mathrm{BAF}_{\mathrm{lw}} = \mathrm{BAF}_{\mathrm{ww}}$) averaged 3.95×10^5. These elevated BAFs are mainly due to high β-endosulfan reported by Kelly (2005).

Table 6
Comparison of range of endosulfan sulfate concentrations in blubber samples (ng/g wet weight) by 3 methods: GC-ECD, GC-negative ion MS and GC-high resolution MS.

Species	Location	Instrumental method			
		N	ECD	GC-NIMS[a]	GC-HRMS[b]
Ringed seal	Central Canadian Arctic	22	–	<0.01–0.09	
Ringed seal	Northern Québec and Labrador[b]	10	–	–	<0.1–0.44
Beluga	Eastern Hudson Bay[c]	14	1.0–8.5	0.01–0.05	–
Beluga	Eastern Hudson Bay[b]	28	–	–	<0.1–2.1
Beluga	Eastern Hudson Bay (Sanikiluaq)[d]	20	34–61	–	–

Results are ranges reported in various studies.

[a] GC-NIMS data for ringed seals and beluga from Muir and Small (2005).

[b] All GC-HRMS data from Kelly (2005) and Kelly et al. (2007). Instrumental detection limit assumed to be 0.1 ng/g for HRMS analyses.

[c] Unpublished data cited by Muir and Small (2005).

[d] Stern et al. (2005b); ng/g lipid weight.

There are numerous studies that have examined endosulfan accumulation in aquatic organisms in laboratory-based studies; some of these earlier studies are presented in Table 8. Data from field studies in temperate regions are also available; for example, DeLorenzo et al. (2002) reported bioconcentration factors (BCF) for freshwater green algae (*Pseudokirchneriella subcapitatum*) and freshwater water flea (*Daphnia magna*) of 2682 and 3278, respectively, with little evidence of bioaccumulation between phytoplankton and zooplankton. In contrast, endosulfan residues in farmed snakehead and carp fish (*Channa striata* and *Catla catla*), from a region in India with intensive agricultural activities, revealed much higher high BAFs of log 4.5 (±0.45) (Amaraneni, 2002).

Table 7 provides BMFs in selected predator/prey species based on results from Kelly (2005) and Kelly et al. (2007) as these were the only published data for endosulfan in marine mammals based on GC-MS analysis. BMFs >1 were apparent for Σendosulfan for beluga (*Delphinapterus leucas*) preying on arctic cod (*Arctogadus glacialus*) and on salmon (*Salmo* sp.), resulting in an overall mean BMF of 1.5 for fish to marine mammals. For land based food webs only modelled data are available. Kelly and Gobas (2003) reported BMFs of β-endosulfan in wolf (*Canis lupus*) ranging from 5.3 to 39.8 (lipid normalised) depending on the age of the wolf. However neither this latter study nor Kelly et al. (2007) actually measured endosulfan in the lichen, caribou and wolf food chain.

7.4.3. Geographical and temporal trends in marine mammals

Extensive datasets are available for endosulfan in minke whales (*Balaenoptera acutorostrata*), beluga whales (*D. leucas*) (Stern et al., 2005b) and polar bears (*Urus maritimus*) (Bentzen et al., 2008), as well as for a wide range of biota collected as part of the Greenland diet survey (Johansen et al., 2004a,b). The endosulfan results in these studies were also obtained with GC-ECD only and are therefore subject to the same analytical uncertainties as discussed before. However, the results are discussed here because of the internal consistency of the data and, in some cases, reasonable agreement with GC-MS data for the same species. Hobbs et al. (2003) measured α-

Table 7
Accumulation of endosulfan in Arctic aquatic biota.[1]

Sample type	Location	Year	α-endo	β-endo	-sulfate	Σ-endo
Seawater (pg/L)[2]	Arctic Ocean	1993–99	2.3	1.5	6.9	10.7
Lake water (pg/L)	Char Lake	2006	2.8	1.5	31.6	35.9
Lake water (pg/L)	Hazen Lake	2005	1.4	0.7	18.9	20.9
BAFs (wet weight)						
Arctic char	Char + Hazen	2005–06	11,050	367	990	1690
Salmon	E. Hudson Bay	1999–02	9640	30,660	1410	7280
Arctic cod	E. Hudson Bay	1999–02	487	21,728	162	3260
BAFs (lipid weight)[3]						
Salmon (whole)	East Hudson Bay	1999–02	1.87×10^5	7.22×10^5	2.74×10^4	1.45×10^5
Arctic cod (whole)	East Hudson Bay	1999–02	4.57×10^4	2.47×10^6	1.52×10^4	3.13×10^5
Beluga blubber (♂)	East Hudson Bay	1999–02	4.57×10^4	1.07×10^7	1.31×10^5	6.76×10^5
Beluga blubber (♀)	East Hudson Bay	1999–02	4.57×10^4	4.14×10^6	8.83×10^4	5.65×10^5
Ringed seal blubber (♂)	East Hudson Bay	1999–02	4.57×10^4	1.92×10^6	4.87×10^4	2.21×10^5
Ringed seal blubber (♂, ♀)	East Hudson Bay	1999–02	1.25×10^5	1.18×10^6	2.05×10^4	2.41×10^5
Arctic char (muscle)	Char Lake	2007	1.86×10^5	5.93×10^3	1.71×10^4	2.98×10^4
Arctic char (muscle)	Hazen Lake	2007	2.45×10^5	1.34×10^4	2.08×10^4	3.52×10^4
BMFs						
Cod to beluga	East Hudson Bay		1.0	4.3	8.6	2.2
Cod to seals	East Hudson Bay		2.7	0.48	1.3	0.77
Salmon to beluga	East Hudson Bay		0.24	2.7	1.8	1.5

[1] Results for eastern Hudson Bay from Kelly (2005); Kelly et al. (2007); results for Char Lake and Hazen Lake from Muir et al. (2007); [2] Seawater concentrations represent Arctic Ocean average from Weber et al. (2006); value for endosulfan sulfate estimated based on results from Morris et al. (2008); [3] Non-detect α-endosulfan (≤0.1 ng/g lipid wt) in arctic cod, beluga blubber and male ringed seals.

endosulfan in blubber of minke whales from the North Atlantic as part of a study in which the pattern of OC pesticides and PCBs was used to identify whales from specific regions. α-endosulfan concentrations were significantly higher in whales from the North Sea than those from all other locations and minkes from the Barents Sea exhibited higher α-endosulfan concentrations than those from Jan Mayen and west Greenland. This pattern is plausible since the North Sea and waters near Norway would be expected to have higher endosulfan concentrations based on atmospheric deposition and riverine inputs.

Bentzen et al. (2008) reported α- and β-endosulfan in the fat and blood of a large number of polar bear samples ($N=57$) from the southern Beaufort Sea. Concentrations of both α- and β-endosulfan averaged 4 ng/g (lipid weight) in subcutaneous adipose tissue of polar bears from three Alaskan Beaufort Sea coast locations (Barrow, Endecott, and Katovik). Average concentrations of α- and β-endosulfan (geometric means) were not significantly different among locations (Bentzen, unpublished data). Concentations of α-endosulfan were significantly higher in females than in males (Bentzen, unpublished data), as observed for total chlordane related compounds (Bentzen et al., 2008), while no differences between the sexes were found for β-endosulfan. Possible false positive results for both α- and β-endosulfan due to chlordane interference cannot be completely ruled out.

Stern et al. (2005) reported endosulfan sulfate in male beluga blubber samples collected between 1993 and 2001 from 11 sites in the Canadian Arctic, ranging from 3.7 to 94 ng/g (lipid weight). Stern et al. (2005) used GC-ECD for the analysis of endosulfan. They did not report α- and β-endosulfan. Higher endosulfan sulfate concentrations were found in male belugas sampled in Lancaster Sound and Jones Sound in the Canadian Arctic archipelago (range 28–94 ng/g) compared to southeastern Baffin Island (Cumberland Sound, Frobisher Bay) of 8.1–23 ng/g. Endosulfan sulfate concentrations for male belugas from eastern Hudson Bay (Sanikiluaq; $N=20$) ranged from 33 to 69 ng/g (lipid weight) while Kelly et al. (2007) reported concentrations ranging from 0.17 to 2.1 ng/g in blubber of male belugas ($N=9$) sampled at the nearby eastern Hudson Bay community of Umiujaq. As noted in the earlier discussion of analytical challenges there is poor agreement between the three detection techniques that have been used (GC-ECD, GC-NIMS, and GC-HRMS) for beluga and ringed seal blubber samples. While it seems likely that the endosulfan sulfate results in beluga determined by GC-ECD are confounded by interferences, further comparisons are needed to confirm the extent of the discrepancy since GC-NIMS and GC-HRMS results are also not in good agreement (Table 6).

Table 8
Examples of bioconcentration factors (BCF) for endosulfan determined in laboratory studies for representative aquatic species.

Compound	Organism	BCF	Reference
α-endosulfan	"Fish"	2006–10,994	Jonsson and Toledo, 1993a; Toledo and Jonsson, 1992
β-endosulfan	"Fish"	1398–9908	Jonsson and Toledo, 1993a; Toledo and Jonsson, 1992
Technical mix	"Phytoplankton"	770–2682	DeLorenzo et al., 2002; Rao and Lal, 1987
Technical mix	"Zooplankton"	3278	DeLorenzo et al., 2002

The Greenland diet study (Johansen et al., 2004a) is the most extensive Arctic dataset for endosulfan in terms of species and tissue analysed. However, age, sex and other biological characteristics of the biota were not available because the objective of the study was to develop a database for assessing human exposure (Johansen et al., 2004b). As with other studies that include top predator mammals there is potential for false positive results for α- and β-endosulfan. Johansen et al. (2004a) did not determine endosulfan sulfate. A review of the original data for this study showed no co-elution of α-endosulfan with cis-chlordane, which is a major problem with data for ringed seals and beluga (Muir and Small 2005). In Fig. 8, geometric mean concentrations of Σ parent endosulfan are arranged by increasing concentration in fat, kidney, liver and muscle. Highest concentrations of α- and β-endosulfan were found in narwhal (*Monodon monoceros*) skin, blubber, and other fats. Harp seal (*Phoca groenlandica*) blubber also had detectable amounts as did ringed seal. The non-detect concentrations of endosulfan in beluga blubber are in general agreement with other analyses of beluga blubber by GC-MS (Kelly 2005; Kelly et al., 2007). Much lower (wet weight) concentrations were found in livers (fish, mammals, and birds) and lower still in muscle samples (Fig. 8). Muir and Small (2005) argue that the results

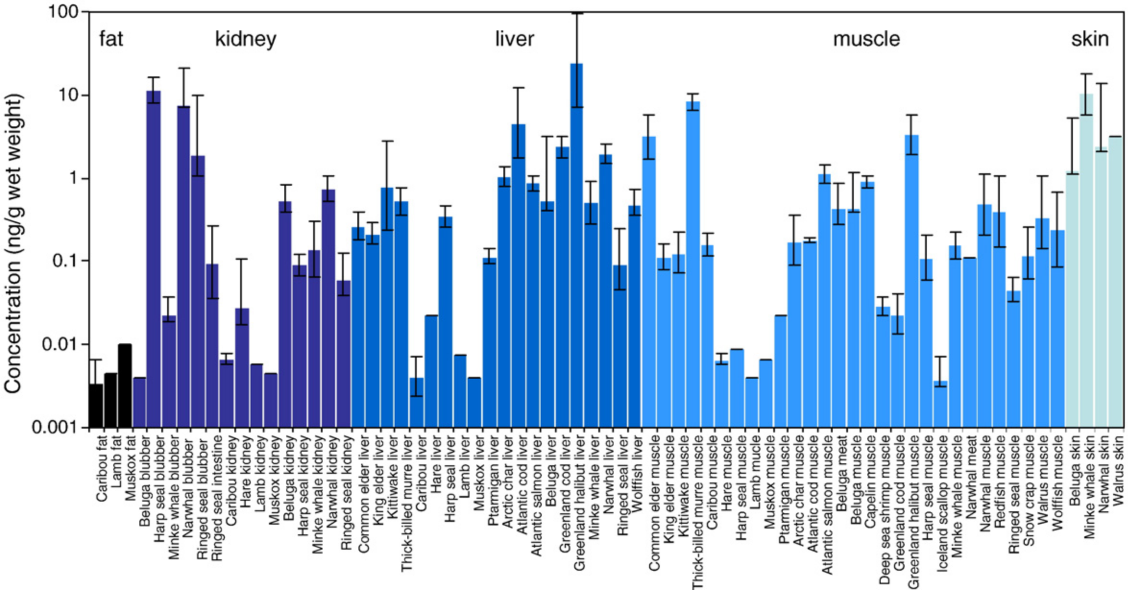

Fig. 8. Geometric mean concentrations (±95% confidence limits) of total endosulfan (sum α- and β-endosulfan) in tissue of key human diet species surveyed in Greenland (see Johansen et al., 2004b). Results below 0.01 ng/g are<MDL. Based on assessment of the results by Muir and Small (2005).

for α-endosulfan in the Greenland samples, although unconfirmed by GC-MS, show a plausible internal consistency with generally highest amounts in fat and liver of top predators e.g., narwhal, beluga, ringed and harp seals, Greenland halibut (*Reinhardtius hippoglossoides*) and Atlantic cod (*Gadus morhua*). Endosulfan was also detectable in seabird livers and muscle, e.g., in thick-billed murre (*Uria lomvia*). There are only limited data for endosulfan in Arctic seabirds. Kelly (2005) detected α-endosulfan in liver of eider ducks (*Somateria mollissima*) from eastern Hudson Bay and endosulfan sulfate in whitewing scoters (*Melanitta fusca*).

Using data from the Greenland diet survey, Small and Solomon (2005) examined the range of exposure concentrations reported in the various marine and terrestrial wildlife species and compared them to diet-based no observed adverse-effect concentrations (NOAEC) for the rat and the grey partridge (based on a 2-yr chronic feeding study (see US-EPA, 2009) as representative mammalian and avian species, respectively. The data are presented in Fig. 9. The upper ranges of Σendosulfan concentrations in biota (wet weight) do not exceed the maximum permissible concentrations (MPC) of endosulfan in the food of both ‘mammals’ and ‘birds’ (combined), calculated as 680 µg/kg-‘food’ (van der Plassche, 1994—cited in OSPAR, 2002). It is also apparent that the upper ranges of the measured endosulfan concentrations in the biota are considerably lower than the NOAEC for the two surrogate species (30,000 µg/kg for the partridge and 15,000 µg/kg for the rat) This suggests that risks from endosulfan exposures in the species in which concentrations were measured are *de minimus*, although the residue data reported in Fig. 9 do not include endosulfan sulfate.

Utilizing the datasets for endosulfan concentrations in Arctic seawater and Greenland biota, Small and Solomon (2005) adopted a stochastic approach to undertake a risk assessment for endosulfan and concluded that the risk of chronic or acute toxic effects to marine mammals and terrestrial wildlife from endosulfan exposure was negligible. Similarly, human dietary risk, based on the biota foodstuff survey in Greenland, was found to be generally negligible, even with the addition of endosulfan residues in imported food. However, in an extreme worst case scenario, an individual could be at risk if there was a heavy reliance upon locally-sourced food items, particularly marine mammals and fish that possessed endosulfan residues at the upper 99th percentile of the concentration distribution (e.g., 10–100 ng/g wet weight). Although endosulfan sulfate was not measured in the Greenland diet study—if it is assumed to be present at similar levels to Σendosulfan (α- and β-isomers) then this would double the exposure. However, due to the order of magnitude difference between the NOAECs for chronic effects and observed concentrations then the overall conclusion would not change. Furthermore, given the uncertainties in quantitative analysis of endosulfan

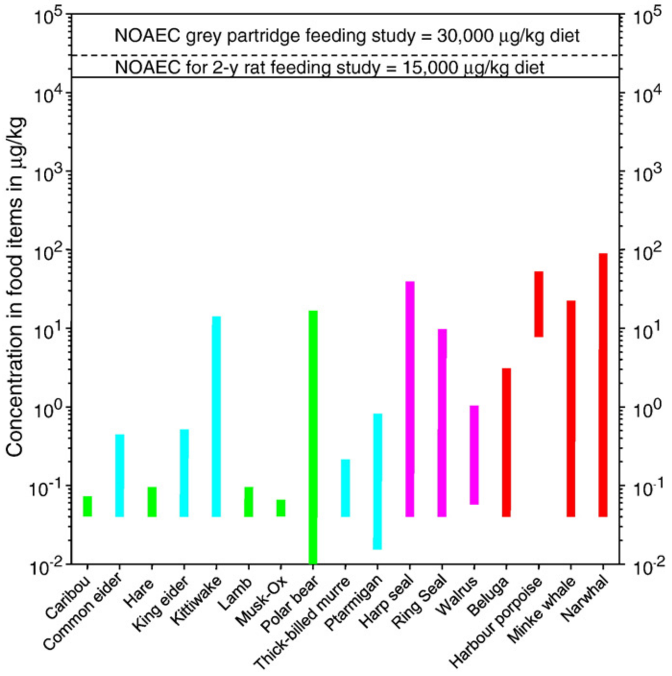

Fig. 9. Range of exposure concentrations of Σ-endosulfan (α- and β-endosulfan) measured in various tissues of polar marine mammals, seabirds and terrestrial birds as compared to no-observed-adverse-effect-concentrations in the diet (NOAECs) in selected avian and mammalian test species (modified from Small and Solomon, 2005).

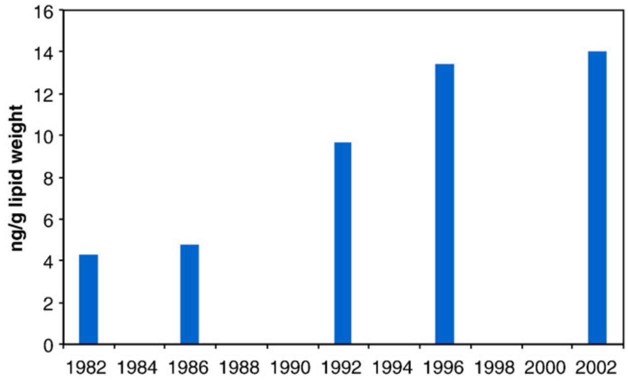

Fig. 10. Temporal profile of endosulfan sulfate concentrations in south–east Baffin Island beluga whale (Stern and Ikonomou (2003). Results are age-adjusted, lipid-normalised concentrations.

(especially using GC-ECD) it is likely that the total endosulfan exposure of wildlife and humans is lower than shown in Fig. 9.

8. Temporal trends

Increasing concentrations of endosulfan sulfate in male beluga whales from Cumberland Sound (Pangnirtung, southeast Baffin Island) have been reported by Stern and Ikonomou (2003), again, as part of results from a larger study of time trends of OC pesticides and PCBs (Stern et al., 2005b). Male belugas were used because they generally show little correlation of major OC pesticides and PCBs with age (Stern et al., 1994). Endosulfan sulfate concentrations were found to have increased significantly during the 1990s, whereby the mean concentrations for 1992 > 1986 or 1982 respectively (Fig. 10). Concentrations in 2002 did not differ from those in 1996. As discussed above the concentrations of endosulfan sulfate in the southeast Baffin Island population reported by Stern and Ikonomou (2003) were approximately 10-fold higher than those reported by Kelly (2005) for eastern Hudson Bay beluga using GC-HRMS for endosulfan analysis and therefore should be regarded with caution until confirmed GC-MS. No other temporal trend data for endosulfan in biota are currently available.

9. Conclusions and areas for further research

Endosulfan is an organochlorine pesticide that continues to have wide use as an insecticide across the globe, with technical formulations dominated by the α-isomer. The physical–chemical properties of endosulfan are similar to some of the 'legacy' OC pesticides, but variations in these properties between the α- and β-isomers and the degradate, endosulfan sulfate, account for differences in their environmental distribution and behaviour. The α- and β-isomers degrade at different rates in temperate aquatic systems but appear to be more recalcitrant in soil, although degradation is highly dependent on the prevailing environmental conditions. There is some evidence to suggest that the β-isomer can be converted to the α-isomer in the environment. Due to their semi-volatility, the α- and β-isomers and endosulfan sulfate are present in the global background atmosphere and are capable of undergoing long-range transport to remote environments. The limited presence of endosulfan sulfate in passive air sampling media suggests that this compound is also transported in the atmosphere, but is more likely to be formed *in situ* following transport of the parent isomers and their subsequent degradative/metabolic transformation. The potential for endosulfan sulfate formation in the atmosphere, while unlikely, needs investigating. There is a need for additional atmospheric data for both β-endosulfan and endosulfan sulfate, as well as accurate temperature-dependent partitioning data for the sulfate.

Measurements of dated lake sediments and snow/ice cores in mountain environments and the Arctic indicate an increase in endosulfan accumulation since the 1980s, in keeping with the ongoing use of this pesticide. Concentrations measured in background atmospheric samples and in deposition appear to have remained stable over the 1990s and early 2000s. Endosulfan, particularly the α-isomer, is present in snow and surface marine waters of the Arctic Ocean and deposition from the atmosphere is likely to be the major source (>85%) with riverine input playing a minor role. Earlier studies of seawater did not measure endosulfan sulfate, which we now know is the major form of endosulfan in Arctic seawater, meltwater, and snow. Thus, a full understanding of the fate and mass balance of endosulfan in the Arctic Ocean will require additional measurements including all likely degradates.

Endosulfan is present in biota within Arctic marine foodwebs and displays relatively large bioaccumulation factors particularly for marine mammals. When calculated for the sum of α-, β-, and endosulfan sulfate however $\mathrm{BAF}_{\mathrm{ww}}$ values in three species of fish do not exceed the 5000 criterion under the POPs convention (UNEP, 2001). Σendosulfan biomagnification factors from fish to beluga and seals exceeded 1 and help to explain the relatively large BAFs for Σendosulfan based on concentrations in beluga and ringed seal blubber (where $\mathrm{BAF}_{\mathrm{lw}} = \mathrm{BAF}_{\mathrm{ww}}$) averaging 3.95×10^5. These elevated BAFs are calculated only for eastern Hudson Bay biota and are mainly due to high β-endosulfan reported by Kelly (2005) and should be confirmed by additional studies. The poor agreement among the three measurement techniques and among laboratories for concentrations of all three endosulfan species in biota means that the BAFs and BMFs for Σendosulfan are highly uncertain as are estimates of human exposure via dietary intake. There is a clear research need to analyse selected biota samples by GC-MS, particularly marine mammals such as ringed seal; and to examine the bioaccumulation potential of endosulfan sulfate in a well-defined food web.

Endosulfan fulfils all of the hazard criteria for classification as a POP under the UN-ECE (LRTAP) Protocol on POPs (UNECE, 1998) and the UNEP Stockholm Convention (UNEP, 2001). Endosulfan is persistent in the environment with the upper range of field-based half-lives >6 months in soil and sediments (α-,β-, and sulfate), with half-lives highly dependent on the prevailing environmental conditions. For example, half-lives for the α- and β-isomers are <2 months in water (i.e. the water column) in warmer temperate/tropical systems, although biologically-mediated degradation yields the more recalcitrant compound, endosulfan sulfate. The concept of 'joint persistence' of both parent isomers and endosulfan sulfate degradate, as proposed by Fenner et al. (2003), would result in considerably longer environmental half-lives for Σendosulfan. Similarly, the toxic potency of Σendosulfan is greater than α-endosulfan alone, as demonstrated for a number of organisms that span several trophic levels in an agricultural freshwater system. While α-endosulfan concentrations in Arctic biota fall well below laboratory-based toxicity thresholds for representative avian and mammalian species, toxicity of Σendosulfan to lower foodweb organisms (that demonstrate high bioaccumulation factors) in 'cold' marine and freshwater systems maybe of concern.

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