

EVALUATION AND INTERPRETATION OF ENVIRONMENTAL DATA ON ENDOSULFAN IN ARCTIC REGIONS

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Dave Arnold

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EVALUATION AND INTERPRETATION OF ENVIRONMENTAL DATA ON ENDOSULFAN IN ARCTIC REGIONS

EXECUTIVE SUMMARY

The classification of compounds as Persistent Organic Pollutants (POPs) under UN ECE Executive Body Decision 1998/2 and in the UNEP Stockholm Convention is based upon toxicity, semi-volatility, persistence and bioaccumulation characteristics. Under Article 1 of the Protocol agreed by the Executive Body of the UN ECE LRTAP Convention, POPs are defined as:

'...organic substances that:

- (i) possess toxic characteristics;*
- (ii) are persistent;*
- (iii) bioaccumulate;*
- (iv) are prone to long-range transboundary atmospheric transport and deposition;*
and
- (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.'*

UN ECE Executive Body Decision 1998/2 sets out more detailed criteria for identifying potential POPs in the form of requirements for a risk profile (the text of this Decision is reproduced in Section 1.5). Criteria *iv* draws heavily upon evidence from monitoring programmes in Arctic/remote region. Detections alone, however, are not evidence of that a chemical is *"likely to cause significant, adverse human health or environmental effects"* (Criteria *v*). A number of factors should be evaluated before making such a determination:

- Temporal trends
- Spatial trends
- Transport mechanisms
- Distribution within the food chain (potential for bioaccumulation/biomagnification)
- Associated ecotoxicological risks due to background and food chain exposure
- Associated human dietary risks, primarily due to potential marine bioaccumulation

A first draft dossier was prepared in support of a proposal for endosulfan to be considered as a candidate for inclusion in the UN-ECE LRTAP protocol on persistent organic pollutants. The draft dossier focused on the specific numeric criteria for the inclusion as a POP, but also presented the findings of endosulfan in remote and Arctic areas in support of the argumentation.

The primary objective of this research exercise is to assemble a broader basis for evaluation of behaviour and exposure of endosulfan by gathering and interpreting monitoring data in key locations, compartments and links within the Arctic food web. Finally, the residues profile within both abiotic and biotic compartments is considered within an ecotoxicological and human health risk context.

Air

- **The temporal trend in endosulfan residues in the air in the Arctic appears to be stable in agreement with its actual use during the 1990 – 2000 decade. The mean levels are very low amounting to approximately < 1 – 15 pg/m³**
- **A distinctive seasonal profile (summer reductions in α -endosulfan concentrations with spring and fall peaks) probably result from a combination of complex environmental fate processes described by Hung, et al. (2002).**
- **Analysis of air trajectories indicates that continental/southerly air masses in North America are likely to be more significant contributors to Arctic contamination than Asian sources.**

Seawater

- The endosulfan levels in seawater were typically approximately $< 1 - 10$ pg/L
- Results of seawater monitoring are highly consistent despite wide geographic separation and analysis being undertaken by a range of institutes.
- The Central Asian Arctic is poorly represented, presenting uncertainties regarding potential riverine routes of entry for endosulfan into the Arctic.
- There are no geographical trends that may suggest that transport from the Pacific Ocean through the Bering and Chukchi seas may be occurring - as observed for other persistent organochlorine pesticides.
- A net air to seawater exchange appears to dominate in some locations (Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) but is reversed at others (Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea), highlighting uncertainties of the trace levels detected in air and water and a potential seasonal sensitivity to ice pack conditions.
- Compounded uncertainties (trace seawater analysis, reliance on a spatially limited air monitoring database and absence of a temperature dependent Henry's law constant) suggest that a high degree of caution must be exercised in interpretation of air - water exchange behaviour.

Snow

- The accumulation profile in snow and ice for the last 50 years reveals that input of endosulfan was higher in the past, although significant post-depositional migration during snow-to-ice metamorphism may obscure this profile.

Biota

- Difficulties with interpretation of biota measurements arise due to former reliance on GC-ECD with associated potential for analytical interference. In particular, differences between the GC-ECD and GC-MS results reported by Kelly (2005) and Stern and Ikononou (2003) warrant further investigation.
- Residues of α -endosulfan were significantly higher in whales from the North Sea, potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species.
- Detections of endosulfan in seals around the Arctic Ocean do not correlate with the findings in seawater.

Trophic Magnification, Biomagnification and Bioaccumulation Potential

- It is concluded that α -endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.
- An average fish to mammal BMF value (10.2) needs to be interpreted recognising a very high degree of variability (± 16.4) and therefore, uncertainty. On this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern.
- There is, however, clear evidence biomagnification for invertebrates to fish and fish to predatory fish does not occur.
- The implications of very high estimated BAF values (ranging from 3.4×10^3 to 2.6×10^7) are unclear. Uncertainties on intermediate micro-organism trophic level and low ambient temperature conditions in the Arctic may increase bioaccumulation by reducing metabolism potential.

Ecotoxicological and Human Dietary Risk Profiles

- There is essentially negligible risk to marine organisms and terrestrial animals associated with exposure to endosulfan in the Arctic
- Human dietary risk was concluded to be generally negligible except with unrealistic, extreme worst-case assumptions (coincidence of very heavy reliance upon marine mammals and fish characterised by 99th centile endosulfan residue profiles).

Based on stable endosulfan levels in the environment, the virtual absence of trophic magnification and biomagnification in the food chain, a negligible ecological risk to marine mammals and a negligible human dietary risk, concerns of adverse effect to human health and the environment cannot be demonstrated that may suggest a classification as a POP.

An abstract of the research findings that support these conclusions are provided overleaf for each of the points summarised above.

Temporal trends

Long-term continuous air sampling is available for comparatively few sites of which Alert in the Canadian high Arctic provides by far the most significant and highest value dataset. The long-term trend in endosulfan residues in air in the Arctic appears to be stable. Usage/emission may have peaked during the period 1990-2001 and may now be in decline but establishing the extent of any delay in parallel decline in air residues will require further (and perhaps more extensive) continuous air sampling. The timescales required to assess this cannot be accurately estimated due to a lack of knowledge about the significance of a wide range of potential confounding influences summarised by Hung *et al.* (2005) as well as more up to date and more accurate usage and emission estimates. The available seawater monitoring database does not constitute a robust enough database to allow firm conclusions to be made regarding temporal trends. A survey of glacial firm and ice has revealed the potential for accumulation α - and β -endosulfan. The accumulation profile for the last 50 years reveals that input of endosulfan has reduced, although significant post-depositional migration may obscure this profile.

Detailed analysis of temporal trends in biota was not possible due to the absence of long-term, site-specific monitoring campaigns. One noteworthy exception is reported by Stern and Ikonomidou (2003), who concluded that endosulfan sulfate residues were increasing in male beluga whales in the Canadian Arctic. However, a 10-20 fold differences between the GC-ECD and GC-MS results reported by Kelly (2005) needs to be investigated further before reaching firm conclusions. The timescales considered, relative to recent trends in emission and air and seawater are probably insufficient to allow firm conclusions to be reached regarding whether endosulfan residues would continue to apparently plateau or decline in the near future.

Spatial trends

As summarised earlier, the NCP (Northern Contaminants Programme) air monitoring station in Alert in the Canadian high Arctic is the most most robust dataset available. Additional monitoring has been conducted at sites in the Canadian sub-Arctic, western Siberia, the Bering Sea and in Norway. Nonetheless, it has been possible to exploit certain databases with the aim of identifying source regions that contribute most significantly to airborne residues at specific locations. Spatial variation in endosulfan concentrations is not pronounced across the Arctic region as a whole, with yearly averages varying by less than a factor of 2. The assembled database of seawater monitoring suggests that most sectors of the Arctic Ocean are included with the Bering Sea, Beaufort Sea, Canadian Archipelago particularly well-represented. However, the Central Asian Arctic is poorly represented. This may have implications when considering the potential of Asian rivers as routes of entry for endosulfan into the Arctic. Concentrations of both α - and β -endosulfan east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain. There is, nonetheless, a relatively high degree of analytical consistency in seawater monitoring results. Analysis of snow has been conducted at a range of sites in Canada and Norway. However, spatial trends in snow and ice are difficult to

determine due to the high variability in snow concentrations. In the Canadian Arctic the two most northerly sample sites, with the coldest air temperatures displayed the widest range in concentrations with higher average concentrations than sites located further south. However, higher rates of precipitation experienced at the more southerly stations result in similar depositional fluxes across the Canadian Archipelago.

Spatial variation in residues of α -endosulfan in biota was specifically considered for ringed seal blubber and minke whales. Further, region-specific data was available in the form of the Greenland diet study (Johansen et al., 2004a). In ringed seals, the highest concentrations of α -endosulfan were found in the Beaufort Sea. Concentrations in the eastern Canadian Arctic, Greenland and Russian Arctic are much lower although in general α -endosulfan was detectable at sub-ng/g in all blubber samples. However, there appears to be no relationship to endosulfan concentrations in seawater. Residues of α -endosulfan were significantly higher in whales from the North Sea than those from all other locations. Minke whales from the Barents Sea had higher α -endosulfan than those from Jan Mayen and west Greenland - potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species.

Transport mechanisms and environmental fate

Key studies conducted in the Canadian sub-Arctic (Tagish, Yukon) have been interpreted with air mass back trajectories to assess potential sources of contaminants into the western Canadian Arctic and other Canadian monitoring locations. This research indicates that continental/southerly air masses in North America are likely to be more significant contributors to Arctic contamination than Asian sources. Attribution of source regions for endosulfan arriving in Arctic regions of eastern North America, Europe and Asia remains uncharacterised.

Although both α - and β -endosulfan concentrations east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain and it has not been possible to attribute oceanic transport sources. Air-water exchange is one of the most important environmental fate processes that will define behaviour in the Arctic. There appears to be significant regional differences in air-sea gas exchange behaviour for α -endosulfan. The use of fugacity ratios to estimate the net transfer air-sea gas exchange behaviour relies very heavily on an estimated temperature dependent Henry's law constant. This is considered to be the single greatest uncertainty in evaluating air-sea gas exchange behaviour (and perhaps behaviour of endosulfan in the Arctic as a whole). Nonetheless, the calculations suggest that in some regions there is a net seawater \rightarrow air transfer mechanism occurring or that air and seawater are at close to equilibrium (e.g. Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea). In other areas (notably the Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) there appears to be a net air \rightarrow seawater transfer mechanism occurring. It is likely that seasonal changes in the ice pack will have a very significant influence on behaviour. There is insufficient data available to accurately estimate net air-sea gas exchange behaviour for β -endosulfan. The lack of clear consistent air-sea gas exchange behaviour is in contrast to γ -HCH where recent results suggest a clear air \rightarrow seawater transfer mechanism in operation.

When taken together, the compounded uncertainties associated with issues such as low level analysis in seawater, reliance on a very limited set of air sampling campaigns, the lack of availability of a temperature dependent Henry's law constant,

suggest that a high degree of caution must be exercised in interpretation and attribution of behaviour as evidence of POP characteristics. It can be argued that the high degree of variability observed would, in fact, favour the combined influence of a far more complex set of processes than is implied in typically simplistic POP profiles where there is a degree of spatial consistency.

Trophic magnification potential

Trophic magnification profiles from three of the four sites for which sufficient data was available to allow analysis (Barrow, Lake Superior, and White Sea) suggest that there is no significant relationship between measured concentration and trophic level for either α -endosulfan or lindane. The evidence for the remaining site (Holman) is ambiguous. At this site, there appears to be a significant relationship between measured concentration and trophic level for all three investigated compounds (α -endosulfan, lindane and PCB 153). However, it is well recognised that lindane does not biomagnify in aquatic food webs (Moisey *et al.* 2001; Hoekstra *et al.* 2003) giving rise to concerns surrounding the interpretation and significance of the dataset for this site. Taking this into account it is concluded that α -endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.

Biomagnification potential

Although there are no biomagnification factor (BMF) triggers within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs, there are criteria applied to bioconcentration or bioaccumulation in aquatic species (BCF (bioconcentration factors) or BAF (bioaccumulation factors) > 5000). BMF values found to be statistically greater than unity are considered to accumulate from prey to predator. Based upon the triggers established for BCF it would be possible to conclude that BMF values of > 10 may also be of consistent concern (Default BCF and BMF values within the EU Technical Guidance Document (ECB, 2003) imply that where BCF of >5000 occurs, BMF values of ca 10 may be expected, although caveats are noted regarding assumed relationships between BCF, BMF and K_{ow}). Calculated biomagnification factors based on residue measurements for a range of Arctic species ranged from 0.056 to 64.7. These ranges both reflect calculations for fish to marine mammal food chain links. The high degree of variability within this food chain links is particularly noteworthy. Further analysis revealed that average invertebrate to fish and fish to predatory fish BMF values were very low (0.38 and 0.60, respectively). The average fish to mammal BMF value was 10.2, lying at a possible threshold of concern. However, this estimate needs to be interpreted recognising a very high degree of variability (± 16.4) and therefore, uncertainty. High fish to mammal BMFs may be due to contribution from an interference in α -endosulfan analysis by GC-ECD that biomagnified e.g a chlordane or toxaphene component, thus artificially raising the BMF. The exact contribution is difficult to assess (because both fish and marine mammals have interferences by GC-ECD) but based on paired GC-ECD and GC-NIMS analysis could result in overestimation by up to 4x. In summary, there is no clear evidence of biomagnification for invertebrates to fish and fish to predatory fish. There is a high degree of uncertainty surrounding fish to marine mammal food chain links – on this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern.

Bioaccumulation potential

Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000. Measured bioaccumulation factors (BAF values) for a range of Arctic species ranged from 3.4 x

10^3 to 2.6×10^7 . The implications of very high BAF values are unclear. The potential for other uptake/retention mechanisms remains a possibility. General consistency is noted despite studies and analysis having been conducted by a number of researchers in different institutes based on monitoring in a range of differing locations. The transfer to zooplankton has been assumed to be mainly *via* water but recent studies suggest that the microbial food web could be important (Wallberg *et al.* 2001) and may unexpectedly influence such calculations. The influence of low temperature on increasing bioaccumulation under Arctic conditions by reducing metabolism potential has been postulated. Such an influence could account for differences between bioconcentration profiles observed under laboratory conditions (BCF: 200-3700, typically measured at 20-25°C; typically 20-25°C) and ambient Arctic conditions (typically <5°C). There is, however, insufficient data to confirm this for endosulfan, although the possibility is considered in studies for other compounds (Buckman *et al.*, 2004).

Ecotoxicological risk

A relatively robust evaluation of ecotoxicological risks has been facilitated through access to a very large database of effects studies. Risks to freshwater or marine animals are minimal. The toxicity value from laboratory studies for the most sensitive animal was about three orders of magnitude greater than the highest measured concentration for Arctic marine waters. This applies to both the acute and the chronic toxicity values. These data clearly show that there is essentially negligible risk to aquatic animals from acute and chronic exposures to endosulfan residues in Arctic marine systems.

Risks to terrestrial animals were assessed by direct comparison of mammalian toxicity data with measured residues in relevant organisms. The results of this assessment support the same conclusion of negligible risks to marine mammals and terrestrial wildlife from endosulfan exposures via the environment and the food chain.

Human dietary risk

The most common criterion for judging human exposures for the purposes of risk assessment is the Reference Dose (RfD) or the Acceptable Daily Intake (ADI). This is determined from the results of laboratory animal studies in which the highest dose that does not cause an adverse acute or chronic response in the most sensitive test species is divided by an uncertainty factor (100) to account for differences between humans and laboratory animals and within humans, such as the elderly or very young. Critical dietary residue profiles were obtained from valuable research conducted in Greenland by Johansen *et al.* (2004a). Probabilistic analysis of exposures, based on residue data for various food items were then used to estimate 90th, 95th, and 99th centiles of intake potential based on limited dietary component analyses carried out in the Arctic (Greenland and Russia).

With the exception of a hypothetical individual in Greenland that consumes all food items with the 99th centile concentration of endosulfan, all other consumption scenarios suggest negligible risk. Similar results were obtained when the concentrations of endosulfan in imported food items were assumed to be the same as those for the US population. Human dietary risk is concluded to be generally negligible except in extreme worst-case situations where there is a coincidence of very heavy reliance upon locally sourced food items drawing heavily upon marine mammals and fish characterised by 99th centile endosulfan residue profiles. It should be noted that even if this unrealistically high uptake profile is compared to the lowest available chronic NOEL from the most sensitive mammalian species tested a safety factor of 21 can be demonstrated.

Research recommendations

A review of strengths and weaknesses in the available datasets was conducted with the aim of identify and characterising uncertainties. Many of the uncertainties highlighted in this review are discussed in this summary and studies that are considered to provide critical, high quality datasets have similarly been identified. This also provided an opportunity to consider how monitoring and risk assessment research in this field might be improved through changes in analytical strategy, monitoring design or other data gathering exercises. A summary of the key recommendations is provided overleaf.

Air

- *Additional quality control procedures should be put in place to periodically confirm the presence of analytes reported by GC-ECD. Further controls such as inter-laboratory round-robins and analysis of quality assurance standards could be regularly implemented.*
- *The long-term air monitoring programme based at Alert in the Canadian high Arctic has provided vital data in understanding the behaviour and trends in many chemicals. It is recommended that this programme be continued to assist in better understanding trends in chemicals with current usage such as endosulfan.*
- *It is further recommended that such monitoring programmes be potentially extended to consider other locations to assist in the development of a more complete understanding of potential source regions for chemicals. The expense and logistical difficulties associated with running such a study are recognised.*

Seawater

- *Additional quality control procedures should be put in place to periodically confirm the presence of analytes reported by GC-ECD. Further controls such as inter-laboratory round-robins and analysis of quality assurance standards could be regularly implemented.*
- *Coupled air /seawater measurements to assess localised air-water exchange during periods of melt and freeze. The work could also be conducted in the vicinity of an ice-lead to quantify the role of polynyas/leads in contributing to air-water exchange during the winter and spring.*
- *Deep water sampling to establish the vertical extent of endosulfan occurrence in the water column. The hypothesis here is that endosulfan residues are unlikely to be detected (unlike HCHs) due to removal via hydrolysis.*
- *Potential for widening seawater monitoring campaigns to include an assessment of the Central Asian Arctic.*
- *Increased accessibility of monitoring databases for large Asian rivers (Ob, Yenisey and Lena Rivers) in order to assess scale of riverine sources into the Arctic*
- *Potential for establishing seawater monitoring designs (seasonal or monthly sampling) for selected sites that would provide a more robust basis for establishing temporal trends.*
- *Further investigation into the role of meltwater as a local source of residues into seawater.*
- *More extensive seawater monitoring from below the ice pack to assist in further understanding seasonal variation in water residues and air-water exchange behaviour.*
- *Of specific relevance to endosulfan, the determination of a temperature dependent Henry's law constant*

Snow

- *Process-based studies are required to examine the fate of endosulfan following snow ageing and melt. Percolation and transport of chemical residues both within and out of the snowpack during periods of thaw are poorly understood and both laboratory simulations and controlled field studies are required to address these areas.*
- *Combined air and snow sampling is required to determine field-based scavenging ratios and relate these to temperature, the physical properties of the snow and theoretically derived values.*
- *Snow-air partitioning studies are required to determine the suitability of Henry's Law (at sub-zero temperatures) in describing the chemical composition in aged snow.*
- *Studies are required to investigate the role of the sea-ice-snowpack in contributing endosulfan to surface seawater.*
- *Photochemical studies are required in photic snow layers to understand chemical degradation/transformation following polar sunrise and 24 h daylight.*

Biota

- *Analytical methodology employed in biota monitoring programmes be upgraded to GC-MS.*
- *Differences between the GC-ECD and GC-MS results reported by Kelly (2005) and Stern and Ikonomou (2003) warrant further investigation to assist in understanding temporal trends.*
- *The influence of low ambient temperature conditions on bioaccumulation and metabolism potential should be investigated with species of relevance to such conditions.*
- *Further understanding of spatial variation in biota residues could be strengthened by widening the range of sites considered to include the Asian Arctic.*

Risk Assessment

- *A more thorough dietary residue analysis for endosulfan would facilitate more robust human dietary risk assessments*
- *A more extensive (population level) and higher resolution (dietary component) dietary profile for a range of Arctic diets should be developed - similar to that employed in conventional human dietary risk assessments for pesticides. This is currently underway in the United States for Alaska but may not be representative of diets in other regions in Canada (Nunavut, Nunavik), Greenland, Scandinavia and Russia.*

1 Introduction

N. Mackay, Cambridge Environmental Assessments-ADAS

1.1 Objectives of the Research Programme

The classification of compounds as Persistent Organic Pollutants (POPs) under UN ECE Executive Body Decision 1998/2 And In The UNEP Stockholm Convention is based upon toxicity, semi-volatility, persistence and bioaccumulation characteristics. Under Article 1 of the Protocol agreed by the Executive Body of the LRTAP Convention, POPs are defined as:

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- (x) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.'*

UN ECE Executive Body Decision 1998/2 sets out more detailed criteria for identifying potential POPs in the form of requirements for a risk profile (the text of this Decision is reproduced in Section 1.5). Criteria *iv* draws heavily upon evidence from monitoring programmes in Arctic/remote region. Detections alone, however, are not evidence of that a chemical is "*likely to cause significant, adverse human health or environmental effects*" (Criteria *v*). A number of factors should be evaluated before making such a determination:

- Temporal trends
- Spatial trends
- Transport mechanisms
- Distribution within the food chain (potential for bioaccumulation/biomagnification)
- Associated ecotoxicological risks due to background and food chain exposure
- Associated human dietary risks, primarily due to potential marine bioaccumulation

A first draft dossier was prepared in support of a proposal for endosulfan to be considered as a candidate for inclusion in the UN-ECE LRTAP protocol on persistent organic pollutants. The draft dossier focused on the specific numeric criteria for the inclusion as a POP, but also presented the findings of endosulfan in remote and Arctic areas in support of the argumentation.

The primary objective of this research exercise is to assemble a broader basis for evaluation of behaviour and exposure (focusing primarily upon bioaccumulative potential and monitoring trends). This is accomplished by gathering and interpreting monitoring data in key locations, compartments and links within the Arctic food web. Finally, the residues profile within both abiotic and biotic compartments is considered within an ecotoxicological and human health risk context.

The Arctic definition accepted within the Arctic Monitoring and Assessment Programme (AMAP) is employed within this assessment. This encompasses the terrestrial and marine areas north of the Arctic Circle, north of 62°N in Asia and 60°N in North America, modified to include the marine areas north of the Aleutian chain, Hudson Bay, and parts of the North Atlantic Ocean including the Labrador Sea (See Figure 1.1.1).

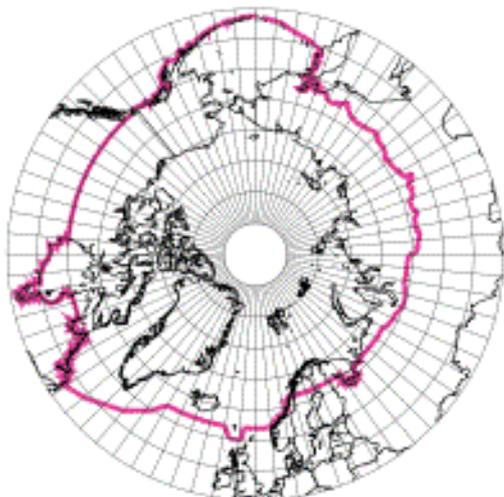
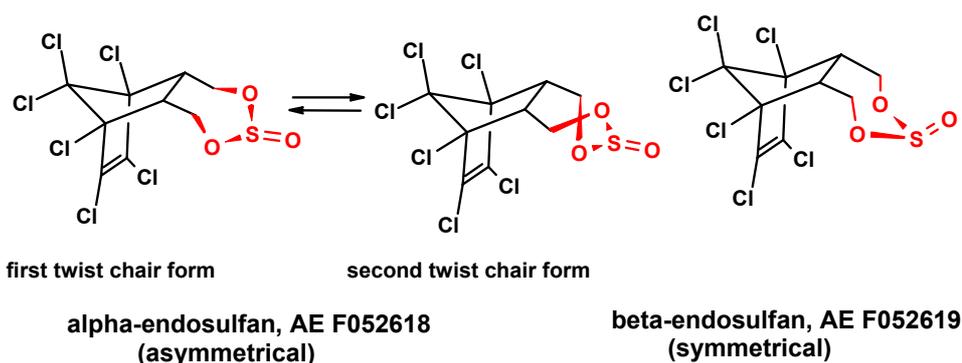


Figure 1.1.1 Arctic regions as defined by AMAP (AMAP, 2004)

1.2 Introduction to Endosulfan and its Uses as a Plant Protection Product

Endosulfan is an insecticide of the type sulfite diester of a chlorinated cyclodiene with the IUPAC nomenclature 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide. It was also known as Thiodan in the former Soviet Union and as Benzoepin in Japan. Endosulfan is mainly formulated as 5 EC and 35 EC formulation and marketed under the trade name Thiodan®. Endosulfan is a mixture of two stereoisomers; alpha-endosulfan and beta-endosulfan. Alpha-endosulfan, also referred to as Endosulfan (I) comprises 64-67% of the technical grade endosulfan with the remainder as beta-endosulfan, or Endosulfan (II). The structural interactions of the isomers of endosulfan was discovered by Schmidt *et al.* (1997) by X-ray crystallography and NMR spectroscopy. The chemical structure of each stereochemical form is illustrated in Figure 1.2.1.



The two twist forms cannot be separated at room temperature

Figure 1.2.1. Stereochemical forms of endosulfan

Endosulfan is subject to both abiotic and biotic degradation to form the primary metabolite, endosulfan sulfate (see Figure 1.2.2). A summary of the physico-chemical

characteristics of α - and β -endosulfan and endosulfan sulfate is reported in Table 1.2.1.

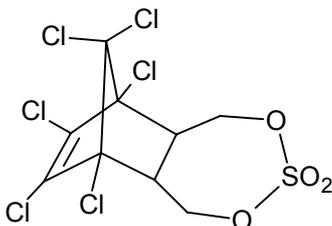


Figure 1.2.2 Structure of endosulfan sulfate

Mode of insecticidal action

Endosulfan acts as a chloride channel antagonist of the GABA (γ -amino butyric acid) receptor in arthropods as summarised in a review by Kern (1990). In insects, it binds to the t-butyl cyclophosphorothionate (TBPS) or the picrotoxin (PTXN) binding site of the multiple GABA receptor and thus affects the chloride ion flux in the postsynaptic membrane. Another effect observed in insects was the drastic increase in glutamate, glutamine, phosphoethanolamine and ethonolamine concentrations during intoxication. An abnormal increase of the glutamate concentration would account for the marked excitation of the insects as a result of endosulfan intoxication. Kern also reported a reduction of trehalose (an insect specific form of sugar storage) and a higher frequency of vacuolization, an atrophy of neurosecretory cells in the insect brain.

Endosulfan does not affect the other targets of insecticides, such as the acetylcholine esterase, the nicotinic acetylcholine receptor, the voltage-dependent sodium channel, the ecdysone receptor, the glutamate receptor, and the chitin and lipid biosynthesis. Due to its unique mode of action, endosulfan does not suffer a cross-resistance with the other insecticides and therefore is very valuable in pest management strategies to reduce selection for resistance.

The mechanistic reasons for lower sensitivity in beneficial insects have been reported in several studies. Schuphan (1987; as cited by Kern, 1990) showed that endosulfan was much more rapidly metabolised in honeybees than in the pest species cabbage white butterfly. The same applied to lady-bird beetles when compared with the Mexican bean beetle (*Epilachna varivestis*). This species selectivity is also a result of the utilisation of different habitat and feeding habits (aphid-eating *versus* leaf-eating).

Registration history

Endosulfan was first synthesized by Frensch and Goebel (1954) and introduced into the European market in 1956 by Hoechst AG under the trade mark Thiodan®. In the USA it also was registered by the FMC Corp. under the same trade mark. Endosulfan is a versatile, but selective insecticide with acaricidal properties and mainly used for the control of chewing and sucking insect pests and broad mites. It penetrates into the insect *via* the tracheas, by ingestion, and has some contact activity. Endosulfan is currently registered in USA, Canada, the South European states including France and the United Kingdom, Middle East, North and South Asia with a major use in India, North and South Africa, Latin America and Australia.

Table 1.2.1. Summary of physico-chemical characteristics for endosulfan and its main metabolite, endosulfan sulfate

	α -endosulfan	β -endosulfan	Endosulfan sulfate
Molecular weight	406.9 g/mol		422.92 g/mol
CAS	technical mixture: 115-29-7 α -endosulfan: 959-98-8 β -endosulfan: 33213-65-9		1031-07-8
Molecular formula	$C_9H_6Cl_6O_3S$		$C_9H_6Cl_6O_4S$
Form	Colourless crystals (tech; cream to brown, mostly beige)		
Melting point	109.2°C	213.3°C	181-201°C
Vapour pressure	9.6 x 10 ⁻⁴ Pa (20°C) 4.40 x 10 ⁻³ Pa (25°C, FAV*)	4.0 x 10 ⁻⁵ Pa (20°C) 4.00 x 10 ⁻³ Pa (25°C, FAV*)	1 x 10 ⁻⁵ Pa (20°C)
<i>Reference</i>	Sarafin (1987); Goerlitz (1987); Shen and Wania (2005)		
Octanol water partition coefficient	Log P _{ow} = 4.63 - 4.74 Log P _{ow} = 4.94 (25°C, FAV*)	Log P _{ow} = 4.34 - 4.79 Log P _{ow} = 4.78 (25°C, FAV*)	Log P _{ow} = 3.77
<i>Reference</i>	Sarafin and Asshauer (1987b); Muehlinger and Lemke (2004); Shen and Wania (2005)		
Henry's law constant	1.48 Pa m ³ mol ⁻¹ (25°C) 0.70 Pa m ³ mol ⁻¹ (25°C, FAV*) Temperature dependence: log H' = -876.14 / T + 0.4463 H (298K) = 7.95 (Pa m ³ / mol)	0.07 Pa m ³ mol ⁻¹ (25°C) 0.045 Pa m ³ mol ⁻¹ (25°C, FAV*)	8.46 x 10 ⁻³ Pa m ³ mol ⁻¹ (20°C, pH 5)
<i>Reference</i>	Weller (1990); Shen and Wania (2005); Rice <i>et al.</i> , (1997)		
Solubility	0.33 mg/L (22°C, pH 5) 0.53 mg/L (25°C, pH 5) 0.0063 mmol/L (25°C, FAV*)	0.32 mg/L (22°C, pH 5) 0.28 mg/L (25°C, pH 5) 0.089 mmol/L (25°C, FAV*)	0.50 mg/L (20°C, pH 5)
<i>Reference</i>	Sarafin and Asshauer (1987a); Goerlitz (1986); Weil <i>et al.</i> (1974); Shen and Wania (2005)		
Hydrolysis DT ₅₀	>1 yr (22°C, pH 5) 22 d (22°C, pH 7) 7 hrs (22°C, pH 9) 68 days (1°C, pH 8)	>1 yr (22°C, pH 5) 17 d (22°C, pH 7) 5 hrs (22°C, pH 9) 68 days (1°C, pH 8)	NA
<i>Reference</i>	Goerlitz and Kloeckner (1982); Sneikus (2005)		
Photostability in water	Both isomers are photolytically stable (direct photolysis) due to the lack of significant light absorption above 290 nm		NA
<i>Reference</i>	Stumpf and Jordan (1993)		

*FAV: final adjusted value by a technique that adjusts a set of physical-chemical property values in such a way that they conform to thermodynamic constraints yet deviate as little as possible from the original values using the algorithms published by Beyer *et al.* (2002).

Endosulfan uses

Endosulfan is worldwide used mainly in cotton (50 %), vegetables (5 %), field crops (15 %), plantation crops (15 %) and soybeans (15 %). These figures are based upon estimated contribution to global use in the year 2000 estimated by Bayer

CropScience against pest organisms of the orders of *Acarina*, *Coleoptera*, *Diptera*, *Heteroptera*, *Hemiptera*, *Homoptera*, *Lepidoptera* and *Thysanoptera*.

Global use of endosulfan

Endosulfan is predominantly used as insecticide in the agriculture. The global use during the last ten years was estimated by the Joint Canada-Philippines Planning Committee (1995) to have peaked in the years 1998 and 2001 with approximately 13,000 tonnes annually. More recent estimates by Li and MacDonald (2005) are consistent with these profiles (See Figure 1.2.3). Cumulative global use of endosulfan for crops was estimated by Li and Macdonald as 338 kt. From 2002, the global use gradually decreased as a consequence of the appearance of new insecticides on the market (pyrethroids, neonicotnoids) and a recent phasing out of some indications. India remains the world's largest user of endosulfan with a total cumulative use of 113 kt from 1958 to 2000, followed by the United States (26 kt from 1954 to 2000). Brazil, Australia, Sudan and the former Soviet Union have also been significant consumers. A summary for the northern and southern hemispheres is provided in Table 1.2.2. The table shows a continuous decrease of endosulfan use in the northern hemisphere and gradual increase of its use in the southern hemisphere. It should be noted that mixing of the air parcels between the northern and the southern hemisphere is limited due to meteorological conditions at the equator with the prevailing wind fluxes not crossing the equator. Within this report endosulfan will be compared against other compounds for which there is a better understanding of transport, fate and bioaccumulation, biomagnification and trophic magnification – most notably HCH (α , β , γ). It should be kept in mind that HCH has been effectively phased out – as such residues in air, seawater and biota for HCH reflect past use, whereas residues of endosulfan in the Arctic represent both current emissions and the influence of past use. This is effectively illustrated in Figure 1.2.4.

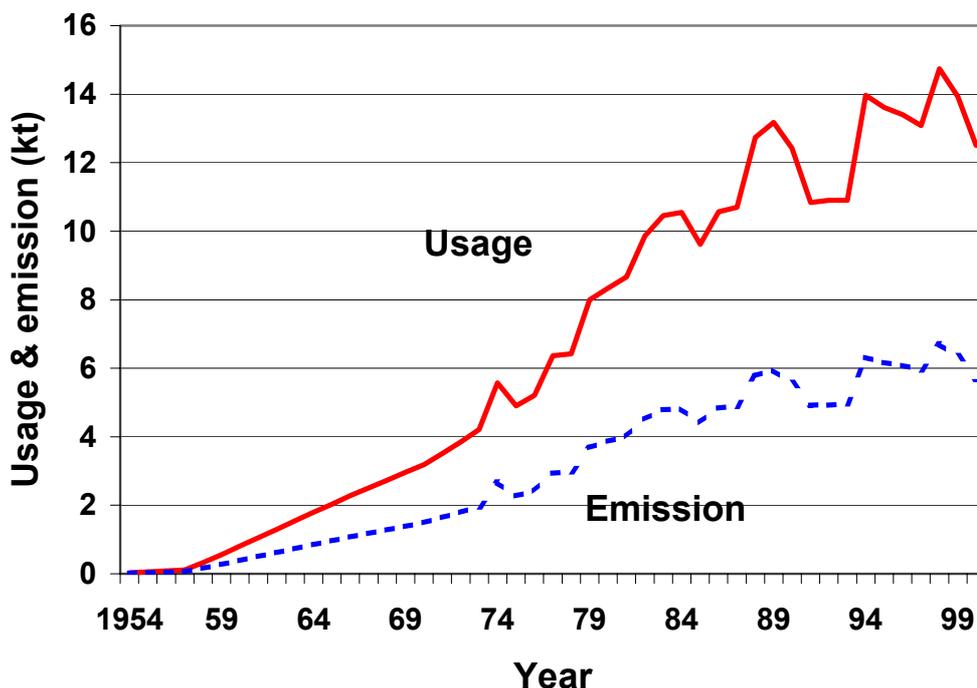


Figure 1.2.3: Temporal trend of endosulfan in usage and emissions* from 1954 to 2000 (Li and MacDonald, 2005).

*During application of pesticides, a portion may be released, or emitted, into the atmosphere at rates that are strongly dependent on the physical and chemical properties of the compound, agricultural practices as well as the prevailing meteorology. The complexity of these processes and variability from site to site precludes highly accurate estimates of emissions into the atmosphere. As a consequence pragmatic 'emission factors' have been proposed to facilitate regional and global gross emission estimates. The methodology employed is described by Li et al. (2004).

Table 1.2.2 Summary of global use trends for endosulfan (Metric Tonnes, Source: Bayer CropScience)

Year	1996	1997	1998	1999	2000	2001	2002	2003	2004
Northern Hemisphere	7900	7500	7300	6900	6150	6250	5800	6200	5350
Southern Hemisphere	4400	5500	5800	5900	6600	6950	6750	6150	6100
Global Use	12300	13000	13100	12800	12750	13200	12550	12350	11450

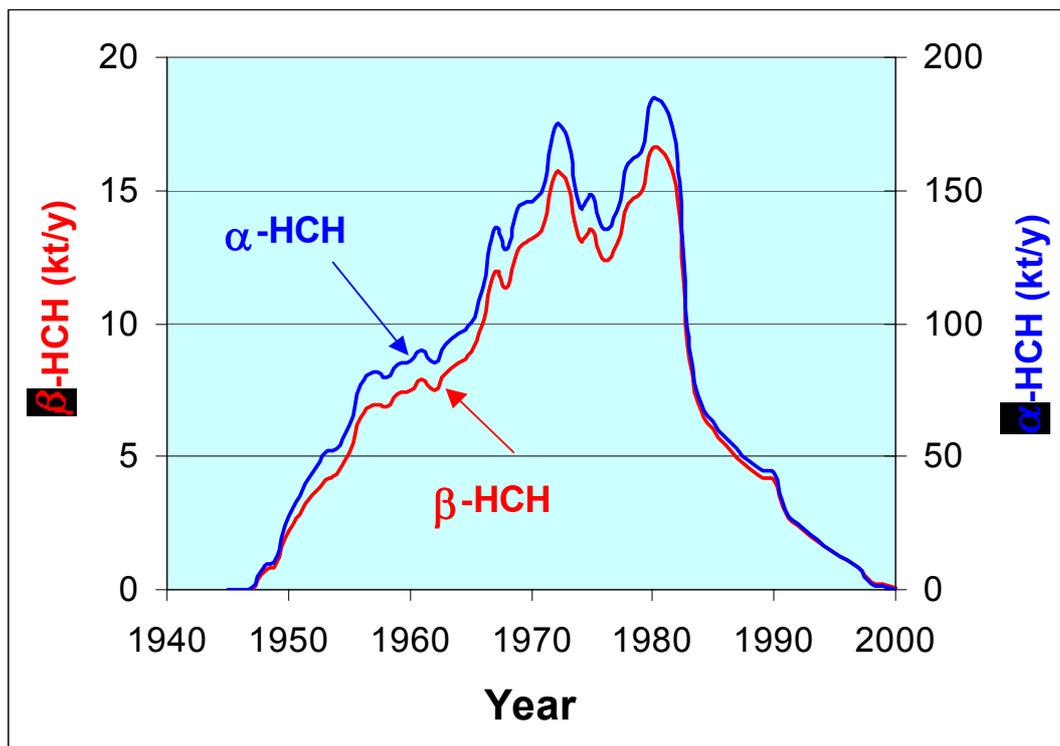


Figure 1.2.4: Annual global emissions of α -HCH (Li et al. 2000) and β -HCH between 1945 and 2000 (Li et al. 2003).

1.3 Background to the Existing Draft Report on Endosulfan to the UN-ECE

The broad aims of the United Nations Economic Commission for Europe (UN-ECE) are to safeguard the environment and human health, and to promote sustainable development in its member countries. The practical aim is to reduce pollution so as to minimize environmental damage and avoid compromising environmental conditions for future generations. Amongst five primary environmental treaties the 'Convention on Long-Range Transboundary Air Pollution' (LRTAP) is of primary interest when considering POP status. The convention entered into force in 1983 and has been extended by eight specific protocols, including the 1998 'Aarhus Protocol on Persistent Organic Pollutants' (entered into force in October 2003).

The Aarhus Protocol has initially focused on a list of 16 substances that have been singled out according to agreed hazard criteria. The substances comprise eleven pesticides, two industrial chemicals and three by-products/contaminants. The ultimate objective is to eliminate any discharges, emissions and losses of POPs. The Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (DDT, heptachlor, hexachlorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that will be banned. It also obliges Parties to reduce their emissions of dioxins, furans, PAHs and HCB below their levels in 1990 (or an alternative year between 1985 and 1995).

The Executive Body for the LRTAP Convention established a task force for POPs at

its 21st session in December 2003. Led by Canada and the Netherlands, the Task Force addresses the technical needs of the reviews and reassessments required by the Aarhus Protocol on POPs and the procedures adopted in Executive Body Decision 1998/2. In setting up the Task Force, the Executive Body agreed decision 2003/10, which identifies the functions of the Task Force, and some of its methods of work. The activities of the Task Force for 2004 were agreed in the Executive Body's work-plan (ECE/EB.AIR/79/Add.2 Paragraph 1.5). The Task Force Co-Chairs will report the results of the meetings of the Task Force to the Convention's Working Group on Strategies and Review, which provides the Parties to the Protocol with the information necessary for their reviews and re-assessments.

Process leading to submission of draft report

In its decision 1998/2 the Executive Body of the LRTAP Convention set out a framework of data and assessments to be provided on substances that Parties may wish to propose when considering potential inclusion of substances within Annexes I, II or III to the Protocol on POPs. The decision lays down that information should be provided on potential for long-range transboundary atmospheric transport of a candidate substances, its toxicity, persistence and bioaccumulation along with indicative values suggesting POP characteristics.

In 2003, The German Federal Environment Agency (Umweltbundesamt; UBA) undertook to provide an assessment of endosulfan against the indicative values set out in decision 98/2 of the Executive Body of the LRTAP Convention. This work was carried out as a voluntary contribution to the *ad hoc* expert group on POP candidates ("forerunner" to Task Force on POPs) and was not included within the Executive Body Work Plan (ECE/EB.AIR/79/Add.2, paragraph 1.5). At the fourth meeting of the ad hoc Expert Group on Persistent Organic Pollutants in Oslo, Norway (March 2003) the first draft of a dossier prepared in support of a proposal of endosulfan to be considered as a candidate for inclusion in the UN-ECE LRTAP protocol on persistent organic pollutants was presented and discussed. The dossier was designed to focus on those specific criteria outlined in the Executive Body's Decision 1998/2 on information to be submitted for adding substances to Annexes I,II or III to the Protocol on POPs. Within this dossier the UBA acknowledged that:

'...the criteria given in Dec. 98/2 for POP characteristics are not very robust regarding specific parameters like study conditions or relevance for the environment conditions spanning wide ranges. This causes quite different interpretation of study results by various stakeholders.'

1.4 Organisational Structure of Arctic Monitoring Programme

The risk profile presented in this report represents joint efforts of a number of organisations funded by and with technical contributions by Bayer CropScience. The refined risk profile presented in this report was prepared by Cambridge Environmental Assessments who co-ordinated other contributors in the following areas:

- Monitoring of air:
 - Lead: C. Halsall (Lancaster University, UK)
 - Contributions: T. Bidleman, H. Hung (Meteorological Services of Canada, Environment Canada)

- Monitoring of snow and ice:
 - Lead: C. Halsall (Lancaster University, UK)
 - Contributions: C. Halsall, J. Weber, B. Herbert (Lancaster University), M.

Hermanson (University of Pennsylvania)

- Monitoring of seawater:
 - Lead: D. Muir, (National Water Resources Institute (NWRI), Environment Canada)
 - Contributions: J. Small (University of Guelph, Canada) and D. Burniston (NWRI, Environment Canada)
- Monitoring of biota:
 - Lead: D. Muir (NWRI, Environment Canada)
 - Contributions: J. Small (University of Guelph, Canada) and C. Teixeira (NWRI, Environment Canada)
- Ecotoxicological risks:
 - Leads: K. Solomon (Guelph University, Canada) and D. Muir (NWRI, Environment Canada)
 - Contributions: J. Small (University of Guelph, Canada)
- Human health risks:
 - Lead: K. Solomon (Guelph University, Canada)
 - Contributions: J. Small (Guelph University, Canada)

1.5 POP Classification Criteria: Opportunities to Place Exposure Into a Risk Context

Definitions of the Executive Body of the LRTAP Convention

Under Article 1 of the Protocol, POPs are defined as:

'...organic substances that: (i) possess toxic characteristics; (ii) are persistent; (iii) bioaccumulate; (iv) are prone to long-range transboundary atmospheric transport and deposition; and (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.'

Executive Body Decision 1998/2 sets out more detailed criteria for identifying potential POPs in the form of requirements for a risk profile. The text of Decision 1998/2 is reproduced here:

INFORMATION TO BE SUBMITTED AND THE PROCEDURE FOR ADDING SUBSTANCES TO ANNEXES I, II OR III TO THE PROTOCOL ON PERSISTENT ORGANIC POLLUTANTS

1. A Party submitting a proposal to amend annexes I, II or III in accordance with article 14, paragraph 6, shall provide the Executive Body with a risk profile on the substance and information on the characteristics below, following the guidance and indicative numerical values, which demonstrate:

(a) Potential for long-range transboundary atmospheric transport: evidence that the substance has a vapour pressure below 1,000 Pa and an atmospheric half-life greater than two days. Alternatively, monitoring data showing that the substance is found in remote regions; and

(b) Toxicity: potential to adversely affect human health and/or the environment; and

(c) Persistence: evidence that the substance's half-life in water is greater than two months, or that its half-life in soils is greater than six months, or that its half-life in sediments is greater than six months. Alternatively, evidence that the substance is otherwise sufficiently persistent to be of concern within the scope of the protocol; and

(d) Bio-accumulation:

(i) Evidence that the BCF or BAF for the substance is greater than 5,000 or the log Kow is greater than 5; or

- (ii) Alternatively, if the bio-accumulative potential is significantly lower than
- (iii) above, other factors, such as the high toxicity of the substance, that make it of concern within the scope of the protocol.

The proposal shall also contain a summary report and include, as available, information on:

- (i) Production/uses/emissions, measured environmental levels in areas distant from sources, abiotic and biotic degradation processes and rates, degradation products, bio-availability; and
- (ii) Socio-economic factors related to the alternatives and/or the techniques available to reduce the emissions of the proposed substance including:
 - Alternatives to the existing uses and their efficacy;
 - Any known adverse environmental or human health effects associated with the alternatives;
 - Process changes, control technologies, operating practices and other pollution prevention techniques which can be used to reduce the emissions of the substance, and their applicability and effectiveness; and
 - The non-monetary costs and benefits as well as the quantifiable costs and benefits associated with the use of these alternatives and/or techniques.

2. Upon receipt of a submission prepared in accordance with paragraph 1 above and if the risk profile is deemed acceptable, the Parties shall, at a meeting of the Executive Body and by consensus, ensure that one or more technical reviews of the proposal are conducted if, on the basis of the submission and any other relevant information submitted to the Executive Body, further consideration of the substance is determined to be warranted. Any such technical reviews shall be in writing and evaluate, *inter alia*:

- (a) The monitoring or equivalent scientific information suggesting long-range transboundary atmospheric transport; and
- (b) Whether sufficient information exists to suggest that the substance is likely to have significant adverse human health and/or environmental effects as a result of its long-range transboundary atmospheric transport; and
- (c) A list of the sources of the substance in the atmosphere, including the use of products, estimates of the total emissions from these sources and the methodologies used; and
- (d) Whether measures exist to reduce the risk of adverse effects on human health and/or the environment as a result of its long-range transboundary atmospheric transport, and whether they are technically feasible, as well as their associated effects and costs.

3. The term risk profile mentioned in paragraphs 1 and 2 above refers to a comprehensive review of the scientific information related to the determination of general human health and environmental risks associated with the uses and releases of a substance. Such a review need not explicitly address risks associated with long-range transboundary air pollution, but must provide suitable information for the assessment of such risk.

4. On the basis of the submission specified in paragraph 1 above and any technical review(s) that may have been prepared in accordance with paragraph 2 above, the Parties shall, at a meeting of the Executive Body, complete their evaluation of the proposal taking into account the objective of the protocol set out in article 2.

Significantly, under Point 2 (above), the Executive body may choose to take into account '*any other relevant material*' that has been submitted in order to determine whether further consideration of the substance is warranted. Specific reference is made, in this regard, to information on environmental monitoring and potential for significant adverse human health and/or environmental effects. As described under Point 3 (above) there is no necessity to conduct a detailed risk assessment as a component of the risk profile, but the data available should provide information suitable for assessment of risks. It is the intention of this submission to more clearly establish the scale and scope of such risks in order to supplement that risk profile for endosulfan, clarifying potential concerns triggered by indicative criteria listed under Point 1 (above).

Stockholm Convention

In 2001 the United Nations Environment Programme (UNEP) completed global negotiations on banning certain POPs with the signing of the Stockholm Convention on Persistent Organic Pollutants. Particularly relevant to this assessment are the criteria for identifying and listing chemicals under the convention. These criteria represent an expansion of the definition provided by the Executive Body of the LRTAP Convention but are viewed as consistent. These criteria are summarised in Table 1.5.1. Notes on endosulfan's persistence, bioaccumulation and toxicity characteristics are provided for comparative purposes.

Table 1.5.1 Criteria for identification of ‘new’ POPs under the Stockholm Convention

Chemistry identity	Structure, including specification of isomers where applicable, and the structure of the chemical class
Persistence	<ol style="list-style-type: none"> 1. The half-life of the chemical in water is greater than two months, or the half-life in soil is greater than six months, or the half-life in sediment is greater than six months. 2. Other evidence that the chemical is sufficiently persistent to justify its consideration
	<p>Environmental fate characteristics of endosulfan:</p> <ul style="list-style-type: none"> ▪ α- and β-endosulfan undergo degradation in soil with half-lives of 12 to 79 days and 42 to 240 days, respectively. ▪ α- and β-endosulfan undergo hydrolysis at pH 7 with half-lives of 22 and 17 days at 22°C, respectively. More rapid hydrolysis occurs under alkali conditions. ▪ Endosulfan sulfate undergoes degradation in soil with half-lives in the range 117-138 days ▪ All isomers are considered photostable in water ▪ α- and β-endosulfan undergo degradation in sediment with a common half life of 38 days
Bioaccumulation	<ol style="list-style-type: none"> 1. Evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000. 2. The logarithm of the octanol-water partition coefficient ($\log K_{ow}$) is greater than 5. 3. Evidence that a chemical presents other reasons for concern, such as high bioaccumulation in other species, high toxicity or ecotoxicity. 4. Monitoring data in biota indicating that the bioaccumulation potential of the chemical is sufficient to justify its consideration.
	<p>Endosulfan BCF and $\log K_{ow}$ characteristics:</p> <ul style="list-style-type: none"> ▪ BCF values of between 350 and 3700 have been determined in more than a dozen studies with a wide range of species. (Note: BCF = 11,000 in a published study of questionable design) ▪ α- and β-endosulfan have $\log K_{ow}$ values of 4.74 and 4.79, respectively
Potential for long-range environmental transport	<ol style="list-style-type: none"> 1. Measured levels of the chemical in locations distant from the sources of its release that are of potential concern. 2. Monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred <i>via</i> air, water, or migratory species. 3. Environmental fate properties and/or model results that demonstrate that there is potential for long-range transport through air, water or migratory species. 4. The half-life in air is greater than two days.
	<p>There are a number of findings of endosulfan at locations distant from the source of its release. The potential for long-range transport is discussed in this report. Endosulfan photo-oxidative degradation profile is summarised below:</p> <ul style="list-style-type: none"> ▪ approx. 2 days (assuming OH concentration of $0.5 \times 10^6 \text{ cm}^{-3}$ at a daily average or approx. 1.3 days at a OH concentration of $1.5 \times 10^6 \text{ cm}^{-3}$ during 12 hours per day) calculated by AOPWIN, v1.88
Adverse effects	<ol style="list-style-type: none"> 1. Evidence of adverse effects to human health or to the environment that justifies consideration. 2. Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

2 Data Mining

C. Halsall, Lancaster University

N. Mackay, Cambridge Environmental Assessments-ADAS

D. Muir, NWRI Environment Canada

2.1 Usefulness of Data and Quality Criteria

Monitoring provides real world data on observed exposure and effects following registration and wide scale usage. The objectives of monitoring exercises vary considerably as pointed out by Trisch and Male (1984). Examples include the provision of data as a basis for the enforcement and development of pollution regulation, to supplement databases for the development calibration and verification of mathematical models of environmental quality to be used in support of other activities and to assure a publicly credible basis for controversial decisions.

Monitoring has the capability of being a very useful 'reality check' on exposure predictions but can be difficult to interpret because of wide range of uncertainties such as spatial (what is the proximity to usage area?) and temporal (how long ago was the release?) issues. These uncertainties can be a significant limitation on the value of monitoring databases as a tool within ecological risk assessment (FOCUS, 2005). When considering the relevance and value of monitoring datasets for substances found at trace levels in the Arctic in assessment of long range transport and persistence potential there are a number of issues that may also frustrate interpretation. The following issues need to be considered with care:

- Which monitoring programmes considered the chemical in question?
- What was the monitoring strategy and aims of the monitoring programme?
- What storage, extraction, purification and identity confirmation strategies have been employed?
- Were the analytical techniques used suitable for characterising the chemical in question at levels of ecological significance?
- What was the environmental, spatial and temporal context in which detections were found?
- When considering monitoring of biota can biological context be established (i.e. age, weight, sex, lipid content vs whole body weight etc...)
- Were any attempts made to track and identify causes for large-scale detections (i.e. point source contamination, back-tracing to usage events/timings etc.)?
- What mathematical treatment has raw data undergone in order to present monitoring profiles (treatment of trace detections at, or below, limit of quantification, use of arithmetic or geometric means or medians, treatment of outliers etc.)

2.2 Selection of Data for Use in Interpretation of Endosulfan in a POP Context.

When considering endosulfan, there are specific issues that require careful consideration. The most significant of these are related to analytical strategy. Endosulfan may be present in α - or β -forms but it is not unusual for analysis to consider either the α -form alone or so-called 'total endosulfan' (α -, β -endosulfan). Issues arise with analytical methodology and rigour and, in particular, potential for interference.

It is noted that interference issues have arisen between endosulfan and other chlorinated pesticides in the analysis of environmental samples. This is particularly relevant for samples analysed using GC-ECD alone, where co-elution with other chlorinated compounds may give rise to peak mis-identification. However, for

contemporary studies (over the last 10 years or so), confirmatory analysis has usually been conducted by GC-MS, although some interference issues have been reported in GC-MS analysis between α -endosulfan and chlordane components in Arctic air samples (Chernyak *et al.*, 1996). In addition, interferences between β -endosulfan and components of toxaphene (a complex organochlorine pesticide comprising of hepta- to nona-chlorinated homologues) can occur, with β -endosulfan possessing a similar chromatographic retention time and qualifier ion (MS operated in NCI mode) as a toxaphene component (Jantunen, *per. comm.*).

When considering the primary datasets summarised later in Section 2.3, care and attention has been paid to these issues in an attempt to ensure that the resulting interpretations are robust and reliable. Under certain circumstances, the full strategy or context that underpins the monitoring data is not available. However, where such data were carried forward into this assessment, the absence of a complete context was not considered to present significant problems with respect to interpretation.

In general, the following profiles are relevant to most of the monitoring datasets employed within this assessment:

Which analytes were considered (α and/or β endosulfan, endosulfan sulfate, other potential/known POPs)?

Most data are held for alpha and beta-endosulfan although some limited data for endosulfan sulfate is held for monitoring programmes in the Great Lakes. Although not classified as Arctic, these later samples may be relevant when considering detection in remote systems and provide indications of bioaccumulative behaviour when compared against biota samples of similar origin. Monitoring datasets often also include various isomers of HCH, specific PCB congeners or total PCBs.

Analytical methodology and rigour (LOD, LOQ, assessment for potential analytical interference)

A range of analytical strategies are employed for endosulfan (α and β). Unfortunately, endosulfan sulfate has not been typically included in most monitoring programmes. Typical strategies are summarised in Table 2.2.1.

Location and dates of monitoring

Temporal context is available at least to the resolution of establishing the year of monitoring. Generally, higher temporal resolution (e.g. season or month) is more typical. Continuous air sampling provides detailed temporal context. Spatial context is often available as routine (air) or seasonal (snow/precipitation/freshwater) monitoring campaigns are based upon fixed locations. Marine sampling from cruises is typically supported by latitude and longitude references.

Biota monitoring

Age, sex and lipid content of tissue analysed is available for mammals except in the Greenland diet study (Johansen *et al.*, 2004) where only lipid content is available. For fish, age and lipid content are generally available for top predators e.g. char, lake trout.

Table 2.2.1 Typical analytical strategies for α - and β -endosulfan

Matrix	Analytical technique	Detection limits*
Biota	GC-ECD (gas chromatography - electron capture detection)	Method Detection Limit for α - and β -endosulfan typically ca 0.0087 and 0.040 ng/g, respectively, typically based on 10 g wet weight samples ($\text{Mean}_{\text{blank}} + (3 \cdot \sigma_{\text{blank}})$)
Seawater	XAD resin extraction of large volume samples (ca 100 L) followed by analyses via GC-ECD or GC-NCIMS.	Method Detection Limits typically range from 0.1 to 0.5 pg/L ($\text{Mean}_{\text{blank}} + (3 \cdot \sigma_{\text{blank}})$)
Snow	GC-NCIMS	Method Detection Limit ca 131 pg/L ($\text{Mean}_{\text{blank}} + (3 \cdot \sigma_{\text{blank}})$) Limit of quantification ca 360 pg/L ($\text{Mean}_{\text{blank}} + (10 \cdot \sigma_{\text{blank}})$)
Air	Sample collection of high air volumes (1,000-10,000 m ³) trapped on polyurethane foam plugs (PUFs) followed by Soxhlet extraction and analysis by GC-ECD	Method Detection Limit for α -endosulfan: 0.05 – 0.3 pg/m ³

* Definition consistent with Gomez-Taylor *et al.* (2003); Limit of Detection (LOD) is equivalent to the Method Detection Limit (MDL; $\text{Mean}_{\text{blank}} + (3 \cdot \sigma_{\text{blank}})$). Limit of Quantification (LOQ) is considered equivalent to $\text{Mean}_{\text{blank}} + (10 \cdot \sigma_{\text{blank}})$.

2.3 Review of Strategy Including Sources of Information on Endosulfan Residues

The measurement of organochlorine pesticides in the Arctic has been largely conducted under the auspices of national programmes funded and organised through the circumpolar nations, particularly Canada, Norway and Sweden. In the early 1990s the Arctic Monitoring Assessment Program (AMAP) was established as part of a wider Arctic Environmental Strategy (AES) to determine, amongst other things, the impact of anthropogenic pollution on the Arctic, and its effect on wildlife and native arctic peoples. Under the framework of national programmes, such as the Canadian Northern Contaminants Program (NCP), both biotic and abiotic data have been gathered through field-based campaigns and monitoring programmes. These data have been subsequently assimilated into national reports and incorporated into the AMAP Assessment reports.

2.3.1 Abiotic Data

The spatial and temporal coverage of semi-volatile organic compounds (SVOCs) for a variety of environmental compartments across the Arctic (including endosulfan data) is not as extensive or as systematic as datasets generated from temperate/industrialised regions. However, data for endosulfan are available for the major arctic compartments of air, surface seawater and snow; primarily for the 1990s. The primary metabolite, endosulfan sulfate, has been included in relatively few monitoring campaigns. Data for this report have been obtained from a variety of sources, mainly from branches within Environment Canada, but also from university/institute-led field campaigns. The purpose for acquiring data for abiotic matrices is to:

- Assess the occurrence and concentrations of α - and β -endosulfan;
- Allow comparisons with another currently-used pesticide (γ -HCH) and;

- Examine chemical transport into the Arctic and transfer between air and arctic surfaces.

The latter will help understand endosulfan fate in the Arctic, its loading to different compartments, and the baseline data necessary to assess biota exposure.

Air monitoring

The most extensive Arctic datasets for endosulfan exist for the atmosphere, under the Canadian Northern Contaminants Program. Air data through systematic air sampling (over periods of >1 year) are available at sites that cover a wide spatial area and are outlined in Table 2.3.1. Air monitoring stations have provided data for the Canadian high Arctic, the Canadian Yukon as well as eastern and western Siberia.

Table 2.3.1. Arctic air sampling locations where endosulfan was included

Sampling location	Grid Reference	Sampling dates	Average sample volume (m ³)	Sampling frequency
¹ Alert, Nunavut Canada	82.47°N, 62.5°W	1992-1999	>10,000	weekly
¹ Tagish, Yukon, Canada	60.30°N 134.12°W	1993-1994	>10,000	weekly
¹ Dunai, E.Siberia	74.10°N 124.50°E	1993-1994	>10,000	weekly
¹ AmDerma, W. Siberia	68.20°N 48.3°E	1998-1999	>10,000	weekly
² Bering Sea (BERPAC)	Various	Aug-Sept 1993	3000	daily
³ Tromsø, Norway	69.65°N, 16.96°E	Feb/March 2003	1100	daily

¹NCP sites - Hung *et al.* (2002); ²Chernyak *et al.* (1996); ³Herbert *et al.* (2005c)

At each of the NCP locations outlined in Table 2.3.1, integrated air samples (over seven days) were taken each week using a High-Volume air sampler fitted with a glass-fibre filter and polyurethane foam to trap the particle and vapour phases respectively. Details of sampling and analytical procedures as well as data handling and quality control issues are provided in Fellin *et al.* (1996). A number of chemical classes have been consistently screened in these air samples. These include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochlorines (OCs). Additional air data are also available for discrete time periods (<1 year) as part of separate air/seawater and air/snow sampling campaigns. These studies are also included in Table 2.3.1 and also utilise high volume air sampling. The study at Tromsø in northern Norway collected daily samples over a two week period in February/March 2003 and, while representing only a brief snapshot in time relative to the NCP sites, does provide the only air data for endosulfan in the European Arctic.

Seawater monitoring

Surface seawater data are restricted to separate sampling campaigns conducted during the Arctic summer when large parts of the Arctic Ocean are ice-free. Much of the OC data are unpublished. Field campaigns have been conducted between 1993 to 2000, through ship-board cruises and are listed in Table 2.3.2. The notable exception is the seawater data collected offshore from Cornwallis Island (Canadian Archipelago) *via* a fixed oceanographic sampling station. This study provided a year

long (1993) time-series of monthly α -endosulfan water concentrations, including winter and summer (ice-free) periods. From Table 2.3.2 different regions of the Arctic Ocean have been subject to ship-based campaigns that provide wide spatial coverage in surface seawater concentrations (the surface defined here as the surface polar mixed layer, ~0-100 m). In most cases, data represent multiple water samples taken over the period of a month or two, usually along a specific cruise track, or within a certain locality/region. Seawater is acquired through large volume grab samples using a submersible pump and stainless-steel collection cans. The seawater is subject to filtration and then solid-phase extraction (e.g. XAD-2, C-18 resins) to trap sufficient chemical residue for analysis. Much of the data gathered are restricted to OC pesticides, although other chemical classes such as the PCBs have been analysed in later campaigns. Details of sampling procedures, extraction protocols, analysis and quality controls, that are typical of the studies presented in Table 2.3.2, are presented in Jantunen & Bidleman (1998).

Table 2.3.2 Arctic seawater sampling locations and details

Cruise name/ study	Sampling Location/ region	Sampling Dates	Sample Volume (L)	<i>n</i>
¹ <i>Bering Sea 93</i>	Bristol Bay (south-west Alaska)	July 93	~75	7
² <i>Cornwallis</i>	Cornwallis Is (Barrow St.) Canadian Archipelago	Jan 93 – Sept 93	200 - 400	NA
¹ <i>JOIS97</i>	Arctic Ocean transect (Bering to Barents Sea)	Sept 1993	NA	10
³ <i>AOS-94</i>	Arctic Ocean transect Chuckchi to Greenland Sea	July – Sept 1994	200	20
⁴ <i>Barrow</i>	Beaufort & Chukchi Seas (northern Alaska)	May-July1999 & May2000	100	9
⁴ <i>Holman</i>	Holman Island Canadian E. Archipelago	May-July 1999	100	3
⁵ <i>White Sea</i>	Onega/Kandalaksha Bay, White Sea	Sept 1999 & July 2000	100	10
¹ <i>Oden 96</i>	Bering Sea and Eastern Arctic Ocean	July-Sept 1999	78 (mean)	43
¹ <i>TNW99</i>	Canadian E. Archipelago	July 1999	~100	6
¹ <i>NOW98</i>	Canadian Archipelago	May 1998	78 (mean)	28

¹Strachan *et al.* (unpublished) ²Hargrave *et al.* (1997); ³Jantunen and Bidleman (1998)

⁴Hoekstra *et al.* (2003), ⁵Muir *et al.* (2003b) ; NA = not available

Snow monitoring

Snow data for SVOCs in the Arctic are scarce. In the scientific literature there are only a handful of studies that report OC concentrations in Arctic snow (e.g. Gregor and Gummer, 1989). Nevertheless, unpublished data for OCs including endosulfan are available for snow from an extensive Canadian survey conducted by Environment Canada (CCIW) during the 1990s, which includes sites located in British Columbia, Yukon and Arctic Canada (NWT and Nunavut). Furthermore, endosulfan concentrations in surface and deep snow are also available from Svalbard in the Norwegian Arctic. Details of these studies which include endosulfan data are given in Table 2.3.3, although spatial coverage is not as extensive as air or seawater data. Snow sampling for SVOCs entails the collection of large volumes of snow to ensure detectable concentrations and is undertaken using aluminium or

stainless steel cans, and in some cases large volume Teflon bags (Garbarino *et al.* 2002). Following collection in the field, snow is then allowed to melt in the sampling container and the meltwater subject to in-line filtration and solid-phase extraction similar to the water samples described above. Details of a low and high-volume snow sampler along with field validation and extraction procedures for SVOCs can be found in Herbert *et al.* (2004). For all the locations listed in Table 2.3.3, with the exception of Svalbard, only surface snow layers and/or freshly fallen snow have been sampled. This is relevant and will be discussed further in Chapter 4, as snow compaction and ageing can significantly reduce the original concentrations of OCs present in fresh snow (Herbert *et al.*, 2005c)

Table 2.3.3. Snow sampling locations and details

Location	Winter Sampling periods	Meltwater (L)	<i>n</i>
¹ Alert, Nunavut, Canada	Dec 92 – April 95	2.0 – 37.5	52
¹ Eureka, Nunavut, Canada	Sept 91 – March 92	5.5 – 12.8	19
¹ Cape Dorset, Nunavut, Canada	Nov 93 – May 95	4.0 – 38.6	32
¹ Dawson, Yukon, Canada	Dec 93 - March 94	4.1 – 19.1	10
¹ Whitehorse, Yukon, Canada	Dec 91 – March 94	7.5 – 60.5	27
¹ Mould Bay, NWT, Canada	Oct 91 – May 95	3.4 – 29.5	86
¹ Snare River, NWT, Canada	Jan 93 – May 95	4.8 – 30.0	38
¹ Fraser River, BC, Canada	Nov 92 – March 95	2.8 – 18.0	27
¹ Tagish, Yukon, Canada	Nov 92 – March 95	3.3 – 17.5	44
² Northwest Alaska, USA	April 1996	~ 1	30
³ Svalbard, Norway	NA	~20	15

¹Strachan *et al.* (unpublished); ²Garbarino *et al.* (2002);

³Hermanson *et al.* (2004)

Environmental data

In some of the field studies outlined above, physical measurements of key environmental parameters are also available and compliment the endosulfan measurements. For the air sampling programmes air temperatures are usually available and air mass back trajectories have been utilised to track the origins or pathway of prevailing air movement for specific sampling periods (e.g. Bailey *et al.* 2000). All the OC air concentrations for the studies outlined in Table 2.3.1 have been previously normalised to standard temperature and pressure (STP), to remove variations in data due to changes in air temperature and pressure. Similarly surface ocean water temperatures have also been recorded at the time of sampling for some of the studies presented in Table 2.3.2, and these often include salinity measurements as well. Snow physical parameters (e.g. density, snow water equivalents (SWE)) for the snow studies (Table 2.3.3) are missing in most cases,

although average precipitation rates and SWEs are available for parts of the Canadian Arctic, through the Meteorological Services of Canada (Environment Canada).

2.3.2 Biotic Data

Endosulfan has been determined in most recent surveys of fish and marine mammals in Alaska, Canada and Greenland. Also limited data exists for endosulfan in marine mammals and fish from Russia. In addition to these results from the Lake Superior foodweb are included because this large lake receives inputs mainly from atmospheric deposition and thus has similar pathways of input to Arctic marine and freshwater systems, although not necessarily 'long-range' transport as historic and recent endosulfan use occurs much closer in the states of Michigan, Wisconsin and Minnesota. These datasets (summarised in Table 2.3.2.1) were examined with a view to assessing the bioaccumulation potential of endosulfan and the exposure of top predators and humans.

Table 2.3.2.1 Summary of fish and marine mammal monitoring exercises in the Arctic including endosulfan

Region	Location	Species	Laboratory	Reference
Alaska, Beaufort Sea	Barrow, AK	Marine food web including bowhead whales	NWRI	Hoekstra <i>et al.</i> (2002) (2003) and unpublished data
Canadian Arctic	Holman, NWT	Marine food web including ringed seals	NWRI	Hoekstra <i>et al.</i> (2003) and Muir, unpublished data
Canada Alaska, Greenland & Russia	20 locations	Ringed seals	NLET/NWRI	Muir <i>et al.</i> (2003a) and unpublished data
Canadian Arctic	E. Hudson Bay	Marine food web including ringed seals & beluga	DFO/IOS	Kelly (2005)
North American Great Lakes	Lake Superior	Food web	NLET/NWRI	Muir unpublished
Greenland	West and East Greenland	Human diet studies including marine fish, marine mammals and seabirds	NLET/NWRI	Johansen <i>et al.</i> (2004a)
Russian Arctic	White Sea	Marine food web including ringed seals and harp seals	Alexeeva Lab, Typhoon Lab	Muir <i>et al.</i> (2003b)
Russian Arctic	Pechora and Kara Seas	Ringed seals	Typhoon Lab	Savinova <i>et al.</i> (2004)

The dataset for endosulfan was developed as part of a much larger dataset on PCBs and organochlorine (OC) pesticides generated mainly by the National Laboratory for Environmental Testing (NLET) located at NWRI (Burlington) in cooperation with D. Muir. The dataset for samples from the Beaufort Sea food web was generated by Dr. Paul Hoekstra (now with Syngenta Crop Protection Canada, Inc) as part of his PhD research (co-supervised by K. Solomon and D. Muir) using facilities at NWRI including analytical standards used by NLET. Results for the East Hudson Bay marine food web were provided by PhD student B. Kelly (co supervised by F. Gobas (Simon Fraser Univ) and M. Ikonou (Fisheries and Oceans)). The results for the

White Sea were provided by the laboratory of Ms. Ludmila Alexeeva of SPA Typhoon (Obninsk, Russia) who used analytical standards, certified reference materials and instrumentation supplied by NWRI. Other results for ringed seals from Russia were also generated at SPA Typhoon under the supervision of L. Alexeeva and A. Konoplev as part of a study funded by the Arctic Monitoring and Assessment Program (Savinova *et al.* 2004).

A substantial amount of data on concentrations of α -endosulfan and β -endosulfan in Arctic biota exists. However, very limited information exists on endosulfan sulfate. Most of the data was generated as a result of projects funded by the Northern Contaminants Program in Canada, the Danish Co-operation for Environment in the Arctic (DANCEA) and the Commission for Scientific Research in Greenland. These programs have extensive quality assurance components (e.g. see Stokker (2003)) that were focused on OC pesticides, PCB congeners and toxaphene. No quality assurance (QA) program specifically targeted endosulfan. However, all projects included blanks and certified reference materials (e.g. NIST (National Institute of Standards and Technology) 1588a cod liver oil) that were analysed for α -endosulfan and β -endosulfan. Thus information on precision and detection limits for endosulfan can be obtained for each dataset reported herein.

The most extensive dataset used in this assessment is from the Greenland diet study. This study determined cadmium, mercury, selenium, PCB, DDT, chlordanes, toxaphene, HCH, chlorobenzenes, mirex, octachlorostyrene, and endosulfan in over 500 samples, mainly from Western Greenland with a subset from East Greenland. An assessment of the significance to human exposure to contaminants of the different diet items has been presented by Johansen *et al.* (2004b).

Detailed methods for the Greenland diet study are given in Johansen *et al.* (2004a) Quantitative analysis was by high resolution capillary GC with electron capture detection using a Agilent 6890 GC equipped with a 30 m x 0.25 mm, 0.25 μ m film thickness DB-5 column programmed at 15°C/min to 150°C and 3°C/min to 265°C. Carrier gas was H₂ (about 1 mL/min) and make-up gas was N₂ (40 mL/min). PCB congeners and OC pesticides were quantified by GC-ECD using a series of authentic external standards. Essentially the same approach was used in all endosulfan analysis outlined in Table 2.3.2.1.

Table 2.3.2.2 shows detection limits and QA data for α and β -endosulfan also calculated from the Greenland dataset. NIST cod liver 1588a and mussels 1974a were used as reference materials. No certified values were available for endosulfan isomers in either reference material but they are reported here for future reference. α -Endosulfan was non-detectable in the mussels. Based on the results for blanks the method detection limit (Gomez-Taylor *et al.* 2003) for α -endosulfan, following blank correction, was 0.0087 ng/g for a 10 g tissue sample or 1 g for a blubber sample.

The results for the NIST reference materials that analyses were generally within acceptable limits (e.g. $\pm 30\%$ of certified values) for PCB congener 153. Although GC-MS has been used extensively for analysis of endosulfan in abiotic samples it has not been used in the analysis of most samples of Arctic biota. Several case studies are discussed below to attempt assess the accuracy of the GC-ECD analysis for endosulfan.

Table 2.3.2.2 QA data from the Greenland database including results for certified reference materials. Data are from Johansen *et al.* (2004a)

Compound	Average method blank value \pm SD (n = 10) ng/g	Detection ¹ limit (3xSD) (ng/g wet wt)	NIST 1588a ² value (% deviation; n=19) ng/g wet wt	NIST 1974a ³ value (% deviation; n=15) ng/g wet wt
α-endosulfan	0.004 \pm 0.0029	0.0087	4.3	<0.04
β-endosulfan	0.011 \pm 0.013	0.040	39.5	<0.01
g-HCH (lindane)	0.004 \pm 0.0029	0.0086	16.9 (-32%)	0.06
PCB 153	0.087 \pm 0.036	0.11	241.6 (-11%)	12.5 (-24%)

¹ Detection limits based on a 10g sample size (all tissues except blubber)

² Cod liver oil reference material available from National Institute of Standards and Technology (www.NIST.gov). Deviation from certified values in parentheses No certified values

³ Mussel reference material available from National Institute of Standards and Technology

Endosulfan confirmation by GC-MS: Arctic char, ringed seal, and beluga sample extracts as well as lake trout extracts were analysed by GC-ECD and by GC-low resolution negative chemical ionization MS (GC-NCIMS). The GC-NIMS conditions for α - and β -endosulfan and endosulfan sulfate were identical to those used for toxaphene analysis except that m/z 406 and 408, as well as m/z 372 and 374 were monitored. 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) and GC-ECD results have been summarized in Muir *et al.* (Muir *et al.* 2003a; 2003c). Methods for extraction and analysis of the lake trout samples (for OCPs including toxaphene) are given in Muir *et al.* (2004). The comparison (Table 2.3.2.3) illustrates the challenges of determining low levels of endosulfan. Clearly both isomers are subject to interference in the analysis by GC-ECD.

While GC-NIMS gave consistently lower concentrations than ECD in all 3 Arctic species which have α -endosulfan close to the MDL, the reverse was true for Lake Superior. 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 lake trout and arctic char samples which yield false positives for this isomer by GC-ECD. Because the interference occurs at m/z 406 under GC-NIMS conditions it is likely due to co-eluting chlordane or toxaphene components. These may be related to the presence of toxaphene which is a major contaminant in lake trout (Muir *et al.* 2004) and is also present at low concentrations in arctic char (Muir *et al.* 2003c). Chlordane is a major contaminant in ringed seal and beluga blubber and has hepta-, octa- and nonachloro- components which could potentially co-elute with endosulfan components.

Kelly (2005) determined α -, β -endosulfan and endosulfan sulfate in ringed seal and beluga blubber samples by GC-high resolution MS (GC-HRMS) using the method of Rayne and Ikononou (2003). The method detection limits for α -, β -endosulfan and -sulfate were 0.34, 0.30, and 0.085 ng/g wet wt for blubber by this method (Kelly, 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).

Table 2.3.2.3. Results of analysis of arctic char (muscle), lake trout (whole fish), ringed seal and beluga samples by GC-ECD and GC-MS. Concentrations are ng/g wet wt.

Species	Location		n	α -endo	α -endo	β -endo	β -endo	EndoSO ₄
				ECD	MS	ECD	MS	MS
GC-Negative ion MS ¹								
Arctic char	Resolute and Char Lakes	Mean	22	0.12	0.06	0.46	0.003	-
		SD		0.09	0.03	0.55	0.003	-
Lake trout	Lake Superior	Mean	10	1.7	2.6	8.1	<0.01	0.23
		SD		1.6	2.4	9.3	-	0.13
Ringed seal	Central Canadian arctic (Arctic Bay, Resolute, Gjoa Haven)	Mean	22	2.00	0.47	1.67	0.21	0.04
		SD		3.19	0.22	2.07	0.19	0.02
Beluga	Eastern Hudson Bay	Mean	4	3.99	0.33	6.51	0.21	0.03
		SD		5.90	0.14	2.75	0.14	0.01
GC-high resolution MS ²								
Ringed seal	Northern Quebec	Mean	8	0.37	0.45	0.88	2.2	0.07
		SD		0.38	0.48	0.78	3.3	0.05
Beluga	Eastern Hudson Bay	Mean	13	16.9	<0.34	10.5	8.0	0.75
		SD		12.3	-	11.0	6.3	0.51

¹GC-NIMS results for char and lake trout 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,2003c).

² GC-high resolution MS (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).

The GC-HRMS results confirm the presence of all 3 endosulfan species in beluga and ringed seal (Table 2.3.2.3) 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 ww) and mean concentrations were similar to those for the central Canadian arctic (Table 2.3.2.3). 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 ¹³C-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 the high-res MS (12 of 13 samples <MDL of 0.34 ng/g). This is in general agreement with the results for α -endosulfan 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 Lake Superior lake trout and in arctic biota (Table 2.3.3).

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.

Conclusions from the GC-MS results

The analysis of samples by NIMS and HRMS shows that while α -, β -endosulfan and -sulfate are present in Arctic biota there is great uncertainty as to actual concentrations determined by ECD. Expressed in percentage terms, the deviation between ECD and MS for α -endosulfan in ringed seals is best, ranging from -22% for 8 Northern Quebec samples analysed by HRMS to +425% for 22 central Arctic samples analysed by NIMS. The deviation for 22 arctic char samples was +100%. While HRMS might be assumed to give the most accurate results because of millimass resolution, higher MDLs and interference from deuterated internal standards may have compromised some of this data particularly for β -endosulfan. The confirmation certainly casts doubt on some endosulfan results by ECD particularly for beluga blubber which appears to have co-eluting interferences for α -endosulfan and endosulfan sulfate.

3 Endosulfan Sources and Dispersion

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3.1 Degradation Pathway and Evidence of Decay in Environmental Media

Upon transport into the Arctic *via* air, water, or migratory species, endosulfan may then undergo transformations. Degradation behaviour of endosulfan has been intensively assessed as a regulatory requirement for its registration as a plant protection product. These assessments are typically intended to have particular relevance to temperate agriculture in Europe and North America but are, nonetheless, instructive in understanding potential fate and behaviour in the Arctic. The transformation pathways are likely to be identical but rates of degradation may be reduced in some cases where there is an obvious dependency on temperature. In the case of photolytic transformation potential following reaction with hydroxyl radicals, there is likely to be a dramatic change due to a differing sunlight intensity and temperature conditions relevant to temperate Europe and North America to those under the extremes of Arctic summer and winter conditions.

Fate and behaviour in soil

Endosulfan is a labile cyclic sulfurous acid diester with a chlorinated (hexachloronorborene ring) group. The presence of this cyclic sulfite group makes the compound susceptible to chemical and biochemical reactions. Endosulfan undergoes a range of transformation processes leading to mineralization that includes biological degradation, oxidation, isomerisation, and dechlorination (Stumpf *et al.*, 1995; Martens, 1977; Gildermeister and Jordan, 1984; Stumpf *et al.*, 1988). Endosulfan is particularly susceptible to hydrolytic transformation in water under alkaline conditions. Hydrolysis of the cyclic sulfite diester group results in formation of the more polar and less toxic endosulfan-diol with release of sulfite from the heterocyclic ring of both isomers. Ester hydrolysis also occurs with the main and only relevant metabolite, endosulfan sulfate. After formation, this metabolite is also subject to microbial degradation itself. The occurrence of endosulfan sulfate in soil has been shown to reach levels equivalent to just over 40% (Czarnecki & Mayasich, 1992) of the original parent (endosulfan) application in a field dissipation study conducted in California. In additional studies conducted in both North America and Europe endosulfan sulfate accounted for maximums of between 7.8% to 34.5% of parent endosulfan (Balluff, 2001; Hacker, 1989; Hardy 2001; Mester, 1990).

In addition, an aerobic soil degradation study was performed with endosulfan sulfate by Schnoeder (2002a,b), in order to investigate the metabolism and degradation rate of this metabolite in four soils. The soil was incubated in the laboratory under aerobic conditions at 20±2°C and a moisture of 30 to 40% of the maximum water holding capacity in the dark for a period of 365 days in total. The resulting degradation half-lives were 117, 134, 138 and 412 days. The later value was concluded to be an outlier as it could be invalidated by a terrestrial field study (with a shorter half life for the sulfate) conducted on the same plot in Spain, where this soil for the original laboratory study had been sampled.

Degradation assessments carried out under laboratory conditions may suffer for declines in microbial activity when studies are conducted over long timescales. This may have the effect of artificially extending the apparent persistence of chemicals. For compounds with potential persistence concerns, it may be more appropriate to interpret the results of field studies as a more realistic basis for assessing degradation behaviour.

α - and β -Endosulfan and endosulfan sulfate are rapidly and strongly adsorbed to soil, confirmed by laboratory studies where high adsorption coefficients were observed (Görlitz and Eyrich, 1988a,b). It was concluded that adsorption was almost completely reversible with K_{des} values approximating K_{ads} values. The results of the adsorption coefficients to organic carbon (K_{oc}) from the studies undertaken by are summarised in Table 3.1.1.

Table 3.1.1 Summary of adsorption coefficients for α - and β -endosulfan, endosulfan sulfate and endosulfan diol

Compound	K_{oc} ranges	
	Agricultural soils	Reference
α -endosulfan	7800 - 21300	Görlitz and Eyrich (1988)
β -endosulfan	8600 - 13900	Görlitz and Eyrich (1988)
Endosulfan sulfate	3800 – 6500	Singer and Chen (1997)
Endosulfan diol	800 – 5300	Singer and Chen (1997)

Fate and behaviour in water

As discussed earlier, endosulfan undergoes relatively rapid hydrolysis under alkali conditions. Some surface waters may have close to neutral pH conditions where hydrolytic degradation proceeds at a slower, but environmentally significant, rate (see Table 3.1.2; Goerlitz and Rutz, 1989; Goerlitz and Kloeckner, 1982; Goerlitz, 1984). Where acidic surface waters are encountered, the rate of hydrolysis decreases markedly and other degradation processes, including microbial mechanisms, may increase in relative importance.

Table 3.1.2 Hydrolytic half-lives for α - and β -endosulfan

	Temperature	pH 5	pH 7	pH 9	Reference
α -Endosulfan	22°C	> 1 year	22 days	7.0 hours	Goerlitz and Kloeckner, 1982
	25°C	> 200 days	19 days	6.2 hours	Goerlitz and Rutz, 1989
β -Endosulfan	22°C	> 1 year	17 days	5.1 hours	Goerlitz and Kloeckner, 1982
	25°C	> 200 days	10.7 days	4.1 hours	Goerlitz and Rutz, 1989

As summarised earlier, adsorption of endosulfan and endosulfan sulfate is relatively strong. As a consequence, the potential for partitioning onto sediment or suspended sediment is a significant dissipation process following pulse loadings (e.g. spray drift or run-off) in relatively small scale systems that are most intimately associated with agricultural systems. In contrast, loadings into Arctic systems will be of a more diffuse nature, associated with scouring by rainfall and airborne particulate matter (dust, aerosols, etc.). Background residues in marine and freshwater systems will be closer to equilibrium with sediment and suspended sediment.

Fate and behaviour in air

The most effective reactive intermediate known in the troposphere is the OH radical which is formed by sunlight. Other intermediates like ozone or nitrosyl radicals

usually have a lower potential of photo-oxidative degradation of organic chemicals. The global mean concentrations of OH radicals in the air is assumed to be a diurnal mean of 500,000 radicals/cm³ (Hewitt and Harrison, 1985). This figure is often adopted as a basis for calculation of photo-oxidative degradation in temperate latitudes. However, in Arctic regions the presence of hydroxyl radicals undergoes a dramatic seasonal shift.

Estimates conducted with AOPWIN v1.88 (Buerkle, 2001) resulting in a photo-oxidative DT₅₀ of 47.1 hours (1.96 days) assuming an OH[•] concentration of 0.5 x 10⁶ cm⁻³ in 24 hours per day and 1.3 days for an OH[•] concentration of 1.5 x 10⁶ cm⁻³ in 12 hours per day. It is noted that there is some uncertainty surrounding the estimated DT₅₀ in air related to the estimation method, the determination of the OH[•] reaction rate and variation in OH[•] concentration.

3.2 Bioaccumulation, Bioconcentration and Biomagnification Potential

Upon transport into the Arctic, chemicals may then be subject to processes leading to bioaccumulation in biota. Hydrophobic compounds may persist in lipid tissues depending upon how fast and completely they are metabolized and may demonstrate cumulative toxicity to organisms. Chemicals with such characteristics are usually assessed in bioconcentration tests that are designed to determine or predict the bioconcentration factor (BCF). The BCF is the ratio of the average concentration of test chemical accumulated in tissues under steady state exposure conditions to the average measured concentration in the water to which the organism is exposed (Rand *et al.*, 1995).

Care should be taken to differentiate the concept of bioaccumulation, bioconcentration and biomagnification. A glossary of terms is provided in Section 10 that may assist the reader in differentiating these concepts. The following very brief summaries provide an outline of the comparative frameworks (based upon Gobas and Morrison, 2000). More detailed definitions are summarised in the glossary of terms, provided towards the end of this report (see Section 11):

- **Bioaccumulation:** Process by which the chemical concentration in an organism exceeds that in the water, as a result of chemical uptake through all possible routes of chemical exposure (combination of bioconcentration and biomagnification)
- **Bioconcentration:** Process by which the chemical concentration in an organism exceeds that in water as a result of absorption only from the water via the respiratory surface (e.g., gills) and/or the skin.
- **Biomagnification:** Process in which the chemical concentration in an organism achieves a level that exceeds that in the organism's diet, due to dietary absorption.

Studies specifically designed to assess bioaccumulation of chemicals in the field are relatively rare. Instead, it is more common in regulatory assessments to consider bioconcentration profiles evaluated under laboratory conditions. Tests have been carried out with endosulfan with a range of fish species and mussels under both laboratory and field exposure conditions. A number of the bioconcentration factors (BCF) measured for fish ranged (with the exception of one study) from 350 to 3700. In the study presenting higher values, these BCF were derived by calculation beyond the range of measured values and are thus suspect because steady state was not reached.

Table 3.2.1. Results of bioconcentration assessments for endosulfan in the laboratory and field

Organism	Exposure	BCF	Reference
Phytoplankton			
<i>P. subcapitatum</i>	100 µg/L; 16 h	2682	De Lorenzo <i>et al.</i> (2002)
<i>Anabaena sp.</i>	100 µg/L; 16 h	770	Rao and Lai (1987)
<i>Aulosira fertilissima</i>	100 µg/L; 16 h	1787	Rao and Lai (1987)
Zooplankton			
<i>Daphnia magna</i>	100 µg/L; 24 h	3278	De Lorenzo <i>et al.</i> (2002)
Grass shrimp			
<i>Palaemonetes pugio</i>	0.2 µg/L; 30 d	200	Wirth (1999)
<i>Palaemonetes pugio</i>	0.16 µg/L; 96 h	81-245	Schimmel <i>et al.</i> (1977)
Oyster			
<i>Crassostrea virginica</i>	0.2 µg/L; 96 h	330	Scott <i>et al.</i> (1990)
Fish			
<i>Fundulus heteroclitus</i>	0.2 µg/L; 96 h	330	Scott <i>et al.</i> (1990)
<i>Lagodon rhomboides</i>	0.15 µg/L; 96 h	1299	Schimmel <i>et al.</i> (1977)
<i>Leiostomus xanthurus</i>	0.076 µg/L; 96 h	895	Schimmel <i>et al.</i> (1977)
<i>Mugil cephalus</i>	0.32 µg/L; 96 h	1344	Schimmel <i>et al.</i> (1977)
<i>Mugil cephalus</i>	0.035 µg/L; 28 d	2429 (edible tissues) 2755 (whole)	Schimmel <i>et al.</i> (1977)
<i>Carassius auratus</i>	1 µg/L	350	Oeser <i>et al.</i> (1991)
<i>Cyprinodon variegatus</i>	Various*	350 - 3700	Hansen & Cripe (1991)
<i>Brachydanio rerio</i>	0.3 µg/L (0.2 - 0.4 µg/L)	2650	Toledo & Jonsson (1992)
<i>Hyphessobrycon bifasciatus</i>	0.3 µg/L (0.2 - 0.4 µg/L)	9900-11600**	Jonsson & Toledo (1993)
Mussels			
<i>Mytilus edulis</i>	0.14 µg/L	600	Ernst (1977)
Field studies			
<i>Lepomis spec.</i> , <i>Micropterus salmoides</i>	0.0641 - 0.195 µg/L	104 – 191***	Cornaby <i>et al.</i> (1989) and Heusel (1992)

* An inter-laboratory precision comparison of the uptake of endosulfan undertaken in a modified early-life stage test was investigated at five contract and two US EPA laboratories. The interlaboratory variability of the results of this test was considered particularly good relative to variability of other tests considering the following: the test was complex; the laboratories were inexperienced; the embryos were from Atlantic and Gulf Coasts; and test water was from the Atlantic, Gulf, and Pacific Coasts. Authors conclude that variation in this and other toxicity and bioconcentration tests using marine species should be considered when judging the environmental implications of results.

** Values calculated beyond measured results

*** Assuming only bioconcentration from water without biomagnification

Of particular interest in considering bioconcentration at lower levels in the aquatic food chain and trophic uptake are the findings of De Lorenzo *et al.*, (2002). This study examined the toxicity of endosulfan to *Pseudokichneriella subcapitatum* (freshwater green algae) and *Daphnia magna* (freshwater cladoceran). The potential for both plankton species to sequester endosulfan from their surrounding media was assessed. In addition, the degree to which endosulfan is accumulated by *D. magna* via food (endosulfan contaminated *P. subcapitatum*) was also considered by exposing *D. magna* to treated water/treated algae and clean water/treated algae combinations in order to assess relative bioaccumulation contributions of water and

food (estimation of BCF_{water} , BCF_{food} and $BCF_{\text{food+water}}$). Although a BCF_{water} of 2682 was calculated for *P. subcapitatum*, the hypothesis that endosulfan would be trophically transferred from phytoplankton to invertebrate grazers was not supported by these experiments. Although *D. magna* neonates rapidly bioaccumulated and concentrated endosulfan from contaminated water, as demonstrated by a BCF_{water} of 3278, *D. magna* neonates accumulated very little endosulfan when exposed to the pesticide via ingestion of contaminated phytoplankton in clean water ($BCF_{\text{food}} = 2.13 \times 10^{-9}$). The gross BCF ($BCF_{\text{food} + \text{water}}$) of 3127 is similar. On this basis, it was concluded that water is the dominant route through which biotic accumulation of endosulfan would occur for plankton.

In conclusion, the results of these assessments provide a good evaluation of the bioaccumulation potential in aquatic and marine species, with the following key conclusions:

- Endosulfan at sublethal concentrations accumulates in laboratory systems by factors between 350 and 3700.
- After the fish are transferred to endosulfan-free water, the residue are rapidly excreted with a half life of 2-4 days (and 6 days for endosulfan sulfate)
- Due to the short elimination half lives from fish and mussel tissues and in combination with the short exposure of aquatic organisms, it is likely that a transfer within the aquatic food-chain is minimal.
- In field systems endosulfan was demonstrated to have undergone significantly less accumulation than observed under laboratory exposure conditions.
- Water represents the primary route of bioconcentration for zooplankton.
- There is evidence that endosulfan contained in phytoplankton is not bioaccumulated by zooplankton.

It should, nonetheless, be noted that BCF values can vary widely depending upon the species tested and the experimental design used (e.g. residue plateau achieved or kinetic calculation from an increasing residue, potential differentiation between bioconcentration and biomagnification). It should also be noted that laboratory studies were carried out at elevated temperatures relative to ambient Arctic conditions.

Adsorption, distribution, metabolism and excretion (ADME) of endosulfan in mammalian systems has been intensively studied as a requirement of the regulatory process as a plant protection product. In studies conducted with rats adsorption potential has been estimated based upon toxicokinetic data gathered following a single dose of (approx. 2 mg/kg bw.) radiolabelled endosulfan as 70-87% of oral dose over 96 hours (Kellner and Eckert, 1983). In metabolism studies endosulfan is extensively metabolised, with ca 13 % unchanged parent in faeces; the main component of which consists of polar and conjugated metabolites (Needham, 2001). The proposed metabolic pathway is summarised in Figure 3.2.1.

Needham *et al.* (1998) studied the toxicokinetics of endosulfan in the rat following repeated daily oral administration of 1 mg/kg bodyweight of radiolabelled endosulfan for up to 28 days, corresponding to approximately 20 mg/kg diet/day. The results show that there was an increase in the concentration of residues in the tissues of male and female rats following repeated daily oral dosing of 1 mg endosulfan/kg bodyweight. In most tissues the residues reached a maximum value (plateau) between 17 and 23 days with the greatest concentration of radioactivity being found in the kidney. Following a 5 day depuration phase, the concentration of residues fell significantly to levels similar to those seen 24 hours after a single oral dose for most tissues – demonstrated specifically for fat tissues (See Figure 3.2.2). The short clearance half life being in the same range as for fish ($DT_{50} = 2-4$ days) is in full

compliance with the low residue levels in organs and tissues of mammals following repeated ingestion. Examination of the residues in the fat and kidney showed that endosulfan sulfate was the major component in the fat and that all of the residue in the kidney was associated with polar compounds.

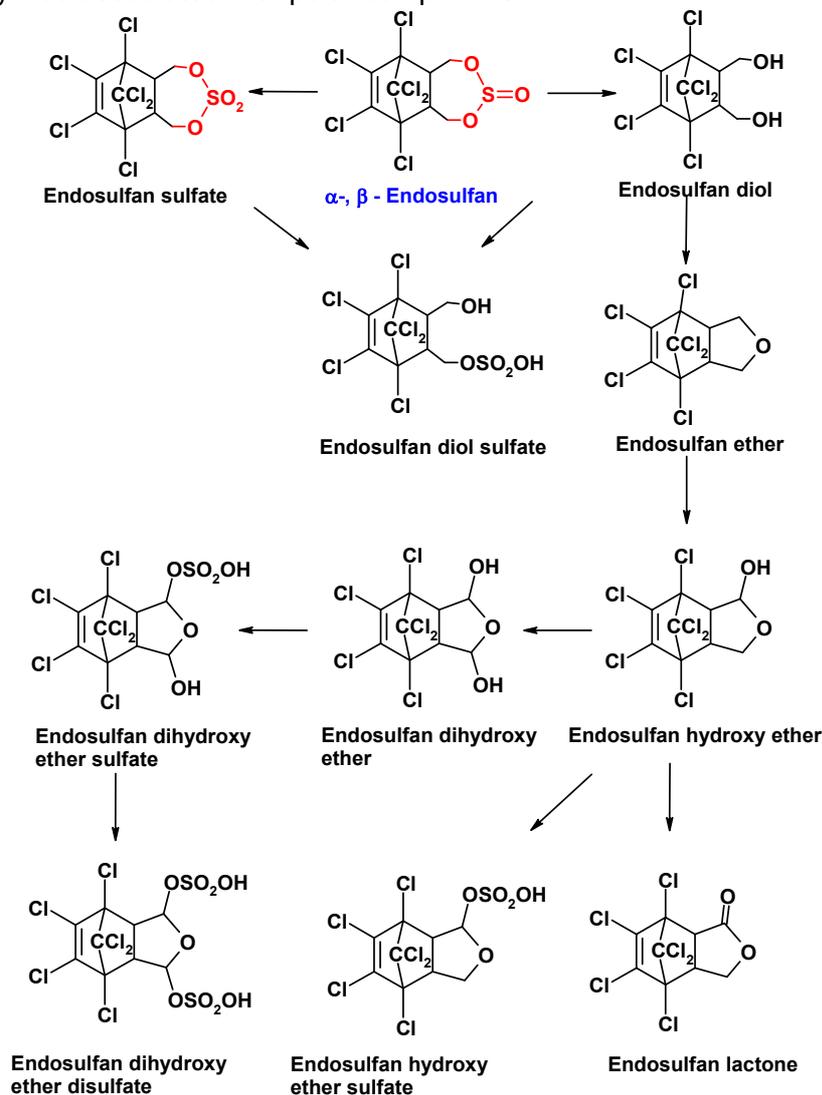


Figure 3.2.1. Proposed metabolism pathway for endosulfan in mammalian systems (Needham, 2001)

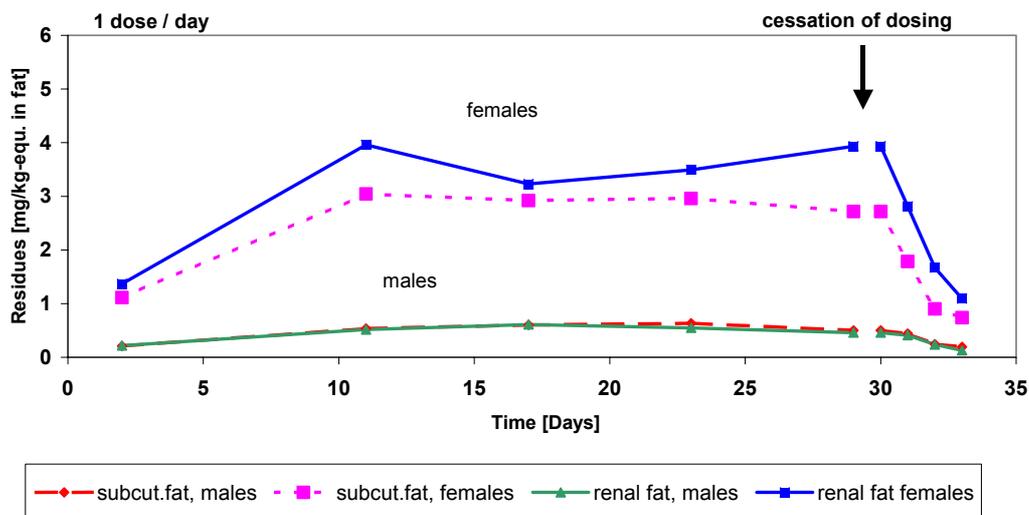


Figure 3.2.2. Total Endosulfan Residues in Subcutaneous Fatty Tissues of Rats Following 28 Oral Administrations of 1 mg/kg bodyweight/day corresponding to 20 mg/kg feed/day

3.3 Potential Routes of Transport to Arctic Regions

The atmosphere, ocean currents, trans-polar ice packs and large Arctic rivers are the main transport routes by which POPs enter Arctic ecosystems (AMAP, 2004). This is illustrated in Figure 3.3.1 (after AMAP, 2004). In addition, migratory animals represent an additional vehicle for transport of POPs. The relative significance of each transport route depends upon physico-chemical and environmental fate characteristics as well as spatial and temporal patterns of production, use and disposal. Since there are no uses of endosulfan within Arctic environments, the presence of the compound in Arctic ecosystems implies transport from agricultural and/or industrial regions in Asia, Europe and North America. Although there are significant uses of endosulfan in the southern hemisphere (notably in cotton production in Australia) transport into the northern hemisphere is likely to be relatively minor.

The significance of various transport processes and factors in defining overall endosulfan transport and accumulation potential in the Arctic is discussed here in brief.

Atmospheric transport

As a highly mobile compartment, transport within air masses represents a significant potential route of transport into the Arctic for many chemicals. Under certain circumstances, transport *via* air into the Arctic from industrialised centres in temperate regions may occur over a matter of days or weeks. The location and intensity of seasonal high and low pressure centres results in dominant patterns of air movements into and out of the Arctic. During the winter, continental high pressure centres combined with deep low pressure centres located in the North Atlantic and Pacific Oceans result in large scale movements of air masses from Asia, Europe,

and North America into the Arctic. North American high pressure ridges in winter result in net transport out of Eurasia, across the Arctic and south across North America. It has been estimated that transport *via* southerlies in the Norwegian Sea (dominated by North Atlantic low pressure), Eastern Europe and Siberia (dominated by Siberian high pressure) and the Bering Sea (dominated by Aleutian low pressure) result in an estimated 40%, 15% and 25% of air transport into the Arctic (Iversen, 1996). The resulting polar fronts cover approximately 80% of the main source areas for POPs (AMAP, 2004).

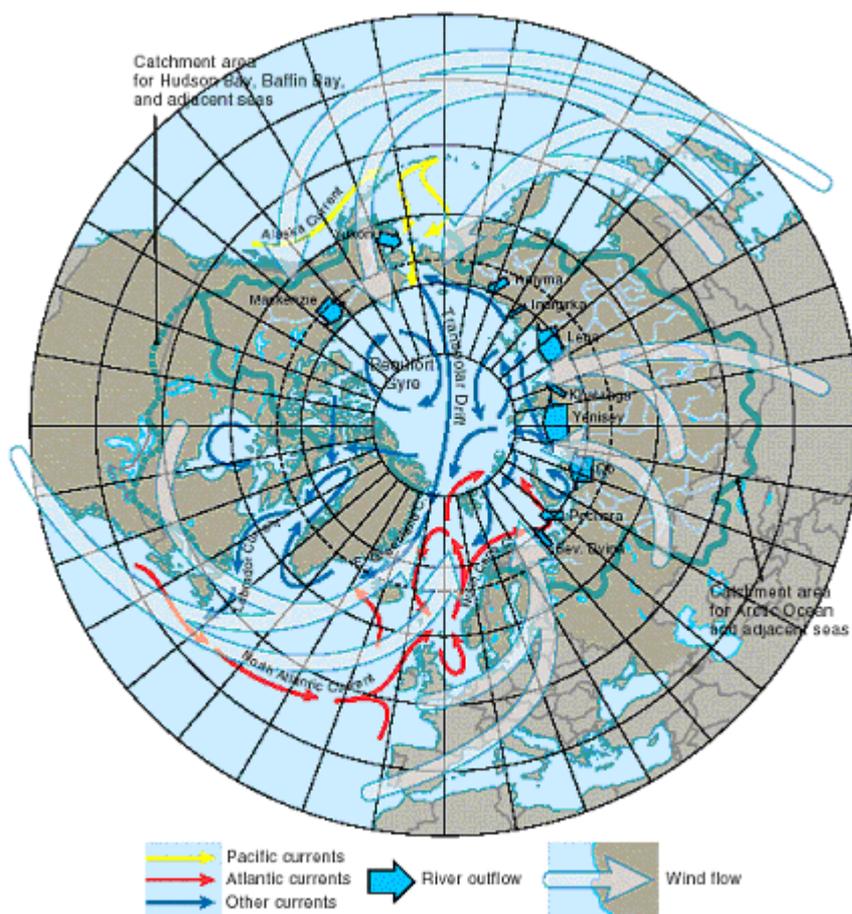


Figure 3.3.1. Illustration of the different physical pathways by which POPs enter the Arctic. Transport into, and within, the Arctic occurs *via* air currents, ocean currents, rivers and transpolar ice movements (After AMAP, 2004).

During the summer, patterns and intensity of pressure centres change with a significant weakening of oceanic lows and elimination of intense continental high pressure centres. This has the effect of significantly reducing the air mass transport potential into the Arctic from temperate regions as the polar front is situated much further north. It has been estimated that approximately 20% of air transport into the Arctic occurs during the summer (10%, 5% and 5% *via* southerlies in the Norwegian Sea, Eastern Europe/Siberia and the Bering Sea, respectively).

Precipitation has been identified as a key factor in the transport of chemicals as a consequence of scavenging processes that lead to deposition on land or water surfaces. However, the significance of these processes may be reduced in the Arctic as a result of characteristic relatively arid conditions. Due to the low annual average

temperatures experienced in these regions snow is the dominant form of precipitation. Wania *et al.* (1999) have demonstrated that precipitation as snow acts as an extremely efficient scavenger of both vapour and particulate (aerosol) phase compounds. Compared with rainfall, snow crystals have a much larger surface area that efficiently adsorb particles and contaminants (Franz and Eisenreich, 1998).

Sea-air exchange processes can be an important indicative transport pathway for POPs in the Arctic. The relative fugacities of PCBs and toxaphene in air and seawater have been employed to demonstrate that the Arctic Ocean continues to act as a 'sink' for residues of these chemicals in the atmosphere, while the reverse is true for α -HCH (Macdonald *et al.*, 2000). Ratios of enantiomers of HCH present in air and seawater have been used to demonstrate that the water-air gas exchange process is dominated by transport from seawater (where biochemical transformation of enantiomeric forms occurs) into air (Falconer *et al.*, 1995; Jatunen and Bidleman, 1996; Jatunen and Bidleman 1997).

Implications for endosulfan

Endosulfan usage regions have been surveyed by Li and Li (2004) and are illustrated in Figure 3.3.2. In the northern hemisphere, significant usage regions are highlighted as follows:

- Asia: India, Thailand, South Korea, Japan and Russia
- Europe: Mediterranean Europe (Spain, Italy, Greece), Russia, the Ukraine
- North America: Eastern, Western and Mid-western USA and Canada

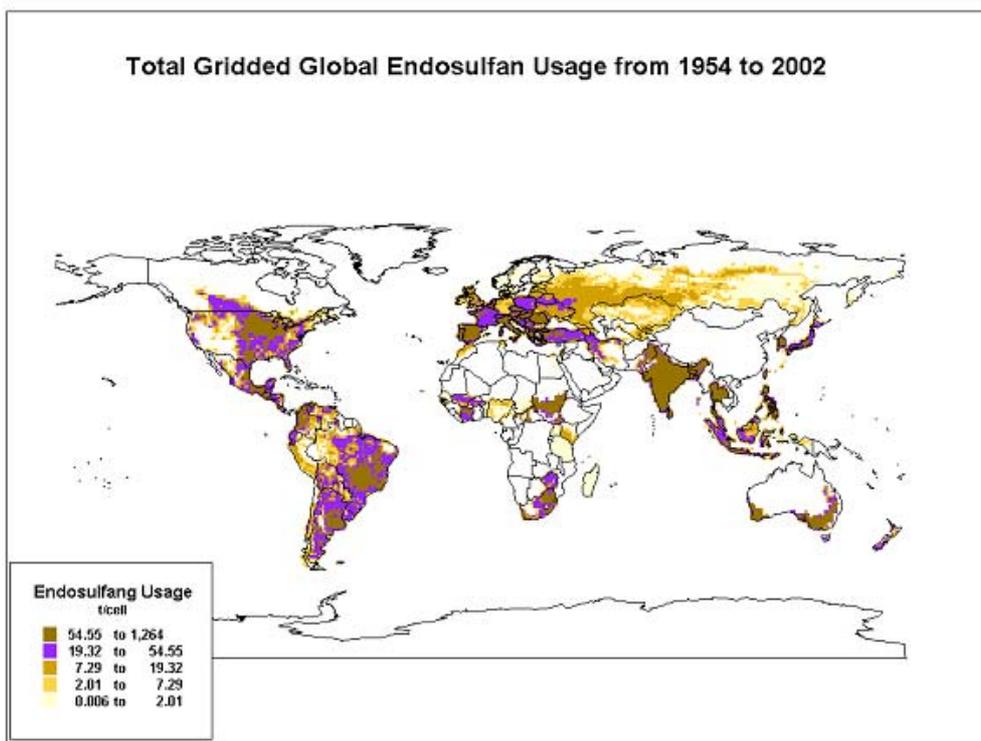


Figure 3.3.2. Global Emission Inventory Activity (Li and Li, 2004)

It should be noted that assumptions have been made in the derivation of these maps regarding potential generalized associations with agricultural land within each country. These are in many cases somewhat misleading in the case of endosulfan as

there are very specific crop associations that may result in misrepresentative profiles, for example within Canada (where key usage regions are British Columbia, Ontario and Prince Edward Island) and the USA (where key usage regions are the east and west coasts). Although assumptions have been made about local usage within each country, the estimates of national total usage implied in Figure 3.3.2 are likely to be reasonably accurate.

Relatively near source transport into the Arctic from east Asia (Japan and South Korea) may occur *via* the Bering Sea as influenced by the Aleutian low pressure centres. Relatively near source transport into the Arctic from the Mediterranean, Russia and the Ukraine *via* Eastern Europe and Siberia may occur as influenced by the Siberian high pressure centres. Contributions from North America may occur *via* the influence of North Atlantic low pressure centres. Timing of usage (late spring and summer) will generally reduce the potential for large scale immediate transport due to the seasonal air movement patterns into the Arctic.

Exchange of residues via air mass transport between hemispheres is assumed to be relatively minor. Hadley cells that occur between the equator and approximately 30°N and S cause strong solar heating along the equator and create a zone of low pressure (the Doldrums) as warm, moist air expands upward and diverges toward the poles, sinking at approx 20-30°N/S latitude. However, seasonal shifts of up to 10° latitude in Hadley cells will result in limited inter-hemispherical transport potential.

The extent of transport in air depends upon a number of further factors including potential for scavenging by wet and/or dry deposition. The scavenging ratio for rainfall can be estimated based upon the Henry's law constant as follows:

$$C_{\text{rainwater}}/C_{\text{air}} = RT/H$$

Where:

$C_{\text{rainwater}}$ = Concentration in rainwater

C_{air} = Concentration in air

R = Universal gas constant (8.314 Pa m³ K⁻¹ mol⁻¹)

T = Temperature (for illustrative purposes assumed to be just over freezing; 0°C or 273.15 K)

H = Temperature dependant Henry's law constant:

$$\log K_{\text{aw}} = -876.14 / T + 0.4463 \text{ (Rice } et al., 1997)$$

$$\log K_{\text{aw}} = -2.76$$

$$H = 1.73 \times 10^{-3} RT = 3.94 \text{ Pa m}^3/\text{mol}$$

$$C_{\text{rainwater}}/C_{\text{air}} = 1/H \text{ (dimensionless)} = 578$$

This indicates that, at low temperatures (lower vapour pressure and Henry's law constant), endosulfan will be scavenged from the vapour phase by rainfall. The efficiency of scavenging will be increased further by snow. It is estimated that scavenging ratios in snowfall may be between one and two orders of magnitude higher. Relationships such as this will also define the potential for air/sea water exchange and the extent to which the air or seawater compartments act as 'sinks' following oceanic and air transport. Representing air/sea water exchange dynamics accurately through interpretation of K_{aw} is critical in developing a more complete understanding of behaviour as a potential POP. There is uncertainty surrounding air/sea water exchange for endosulfan as a temperature dependant Henry's law constant has not been determined with accuracy. Based on the relationships summarised above, endosulfan appears to lie in an intermediate volatility band where it is unclear whether air → water or water → air partitioning dominates. Further

consideration of monitoring results and dominant transport mechanisms would be instructive.

The potential for degradation *via* photolytic processes needs to also be considered. Endosulfan has been shown to undergo photo-oxidative degradation in the gaseous phase following exposure to Xenon light at > 290 nm (Parlar, 1988). An estimation method for the determination of the rate of reaction with hydroxyl radicals based upon Atkinson's increment method (Atkinson 1987) revealed a half life of 1.96 or 1.4 days assuming the concentration of hydroxyl radicals of $0.5 \times 10^6 \text{ cm}^{-3}$ for 24 hours per day or $1.5 \times 10^6 \text{ cm}^{-3}$ for 12 hours per day (see section 3.1; a figure relevant for temperate Europe). It should be noted that, in the Arctic there is a significant seasonal shift in hydroxyl radical occurrence as reactivity with sunlight increases during the summer and is eliminated during the Arctic winter.

Oceanic transport

The main surface circulation features in the Arctic Ocean are the Beaufort Gyre and the Transpolar Drift, which flows from Siberia, across the pole and then southward to form the East Greenland Current (Gregor *et al.*, 1998; Macdonald *et al.*, 2003). The major currents that result in exchange between the Arctic Ocean and other Oceans are found in the Fram strait.

Oceanic transport mechanisms may be important for certain compounds with low Henry's law constants as compounds may be partitioned into seawater from air and scavenged from air by precipitation. The extended persistence of compounds under lower temperatures in the Arctic combined with efficient biomagnification and bioaccumulation of POPs may give rise to elevated concentrations in higher trophic levels in Arctic ecosystems.

Implications for endosulfan

As discussed earlier, air/seawater exchange processes for endosulfan will need to be considered with great care due to the intermediate volatility characteristics where exchange may be limited to some extent by both air and water phase diffusion processes.

Endosulfan undergoes relatively rapid hydrolysis under alkaline conditions (See Table 1.2.1);

- Hydrolytic DT₅₀ values of 22 d and 17 d for α - and β -endosulfan, respectively, at pH 7 and 22°C;
- Hydrolytic DT₅₀ values of 7 h and 5 h for α - and β -endosulfan, respectively, at pH 9 and 22°C;
- Hydrolytic DT50 values of 68 days for both α - and β -endosulfan at pH 8 and 1°C.

It is anticipated that, under typical seawater pH conditions, endosulfan would readily undergo hydrolysis to endosulfan diol, although more slowly than observed in laboratory studies due to reduced temperature.

Riverine inputs

For certain chemicals, input *via* river transport represents an important transport process (Barrie *et al.*, 1992; Pavlov and Pfirman, 1994; de March *et al.*, 1998; Gregor *et al.*, 1998). Large scale transport of chemicals in water and associated with particulate matter occurs in large Russian Arctic Rivers such as the Yenisey, Ob, Lena and Pechora. The rivers extend into industrial areas of the northern Urals and western Siberia and may be significant for certain contaminants such as PCBs. In North America, the only river of a comparable scale is the Mackenzie river with a

drainage basin extending south in the Northwest Territories (N.W.T.) and Alberta in Canada.

Implications for endosulfan

As illustrated in Figure 3.3.2, the most relevant regions for use of endosulfan in North America and Europe are associated with agricultural areas draining directly into the Atlantic, Pacific or *via* the Gulf of Mexico or the Mediterranean Sea. There is some uncertainty surrounding the scale of use in the catchments of large Asian rivers that drain north into the Arctic Ocean.

Biotic transport

Chemical transport in migratory species may be a significant pathway for POPs into the Arctic. Relevant species include various seabirds and cetaceans (particularly beluga, bowhead whales, minke whales), pinnipeds (harp seals), salmon and Atlantic cod. Numerous species migrate between industrialized regions and the Arctic where they may then become prey of residents in the upper food chain such as polar bears and, in some cases, man.

Wania (1998) has estimated that the amount of POPs transferred into and out of the Canadian Arctic to the northwest Atlantic *via* migratory seabirds was in the range of grams to kilograms per year. Similarly, Wania estimated that the total amounts of PCBs and DDT contained in gray whale populations that migrate between the Bering and Chukchi Seas and the Pacific Coast of California and Mexico was in the range of 20 to 150 kg and 1 to 40 kg, respectively. Considering all migratory whale populations, Wania concluded that the total amounts of PCBs and DDT transported in this manner was likely to be on the order of tens of tonnes per year. For DDT, it was considered that this was comparable to quantities transported *via* air and ocean currents. For more water soluble, more volatile and less bioaccumulative compounds such as HCHs the amounts in organisms remain relatively low by comparison with amounts in the water column.

Implications for endosulfan

The importance of biological transport media increases with decreasing volatility and water solubility and with increasing bioaccumulation potential (AMAP, 2004). Although endosulfan residues have been detected in certain migratory species (e.g. minke whales, Hobbs *et al.*, 2003), this route of transport is not considered to be significant in this case. It should, however, be kept in mind that pollutants in biological transport media are themselves more readily available for bioaccumulation than those in abiotic media.

The most significant implications of biotic transport potential lie in the potential for misinterpretation of detections in migratory species as evidence of POP behaviour. The occurrence in species such as minke whales may be less indicative of bioaccumulation potential following exposure in the Arctic than of bioaccumulation following exposure in industrialized regions.

3.4 Endosulfan and POPs Criteria: Establishing a Broader Context

The classification of compounds as POPs is based upon semi-volatility, persistence, bioaccumulation and toxicity characteristics, supported by evidence from monitoring programmes that confirm detections in Arctic/remote region. It can be argued that simplistic classification/categorisation of POP behaviour based upon these criteria may disregard a broader context – including the need for human and ecotoxicological risk criteria as mentioned:

- ◆ in the UNECE EXECUTIVE BODY DECISION 1998/2 on Information to be Submitted and the Procedure for Adding Substances to Annexes I, II of III on the Protocol of Persistent Organic Pollutants (ECE.EB/AIR/60), paragraph 2:

“... Any such technical review shall be in writing and evaluate, *inter alia*: ...
(b) Whether sufficient information exists to suggest that a substance is likely to have significant adverse human health and /or environmental effects as a result of its long-range transboundary atmospheric transport; and ...”

paragraph 3
“The term risk profile mentioned in paragraphs 1 and 2 above refers to a comprehensive review of the scientific information related to the determination of general human health and environmental risks associated with long-range transboundary air pollution. ...”
- ◆ in Annex II of the UNECE report on Technical Input for Reviewing the Protocol on Persistent Organic Pollutants (EB.AIR/WG.5/2004/1), annex II, paragraph 4:

“Article 10 states that this review should take into account the effects of deposition of POPs. ... Consideration of effects will include simple comparison of the deposition levels and levels in biota to various available indicators of significance (e.g. lowest observed effect levels for similar species, tolerable daily intake levels for humans).
...”

paragraph 5:

“The review will consider ... and other substances with POP characteristics whose effects due to their deposition from long-range atmospheric transport cause concerns. ...”
- ◆ and also mentioned in the preamble of the UNEP STOCKHOLM CONVENTION on POPs:

“The Parties of this convention ...
Acknowledging that the Arctic ecosystems and indigenous communities are particularly at risk because of the biomagnification of persistent organic pollutants and that contamination of their traditional foods is a public health issue, ...
Conscious of the need to take measures to prevent adverse effects caused by persistent organic pollutants at all stages of their life cycle, ...
Determined to protect human health and the environment from harmful impacts of persistent organic pollutants, ...
Have agreed as follows: ...”

To address these aspects additional information should be included on:

- Temporal trends (monitoring)
- Spatial trends (monitoring)
- Extent of transport (short-term versus long-term)
- Distribution within the food chain (potential for bioaccumulation/biomagnification)
- Associated ecotoxicological risks due to background and food chain exposure
- Associated human dietary risks, primarily due to potential marine bioaccumulation

A broader basis for evaluation of behaviour and exposure (focusing initially upon spatial/temporal trends and bioaccumulative potential and subsequently upon implications for ecotoxicological and human health risk) can be investigated by gathering monitoring data in key locations, compartments and links in the Arctic food web. Three criteria (spatial and temporal trends and bioaccumulative profiles) are discussed in further detail below.

3.4.1 Temporal Trends: Air

As summarised earlier in this chapter, air is an important route of entry for chemicals in the Arctic. There are several extensive monitoring datasets (e.g. long-term,

continuous monitoring campaigns at Alert, Tagish, and Dunai in the Canadian Arctic) that will assist in clarifying a number of key issues, as summarised here.

Source regions

The most significant current and historic usage regions for endosulfan are remote from the Arctic (India is by far the largest user but there have been significant uses in the northern hemisphere in the contiguous United States and cotton growing regions in the former Soviet Union). Primary source regions for the Arctic may be identified by assessing seasonal air flow patterns. More detailed attribution of source regions may be possible in certain cases where back trajectories have been calculated. Examples include the attribution of Asian sources of organochlorine pesticides in the western Canadian Arctic undertaken by Bailey *et al.* (2000) that included endosulfan.

Understanding seasonal behaviour

As discussed earlier, monitoring of endosulfan in Arctic air follows distinctive seasonal shifts. This has been attributed to be the result of a combination of factors, including (Gouin *et al.*, 2002):

- Polar sunrise
- Atmospheric circulation
- OC usage/ primary emission patterns
- “Spring pulse” due to snow-/ice-melt
- Secondary emission according to T increase
- Scavenging by forests/vegetation along path
- Spatial distribution of the sources

Implications of atmospheric deposition

In addition to air/sea exchange processes, deposition associated with precipitation may also be an important route of the terrestrial, freshwater and marine environments. As summarised earlier, scouring by precipitation can be significant for some compounds where efficient scouring of both particle bound and vapour phase semi-volatile compounds by the increased surface area of snowfall dominates. Routine snow sampling and analysis remains relatively rare but recent monitoring campaigns employing snow sampling (Herbert *et al.*, 2004) will be assessed to provide additional information on the potential scale of this route of entry. Implications of seasonal melt on availability in water and *via* volatilisation into air should be considered.

Consideration of long-term temporal trends

A final critical consideration is the interpretation of long-term monitoring in order to assess whether concentrations of endosulfan in air are increasing. It is important to more fully understand whether temporal trends reflect current usage and the extent to which current levels of exposure are influenced by historic usage following long-term transport into Arctic regions (e.g. consistent with the so-called ‘grasshopper’ effect; Mackay and Wania, 1996). Recent assessments (Hung *et al.*, 2002) have suggested that α -endosulfan levels in air in the Canadian Arctic (Alert, Nunavut) between 1993 and 1997 appear to have increased or remained constant. Further investigation of temporal trends that could include evidence from other sites or the opportunity to include more recent monitoring conducted at Alert may be helpful in developing a clearer understanding of temporal trends.

Actions:

- Summarise available air monitoring profiles
- Generally identify likely short-term transport source regions (e.g. Europe, North America, Asia) through consideration of seasonal air currents and, where available, back trajectories.

- Characterise and interpret seasonal exposure profiles in Arctic air
- Characterise and interpret atmospheric deposition processes
- Summarise and interpret long-term temporal trends in air monitoring for endosulfan

3.4.2 Characterising Behaviour in Seawater

Under certain circumstances, ocean currents may represent the most significant route of entry into the Arctic. For other compounds, transport into the Arctic *via* air followed by deposition and/or air/seawater exchange are the critical routes of entry into this compartment. Behaviour in seawater is then important when considering potential for bioaccumulative uptake. Various aspects will be considered when interpreting available air and seawater monitoring data as summarised below:

Spatial trends

An evaluation of spatial trends in seawater concentrations will assist in understanding the significance of transport *via* ocean currents. Where there is a high degree of spatial consistency, this may imply that this route of entry is less significant than air/seawater exchange processes.

Air/seawater exchange processes

In order to more completely understand the significance of air as a route of entry into the Arctic it is important to characterise the extent of likely air-to-sea exchange processes. Factors such as spatial homogeneity in air and seawater concentrations need to be considered together with implications of seasonality (shifts in air concentrations, dynamic Arctic sea ice cover). The information provided will form a logical progression towards consideration of seawater monitoring and establish a background for more fully understanding bioaccumulation behaviour.

Dissipation and degradation mechanisms in seawater

Having established the likely primary route of entry into Arctic seawater it is then appropriate to consider, in brief, the likely dissipation and degradation mechanisms in seawater before evaluating the potential for bioaccumulation in the Arctic marine food web.

Actions:

- Summarise available seawater monitoring profiles
- Characterise and interpret air/seawater exchange profiles
- Characterise potential degradation and dissipation mechanisms in seawater

3.4.3 Potential for Bioaccumulation, Bioconcentration and Biomagnification

As discussed earlier (see section 3.2), endosulfan is rapidly excreted from aquatic organisms ($t_{1/2}$ of endosulfan = 2-4 days, fish) and therefore does not result in toxic plateau concentrations from successive steps of biomagnification. Similar observations are made in ADME (Absorption, Distribution, Metabolism and Excretion studies) studies in mammals. Therefore, it is expected that if Arctic food chain were subject to analysis and endosulfan levels compared, the degree of biomagnification in the food chain would be very limited. Earlier reviews, designed to address temporal and spatial criteria would potentially identify sources of data collected at approximately the same location and within a confined time window.

The Arctic food chain schematic described by Borgå *et al.* (2004) is instructive in identifying potential targets for consideration (see Figure 3.4.3.1). It is not practical to sample or evaluate each of the links in the Arctic food web. Instead, it is proposed that key links are considered where the food chains converge and/or are significant components of indigenous diet (Figure 3.4.3.1). Borgå *et al.* (2004) considers that Arctic marine ecosystems provide an excellent basis for studying food web dynamics of organochlorine compounds because:

- The contribution of point sources to regional contamination is relatively minor
- A high dependence upon lipids is found in Arctic food webs
- The food webs tend to be long and simple.
- Reduced diversity of species
- Multiple and widely separated areas with similar food webs
- Limited influence from pollution point sources

Depending on the data/samples available sampling should at least be focused to the following marine groups of organisms that have commonly featured within monitoring programmes such as Hoekstra *et al.* (2003):

- Marine mammals:
 - Bearded seal (*Erignathus barbatus*)
 - Ringed seal (*Phoca hispida*)
 - Bowhead whale (*Balaena mysticetus*)
 - Beluga whales (*Delphinapterus leucas*) feature prominently in monitoring campaigns but certain species undergo long-range migrations out of Arctic waters. As a consequence, care should be taken with interpretation of results from beluga monitoring.
- Fish:
 - Capelin (*Mallotus vallosus*; pelagic; oceanodromous fish)
 - Polar cod (*Arctogadus glacialis*; bathypelagic; non-migratory; marine fish).
 - Arctic char (*Salvelinus alpinus alpinus*; benthopelagic; anadromous; freshwater and marine fish)
 - Pink salmon (*Oncorhynchus gorbuscha*; demersal; anadromous; freshwater and marine)
 - Fourhorn sculpin (*Myoxocephalus quadricornis*; demersal, freshwater and marine)
 - Zooplankton (various – calanoids)

It should be noted that a number of biological factors will influence the bioaccumulation and trophic transfer in Arctic marine biota. Borgå *et al.* (2004) point out that none of the factors are completely independent in nature, and they are correlated to some degree. They include:

- seasonality (e.g. altering lipid content, bioavailability, feeding preferences, migration)
- life cycle and reproduction (e.g. transfer of lipids to offspring)
- life cycle, sex and body size (e.g. because of physiological and ecological changes, e.g. diet and age)
- biotransformation
- habitat use (e.g. exposure and diet change)
- migration (e.g. exposure and diet change)
- feeding ecology
- biotransformation potential



Fig. 3.4.3.1. Diagram of simplified Arctic marine food web, including ice-associated (italic) and pelagic organisms. The diagram includes only some of the dominant species (by numbers and biomass), and the arrows illustrate trophic links by pointing to the organism that serve as food. For simplicity, some of the trophic interactions, such as seabirds feeding on ice fauna, are not shown, and the strength of trophic links is not represented (After Borgå *et al.*, 2004).

The influence of these factors is discussed at length by Borgå *et al* (2004). In addition to the uncertainties related to these factors there are a number of practical limitations in the development of a detailed and robust representation of an Arctic food web. Borgå *et al* (2004) point out that zooplankton and phytoplankton have typically either not been included in monitoring campaigns or were included but assessed without separation into taxonomic or functional groups. As a consequence, it will only be possible to represent a very general picture of bioaccumulation profiles across a range of broad trophic levels.

Nonetheless, Hoekstra *et al* (2002, 2003) have provided an effective demonstration of how trophic transfer of persistent organochlorine contaminants can be effectively characterised within Arctic marine food webs employing stable isotope analysis. Samples of whole zooplankton and muscle tissue of various fish and marine

mammals were analysed in triplicate for both stable $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ isotope ratios. These ratios are increased in succeeding trophic levels as a consequence of metabolic transformations. It was assumed that the *Calanus* copepods were primary herbivores and occupied a secondary trophic level (TL=2.0). Isotopically derived trophic level for all other species were determined using the relationship developed by Fisk *et al.*, 2001):

$$\text{TL} = 2.0 + (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{Calanus}})/3.8$$

Where TL is the trophic level, $\delta^{15}\text{N}_{\text{consumer}}$ is the $\delta^{15}\text{N}$ signature in the specified organism, $\delta^{15}\text{N}_{\text{Calanus}}$ is the mean (± 1 SE) $\delta^{15}\text{N}$ value for *Calanus* spp. (9.8 ± 0.2) and 3.8 is the trophic enrichment factor for $\delta^{15}\text{N}$ in an Arctic food web (Hobson *et al.*, 2002). The trophic levels of organisms in the study of Hoekstra *et al.* (2003) are summarised in Table 3.4.3.1. An illustration of the results of a trophic analysis for ΣDDT is provided in Figure 3.4.3.2. This technique represents a powerful basis for demonstrating biomagnification potential in Arctic food webs and may be employed to assess the biomagnification profiles for α - and β -endosulfan.

Actions:

- Develop a database of biotic monitoring data to establish temporal and trophic trends and clarify bioaccumulation status of endosulfan residues at a range of trophic levels (calculation and interpretation of BAF values).
- Use probabilistic approaches to summarise endosulfan distributions in marine organisms.
- Consider potential human dietary implications of endosulfan residues in fish and marine mammals (carry out a comparison of residue levels to regulatory human reference dose (RfD), and the acceptable daily intake (ADI) with realistic diet profiles)

Table 3.4.3.1. Trophic levels for Arctic marine species from the Barrow (Alaska) food web determined by Hoekstra *et al.* (2003)

Species	TL
Zooplankton (various – undistinguished)	2.0 ± 0.1
Pink salmon (<i>Oncorhynchus gorbuscha</i>)	2.3 ± 0.1
Arctic char (<i>Salvelinus alpinus alpinus</i>)	3.1 ± 0.1
Polar cod (<i>Arctogadus glacialis</i>)	3.3 ± 0.1
Fourhorn sculpin (<i>Myoxocephalus quadricornis</i>)	3.5 ± 0.2
Bearded seal (<i>Erignathus barbatus</i>)	3.8 ± 0.1
Ringed seal (<i>Phoca hispida</i>)	4.1 ± 0.2
Bowhead whale (<i>Balaena mysticetus</i>)	2.8 ± 0.1
Beluga whales (<i>Delphinapterus leucas</i>)	3.8 ± 0.2

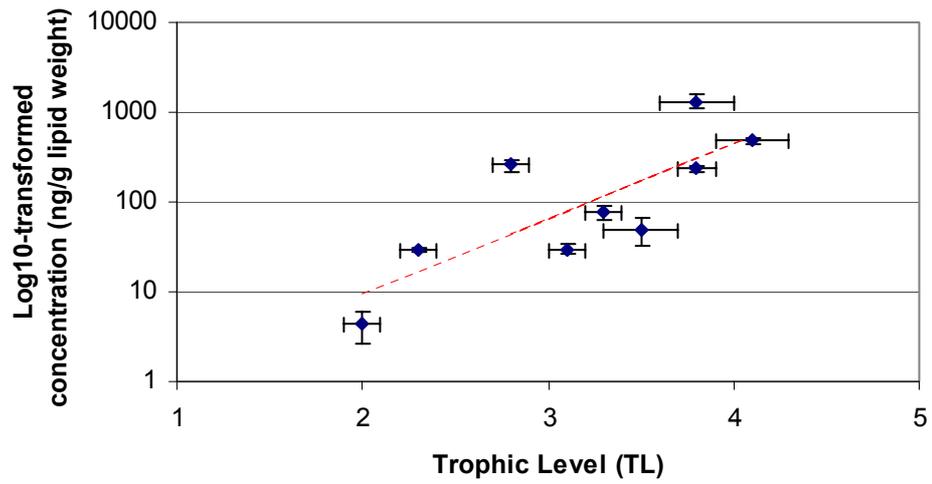


Figure 3.4.3.2. Relationship between log₁₀-transformed, lipid normalised concentrations for Σ DDT and trophic levels in the Arctic food chain (Barrow, Alaska; Hoekstra *et al.*, 2003)

4 Overview of abiotic monitoring data

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4.1 Air

Air concentrations of α -endosulfan in the Arctic average between $\sim 3\text{-}6\text{ pg/m}^3$ (annual averages throughout the 1990s) compared to γ -HCH which averages $\sim 9\text{-}13\text{ pg/m}^3$. Table 4.1.1 provides a summary for the various Canadian NCP sample sites that have provided the longest time-series of continuous measurements. β -endosulfan has not been reported from the NCP air monitoring stations and data for this isomer are scarce, although concentrations reported from the Bering-Chukchi sea region during August/Sept 1993 ranged between $<0.27\text{ -}1\text{ pg/m}^3$ (Chernyak *et al.*, 1996). The absence of β -endosulfan in the air monitoring records is likely to be, in large part, related to significant differences in physico-chemical properties between the two isomers (it is noted that the β -isomer has a vapour pressure at least an order of magnitude lower than the α -isomer). Large spatial differences across the Arctic in endosulfan concentrations are not evident, although a seasonal pattern in air concentrations marked by elevated concentrations during the spring months of April/May and a later peak in Oct/Nov has been observed at a number of stations including Alert, Dunai and to a lesser extent Amderma and Tagish. 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/August. In order to place α -endosulfan concentrations in context with temperate areas, summertime concentrations in the North American Great Lakes region are typically factors of 5-25 greater than the spring maximum concentrations observed in the Arctic, with concentrations close to agricultural areas across Canada/US ranging from 100s to $>1000\text{ pg/m}^3$ (Harner *et al.*, 2004; Shen *et al.*, 2005).

Table 4.1.1. A summary of α -endosulfan and γ -HCH air concentrations (pg/m^3) measured at the Canadian Northern Contaminant Program (NCP) monitoring stations.

Sampling location	Sampling dates	α -endosulfan Mean (range)	γ -HCH Mean (range)
Alert, Nunavut, Canada	1992-1999	4.24(<0.01-16.5)	8.36 (<0.05 – 59.2)
Tagish, Yukon, Canada	1993-1995	5.82 (<0.06 – 15.3)	12.1 (0.18-138)
Dunai, E.Siberia	1993-1994	2.99 (<0.05 - 7.18)	9.83 (3.68-22.7)
Amderma, W. Siberia	1999-2000	3.66 (<0.03 - 13.2)	7.79 (0.78-24.24)

Following an extensive atmospheric survey conducted across the North American continent, Shen *et al.* (2005) reported a number of organochlorine pesticides, including α - and β -endosulfan, through the deployment of passive air samplers (PAS). These devices consisted of a polymer/resin (XAD-2) wrapped in steel mesh and suspended in a metal tube with an open bottom to allow contact with the ambient air. Unlike Hi-Vol air samplers, PAS operate without actively pumping the air, accumulating SVOCs onto the XAD-2 by passive diffusion. PAS 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 Figure 4.1.1, and arise through the year-long deployment of the PAS devices during 2000/01. The year-long integrated air concentrations provide useful geographical trends, allowing arctic air concentrations to be placed in context with

temperate regions. From Figure 4.1.1 the lowest endosulfan concentrations clearly occur at the arctic sites, with much higher concentrations evident in Mexico and the western (British Columbia) and eastern fringes (Prince Edward Island) of Canada reflecting the agricultural use of endosulfan. Importantly, time-averaged air concentrations were also estimated for the PAS devices by dividing the mass of chemical on the PAS by the product of the uptake rate and the deployment period. The concentrations reported from Arctic Canada were found to be in close agreement with the air concentrations observed separately at Alert as part of the Canadian Northern Contaminants Program (see Table 4.1.1), thereby highlighting the usefulness of PAS as long term air monitoring tools, but also providing a degree of quality assurance for both programmes.

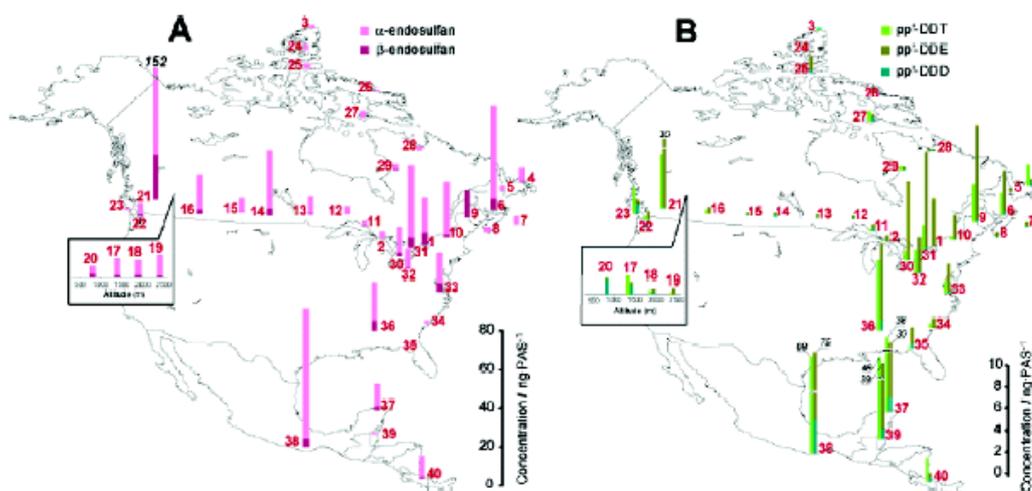


Figure 4.1.1. The spatial distribution of Endosulfan (A) and DDT compounds (B) across the north American continent through the deployment of Passive Air Samplers (PAS). From Shen *et al.* (2005) with kind permission from the American Chemical Society.

Direct atmospheric transport from agricultural regions to the Arctic, would presumably result in the temperate summertime 'peak' in concentrations being reflected at the high Arctic monitoring stations. The fact that this is not the case, and the occurrence of a 'spring event' for endosulfan would suggest that there is significant environmental processing of endosulfan (e.g. atmospheric depletion, air-surface exchange etc), that occurs either during long range transport and/or within the Arctic itself. This is illustrated in Figure 4.1.2. There are many potential factors that may account for the observed seasonal profile in the Arctic and these are discussed in Hung *et al.* (2005). In the case of γ -HCH, clear peaks in April followed by less distinct peaks in October/November have been directly attributed to agricultural practices. Peaks in spring coincide with increased applications of γ -HCH and associated tillage of land. Secondary autumn peaks have been attributed to increased ploughing activities releasing the chemical to the atmosphere. Hung *et al.* (2002) suggest that this may not be the case for α -endosulfan, as well as *trans*-chlordane, *o,p'*-DDT and dieldrin. In these cases the possibility of increased photodegradation or depletion reactions with OH radicals may be an important factor. Another potentially significant factor relates to the role of forests as scavengers of semi-volatile organic compounds (e.g. air-water partition coefficients ($\text{Log } K_{aw}$) of >-6). Wania and McLachlan (2001) have suggested that because compounds would pass through significant forested areas during long-range transport to higher latitudes there is the potential for scavenging of airborne residues that may result in

seasonal depletion by up to a factor of 5 during the growing season. Hung *et al.* (2002) point out that, in monitoring campaigns conducted in the Canadian Arctic, there were summer reductions in α -endosulfan levels of between a factor of 3-5 relative to spring and fall periods. In essence, the seasonal profile probably results through a combination of processes including;

- Changing air flow patterns/meteorology following the transition from arctic winter to spring that reduces the incursion of temperate air masses to the high Arctic during summer;
- Enhanced photochemical depletion with the onset of polar sunrise and 24 h daylight,
- Enhanced air-surface exchange processes during snow melt in sub-Arctic regions, that may serve to increase air concentrations during the spring;
- Scavenging via vegetation ('forest filter effect') during long-range transport to the Arctic.

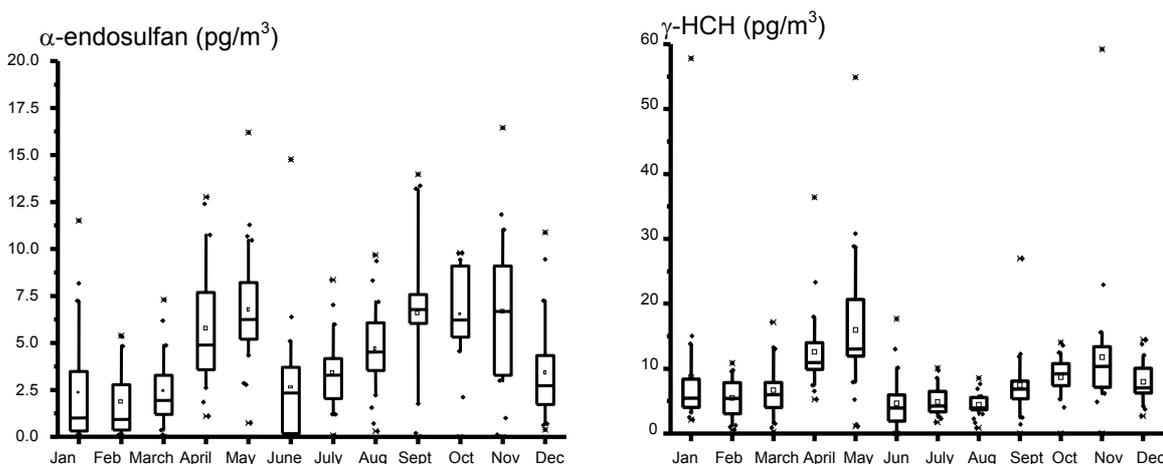


Figure 4.1.2 Box-and-whisker plots providing monthly summaries for α -endosulfan and γ -HCH concentrations at Alert for the years 1992-1998.

Losses of chemicals from air masses in the Arctic may occur as a result of photolysis, scavenging *via* precipitation and partitioning (dominated by sea-air gas exchange processes). Because of dramatic seasonal shifts in light conditions (ranging from the 'polar night' in winter and 'midnight sun' at latitudes greater than 80°N) for certain chemicals, there is a dramatic influence on persistence and behaviour. For example, seasonally dependent photolytic degradation has been proposed as an explanation for patterns of year-round air sampling for chlordane in research campaigns conducted in Ny Alesund (Svalbard, Norway) and Alert (Ellesmere Island, Canada) (Oehme, 1991; Halsall *et al.*, 1998). The significant seasonal shift in light conditions has been suggested as a possible contributing factor in the characteristic seasonal air concentration profiles for endosulfan, although direct evidence is scarce (Hung *et al.*, 2002).

Air-mass back trajectory analysis is frequently used to explain fluctuations or 'spikes' in atmospheric concentrations of anthropogenic semi-volatile organic compounds, whereby elevated levels may arise due to the prevailing air mass having originated, or passed over, a source region. For weekly integrated air samples (i.e. those taken as part of the Canadian NCP programme), it is often difficult to assign a prevailing air mass direction due to changing winds/meteorology during the sampling period. However, for systematic sampling over the course of a year then it is possible to identify a significant number of sample weeks where the air mass origins/direction can be clearly assigned. For example, at the air sampling station of Tagish in the

Yukon, the prevailing air flow is predominantly westerly from the Pacific Ocean and unusually high concentrations of several OC pesticides, including α/γ -HCH, DDT and chlordanes, have been observed when the air flow has originated from as far as eastern Asia. This has prompted concern over trans-Pacific transport of pesticides and subsequent contamination of the western sub-Arctic/Arctic by Asian sources (Bailey *et al.*, 2000; Killin *et al.*, 2004). To investigate the likelihood of endosulfan undergoing trans-Pacific transport from Asia, sample weeks from the Tagish database (collected between 1993-1995) were identified when the upwind air shed had originated over the Asian landmass. Figure 4.1.3 illustrates the 5-day airmass back trajectory for two periods of strong trans-Pacific air flow. Periods of strong trans-Pacific air flow generally occur during the winter due to the prevailing meteorology, resulting in selected sample weeks showing elevated OC pesticide concentrations (Bailey *et al.*, 2000). To demonstrate the influence of the east Asian landmass on air concentrations at Tagish, sample weeks ($n=15$) were selected which had experienced strong trans-Pacific airflow. Interestingly, the HCH concentrations were correlated to the fraction of time (f) that the air had spent over the Asian landmass during the 5-day trajectory period. Figure 4.1.4 shows this relationship between f and concentrations of both γ -HCH and α -endosulfan for these 15 sample weeks. The relationship is statistically significant for γ -HCH but not for α -endosulfan, indicating that transpacific transport, and the amount of time that the air has spent over eastern Asia, does not significantly affect concentrations of α -endosulfan observed at Tagish.

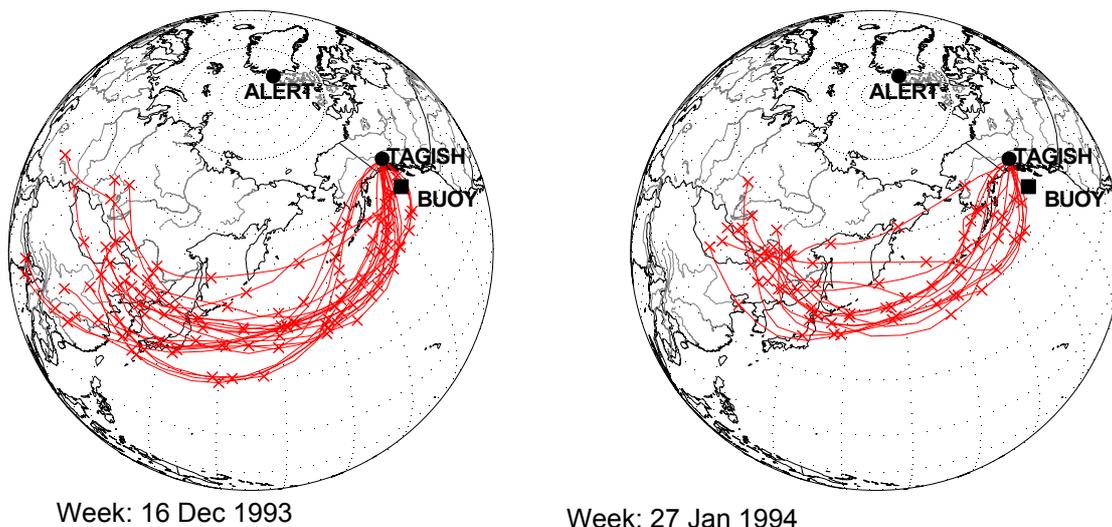


Figure 4.1.3. Lagrangian 5-day air mass back trajectories to Tagish, arriving at the 700 mb pressure height (sample site is located ~2000 m.a.s.l.) and illustrating periods of strong trans-Pacific air flow to the western Arctic (Bailey *et al.*, 2000)

This finding is supported by recent work conducted in the lower Fraser Valley in British Columbia (Harner *et al.*, 2005). In this study, air samples were taken at ground level and at high altitude (4400 m) concurrently; the latter via use of an aircraft. Elevated concentrations of α -HCH were observed in the high altitude samples when the air mass (at this altitude ~700 mb pressure height) had originated from eastern Asia. Endosulfan on the other hand was not detected in these samples (along with other higher MW pesticides), indicating that the east Asia does not significantly influence endosulfan concentrations in western Canada or the western Arctic.

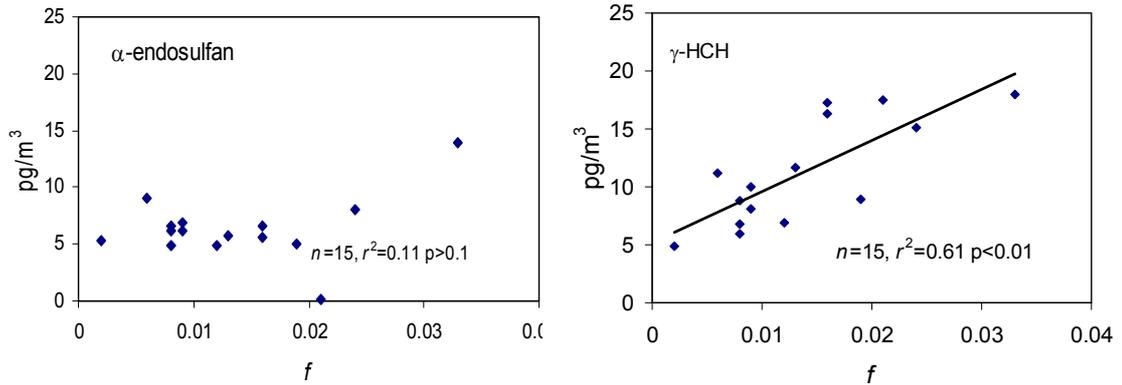


Figure 4.1.4 α-endosulfan and γ-HCH concentrations observed at Tagish, correlated to the fraction of time (*f*) that the 5-day air mass back trajectory has spent over the Asian landmass.

To examine the influence of the North American land mass on endosulfan concentrations, the 1993-95 Tagish database was further utilised and sample weeks identified where the air had predominantly originated from western Canada and the US. Figure 4.1.5 compares the 'Canada/US' average (for 8 weeks identified when the air clearly originated from the south and within the N. American continent) to the overall 1993-95 average (105 weeks). The average concentration for the sample weeks influenced by the continental/southerly air masses was significantly higher than the Tagish 1993-95 average (t-test where $t=1.99, df=111, p < 0.05$) indicating that incursions of endosulfan into the western sub-Arctic, may be attributable to agricultural areas in western Canada and the US.

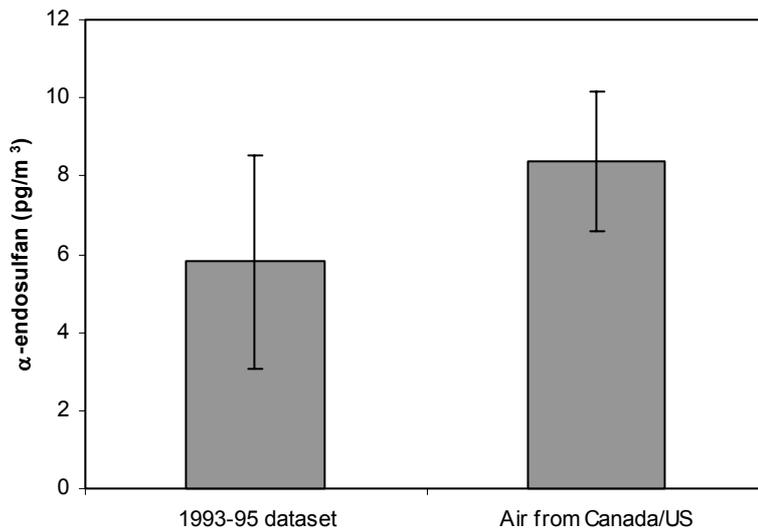


Figure 4.1.5 α-endosulfan concentrations at Tagish. A comparison of the 1993-1995 average to the average concentration for those sample weeks ($n=8$) when the air originated from western Canada/US. Bars represent 1xSD around the mean.

4.2 Endosulfan in Seawater and Assessment of Air-Gas Exchange

Endosulfan is present in Arctic air predominantly in the vapour phase, even during the colder winter months (e.g. α -endosulfan >98% vapour phase; Hung *et al.*, 2002 and personal communication). As such, endosulfan contamination of arctic surfaces will be through vapour sorption (gas exchange) and vapour scavenging by precipitation, rather than by dry or wet particle deposition. For OC pesticides present in the Arctic atmosphere vapour exchange (absorption and volatilisation) with ice-free surface ocean waters is a significant route of transfer to the marine system, alongside input through ocean currents and northerly draining rivers (AMAP, 2004). To-date, knowledge on air-sea transfer in the Arctic has been gained through studies on α -HCH, due to the relatively wide number of seawater measurements for this chemical and reliable measurements of its temperature-dependent Henry's Law constant (H); a key physical-chemical property required to describe air-water partitioning. As H is sensitive to changes in temperature then colder conditions such as those encountered in the Arctic, drive air-water partitioning in favour of water and this can account for the enrichment of α -HCH in the surface waters of the Arctic Ocean relative to temperate oceans (Wania and Mackay, 1996). Over the last 15-20 years the decline in atmospheric levels of α -HCH in the Arctic has resulted in surface waters becoming oversaturated with respect to the atmosphere, resulting in the reversal of air-water gas exchange and net volatilisation to the atmosphere in some regions of the Arctic Ocean (Jantunen and Bidleman, 1995; Jantunen and Bidleman, 1996). Interpretation of the volatility characteristics of endosulfan will also be extremely important in defining air/seawater exchange processes. Although there is obvious uncertainty through lack of a recently measured temperature-dependent Henry's law constant, an estimated air/water partition coefficient (K_{aw}) at near 0°C of approximately 1.7×10^{-3} (α -isomer) suggests that volatility and air/seawater exchange will be controlled to some extent by both air and water phase diffusion processes. As K_{aw} increases the relative importance of water phase control increases and air phase control decreases (and vice versa as K_{aw} decreases). Endosulfan would appear to lie within an intermediate volatility band in which both resistances are important.

An assessment of air-water exchange for the endosulfan isomers is required to understand their equilibrium status, with regards to deposition or volatilisation between the surface seawater and the atmosphere for different regions of the Arctic Ocean. Seawater measurements of endosulfan are not as extensive as the HCHs, but are available from most of the ocean studies outlined in Table 2.3.2, which effectively cover a wide part of the Arctic Ocean for different summer periods throughout the 1990s. Endosulfan is considered to be almost totally present in dissolved form, with only a small fraction (<1%) associated with particles, although for α -HCH and chlordanes a substantial increase in the particle fractions (16-28% α -HCH, 32-66% chlordanes) were found in select areas of high productivity due to the presence of suspended particles/plankton (Jantunen and Bidleman, 1998).

Table 4.2.1 provides a summary of surface (<100m depth) seawater concentrations for α - and β -endosulfan. The units are reported in pg/m^3 to allow direct use with air concentration data (see next section 4.2.1), but may be simply divided by 1000 to yield pg/L . The studies presented in Table 4.2.1 report seawater concentrations of α - and β -endosulfan analysed by both GC-ECD and GC-NCIMS techniques, depending on the study in question. The fact that large discrepancies (i.e. concentrations ranging over 2-3 orders of magnitude) are not apparent between these studies, adds confidence in the qualification and quantification of the two isomers.

Table 4.2.1 Average (range) concentrations for α and β -endosulfan in surface seawater for different regions of the Arctic Ocean.

Cruise/ study	Location/region	Sampling period	α -endosulfan pg/m ³	β -endosulfan pg/m ³
¹ Bering Sea 93	Bristol Bay (south-west Alaska)	July 1993	4100 (80 – 8800)	3400 (<100 – 27000)
² BERPAC	Bering Sea/Gulf of Anadyr	Aug – Sep 1993	4300 <2000 - 5000	100,000*
³ Cornwallis	Cornwallis Is (Barrow St.) Canadian Archipelago	Jan-Sep 1993	2600	NR
¹ JOIS97	Central Canadian Archipelago	Sep 1997	1400 (<100 – 5100)	600 <100 -2300
⁴ AOS-94	Arctic Ocean transect Chukchi to Greenland Sea	July–Sep 1994	3500 (400 – 8800)	1500 (100 – 7800)
⁵ Barrow	Beaufort & Chukchi Seas (northern Alaska)	May-July 1999 & May 2000	1600 (ND – 2100)	800 (ND – 1900)
⁵ Holman	Holman Island Canadian W. Archipelago	May 1999	2000 (500 – 3100)	700 (ND – 1200)
⁶ White Sea	Onega & Kandalaksha Bay White Sea (Russia)	Sep1999 & July 2000	3200 (950 – 7600)	500 (ND – 1800)
¹ Oden 96	Barents Sea and eastern Arctic Ocean	July–Sep 1996	2000 (<100 – 3400)	1400 (<100 – 5400)
¹ TNW99	Canadian E. Archipelago	July 1999	NR**	NR**
¹ NOW98	East Canadian Archipelago Baffin Bay	May 1998	1900 (<400 -5800)	900 (<400 – 3100)

¹Strachan *et al* (unpublished); ²Chernyak *et al.* (1996); ³Hargrave *et al.* (1997); ⁴Jantunen and Bidleman (1998); ⁵Hoekstra *et al* (2003); ⁶Muir *et al.* (2002); ND = not detected; NR = not reported.* β -isomer present in a few samples taken from the Gulf of Anadyr (Russia), however analytical uncertainties were noted. Possible 'local run-off' may have contributed to this high value. ** Interferences in fraction II of the clean-up procedure resulted in loss of most OC pesticides.

Seawater concentrations of the endosulfan isomers are typically 100-fold less than γ -HCH, with average concentrations of γ -HCH ranging from 440 to 600 ng/m³ in the western Arctic Ocean (south Bering sea to the Beaufort Sea; Sahuvar *et al.*, 2003). Average concentrations of β -endosulfan are approximately 2-fold lower than the α -isomer for the studies in Table 4.2.1, although there is considerable variability in concentrations within each study. For example, in the 'Oden 96' cruise which covered the north Barents Sea and eastern/central Arctic Ocean and comprises the highest number of seawater samples, β -endosulfan ranged from detection limits to 5400 pg/m³ and was more frequently detected in this study than α -endosulfan. This is in contrast to other seawater monitoring in which α -endosulfan dominates. In the earlier studies conducted in the Bering Sea ('Bering Sea 93' and 'BERPAC') β -endosulfan was detected at high concentrations in a small number of samples, although in the BERPAC study (Chernyak *et al.*, 1996) the authors raise analytical uncertainties with regard to the β -endosulfan measurements. From the averages presented in Table 4.2.1 the ratios of α/β in seawater are $\approx 2:1$ (comparable to the ratio found in the endosulfan technical mixture). However the variability in both absolute concentrations and ratios is large in many of the studies. For example, in the 'Oden 96' cruise many of the water samples were collected above 80°N and out of 23 samples collected that contained either α or β -endosulfan, only three had α -endosulfan above detection limits (but at relatively high concentrations), whereas β -endosulfan was detected in 18 of the samples. These samples contained either only

β -endosulfan, or had an α/β ratio of 1:1-4 in favour of the β isomer. Jantunen and Bidleman (1998) reported a similar variability in 'AOS-94' with some seawater samples enriched in the β -isomer and others with β below detection limits. The enrichment of β -isomer in seawater may be due to its lower Henry's Law constant relative to α -endosulfan, whereby air-water partitioning would favour the water side, resulting for example, in enhanced precipitation scavenging. However, the lack of air measurements for this isomer presents a major knowledge gap with respect to the source and transfer pathways of β -endosulfan within the Arctic. β -endosulfan has not been detected in the Canadian NCP air programme and there appear to be only two studies that have reported air concentrations alongside seawater measurements (BERPAC and JOIS97 listed in Table 4.2.1).

Figure 4.2.1 illustrates the spatial variability of endosulfan across the Arctic Ocean for the studies presented in Table 4.2.1, with data grouped either as monthly averages or representative of a certain location, rather than the average of a whole cruise track. Spatial trends are difficult to ascertain, although there are general features which deserve comment. A geographical trend in α -endosulfan concentrations is not readily apparent, although the highest levels are in the Bering/Chukchi and Greenland seas with lower concentrations in the central Arctic Ocean (presumably under sea-ice). β -endosulfan concentrations broadly follow a concentration gradient of higher levels in the western Arctic and lower in the eastern Arctic, although levels in the Canadian Archipelago are typically less than 1000 pg/m^3 .

Trends for γ -HCH reported for AOS-94 by Jantunen and Bidleman (1998) reveal a slight increase in concentrations from the Chukchi Sea to the North Pole, followed by ~2-3 fold decrease at sample sites in the Eurasian Basin and the Greenland sea (towards the eastern Arctic). Similarly, a contemporary assessment of spatial patterns for Σ HCHs across the Arctic (including studies listed in Table 4.2.1) reveal concentrations to be highest in the central Canadian Archipelago, intermediate in the Bering/Chukchi Seas and North Pole and lowest in the Greenland Sea and northern Barents Sea. In contrast, levels of α -endosulfan do not appear to be higher in the Canadian Archipelago compared to the Chukchi/Bering Seas and do not show the west to east gradient unlike the β -isomer.

In a recent assessment of γ -HCH input to the North American Arctic Ocean, the atmosphere was estimated to contribute only 10% of the total input, compared to ~90% attributed to inflow of Pacific waters through the Bering Strait (CACAR, 2003). The atmospheric contribution has largely declined since the 1980s due to decreasing air concentrations of γ -HCH and it is likely that input via the atmosphere will continue to decline. For α -endosulfan, however, the atmosphere is likely to be a significant contemporary source to the Arctic Ocean for a number of reasons. Firstly, atmospheric concentrations have not shown a decline throughout the 1990s in contrast to γ -HCH. Secondly, α -endosulfan has a Henry's Law constant which is approximately 3-4-fold higher than γ -HCH (Shen and Wania, 2005; Sahuvar *et al.*, 2003) and is therefore less likely to be removed by either precipitation scavenging or direct partitioning to ocean surfaces during atmospheric transport to the Arctic. For the Arctic Ocean as a whole, river drainage into the coastal arctic seas may be a significant source of endosulfan, similar to other chlorinated pesticides, but river water measurements for endosulfan are currently lacking.

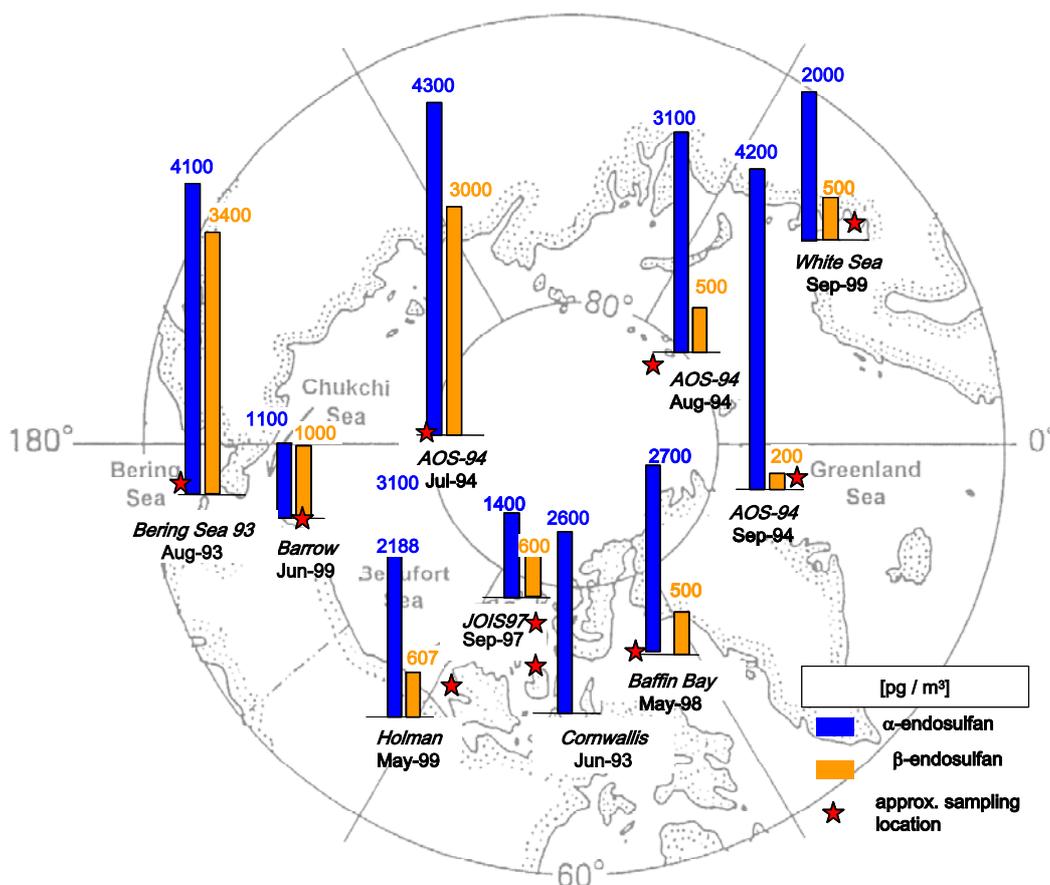


Figure 4.2.1. Monthly average α- and β-endosulfan concentrations across the Arctic Ocean. Numbers above the bars represent the monthly average concentration at that location or region.

4.2.1 Air-water exchange

To assess the status of gaseous air-water transfer of endosulfan - in other words to determine whether the chemical is at equilibrium, or undergoing net deposition or volatilisation - air and seawater data were grouped both spatially and temporally to ascertain transfer for different regions of the Arctic Ocean. For example, June-September air concentrations were selected from Alert for the appropriate year to couple with summer seawater concentrations measured in the Canadian Archipelago. In addition, seawater data from the White Sea (western Russia) were coupled to air concentrations measured at Amderma in western Siberia. Table 4.2.1.1 provides a summary of coupled air and water endosulfan concentrations. In each case, seawater data were compared to atmospheric data from the same month and from broadly the same region. For example, seawater concentrations measured during June/July 1999 in the Canadian/US Arctic were coupled to Alert air concentrations, although in this case air concentrations from the previous summer were used due to the lack of data from Alert for 1999 onwards.

Using the paired data in Table 4.2.1.1, water-air fugacity ratios (f_w/f_a) were calculated using H adjusted to the ambient water temperature. In this case, fugacity provides a simple but useful criterion to assess the equilibrium status of endosulfan between air and water. In other words, fugacity represents the 'pressure' or 'fleeing tendency' exerted by endosulfan in both air and water, and a simple ratio of the two provides a

useful assessment on the net direction of chemical transfer, i.e. water to air, air to water, or no overall net transfer whereby the system is at equilibrium. This approach has been used successfully to examine the air-water transfer for the HCHs across the Arctic Ocean (e.g. Jantunen and Bidleman, 1995; Sahsuvar *et al.*, 2003). The fugacity in water (f_w) can be calculated according to:

$$f_w = C_w H(T_w) / M10^{-12} \quad (1)$$

where C_w is the dissolved concentration in water (pg m^{-3}), $H(T_w)$ is the temperature dependent Henry's law constant ($\text{Pa m}^3 \text{mol}^{-1}$) at the temperature of the water (K) and M is the molecular weight of endosulfan (g mol^{-1}), multiplied by 10^{-12} to convert g to pg. The fugacity in air (f_a) is calculated according to:

$$f_a = C_a R T_a / M10^{-12} \quad (2)$$

where C_a is vapour air concentration (pg/m^3), R is the gas constant, ($8.31 \text{ Pa m}^3 \text{K}^{-1} \text{mol}^{-1}$) and T_a is the ambient air temperature (K). The fugacity ratio (FR) is therefore:

$$\text{FR} = f_w / f_a = C_w H / C_a R T_a \quad (3)$$

Table 4.2.1.1 Paired seawater and air data used to determine air-water transfer of endosulfan for different regions of the Arctic Ocean

Seawater			Air		
Data source/ location	Month/ Date	Water [pg/m ³]	Data source/ Location	Month/ Date	Air [pg/m ³]
α-endosulfan					
<i>Bering & Chukchi Sea</i>	Aug 1993	4100	<i>Alert</i>	Aug 1993	0.70
<i>Barrow/ Beaufort Sea</i>	June 1999	1100	<i>Alert</i>	June 1998	4.06
<i>Holman/ W. Archipelago</i>	June 1999	3100	<i>Alert</i>	June 1998	4.06
<i>Baffin Bay/ E. Archipelago</i>	May 1998	2700	<i>Alert</i>	May 1998	9.34
<i>Western Arctic Ocean</i>	July 1994	4400	<i>Alert</i>	July 1994	4.77
<i>Central Arctic Ocean</i>	Aug 1994	2000	<i>Alert</i>	Aug 1994	5.22
<i>Greenland Sea</i>	Sept 1994	4200	<i>Alert</i>	Sept 1994	5.87
<i>White Sea, Russia</i>	Sept 1999	2000	<i>Amderma</i>	Sept 1999	3.73
β-endosulfan					
<i>Canadian Archipelago (JOIS-97)</i>	Sept 1997	600	<i>Canadian Archipelago (JOIS-97)</i>	Sept 1997	0.29
<i>Bering & Chukchi Sea</i>	Aug 93	3400	<i>Bering Sea, Gulf of Anadyr</i>	Aug 1993	1.00

Values of $\text{FR} > 1$ correspond to oversaturation in the seawater and hence net volatilisation, whereas $\text{FR} < 1$ shows undersaturation in the water and therefore net

deposition, whereas $FR = 1$ indicates air-water equilibrium and no overall net transfer.

Regression parameters to allow calculation of a temperature dependent Henry's law constant for α -endosulfan are restricted to one study by Rice *et al.* (1997), whereby H' is the dimensionless form of H (the air-water partition coefficient), given by:

$$\log H' = -876.14 / T + 0.4463 \quad (4)$$

Where H' can be converted to H by simply dividing through by RT . Rice *et al.* were not successful in measuring the temperature dependence of H for β -endosulfan. Therefore H was estimated for the β -isomer, based on the ratio of H values for both isomers ($H_{\alpha-ES}$ and $H_{\beta-ES}$) measured at 25°C (298K), according to:

$$H(T)_{\beta-ES} = \frac{H(T)_{\alpha-ES}}{H(298K)_{\alpha-ES} / H(298K)_{\beta-ES}} = \frac{H(T)_{\alpha-ES}}{15.6} \quad (5)$$

Where $H(298)_{\alpha-ES}$ and $H(298)_{\beta-ES}$ in the denominator of equation (5) were recently derived by Shen and Wania (2005). Temperature adjusted values for the β -isomer ($H(T)_{\beta-ES}$) can only be considered as estimates using this approach and it must be noted that the Henry's Law constant for the α -isomer at 298 K using the Rice *et al.* regression (equation 4), results in a value of 7.95 Pa m³ mol⁻¹ which is a factor of 11.4 greater than 0.7 Pa m³ mol⁻¹, the 'final adjusted' value given by Shen and Wania (2005).

The fugacity ratios presented in Table 4.2.1.2 for α -endosulfan provide evidence of a regional difference in air-water transfer. The FR values are significantly lower than 1, indicating net deposition from the air into surface waters, for the Canadian Archipelago and ice-free parts of the central Arctic Ocean. However, the FR values are at 1 or significantly exceed 1, indicating either equilibrium or net volatilisation respectively, for the western reaches of the Arctic Ocean as well as the Bering/Chukchi Seas, the Greenland Sea and the White Sea (close to Russia in the eastern Arctic). Some of the highest α -endosulfan seawater concentrations are reported in these regions. For the White Sea, a relatively shallow coastal sea and almost landlocked by western Siberia, the contribution of riverine inputs to the pesticide loading may be significant (the Onega and Dvina rivers drain into the eastern part of the White Sea) and may serve to increase seawater concentrations. Water concentrations for selected pesticides, excluding endosulfan, have been reported for several of the larger Russian rivers that drain into the arctic coastal seas (Alexeeva *et al.*, 2001). As a result, levels of γ -HCH are relatively high in the White Sea (averaging 374 ng/m³ compared to 220 ng/m³ in the Barents Sea) resulting in an FR value close to 1, indicating equilibrium or near equilibrium conditions with the atmosphere, unlike other parts of the Arctic Ocean where γ -HCH is undergoing net deposition.

The variability of α -endosulfan FR values across these regions is illustrated in Figure 4.2.2. Towards the western and eastern fringes of the Arctic Ocean (coastal seas) the FR values are >1 indicating that the seawater is oversaturated with respect to the air, resulting in net volatilisation. This is also the case for the Greenland Sea and White Sea where ratios also exceed 1. For the Canadian Archipelago and central Arctic Ocean the situation appears to be reversed, with FR values generally <1, indicating net deposition. However, a degree of caution must be emphasised when

interpreting these FR values. For example, the error bars displayed in Figure 4.2.2 for several of the western Arctic locations including Bering/Chukchi, Holman and the western Arctic Ocean result in FR values that are not significantly different from 1 for these sites (i.e. equilibrium). This is also the case for several of the Canadian Archipelago sites (i.e. the JOIS 97 cruise) as well as the White Sea in the Russian Arctic. The wide error bars arise due to the variability in seawater concentrations measured within particular studies, and the picture is further complicated by the presence of ice which will effectively inhibit air/water transfer. This is particularly relevant for those campaigns conducted in May before substantial ice melt has occurred in the high Arctic. The reduction in FR values within the Canadian Archipelago probably reflects the lower water concentrations relative to the Bering/Chukchi seas further west. However, within the Archipelago, fluctuations in α -endosulfan seawater concentrations over an annual time frame have been observed by Hargrave *et al.* (1997). In their study, year-round water samples were taken near Cornwallis Island located in the central Archipelago, and α -endosulfan concentrations were found to increase during ice-free summer periods, unlike γ -HCH.

Table 4.2.1.2 Fugacity ratios (FR) for endosulfan and γ -HCH calculated for different regions of the Arctic Ocean.

Location	Air Temp (K)	Water Temp (K) [§]	FR α -endosulfan	FR β -endosulfan	FR γ -HCH
Bering/Chukchi Seas	276.7	278	1.57 (\pm 1.38) [†]		0.31-0.52*
Barrow/Beaufort Sea	270.7	271	0.43 (\pm 0.20)		0.30-0.38**
Holman W. Archipelago	273.4	273	3.11 (\pm 4.61) [†]		0.43
Baffin Bay E. Archipelago	267.5	273	0.64 (\pm 0.37)		0.46
Western Arctic Ocean	278.1	272	2.12 (\pm 1.92)		0.45
Central Arctic Ocean	273.4	272	0.63 (\pm 0.21)		0.97 [†]
Greenland Sea	264.7	274	1.31 (\pm 0.30)		0.57
White Sea, Russia	276.7	272	1.21(\pm 0.34) [†]		1.01 [†]
Canadian Archipelago (JOIS 97)	262.4	271		0.22 (0.10)	1.14 [†]
Bering Sea, Gulf of Anadyr	279.2	278		0.43	

[§]Seawater temperatures taken during the cruise/study or obtained from NOAA satellite database.*Range of fugacity ratios reported by Sahuvar *et al.* (2003) for the south Bering Sea and Chukchi Sea using temperature adjusted Henry's Law constants for α -HCH derived from their own work.** Range reported by Sahuvar *et al.* (2003) for the Northern Canada Basin ('western Arctic Ocean') and the Beaufort Sea.[†] not significantly different from FR=1

The relatively shallow waters of the Archipelago become highly stratified during ice-free periods due to the incursion of meltwater and localised air-water exchange may strongly influence seawater concentrations due to the lack of vertical mixing (Hargrave *et al.*, 1997). As a result, changeable seawater concentrations coupled to seasonal changes in air concentrations (i.e. spring maximum events) will affect the

FR values over the short term and this is reflected by the error bars in Fig 4.2.2. for the JOIS '97 and Baffin Bay studies.

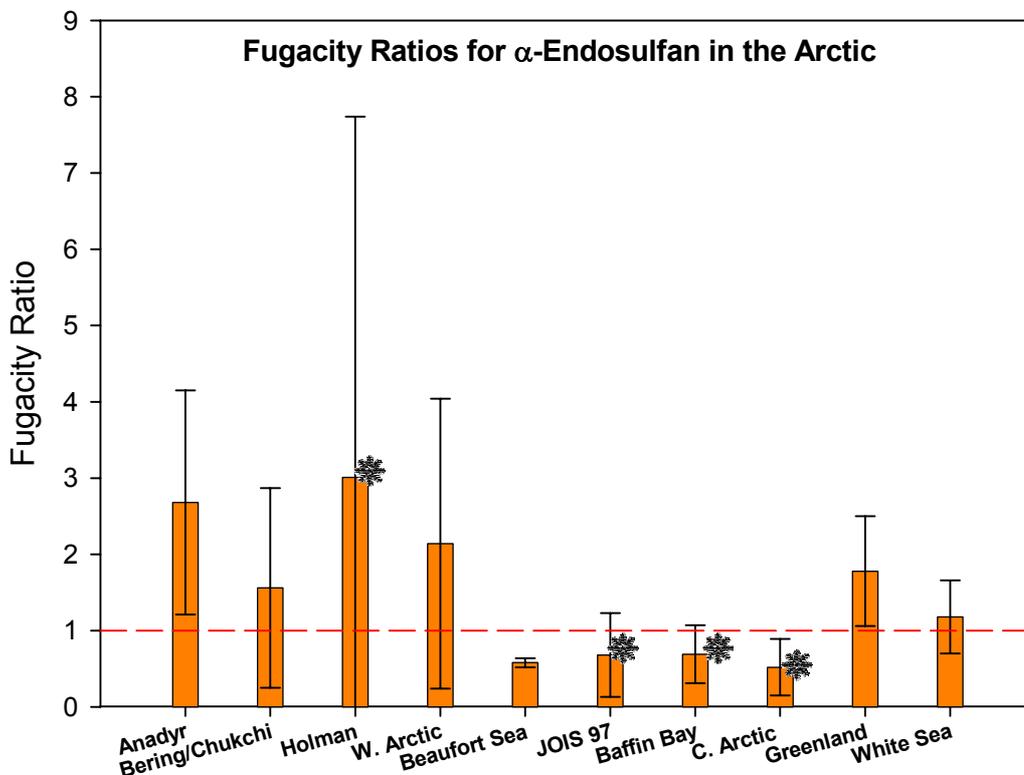


Figure 4.2.2. Fugacity ratios of α -endosulfan for different regions of the Arctic Ocean. Note the locations on the x-axis broadly represent a west to east transect (i.e. Bering to the White Sea).

* Sea-ice cover likely to be impeding air-water transfer; JOIS 97 = Canadian Archipelago

It is plausible that endosulfan residues present in the winter snow pack will be flushed into surface seawater with the melting sea-ice and associated snow. Helm *et al.* (2002) highlighted the importance of meltwater as a source of α -endosulfan to a freshwater lake (Amituk Lake) on Cornwallis Island. A mass balance of the lake over a three year period revealed that endosulfan present in the water column was rapidly removed over the course of a year unlike γ -HCH (i.e. ~90% reduction in the water concentration), but was re-supplied each June by the input of meltwater. Losses through sedimentation and volatilisation were considered negligible compared to export from the lake with water outflow and degradation (both chemical and biological). Degradation in this case was considered to be an important loss process for endosulfan (~40%) relative to γ -HCH (~15%).

To summarise, α -endosulfan appears to be undergoing net volatilisation in the western and eastern fringes of the Arctic Ocean, and yet undergoing net deposition to surface waters in the Canadian Archipelago and the central Arctic Ocean. This variation between regions is likely to be driven by fluctuations in seawater concentrations which in turn may be affected by water stratification and the input of meltwater. For those regions where air data exists for α -endosulfan (the Bering Sea and Canadian Archipelago) the FR values are <1 indicating net deposition. However

the paucity of air concentrations and the lack of a measured temperature-dependent Henry's Law constant for this isomer results in greater uncertainty in these values. γ -HCH is undergoing net deposition or at equilibrium for the regions of the Arctic Ocean provided in Table 4.2.1. Interestingly, the γ -HCH FR values reported in Table 4.2.1.2 also include the range of values reported by Sahuvar *et al.* (2003) for the Bering/Chukchi Seas and other parts of the western Arctic Ocean. These data were effectively a re-evaluation of existing sea and air concentrations but using the most accurate Henry's Law constant for γ -HCH. Use of this later Henry's Law constant resulted in a re-assessment of the equilibrium status of γ -HCH, whereby FR values which were previously >1 for the Bering and Chukchi Seas, changed to values that were <1 . This serves to highlight the importance of up to-date and accurate Henry's Law constants in order to conduct a thorough assessment of air-water transfer. For α -endosulfan, temperature dependent values of H are accessible from only one study and are non-existent for the β -isomer. This adds considerable uncertainty to the data presented in Table 4.2.1.2. Furthermore, the presence of salt in seawater reduces chemical solubility thereby increasing the Henry's Law constant. This 'salting out effect' can be determined with use of the Setschenow constant (Xie *et al.*, 1997) and will have the effect of increasing the endosulfan Henry's Law constants by ~ 1.5 , thereby increasing the FR values presented in Table 4.2.1.2 and Figure 4.2.2.

4.3 Snow & Ice

Snow and ice play an important role in transferring organic contaminants to Arctic terrestrial and marine systems. Much of the precipitation that falls in the Arctic is in the form of snow and the efficient scavenging of semi-volatile organic compounds by snowfall (see section 3.3) makes this an important transfer route for chemicals present in the atmosphere (CACAR, 2003; Herbert *et al.*, 2005a). The extensive arctic snowfields also receive dry deposition through particle deposition and chemical sorption, with snow providing an ideal porous medium suitable for chemical exchange with the atmosphere (Hallsall, 2004). While there are a limited number of studies that report organochlorine pesticides in arctic snow, there are very few 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) provided snow and meltwater data that were utilised to develop a chemical snow model to simulate the behaviour of SVOCs with snow ageing and melt (Wania *et al.*, 1999). During snow melt, chemicals were found to follow an elution order from the snowpack, whereby those SVOCs 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 solubility. Interestingly, those chemicals which had aqueous solubilities similar to α -endosulfan, but possessed much higher K_{ow} values, were not considered as 'first flush' chemicals (i.e. initially released with the first snowmelt) as significant re-partitioning occurred within the melting snowpack due to the presence of particulate/organic material. This had the effect of delaying or even preventing their release with outflowing meltwater. While detailed laboratory investigations are required to verify model results, there is some evidence from field work to suggest that α -endosulfan is released annually from the melting snowpack. For example, a seasonal increase in water concentrations has been observed in Amituk Lake, coinciding with periods of meltwater input during early summer (Helm *et al.*, 2002) and has been discussed earlier in this chapter (see Section 4.2).

Arctic snow concentrations

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.* (2005b). In general, pesticide snow concentrations (reported as mass of chemical per volume of snow meltwater) display a wide range in values and there are a number of factors which account for this (Herbert *et al.* 2005b), although in essence this is due to the sampling of different snow types/layers within the same study (i.e. fresh snow versus aged snow), whereby different snow layers may contain significantly different concentrations. The heterogeneous nature of snowpack contamination, coupled to the scarcity of field studies, makes identification of geographical or temporal trends for a particular chemical difficult to establish. A notable study conducted in 1986, reported a number of OC pesticides in snow, including γ -HCH and α -endosulfan, for 12 sample sites located across the Canadian Archipelago (Gregor and Gummer, 1989). Snow concentrations for γ -HCH and α -endosulfan ranged from 0.22 – 4.46 and 0.09 - 1.09ng/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 less data available for endosulfan. For example, γ -HCH concentrations measured during 2001 at Ny-Ålesund (Svalbard, Norwegian Arctic) ranged from 0.18 – 3.09 ng/L for a series of fresh snowfall events (Herbert *et al.* submitted). Garabarino *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 bulk of endosulfan snow data exist for northern Canada, where fresh snow samples have been collected at a frequency of every two to four weeks for several locations through the winter months of 1992-1995 (Strachan *et al.* unpublished data). Details of the sample locations are presented in Table 2.3.3, but these effectively cover a wide part of northern Canada, stretching from the Fraser valley in British Columbia, to sites across Nunavut in the Canadian Archipelago, and as far north as Alert. A summary of concentrations for γ -HCH and the endosulfan isomers are presented in Table 4.3.1 for six Canadian sites that represent a wide geographical area and have measurements reported for 1995, the final year of sampling. In addition, concentrations are also included from recent studies conducted in the Norwegian Arctic, where surface glacial snow was sampled on Svalbard Island (Hermanson *et al.* 2004) and fresh snow was sampled near the town of Tromsø on the Norwegian mainland (Herbert *et al.* 2005a). In the latter study, snow extracts were re-analysed by GC-NIMS 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.

From Table 4.3.1, the average snow concentrations at Alert for α -endosulfan and γ -HCH were not significantly different; similarly there was no significant difference between the mean concentrations at Cape Dorset (Kingait) and Fraser River. Nevertheless, γ -HCH concentrations were greater at Eureka, which like Alert, is also located on Ellesmere Island in the Canadian high Arctic, although snow sampling at this site did not extend into 1994/95 with the concentrations representing 1992/93. In general, levels of α -endosulfan in surface snow are comparable to γ -HCH which is in contrast to levels observed in arctic seawater. This reflects the efficiency by which falling snow will remove SVOCs 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. Indeed the snow/air partition coefficient (K_{sa}) for α -endosulfan is estimated to be 2-3

fold greater than γ -HCH at ca. -5°C (estimated using a method developed by Lei and Wania, 2004) and can account for the similar concentrations in fresh snow. It is worth noting however, that the studies selected in Table 4.3.1 represent relatively fresh snow, whereas the earlier Canadian study conducted by Gregor and Gummer (1989) (which reported higher levels of γ -HCH on average) sampled composite snow, comprising of older snow layers taken towards the end of the winter season. Post-depositional loss of SVOCs following the ageing of fresh snow is significant and is addressed further (with respect to α -endosulfan) in the following section. Concentrations of β -endosulfan were considerably lower (~ 10 - 50 -fold) than those of the α -isomer, and was detected in a much smaller number of samples. For example, at both Fraser River and Alert, the β -isomer was only detected in <5 samples out of a total of 15 taken during the 1994/95 winter periods, whereas α -endosulfan was consistently present in all samples. Nonetheless, 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.

Table 4.3.1. Mean (SD) surface snow concentrations measured at different locations within Arctic Canada and Norway

ng/L	γ -HCH	α -endosulfan	β -endosulfan
CANADA 1994/5 ¹			
Alert	2.35 (2.02)	1.59 (1.33)	0.007 (0.007) ²
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 ³
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 ⁴	0.169	0.136	0.037
Tromsø ⁵	1.50 (0.335)	0.830 ⁶	$<\text{MDL}$ ⁷

¹Strachan et al (unpublished data); ²detected in only 5 samples ($n=5$); ³ $n=2$; ⁴Hermanson et al.(unpublished data), values for a surface snow layer; ⁵Re-analysis of surface snow extracts (for details see Herbert et al. (2005a)); ⁶ $n=3$ (relatively high method detection limits (MDL = 0.410 ng/L) resulted in the exclusion of most samples); ⁷ β -isomer was below the method detection limits (MDL = 0.060 ng/L) for all samples.

Figure 4.3.2 illustrates the range of snow concentrations for α -endosulfan and γ -HCH for a selection of the Canadian studies taken from Table 4.3.1. 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 is the only site not located within the Canadian Archipelago. The largest range in concentrations for both compounds was observed at the more northerly sites of Alert and Eureka. These sites experience the coldest annual air temperatures and yet displayed some of the highest snow concentrations. The scavenging efficiency of falling snow is estimated to increase by an order of magnitude for γ -HCH, when air temperatures drop from -10°C to -20°C (Lei and Wania, 2004) and this is also likely to be the case for α -endosulfan. As wintertime air concentrations do not vary significantly over the Canadian Arctic for both compounds, then temperature differences between these sites (where colder temperatures result in enhanced vapour scavenging by snow) is likely to account for the higher snow concentrations at the two most northerly sites. It is worth bearing in

mind that the relative loading of γ -HCH and α -endosulfan between these sites is dependent on the amount of snowfall. Alert has the lowest precipitation rate out of all of the sample sites (~150 mm water/year), and taking the average snow concentration of α -endosulfan as 1.59 ng/L (Table 4.3.1) yields a flux of 239 ng/m²/yr. Cape Dorset, on the other hand, has an average snow concentration 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/m²/yr, which is a factor of only 1.6 less than Alert.

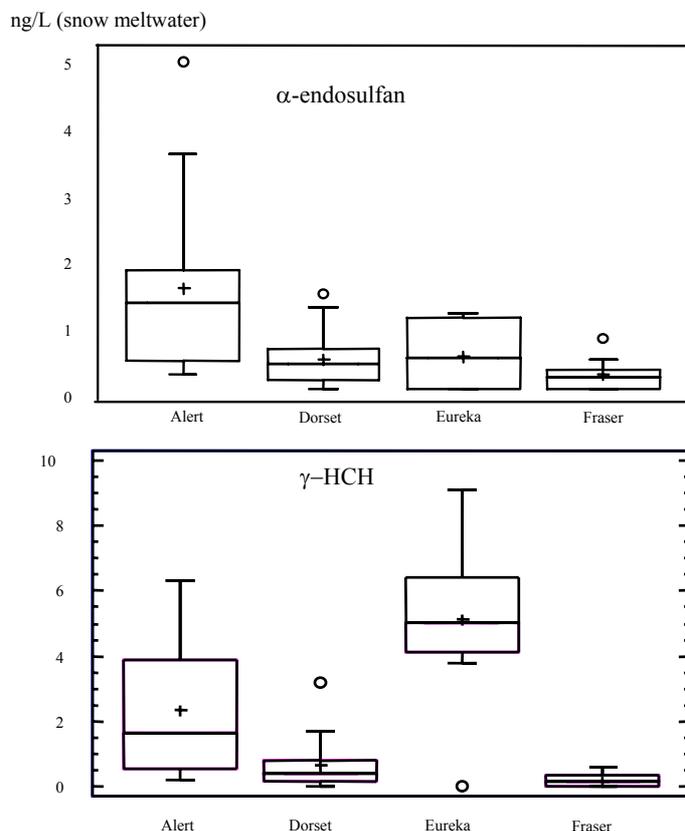


Figure 4.3.2. Box-and-whisker plot of α -endosulfan and γ -HCH concentrations measured systematically in surface snow at sites located across northern Canada during winter months 1994/95.

Alert, Ellesmere Is (82°N), Cape Dorset (Kingait) (64°N), Eureka, Ellesmere Is (80°N), Fraser River, Yukon/BC (61°N). For each box-and-whisker, the central line represents the median, the cross the mean, then upper and lower ends of the box are the 75th and 25th percentiles and the ends of the whiskers the 90th and 10th percentiles. Outliers are represented by the circles.

Post-depositional fate of endosulfan

To understand the significance of the snowpack in providing pesticides such as endosulfan to arctic watersheds, it is necessary to consider the fate of SVOCs following deposition with fresh snowfall. Snow is a highly transient medium, with physical properties open to rapid change over a short period of time. Snow metamorphism arises due to ice-crystal compaction, abrasion and sublimation that almost always results in a decrease in snow surface area (Cabanès *et al.* 2003). A decrease in the specific snow surface area (SSA) (cm²/g) results in a marked reduction in the vapour-sorbed quantity of trace VOCs in snow (Cabanès *et al.*, 2003) and indeed a significant loss of vapour-sorbed SVOCs has been recently

observed during the ageing of fresh snow sampled in Tromsø in the Norwegian Arctic (Herbert *et al.* 2005a). In this case, snow density (ρ) was used as a surrogate for SSA, whereby increases in ρ were found to be inversely related to vapour-sorbed concentrations for a range of different compounds including polychlorinated biphenyls (PCBs) and OC pesticides such as γ -HCH. Figure 4.3.2 illustrates the exponential relationship between the fraction of chemical remaining in a fresh snow layer (ϕ_s) following changes to its density ($\Delta\rho$) with time. Re-analysis of the Tromsø snow extracts for endosulfan resulted in only three of the ten samples (comprising the time-series) with concentrations exceeding the method detection limits (both α - and β -endosulfan were present at relatively high levels in the field blanks). The average concentration of α -endosulfan in the three samples was 0.830 ng/L (Table 4.3.1), but individually the concentrations were 1.48, 0.53 and 0.48 ng/L, corresponding to the snow sample taken immediately after snowfall (time, $t=0$ h), the 72 h sample ($t=72$ h) and the 96 h sample ($t=96$ h) respectively. Fitting these data to the plot in Figure 4.3.2 resulted in α endosulfan confirming to the rapid first order loss observed for other SVOCs, including γ -HCH. The relationship between ϕ_s for α -endosulfan and snow density, ρ may be given by:

$$\phi_{S, \alpha\text{-endo}} = 0.69e^{-6.26\Delta\rho}$$

To illustrate the use of this equation, an increase in snow density of $\Delta\rho = 0.1$, which is often typical for fresh snow subject to changes in temperature or windspeed, would result in a $\phi_{S, \alpha\text{-endo}}$ value of 0.36, or alternatively, a 64% reduction in the initial snow concentration. It is therefore not advisable to use the fluxes calculated for Alert and Cape Dorset as estimates of α -endosulfan loading to nearby catchments, as these would result in gross overestimations.

Given the relatively low precision associated with snow sampling (Herbert *et al.*, 2004) it is not possible to distinguish separate loss rates for the range of compounds shown in Figure 4.3.2. However, in a separate study conducted at the same location, fresh snow was artificially spiked with a number of different organochlorine pesticides, and loss rates from snow (k_s) were found to be strongly correlated to temperature-adjusted Henry's Law constants rather than chemical vapour pressures (Villa *et al.*, 2004) In other words, following snowfall, organochlorine pesticides will strive to attain equilibrium according to their Henry's Law constants, with the rate being driven by the changing surface area/density of the snow layer. In this case, snow can be considered akin to a simple aqueous phase and with time, the relative proportions in aged snow should reflect those predicted by the pesticides' Henry's Law constants. This will account for the preferential loss of α -endosulfan in aged snow relative to γ -HCH, and explains the enrichment of γ -HCH in older snow and firn (Gregor and Gummer, 1989) compared to fresh snow.

The occurrence of endosulfan in glacial firn and ice has been observed in both the Norwegian Arctic (Svalbard) (Hermansen *et al.* in press and unpublished data) and a temperate glacier located in the Canadian Rockies (Donald *et al.*, 1999). Concentrations of α -endosulfan were typically much lower than fresh snow and ranged between 0.01-0.09 ng/L. However, there is considerable variation in concentrations between ice-cores taken in the Svalbard Archipelago. For example, Hermansen *et al.* (in press) analysed ice cores taken from Austfonna, an ice cap located towards eastern Svalbard and found elevated concentrations of both organochlorine and organophosphorus pesticides, including endosulfan. The peak concentration of α -endosulfan was 10 ng/L corresponding to an ice layer representing the accumulation period 1986-1992, with similar concentrations of γ -HCH. Agricultural regions in northern Russia were suspected as the major sources of

these pesticides to this low altitude glacier. For ice and snow analysed at Lomonosovfonna, a glacier also located in the Svalbard Archipelago but at higher altitude, concentrations of γ -HCH and endosulfan were ~ 10 -fold less and a longer time-series was established. Data from Lomonosovfonna are presented in Figure 4.3.3 and show the abundance of γ -HCH relative to endosulfan. Figure 4.3.3 B illustrates the profile of endosulfan only and warrants further discussion. The uppermost surface layers (snow and firn) show the highest concentrations of both isomers, ranging between 0.120-0.140 ng/L, although these are still less than half the concentrations observed in fresh snow (Table 4.3.1). The increase in concentrations in the most recent layers corresponds to the late 1990s/2000 but should not be interpreted as an upward trend in endosulfan deposition. Firstly, the concentrations do not take into account the difference between the rates of precipitation between the years (i.e. fluxes are not reported), secondly and more importantly, the concentrations are likely to decrease as further compaction takes place due to subsequent snow burial and conversion of snow to firn. From Figure 4.3.3 B, it is interesting to note that in the uppermost snow layers β -endosulfan concentrations are ~ 4 -fold less than the α -isomer, but in deeper layers the predominance of the α -isomer declines. This is presumably due to the preferential loss of the α -isomer through re-partitioning to interstitial pore air (due to its relatively higher Henry's Law constant); a process which is likely to be enhanced during firnification and the formation of glacial ice. It should be noted that post-depositional processes will obscure temporal trends to some extent. This is apparent in the case of endosulfan which had not been discovered and produced until the 1950's (see Figure 4.3.3).

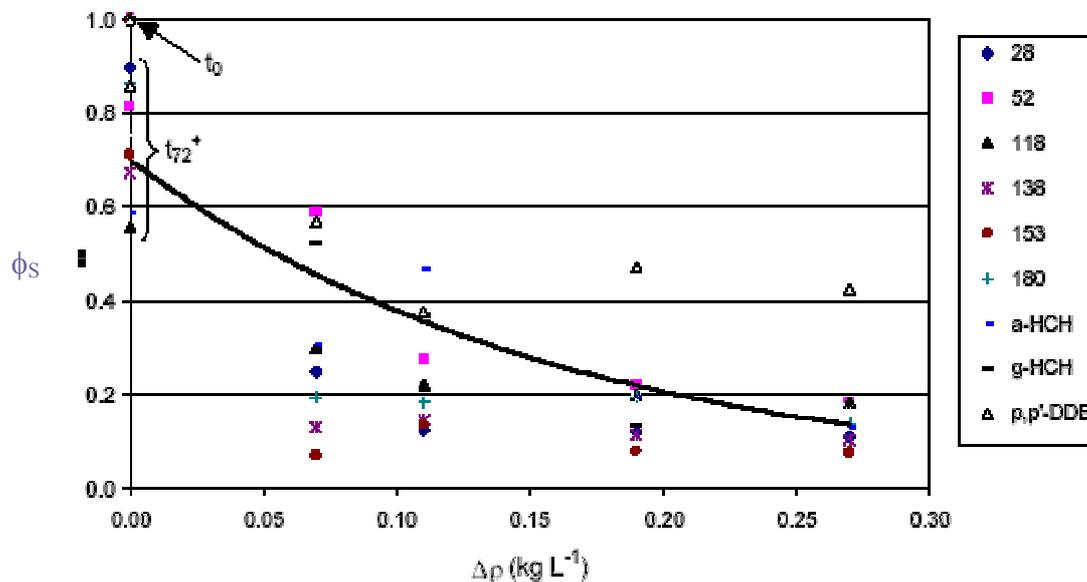


Figure 4.3.2 Relationship between the chemical fraction (ϕ_s) remaining in a fresh snow layer and changes to its snow density ($\Delta\rho$). The fresh snow was sampled immediately following snowfall ($t=0$) and then repeatedly over a 10 day period ($t=240$ h). The line is fitted to the average of the data since significant differences could not be distinguished between the various chemicals. Note that increases in snow density could not be detected between $t=0$ and $t=72$.

Legend: the numbers 28, 52, 115, 138, 153 and 180 are the IUPAC numbers assigned to individual PCB congeners of varying chlorination.

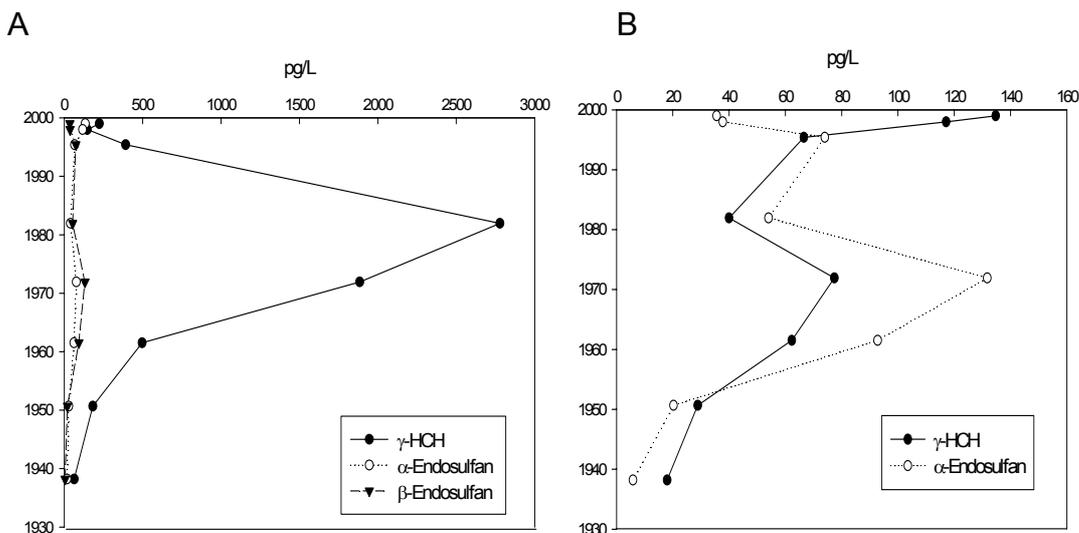


Figure 4.3.3 Concentrations of γ -HCH and endosulfan in a snow/ice core taken from Lomonosovfonna (glacier) in Svalbard (Norwegian Arctic) (Hermanson et al. unpublished data). Both γ -HCH and α/β -endosulfan are shown in A with α - and β -endosulfan depicted in B.

4.4 Data Gaps and Uncertainties

Air

Scope

In general, endosulfan has only been added to lists of routine monitoring analytes relatively recently. The vast majority of the monitoring of endosulfan conducted to-date has focused upon α -endosulfan. More extensive endosulfan monitoring campaigns suggest that β -endosulfan residues in air are comparatively minor. Endosulfan sulfate is not considered in typical monitoring and therefore has not been reported or detected in the abiotic Arctic environment to the authors' knowledge. However, endosulfan sulfate occurs, and is expected to be formed, in Arctic biota.

Spatial uncertainty

Long-term continuous air sampling is available for comparatively few sites of which Alert in the Canadian high Arctic provides the most significant dataset (weekly sampling during the period 1992-99). An additional limited monitoring programme has been conducted at a sub-Arctic (but considered Arctic under the conventions of AMAP) site in the Yukon, Canada (Tagish; 1993-94). Limited additional monitoring at Arctic sites in Asia has similarly been conducted in eastern and western Siberia (Dunai, 1993-94; AmDerma, 1998-99). Very short but intensive monitoring exercises have been carried out in the Bering Sea (August-September, 1993) and in the European Arctic in Tromsø, Norway (February-March, 2003). The available network of monitoring programmes that were utilised for this assessment are summarised in Table 2.3.1. From this summary it is apparent that the network of long-term, continuous air monitoring sites in the Arctic remains extremely limited and, as a consequence, there are obvious associated spatial uncertainties in the interpretation of air monitoring results. This is not surprising given the logistical difficulties of mounting such research campaigns. Nonetheless, the results of these exercises do

provide some critical insights into spatial variability and, in some cases, presents the opportunity for attributing significant likely source regions for contaminants.

Attribution of sources and transport behaviour

Air mass back trajectories at Tagish have been employed to assess potential sources of contaminants into the western Canadian Arctic. Similar detailed assessments have not been conducted for endosulfan at other monitoring sites. However, interpretation of data from Tagish in conjunction with air sampling conducted in the Fraser River valley of British Columbia has indicated that continental/southerly air masses in North America are likely to be more significant contributors to Arctic contamination than Asian sources. Attribution of source regions for endosulfan arriving in Arctic regions of eastern North America, Europe, eastern and western Asia remains uncharacterised.

Temporal uncertainty

The long-term trend in endosulfan residues in air in the Arctic appears to be stable. Usage/emission may have peaked and may now be in decline but establishing the extent of any delay in parallel decline in air residues will require further (and perhaps more extensive) continuous air sampling. The timescales required to assess this cannot be accurately estimated due to a lack of knowledge about the significance of a wide range of potential confounding influences summarised by Hung *et al.* (2005) as discussed earlier in this chapter, as well as more up to date and more accurate usage and emission estimates.

Seawater

Scope

Both α and β endosulfan have been included in seawater monitoring campaigns and have been detected in surface water in most regions of the Arctic Ocean. The concentrations found in monitoring studies are typically very small, resulting in significant analytical challenges. The Method Detection Limits for endosulfan typically range from 100 to 500 pg/m^3 ($\text{Mean}_{\text{blank}} + (3 \cdot \sigma_{\text{blank}})$). By comparison, averaged measurements of α - and β -endosulfan have been reported in the ranges 1400 to 4300 pg/m^3 and 500 to 3400 pg/m^3 , respectively. In particular, uncertainties have been pointed out by some researchers in the robustness of β -endosulfan measurements (Chernyak *et al.*, 1996). Endosulfan sulfate has not been typically included in monitoring campaigns and, therefore, seawater profiles remain unknown for this metabolite.

Spatial uncertainty

Seawater monitoring profiles are available for a reasonable distribution of sites in the Arctic. Most sectors of the Arctic are included with the Bering Sea, Beaufort Sea, Canadian Archipelago particularly well-represented. Much of this data has been gathered from 'near coast' sampling, but a few more isolated sampling campaigns have been carried out on cruises such as the Barents Sea and Eastern Arctic sampling campaign mounted by the Swedish research vessel *Oden* in 1996. The Central Asian Arctic (e.g. region around the Kara and Laptev Seas where several large Asian rivers such as the Ob, Yenisey and Lena Rivers discharge) is poorly represented. This may have implications when considering the potential of Asian rivers as routes of entry for endosulfan into the Arctic.

Attribution of sources and transport behaviour

The extent to which oceanic transport acts as a major route of entry remains unclear. Concentrations of both α - and β -endosulfan east of the Beaufort Sea in the

Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain. There are no clear geographical trends that may suggest, for example, that transport from the Pacific Ocean through the Bering and Chukchi seas may be occurring. Input via Pacific waters through the Bering Strait may be significant but this does not appear to be consistent with long-range transport observations from the Asian Pacific Rim (see earlier comments regarding sources of air contaminant).

The limited geographical trend discussed above is in contrast to more intensively studied compounds such as γ -HCH, for which transport routes and fate are comparatively well understood. Endosulfan does not appear to be behaving or entering the Arctic in the same manner as this better characterised compound.

Under certain circumstances water monitoring results have been found to be highly variable (both in terms of the scale of detection but, notably, also in terms of the ratios of α - to β -endosulfan). It has been suggested that this may reflect local influences such as entry of meltwater. This is consistent with observations made in certain coastal locations (e.g. Cornwallis Island) where meltwater has been attributed as a significant local source of endosulfan residues.

Uncertainties in air-water exchange potential

As highlighted earlier, high quality air monitoring results are available for a very limited number of sites that limit the ability to accurately cross reference to seawater monitoring when estimating air-water exchange potential. The lack of air data (generally levels below detection) for the β -isomer frustrate attempts to estimate air-sea gas exchange potential. However, considering the very small quantities of β -endosulfan found in air, there appears to be an enrichment process occurring for this isomer in seawater related to a lower Henry's law constant compared with the α -isomer.

Despite this, there appear to be significant regional differences in air-sea gas exchange behaviour for α -endosulfan. Sampling of seawater in some regions suggest that there is a net seawater \rightarrow air transfer mechanism occurring or that air and seawater are at close to equilibrium (e.g. Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea). In other areas (notably the Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) there is a net air \rightarrow seawater transfer mechanism occurring. In some cases there is a high degree of ambiguity (e.g. Holman in the Western Canadian Archipelago; where different sampling events suggest reversal of the net transfer mechanism with contrasting fugacity ratios estimated of 0.25 and 1.34). In several other cases there is a high degree of uncertainty that is characteristic of low level analysis. There is insufficient data available to accurately estimate net air-sea gas exchange behaviour for β -endosulfan. The lack of clear consistent air-sea gas exchange behaviour is in contrast to γ -HCH where recent results suggest a clear air \rightarrow seawater transfer mechanism in operation.

Fugacity ratios have been used to estimate the net transfer air-sea gas exchange behaviour. This relies very heavily on an estimated temperature dependent Henry's law constant. This leads to significant uncertainties and potential for inaccuracies in attributing net transfer behaviour, particularly when fugacity ratios are close to unity (e.g. implication that the system is at equilibrium). This is considered to be the single greatest uncertainty in evaluating air-sea gas exchange behaviour (and perhaps behaviour of endosulfan in the Arctic as a whole). The uncertainty in the estimated

value is underscored by comparison with the 'final adjusted value' proposed by Shen and Wania (2005) (a difference of just over one order of magnitude).

These uncertainties are further compounded by salinity effects that have not been taken into account when estimating fugacity ratios. The influence of 'salting out' may result in a general underestimate in the seawater → air transfer potential by a factor of ca 1.5. When taken together, the compounded uncertainties associated with low level analysis in seawater, reliance on a very limited set of air sampling campaigns (two locations in the Canadian High Arctic and Siberia), the lack of availability of a temperature dependent Henry's law constant and the influence of 'salting out', suggest that a high degree of caution must be exercised in interpretation and attribution of behaviour as evidence of POP characteristics. It can be argued that the high degree of variability observed would, in fact, favour the combined influence of a far more complex set of processes than is implied in typical simplistic POP characterisation more relevant for compounds such as γ -HCH where there is a degree of spatial consistency.

Temporal uncertainty

The available monitoring database is spatially and temporally sporadic. The majority of the seawater monitoring data utilised in this assessment has been gathered during summer months during the mid- to late 1990's. It does not constitute a robust enough database that would allow firm conclusions to be made regarding temporal trends.

The almost complete reliance on monitoring during summer months in ice-free areas has additional implications regarding understanding environmental fate in the Arctic. Ice cover effectively eliminates air-sea gas exchange potential. The seasonal influence of this remains an uncertainty as sampling has been conducted below the ice pack to investigate any seasonal variation in seawater residues due to shut down of the air-sea gas exchange process. This is particularly important in the Central Arctic where the ice pack remains throughout the summer period.

Snow and ice

Scope

Both α - and β -endosulfan have been detected in arctic snow, with systematic measurements available for a number of sites across the Canadian Arctic for the mid-1990s. β -endosulfan was detected less frequently than the α -isomer with concentrations ~10-fold lower. This was confirmed by later studies conducted in the Norwegian Arctic, although concentrations in fresh snow could not be determined due to its presence in field blanks, resulting in high method detection limits for the β -isomer. Concentrations of α -endosulfan and γ -HCH in fresh snow are comparable, which is in contrast to seawater where γ -HCH is the predominant compound (typically a 100-fold higher than α -endosulfan). In fresh snowfall however, concentrations of a range of semi-volatile organic compounds (SVOCs), including α -endosulfan, were found to decrease rapidly due to snow metamorphosis, with concentrations declining according to first order kinetics. Subsequent re-emission from the snowpack to the atmosphere is considered to be the most likely loss process over the short term.

Spatial uncertainty

Spatial differences are difficult to determine due to the high variability in snow concentrations. In the Canadian Arctic the two most northerly sample sites, with the coldest air temperatures displayed the widest range in concentrations with higher average concentrations than sites located further south. However, higher rates of

precipitation experienced at the more southerly stations result in similar depositional fluxes across the Canadian Archipelago.

Measurements in aged snow are limited to single studies in Canada and Norway, but reveal levels that are markedly lower than those observed in fresh snow. It is these residues that will be available to meltwater during spring thaw, and not residues present in fresh snow. Limited evidence suggests that in aged snow the chemical composition can be described by the Henry's Law constants, which accounts for the preferential loss of α -endosulfan over γ -HCH. Chemical (photo)degradation may also play a role in chemical loss particularly following polar sunrise in the high Arctic.

Temporal uncertainty

A survey of glacial firn and ice in the Norwegian Arctic revealed the accumulation of SVOCs including α - and β -endosulfan. In this study, the chemical profile in deeper layers of firn/ice was dominated by the β -isomer, presumably due to the post-depositional loss of the α -isomer. The accumulation profile for the last 50 years reveals that input of endosulfan was higher in the past, although significant post-depositional migration may blur this profile to some extent.

5 Residue Transfer

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The concepts of bioaccumulation, bioconcentration and biomagnification have been discussed briefly in Sections 3.2 (providing an overview of uptake profiles for endosulfan in laboratory and/or temperate evaluation context) and 3.4.3 (outlining a strategy for extending this interpretation into an Arctic context based on biotic monitoring data). Detailed definitions of bioaccumulation, bioconcentration and biomagnification are provided in the glossary of terms towards the end of this report (see Section 11). It is appropriate at this stage to simply summarise the benchmarks or triggers of regulatory concern:

Bioaccumulation and bioconcentration

Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000 (Log BAF or Log BCF > 3.7).

Biomagnification and trophic magnification

Although there are no biomagnification factor (BMF) or trophic magnification factor (TMF) triggers within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs, there are criteria applied to bioconcentration or bioaccumulation in aquatic species (BCF (bioconcentration factors) or BAF (bioaccumulation factors) > 5000). BMF values found to be statistically greater than unity are considered to accumulate from prey to predator. Based upon the triggers established for BCF it would be possible to conclude that BMF values of > 10 may also be of consistent concern (Default BCF and BMF values within the EU Technical Guidance Document (ECB, 2003) imply that where BCF of >5000 occurs, BMF values of *ca* 10 may be expected, although caveats are noted regarding assumed relationships between BCF, BMF and K_{ow}). TMF values found to be statistically greater than unity are considered to accumulate within the food web. For context setting, in assessments of Arctic food chains off of Barrow, Alaska (Hoekstra *et al.*, 2003) provided FWMF (food web magnification factors; equivalent to TMF) as summarised in Table 5.1.

Table 5.1 Illustrative Food Web Magnification Factors (equivalent to Trophic Magnification Factors) for an Arctic food web off of Barrow, Alaska

Contaminant	FWMF (=TMF)
α -HCH	1.58 ($r^2=0.19$)
β -HCH	2.89 ($r^2=0.51$)
γ -HCH	0.65 ($r^2=0.08$)
Σ -HCH	3.22 ($r^2=0.54$)
<i>cis</i> -Chlordane	0.72 ($r^2=0.54$)
<i>trans</i> -chlordane	0.98 ($r^2=0.09$)
<i>p,p'</i> -DDE	5.35 ($r^2=0.48$)
<i>p,p'</i> -DDT	1.53 ($r^2=0.05$)
Σ -DDT	2.95 ($r^2=0.31$)
PCB 153	6.69 ($r^2=0.64$)
Σ -PCB	3.26 ($r^2=0.47$)

Illustrative uptake profiles

In order to provide a broader context for interpretation of the significance of the BAF, BCF and TMF values for endosulfan discussed in this chapter, a summary table is provided (Table 5.2) for a range of compounds exhibiting contrasting uptake profiles.

Table 5.2 Illustrative BAF, BCF and BMF profiles for a range of compounds based upon theoretical calculations reported by Gobas and Morrison (2000) and available data for endosulfan from laboratory and semi-field studies conducted under temperate conditions

Chemical	Log K _{ow}	Log BAF Fish	Log BCF Algae	Log BCF Macrophytes	Log BCF Zooplankton	Log BCF Fish	Log BMF Fish
Lindane	3.70	2.71	1.70	1.70	2.18	2.69	0.09
Anthracene	4.54	3.60	2.53	2.53	3.02	3.49	0.54
Pentachlorobenzene	5.03	4.18	3.01	3.01	3.51	3.89	1.34
PCB 52	6.10	5.41	3.90	3.90	4.58	4.26	3.06
2,3,7,8-TCDD	6.85	6.44	4.23	4.23	5.33	4.44	4.18
PCB 153	6.90	6.49	4.24	4.24	5.38	4.45	4.14
PCB 209	8.25	7.48	4.34	4.34	6.73	4.59	1.35
Endosulfan	4.94 (α^1) 4.78 (β^1)	NA	2.54 – 3.57 ²				NA

1: FAV reported by Shen and Wania (2005)

2: See Tables 1.5.1 and 3.2.1 - BCF values of between 350 and 3700 have been determined in more than a dozen studies with a wide range of species. (Note: BCF = 11,000 in a published study of questionable design)

5.1 Trophic Magnification and Dilution

Notwithstanding the uncertainties in endosulfan analysis, we selected datasets for which there is substantial published background information to examine biomagnification in the Arctic marine and Lake Superior food web as discussed in Section 2.1.2. In addition to data on endosulfan these data sets all had % lipid, $\delta^{15}\text{N}$ and results for lindane and PCB 153 in the same samples facilitating comparison with endosulfan. It is noted that lindane does not biomagnify in aquatic food webs (Moisey *et al.* 2001; Hoekstra *et al.* 2003) while PCB 153 is an example of a recalcitrant chemical with a high degree of biomagnification in Arctic marine food web and freshwater food webs (Fisk *et al.* 2001).

While changes in the concentration of OC pesticides and PCBs through the food web can partially be explained by changes in lipid content, biomagnification of highly recalcitrant organochlorines can also occur (Kidd *et al.*, 1997; Fisk *et al.*, 2001; Hoekstra *et al.*, 2003) i.e. even when the increase in fraction lipid is accounted for (by use of lipid normalized or adjusted data).

It has been shown that ^{15}N is preferentially enriched over lighter isotopes and increases with trophic level in aquatic food webs (Peterson and Fry 1987). Although the use of nitrogen isotopes in assessing trophic structure is a simplification of an inherently complex system, it is a useful technique because it incorporates diet over a longer period of time than stomach contents and they are consistent with documented feeding strategies (Bradstreet and Cross 1982; Fisk *et al.*, 2001; Hoekstra *et al.*, 2003). The trophic levels for various organisms in the food web were determined, based on their $^{15}\text{N}/^{14}\text{N}$ ratios. Then trophic level was assigned based on ^{15}N isotope ratio, using the following equation (Hobson and Welch 1992):

$$\text{TL} = 2 - (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{zooplankton}})/3.8$$

As discussed earlier, Trophic Magnification Factors (TMFs) can be calculated as $TMF = 10^B$ where $B =$ slope of the regression of \log [endosulfan lipid wt] vs TL. In this application we have regressed arithmetic mean concentrations (lipid wt) versus TL rather than use all data as some authors have done previously. This reduces the bias in the linear regression analysis associated with unequal sample sizes at each trophic level.

Southern Beaufort Sea food web

Figure 5.1.1 (A-F) show the trends of α -endosulfan, lindane and PCB 153 throughout the food web in the southern Beaufort Sea off Barrow, Alaska. Further details on this food web are given in Hoekstra *et al.* (2003). We did not include results for α -endosulfan in beluga because of the uncertainty in ECD analysis of in this species discussed in Section 2.1.2. Figure 5.1.1A includes results with bowhead whales, ringed and bearded seals and Figure 5.1.1B with them removed. No significant regression was found between \log -transformed α -endosulfan concentrations and trophic level with all biota included. because there is a decrease in concentration of α -endosulfan from zooplankton to Arctic char, Arctic cod and salmon, along with an apparent increase in concentration from fish to bearded seal and ringed seal. Omitting all mammals gives a significant negative regression of α -endosulfan and TL (Figure 5.1.1B).

There was no significant regression between lindane and trophic level (Figure 5.1.1C,D). In contrast, there is a significant regression between PCB 153 concentration and trophic level, whether or not sculpin and bowhead were present or absent (Figures 5.1.1E, F). This trend has been shown in other studies such as Fisk *et al.* (2003).

The TMF for α -endosulfan is nominally greater >1 with marine mammals included and (Table 5.1.1) and <1 with them omitted. The actual TMF may lie between these values. We believe the α -endosulfan values for seals are overestimated (as discussed in Section 2.1.2), however, it was not possible to reanalyse these specific samples by GC-MS. With marine mammals omitted the slopes of the \log α -endosulfan vs TL relationship was negative while it still remained positive for lindane and PCB153 (Figure 5.1.1 D and F).

Amundsen Gulf food web

Figures 5.1.2 (A-F) shows the concentrations of α -endosulfan in various species in the arctic food web from Holman, NT on the Amundsen Gulf in the western Canadian Arctic. Fewer species were available for comparison, nevertheless they represent part of a likely food web although adult Greenland cod (*Gadus ogac*) may not be consumed by ringed seals. In addition to data from other regions, this database contains α -endosulfan values from samples of marine algae, which is advantageous because it shows the behaviour of endosulfan across all trophic levels, from primary producers to top carnivore. As with the southern Beaufort Sea food web, there is a significant increase in α -endosulfan concentration with trophic level ($r^2 = 0.44$, $p = 0.34$). The calculated TMF is nominally >1 with ringed seals included but has a large error term (Table 5.1). With ringed seals removed there is no trend with TL (Figures 5.1.2B). Lindane and PCB 153 show stronger relationships with TL than α -endosulfan, with or without the inclusion of seals (5.1.2C-F). Omitting ringed seals gives a lower TMF for α -endosulfan but increases for lindane and PCB 153 (Table 5.1.1).

White Sea marine food web

Figure 5.1.3A presents log-transformed α -endosulfan concentrations in various species in the White Sea food web. Further details on the food web are given in Muir *et al.* (2003b). There is an increase in concentration of α -endosulfan from zooplankton to fish, however, unlike the Southern Beaufort Sea and Holman results there appears to be a decrease in concentration from fish to ringed seal. Overall, there was no significant regression between log-transformed α -endosulfan concentration and trophic level with or without the removal of seals (Figure 5.1.3B). A positive relationship for α -endosulfan with TL if seals and sculpin are omitted ($r^2 = 0.53$, $p = 0.17$). Corresponding α -endosulfan TMFs were not significantly different from 1. Food web accumulation of lindane and PCB 153 in the White Sea data has been described by Muir *et al.* (2003b). Using all biota, lindane did not biomagnify (TMF < 1) while PCB153 was significantly accumulated (TMF = 2.9).

Lake Superior pelagic food web

Figure 5.1.4A-C show the trends in α -endosulfan, lindane and PCB 153 in the Lake Superior food web. Further details on this food web are given in Muir *et al.* (2004). Phytoplankton were not included in the analysis in this case because there is some debate as to whether or not the concentrations of organochlorine compounds should be normalized with respect to lipid or organic carbon content, in this organism (Muir *et al.* 2004). As with the marine food webs, there is no significant regression between log-transformed α -endosulfan concentration and trophic level ($R^2 = 0.26$, $p = 0.30$) between invertebrates and fish. There appears to be a decrease in α -endosulfan concentration from all of the prey species to lake trout, which is at the top of the Lake Superior food web, although there is no significant regression. In comparison, the regression of log-transformed PCB 153 concentration vs. trophic level shows a significant regression while lindane does not. TMFs for α -endosulfan and lindane were not significantly different from 1.

Summary

From the information summarised in Table 5.1.1 and in Figures 5.1.1-5.1.4 the following conclusions may be reached:

- ◆ Regressions of PCB 153 concentrations in biota versus trophic level lie in the range $r^2 = 0.28 - 0.98$. A significant relationship can be clearly demonstrated based on data available from monitoring at Holman (NT). A much less significant relationship may exist based upon data available from Barrow (AK).
- ◆ Similar profiles for α -endosulfan, lindane and PCB 153 can be demonstrated based upon analysis of the Holman datasets, but are quite different in the case of Lake Superior and White Sea datasets.
- ◆ Lindane is not recognised as having bioaccumulative and biomagnification profiles that are characteristics of POPs. Therefore, apparent uncharacteristically high TMF values for lindane may frustrate the potential for secure assertions regarding POP status of α -endosulfan based on the Holman dataset.
- ◆ With the exception of the Holman dataset, regressions of α -endosulfan concentrations in biota versus trophic level are clearly not significant.

In summary, the TMF profiles from three of the four sites (Barrow, Lake Superior, and White Sea) suggest that there is no significant relationship between measured concentration and trophic level for either α -endosulfan or lindane. The evidence for the remaining site is ambiguous. There appears to be a significant relationship between measured concentration and trophic level for all three compounds (α -endosulfan, lindane and PCB 153). However, it is well recognised that lindane does not biomagnify in aquatic food webs (Moisey *et al.* 2001; Hoekstra *et al.* 2003). Therefore, there is a high degree of uncertainty surrounding the interpretation and significance of the Holman dataset. Taking this into account it is concluded that α -

endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.

Table 5.1.1. Trophic magnification factors (TMF) for endosulfan, lindane and PCB 153. TMF<1 implies trophic dilution. TMF is reported ± SE of the back-transformed slope of the regression line of mean concentrations vs trophic level

Location/food web ²	TMF	TMF	TMF
	α-endosulfan	lindane	PCB 153
Barrow AK, all biota	1.5±1.5 (r ² = 0.06)	1.2±1.1 (r ² = 0.01)	5.4±5.0 (r ² = 0.57)
Barrow AK, - BH and seals	0.30±0.18 (r ² = 0.60)	2.2±2.4 (r ² = 0.20)	4.5±7.0.1 (r ² = 0.33)
Lake Superior	0.78±0.18 (r ² = 0.26)	1.4±1.1 (r ² = 0.09)	7.8±5.2 (r ² = 0.80)
White Sea, all biota ³	0.72±1.8 (r ² = 0.01)	0.62±0.07 (r ² = 0.20)	2.9±0.59 (r ² = 0.28)
White Sea, - seals	0.43 ±2.8 (r ² = 0.04)	-	-
White Sea, - seals and Sc ²	4.7±4.4 (r ² = 0.53)	-	-
Holman NT, all biota	3.3±5.3 (r ² = 0.44)	7.6±7.5 (r ² = 0.81)	6.0±1.7 (r ² = 0.96)

¹ Calculated with arithmetic mean lipid weight concentrations and average TL for each species/trophic level except for lindane and PCB153 results from the White Sea

² BH: Bowhead whales; Sc: Sculpin;

³ Results for lindane and PCB153 from Muir et al. 2003

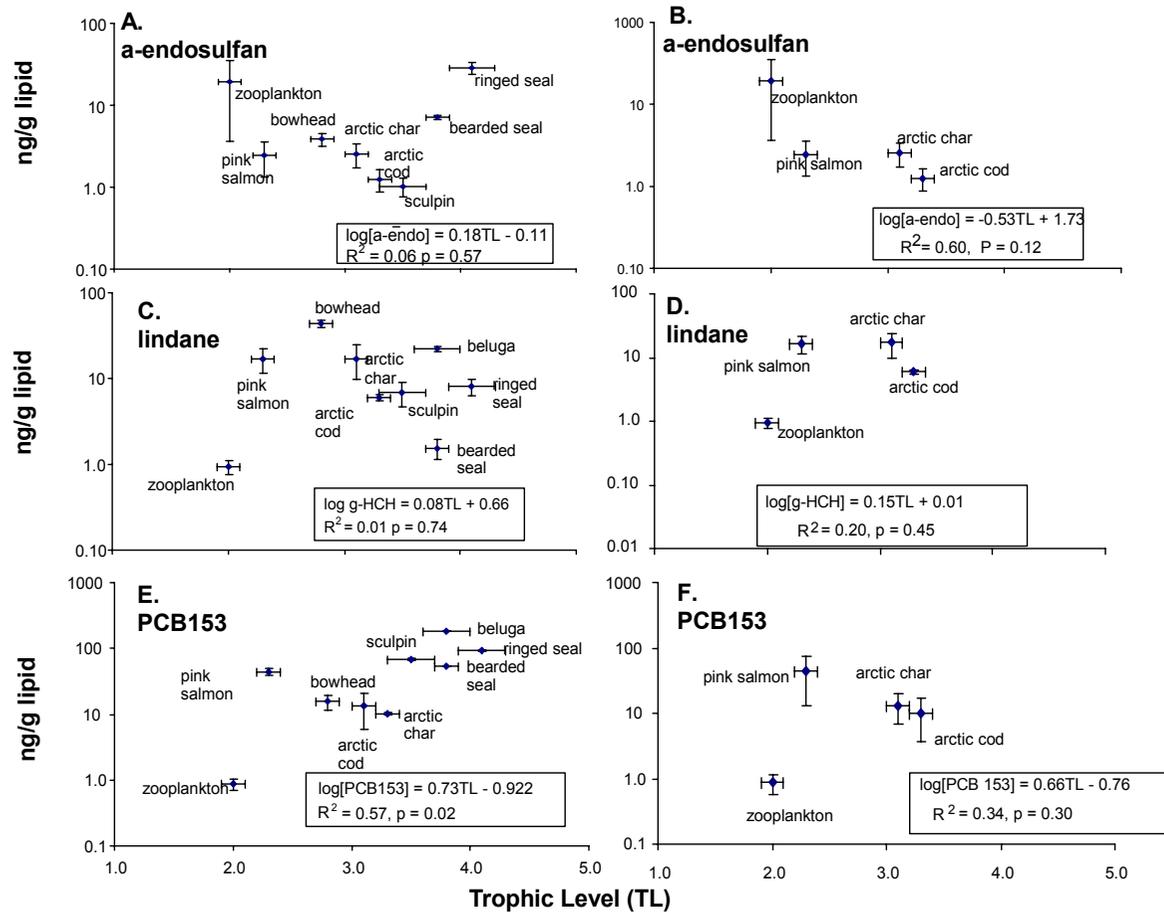


Figure 5.1.1: Relationship of α -endosulfan and trophic level (TL) in the Arctic marine food web at Barrow, Alaska. A. All biota except beluga included for α -endosulfan. B. All marine mammals removed from the analysis. C. Regression between log-transformed lindane concentration and TL, D. lindane concentration vs TL with marine mammals removed. E. Trophic level vs logPCB 153 concentration with all biota shows strong relationship. F. log PCB 153 concentration vs. TL with marine mammals removed still shows positive relationship with TL

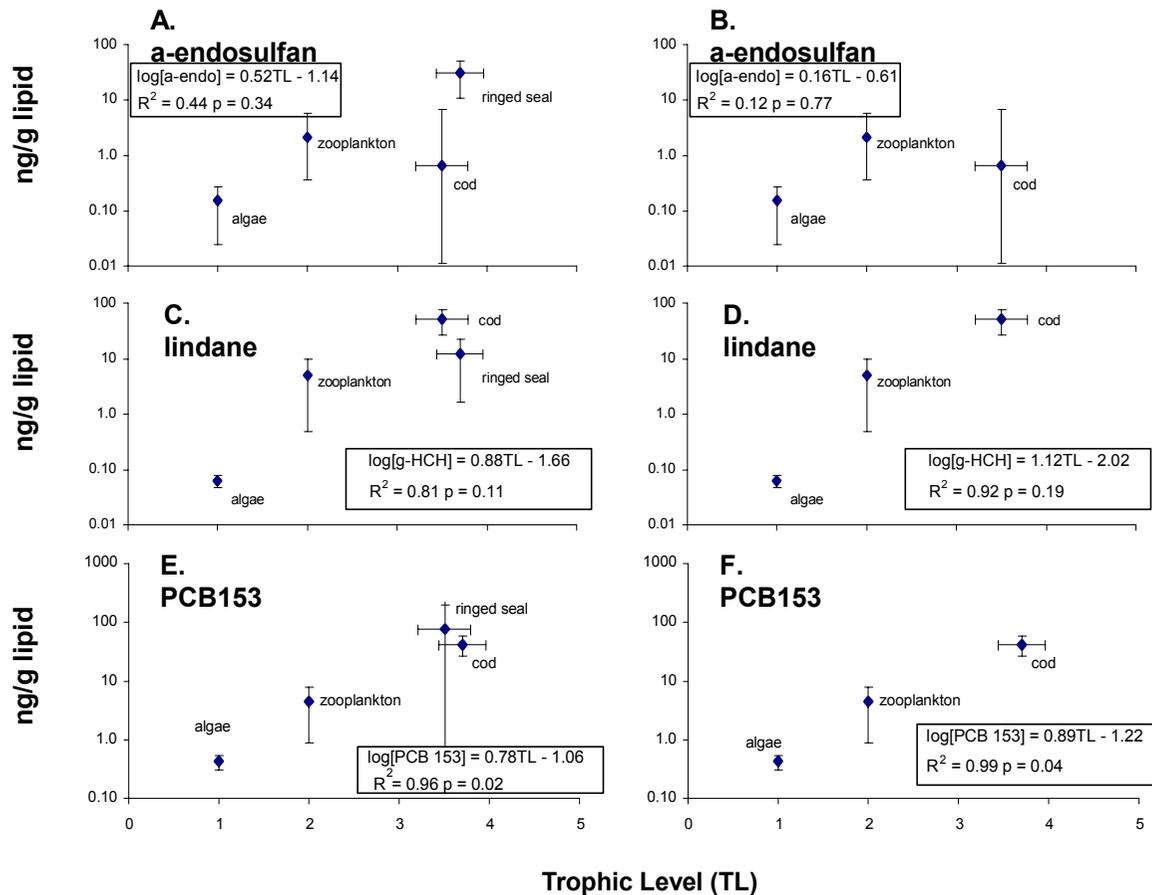


Figure 5.1.2. Arctic Ocean marine food web at Holman NT. A. Log-transformed α -endosulfan concentration. There is an increase in concentration between cod and ringed seal, however, concentrations may be overestimated in seals. B. α -endosulfan versus TL with seals removed. C. Lindane: no significant regression between log-transformed lindane concentration and trophic level. D. Lindane versus TL with seals removed. E. Log-transformed PCB 153 concentration in the Holman food web. There is a significant regression between PCB 153 and trophic level with or without (F) seals.

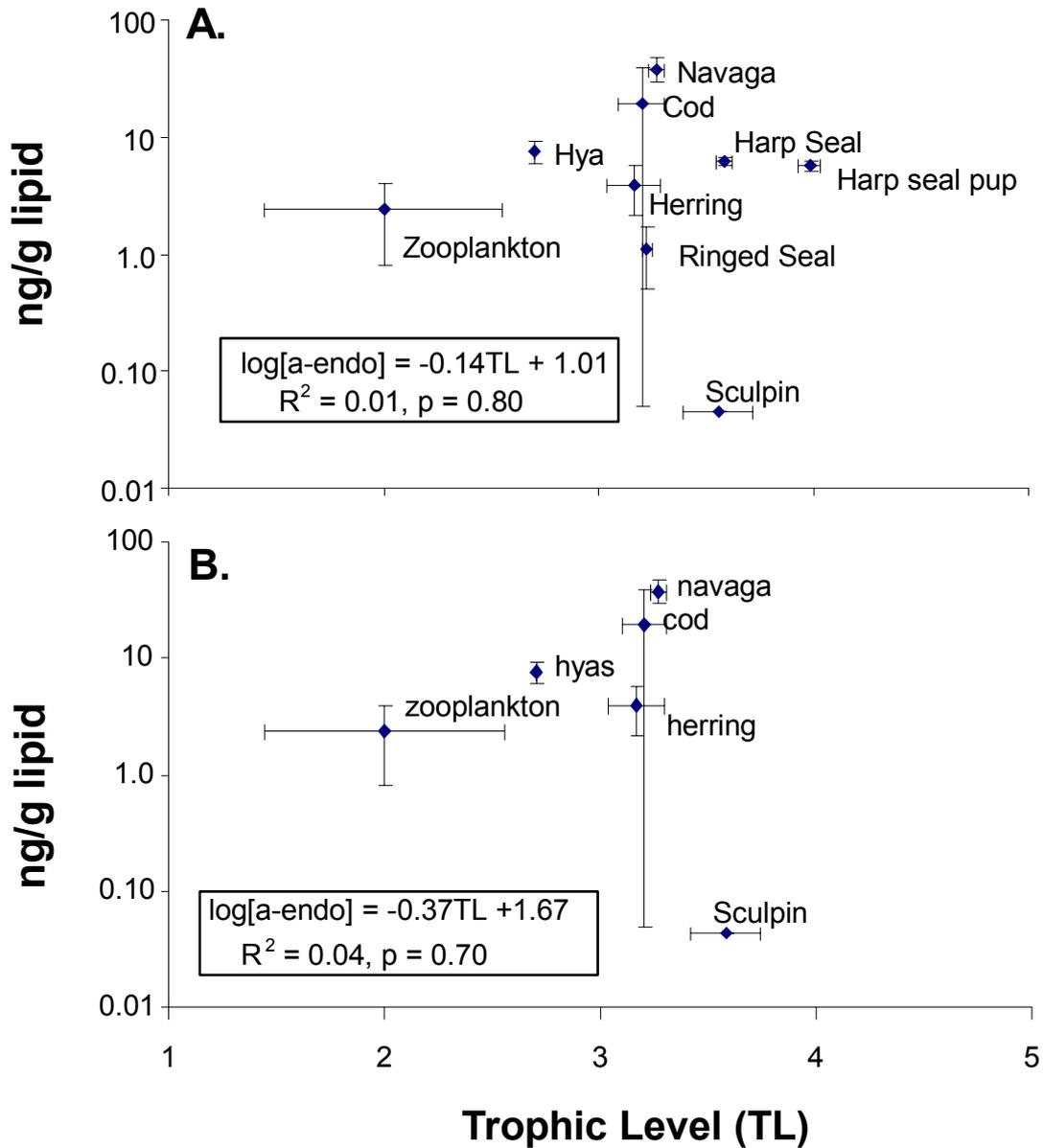


Figure 5.1.3. White Sea marine food web. A. No significant regression between α -endosulfan and trophic level with all biota included. There is an increase in α -endosulfan concentration from zooplankton to cod and navaga (TL 2-3). B. With seals removed there is a greater decline of α -endosulfan concentrations with TL although the relationship is not statistically significant.

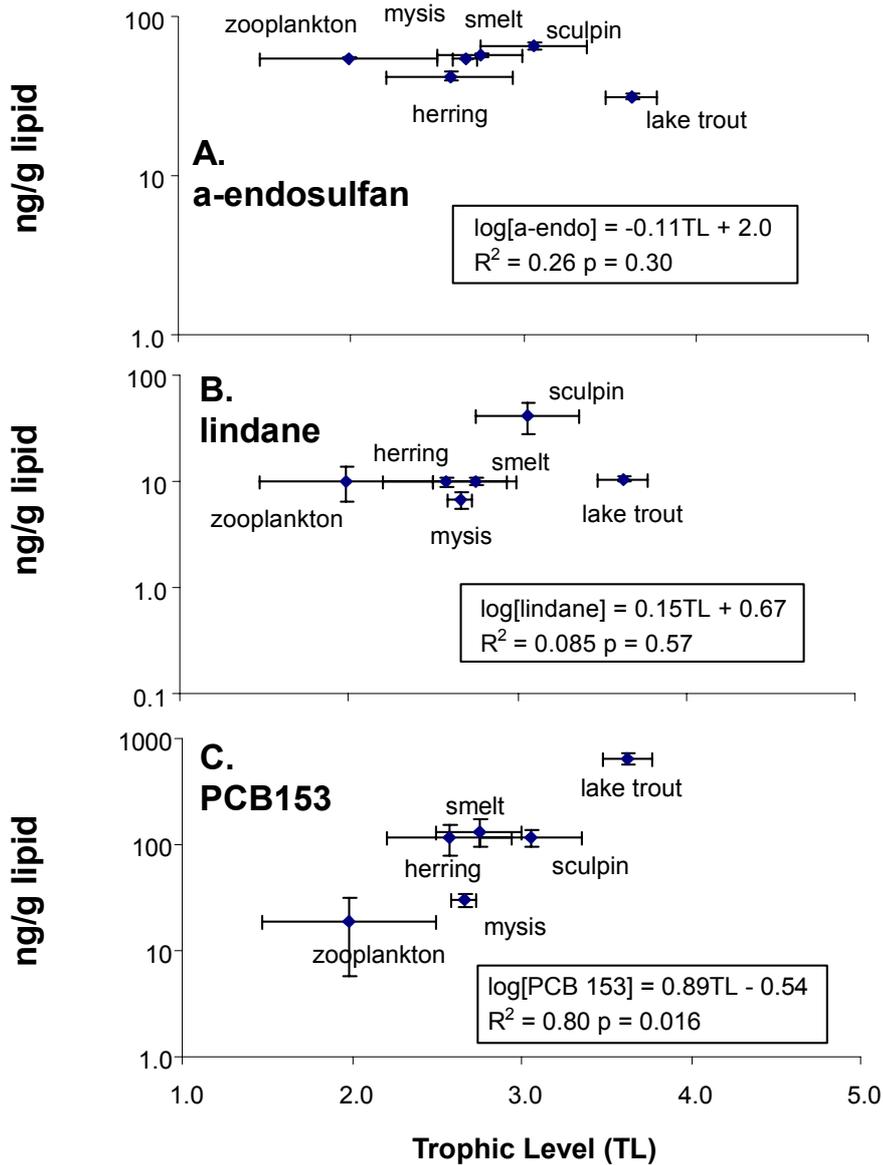


Figure 5.1.4 Lake Superior food web. A. Significant regression between α -endosulfan and trophic level. There is a significant increase in α -endosulfan from zooplankton to fish, however there appears to be a decrease in concentration from lake trout, which are feeding at the top of the food web. B. No significant regression between log-transformed lindane concentration and trophic level. C. Significant regression between PCB 153 and trophic level

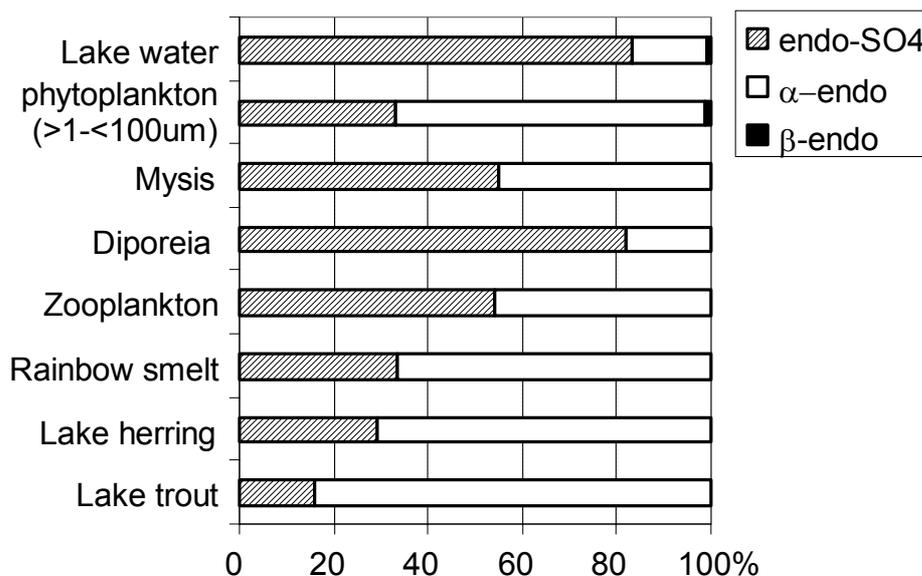


Figure 5.1.5. Proportions of endosulfan sulfate (endo-SO₄) in the Lake Superior food web based on GC-NIMS analysis of a subset of samples in the food web study by Muir et al. (2004)

5.2 Bioaccumulation and Biomagnification Factors

Biomagnification factors

The TMFs for α-endosulfan were generally <1 when the food web was restricted to algae, zooplankton, and various species of fish. This is generally also the case for lindane but not for PCB153. This suggests that averaged over at least 3 trophic levels endosulfan is not biomagnifying in aquatic food webs. The apparent biomagnification when seals are included in the Southern Beaufort Sea and Holman food webs may be due, at least in part, to an interference in the GC-ECD analysis which also biomagnifies. Chlordane and toxaphene components are both possible candidates. Further investigation of the endosulfan concentrations in this food web should be made.

Although endosulfan is not expected to biomagnify because of its relatively short half-life in biota, there were apparent increases in α-endosulfan from prey to predator within each food web particularly from fish to seals. Table 5.2.1 shows BMFs for all of the species previously described. Ringed seal to cod BMF's were available from almost all of the data sets and vary by several orders of magnitude depending on the location of the sampling, although they were greater than 1 for all locations, except the White Sea. BMF's in the Lake Superior food web were less than 1 for all species monitored. The highest BMF was for ringed seal/arctic cod, followed by harp seal/Arctic cod. Overall mean BMFs for α-endosulfan = 10.2±16.4 for fish to marine mammals (Table 5.2.1). Omitting results for large cod to ringed seal (Greenland cod and cod in the White sea (*Gadus morhua*)) because of lack of a clear predator-prey relationship lowers the overall BMF to 7.2. On the other hand, BMFs were <1 for forage fish to predatory fish and from invertebrates to fish. Overestimation of α-endosulfan concentrations due to co-contaminants such as chlordane or toxaphene might lower the fish to marine mammal BMFs but it is difficult to estimate by how much from the limited data available for both predator and prey. For example, the BMF for salmon to seals in East Hudson Bay = 0.73 from Kelly (2005). However,

Kelly (2005) also found salmon-ringed seal BMFs 2.6 for β -endosulfan and 1.8 for endosulfan sulfate.

Table 5.2.1. Biomagnification factors for α -endosulfan in selected species in the arctic food web. Biomagnification factors were calculated as the average (lipid wt) concentration of α -endosulfan in the predator divided by the average concentration in prey¹.

Species	Barrow, AK	Holman, NT	East Hudson Bay	White Sea	Greenland		Lake Superior
					East	West	
Harp seal/ Cod				0.32		9.67	
Harp seal/ Arctic char				1.57		3.31	
Ringed Seal/ Arctic char	11.2				6.5	12.8	
Ringed Seal/ Arctic cod	22.7				2.61	5.14	
Ringed Seal/ Salmon	11.6		0.73				
Ringed Seal/ Greenland cod		64.7		0.056			
Ringed seal/ Herring				0.28			
Herring / Zooplankton				1.65			
Cod/ Zooplankton	0.07	0.24					
Arctic char/ Zooplankton	0.13						
Lake trout/ Herring							0.75
Lake trout/ Smelt							0.56
Lake trout/ Mysis							0.58
Lake trout/ Sculpin							0.48
Overall average BMFs	Mean			SD			
Fish to mammals (N=14)	10.2			16.4			
Fish to predatory fish (N=4)	0.60			0.14			
Invertebrates to fish (N=7)	0.38			0.59			

¹Data sources are listed in Table 2.3.2.1

Bioaccumulation factors

Bioaccumulation factors (BAFs) for α -endosulfan were calculated by using seawater concentrations and are shown in Table 5.2.2 on both a wet weight (BAF_{ww}) and lipid weight (BAF_{lw}) basis. BAFs assume uptake from water and food and should not be confused with bioconcentration factors (BCFs) which are laboratory based measurements where exposure is only from water. Both BAFs and BCFs can be predicted from physical properties and, in the case of BAF, generic food web characteristics. Predicted BAFs using food chain model for chemicals with $\log K_{ow}$'s =4.9 (Table 1.2.1) yield values of $\log BAF_{ww}$ =4.1 (1.26×10^4) by the Gobas model and $\log BCF$ (wet wt) = 3.1 (1.26×10^3) by BCFWIN. The Gobas model is based on Great Lakes food webs and therefore the results from Lake Superior are perhaps the most

appropriate comparison. Including marine mammals in the food web adds a trophic level and potentially a food chain magnification factor as well. Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000 (Log BAF or Log BCF > 3.7; e.g. BAF and BCF values of just over 5000). Therefore, on the basis of these estimates the threshold of concern for bioconcentration is not exceeded, but the threshold of concern for bioaccumulation is exceeded, slightly.

Table 5.2.2. Bioaccumulation factors for selected species in the Arctic food web (wet weight and lipid weight normalized), calculated as the average concentration of α -endosulfan in the organism divided by the average concentration in water.

Water/organism	Barrow, AK	White Sea	Holman	Lake Superior
$[\alpha\text{-endosulfan}]_{\text{water}}$	1.7± 0.76 pg/L	3.1 ±2.0 pg/L	3.0± 0.97 pg/L	2.3 ± 2.7 pg/L
BAF wet wt basis				
Water/zooplankton	6.1x10 ⁵	6.6x10 ⁴	2.0x10 ⁵	6.7x10 ⁵
Water/herring		1.0x10 ⁵		2.7x10 ⁵
Water/cod	3.0x10 ⁴	5.6x10 ⁴	3.4x10 ³	
Water/char	9.7x10 ⁴			
Water/salmon	1.8x10 ⁴			
Water/smelt				1.8x10 ⁵
Water/navaga		2.0x10 ⁵		
BAF lipid wt basis				
Water/zooplankton	2.2x10 ⁶	8.0x10 ⁵	7.5x10 ⁵	2.4x10 ⁷
Water/herring		1.3x10 ⁶		1.9x10 ⁷
Water/cod	7.3x10 ⁵	6.5x10 ⁶	7.2x10 ⁵	
Water/char				
Water/smelt				2.6x10 ⁷
Water/navaga		1.3x10 ⁷		

It is, therefore appropriate to consider measured profiles. Table 5.2.2 shows the BAF_{ww} values for four locations. Greenland was not included because data for α -endosulfan in water samples were not available in this dataset. BAF_{ww}s range from 3.4x10³ to 6.1x10⁵ in the Arctic Ocean food webs and from 1.8 to 6.7 x10⁵ in Lake Superior. Given the uncertainty of endosulfan measurements at low levels in biota and the possible spatial and temporal variation in water concentrations of α -endosulfan these BAFs need to be viewed with caution. As expected, the BAF_{lw}s are higher than the BAF_{ww}s by at least 1 order of magnitude. The largest BAF's were found in the Lake Superior food web. Possible reasons for higher than anticipated

BAFs for PCBs have been discussed by Borgå *et al.* (2005) and some of the factors these authors considered may apply for endosulfan. BAF_{ww} s are high even for water to zooplankton (10^4 - 10^5) and are usually lower for fish because of lack of biomagnification from invertebrates to fish that is apparent in the food web studies. The transfer to zooplankton has been assumed to be mainly via water but recent studies suggest that the microbial food web could be important (Wallberg *et al.* 2001). In this regard it is interesting to note that α -endosulfan was detectable in Lake Superior phytoplankton (a mixed suspended solids phase (>1 to <100 μ m) obtained by continuous centrifugation) at 1.91 ng/g (dry wt) (Table 5.2.3). BAF_{ww} for phytoplankton were about 8.2×10^4 (assuming 10% dry weight basis). It is possible that endosulfan is not degraded rapidly by aquatic microbial communities in oligotrophic lakes and degradation is mainly occurring in higher organisms. Hence the lower BAFs for water-fish than water-zooplankton or water-phytoplankton.

The influence of temperature on bioaccumulation potential also needs to be considered. Temperature could be an important variable that has not been taken into account in comparisons of BCFs from lab studies with field studies. It is suggested that the effect of decreased ambient temperature conditions relative to those characterising standard laboratory tests could decrease metabolism of endosulfan both by invertebrates and fish. In the case of fish Buckman *et al.* (2004) found longer half-lives for PCBs and higher BMFs in rainbow trout. There was also no measurable production of OH-PCBs at 8°C compared the same fish species previously studied at 12°C. Also Blais *et al.* (2004) concluded that growth rate was the major factor explaining higher OC pesticide concentrations, including α -endosulfan, in amphipods along an elevation gradient in mountain lakes in Canada (i.e. higher concentrations could be explained by the lower growth rates of the amphipods in the colder lakes). Unfortunately there do not seem to be any studies of the direct influence of temperature on bioaccumulation of endosulfan or other metabolisable compounds. This is specifically highlighted as an important knowledge gap that limits the ability to interpret BAF values calculated in this assessment.

The BCF and BAF trigger criteria for evaluation of POPs were proposed primarily on the basis of laboratory evidence (e.g. studies conducted at 20-25°C). It should be noted that the impact of temperature differences between ambient Arctic and laboratory conditions will be decreased for highly persistent, non- or slowly-metabolisable substances such as PCBs and increased for compounds that have been demonstrated to be readily metabolised. A number of studies, including a number of those summarised in Section 3.2 have demonstrated that endosulfan is readily metabolised. As a consequence, it is likely that the BAF values calculated for endosulfan based on Arctic monitoring results are significantly influenced by temperature conditions.

BCF values of between 350 and 3700 have been determined in more than a dozen studies with a wide range of species (summarised in Tables 15.1 and 3.2.1). Assuming that laboratory-based BCF criteria are then the primary basis for decision-making, endosulfan does not fulfil the criteria proposed within the Stockholm Convention (2001) and UN-ECE Convention on POPs (e.g. BCF values > 5000).

Endosulfan sulfate

We were unable to find any published endosulfan sulfate in Arctic food web organisms although a small amount of GC-ECD data was available for beluga whales (Stern and Ikonoumou 2003) and in Northern Québec seals and beluga (Kelly (2005). Samples from the Lake Superior study by Muir *et al.* (2004) have been analysed for endosulfan sulfate by GC-NIMS using parent ions (M^+ , m/z 422, 424) and $M-HCl^-$ (m/z 386, 388). M/z 386 was used for quantification with confirmation

using m/z 388. GC-MS conditions were otherwise identical to those used for toxaphene analysis in the same samples (Muir *et al.* 2004). Results are presented in Table 5.2.3.

Table 5.2.3. Concentrations of endosulfan sulfate and α -endosulfan in Lake Superior waters (ng/L) and food web samples (ng/g ww).

		Endosulfan sulfate	α -Endosulfan
Sample	N	ng/g ww	ng/g ww
Lake trout	10	0.23±0.13	1.68±1.62
Lake herring	2	0.18	0.68
Rainbow smelt	2	0.17	0.40
Zooplankton	3	0.21±0.03	0.18±0.02
Diporeia	3	0.55±0.24	0.11±0.09
Mysis	2	0.04	0.08
Surface waters	4	0.056±0.001	0.012±0.014
phytoplankton (>1-<100um) ¹	3	0.88±0.30	1.91±1.01

¹ Dry weight concentration

Endosulfan sulfate was detected mainly in water and invertebrate samples and was present at lower proportions in forage fish and lake trout (Table 5.2.3). From this figure it is clear that endosulfan sulfate does not biomagnify and if concentrations in water are compared to those in fish, it has low bioaccumulation factors compared to α -endosulfan. Phytoplankton and the amphipod, *Diporeia* (*Diporeia hoyi*), had the highest concentrations of endosulfan sulfate of all organisms analysed (Table 5.2.3).

Endosulfan sulfate has also been reported in beluga whale blubber samples from the Canadian Arctic (Muir, unpublished data 1998; Stern and Ikonomou (2003)). The AMAP POPs assessment (p. 156; (de Wit *et al.* 2004) reports temporal trends of endosulfan sulfate attributed to Stern and Addison (1999) although it is actually from Stern and Ikonomou (2003).

The analysis of endosulfan sulfate in beluga blubber was conducted by high resolution GC-ECD using 60m x 0.25 mm i.d. capillary GC with H₂ carrier gas and quantification of endosulfan-sulfate using external standard calibration. Unfortunately, to our knowledge, none of the results for endosulfan-sulfate data in beluga blubber have been confirmed by GC-MS and thus there is the potential for false positives as noted previously for α - and β -endosulfan.

Kelly (2005) found that α -endosulfan was generally non-detectable in beluga blubber, (Table 5.2.4). α -endosulfan was also not detected in beluga blubber samples from Western Greenland analysed as part of the Greenland human diet study discussed below (Johansen *et al.* 2004).

However, Kelly (2005) detected β -endosulfan in most beluga blubber samples and also endosulfan sulfate, although less frequently. Geometric mean concentrations of endosulfan sulfate ranged from 0.31-0.86 ng/g lipid wt in beluga and from 0.19-0.32 in ringed seal blubber.

Table 5.2.4. Concentrations of α - and β -endosulfan and endosulfan-sulfate (ng/g lipid wt) reported for beluga and ringed seals by Kelly (2005) using high resolution mass spectrometry.

Species	Sex	Tissue	n	age	% lipid	α -endosulfan		β -endosulfan		endosulfan sulfate	
						GM	(95% CL)	GM	(95% CL)	GM	(95% CL)
Beluga	Male	blubber	21	16-35	89 \pm 0.53	-		12.6	4.5-35	0.86	0.21-3.5
Beluga	Female	blubber	14	5-35	90 \pm 0.17	-		4.87	1.2-19	0.58	0.11-3.0
Beluga	Female	(Milk)	8		37 \pm 8.6	-		2.75	0.65-12	0.31	0.13-0.74
Beluga	Calves	blubber	9	~1	90 \pm 1.8	-		4.13	1.9-9.0	0.35	0.035-3.6
Beluga	Male	blood	7		0.59 \pm 0.08	-		371	77-1,800	-	-
Beluga	Male	liver	16		2.1 \pm 0.44	0.59	0.24-1.3	384	21-6,880	-	-
Beluga	Female	blood	7		0.56 \pm 0.10	-	-	122	41-356	-	-
Beluga	Female	liver	3		1.7 \pm 0.55	-		-		-	
Ringed seals	Female	blubber	7		71 \pm 2.8			3.02	0.27-34	0.19	
Ringed seals	Male	blubber	7		73 \pm 4.6	0.3	0.10-0.87	2.26	0.62-8.2	0.32	0.10-1.01

Summary

There are no biomagnification factor triggers within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs. BMF values found to be statistically greater than unity are considered to accumulate from prey to predator. Based upon the triggers established for BCF it would be possible to conclude that BMF values of > 10 would be of consistent concern. Calculated biomagnification factors based on residue measurements for a range of Arctic species ranged from 0.056 (Greenland cod \rightarrow ringed seal; Barrow, AK) to 64.7 (Both Greenland cod \rightarrow ringed seal; White Sea and Holman, respectively). The high degree of variability within similar food chain links is particularly noteworthy. Further analysis revealed that average invertebrate to fish and fish to predatory fish BMF values were very low (0.38 ± 0.59 and 0.60 ± 0.14 , respectively). The average fish to mammal BMF value was 10.2, lying at a possible threshold of concern. However, this estimate needs to be interpreted recognising a very high degree of variability (± 16.4) and therefore, uncertainty. In summary, there is no clear evidence of biomagnification for invertebrates to fish and fish to predatory fish. There is a high degree of uncertainty surrounding fish to marine mammal food chain links – on this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern.

Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor or bioaccumulation factor in aquatic species is greater than 5000 (Log BAF or Log BCF > 3.7; e.g. BAF or BCF values of just over 5.0×10^3). Measured bioaccumulation factors for a range of Arctic species ranged from 3.4×10^3 (BAF_{ww} cod; Holman) to 2.6×10^7 (BAF_{lw}; smelt; Lake Superior). As discussed earlier, the transfer to zooplankton has been assumed to be mainly *via* water but recent studies suggest that the microbial food web could be important (Wallberg *et al.* 2001). In this regard it is interesting to note that α -endosulfan was detectable in Lake Superior phytoplankton. The range decreases slightly if the Lake Superior dataset is set aside in order to potentially eliminate other influences potentially present in this oligotrophic system. The maximum bioaccumulation factor is then slightly lower; 1.3×10^7 (BAF_{lw}; navaga; White Sea). Interpretation of the bioaccumulation potential for the navaga in the White Sea may be frustrated somewhat because of its life cycle (shoals even enter lakes and river estuaries – particularly during the autumn reproduction season) and (as noted in Section 4.2) the contribution of riverine pesticide loads may be significant (the Onega and Dvina rivers drain into the eastern part of the White Sea). Nonetheless, even if this evidence were set aside bioaccumulation factors approaching 1 million (BAF_{lw}) can be readily demonstrated for zooplankton and fish for other locations (e.g. Barrow and Holman). The implications of such high BAF values are unclear, particularly when considered alongside the ambiguous trophic magnification and biomagnification profiles discussed earlier. The potential for other uptake/retention mechanisms such as highlighted by Wallberg *et al.* (2001) remains a possibility, but there is no direct evidence. The influence of temperature on bioaccumulation potential also needs to be considered. It is suggested that the effect of decreased ambient temperature conditions relative to those characterising standard laboratory tests could decrease metabolism of endosulfan both by invertebrates and fish.

5.3 Endosulfan Residue Trends in Biotic Compartments

Geographical trends: Ringed seals

Figure 5.3.1 shows geometric mean concentrations for α -endosulfan in ringed seal blubber across the Arctic. These results are from GC-ECD analysis of blubber samples and are part of much larger datasets of PCBs and OC pesticides as discussed in Section 2.1.2. The results for the Canadian Arctic, except for Holman NT, are for female seals only because they are part of temporal trend studies which use females because of the lack of correlation with age which facilitates time trend comparisons (Muir *et al.* 2003a). Inclusion of males could influence the results because results for males only were available from Barrow AK while at Holman results for both males and females were available. Concentrations of α -endosulfan averaged 29 ng/g in males and 19 ng/g in females at Holman (Hoekstra *et al.* unpublished data, 2002). The highest concentrations of α -endosulfan were found in the western Canadian Arctic and at Barrow AK. Concentrations in the eastern Canadian Arctic, Greenland and Russian Arctic are much lower although in general α -endosulfan was detectable at sub-ng/g in all blubber samples (Table 5.3.1). This pattern of higher concentrations in the Beaufort Sea area has also been observed for α -HCH in ringed seals (Muir *et al.* 2000a) and polar bears (Norstrom *et al.* 1998) and coincides with elevated α -HCH in the Beaufort Sea and Canada basin (Li *et al.* 2002). However, there appears to be no relationship to endosulfan concentrations in seawater (see Section 4.2). It should be kept in mind that analysis of ringed seal samples employed GC-ECD rather than GC-MS techniques. As a consequence α -

endosulfan is likely to be overestimated but whether this is an issues of specific or greater significance to selected sites/samples could not be determined.

Table 5.3.1. Mean concentrations (ng/g lipid weight) of α -endosulfan in ringed seal blubber

Region/sea	Community	Sex	N	Geometric mean (ng/g lipid weight)	Lower 95% CI	Upper 95% CI	Data source
Beaufort/Chukchi Sea	Barrow	M	14	22.6	11.77	43.39	Hoekstra <i>et al.</i> Unpublished
Eastern Beaufort Sea	Sachs Harbour	M&F	10	1.44	0.75	2.78	Muir <i>et al.</i> unpublished
Amundsen Gulf	Holman	F	5	18.9	8.92	42.41	Hoekstra <i>et al.</i> Unpublished
Queen Maud Gulf	Gjoa Haven	F	10	0.88	0.25	3.08	"
Lancaster Sound	Resolute	F	6	0.21	0.09	0.47	"
Western Hudson Bay	Arviat	F	11	1.48	0.79	2.77	"
Lancaster Sound	ArcticBay	F	6	0.70	0.31	1.58	"
Jones Sound	GriseFiord	F	6	0.23	0.10	0.51	"
Eastern Hudson Bay	Inukjuak	F	7	0.49	0.23	1.06	"
Hudson Strait	Quartaq/Salluit	F	9	0.62	0.31	1.23	"
Ungava Bay	Kangiarsualujaq	F	8	0.38	0.18	0.78	"
Cumberland Sound	Pangnirtung	F	9	0.82	0.41	1.64	"
Labrador Sea	Nain	F	5	0.62	0.26	1.48	"
West Baffin Bay	W. Greenland	M&F	10	0.36	0.02	0.07	Johansen <i>et al.</i> 2004
Scoresbysund	E. Greenland	M&F	19	0.18	0.02	0.04	Johansen <i>et al.</i> 2004
Northwestern Russia White Sea	Divina Bay	Juv	17	1.09	0.004	1.05	Muir <i>et al.</i> 2003b
Northwestern Russia White Sea	Onega Bay	M&F	24	0.03	0.03	0.03	Muir <i>et al.</i> 2003b
Northwestern Russia	Barents Sea, Vaygach Island	M&F	8	0.12	0.09	0.17	Savinova <i>et al.</i> 2004
Northern Russia	Kara Sea, Dikson Island	M&F	6	0.56	0.20	1.60	Savinova <i>et al.</i> 2004

Geographical trends: Minke whales

Hobbs *et al.* (2003a) determined α -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. As with other studies on α -endosulfan in marine mammals, the analyses were conducted by GC-ECD and not confirmed by GC-MS. Results were compared using ANCOVA. Geometric mean concentrations \pm 95% confidence limits are plotted in Figure 5.3.2 (redrawn from Hobbs *et al.* using the original data). α -Endosulfan was significantly higher in whales from the North

Sea than those from all other locations and minkes from the Barents Sea had higher α -endosulfan than those from Jan Mayen and west Greenland (Figure 5.3.2). This pattern is plausible since the North Sea and waters near Norway would be expected to have higher endosulfan based on atmospheric deposition and riverine inputs.

Greenland diet study

Tables 5.3.3 to 5.3.5 show geometric mean α -endosulfan in various tissues, liver and muscle tissue respectively, in various species analysed for the Greenland diet study (Johansen *et al.* 2004 a).

This is the most extensive Arctic dataset for α -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).

In Figure 5.3.3, mean concentrations are arranged by increasing concentration in fat, kidney, liver and muscle. Highest concentrations of α -endosulfan were found in narwhal skin and blubber and other fats (Table 5.3.3). Harp seal blubber also had detectable amounts as did ringed seal (shown in Table 5.3.1). The non-detect concentrations in beluga blubber are in general agreement with other analyses of beluga blubber (Table 5.2.4). Much lower (wet weight) concentrations were found in livers (fish, mammals and birds) and lower still in muscle samples (Figure 5.3.3).

Although unconfirmed by GC-MS the results for α -endosulfan in the Greenland samples 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, Atlantic cod. Endosulfan was also detectable in seabird livers and muscle e.g. thick-billed murre. There are only limited data for α -endosulfan in Arctic seabirds. Kelly (2005) detected α -endosulfan in liver of eider ducks from Eastern Hudson Bay (*Somateria mollissima*) and endosulfan sulfate in white winged scoters (*Melanitta fusca*).

Temporal trends studies

Stern and Ikonomou (2003) reported increasing concentrations of endosulfan sulfate in male beluga whales from Cumberland Sound (Pangnirtung, Southeast Baffin Is.) as part of results from a larger study of time trends of OC pesticides and PCBs. Male beluga were used because they generally show little correlation of major OCPs and PCBs with age (Stern *et al.* 1994). The authors reported that they age-adjusted the data using ANCOVA although it is unlikely that endosulfan sulfate were related to age. Correlation analysis of endosulfan sulfate results for beluga listed in Table 5.2.4 showed no significant correlations. Whether age adjustment would have altered the results i.e. if there were large differences in age between sampling years cannot be determined. It is not clear whether the age adjustment is justified in the case of endosulfan sulfate as has been demonstrated for other compounds. Endosulfan sulfate concentrations were found to have increased significantly during the 1990s (means for 1992 > 1986 or 1982) (Figure 5.3.4). Concentrations in 2002 did not differ from those in 1996.

The concentrations of endosulfan sulfate in the Southeast Baffin Island population reported by Stern and Ikonomou (2003) were approximately 10-fold higher than reported by Kelly (2005) for East Hudson Bay beluga using GC-HRMS. In another recent report, Stern *et al.* (2005a) have reported geometric mean concentrations of endosulfan-sulfate in beluga blubber ranging from 7 to 70 ng/g (lipid wt) from 11 locations in the Canadian arctic. The 10-20 fold differences between the GC-MS and

GC-ECD results that have been identified for endosulfan-sulfate in beluga need to be investigated further. In addition, the use of archived samples such as these brings with it uncertainties surrounding storage stability. The stability of endosulfan sulfate in matrices such as these over almost 20 years has, to the knowledge of the author, not been assessed.

Stern *et al.* (2005b) reported the detection of α -endosulfan in a laminated core from Devon Island in the Canadian arctic. This core was shown to preserve an accurate record of PCB and toxaphene deposition and thus could be useful for assessing endosulfan time trends as well. The endosulfan analysis was by GC-ECD. The endosulfan concentrations were highest at the sediment surface, and rapidly decreased to below detection limits in core slices dated prior to 1988 (at about 2 cm depth). The authors concluded that the rapid decline in endosulfan with sediment age was due to abiotic and/or biotic degradation. They also noted that α -endosulfan was the only endosulfan species detected in Arctic air.

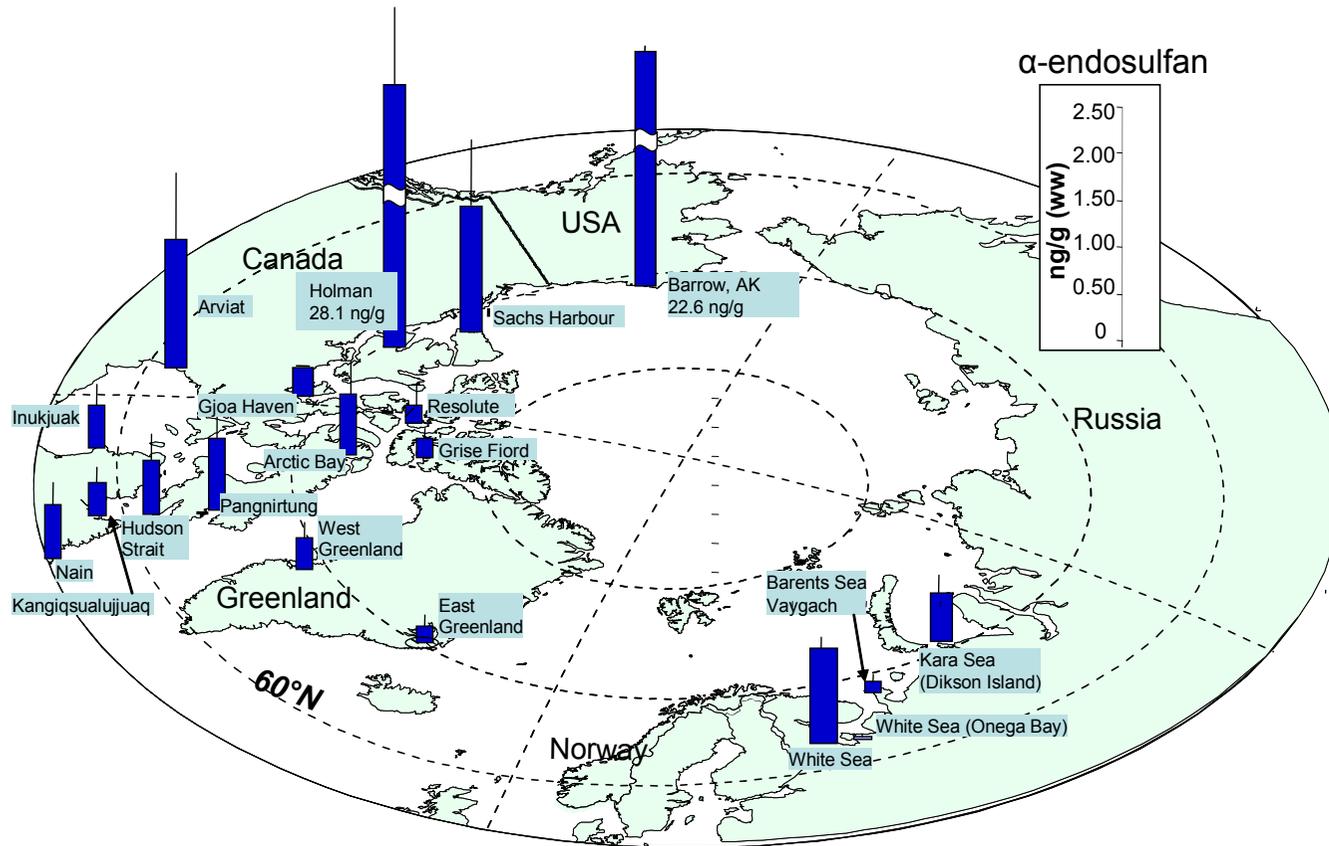


Figure 5.3.1. Geometric mean concentrations of α -endosulfan in ringed seal blubber (combined males and females) across the Arctic

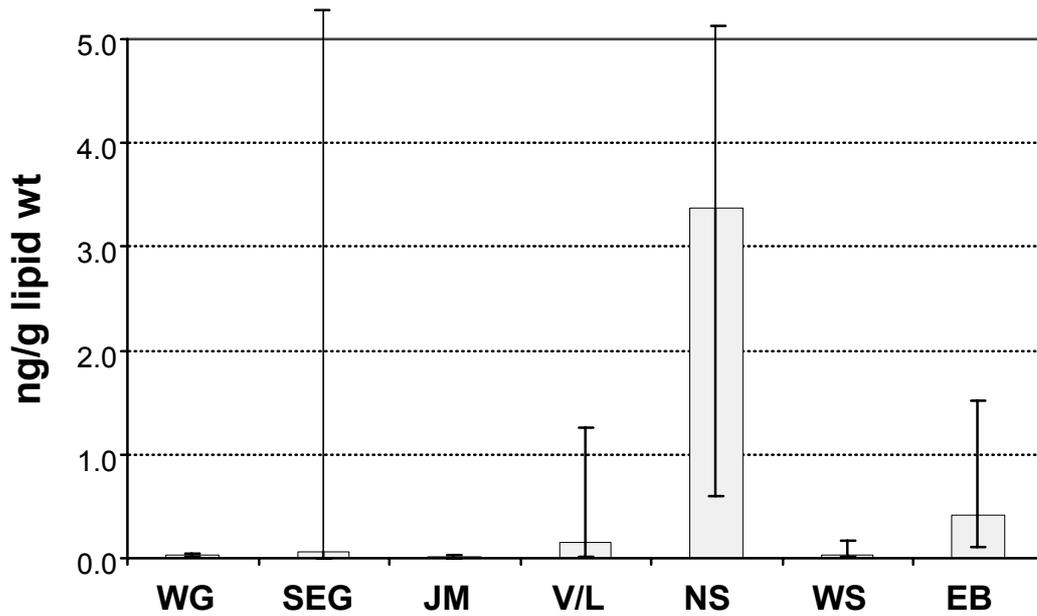


Figure 5.3.2. α -Endosulfan concentrations in minke whale blubber (ng/g lipid wt, combined males and females) from defined whaling areas in the North Atlantic Ocean. Vertical bars refer as follows: WG=west Greenland, SEG = Southeast Greenland, JM=Jan Mayan, V/L = Vestfjorden/Lofoten, NS = North Sea, WS = West Svalbard (Barents Sea), EB = East Barents Sea

Table 5.3.3. Geometric mean concentrations of α -endosulfan and β -endosulfan in kidney, muscle and various tissues (ng/g wet weight) analysed in the Greenland diet study (Johansen *et al.* 2004 a)

Various Tissue	Sample Number (n)	α -endosulfan (\pm 95% CI)	β -endosulfan (\pm 95%CI)
Hare kidney	5	0.016 \pm 0.018	0.042 \pm 0.0037
Lamb fat	5	0.0087	0.040
Lamb kidney	5	0.0087	0.040
Muskox fat	4	0.013 \pm 0.0077	0.040
Muskox kidney	5	0.0087	0.0400
Beluga blubber	10	0.0087	0.04 \pm 0.000
Beluga meat	14	0.25 \pm 0.18	0.32 \pm 0.12
Beluga skin	5	0.88 \pm 0.49	0.24 \pm 0.54
Narwhal blubber	6	5.78 \pm 11.1	0.68 \pm 14.55
Narwhal meat	7	0.12 \pm 0.14	0.04
Narwhal skin	5	1.43 \pm 0.92	0.56 \pm 0.97
Caribou fat	5	0.01 \pm 0.0094	0.04

Table 5.3.4: Geometric mean concentrations in liver tissue of various terrestrial and aquatic Arctic species (ng/g wet weight) analysed in the Greenland diet study (Johansen *et al.* 2004 a)

Liver Tissue	Sample Number (n)	α -endosulfan ng/g (ww) (\pm 95% CI)	β -endosulfan ng/g (ww) (\pm 95%CI)
Common eider	5	0.090 \pm 0.015	0.162 \pm 0.08
King eider	5	0.109 \pm 0.012	0.095 \pm 0.06
Thick-billed murre	5	0.053 \pm 0.024	0.468 \pm 0.15
Ptarmigan	5	0.0553 \pm 0.037	0.0522 \pm 0.02
Hare	5	0.021 \pm 0.0048	0.040
Kittiwake	5	0.039 \pm 0.037	0.401 \pm 0.69
Lamb	5	0.013 \pm 0.018	0.040
muskox	5	0.0087	0.040
Greenland cod	5	0.103 \pm 0.15	2.208 \pm 0.52
Arctic char	5	0.181 \pm 0.048	0.853 \pm 0.23
Minke whale	5	0.01	0.50 \pm 0.28
wolffish	5	0.01	3.14 \pm 1.75
Atlantic cod	5	0.18 \pm 0.21	4.29 \pm 3.21
Atlantic salmon	5	0.07 \pm 0.056	0.76 \pm 0.13
Greenland halibut	5	1.66 \pm 2.2	22.17 \pm 45
Snow crab	5	0.03 \pm 0.016	0.10 \pm 0.06

Table 5.3.5. Geometric mean concentrations of endosulfan in muscle tissue of various Arctic species (ng/g wet weight) analysed in the Greenland diet study (Johansen *et al.* 2004a)

Muscle Tissue	Sample Number (n)	α-endosulfan (±95% CI)	β-endosulfan (±95% CI)
Common eider	10	0.038±0.0088	0.084±0.02
King eider	10	0.027±0.0178	0.107±0.07
Thick-billed murre	19	0.027±0.0142	0.127±0.05
Ptarmigan	5	0.022±0.0129	0.040
Hare	5	0.012±0.0064	0.040
Kittiwake	9	0.327±0.0560	7.885±1.86
Lamb	5	0.009	0.040
Muskox	5	0.011±0.0065	0.040
Greenland cod	5	0.009±0.0015	0.041±0.00
Arctic char	5	0.028±0.0164	0.143±0.10
Atlantic cod	9	0.07±1.1152	0.05±0.01
Redfish	5	0.03±0.0423	0.36±0.36
Atlantic Salmon	9	0.14±0.0477	0.97±0.26
Greenland halibut	10	0.30±0.3410	2.97±3.54
Capelin	10	0.08±0.0288	0.81±0.13
Deep sea shrimp	11	0.01	0.04±0.00
Snow crab	5	0.03±0.0156	0.10±0.06
Minke whale	10	0.01	0.15±0.13
Wolffish	5	0.01	0.24±0.23
Scallop	8	0.01	0.04±0.00

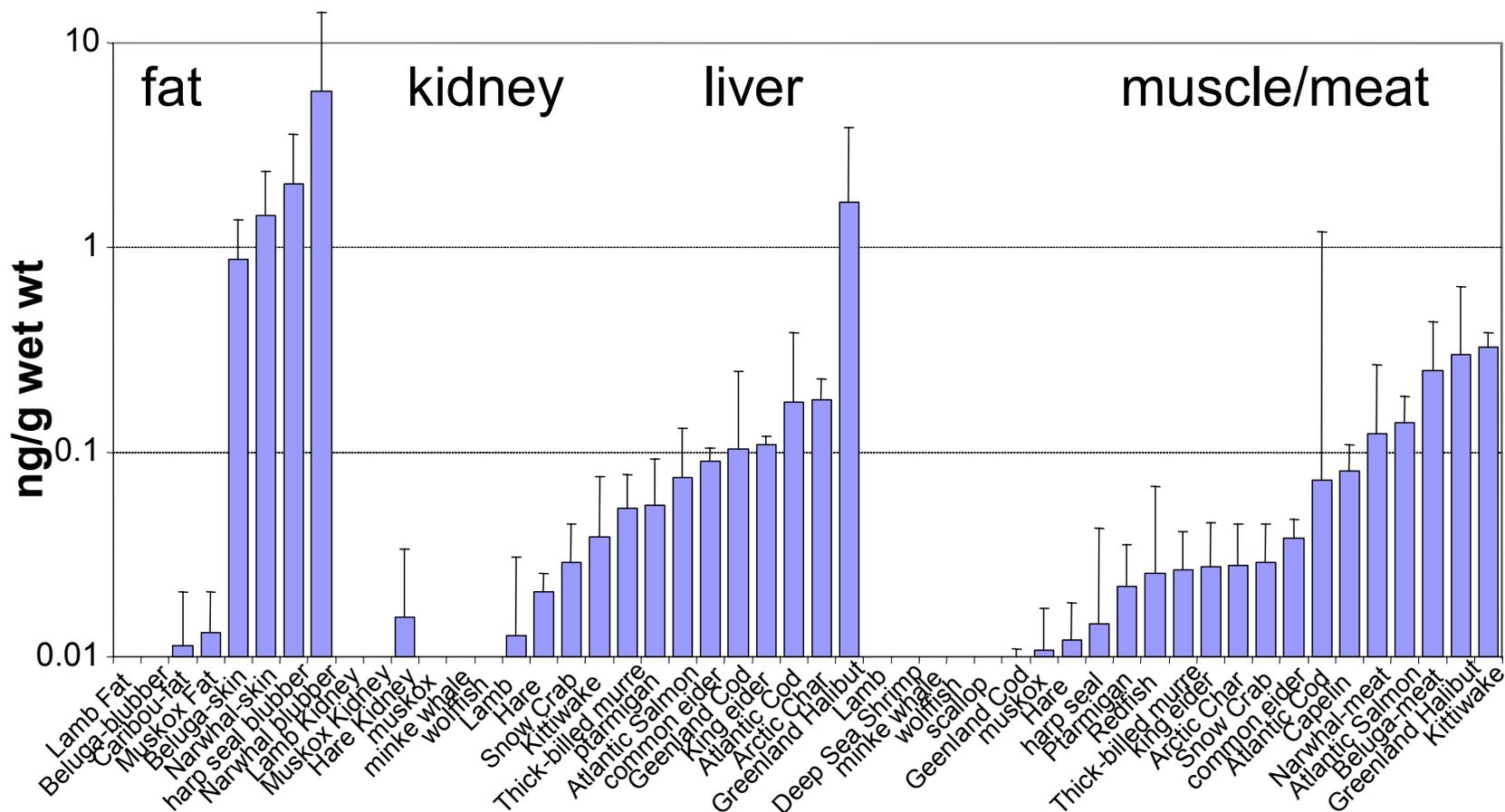


Figure 5.3.3. α -Endosulfan concentrations in tissues of important human diet species from Greenland (ng/g wet wt; geometric means \pm 95% confidence intervals). A log scale is used to visualize samples with very low concentrations. Nondetect concentrations were replaced by $\frac{1}{2}$ detection limit for calculation of means.

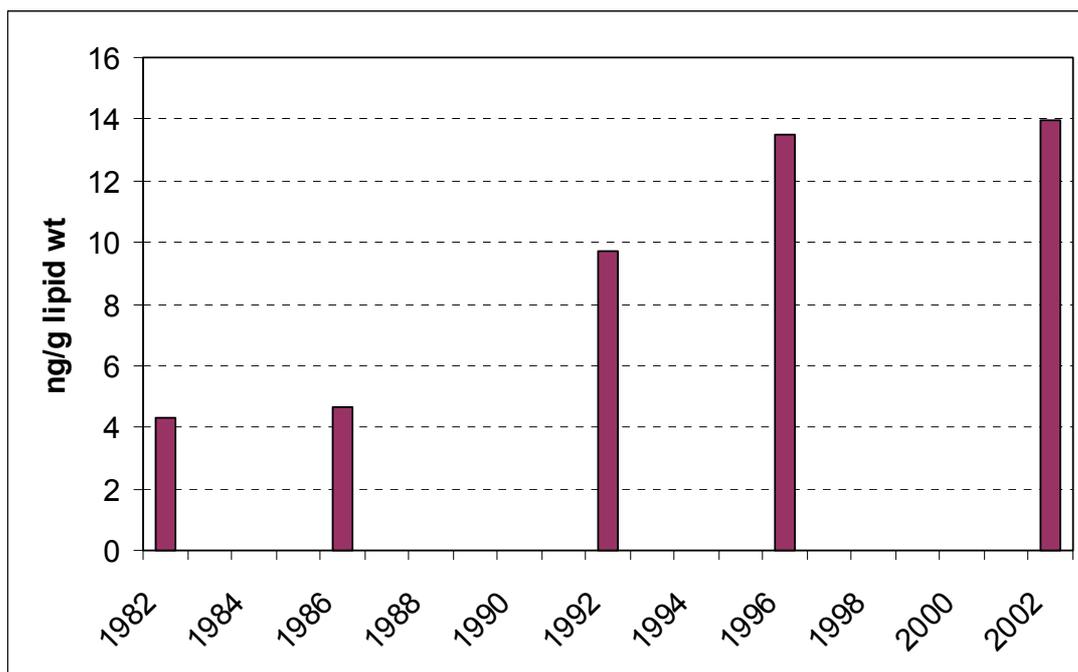


Figure 5.3.4 Temporal trends of endosulfan sulfate in south-east Baffin Island beluga whale reported by Stern and Ikonou (2003). Results are age-adjusted, lipid weight concentrations

5.4 Data Gaps and Uncertainties

Scope

The database for analysis of α -endosulfan in biota is far more significant than that available for either β -endosulfan or endosulfan sulfate. Notably, however, β -endosulfan has been included in the Greenland diet study (Johansen et al., 2004a) and endosulfan sulfate has been considered in analyses of seals and beluga conducted by Stern and Ikonou (2003) and Kelly (2005). There remain significant uncertainties surrounding analytical differences between these studies.

Analysis

A major shortcoming of the data for endosulfan in arctic biota is the lack of confirmation of results by GC-MS. While GC-MS is also subject to problems due to interfering ions (Section 2.1.2) it is nevertheless much more specific than GC-ECD. The problem is particularly acute for marine mammals where there is clearly interference with α -endosulfan from chlordane and/or toxaphene components for the ECD data based on the lower results obtained by both low resolution GC-NIMS and GC-HRMS. The high values obtained by GC-HRMS for β -endosulfan are difficult to reconcile with other results e.g. by GC-NIMS, from the sample collection and deserve further investigation as well.

Overall the uncertainty in α -, β -endosulfan and –sulfate is of the order of 10x in the case of marine mammals, which does significantly affect our conclusions in terms of magnitude of TMFs, BMFs and BAFs. There are also uncertainties in endosulfan concentrations in fish and invertebrates but based on limited GC-NIMS confirmation (Table 2.3.2.3) these are <2-fold and thus will not greatly impact the observed BAFs

or invertebrate to fish BMFs or TMFs based on the invertebrate-forage fish-predatory fish food web.

Spatial trends

Spatial variation in residues of α -endosulfan was considered for ringed seal blubber and minke whales. Further, region-specific data was available in the form of the Greenland diet study (Johansen *et al.*, 2004a). In ringed seals, the highest concentrations of α -endosulfan were found in the western Canadian Arctic and at Barrow AK. Concentrations in the eastern Canadian Arctic, Greenland and Russian Arctic are much lower although in general α -endosulfan was detectable at sub-ng/g in all blubber samples. This pattern of higher concentrations in the Beaufort Sea area has also been observed for α -HCH in ringed seals (Muir *et al.* 2000a) and polar bears (Norstrom *et al.* 1998) and coincides with elevated α -HCH in the Beaufort Sea and Canada basin (Li *et al.* 2002). However, there appears to be no relationship to endosulfan concentrations in seawater. Residues of α -endosulfan were significantly higher in whales from the North Sea (potentially reflecting a 'near source' influence) than those from all other locations. Minke whales from the Barents Sea had higher α -endosulfan 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 based on atmospheric deposition and riverine inputs. It was not possible to derive any further spatial trends.

Temporal trends

Detailed analysis of temporal trends was not possible due to the absence on long-term, site-specific monitoring campaigns of biota. One exception is the assessment conducted by Stern and Ikonou (2003) who reported increasing concentrations of endosulfan sulfate in male beluga whales from Cumberland Sound (Pangnirtung, Southeast Baffin Is.) as part of results from a larger study of time trends of OC pesticides and PCBs. Endosulfan sulfate concentrations were found to have increased significantly during the 1990s (means for 1992 > 1986 or 1982) (Figure 5.3.4). Concentrations in 2002 did not differ from those in 1996. However, 10-20 fold differences between the GC-ECD and GC-MS results reported by Kelly (2005) need to be investigated further. The timescales considered, relative to recent trends in emission and air and seawater are probably insufficient to allow firm conclusions to be reached regarding whether endosulfan residues would continue to increase, plateau or decline in the near future.

Trophic magnification and biomagnification

There is ambiguous evidence of trophic magnification potential for endosulfan. It was concluded that endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP. There is no clear evidence of biomagnification for invertebrates to fish and fish to predatory fish. There is, however, a high degree of uncertainty surrounding fish to marine mammal food chain links – on this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern.

Bioaccumulation

Bioaccumulation factors approaching 1 million (BAF_{lw}) can be readily demonstrated for zooplankton and fish for other locations (e.g. Barrow and Holman). The implications of such high BAF values are unclear, particularly when considered alongside ambiguous trophic magnification and biomagnification profiles (particularly for fish \rightarrow marine mammals). The potential for other uptake/retention mechanisms much lower in the food chain such as highlighted by Wallberg *et al.* (2001) remains a possibility, but there is no direct evidence. The influence of temperature on

bioaccumulation potential also needs to be considered. Temperature could be an important variable that has not been taken into account in comparisons of BCFs from lab studies with field studies. It is suggested that the effect of decreased ambient temperature conditions relative to those characterising standard laboratory tests could significantly decrease metabolism of endosulfan both by invertebrates and fish.

6 Risk Profile for Endosulfan in the Arctic Region

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Estimation of risks for wildlife and humans requires the integration of exposure and effects data (NRC 1993, USEPA 1992). This can be done deterministically to characterize hazard (whether one of the exposure concentration, usually the greatest, exceeds one of the effect concentrations, usually the smallest) or probabilistically (calculating the likelihood that exposure concentrations will exceed effects concentrations). Risks were assessed for non-mammal marine animals, terrestrial animals and humans in the following sections.

6.1 Risks to Non-Mammalian Marine Species

To characterize risks to marine and freshwater invertebrates and vertebrates, concentrations in the exposure matrix (water) were compared to those causing adverse effects in toxicity tests conducted in laboratory studies with a variety of test organisms. In this process it was assumed that other routes of exposure, such as food, were of relatively less important than direct uptake from the water. Studies in *Daphnia magna* have shown that uptake of endosulfan via food is relatively minor when compared to uptake from water (De Lorenzo et al. 2002), suggesting that this assumption is valid, at least for fully aquatic species (See discussion of bioaccumulation in Section 3.2). Although environmental concentrations are frequently reported for the isomers of endosulfan, toxicity data are usually based on total endosulfan. For this reason, total endosulfan residues were used to characterize exposures for risk assessment purposes.

Characterization of the toxicity of endosulfan to aquatic animals

Toxicity data for aquatic animals were obtained from the US EPA ECOTOX database (USEPA 2001). Data were processed to exclude values where the endpoint was physiological or not clearly related to survival, mortality, or reproduction. Endpoints such as 0 or 100% mortality were excluded for acute tests but NOECs, LOECs, and MATCs were retained for chronic tests. All effect measures were converted to ng/L. Saltwater and freshwater studies were analyzed separately. Exposures less than 24 h were excluded and, for acute studies where different exposure durations were reported, data for the longest duration up to 120 h were retained if this was the only exposure time available in the data set. For other species with multiple exposure times, the longest time up to 96 h was selected to represent an acute exposure.

Acute data

Where multiple values were reported for the same species, data from flow-through studies were selected over static renewal, over static exposures. If more than one value remained, the geometric mean of the values was used so that each species was represented only once in the data set. Because endosulfan is selective in its action, data were separated into taxa, such as, arthropods, fish and amphibians, and other aquatic animals (Appendix 10, Tables 1 and 2). The data were ranked and plotted to produce several Species Sensitivity Distributions (SSDs) using published procedures (Solomon and Takacs 2002).

Chronic data

Chronic data (Appendix 10, Tables 3 and 4) were too few to be plotted as distributions. The most sensitive effect measure for each species was retained for the purposes of risk assessment; however, the smallest of these values (Appendix 10) was not less than the most sensitive acute effect measure (Figure 6.1.1). This is

likely because endosulfan is a rapidly acting neurotoxin and does not bioaccumulate to greater and more toxic body burdens over exposure times longer than those used in most acute toxicity tests.

Characterisation of the concentrations of endosulfan in marine waters

Concentrations of endosulfan in Arctic marine waters were obtained from data compiled from several sources collected over a period of years from 1993 to 2000 (See Section 4.3). A smaller data set from Lake Superior (D Muir, unpublished, see Section 2) was also used for the analysis. For the purposes of the risk assessment, the concentrations for α -endosulfan and β -endosulfan were summed. If either isomer was found below the method detection limit (MDL), the MDL for the isomer was assumed. Thus, the total for both isomers is a somewhat conservative number. If both isomers were found below the MDL, the MDL for only one isomer was assumed. The concentrations are thus slightly greater than the actual values and the assessments therefore somewhat conservative.

Discussion and risk assessment

The toxicity and exposure data were plotted on the same graph to illustrate potential risks of acute toxicity (Figure 6.1.1). The toxicity data show that endosulfan is, in general, more toxic to fish than to arthropods and, in addition, is somewhat more toxic to saltwater than freshwater fish – an observation that is consistent with general observations in the literature. Toxicity to freshwater and saltwater arthropods was similar. Other aquatic animals were less sensitive than fish or arthropods, most likely because this group included mollusks and rotifers, organisms that are in general insensitive to insecticides.

Risks to freshwater or marine animals are minimal. The toxicity value for the most sensitive animal was about three orders of magnitude greater than the highest measured concentration for Arctic marine waters (Figure 6.1.1). This applies to both the acute and the chronic toxicity values. Concentrations in freshwater were smaller and the risks are even less for freshwater organisms (Table 6.1.1). These data clearly show that there is essentially negligible risk to aquatic animals from acute and chronic exposures to endosulfan residues in Arctic marine systems. The same conclusion applies to the exposures in Lake Superior.

Table 6.1.1 Regression coefficients and intercepts for the toxicity data distributions for acute exposures of aquatic organisms to endosulfan and concentrations in Arctic marine water and Lake Superior

Data source			y = ax + b		Centile intercepts (ng/L)		Probability of exceeding the 10 th centile of the toxicity distributions	
	n	r ²	A	b	10%	90%	FW fish	SW arthropods
FW Arthropods	33	0.98	0.69	-2.89	214			
FW Fish	61	0.84	0.93	-3.36	173			
FW Other	15	0.89	0.88	-5.56	70,946			
SW Arthropods	17	0.97	0.54	-2.16	44			
SW Fish	12	0.91	1.66	-4.69	115			
SW Other	11	0.96	0.78	-4.21	5,813			
Arctic marine	120	0.89	1.24	3.87		0.01	<0.001%	<0.001%
Lake Superior	14	0.83	1.33	3.92		0.01	<0.001%	<0.001%

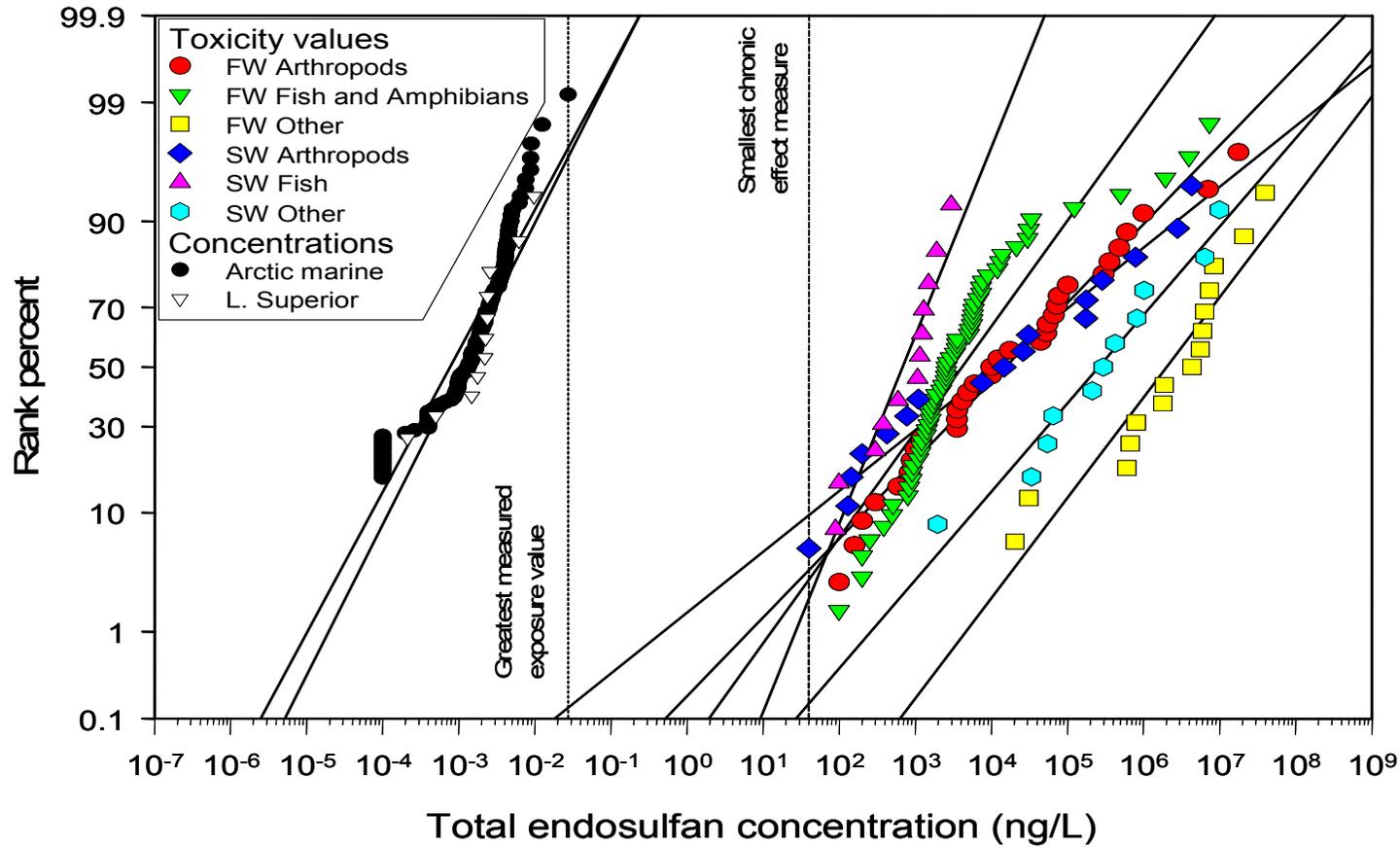


Figure 6.1.1 Distributions of toxicity values for endosulfan in freshwater and saltwater animals and concentration values for Arctic marine waters and Lake Superior.

6.2 Risks to Indigenous Human Populations

Exposures of Humans in the Arctic to Endosulfan

Risks to humans usually consider all routes of exposure. In the case of humans in the arctic, direct exposure through use of endosulfan in agriculture is not relevant. Inhalation exposure from the atmosphere is small (Section 4.1) and was considered to be irrelevant. Therefore exposures via food and drinking water were used in the exposure characterization. Since multiple food and drinking-water concentration data are available, these concentrations could be characterized probabilistically. Since there are no toxicity data for humans, laboratory animal data were used. The most common criterion for judging human exposures for the purposes of risk assessment is the Reference Dose (RfD) or the Acceptable Daily Intake (ADI). This is determined from the results of laboratory animal studies in which the greatest dose that causes no adverse acute or chronic response in the most sensitive test species is divided by an uncertainty factor to account for differences between humans and laboratory animals and within humans, such as the elderly or very young. In the case of endosulfan, the chronic RfD used by the US EPA is 0.006 mg/kg/day, based on reduced body weight gain in male and female rats; increased incidence of marked progressive glomerulonephrosis and blood vessel aneurysms in male rats (USEPA 2005). This RfD incorporates an uncertainty factor of 100.

Table 6.2.1 Average food intake in Greenland (Data from AMAP, 2003)

Source	Intake in g/day
Walrus	14
Polar bear	23
Whale meat and blubber	37
Seal meat and blubber	41
Reindeer, hare, muskox	50
Fish	78
Imported food	638

Table 6.2.2 Food intake in the Russian Arctic by indigenous people (Data from AMAP, 2003)

Source	Ustj-Yeniseyskiy district		Dudinka area
	Male g/day	Female g/day	Female g/day
Reindeer	402	380	140
Fish (fresh or treated)	511	484	361
Game	50	45	44
Vegetables	180	156	168
Imported meat	98	86	100
Dairy	118	113	100

Food exposure data

Food exposure data were taken from analyses conducted in Greenland. For the purposes of the risk assessment, the residues for α -endosulfan and β -endosulfan were summed and data from west and east Greenland were grouped together. If either isomer was found below the method detection limit (MDL) the MDL for the isomer was assumed. Thus the total for both isomers is a somewhat conservative number. Values for fish and marine invertebrates were grouped together under the generic category of "fish". Data were from Arctic char, Atlantic cod, Atlantic salmon,

capelin, deep sea shrimp, Greenland cod, Greenland halibut, Iceland scallop, redfish, snow crab, and wolf fish (Johansen et al. 2004). Only values for fish muscle were used in the assessment.

For terrestrial mammals and birds (game), data from all tissues analyzed (muscle, liver, kidney, and fat) were used in the characterization. Data were from analyses of caribou, common eider, hare, king eider, kittiwake, lamb, musk-ox, ptarmigan, and thick-billed murre (Johansen et al. 2004). Data for polar bears were obtained from samples taken in Svalbard and Bering-Chukchi (D Muir, personal communication). As for the other data, the concentrations of both isomers were added together and the assessment done on total endosulfan.

For marine mammals, whales, walruses, and seals were analyzed separately. Only data from muscle, skin, and blubber were used in the characterization. Whale species analyzed included beluga, harbor porpoise, narwhal and minke whale. Seals included harp seal, and ring seal (Johansen et al. 2004).

Water exposure data

Concentration data for snow were used as a surrogate for drinking water exposures to endosulfan. Endosulfan concentration data (Strachan et al. 2005) from analyses of samples of snow samples collected between 1992 and 1996 in Cape Dorset, Dawson, Eureka, Mould Bay, Snare River, Tagish, and Whitehorse were combined for the purposes of the risk assessment. These data were converted to $\mu\text{g/L}$ to allow direct comparison to the concentration data for food items.

Probabilistic characterization of the measured endosulfan concentrations

For probabilistic graphical analysis of exposures, data from food and snow were ranked from smallest to greatest and plotted using published methods to produce concentration distributions for food and drinking water (Solomon and Takacs 2002). Values where the total endosulfan concentration was below the MDL were included in the ranking but were assigned a dummy value of 0. These data were not plotted on the graphs (Figures 6.2.1 and 6.2.2). The 90th, 95th, and 99th centiles were estimated from the slope and intercept of the regression line and used to determine the total exposure to endosulfan in food, assuming that people ate only food with the 90th centile concentrations, etc. (Table 6.2.3). Since the source of the vegetables was not specifically known, these food items and imported food, dairy, and meat were assigned a value of 0.5 ng/g, the 90th centile value for reindeer meat (Table 6.2.3). As an alternate method, these imported food items were assigned a concentration derived from the total food exposure to endosulfan as estimated by the USEPA (USEPA 2002) but adjusted for the proportion of "imported food" in the diet (Tables 6.2.1 and 6.2.2) and then the 50th, 90th, etc. centile of the estimated dietary exposures in the US (USEPA, 2002) were used to calculate total exposures (Table 6.2.4).

To estimate total exposures from food and water, the concentrations of endosulfan in food and water were multiplied by the intake of food items (Table 6.2.1 and 6.2.2). Water consumption was assumed to be 2 L per day. The margin of exposure for the 50th centile exposure through diet and water was then calculated using the chronic Reference Dose (RfD) for endosulfan (0.006 mg/kg/day) as determined by the US EPA (USEPA, 2005) while that for the 90th, 95th, and 99th centiles was calculated using the acute RfD for endosulfan (0.015 mg/kg/day) (USEPA 2002).

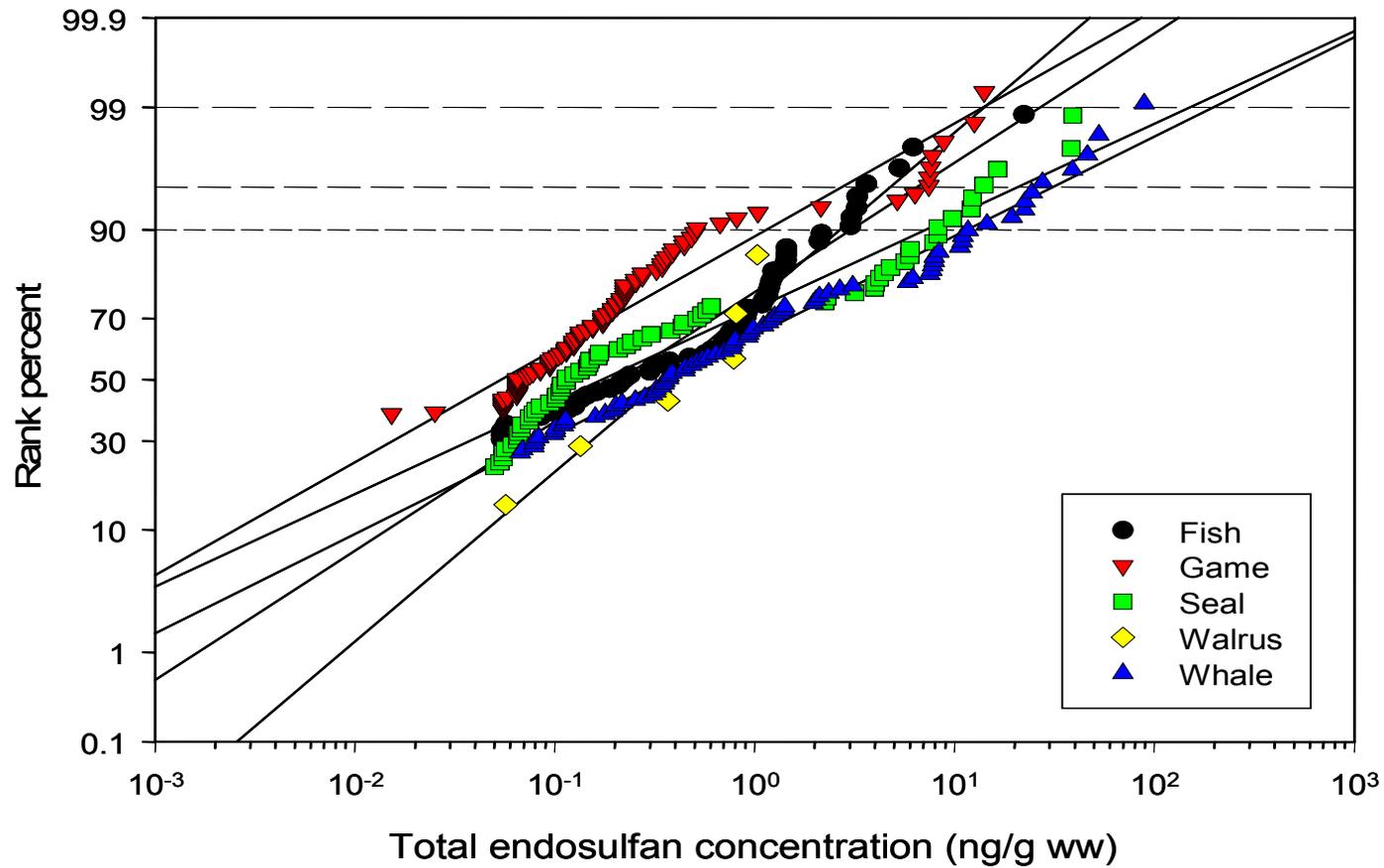


Figure 6.2.1. Distributions of total endosulfan concentrations in food items from Greenland. The horizontal lines show the 90th, 95th, and 99th centiles and intercept of these with the regression lines was used to determine the respective concentrations associated with these centiles.

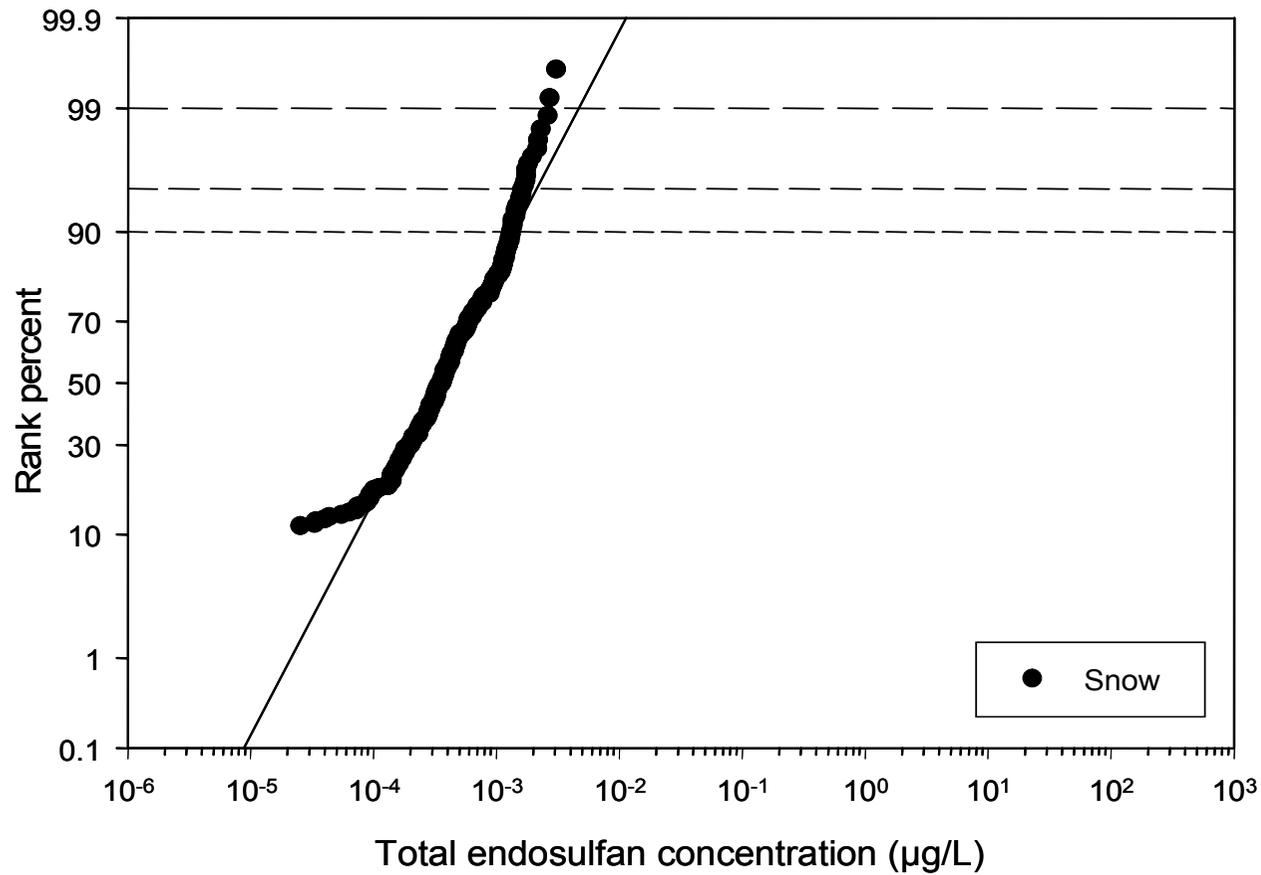


Figure 6.2.2. Distributions of total endosulfan concentrations in Snow from the arctic. The horizontal lines show the 90th, 95th, and 99th centiles and intercept of these with the regression lines was used to determine the respective concentrations associated with these centiles.

Table 6.2.3 Centiles of total endosulfan concentration in food items from Greenland (RfD from USEPA, 2005; incorporates an uncertainty factor of 100)

Food Group	Centiles ng/g			
Food Group	50%	90%	95%	99%
Fish	0.2	3.0	6.5	26.9
Game	0.1	1.1	2.7	13.9
Seals	0.2	7.1	20.5	149.5
Walrus	0.4	2.7	4.8	14.2
Whale	0.4	11.5	31.0	197.1
Imported food	0.5	0.5	0.5	0.5
Dairy	0.5	0.5	0.5	0.5
Total daily intake (mg/kg/day) based on a 60 kg person				
Greenland	0.000006	0.000297	0.001953	0.071250
Russia U-Y male	0.000006	0.000038	0.000079	0.000337
Russia U-Y female	0.000005	0.000036	0.000075	0.000319
Russia D female	0.000005	0.000025	0.000051	0.000208
Margin of safety over RfD of 0.006 mg/kg/day				
Greenland	965	51	7.7	0.21
Russia U-Y male	1091	158	76	18
Russia U-Y female	1190	168	80	19
Russia D female	1332	241	119	29

Table 6.2.4 Centiles of total endosulfan concentration in food items from Greenland and from drinking water sources using US values for concentrations in imported foods (RfD from USEPA, 2002; incorporates an uncertainty factor of 100)

Food Group	Centiles ng/g or µg/L (water)			
Food Group	50%	90%	95%	99%
Fish	0.2	3.0	6.5	26.9
Game	0.1	1.1	2.7	13.9
Seals	0.2	7.1	20.5	149.5
Walrus	0.4	2.7	4.8	14.2
Whale	0.4	11.5	31.0	197.1
Proportion of imported food in the diet (%)	72%	29%	28%	40%
Contribution of imported food to daily dose (mg/kg/day)	0.000038	0.000159	0.000239	0.000511
Drinking water concentration (µg/L)	0.00032	0.00140	0.00214	0.00470
Total daily intake from food and water (mg/kg/day) based on a 60 kg person				
Greenland	0.000028	0.000406	0.002119	0.071613
Russia U-Y male	0.000013	0.000081	0.000145	0.000482
Russia U-Y female	0.000013	0.000079	0.000143	0.000477
Russia D female	0.000017	0.000098	0.000171	0.000538
Margin of safety over chronic RfD of 0.006 mg/kg/day or acute RfD of 0.015 mg/kg/day				
Greenland	212	37	7	0.21
Russia U-Y male	454	186	103	31
Russia U-Y female	467	190	105	31
Russia D female	345	153	88	28

Conclusions and risk assessment

With the exception of a hypothetical individual in Greenland that consumes all food items with the 99th centile concentration of endosulfan (Table 6.2.3), all other consumption scenarios suggest negligible risk. Similar results were obtained when the concentrations of endosulfan in imported food items were assumed to be the same as those for the US population (Table 6.2.4). It is observed that significance of residues in imported food assumes a greater significance to the total load at the 50th centile exposures, while the significance of locally sourced food items is greater in higher centiles of exposure. Human dietary risk is concluded to be generally negligible except in extreme worst-case situations where there is a coincidence of very heavy reliance upon locally sourced food items drawing heavily upon marine mammals and fish characterised by 99th centile endosulfan residue profiles. It should be noted that even if this unrealistically high uptake profile is compared to the lowest available chronic NOEL from the most sensitive mammalian species tested a safety factor of 21 can be demonstrated.

6.3 Risks to Terrestrial Animals

Since no toxicity data were available for terrestrial animals from polar regions, surrogate data were used for the assessment of possible effects. The approach was similar to that used above for risk to humans.

Toxicity data

Because of lack of experience and the large sized of some of the animals, the allometric scaling factors (Sample, 1996, 1999) recommended for wildlife risk assessment were not used. Instead, for mammals, the NOAEL for the chronic 2-year rat feeding study (= 0.6 mg/kg/day = 600 µg/kg/day; USEPA, 2005) was used. This was used in two ways. Firstly, the dose derived from the food was assumed to represent the body dose. Secondly, the body dose from the above study was adjusted for the accumulation observed in pharmacological studies in rats (Figure 6.3.1) where the measured concentration in fat was four times greater than the actual body dose used in the experiment.

Exposure data

Exposure data were taken from studies in food organisms from Greenland (as for humans, Section 6.2, above) and from samples collected in polar bears (D Muir, personal communication).

Assessment and conclusions

Centiles of the exposure data were compared to the rat NOAEL value above and the margin of exposure calculated (Table 6.3.1). In addition, maximum and minimum concentrations reported in individual species from Greenland were compared to the NOAEL dose for the rat and to the NOAEL dose for the grey partridge (Sample, 1996) as representing birds (Figure 6.3.1).

The margins of exposure (Table 6.3.1) for all centiles are all more than 1, suggesting that these groups of animals are exposed to body doses less than the NOAEL for the most sensitive test species, the rat. This suggests minimal to negligible risks.

When the maximum body concentrations for various species of animals are compared to NOAEL values for the rat and the grey partridge, none of the measured values exceed any of the toxicity values (Fig. 6.3.1), supporting the same conclusion

of negligible risks to marine mammals and terrestrial wildlife from endosulfan exposures via the environment and the food chain.

Table 6.3.1. Centiles of total endosulfan concentration in terrestrial wildlife from Greenland

Organism group	Centiles ug/kg			
	50%	90%	95%	99%
Game	0.05	1.15	2.73	13.92
Seals	0.17	7.13	20.54	149.47
Polar bear	3.17	10.32	14.43	27.05
Walrus	0.35	2.69	4.79	14.16
Whale	0.36	11.55	30.97	197.07
	Margin of exposure over chronic NOAEL from 2-y rat feeding study = 0.6 mg/kg/day = 600 ug/kg/day (USEPA, 2005)			
Game	11,160	523	220	43
Seals	3,513	84	29	4
Polar bear	189	58	42	22
Walrus	1,711	223	125	42
Whale	1,686	52	19	3
	Margin of exposure over maximum estimated body dose at chronic NOAEL from 2-y rat feeding study = 0.6 mg/kg/day x 4 = 2400 ug/kg/day (USEPA, 2005)			
Game	44,640	2,091	878	172
Seals	14,053	337	117	16
Polar bear	758	233	166	89
Walrus	6,843	892	501	170
Whale	6,745	208	77	12

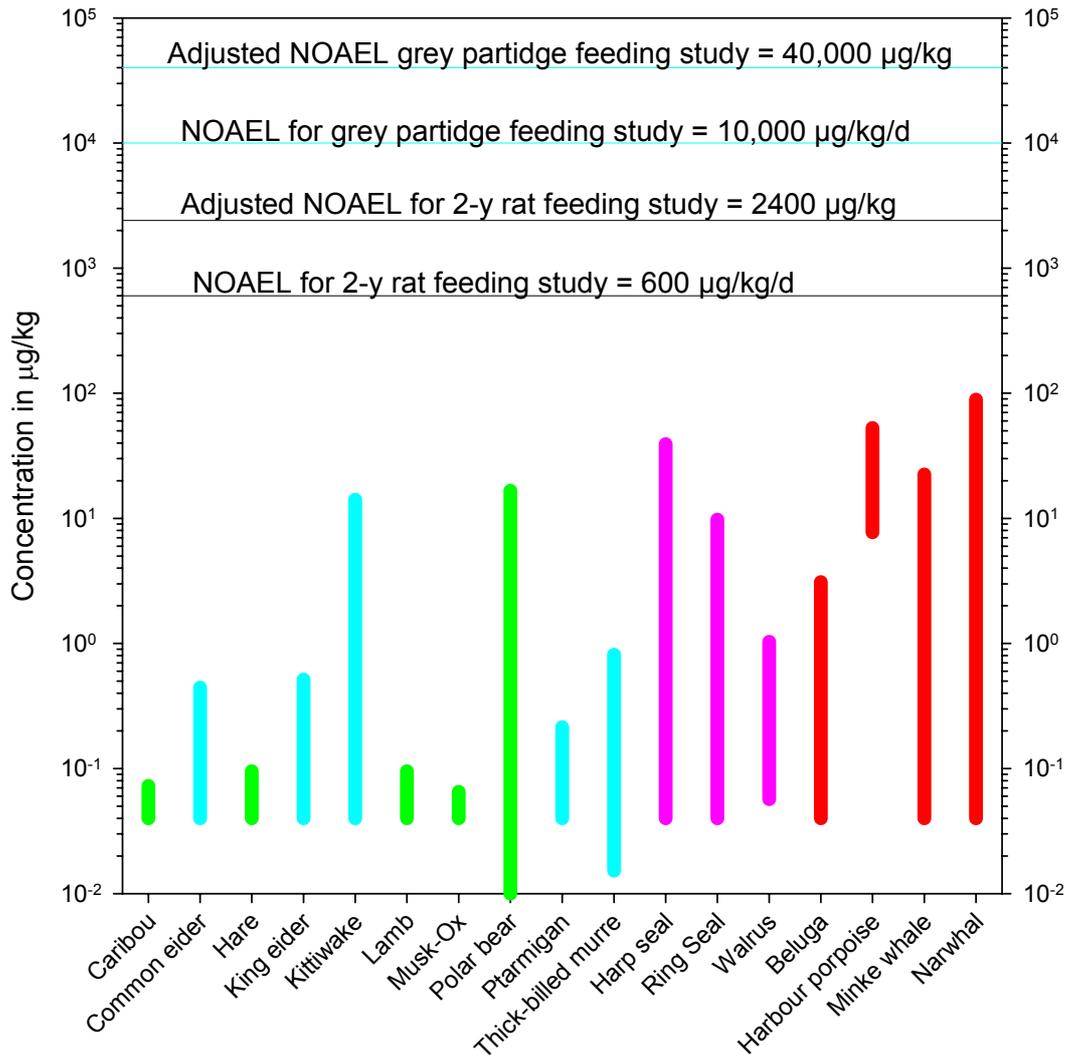


Figure 6.3.1. Range of exposure concentrations measured in various polar marine and terrestrial wildlife species as compared to NOEL doses in test species.

6.3 Data Gaps and Uncertainties

Risks to non-mammalian marine species

Concentration profiles for endosulfan were relatively few and, by necessity, were grouped over several years and locations to facilitate assessment. An expanded dataset including further data from each location would allow assessment of spatial differences in the concentration of endosulfan in marine waters. Data for Lake Superior data were also limited but were included only for the purposes of comparison to a more southerly location. Toxicity data were robust, particularly for freshwater organisms (see appendix 10). There were fewer data for salt-water fish, however, these were still considered appropriate for risk assessment. There is uncertainty in the extrapolation of data from mostly temperate test organisms to those in the arctic. However, arctic arthropods have been reported to have similar sensitivity to metals as temperate species (Chapman 1993) and data on insecticides has shown similarity in response between tropical and temperate organisms (Maltby *et al.* 2005).

Risks to indigenous human populations

There are several uncertainties in this assessment. The endosulfan concentration data were based on samples from Greenland only and may not be representative of other areas. Endosulfan concentrations in ring-seal from Greenland were less than concentrations reported from Holman and Barrow (Table 5.3.2), however, they were similar to those reported in a number of other locations (Table 5.3.2). The number of samples of each food item was also small and, although food items were combined for analysis, the 99th centile of exposure was based on an extrapolated value for fish, seal, and walrus. It should, nonetheless, be noted that this evaluation is based on a RfD that already incorporates an uncertainty factor of 100.

There are two uncertainties in the food consumption data. Firstly, the dietary intake values for Greenland from the AMAP survey were based on only 180 individuals surveyed for food intake in 24 h (AMAP 2003) while those from Russia are not well described. In addition, insufficient data were available to characterize individual variability in day to day consumption of food items. These uncertainties should be addressed in future research in the Arctic as they will be useful in assessing risks from a number of other substances found in foods. However, these uncertainties are to some extent balanced by the conservative assumption that endosulfan residues in all food items will be at high centiles of concentration on a particular day. Over an extended period, residues consumed will tend to the 50th centile which has a greater margin of exposure and presents negligible long term chronic risks (Table 6.2.3 and 6.2.4).

Risks to terrestrial animals

As this risk assessment draws upon the same exposure database as was employed in the human dietary risk assessment, many of the same uncertainties are also applicable here. It should be noted however, that the databases was widened slightly to include samples collected in polar bears (D Muir, personal communication).

7 Summary of Principal Strengths and Weaknesses

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An important component of any assessment of a potential POP is a consideration of transport behaviour, temporal trends and spatial trends in remote regions. In the Arctic (where much of the focus of research on POPs has taken place due to anticipated accumulation in polar regions) ascertaining clear trends is often hampered by difficulties of accessibility and the associated problems of logistics when establishing long-term, or even short-term, research facilities. As a consequence there are often significant uncertainties and data gaps that may confound efforts to provide clear interpretations of behaviour. This is often compounded for compounds that have complex analytical profiles by issues such as potential for interference and the development of robust methods capable of accurately quantifying trace levels in matrices ranging from air to blubber. A short summary is provided in tabular form of the principal issues highlighted by this research that may frustrate attempts to develop a clear interpretation of behaviour.

In many cases, high quality studies are available that have greatly assisted in the interpretation of fate and behaviour. It is appropriate to recognise the value and scientific contribution of these studies, particularly in the context of any further research recommendations that may build upon their foundation. Accordingly, the strengths of the available datasets are specifically highlighted in the summary Tables presented in this chapter. Finally, a set of bullet point recommendations are provided that may be carried forward into future monitoring exercises. It is intended that these would have not only specific value in assessing endosulfan, but also broader generic value in the assessment of other chemicals as well.

Table 7.1. Summary of principal strengths and weaknesses - Air

<p>SCOPE</p> <p>Strengths: The main focus of monitoring has been upon α-endosulfan and there are substantial datasets available on this compound – particularly from the long-term NCP monitoring station in Alert.</p> <p>Weaknesses and uncertainties: β-endosulfan has been included in only a selected number of monitoring campaigns. Endosulfan sulfate does not appear to have been considered in typical monitoring campaigns. Analysis has typically relied on GC-ECD, rather than the more robust GC-MS. Therefore, the potential for analytical interferences cannot be ruled out.</p>
<p>SPATIAL TRENDS</p> <p>Strengths: A high quality, long-term continuous air sampling programme based in Alert in the Canadian High Arctic has provided important information on long-term and seasonal trends in air concentrations of endosulfan and a range of other chemicals. Additional limited monitoring datasets are available for sites in the Canadian sub-Arctic, western Siberia, the Bering Sea and in Norway.</p> <p>Weaknesses and uncertainties: Long-term continuous air sampling is available for comparatively few sites. The network of long-term, continuous air monitoring sites in the Arctic remains extremely limited and, as a consequence, significant spatial gaps and uncertainties remain.</p>
<p>TEMPORAL TRENDS</p> <p>Strengths: As discussed above, the long-term NCP air monitoring station in Alert provides the highest quality basis for assisting in the better understanding of temporal trends of many chemicals, including endosulfan.</p> <p>Weaknesses and uncertainties: The long-term trend in endosulfan residues in air in the Arctic appears to be stable. Usage/emission may have peaked and may now be in decline but establishing the extent of any delay in parallel decline in air residues will require further (and perhaps more extensive) continuous air sampling. The timescales required to assess this cannot be accurately estimated due to a lack of knowledge about the significance of a wide range of potential confounding influences summarised by Hung <i>et al.</i> (2005) as well as more up to date and more accurate usage and emission estimates.</p>
<p>SOURCES AND ENVIRONMENTAL FATE</p> <p>Strengths: Air mass back trajectories have been employed to assess potential sources of contaminants into the western Canadian Arctic and other Canadian monitoring locations.</p> <p>Weaknesses and uncertainties: Attribution of source regions for endosulfan arriving in Arctic regions of eastern North America, Europe, eastern and western Asia remains uncharacterised.</p>
<p>RESEARCH RECOMMENDATIONS</p> <ul style="list-style-type: none"> • Additional quality control procedures should be put in place to periodically confirm the presence of analytes reported by GC-ECD. Further controls such as inter-laboratory round-robins and analysis of quality assurance standards could be regularly implemented. • The long-term air monitoring programme based at Alert in the Canadian high Arctic has provided vital data in understanding the behaviour and trends in many chemicals. It is recommended that this programme be continued to assist in better understanding trends in chemicals with current usage such as endosulfan. • It is further recommended that such monitoring programmes be potentially extended to consider other locations to assist in the development of a more complete understanding of potential source regions for chemicals. The expense and logistical difficulties associated with running such a study are recognised.

Table 7.2. Summary of principal strengths and weaknesses - Seawater

SCOPE
<p>Strengths: Monitoring has been conducted for both α- and β-endosulfan in many regions of the Arctic. This has included not only 'near coast' monitoring but also extensive research cruises such as those conducted under BERPAC and by the research vessel <i>Oden</i>. A high degree of consistency is noted despite studies and analysis having been conducted by a number of researchers in different institutes.</p> <p>Weaknesses and uncertainties: The very small levels present result in significant analytical challenges. In particular, uncertainties have been pointed out by some researchers in the robustness of β-endosulfan measurements. Endosulfan sulfate has not been typically included in monitoring campaigns and, therefore, seawater profiles remain unknown for this metabolite.</p>
SPATIAL TRENDS
<p>Strengths: Most sectors of the Arctic have been included in seawater monitoring campaigns although 'near coast' monitoring accounts for the majority of these research efforts.</p> <p>Weaknesses and uncertainties: The Central Asian Arctic, where several large Asian rivers such as the Ob, Yenisey and Lena Rivers discharge, is poorly represented. This may have implications when considering the potential of Asian rivers as routes of entry for endosulfan into the Arctic.</p>
TEMPORAL TRENDS
<p>Strengths: Results of limited monitoring conducted at different time periods at similar locations has given indications of the possibility of meltwater contributions to residues of endosulfan in seawater. Results of limited monitoring conducted within and outside the icepack has assisted in potentially better understanding seasonal changes in air-water exchange behaviour.</p> <p>Weaknesses and uncertainties: The available monitoring database is temporally sporadic. There are no continuous seawater monitoring campaigns in existence in the manner operated by the Canadian government for air monitoring. There is an almost complete reliance on monitoring during summer months in ice-free areas. Assessment of the seasonal variation in seawater residues due to shut down of the air-sea gas exchange process during ice cover remains an uncertainty worthy of further research. This is particularly important in the Central Arctic where the ice pack remains throughout the summer period.</p>

Table 7.2. Summary of principal strengths and weaknesses – Seawater (cont'd)

<p>SOURCES AND ENVIRONMENTAL FATE</p> <p>Strengths: The value of monitoring undertaken during cruises through the ice pack in understanding air-sea exchange behaviour is particularly recognized. The availability of the long-term continuous air monitoring programme run by the Canadian government in Alert has been very useful in assisting in beginning to interpret air-sea exchange behaviour for endosulfan.</p> <p>Weaknesses and uncertainties: Concentrations of both α- and β-endosulfan east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain. Under certain circumstances water monitoring results have been found to be highly variable (both in terms of the scale of detection but, notably, also in terms of the ratios of α- to β-endosulfan). It has been suggested that this may reflect local influences such as entry of meltwater but this remains uncertain.</p> <p>The availability of air monitoring data for a broader range of site severely limits accurate estimation of air-water exchange potential. It has been necessary to rely upon air monitoring for a limited number of locations – sometimes far removed from the parallel seawater monitoring site. There is, therefore, an assumption that the air monitoring has 'regional' relevance despite sometimes very large spatial separation. The single greatest uncertainty in evaluating air-sea gas exchange behaviour is the reliance upon an estimated temperature dependent Henry's law constant. Significant regional differences in air-sea gas exchange behaviour for α-endosulfan cannot readily be explained. There is insufficient data available to accurately estimate net air-sea gas exchange behaviour for β-endosulfan.</p> <p>When taken together, the compounded uncertainties associated with low level analysis in seawater, reliance on a very limited set of air sampling campaigns (two locations in the Canadian High Arctic and Siberia), the lack of availability of a temperature dependent Henry's law constant and the influence of 'salting out', suggest that a high degree of caution must be exercised in interpretation and attribution of behaviour as evidence of POP characteristics.</p>
<p>RESEARCH RECOMMENDATIONS</p> <ul style="list-style-type: none"> • Additional quality control procedures should be put in place to periodically confirm the presence of analytes reported by GC-ECD. Further controls such as inter-laboratory round-robins and analysis of quality assurance standards could be regularly implemented. • Coupled air /seawater measurements to assess localised air-water exchange during periods of melt and freeze. The work could also be conducted in the vicinity of an ice-lead to quantify the role of polynyas/leads in contributing to air-water exchange during the winter and spring. • Deep water sampling to establish the vertical extent of endosulfan occurrence in the water column. The hypothesis here is that endosulfan residues are unlikely to be detected (unlike HCHs) due to removal via hydrolysis. • Potential for widening seawater monitoring campaigns to include an assessment of the Central Asian Arctic. • Increased accessibility of monitoring databases for large Asian rivers (Ob, Yenisey and Lena Rivers) in order to assess scale of riverine sources into the Arctic • Potential for establishing seawater monitoring designs (seasonal or monthly sampling) for selected sites that would provide a more robust basis for establishing temporal trends. • Further investigation into the role of meltwater as a local source of residues into seawater. • More extensive seawater monitoring from below the ice pack to assist in further understanding seasonal variation in water residues and air-water exchange behaviour. • Of specific relevance to endosulfan, the determination of a temperature dependent Henry's law constant

Table 7.3. Summary of principal strengths and weaknesses – Snow and ice

<p>SCOPE</p> <p>Strengths: Both α- and β-endosulfan have been detected in Arctic snow, with measurements available for a number of sites across the Canadian Arctic and Norway. Analysis has generally been via GC-NCIMS.</p> <p>Weaknesses and uncertainties: Endosulfan sulfate was not detected in bulked snow samples, which calls into doubt the atmosphere as a major source of this chemical to the arctic system.</p>
<p>SPATIAL TRENDS</p> <p>Strengths: An extensive survey of surface fresh snow across northern/Arctic Canada during the early/mid-1990s has provided insight into the geographical distribution of endosulfan. The sampling and analytical methodology are uniform for all the sites surveyed providing a high degree of confidence in the data.</p> <p>Weaknesses and uncertainties: Spatial differences are difficult to determine due to high variability in snow concentrations. In the Canadian Arctic the two most northerly sample sites, with the coldest air temperatures displayed the widest range in concentrations with higher average concentrations than sites located further south. However, higher rates of precipitation experienced at the more southerly stations result in similar depositional fluxes across the Canadian Archipelago.</p>
<p>TEMPORAL TRENDS</p> <p>Strengths: A survey of glacial firn and ice in the Norwegian Arctic revealed the accumulation of SVOCs including α- and β-endosulfan. In this study, the chemical profile in deeper layers of firn/ice was dominated by the β-isomer, presumably due to the post-depositional loss of the α-isomer.</p> <p>Weaknesses and uncertainties: There remain significant uncertainties associated with attributing processes post-depositional dissipation, including the extent of migration, volatilisation and photolysis.</p>
<p>RESEARCH RECOMMENDATIONS</p> <ul style="list-style-type: none"> • Process-based studies are required to examine the fate of endosulfan following snow ageing and melt. Percolation and transport of chemical residues both within and out of the snowpack during periods of thaw are poorly understood and both laboratory simulations and controlled field studies are required to address these areas. • Combined air and snow sampling is required to determine field-based scavenging ratios and relate these to temperature, the physical properties of the snow and theoretically derived values. • Snow-air partitioning studies are required to determine the suitability of Henry's Law (at sub-zero temperatures) in describing the chemical composition in aged snow. • Studies are required to investigate the role of the sea-ice-snowpack in contributing endosulfan to surface seawater. • Photochemical studies are required in photic snow layers to understand chemical degradation/transformation following polar sunrise and 24 h daylight.

Table 7.4. Summary of principal strengths and weaknesses – Biota analysis

<p>SCOPE</p> <p>Strengths: The Greenland diet study conducted by Johansen et al. (2004a) is recognised an important contribution in characterising residues for a range of organisms in both the Arctic food web and human diet. Much of the monitoring has focused on α-endosulfan, but the Greenland diet study also includes β-endosulfan.</p> <p>Weaknesses: Significant uncertainties remain for β-endosulfan and endosulfan sulfate. Endosulfan sulfate has been considered in analyses of seals and beluga conducted by Stern and Ikonomou (2003) and Kelly (2005). However, a 10-20 fold differences between the GC-ECD and GC-MS results reported by Kelly (2005) needs to be investigated further before reaching firm conclusions.</p>
<p>ANALYSIS:</p> <p>Strengths: Recent GC-MS analysis results conducted by Kelly (2005)</p> <p>Weaknesses: Lack of confirmation of results by GC-MS represents a major analytical limitation. Problems due to interfering chromatographic peaks are particularly acute for marine mammals where there is clearly interference with α-endosulfan from chlordane and/or toxaphene components for the ECD compared with GC-NIMS and GC-HRMS. High values obtained by GC-HRMS for β-endosulfan are difficult to reconcile with other results e.g. by GC-NIMS, from the sample collection and deserve further investigation as well.</p> <p>Overall the uncertainty in α-, β-endosulfan and –sulfate is of the order of 10x in the case of marine mammals, which does significantly affect our conclusions in terms of magnitude of TMFs, BMFs and BAFs. There are also uncertainties in endosulfan concentrations in fish and invertebrates but based on limited GC-NIMS confirmation these are <2-fold.</p>
<p>TROPHIC MAGNIFICATION AND DILUTION</p> <p>Strengths: TMF profiles from three of the four sites considered in the assessment suggest that there is no significant relationship between measured concentration and trophic level for either α-endosulfan or lindane.</p> <p>Weaknesses: A high degree of uncertainty surrounding the interpretation and significance of the final dataset (Holman) that may be related to analytical issues discussed above.</p>
<p>BIOMAGNIFICATION</p> <p>Strengths: The available database allows consideration of two critical links in the Arctic food web for a range of species and locations. Based on these results there is no clear evidence of biomagnification for invertebrates to fish and fish to predatory fish.</p> <p>Weaknesses: A high degree of variability in calculated BMF values within similar food chain links (fish → marine mammals) was considered particularly noteworthy. The average fish to mammal BMF value was 10.2, lying at a possible threshold of concern. However, this estimate needs to be interpreted recognising a very high degree of variability (± 16.4) and therefore, uncertainty.</p>
<p>BIOACCUMULATION</p> <p>Strengths: The available database allows consideration of bioaccumulation potential for a range of species and locations. Generally consistency of profiles is noted despite studies and analysis having been conducted by a number of researchers in different institutes.</p> <p>Weaknesses: Transfer to zooplankton has been assumed to be mainly <i>via</i> water but recent studies suggest that the microbial food web could be important (Wallberg <i>et al.</i> 2001). Uncertainties were highlighted surrounding the interpretation of the Lake Superior dataset because the potential for confounding influences such as these. Further uncertainties were highlighted for anadromous species because of the potentially significant contribution of riverine pesticide loads may be significant. The implications of very high BAF values estimated for other species are unclear. The potential for other uptake/retention mechanisms remains a possibility. The influence of low temperature on increasing bioaccumulation under Arctic conditions by reducing metabolism potential has been postulated. Such an influence could account for differences between bioconcentration profiles observed under laboratory conditions (typically 20-25°C) and ambient Arctic conditions (typically <5°C). There is, however, insufficient data to confirm this for endosulfan, although the possibility is considered in studies for other compounds (Buckman <i>et al.</i>, 2004).</p>

Table 7.4. Summary of principal strengths and weaknesses – Biota analysis (cont'd)

SPATIAL TRENDS
<p>Strengths: Analysis of biota has been conducted for a range of sites through the Arctic with the Canadian Arctic and Greenland particularly well-represented.</p> <p>Weaknesses: Spatial analysis for endosulfan in marine mammals is highly uncertainty. In ringed seals, the highest concentrations of α-endosulfan were found in the Beaufort Sea – there appears to be no relationship to endosulfan concentrations in seawater. Residues of α-endosulfan were significantly higher in whales from the North Sea than those from all other locations – potentially reflecting a ‘near source’ influence and highlighting potential confounding influences for migratory species.</p>
TEMPORAL TRENDS
<p>Weaknesses: Detailed analysis of temporal trends was not possible due to the absence on long-term, site-specific monitoring campaigns of biota. Stern and Ikonomou (2003) represent a critical exception, reporting increasing concentrations of endosulfan sulfate in male beluga whales in the Canadian Arctic. However, a 10-20 fold differences between the GC-ECD and GC-MS results reported by Kelly (2005) is worthy of further consideration. The timescales considered, relative to recent trends in emission and air and seawater are probably insufficient to allow firm conclusions to be reached regarding whether endosulfan residues would continue to apparently plateau or decline in the near future.</p>
RESEARCH RECOMMENDATIONS
<ul style="list-style-type: none"> • Analytical methodology employed in biota monitoring programmes be upgraded to GC-MS. • Differences between the GC-ECD and GC-MS results reported by Kelly (2005) and Stern and Ikonomou (2003) warrant further investigation to assist in understanding temporal trends. • The influence of low ambient temperature conditions on bioaccumulation and metabolism potential should be investigated with species of relevance to such conditions. • Further understanding of spatial variation in biota residues could be strengthened by widening the range of sites considered to include the Asian Arctic.

Table 7.5. Summary of principal strengths and weaknesses – Risk assessment

ECOTOXICOLOGICAL RISKS
<p>Strengths: A relatively robust evaluation of ecotoxicological risk potential has been facilitated through access to the very large database of effects studies – particularly for freshwater organisms, as summarised in Appendix 10.</p> <p>Weaknesses: Concentration profiles for endosulfan in water were relatively few and, by necessity, were grouped over several years and locations to facilitate assessment. There were fewer data for salt-water fish, however, these were still considered appropriate for risk assessment. There is uncertainty in the extrapolation of data from mostly temperate test organisms to those in the Arctic. However, Arctic arthropods have been reported to have similar sensitivity to metals as temperate species (Chapman 1993) and data on insecticides has shown similarity in response between tropical and temperate organisms (Maltby et al. 2005).</p>
HUMAN DIETARY RISKS
<p>Strengths: The Greenland diet study conducted by Johansen <i>et al.</i> (2004a) is recognised an important contribution in characterising residues for a range of organisms in both the Arctic food web and human diet. Much of the monitoring has focused on α-endosulfan, but the Greenland diet study also includes β-endosulfan.</p> <p>Weaknesses: An evaluation based upon dietary profiles for Greenland may not be representative of other areas. There are also significant uncertainties associated with the spatial variability in residues of endosulfan in ringed seals. The number of samples of each food item was also small and, although food items were combined for analysis, the 99th centile of exposure was based on an extrapolated value for fish, seal, and walrus.</p> <p>There are two additional uncertainties in the food consumption data. Firstly, the dietary intake values for Greenland from the AMAP survey were based on only 180 individuals surveyed for food intake in 24 h (AMAP 2003) while those from Russia are not well described. In addition, insufficient data were available to characterize individual variability in day to day consumption of food items. I should be noted that these uncertainties are to some extent balanced by the conservative assumption that endosulfan residues in all food items will be at high centiles of concentration on a particular day.</p>
TERRESTRIAL ANIMAL
<p>Strengths: The Greenland diet study conducted by Johansen <i>et al.</i> (2004a) is recognised an important contribution in characterising residues for a range of organisms in both the Arctic food web and human diet. Much of the monitoring has focused on α-endosulfan, but the Greenland diet study also includes β-endosulfan. This has been supplemented by further information for polar bears from samples taken in Svalbard and Bering-Chukchi. Risks were assessed by direct comparison of mammalian toxicity data with measured residues in relevant organisms.</p> <p>Weaknesses: The available wildlife residues database reflects exposure profiles for a relatively limited range of locations.</p>
RESEARCH RECOMMENDATIONS
<ul style="list-style-type: none"> • A more thorough dietary residue analysis for endosulfan would facilitate more robust human dietary risk assessments • A more extensive (population level) and higher resolution (dietary component) dietary profile for a range of Arctic diets should be developed - similar to that employed in conventional human dietary risk assessments for pesticides. This is currently underway in the United States for Alaska but may not be representative of diets in other regions in Canada (Nunavut, Nunavik), Greenland, Scandinavia and Russia.

8 Discussion

The primary objective of this research exercise is to assemble a broader basis for evaluation of behaviour and exposure (focusing primarily upon bioaccumulative potential and monitoring trends). Abiotic and biotic residues from high quality monitoring exercises were then considered within an ecotoxicological and human health risk context in order to develop risk profiles. The issues raised during the assessments of the available monitoring data are summarised in this section for the following topics:

- Scope of available data
- Temporal trends
- Spatial trends
- Transport mechanisms and environmental fate
- Trophic magnification potential
- Biomagnification potential
- Bioaccumulation potential
- Ecotoxicological risk
- Human dietary risk

A series of research recommendations are then provided based upon an evaluation of weaknesses in the assembled database, as discussed in Chapter 7.

8.1 Scope of available data

Assessment of endosulfan is made challenging by virtue of the fact that there is a potentially important metabolite (endosulfan sulfate) that is worthy of consideration, in addition to two distinctive isomeric forms; α - and β -endosulfan. The vast majority of air monitoring of endosulfan conducted to-date has focused upon α -endosulfan. However, there is evidence to suggest that β -endosulfan residues in air are comparatively minor. Endosulfan sulfate does not appear to have been considered in typical air monitoring campaigns.

A relatively high degree of consistency is noted despite studies and analysis having been conducted by a number of researchers in different institutes. The concentrations found in monitoring studies are typically very small, resulting in significant analytical challenges. In particular, uncertainties have been pointed out by some researchers in the robustness of β -endosulfan measurements. Endosulfan sulfate has not been typically included in monitoring campaigns and, therefore, seawater profiles remain unknown for this metabolite.

Both α - and β -endosulfan have been detected in Arctic snow. β -endosulfan was detected less frequently than the α -isomer with concentrations \sim 10-fold lower. Concentrations of α -endosulfan and γ -HCH in fresh snow are comparable, which is in contrast to seawater where γ -HCH is the predominant compound (typically a 100-fold higher than α -endosulfan). In fresh snowfall, however, concentrations of a range of semi-volatile organic compounds (SVOCs), including α -endosulfan, were found to decrease rapidly due to snow metamorphosis. Subsequent re-emission from the snowpack to the atmosphere is considered to be the most likely loss process over the short term.

The database for analysis of α -endosulfan in biota is far more significant than that available for either β -endosulfan or endosulfan sulfate. Notably, however, β -endosulfan has been included in the Greenland diet study (Johansen et al., 2004a) and endosulfan sulfate has been considered in analyses of seals and beluga

conducted by Stern and Ikonou (2003) and Kelly (2005). However, a 10-20 fold differences between the GC-ECD and GC-MS results reported by Kelly (2005) needs to be investigated further before reaching firm conclusions.

8.2 Temporal trends

Long-term continuous air sampling is available for comparatively few sites of which Alert in the Canadian high Arctic provides by far the most significant and highest value dataset. The long-term trend in endosulfan residues in air in the Arctic appears to be stable. Usage/emission may have peaked between 1990 and 2001 and may now be in decline but establishing the extent of any delay in parallel decline in air residues will require further (and perhaps more extensive) continuous air sampling. The timescales required to assess this cannot be accurately estimated due to a lack of knowledge about the significance of a wide range of potential confounding influences summarised by Hung *et al.* (2005) as well as more up to date and more accurate usage and emission estimates.

The available seawater monitoring database is spatially and temporally sporadic. It does not constitute a robust enough database that would allow firm conclusions to be made regarding temporal trends. The almost complete reliance on monitoring during summer months in ice-free areas has additional implications regarding understanding environmental fate in the Arctic. Ice cover effectively eliminates air-sea gas exchange potential. The seasonal influence of this remains an uncertainty as sampling has been conducted below the ice pack to investigate any seasonal variation in seawater residues due to shut down of the air-sea gas exchange process. This is particularly important in the Central Arctic where the ice pack remains throughout the summer period.

A survey of glacial firn and ice in the Norwegian Arctic revealed the potential for accumulation of SVOCs including α - and β -endosulfan. In this study, the chemical profile in deeper layers of firn/ice was dominated by the β -isomer, presumably due to the post-depositional loss of the α -isomer. The accumulation profile for the last 50 years reveals that input of endosulfan was higher in the past, although significant post-depositional migration may obscure this profile.

Detailed analysis of temporal trends in biota was not possible due to the absence on long-term, site-specific monitoring campaigns. One noteworthy exception is reported by Stern and Ikonou (2003) who concluded that endosulfan sulfate residues were increasing in male beluga whales from Cumberland Sound in the Canadian Arctic. As discussed earlier, there remain significant uncertainties surrounding analytical differences between these studies. The timescales considered, relative to recent trends in emission and air and seawater are probably insufficient to allow firm conclusions to be reached regarding whether endosulfan residues would continue to apparently plateau or decline in the near future.

8.3 Spatial trends

As summarised earlier, the NCP (Northern Contaminants Programme) air monitoring station in Alert in the Canadian high Arctic is the most most robust dataset available. Additional monitoring has been conducted at sites in the Canadian sub-Arctic (Tagish, YK), western Siberia (Dunai and AmDerma), the Bering Sea and in Norway (Tromsø). It is apparent that the network of long-term, continuous air monitoring sites in the Arctic remains extremely limited and, as a consequence, significant spatial gaps and uncertainties remain. Nonetheless, it has been possible to exploit certain

databases with a view towards identifying source regions that contribute most significantly to airborne residues at specific locations. Spatial variation in endosulfan concentrations is not pronounced across the Arctic region as a whole, with yearly averages varying by less than a factor of 2.

The assembled database of seawater monitoring suggests that most sectors of the Arctic Ocean are included with the Bering Sea, Beaufort Sea, Canadian Archipelago particularly well-represented. Much of this data has been gathered from 'near coast' sampling, but a few more isolated sampling campaigns have been carried out on cruises such as the Barents Sea and Eastern Arctic sampling campaign mounted by the Swedish research vessel *Oden* in 1996. The Central Asian Arctic (e.g. region around the Kara and Laptev Seas where several large Asian rivers such as the Ob, Yenisey and Lena Rivers discharge) is poorly represented. This may have implications when considering the potential of Asian rivers as routes of entry for endosulfan into the Arctic. Concentrations of both α - and β -endosulfan east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain. There is, nonetheless, a relatively high degree on analytical consistency in seawater monitoring results.

As summarised earlier, analysis of snow has been conducted at a range of sites in Canada and Norway. However, spatial trends in snow and ice are difficult to determine due to the high variability in snow concentrations. In the Canadian Arctic the two most northerly sample sites, with the coldest air temperatures displayed the widest range in concentrations with higher average concentrations than sites located further south. However, higher rates of precipitation experienced at the more southerly stations result in similar depositional fluxes across the Canadian Archipelago.

Spatial variation in residues of α -endosulfan in biota was specifically considered for ringed seal blubber and minke whales. Further, region-specific data was available in the form of the Greenland diet study (Johansen *et al.*, 2004a). In ringed seals, the highest concentrations of α -endosulfan were found in the western Canadian Arctic and at Barrow AK. Concentrations in the eastern Canadian Arctic, Greenland and Russian Arctic are much lower although in general α -endosulfan was detectable at sub-ng/g in all blubber samples. This pattern of higher concentrations in the Beaufort Sea area has also been observed for α -HCH in ringed seals (Muir *et al.* 2000a) and polar bears (Norstrom *et al.* 1998) and coincides with elevated α -HCH in the Beaufort Sea and Canada basin (Li *et al.* 2002). However, there appears to be no relationship to endosulfan concentrations in seawater. Residues of α -endosulfan were significantly higher in whales from the North Sea than those from all other locations. Minke whales from the Barents Sea had higher α -endosulfan than those from Jan Mayen and west Greenland - potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species. This pattern is plausible since the North Sea and waters near Norway would be expected to have higher endosulfan based on atmospheric deposition and riverine inputs. It was not possible to derive any further spatial trends.

8.4 Transport mechanisms and environmental fate

Key studies conducted in the Canadian sub-Arctic (Tagish, Yukon) have been interpreted with air mass back trajectories to assess potential sources of contaminants into the western Canadian Arctic and other Canadian monitoring locations. This research indicates that continental/southerly air masses in North

America are likely to be more significant contributors to Arctic contamination than Asian sources. Attribution of source regions for endosulfan arriving in Arctic regions of eastern North America, Europe and Asia remains uncharacterised.

As discussed earlier, concentrations of both α - and β -endosulfan east of the Beaufort Sea in the Canadian Arctic are lower than those found in the Bering, Chukchi and Greenland Seas – the reasons for this is uncertain. There are no clear geographical trends that may suggest, for example, that transport from the Pacific Ocean through the Bering and Chukchi seas may be occurring. Under certain circumstances water monitoring results have been found to be highly variable (both in terms of the scale of detection but, notably, also in terms of the ratios of α - to β -endosulfan). It has been suggested that this may reflect local influences such as entry of meltwater.

Air-water exchange is one of the most important environmental fate processes that will define behaviour in the Arctic. Despite problems with availability of a network of long-term air monitoring sites and the lack of air monitoring data for the β -isomer, there appear to be significant regional differences in air-sea gas exchange behaviour for α -endosulfan. The use of fugacity ratios to estimate the net transfer air-sea gas exchange behaviour relies very heavily on an estimated temperature dependent Henry's law constant. This leads to significant uncertainties and potential for inaccuracies in attributing net transfer behaviour. This is considered to be the single greatest uncertainty in evaluating air-sea gas exchange behaviour (and perhaps behaviour of endosulfan in the Arctic as a whole).

Nonetheless, the calculations suggest that in some regions there is a net seawater \rightarrow air transfer mechanism occurring or that air and seawater are at close to equilibrium (e.g. Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea). In other areas (notably the Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) there appears to be a net air \rightarrow seawater transfer mechanism occurring. It is likely that seasonal changes in the ice pack will have a very significant influence on behaviour. In some areas, such as the Canadian Archipelago, there is a degree of variability in seawater concentrations which may arise due to marked stratification of surface layers through the influence of meltwater input. There is insufficient data available to accurately estimate net air-sea gas exchange behaviour for β -endosulfan. The lack of clear consistent air-sea gas exchange behaviour is in contrast to γ -HCH where recent results suggest a clear air \rightarrow seawater transfer mechanism in operation.

When taken together, the compounded uncertainties associated with low level analysis in seawater, reliance on a very limited set of air sampling campaigns, the lack of availability of a temperature dependent Henry's law constant and the influence of 'salting out', suggest that a high degree of caution must be exercised in interpretation and attribution of behaviour as evidence of POP characteristics. It can be argued that the high degree of variability observed would, in fact, favour the combined influence of a far more complex set of processes than is implied in typically simplistic POP profiles where there is a degree of spatial consistency.

8.5 Trophic magnification potential

Trophic magnification profiles from three of the four sites for which sufficient data was available to allow analysis (Barrow, Lake Superior, and White Sea) suggest that there is no significant relationship between measured concentration and trophic level for either α -endosulfan or lindane. The evidence for the remaining site (Holman) is ambiguous. At this site, there appears to be a significant relationship between

measured concentration and trophic level for all three compounds (α -endosulfan, lindane and PCB 153). However, it is well recognised that lindane does not biomagnify in aquatic food webs (Moisey *et al.* 2001; Hoekstra *et al.* 2003). Therefore, there is a high degree of uncertainty surrounding the interpretation and significance of the Holman dataset. Taking this into account it is concluded that α -endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.

8.6 Biomagnification potential

Although there are no biomagnification factor (BMF) triggers within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs, there are criteria applied to bioconcentration or bioaccumulation in aquatic species (BCF (bioconcentration factors) or BAF (bioaccumulation factors) > 5000). BMF values found to be statistically greater than unity are considered to accumulate from prey to predator. Based upon the triggers established for BCF it would be possible to conclude that BMF values of > 10 may also be of consistent concern (Default BCF and BMF values within the EU Technical Guidance Document (ECB, 2003) imply that where BCF of >5000 occurs, BMF values of ca 10 may be expected, although caveats are noted regarding assumed relationships between BCF, BMF and K_{ow}). Calculated biomagnification factors based on residue measurements for a range of Arctic species ranged from 0.056 to 64.7. The ranges are both based on calculations for Greenland cod to ringed seal food chain links. The high degree of variability the same food chain links is particularly noteworthy. Further analysis revealed that average invertebrate to fish and fish to predatory fish BMF values were very low (0.38 ± 0.59 and 0.60 ± 0.14 , respectively). The average fish to mammal BMF value was 10.2, lying at a possible threshold of concern. However, this estimate needs to be interpreted recognising a very high degree of variability (± 16.4) and therefore, uncertainty. In summary, there is no clear evidence of biomagnification for invertebrates to fish and fish to predatory fish. There is a high degree of uncertainty surrounding fish to marine mammal food chain links – on this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern.

8.7 Bioaccumulation potential

Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor (BCF) or bioaccumulation factor (BAF) in aquatic species is greater than 5000 (Log BAF or Log BCF > 3.7). Measured bioaccumulation factors for a range of Arctic species ranged from 3.4×10^3 (BAF (wet weight basis) cod; Holman) to 2.6×10^7 (BAF (lipid weight basis); smelt; Lake Superior). The implications of very high BAF values estimated for other species are unclear. The potential for other uptake/retention mechanisms remains a possibility. The transfer to zooplankton has been assumed to be mainly *via* water but recent studies suggest that the microbial food web could be important (Wallberg *et al.* 2001) and may unexpectedly influence such calculations. The influence of low temperature on increasing bioaccumulation under Arctic conditions by reducing metabolism potential has been postulated. Such an influence could account for differences between bioconcentration profiles observed under laboratory conditions (typically 20-25°C) and ambient Arctic conditions (typically <5°C). There is, however, insufficient data to confirm this for endosulfan, although the possibility is considered in studies for other compounds (Buckman *et al.*, 2004).

8.8 Ecotoxicological risk

A relatively robust evaluation of marine ecotoxicological risks has been facilitated through access to a very large database of effects studies. Risks to freshwater or marine animals are minimal. The toxicity value for the most sensitive animal was about three orders of magnitude greater than the highest measured concentration for Arctic marine waters. This applies to both the acute and the chronic toxicity values. These data clearly show that there is essentially negligible risk to aquatic animals from acute and chronic exposures to endosulfan residues in Arctic marine systems. The same conclusion applies to the exposures in Lake Superior.

Risks to terrestrial animals were assessed by direct comparison of mammalian toxicity data with measured residues in relevant organisms. The results of this assessment support the same conclusion of negligible risks to marine mammals and terrestrial wildlife from endosulfan exposures via the environment and the food chain.

8.9 Human dietary risk

The most common criterion for judging human exposures for the purposes of risk assessment is the Reference Dose (RfD) or the Acceptable Daily Intake (ADI). This is determined from the results of laboratory animal studies in which the lowest dose that causes an adverse acute or chronic response in the most sensitive test species is divided by an uncertainty factor (100) to account for differences between humans and laboratory animals and within humans, such as the elderly or very young. Food exposure data were taken from analyses conducted in Greenland. Probabilistic analysis of exposures, based on residue data for various food items were then used to estimate 90th, 95th, and 99th centiles of intake potential based on limited dietary component analyses carried out in the Arctic (Greenland and Russia).

With the exception of a hypothetical individual in Greenland that consumes all food items with the 99th centile concentration of endosulfan, all other consumption scenarios suggest negligible risk. Similar results were obtained when the concentrations of endosulfan in imported food items were assumed to be the same as those for the US population. Human dietary risk is concluded to be generally negligible except with extreme worst-case assumptions where there is a coincidence of very heavy reliance upon locally sourced food items drawing heavily upon marine mammals and fish characterised by 99th centile endosulfan residue profiles. It should be noted that even if this unrealistically high uptake profile is compared to the lowest available chronic NOEL from the most sensitive mammalian species tested a safety factor of 21 can be demonstrated.

9 Conclusions

The classification of compounds as Persistent Organic Pollutants (POPs) is based upon toxicity, semi-volatility, persistence and bioaccumulation characteristics. Under Article 1 of the Protocol agreed by the Executive Body of the LRTAP Convention, POPs are defined as:

- ‘...organic substances that:*
- (i) possess toxic characteristics;*
 - (ii) are persistent;*
 - (iii) bioaccumulate;*
 - (iv) are prone to long-range transboundary atmospheric transport and deposition;*
and
 - (v) are likely to cause significant adverse human health or environmental effects near to and distant from their sources.’*

Executive Body Decision 1998/2 sets out more detailed criteria for identifying potential POPs in the form of requirements for a risk profile (the text of this Decision is reproduced in Section 1.5). The final two criteria draw heavily upon evidence from monitoring programmes in Arctic/remote region. Detections alone, however, do not pose a risk *per se* to the environment or to humans. A number of factors should be evaluated before making such a determination:

- Temporal trends
- Spatial trends
- Transport mechanisms
- Distribution within the food chain (potential for bioaccumulation/biomagnification)
- Associated ecotoxicological risks due to background and food chain exposure
- Associated human dietary risks, primarily due to potential marine bioaccumulation

The primary objective of this research exercise is to assemble a broader basis for evaluation of behaviour and exposure (focusing primarily upon bioaccumulative potential and monitoring trends). This is accomplished by gathering and interpreting monitoring data in key locations, compartments and links within the Arctic food web. Finally, the residues profile within both abiotic and biotic compartments is considered within an ecotoxicological and human health risk context. Development of clear and consistent profiles is important when considering attribution as a potential POP. The primary conclusions of this research exercise are summarised, in brief, below.

Temporal Trends	
Air	<p>Long-term continuous air sampling is available for comparatively few sites of which Alert in the Canadian high Arctic provides by far the most significant and highest value dataset. On the basis of this high quality database the following conclusions are made:</p> <ul style="list-style-type: none"> • The temporal trend in endosulfan residues in the air in the Arctic appears to be stable in agreement with its actual use between 1990 and 2000. • A distinctive seasonal profile (summer reductions in α-endosulfan concentrations with spring and fall peaks) probably result from a combination of complex environmental fate processes described by Hung, et al. (2002). • Significant seasonal variation in air residues is noted with summer reductions in α-endosulfan levels of between a factor of 3-5 relative to spring and fall peaks. • The seasonal profile probably results through a combination of

	<p>processes ranging from enhanced photochemical depletion with the onset of polar sunrise to scavenging via vegetation ('forest filter effect') during long-range transport (consistent with Hung, et al., 2002).</p>
Seawater	<p>The available seawater monitoring database does not constitute a robust enough database that would allow firm conclusions to be made regarding temporal trends. The following issues were highlighted as being of specific concern as deficiencies in the available database:</p> <ul style="list-style-type: none"> • The almost complete reliance on monitoring during summer months in ice-free areas has additional implications regarding understanding environmental fate in the Arctic as it is not possible to evaluate seasonal variation due to shut down of the air-sea gas exchange process whilst the ice pack is present.
Snow	<p>A survey of glacial firn and ice in the Norwegian Arctic revealed the potential for accumulation of SVOCs including α- and β-endosulfan:</p> <ul style="list-style-type: none"> • The accumulation profile for the last 50 years reveals that input of endosulfan was higher in the past, although significant post-depositional migration during snow-to-ice metamorphism may obscure this profile.
Biota	<p>Detailed analysis of temporal trends in biota was not possible due to the absence on long-term, site-specific monitoring campaigns for which data was available for detailed re-interpretation. However, in one study (Stern and Ikonomou, 2003) it was concluded that endosulfan sulfate residues were increasing in male beluga whales from the Canadian Arctic. There remain significant uncertainties surrounding analytical differences between this study and a more recent study conducted by Kelly (2005) which suggest lower endosulfan residues may be present when analysis is conducted by GC-MS.</p> <ul style="list-style-type: none"> • Difficulties with interpretation of biota measurements arise due to former reliance on GC-ECD with associated potential for analytical interference. In particular, differences between the GC-ECD and GC-MS results reported by Kelly (2005) and Stern and Ikonomou (2003) warrant further investigation. • Residues of α-endosulfan were significantly higher in whales from the North Sea, potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species.
Spatial Trends	
Air	<p>The NCP (Northern Contaminants Programme) air monitoring station in Alert in the Canadian high Arctic is the most most robust dataset available, although additional monitoring has been conducted at sites in the Canadian sub-Arctic, western Siberia and in Norway. Despite the very limited network of long-term, continuous air monitoring sites available in the Arctic it has been possible to exploit certain databases with a view towards identifying source regions that contribute most significantly to airborne residues at specific locations.</p> <ul style="list-style-type: none"> • The mean levels are very low amounting to approximately < 1 – 15 pg/m³
Seawater	<p>The assembled database of seawater monitoring suggests that most sectors of the Arctic are included with the Bering Sea, Beaufort Sea, Canadian Archipelago particularly well-represented. It is noteworthy that there is a relatively high degree on analytical consistency in seawater monitoring results.</p> <ul style="list-style-type: none"> • Endosulfan concentrations in seawater were typically approximately < 1 – 10 pg/L <p>The following significant limitation was highlighted:</p> <ul style="list-style-type: none"> • The Central Asian Arctic (where several large Asian rivers such as the Ob, Yenisey and Lena Rivers discharge) is poorly represented, presenting uncertainties regarding potential riverine routes of

	entry for endosulfan into the Arctic.
Snow	<p>Spatial trends in snow and ice are difficult to determine due to the high variability in snow concentrations.</p> <ul style="list-style-type: none"> • In the Canadian Arctic the two most northerly sample sites, with the coldest air temperatures displayed the widest range in concentrations with higher average concentrations than sites located further south. • However, higher rates of precipitation experienced at the more southerly stations result in similar depositional fluxes across the Canadian Archipelago.
Biota	<p>Spatial variation in residues of α-endosulfan in biota was specifically considered for ringed seal blubber and minke whales.</p> <ul style="list-style-type: none"> • In ringed seals, the highest concentrations of α-endosulfan were found in the western Canadian Arctic and at Barrow, Alaska. • There appears to be no reliable relationship to endosulfan concentrations in seawater. • Residues of α-endosulfan were significantly higher in whales from the North Sea potentially reflecting a 'near source' influence and highlighting potential confounding influences for migratory species.
Transport Mechanisms and Environmental Fate	
Air	<p>Key studies conducted in the Canadian sub-Arctic (Tagish, Yukon) have been interpreted with air mass back trajectories to assess potential sources of contaminants into the western Canadian Arctic and other Canadian monitoring locations.</p> <ul style="list-style-type: none"> • This research indicates that continental/southerly air masses in North America are likely to be more significant contributors to Arctic contamination than Asian sources. • Attribution of source regions for endosulfan arriving in Arctic regions of eastern North America, Europe and Asia remains uncharacterised.
Seawater	<ul style="list-style-type: none"> • There are no clear geographical trends that may suggest, for example, that transport from the Pacific Ocean through the Bering and Chukchi seas may be occurring. • Under certain circumstances water monitoring results have been found to be highly variable and it has been suggested that this may reflect local influences such as entry of meltwater.
Air-water exchange	<p>Despite problems with availability of a network of long-term air monitoring sites and the lack of air monitoring data for the β-isomer, there appear to be significant regional differences in air-sea gas exchange behaviour for α-endosulfan.</p> <ul style="list-style-type: none"> • A net air to seawater exchange appears to dominate in some locations (Barrow, Beaufort and White Seas, Baffin Bay and the Canadian Arctic Archipelago) but is reversed at others (Bering/Chukchi Seas, Western Arctic Ocean, Greenland Sea), highlighting uncertainties of the trace levels detects in air and water and a potential seasonal sensitivity to ice pack conditions. • When taken together, the compounded uncertainties associated with low level analysis in seawater, reliance on a very limited set of air sampling campaigns, the lack of availability of a temperature dependent Henry's law constant and the influence of 'salting out', suggest that a high degree of caution must be exercised in interpretation and attribution of behaviour as evidence of POP characteristics.

Residue Transfer	
Trophic magnification potential	<p>Trophic magnification profiles from three of the four sites for which sufficient data was available to allow analysis (Barrow, Lake Superior, and White Sea) suggest that there is no significant relationship between measured concentration and trophic level for either α-endosulfan or lindane. The evidence for the remaining site (Holman) is ambiguous.</p> <ul style="list-style-type: none"> • It is concluded that α-endosulfan does not exhibit clear trophic magnification potential that is a classical characteristic of a POP.
Biomagnification potential	<p>There are no biomagnification factor (BMF) triggers within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs. BMF values of > 10 may also be of consistent concern with thresholds established for BAF (bioaccumulation factor).</p> <ul style="list-style-type: none"> • An average fish to mammal BMF value (10.2) needs to be interpreted recognising a very high degree of variability (± 16.4) and therefore, uncertainty. On this basis it is not possible to conclude with any certainty whether there is potential for biomagnification occurring at a scale of potential concern. • There is, however, clear evidence of the absence of biomagnification for invertebrates to fish and fish to predatory fish.
Bioaccumulation potential	<p>Within the framework of the Stockholm Convention (2001) and UN-ECE Convention on POPs concerns are triggered by evidence that the bioconcentration factor (BCF) or bioaccumulation factor (BAF) in aquatic species is greater than 5000 (Log BAF or Log BCF > 3.7).</p> <ul style="list-style-type: none"> • The implications of very high estimated BAF values (ranging from 3.4×10^3 to 2.6×10^7) are unclear. Uncertainties on intermediate micro-organism trophic level and low ambient temperature conditions in the Arctic may increase bioaccumulation by reducing metabolism potential. • The influence of low temperature on increasing bioaccumulation under Arctic conditions by reducing metabolism potential has been postulated. There is, however, insufficient data to confirm this for endosulfan, although the possibility is considered in studies for other compounds (Buckman et al., 2004).
Ecotoxicological and Human Risk Profiles	
Ecotoxicological risk	<p>A relatively robust evaluation of ecotoxicological risks has been facilitated through access to a very large database of effects studies.</p> <ul style="list-style-type: none"> • There is essentially negligible risk to marine organisms from acute and chronic exposures to endosulfan residues in Arctic marine systems. • The toxicity value for the most sensitive animal was about three orders of magnitude greater than the highest measured concentration for Arctic marine waters. • There is similarly a negligible risk to terrestrial animals from exposures to endosulfan residues.
Human dietary risk	<p>A probabilistic human dietary risk assessment was based upon i) a US EPA Reference Dose (RfD) and ii) limited dietary component analyses carried out in the Arctic (Greenland and Russia).</p> <ul style="list-style-type: none"> • Human dietary risk was concluded to be generally negligible

	except with unrealistic, extreme worst-case assumptions (coincidence of very heavy reliance upon locally sourced food items drawing heavily upon marine mammals and fish characterised by 99th centile endosulfan residue profiles).
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Based on stable endosulfan levels in the environment, the virtual absence of trophic magnification and biomagnification in the food chain, a negligible ecological risk to marine mammals and a negligible human dietary risk, concerns of adverse effect to human health and the environment cannot be demonstrated that may suggest a classification as a POP.

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11 Glossary of Terms and Abbreviations

$\delta^{13}\text{C}$	$^{13}\text{C}/^{12}\text{C}$ stable isotope ratio.
$\delta^{14}\text{N}$	$^{15}\text{N}/^{14}\text{N}$ stable isotope ratio.
ΣDDT	Sum of DDT, DDD, and DDE (concentrations).
ΣHCH	Sum of (concentrations of) α -, β -, and γ -HCH isomers.
ΣPCB	Sum of a number of individual polychlorinated biphenyl (PCB) congeners. A method of expressing the PCB content of a sample by measuring and summing the quantities of specific PCB congeners. The number and identification of the congeners determined varies from laboratory to laboratory and for different types of samples. It is generally given in explanatory notes. (See also Total PCB).
ADI	Acceptable Daily Intake.
AK	Alaska
AMAP	Arctic Monitoring and Assessment Programme (Arctic Council Working Group).
Beaufort Gyre	Major current system in the Arctic Ocean: clockwise surface circulation in the Beaufort Sea.
BERPAC	BERing PACific Russia/US Cooperative Research Program
Bioaccumulation	<p>This is the process by which the chemical concentration in an aquatic organism achieves a level that exceeds that in the water, as a result of chemical uptake through all possible routes of chemical exposure (e.g., dietary absorption, transport across the respiratory surface, dermal absorption, inhalation).</p> <p>Bioaccumulation takes place under field conditions. It is a combination of chemical bio-concentration and biomagnification (Gobas and Morrison, 2000).</p>
Bioaccumulation Factor	<p>The extent of chemical bioaccumulation factor (BAF), which is the ratio of the chemical concentrations in the organism (C_B) to those in water (C_W):</p> $\text{BAF} = C_B/C_W$ <p>Because chemical sorption to particulate and dissolved organic matter in the water column can reduce substantially the fraction of chemical in water that can be absorbed by aquatic organisms (see discussion on bioavailability), the BAF also can be expressed in terms of the freely dissolved chemical concentration (C_{WD}):</p> $\text{BAF} = C_B/C_{WD}$ <p>Defining BAF this latter way keeps it independent of the concentrations of particulate and dissolved organic matter in the water phase and thus makes it more universally</p>

applicable from site to site.

The chemical concentration in the organism usually is expressed in units of mass of chemical per kg of organism, whereas the concentration in water is expressed in mass per litre. The weight of the organism can be expressed on a wet weight (WW), dry weight (DW), or lipid weight (LW) basis.

Most commonly, the weight of the organism is expressed on a wet weight basis, and the units of the BAF are L/kg. However, when concentration measurements are made in specific tissues of the organism (rather than the whole organism), it is preferable to report the concentration on a lipid weight basis, as organs and tissues can vary substantially in their lipid content. The lipid content is an important factor controlling the extent of chemical bioaccumulation of organic substances (Gobas and Morrison, 2000).

Bioavailability

Definitions of chemical bioavailability vary widely among environmental chemists, pharmacologists, physiologists, and ecologists. In this chapter, bioavailability of a chemical substance in a particular environmental media such as water, sediment, and food is defined as “the fraction of chemical in a medium that is in a state which can be absorbed by the organism.” Bioavailability is expressed as a fraction or a percentage and is specific to the medium and route of exposure (Gobas and Morrison, 2000).

Bioconcentration

The process in which the chemical concentration in an aquatic organism exceeds that in water as a result of exposure to waterborne chemical. Bioconcentration refers to a condition, usually achieved under laboratory conditions, where the chemical is absorbed only from the water via the respiratory surface (e.g., gills) and/or the skin (Gobas and Morrison, 2000).

Bioconcentration Factor

Bioconcentration can be described by a bioconcentration factor (BCF), which is the ratio of the chemical concentration in an organism (C_B) to the concentration of water (C_W):

$$BCF = C_B/C_W$$

The BCF, like the BAF, also can be expressed in terms of the dissolved chemical concentration (C_{WD}). The concentration in biota is expressed as wet weight (ww) or lipid weight (lw).

$$BCF = C_B/C_{WD}$$

(Gobas and Morrison, 2000).

Biomagnification

This is the process in which the chemical concentration in an organism achieves a level that exceeds that in the organism's diet, due to dietary absorption. The extent of chemical biomagnification in an organism is best determined under laboratory conditions, where organisms are administered diets containing a known concentration of chemical, and there is no chemical uptake through other exposure routes (e.g., respiratory surface, dermis).

Biomagnification also can be determined under field conditions, based on chemical concentrations in the organism and its diet. Biomagnification factors derived under controlled laboratory conditions, which exclude uptake through routes other than diet, are different from those determined under field conditions, because field-based biomagnification factors are inevitably the result of chemical uptake by all routes of chemical uptake, rather than dietary absorption alone (Gobas and Morrison, 2000).

Biomagnification Factor

Biomagnification can be described by a biomagnification factor (BMF), which is the ratio of the chemical concentration in the organism to the concentration in the organism's diet:

$$BMF = C_B/C_D$$

The chemical concentration of the organism (C_B) and the diet of the organism (C_D) usually are expressed in units of mass of chemical per kg of the organism and mass chemical per kg of food, respectively. Again the weight of the organism and food can be expressed on a wet weight (WW), dry weight (DW), or lipid weight (LW) basis. Most commonly, the weight of the organism is expressed on a wet weight basis (Gobas and Morrison, 2000).

DDE

1,1-dichloro-2,2-bis (4-chloro-phenyl) ethylene.

DDT

Dichlorodiphenyltrichloroethane (an organochlorine pesticide).
1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane.

Dry deposition

Delivery of airborne contaminants to the surface by particle fallout, diffusion, and air movements (including irregular air movements in the turbulent boundary layer close to the ground and diffusion through the laminar surface layer).

dw

Dry weight – basis of determination of concentration.

EC₅₀

Effective concentration causing a response in 50% of the treated organisms.

Endosulfan

Insecticide of the type sulfite diester of a chlorinated cyclodiene with the IUPAC nomenclature 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide.

Endosulfan is a mixture of two stereoisomers; α -endosulfan and β -endosulfan. Alpha-endosulfan, also referred to as Endosulfan (I) comprises 64-67% of the technical grade endosulfan with the remainder as beta-endosulfan, or Endosulfan (II).

The α -isomer is asymmetrical, and the β -isomer is the symmetrical structural form.

Endosulfan sulfate

Principal metabolite of endosulfan.

FAV

Final Adjusted Value: A set of physico-chemical properties was adjusted in such a way that they conform to thermodynamic constraints yet deviate as little as possible

from the original values.

Firn	Rounded, well-bonded snow that is older than one year. Firn has a density greater than 550 kg/m ³ (35 lb/ft ³). Also called névé.
Food web	A series of interconnected food chains.
Fram Strait	Strait between Greenland and Svalbard; major exit route for water and ice exiting the Arctic Ocean.
HCB	Hexachlorobenzene.
HLC	Henry's Law constant.
HCH	Hexachlorocyclohexane (organochlorine insecticides; including the γ -HCH isomer, lindane).
Isomer	Member of a group of molecules with the same empirical formula, however with a different sequence or different spatial arrangement of the atoms.
IUPAC	International Union of Pure and Applied Chemistry.
K_{ow}	Partitioning coefficient between octanol and water (also referred to as P _{ow}).
LRTAP	(UN-ECE Convention on) Longrange Transboundary Air Pollution.
MDL	Method Detection Limit
MS	Mass spectrometer.
lw	Lipid weight - – basis of determination of concentration.
NWT	Northwest Territories, Canada (former abbreviated designation).
NT	Northwest Territories, Canada.
OC	Organochlorine.
Oden	<i>Oden</i> is one of seven icebreakers operated by the Swedish Maritime Administration. Icebreaker <i>Oden</i> is designed for escort ice-breaking and for Arctic research operations.
OSPAR	Oslo and Paris Convention for the Protection of the Marine Environment of the North East Atlantic, 1992.
OSPARCOM	Oslo and Paris Commissions and pollution.
PAH	Polyaromatic hydrocarbon.
PCBs	Polychlorinated biphenyls.
Plankton	Animals and plants, many of them microscopic, that float or swim very weakly in fresh- or salt water bodies. They are moved passively by winds, waves or currents.

Polynya	Open water regions, ranging in area up to thousands of square kilometers, that persist within closed sea-ice cover.
POP	Persistent organic pollutant.
P_{ow}	Partitioning coefficient between octanol and water (also referred to as P _{ow}).
PUF	Polyurethane foam plug.
r²	Coefficient of correlation.
RfD	Reference dose employed in dietary risk assessment based upon mammalian toxicological endpoints.
SD	Standard deviation.
SE	Standard error.
Stockholm Convention	Global treaty of UNEP to protect human health and the environment from persistent organic pollutants (POPs). In implementing the Convention, Governments will take measures to eliminate or reduce the release of POPs into the environment.
SVOC	Semi-Volatile Organic Chemical
SWE	Snow Water Equivalents
TL	Trophic Level (quantitative representation of position within the food chain).
TGD	Technical Guidance Document
Total PCB	An (older) method for expressing the PCB content of a sample in which the sample is quantitated against a technical PCB product (such as Aroclor 1254) as the standard. The analysis is carried out using packed column chromatography. Also termed PCB on a formulation basis.
Toxaphene	Polychlorobornanes and camphenes.
Transpolar Drift	Major current system in the Arctic Ocean: surface current traversing the Arctic Ocean from the Chukchi Sea to the North Greenland Sea. (See also Beaufort Gyre.)
Trophic Magnification Factor	Trophic magnification factors (TMFs) are a means of representing the extent of trophic transfer of chemicals. TMFs can be calculated as $TMF = 10^B$ where B = slope of the regression of log [endosulfan lipid wt] vs Trophic Level (TL). Trophic Level (TL) is characterised by stable isotope analysis. Samples of whole zooplankton and muscle tissue of various fish and marine mammals are analysed for both stable isotope ratios, such as ¹⁵ N/ ¹⁴ N and ¹³ C/ ¹² C. These ratios are increased in succeeding trophic levels as a consequence of metabolic transformations and provide a means of quantifying the trophic position in the food chain. TMF values are mathematically equivalent to results reported as food web magnification factors (FWMFs) by Fisk <i>et al.</i> (2001), Hoekstra <i>et al.</i> (2003) and Muir <i>et al.</i> (2003). TMFs

significantly >1 imply biomagnification. The use of TMFs makes possible comparisons among food webs and chemicals that incorporate the entire food chain rather than merely predator-prey relationships used to calculate Biomagnification factors (BMFs). TMFs represent the average increase in bioaccumulative contaminant concentration in food webs rather than the variability shown between species and compounds in BMF which represent only specific predators (Borga *et al.*, 2004).

UBA	Umweltbundesamt (Federal Environment Agency, Germany).
UN ECE	United Nations Economic Commission for Europe.
UNEP	United Nations Environment Programme
Wet deposition	Delivery of airborne contaminants to the surface as a result of their incorporation into rain or snow which subsequently falls to the ground.
ww	Wet weight - basis of determination of concentration.

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APPENDIX 1 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Bearded Seal (*Erignathus barbatus*)

The following overview has been abstracted from the Alaska Department of Fisheries and Game and the Digital Collection Programme of Industry Canada. The bearded seal inhabits areas of the Bering, Chukchi, and Beaufort seas where sea ice forms during the winter. Inuit who speak the Yupik and Inupik languages (Alaska) refer to this seal as *mukluk* and *oogruk*, respectively. The Inuktitut name (eastern Arctic Canada) is *ugyuk*.

General Description: Bearded seals are heaviest during winter and early spring when they may attain a weight of more than 341 kg. From June through September adults usually weigh from 216 to 239 kg. This seasonal loss of weight results from decreased feeding during spring and summer and is most obvious in changes of the thick layer of blubber under the skin. Measured from nose to tip of tail (not including hind flippers), adults average about 2.4 m. Colour varies from a tawny-brown or silver-gray to dark brown (See Figure 1). Unlike other Alaska seals, adult bearded seals have neither spots nor bands. They have comparatively long whiskers (mystacial vibrissae), rounded foreflippers of which the middle one of the five digits is longest, relatively small eyes, and four mammary teats rather than two as on other Alaska seals. Bearded seals normally have 34 teeth—six incisors on the upper jaw and four on the lower, two canines upper and lower, eight postcanines on upper and eight lower, and two molars on the upper and two on the lower jaw. Teeth are small and their wear is rapid; most bearded seals older than 9 years appear toothless, although roots persist beneath the gum line.



Figure 1 Bearded seal (Digital Collection Programme, Industry Canada)

Life history: Females bear a single pup, usually during late April or early May. The average weight of pups at birth is around 34 kg, and average length is about 1.3 m. By the end of a brief nursing period lasting from 12 to 18 days, pups increase their weight almost three times, to around 86 kg. This gain is due mainly to an increase in thickness of the blubber layer.

Most females breed again within two weeks after their pup has been weaned. Embryonic development is delayed for 2½ months after conception, until mid- to late

July when implantation occurs and the embryo begins to develop rapidly. The reproductive cycle is annual and the gestation period is about 11 months, including the period of delayed implantation.

Some female bearded seals begin to ovulate at 3 years of age, but reproductive maturity (the ability to conceive successfully) is not attained until they are 5 or 6 years old. Males become sexually mature at 6 or 7 years. Bearded seals commonly become reproductively active before they attain maximum growth. The incidence of pregnancy in adult females is about 85 percent, and the sex ratio of Alaska samples consistently shows slightly more females in the population.

Food habits: Bearded seals eat a wide variety of invertebrates and some fishes found in and on the rich bottom of the shallow Bering and Chukchi seas. The main food items are crabs, shrimp, clams and snails.

Seasonal movements and distribution: Bearded seals usually are solitary animals. They make seasonal migrations as they follow the movement of sea ice. The density of animals in a given area varies widely. In late winter, when ice occupies a large area of the northern seas, bearded seals are widely dispersed. During their northward spring migration through the constricted waters of Bering Strait and during late summer when sea ice has receded to the Arctic Ocean they are more concentrated. Adult bearded seals are almost always associated with ice, but young seals sometimes remain in ice-free areas where they frequent bays and estuaries.

Behavior: Bearded seals vary in their alertness or wariness depending upon the time of year. In the spring when they are basking on the ice, bearded seals frequently show little concern about the presence of a boat or humans. One might judge that this seal's senses of sight, smell, and hearing are very poor. In fact, bearded seals have good vision and hearing, and at least a fair sense of smell. During late fall when boats are used in the hunt, it is common to see a bearded seal surface several hundred yards from a boat, trying hard to identify the source of disturbance. During winter hunts on the ice, the slightest sound of a hunter will cause a seal to flee amidst a mighty splash of water. A hunter must remain well hidden, and if exposed, move very slowly so as not to alarm the seal. It is a common occurrence to see a bearded seal surface, immediately dive and resurface far out of effective rifle range, obviously aware of something strange in the vicinity.

Judging by the number of freshly scarred adults taken by hunters during May and June, fighting is very common during the breeding season. With imagination, it is easy to misinterpret the cause of these wounds and attribute them to a bearded seal's desperate struggle to escape from the grasp of a polar bear. Polar bears do eat bearded seals, but the number of bears present in central Bering Sea is relatively small, while the incidence of adults with fresh scars during the spring is high.

During April, adult male bearded seals begin underwater "singing." The song is a highly characteristic and complex frequency-modulated whistle, parts of which are audible to humans. Hunters are sometimes guided to a seal by its whistle. Singing males are designated by the Inuit word *au-uk-touk*.

Hunting: Residents of western coastal villages depend upon bearded seals and other seals for hides and a large part of their food. Bearded seal meat is the most desirable of the seals, and the hides are necessary for boat covers, raw-hide line, boot soles, and numerous other uses. Bearded seals are hunted whenever they are available. Spring hunts (which coincide with the northern migration of seals) are the most successful. In the spring, boats can be used to hunt in the loose drifting ice.

Productive bearded seal hunting begins during late April in the northern Bering Sea area and is progressively later at the more northerly villages.

APPENDIX 2 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Ringed Seal (*Phoca hispida*)

The following overview has been abstracted from the Alaska Department of Fisheries and Game and the Digital Collection Programme of Industry Canada. Ringed seals (*Phoca hispida*) are the most common and most widespread seals in the arctic. In Alaska, ringed seals inhabit the northern Bering, Chukchi and Beaufort seas. They have been found as far south as the Aleutian Islands. During winter, ringed seals are most abundant close to shore in the shorefast ice. As a result they have been important in the economy of the coastal Inuit as a source of food and usable products. Inupiat Inuit refer to the ringed seal as *natchek*; to the Yupik-speaking Inuit of the Bering Strait it is *niknik*.

General description: Ringed seals are the smallest of all pinnipeds (seals, sea lions, and walruses) with adults in Alaska rarely exceeding 1.5 meters in length and 68 kg in weight. Ringed seals weigh the most in the winter and early spring when they have a thick layer of blubber under their skin. The blubber serves as insulation and as an energy source during the breeding and pupping season. The weight of ringed seals declines with the decrease in feeding during the reproductive and molting season.

The colouration of ringed seals is quite variable, but the basic pattern is a gray back with black spots and a light belly (See Figure 1). The seal gets its name from the black spots ringed with light marks.



Figure 1 Ringed seal (Digital Collection Programme, Industry Canada)

Food habits: Ringed seals eat a variety of invertebrates and fish. The particular species eaten depends on availability, depth of water, and distance from shore. In Alaska waters, the important food species are arctic cod, saffron cod, shrimps, and other crustaceans.

Life history: Females give birth to a single, white-coated pup in snow dens on either landfast or drifting pack ice during March and April. Female seals build lairs in pressure ridges or under snowdrifts for protection from predators and severe weather. There is some evidence that females lacking maternal experience give birth in marginal habitat—drifting pack ice—and may be more subject to polar bear

predation. More experienced females give birth in the better habitat—landfast ice—and may have higher reproductive success.

The average weight of pups at birth is 4.5 kg. Females nurse pups for about two months and during that time the pup doubles its birth weight. Increasing blubber thickness provides the pup with insulation to reduce heat loss and an energy reserve to use while it learns to find its own food. Weaning usually takes place at ice breakup.

Most females breed again within a month after the birth of the pup. Implantation of the embryo is delayed until mid-July or early August. Pregnancy lasts about 11 months. Most female ringed seals first ovulate at 5 or 6 years of age and first give birth at 6 to 8 years old. Males become sexually mature at the same age.

Migration and distribution: Ringed seals generally occur in association with sea ice; however, some ringed seals are seen during ice-free periods in the Bering and Chukchi seas. Seals appear at various coastal locations with the formation of shorefast ice in the fall. They disappear in the spring with the ice breakup. Seals wintering in the Bering Sea probably summer in the northern Chukchi Sea or Arctic Ocean. The density of ringed seals varies greatly with the area and the season. In addition to humans, predators of ringed seals include polar bears (the chief predator), arctic and red foxes, walruses, dogs, wolves, wolverines, and ravens. Arctic foxes and polar bears can locate seal lairs by their smell. During pupping, they enter the lairs in an effort to kill and eat the pups.

Behavior: Ringed seals emit several types of vocalizations underwater which are not readily audible above water. The function of these calls is unknown. The behavior of ringed seals is poorly understood since both males and females spend the greater part of the year in lairs or in the water. Ringed seals molt in May and June. During this time they spend long periods hauled out on the ice “basking” in the sun. It is thought that warmer skin temperatures cause the new hair to grow more quickly. When hauled out on the ice, ringed seals are very wary, raising their heads every 20 seconds or so to look around. They rapidly enter the water when they detect an approaching human or other predator. Male ringed seals may be territorial during the breeding season.

Hunting: Ringed seals are hunted by Alaska coastal residents from Mekoryuk to Kaktovik for human and dog food and skins for clothing, equipment, and crafts. Several thousand seals are harvested annually.

APPENDIX 3 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Bowhead whale (*Balaena mysticetus*)

General description: The bowhead whale is an Arctic baleen whale, a right whale with a large, bow-shaped head that is up to 40% of its body length. The arched mouth is up to 3 m wide and 6 m deep. The eyes are very small and lips are huge. Bowheads live in pods, are rich in blubber (up to 50 cm subcutaneous layer), and have 2 blowholes. The bowhead whale's skin is usually black with a white spot on the lower snout. Calves are blue to gray coloured. Bowheads have no dorsal fin and no throat grooves. Bowhead whales are not extremely social and congregate in small pods of about 3 whales in the spring and pods of about 50 whales in the fall. They have short, narrow flippers; the flukes are 8.1 m wide. See Figure 1.

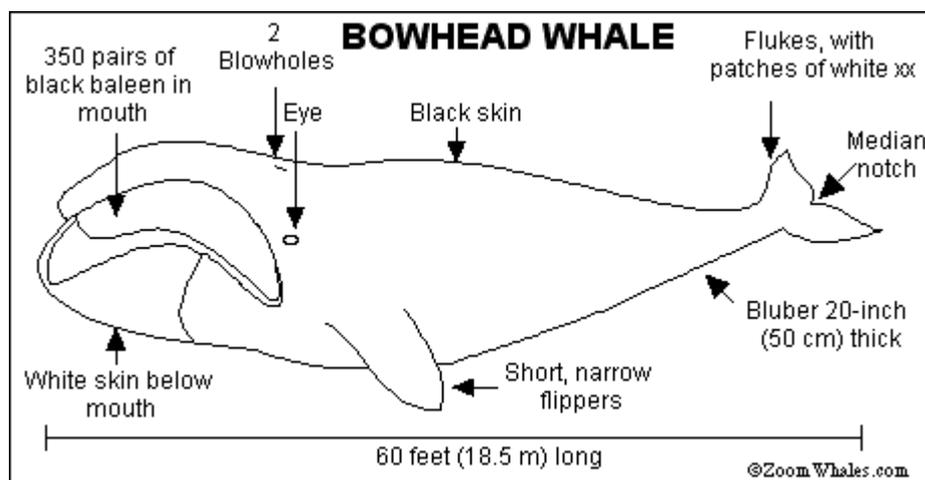


Figure 1 Bowhead whale

Size: Bowhead whales grow to be about 15-18.5 m long, weighing over 72-91 tonnes. The females are slightly larger than males, as with all baleen whales.

Diet: Bowhead whales (like all baleen whales) are seasonal feeders and carnivores that filter feed plankton and tiny crustaceans like krill, copepods, pteropods, etc., from the water. Bowheads are skimmers, filter feeders that swim slowly with their mouth open, constantly eating. On occasion, they are also bottom feeders, eating benthic prey from the mud on the ocean floor. The fine baleen hairs can filter out very tiny prey including copepods, steropods, euphasids and mysids.

Migration: Bowhead whales stay in Arctic waters, making a northern migration in the spring to rich feeding waters. They migrate south again in the fall to breed and calve.

Reproduction: The bowhead gestation period is about 12-16 months and the calf is born tail first (this is normal for cetaceans) and near the surface. The newborn instinctively swims to the surface within 10 seconds for its first breath; it is helped by its mother, using her flippers. Within 30 minutes of its birth the baby whale can swim. The newborn calf is about 5 m and weighs about 4.5-5.4 tonnes. Twins are rare; there is usually one calf. The baby is nurtured with its mother's milk and is weaned in about 1 year. The mother and calf may stay together for a year or longer. Bowhead whales reach puberty at 6 years.

APPENDIX 4 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Beluga whale (*Delphinapterus leucas*)

General description: The beluga whale (meaning 'white one' in Russian) is a small, toothed whale that is white as an adult. The beluga's body is stout and has a small, blunt head with a small beak, tiny eyes, thick layers of blubber, and a rounded melon. They have one blowhole. It belongs to the genus *Delphinapterus*, meaning "whale without fins". The species, *leucas*, refers to the white colouration. Unlike most other cetaceans, the beluga's seven neck vertebrae are not fused, giving it a flexible, well-defined neck. See Figure 1.

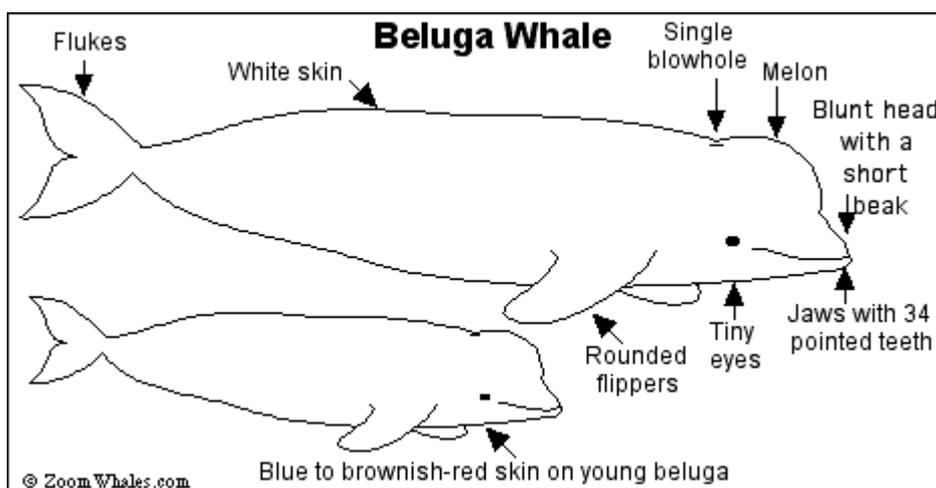


Figure 1 Beluga whale

Size: Beluga whales grow to be about 4.6 m long on average, weighing up to about 1,500 kg. Males are slightly larger than females.

Diet: Belugas are toothed whales with 34 teeth. The teeth are not designed for chewing, but for grabbing and tearing prey. They swallow their prey whole. They are opportunistic feeders, eating a varied diet of fish, squid, crustaceans, octopi and worms. They are both benthic (bottom) and pelagic (oceanic) feeders (in shallow water). Belugas sometimes hunt schools of fish cooperatively in small groups. An adult beluga will eat about 2.5% to 3% of its body weight per day, or 25 kg of food a day, or more.

Migration: Belugas live in frigid Arctic and sub-Arctic waters, but some populations migrate south to warmer water in the summer. Beluga's Arctic habitat overlaps with narwhal habitat (its closest relative). Belugas also travel up northern rivers into brackish (partly salty) water and estuaries (where a river meets the seas) to hunt prey during the summer. Belugas sometimes migrate with bowhead whales.

Reproduction: The gestation period of the beluga is about 14-15 months and the calf is born tail or head first and near the surface in warm, shallow waters. They breed in warm, shallow waters or estuaries (where rivers meet seas). The newborn instinctively swims to the surface within 10 seconds for its first breath; it is helped by its mother, using her flippers. The newborn calf is about 1.2-1.5 m long and weighs over 45-64 kg. Single births are the norm; twins are very rare. Calves are not white like the adults; they are blue to brownish-red for the first year of life. During the

second year they are gray to blue. Their pigment (melanin) fades slowly, and by 6 years old, they are white. The baby is nurtured with its mother's fat-laden milk (it is 28% fat) and is weaned in about 12-24 months. Beluga whales reach maturity at 7-9 years.

APPENDIX 5 – Illustrative Profiles of Organisms in Arctic Marine Food Web –Capelin (*Mallotus vallosus*)

Information summarised from www.fishbase.org

Family:	<u>Osmeridae</u> (Smelts)
Order:	<u>Osmeriformes</u> (smelts)
Class:	Actinopterygii (ray-finned fishes)
Max. size:	20.0 cm TL (male/unsexed); 25.2 cm TL (female); max. reported age: 5 years
Environment:	pelagic; oceanodromous; freshwater; brackish; marine ; depth range 0 - 300 m
Climate:	polar; 74°N - 34°N, 180°W - 180°E
Importance:	fisheries: highly commercial
Resilience:	Medium, minimum population doubling time 1.4 - 4.4 years (K=0.3-0.5; tm=3; tmax=5; Fec=6000)
Distribution:	Circumpolar in the Arctic. North Atlantic: Barents Sea up to Bear Island, in the White and Norwegian seas, off the coast of Greenland up to 74°N and from Hudson Bay in Canada to Gulf of Maine, USA. North Pacific: south to Korea and Juan de Fuca Strait, Canada.
Morphology:	<u>Dorsal spines</u> (total): 0; <u>Dorsal soft rays</u> (total): 10-14; <u>Anal spines</u> : 0; <u>Anal soft rays</u> : 16-23; <u>Vertebrae</u> : 62-73. Adipose with long base, about 1.5 times as long as the orbit or longer, outer margin only slightly curved – See Figure 1. Olive green on dorsal surface, merging into silvery on sides and ventral surface.



Figure 1 Capelin (*Mallotus vallosus*). Illustration taken from the book "Encyclopedia of Canadian Fishes" by Brian W. Coad with Henry Waszczuk and Italo Labignan, 1995, courtesy of the Canadian Museum of Nature

Biology:	Oceanic species found in schools. Feeds on planktonic crustaceans, copepods, euphausiids, amphipods, marine worms, and small fishes. Moves inshore in large schools to spawn. In the spring large spawning shoals migrate toward the coasts, males usually arrive first. Often entering brackish and freshwater. Produces 6,000-12,000 adhesive eggs. Females are valued for their roe, males are utilized as fishmeal. Marketed canned and frozen; eaten fried and dried. Possibly to 725 m depth.
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APPENDIX 6 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Polar cod (*Arctogadus glacialis*)

Information summarised from www.fishbase.org

Family:	<u>Gadidae</u> (Cods and haddocks)
Order:	<u>Gadiformes</u> (cods)
Class:	Actinopterygii (ray-finned fishes)
Max. size:	32.5 cm TL (male/unsexed)
Environment:	bathypelagic; non-migratory; marine ; depth range 0 - 1000 m
Climate:	deep-water; 85°N - 72°N
Importance:	fisheries: minor commercial
Resilience:	Medium, minimum population doubling time 1.4 - 4.4 years (Preliminary K or Fecundity.)
Distribution:	Arctic and North Atlantic: widely distributed in western part of Arctic basin, also northwest and northeast coasts of Greenland.
Morphology:	<u>Dorsal spines</u> (total): 0; <u>Anal spines</u> : 0. Chin barbels rudimentary or absent. See Figure 1.

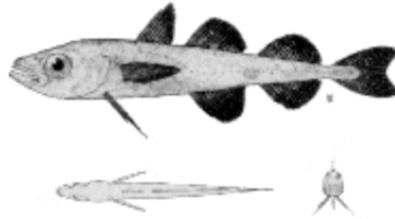


Figure 1 Polar cod (*Arctogadus glacialis*). Illustration taken from the book "Encyclopedia of Canadian Fishes" by Brian W. Coad with Henry Waszczuk and Italo Labignan, 1995, courtesy of the Canadian Museum of Nature

Biology: Associated with ice, found mainly in offshore waters, at or beyond the edge of the continental shelf.

APPENDIX 7 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Arctic char (*Salvelinus alpinus alpinus*)

Information summarised from www.fishbase.org

Family:	<u>Salmonidae</u> (Salmonids) , subfamily: Salmoninae
Order:	<u>Salmoniformes</u> (salmons)
Class:	Actinopterygii (ray-finned fishes)
Max. size:	107 cm TL (male/unsexed); max. published weight: 15.0 kg; max. reported age: 40 years
Environment:	benthopelagic; anadromous; freshwater; brackish; marine ; depth range 30 - 70 m
Climate:	temperate; 4 - 16°C; 85°N - 42°N, 180°W - 180°E
Importance:	fisheries: minor commercial; aquaculture: commercial; gamefish: yes
Resilience:	Low, minimum population doubling time 4.5 - 14 years (tm=7-10; tmax=24; Fec=400)
Distribution:	Europe: northern Atlantic southward to southern Norway, also Iceland and southern Greenland. Isolated populations in Northern UK, Scandinavia, Finland and the Alps. Landlocked populations in Quebec, Canada and in Maine and New Hampshire in USA.
Morphology:	<u>Dorsal spines</u> (total): 4-5; <u>Dorsal soft rays</u> (total): 8-16; <u>Anal spines</u> : 3-4; <u>Anal soft rays</u> : 7-15; <u>Vertebrae</u> : 62-68. See Figure 1. Distinguished by the presence of 23 to 32 gill rakers, 37 to 75 pyloric caeca and, on the sides and back, pink to red spots, the largest of which are usually larger than the pupil of the eye. Lateral line curves slightly downward from the head. Pelvic fins with axillary process; caudal emarginate. Colour highly variable, depending on location, time of year and degree of sexual development. In general, back is dark, usually rather brown but sometimes with a green cast; the sides are lighter, belly pale; sides and back are liberally sprinkled with pink to red spots, the largest spots along the lateral line usually larger than the pupil of the eye; forward edges of pectoral, pelvic and anal fins, and sometimes the caudal, with a narrow white margin; fins pale in young, dorsal and caudal dark in adults. Spawning adults, especially males, are brilliant orange-red to bright red on the ventral side and on the pectoral, pelvic and anal fins. Young have about 11 dark parr marks on each side. Caudal fin with 19 rays.



Figure 1 Arctic char (*Salvelinus alpinus alpinus*). Illustration courtesy of J. Jensen

Biology: Occurs in deep runs and pools of medium to large rivers, and

lakes. Anadromous forms spend a considerable time of their lives at sea; non-migratory populations remain in lakes and rivers. Freshwater populations feed on planktonic crustaceans, amphipods, mollusks, insects and fishes. Extremely sensitive to water pollution (cold water and oxygen oriented).

APPENDIX 8 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Pink salmon (*Oncorhynchus gorbuscha*)

Information summarised from www.fishbase.org

Family:	<u>Salmonidae</u> (Salmonids) , subfamily: Salmoninae
Order:	<u>Salmoniformes</u> (salmons)
Class:	Actinopterygii (ray-finned fishes)
Max. size:	76.0 cm TL (male/unsexed; max. published weight: 6,800 g; max. reported age: 3 years)
Environment:	demersal; anadromous; freshwater; brackish; marine ; depth range 0 - 250 m
Climate:	subtropical; 21°C; 72°N - 27°N
Importance:	fisheries: highly commercial; aquaculture: commercial; gamefish: yes
Resilience:	Medium, minimum population doubling time 1.4 - 4.4 years (tm=2; tmax=3; Fec=800)
Distribution:	Arctic and Eastern Pacific: Alaska and the Aleutian Islands, drainages from Northwest Territories in Canada to southern California in USA; the Bering and Okhotsk seas. Western Pacific: Russian Federation, eastern Korea and Hokkaido, Japan. Import restricted in Germany (Anl.3 BArtSchV). Occasionally hybridizes with <i>Oncorhynchus keta</i> producing fertile offspring. Asia: Iran.
Morphology:	<u>Dorsal spines</u> (total): 0; <u>Dorsal soft rays</u> (total): 10-15; <u>Anal spines</u> : 0; <u>Anal soft rays</u> : 13-19; <u>Vertebrae</u> : 63-72. See Figure 1. Distinguished by the presence of large black spots on the back and on both lobes of the caudal fin; the young have no parr marks. Body fusiform, streamlined, somewhat laterally compressed; moderately, deeper in breeding males. Mouth terminal, normally very little oblique but greatly deformed in breeding males, with lower jaw enlarged, turned up at tip, mouth unable to close. Adipose fin large; pelvic fins with axillary process. Fish in the sea are steel blue to blue-green on the back, silver on the sides and white on the belly; large oval spots present on the back, adipose fin and both lobes of the caudal fin. Breeding males become dark on the back, red with brownish green blotches on the sides; breeding females are similar but less distinctly coloured.

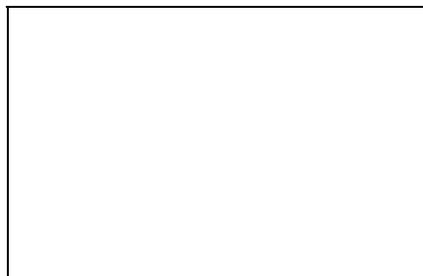


Figure 1 Pink salmon (*Oncorhynchus gorbuscha*). Illustration taken from the book "Encyclopedia of Canadian Fishes" by Brian W. Coad with Henry Waszczuk and Italo Labignan, 1995, courtesy of the Canadian Museum of Nature

Biology:

Spends 18 months at sea after which spawning migration to the natal river or stream occurs; but because the species is less certain of its homing and there is a certain degree of wandering, streams as much as 640 km from natal streams may be used. Upon emerging from the gravel, fry immediately move downstream and remain inshore for a few months before going out to sea. Fry may feed on nymphal and larval insects while in fresh water, but may not feed at all. In the sea, young feed on copepods and larvacean tunicates, its diet shifting to amphipods, euphausiids and fishes as the fish grows. Other food include ostracods, decapod larvae, cirripeds, tunicates, dipterous insects. Fry may be preyed upon by birds and mammals while adults by marine mammals and large fish.

APPENDIX 9 – Illustrative Profiles of Organisms in Arctic Marine Food Web – Fourhorn sculpin (*Myoxocephalus quadricornis* also reported as *Trigloopsis quadricornis*)

Information summarised from www.fishbase.org

Family: Cottidae (Sculpins)
Order: Scorpaeniformes (scorpionfishes and flatheads)
Class: Actinopterygii (ray-finned fishes)
Max. size: 60.0 cm TL (male/unsexed); max. published weight: 260 g; max. reported age: 14 years
Environment: demersal; freshwater; brackish; marine ; depth range 1 - 100 m
Climate: polar; 83°N - 51°N, 5°E - 168°W
Importance: fisheries: subsistence fisheries
Resilience: Low, minimum population doubling time 4.5 - 14 years (tm=3-5; tmax=14; Fec=792)
Distribution: North Atlantic and Arctic: normally above 60°N but reaching 45°N in Nova Scotia. Relict populations in deep and cold freshwater lakes of North America and northern Europe. In Appendix III of the Bern Convention (protected fauna).
Morphology: Dorsal spines (total): 7-9; Dorsal soft rays (total): 13-16; Anal spines: 0; Anal soft rays: 13-17; Vertebrae: 37-42 (see Figure 1). Identified by the four bony protuberances on the top of the head (the protuberances are smaller in females and young and absent in the freshwater form), the chainlike lateral line, the sharp spines on the preoperculum, and the absence of palatine teeth. Gill rakers reduced to rounded, spiny protuberances. Soft dorsal often much enlarged in adult males; caudal truncate to slightly rounded. Young gray above, with three or four dark saddles below dorsal fins and a dark spot on dorsal side of caudal peduncle; adults are darker; spiny dorsal fin dusted with black; soft dorsal, anal, pectoral and caudal fins have dark bars; pelvic fins pale.



Figure 1 Fourhorn sculpin (*Myoxocephalus quadricornis* also reported as *Trigloopsis quadricornis*)- Illustration taken from the book "The Freshwater Fishes of Northwestern Canada and Alaska" The Freshwater Fishes of Northwestern Canada and Alaska. *Fisheries Research Board of Canada Bulletin* 173. 381 pp. McPhail, J.D., and C.C. Lindsey. 1970.

Biology: Occurs in cold brackish and moderately saline water near the coast; enters coastal rivers and may occur as far as 120 miles inland. Movements are limited to short onshore-offshore seasonal movements and mass movements of fry into shallow water in autumn. Moreover, there are no migrations of large numbers; movement into freshwater and long distances up rivers are apparently undertaken by relatively few individuals at a time.

Diurnal from November to April but is largely nocturnal the rest of the year. Feeds on small crustaceans and fishes, also worms. Spawning takes place in shallow waters, male digs a groove in the gravel where pairing and egg laying occur. Move to deeper water in the spring, where they stay in summer.

APPENDIX 10: Aquatic Ecotoxicology Database for Endosulfan

Table 1. Acute Toxicity Data for Endosulfan in Freshwater Animals

Scientific Name	Endpoint	Effect	Test duration (h)	Effect measure (ng/L)	n
Arthropods, FW					
<i>Eucyclops sp.</i>	LC ₅₀	Mortality	48	100	1
<i>Paratelphusa jacquemontii</i>	LC ₅₀	Mortality	96	159	1
<i>Alonella sp.</i>	LC ₅₀	Mortality	48	200	1
<i>Daphnia longispina</i>	LC ₅₀	Mortality	48	300	1
<i>Atalophlebia australis</i>	LC ₅₀	Mortality	72	600	1
<i>Cheumatopsyche sp.</i>	LC ₅₀	Mortality	48	849	2
<i>Cypria sp.</i>	LC ₅₀	Mortality	48	900	1
<i>Amphipoda</i>	LC ₅₀	Mortality	24	1,000	1
<i>Jappa kutera</i>	LC ₅₀	Mortality	96	1,200	1
<i>Macrobrachium lamarrei</i>	LC ₅₀	Mortality	96	3,520	1
<i>Diaptomus sp.</i>	LC ₅₀	Mortality	48	3,550	2
<i>Pteronarcys californicus</i>	LC ₅₀	Mortality	48	3,589	2
<i>Macrobrachium dayanum</i>	LC ₅₀	Mortality	96	4,100	1
<i>Macrobrachium rosenbergii</i>	LC ₅₀	Mortality	96	4,899	2
<i>Gammarus fasciatus</i>	LC ₅₀	Mortality	96	6,062	3
<i>Asellus aquaticus</i>	LC ₅₀	Mortality	24	10,000	1
<i>Eretes sticticus</i>	LC ₅₀	Mortality	48	10,000	1
<i>Sigara alternata</i>	LC ₅₀	Mortality	48	12,300	1
<i>Enallagma sp.</i>	LC ₅₀	Mortality	96	17,500	1
<i>Spicodiptomus chilospinus</i>	LC ₅₀	Mortality	24	44,721	2
<i>Chironomus plumosus</i>	LC ₅₀	Mortality	24	53,000	1
<i>Daphnia magna</i>	LC ₅₀	Mortality	96	54,428	2
<i>Culex pipiens quinquefasciata</i>	LC ₅₀	Mortality	24	66,000	1
<i>Limnephilus sp.</i>	EC ₅₀	Development	24	72,000	1
<i>Ischnura sp.</i>	LC ₅₀	Mortality	120	77,311	4
<i>Procambarus clarkii</i>	LC ₅₀	Mortality	96	100,757	2
<i>Daphnia pulex</i>	LC ₅₀	Mortality	24	300,000	1
<i>Potamonautes sp.</i>	LC ₅₀	Mortality	48	360,000	1
<i>Daphnia carinata</i>	LC ₅₀	Mortality	48	478,000	1
<i>Chironomidae</i>	LC ₅₀	Mortality	24	607,000	1
<i>Aedes aegypti</i>	LC ₅₀	Mortality	24	1,000,000	1
<i>Oziotelphusa senex senex</i>	LC ₅₀	Mortality	96	7,060,041	5
<i>Barytelphusa guerini</i>	LC ₅₀	Mortality	96	17,780,000	1
Fish and amphibians FW					
<i>Carassius auratus</i>	LC ₅₀ *	Mortality	48	100	2
<i>Nematolosa erebi</i>	LC ₅₀	Mortality	96	200	1
<i>Rasbora heteromortalitypha</i>	LC ₅₀	Mortality	96	200	1
<i>Mortalityone saxatilis</i>	LC ₅₀	Mortality	96	253	8
<i>Macquaria ambigua</i>	LC ₅₀	Mortality	96	387	2
<i>Melanotaenia duboulayi</i>	LC ₅₀	Mortality	96	500	1
<i>Tilapia mossambica</i>	LC ₅₀	Mortality	96	508	2
<i>Oncorhynchus mykiss</i>	LC ₅₀	Mortality	96	804	46
<i>Tilapia zillii</i>	LC ₅₀	Mortality	96	826	1
<i>Salmo trutta</i>	LC ₅₀	Mortality	96	900	1
<i>Barbus sophore</i>	LC ₅₀	Mortality	96	912	2
<i>Pimephales promelas</i>	LC ₅₀	Mortality	96	952	15
<i>Heteropneustes fossilis</i>	LC ₅₀	Mortality	96	1,100	1

Table 1. Acute Toxicity Data for Endosulfan in Freshwater Animals

Scientific Name	Endpoint	Effect	Test duration (h)	Effect measure (ng/L)	n
<i>Labeo rohita</i>	LC ₅₀	Mortality	96	1,173	2
<i>Anabas testudineus</i>	LC ₅₀	Mortality	96	1,200	1
<i>Barbus sp.</i>	LC ₅₀	Mortality	24	1,220	1
<i>Cyprinus carpio</i>	LC ₅₀	Mortality	96	1,393	3
<i>Tilapia nilotica</i>	LC ₅₀	Mortality	96	1,420	1
<i>Ictalurus punctatus</i>	LC ₅₀	Mortality	96	1,500	1
<i>Danio rerio</i>	LC ₅₀	Mortality	24	1,600	1
<i>Gymnocorymbus ternetzi</i>	LC ₅₀	Mortality	96	1,600	1
<i>Catla catla</i>	LC ₅₀	Mortality	96	1,636	5
<i>Gambusia affinis</i>	LC ₅₀	Mortality	96	1,729	2
<i>Rana tigrina</i>	LC ₅₀	Mortality	96	1,800	1
<i>Mystus cavasius</i>	LC ₅₀	Mortality	96	1,900	1
<i>Mystus vittatus</i>	LC ₅₀	Mortality	96	2,200	1
<i>Bidyanus bidyanus</i>	LC ₅₀	Mortality	96	2,349	2
<i>Cirrhinus mrigala</i>	LC ₅₀	Mortality	96	2,500	1
<i>Tilapia aurea</i>	LC ₅₀	Mortality	96	2,558	8
<i>Aplocheilichthys johnstonii</i>	LC ₅₀	Mortality	24	2,570	1
<i>Hyphessobrycon bifasciatus</i>	LC ₅₀	Mortality	24	2,600	1
<i>Poecilia reticulata</i>	LC ₅₀	Mortality	96	2,700	1
<i>Catostomus commersoni</i>	LC ₅₀ *	Mortality	120	2,928	4
<i>Scardinius erythrophthalmus</i>	LC ₅₀	Mortality	48	3,347	2
<i>Macragnathus aculeatus</i>	LC ₅₀	Mortality	96	3,500	1
<i>Lepomis macrochirus</i>	LC ₅₀	Mortality	96	3,569	10
<i>Oryzias latipes</i>	LC ₅₀	Mortality	48	3,571	2
<i>Schilbe mystus</i>	LC ₅₀	Mortality	24	5,110	1
<i>Cyprinus carpio communis</i>	LC ₅₀	Mortality	96	5,200	1
<i>Synodontis sp.</i>	LC ₅₀	Mortality	24	5,570	1
<i>Hypophthalmichthys molitrix</i>	LC ₅₀	Mortality	24	5,690	1
<i>Channa punctata</i>	LC ₅₀	Mortality	96	5,769	3
<i>Tilapia sp.</i>	LC ₅₀	Mortality	48	5,900	1
<i>Gasterosteus aculeatus</i>	LC ₅₀	Mortality	48	6,000	1
<i>Clarias batrachus</i>	LC ₅₀	Mortality	96	6,743	4
<i>Channa orientalis</i>	LC ₅₀	Mortality	96	7,326	5
<i>Tilapia sparrmanii</i>	LC ₅₀	Mortality	24	7,350	1
<i>Caridina weberi</i>	LC ₅₀	Mortality	96	7,761	4
<i>Leuciscus idus</i>	EC ₅₀	Mortality	96	9,000	1
<i>Rana limnocharis</i>	LC ₅₀	Mortality	48	12,000	1
<i>Nuria danrica</i>	LC ₅₀	Mortality	120	13,038	2
<i>Anguilla japonica</i>	LC ₅₀	Mortality	48	14,000	1
<i>Barbus conchoniuis</i>	LC ₅₀	Mortality	48	21,360	1
<i>Lepidocephalichthys thermalis</i>	LC ₅₀	Mortality	96	30,000	1
<i>Anguilla anguilla</i>	LC ₅₀	Mortality	96	31,133	10
<i>Cyprinus carpio carpio</i>	LC ₅₀	Mortality	48	33,600	1
<i>Bufo melanostictus</i>	LC ₅₀	Mortality	96	123,000	1
<i>Cambarus sp.</i>	LC ₅₀	Mortality	24	500,000	1
<i>Bufo vulgaris formosus</i>	LC ₅₀ *	Mortality	24	1,946,382	4
<i>Channa striata</i>	LC ₅₀	Mortality	96	4,000,000	1
<i>Rana clamitans</i>	LC ₅₀	Mortality	96	7,431,353	2
Other aquatic animals FW					
<i>Lamellidens marginalis</i>	LC ₅₀	Mortality	96	20,520	3

Table 1. Acute Toxicity Data for Endosulfan in Freshwater Animals

Scientific Name	Endpoint	Effect	Test duration (h)	Effect measure (ng/L)	n
<i>Lamellidens corrianus</i>	LC ₅₀	Mortality	96	31,045	3
<i>Pisidium sp.</i>	LC ₅₀	Mortality	24	607,000	1
<i>Hydra viridissima</i>	LC ₅₀	Mortality	96	670,000	1
<i>Hydra vulgaris</i>	LC ₅₀	Mortality	96	810,000	1
<i>Bellamyia dissimilis</i>	LC ₅₀	Mortality	96	1,800,000	1
<i>Aplexa hypnorum</i>	LC ₅₀	Mortality	96	1,890,000	1
<i>Lymnaea natalensis</i>	LC ₅₀	Mortality	48	4,370,000	1
<i>Brachionus calyciflorus</i>	EC ₅₀	Mortality	165	5,607,264	5
<i>Tubifex tubifex</i>	LC ₅₀	Mortality	24	6,000,000	1
<i>Physella acuta</i>	LC ₅₀	Mortality	48	6,400,000	1
<i>Semisulcospira libertina</i>	LC ₅₀	Mortality	48	7,400,000	1
<i>Cipangopaludina malleata</i>	LC ₅₀	Mortality	48	8,500,000	1
<i>Indoplanorbis exustus</i>	LC ₅₀	Mortality	48	21,000,000	1
<i>Melanopsis dufouri</i>	LC ₅₀	Mortality	96	39,891,812	3

Table 2. Acute Toxicity Data for Endosulfan in Saltwater Animals

Scientific Name	Endpoint	Effect	Test duration (h)	Effect measure (ng/L)	n
Arthropods, SW					
<i>Penaeus duorarum</i>	LC ₅₀	Mortality	96	40	1
<i>Penaeus indicus</i>	LC ₅₀	Mortality	96	130	1
<i>Acartia tonsa</i>	LC ₅₀	Mortality	96	144	6
<i>Crangon septemspinosa</i>	LC ₅₀	Mortality	96	200	1
<i>Gammarus palustris</i>	LC ₅₀	Mortality	96	430	1
<i>Palaemon macrodactylus</i>	LC ₅₀	Mortality	96	774	25
<i>Americamysis bahia</i>	LC ₅₀	Mortality	96	1,107	16
<i>Palaemon macrodactylus</i>	LC ₅₀	Mortality	96	7,625	2
<i>Cancer magister</i>	LC ₅₀	Mortality	96	14,800	1
<i>Penaeus monodon</i>	LC ₅₀	Mortality	96	26,320	1
<i>Nanosesarma sp.</i>	LC ₅₀	Mortality	96	31,000	1
<i>Eucalanus sp.</i>	LC ₅₀	Mortality	24	176,000	1
<i>Scylla serrata</i>	LC ₅₀	Mortality	96	178,000	1
<i>Lucifer sp.</i>	LC ₅₀	Mortality	24	290,000	1
<i>Uca pugilator</i>	LC ₅₀	Mortality	48	789,500	1
<i>Artemia salina</i>	LC ₅₀	Mortality	24	2,830,000	1
<i>Artemia parthenogenetica</i>	LC ₅₀	Mortality	24	4,285,755	2
Fish SW					
<i>Leiostomus xanthurus</i>	LC ₅₀	Mortality	96	90	1
<i>Mortalityone saxatilis</i>	LC ₅₀	Mortality	96	100	2
<i>Lagodon rhomboides</i>	LC ₅₀	Mortality	96	300	1
<i>Mugil cephalus</i>	LC ₅₀	Mortality	96	380	1
<i>Mugil curema</i>	LC ₅₀	Mortality	48	600	1
<i>Cymatogaster aggregata</i>	LC ₅₀	Mortality	96	1,080	2
<i>Fundulus heteroclitus</i>	LC ₅₀	Mortality	96	1,150	2
<i>Cymatogaster aggregata</i>	LC ₅₀ *	Mortality	96	1,237	15
<i>Atherinops affinis</i>	LC ₅₀	Mortality	96	1,300	1
<i>Menidia beryllina</i>	LC ₅₀	Mortality	96	1,500	1
<i>Barbus stigma</i>	LC ₅₀	Mortality	96	1,930	1
<i>Poecilia reticulata</i>	LC ₅₀	Mortality	48	2,980	2

Table 2. Acute Toxicity Data for Endosulfan in Saltwater Animals

Scientific Name	Endpoint	Effect	Test duration (h)	Effect measure (ng/L)	n
Other aquatic animals SW					
<i>Paphia laterisulca</i>	LC ₅₀	Mortality	96	1,960	1
<i>Strongylocentrotus droebachiensis</i>	LC ₅₀	Mortality	96	33,891	2
<i>Crassostrea gigas</i>	EC ₅₀	Development	48	55,000	1
<i>Crassostrea virginica</i>	EC ₅₀	Shell growth	96	65,000	1
<i>Mytilus edulis</i>	EC ₅₀	Development	72	212,300	1
<i>Dinophilus gyrociliatus</i>	LC ₅₀	Mortality	96	295,631	4
<i>Sagitta sp.</i>	LC ₅₀	Mortality	24	424,000	1
<i>Dendraster excentricus</i>	EC ₅₀	Development	72	822,100	2
<i>Dinophilus gyrociliatus</i>	LC ₅₀	Mortality	96	1,029,331	2
<i>Brachionus plicatilis</i>	LC ₅₀	Mortality	24	6,432,130	3
<i>Cerastoderma edule</i>	LC ₅₀	Mortality	48	10,000,000	2

Table 3. Chronic Toxicity Data for Endosulfan in Freshwater Animals

Scientific Name	Endpoint	Effect	Test duration (d)	Effect measure (ng/L)
Arthropods, FW				
<i>Ceriodaphnia dubia</i>	NOEC	Reproduction	14	10,000
<i>Moinodaphnia macleayi</i>	NOEC	Reproduction	14	20,000
<i>Daphnia cephalata</i>	LOEC	Growth	14	22,000
<i>Daphnia magna</i>	MATC	Growth	21	170,000
Fish and amphibians FW				
<i>Clarias batrachus</i>	LC ₅₀	Mortality	28	300
<i>Pimephales promelas</i>	LC ₅₀	Mortality	7	860
<i>Cyprinus carpio</i>	LC ₅₀	Mortality	7	900
<i>Nuria danrica</i>	LC ₅₀	Mortality	7	8,000
<i>Rana clamitans</i>	LC ₅₀	Mortality	16	15,000
Other aquatic animals FW				
<i>Hydra vulgaris</i>	NOEC	Reproduction	6	40
<i>Hydra viridissima</i>	NOEC	Reproduction	6	60
<i>Brachionus calyciflorus</i>	EC ₅₀	Reproduction	10	1,000,000

Table 4. Chronic Toxicity Data for Endosulfan in Saltwater Animals

Scientific Name	Endpoint	Effect	Test duration (d)	Effect measure (ng/L)
Arthropods, SW				
<i>Americamysis bahia</i>	MATC	Mortality	38	120
Fish SW				
<i>Cyprinodon variegatus</i>	NOEC	Growth	28	170
Other aquatic animals SW				
<i>Nereis arenaceodentata</i>	LC ₅₀	Mortality	28	80,000
<i>Nereis virens</i>	LC ₅₀	Mortality	12	100,000
<i>Strongylocentrotus purpuratus</i>	EC ₅₀	Development	5	227,000
<i>Dendraster excentricus</i>	EC ₅₀	Development	5	352,000
<i>Strongylocentrotus droebachiensis</i>	EC ₅₀	Development	5	549,000