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Review

# Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations ☆

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ABSTRACT

This article provides an overview of key findings in the reviews in this special issue on the assessment of persistent organic pollutants (POPs) under the Arctic Monitoring and Assessment Program (AMAP), identifies knowledge gaps, and presents conclusions and recommendations for future work. The articles in this special issue summarize the peer reviewed literature and selected technical reports on trends of concentrations and possible biological effects of POPs in the Arctic published up to early 2009.

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**Contents**



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

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## 1. Introduction

Previous assessments of persistent organic pollutants (POPs) (de March et al., 1998; de Wit et al., 2004) by the Arctic Monitoring and Assessment Program (AMAP) made recommendations and identified information gaps based on the information up to early 2003. The series of articles in this special issue has extended this to peer reviewed literature and selected technical reports published up to early 2009. A distinctive aspect of the literature reviewed in this special issue is the broad range of persistent halogenated compounds measured including most of the substances banned or phased out by the Stockholm Convention, at least 10 current use pesticides, chlorinated naphthalenes, perfluorinated carboxylates (PFCAs) and perfluorinated alkyl sulfonates (PFSAs), polybrominated diphenyl ethers (PBDEs) plus at least 6 other brominated flame retardants (BFRs). One characteristic of the majority of these chemicals is that they, or precursors, have been at one time, high production volume chemicals i.e. >454 t/y in USA or >1000 t/y globally. Another is that they have molecular structures which convey sufficient stability and physical–chemical properties for transport to remote areas. Previous assessments of POPs have emphasized the semi-volatile characteristics and relatively high Henry's law constants which give rise to global fractionation and multi-hopping. However, recent results suggest that many non-volatile but highly stable compounds such as decabromodiphenyl ether (decaBDE), and other highly brominated compounds, as well the PFCAs and PFSAs are present in the Arctic. Their presence is either due to atmospheric transport on particles (particularly decaBDE) or to degradation of volatile precursors (particularly perfluoro-alkyl and -sulfonamide alcohols). The potential for ocean transport has also been studied in more detail recently, particularly for PFCAs.

Here we review the highlights of the reviews in this special issue, identify knowledge gaps, and present conclusions and recommendations for future work.

## 2. Legacy POPs

Time series are available for 8 groups of legacy POPs in Arctic biota, α-, β- and γ-hexachlorocyclohexane (HCH); total chlorobenzenes (ΣCBz = sum of tetra- penta- and hexachlorobenzene) and hexachlorobenzene (HCB); total chlordanes (ΣCHL = sum of trans-nonachlor, cis-nonachlor, trans-chlordane, cis-chlordane and oxychlordane) as well as trans-nonachlor and heptachlor epoxide; total DDTs (ΣDDT = sum of p,p′-DDD, p,p′-DDE, p,p′-DDT) and p,p′-DDE; sum of 10 PCB congeners (Σ10PCB = sum of congeners 28, 31, 52, 101, 105, 118, 138, 153, 156, 180) and PCB-153; dieldrin; mirex and toxaphene. Time series are available for most of the same groups of POPs in atmospheric samples from 4 stations Alert (Canada), Pallas (Finland), Storhofdi (Iceland) and Zeppelin (Svalbard/Norway) where long term monitoring have been carried out since the early 1990s. There are insufficient time series data for chlorinated dioxins/furans and for aldrin and heptachlor, however, the latter two are precursors of dieldrin and heptachlor epoxide, respectively and thus covered by dieldrin and ΣCHL. Time series for mirex in air are available only at Alert while no continuous atmospheric time series, and very limited biological time series, are available for toxaphene (Hung et al., (2010-this issue)).

In this special issue, Rigét et al. (2010-this issue) have assessed the time series available for legacy POPs in the Arctic biota while Hung et al. (2010-this issue) have examined the trends in air concentrations; both assessments employed a standardised statistical methodology. Both reviews note that levels of most of the legacy POPs have declined in the Arctic environment. Declines were observed in studies of marine and freshwater biota across the Arctic and in reindeer from northern Sweden (the only terrestrial mammal studies). Declining concentrations of PCBs, DDT- and chlordane-compounds, as well as HCHs and dieldrin in air were also observed at one or more Arctic air monitoring stations. These declines are a consequence of past national and regional bans and restrictions on uses and emissions in circumpolar and neighboring countries which began in the 1970s for chlorinated pesticides and PCBs. Phaseouts of technical HCH use in China and Russia have been shown to coincide with declining concentrations in Arctic air previously (Li and Macdonald, 2005) while the phase out of toxaphene use in the southern USA in the 1980s also was apparent in Arctic air measurements (Li and Macdonald, 2005). Whether the more recent geographically broader bans of the 12 POPs brought about with the implementation of the UN ECE LRTAP POPs Protocol (that entered into force in 2003) and particularly the Stockholm Convention (that came into force in 2004) have contributed to the trends is probably too early to say since most of the studies involve measurements of samples only up to 2005 or 2006. They do, however, provide a baseline with which to follow the effectiveness of these conventions in the future.

Declining atmospheric concentrations of some legacy POPs is also reflected to some extent in biological time series. In biota, compounds such as α-HCH, γ-HCH and ΣDDT had a relatively higher proportion of time-series showing significantly decreasing trends; ΣCHL had the lowest proportion. β-HCH was an exception showing significantly increasing trends in seabirds and beluga. Also a recent study has shown β-HCH increasing in ringed seals in the western Canadian Arctic (Addison et al. 2009). This is thought to be due to differences in the water solubilities of α- and β-HCH, with β-HCH partitioning more strongly to water, resulting in its delayed arrival to the Arctic via ocean currents through the Bering Strait (Li and Macdonald, 2005). $\Sigma_{10}$PCB and PCB153 have declined significantly in almost all time series studies albeit with relatively low annual % declines (annual decrease of 1.9% ($\Sigma_{10}$PCB) and 1.2% PCB153). DDE (p,p′-isomer) and ΣDDT, declined 1.9% and 4.4.%, respectively and DDE had one of the highest proportions of time-series showing no trend or significant non-exponential trends, most often with a period of relatively stable levels followed by a decrease. By contrast, the mean annual change in α-HCH in all biological time series was a decrease of 7.4%.

## 3. Screening for new or potential POPs

An interesting development in the assessment of potential POPs in the Arctic has been recent screening of chemicals in commerce using models, which indicates that many current-use organic compounds have chemical characteristics that make them similar to POPs and thus with potential to transport to the Arctic. Brown and Wania (2008) used a data set of more than 100,000 distinct industrial chemicals, subjected it to their screening system of models and identified 120 high production volume chemicals which were structurally similar to known Arctic contaminants and/or have partitioning properties that suggest they are potential Arctic contaminants. Their list included several known POPs such as p,p′-DDT as well as PBDEs and several current use pesticides (e.g. chlorothalonil, nitrapyrin, picloram, endosulfan, dicofol) as well as many other halogenated chemicals that have not been measured previously in the Arctic. Muir and Howard (2006), using 11,000 organic chemicals on the Canadian Domestic Substances List, also identified 28 chemicals with long range transport potential based on predicted atmospheric oxidation half-lives >2 days. Among these 28 only 8 were thought to have been measured in environmental samples and none in Arctic samples. Combined modelling for long range atmospheric or oceanic transport and for food web bioaccumulation would appear to be the best approach for screening the thousands of chemicals in commerce. This information is relevant to ongoing consideration of new chemicals for inclusion under existing national, regional and global agreements to regulate use and emissions of POPs. However, there is great potential for false positives and negatives in the application of these models to screening due to lack of key data, such as rates of biodegradation and other environmental transformations, as well lack of information on emissions and quantities in production for thousands of organic chemicals (Muir and Howard, 2006). Also there is the need for

confirming model predictions by use of targeted environmental measurement campaigns.

## 4. New results for various classes of POPs

### 4.1. Brominated flame retardants (BFRs)

In this special issue, de Wit et al. (in press) review the recent literature on the presence of BFRs in Arctic media. PBDEs have been reported in Arctic biota and in passive and high-volume air samples since the early to mid 2000s (de Wit et al., 2004, 2006). However, new observations of BFRs continue to be made. Perhaps the most surprising is the predominance of decabromodiphenyl ether (decaBDE, BDE-209) in Arctic air samples. First observations of decaBDE in air particles were made by Wang et al. (2005) from ship board measurements and then in weekly samples taken at Alert (the long term monitoring station on northern Ellesmere Island) by Su et al. (2007). All the decaBDE was detected in the particle phase which is consistent with its low vapor pressure. Confirming this, BDE-209 was not detected using passive samplers, probably because these devices sample mainly gas phase chemicals (Pozo et al., 2006). Unfortunately decaBDE measurements in air are limited to Alert; it has been reported as non-detectable at Zeppelin in Svalbard. This lack of detection is surprising but was related to measurable concentrations in field blanks and high detection limits.

The presence of BDEs, including BDE-209, in the Arctic terrestrial environment and foodchains involving herbivores is also a new observation. The detection of BDE-209 and other BDEs in moose and grouse in northern Norway provides evidence for entry of these BFRs into the terrestrial food web. However, the BDE concentrations were very low (sub-ng/g lipid weight).

Additional observations of PBDEs in Arctic lake sediments, from Alaska, Svalbard and northern Norway, including Lake Ellasjøen on the island Bjørnøya and in Canada, have been published in the past few years, broadening our knowledge of the deposition of PBDEs. In general deposition rates are much lower than in mid-latitude lakes (Landers et al., 2008; Breivik et al., 2006). An interesting aspect of this new data is that sediments in lakes on Svalbard, northern Norway as well as in Lake Ellasjøen seem to be influenced by the input of seabird guano.

There is some evidence that environmental levels of pentaBDE-related congeners are now starting to level off or decline due to national regulations and reductions in use and production. Long term temporal trend studies of tetra- to hexaBDE congeners in biota are ongoing using archived and present day samples, in Arctic char, burbot, lake trout, ringed seals from Canada and Greenland, northern fulmar and thick-billed murres from Canada, Brünnich's guillemots from Svalbard and Bjørnøya, and in beluga from Canada. Most studies are now showing a leveling off or decline of BDE-47 and BDE-99. It seems likely that the reduced emissions of penta- and octa-BDEs formulations due to regulatory measures in the early 2000s in Europe and mid-decade in the US and Canada are having an effect on concentrations observed in Arctic biota. They are also no longer produced in Russia and use there is very limited compared to North America (ACAP/AMAP, 2007). However, no declining trend is seen in BDE-47 and -99 concentrations in air at Alert. BDE-209 concentrations appear to be increasing in air (Hung et al., 2010-this issue). Strong seasonal trends in air concentrations of all the PBDEs make interpretation of air trends challenging. Trend data for PBDEs in air are not yet available for other air monitoring sites. Spatial trends show lower PBDE concentrations and higher proportions of lower brominated BDE congeners with increasing latitude. Circumpolar trends in seabirds and marine mammals show highest concentrations in populations on East Greenland and Svalbard, lower concentrations in the Canadian Arctic and lowest concentrations in Alaska, similar to spatial trends for polychlorinated biphenyls (PCBs).

The presence of hexabromocyclododecane (HBCD) in Arctic biota is another recent observation. The γ-HBCD isomer predominates in air at Svalbard, and the α-HBCD isomer in biota, while similar concentrations of α-, β- and γ-HBCD were found in marine sediments. Spatial trends of HBCD in seabirds and marine mammals are similar to those seen previously for PCBs and PBDEs, with highest concentrations found in organisms (e.g. polar bears) from East Greenland and Svalbard. These trends suggest that western Europe and eastern North America as important source regions of both PBDEs and HBCD and indeed HBCD is a major replacement compound for the pentaBDEs in Europe (BSEF, 2006). Eight time trend studies on biota have included HBCD, but most of them could not identify any clear trends, as the HBCD concentration was very variable. Increases were found in northern fulmar eggs (Canada) and ringed seal from several sites in Canada, while decreases were reported for ivory gull eggs (Canada) and beluga (Canada). There is very little current information on global BFR production volumes or geographical use patterns and this information is needed in order to understand temporal and spatial trends. For example, China is now producing BFRs but production volumes are unknown.

The period 2005–2008 has also seen the first reports of BFRs that are used as substitutes for phased-out substances. These include bis(tribromophenoxy) ethane (BTBPE) and 1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane (TBECH), as well as older BFRs that have not been reported previously such as hexabromobenzene (HxBBz), pentabromoethylbenzene (PBEB), and pentabromotoluene (PBT) in seabirds and/or marine mammals. This indicates that these compounds reach the Arctic, most probably by long range atmospheric transport and bioaccumulate in higher trophic level organisms. Another BFR, tetrabromobisphenol is present at low levels in several Arctic animals and plants, but more data are needed to assess its potential to undergo long-range transport. The presence of these BFRs in the Arctic indicates that they undergo long range atmospheric transport and are bioaccumulating in food webs. Their presence in the Arctic is a warning sign that they may have some POP characteristics. If the PBDE substitutes are undergoing increasing use it is reasonable to assume, based on the time trends for PBDEs, that this will lead to increasing concentrations over time.

### 4.2. Fluorinated compounds

Perfluorinated compounds (PFCs) have only been detected in the Arctic relatively recently; in the previous POPs assessment (de Wit et al., 2004) only data from the initial studies of Giesy and Kannan (2001) were available. However, a large body of literature, at least for the marine environment as well as for selected freshwater and terrestrial biota, lake sediments, and air, is reviewed in this special issue by Butt et al. (2010-this issue). Several modeling studies have attempted to resolve the debate about the dominant transport pathway of PFCs to the Arctic–atmospheric transport of precursors versus direct transport via ocean currents. The focus of modeling has been on PFOA and it is unknown to what extent those results apply to other perfluoroalkyl acids (PFAs). All models generally agree that inputs of PFOA to the Arctic Ocean via the ocean currents, are about 2 orders of magnitude greater than those from volatile precursor degradation in the atmosphere. However, whether ocean transport entirely explains the PFA exposure of biota feeding at or near the surface of the ocean is unresolved. There have been some efforts to characterize the spatial distribution of PFAs via measurements in the Canadian Arctic and subarctic seawater (Rosenberg et al., 2008) and in the Greenland Sea (Theobald et al., 2007) and Labrador Sea (Yamashita et al., 2008). However, only the Yamashita et al. data have been published in peer-reviewed literature and they are actually more relevant to the North Atlantic than the Arctic Ocean proper.

Production of products containing perfluorooctane sulfonate (PFOS) was substantially reduced in 2001, but PFOS continues to be produced in China (UNEP, 2008). In May 2009 PFOS and its related compounds were added to the Stockholm Convention but with many "acceptable purposes" such as in fire fighting foams and use as sulfluramid insecticide (N-ethyl perfluorooctanesulfonamide), and

"exemptions" such as for use or as an intermediate in production of stain repellent surface coatings (UNEP, 2009). Since China has been a source region for other Arctic contaminants e.g. HCH isomers and DDT (Li and Macdonald, 2005), due to atmospheric and oceanic transport to the northwest Pacific, Bering Sea and Chukchi Sea, there is potential for continued inputs despite reduced inputs from North America and Western Europe. As well, products that contain PFOS and other fluorinated compounds can still serve as sources to the environment.

Leveling off or decline in PFOS concentrations has generally been observed for PFOS in Alaska, the Canadian Arctic and northern Norway, but not in Greenland. Declining concentrations have been reported in sea otter from Alaska, and in ringed seal and beluga whale from the Canadian Arctic, whereas, ringed seals and polar bears from Greenland continue to show increasing PFOS levels from the 1980s to 2006. Declining PFOS was also observed in two freshwater species, burbot and lake trout, from the western Canadian Arctic.

PFOA and its perfluorotelomer alcohol precursors continue to be produced with large increases in emissions of predicted during the period 2000–2005 (Schenker et al., 2008). In temporal trend studies showing PFOS declines/leveling off, concentrations of major perfluorocarboxylates (PFCAs) such as PFNA, PFDA and PFUnA, in Arctic marine biota have generally not declined or are increasing, consistent with the emissions estimates. For the two available freshwater studies, PFCAs trends were variable with some increases and some declines.

The inconsistencies observed between temporal studies in the marine environment may be due to differences in emissions from source regions. Based on spatial trends in polar bears and ringed seals, which show highest PFOS and PFCAs in Svalbard and eastern Greenland, North America and Western Europe appear to be major source regions for East Greenland and Svalbard similar to what is observed for PBDEs and PCBs. Relatively high PFAs in ringed seals in Hudson Bay also point to North American sources. The lack of declining trends of PFOS in Greenland may thus be due to different seawater sources there (south flowing East Greenland current) compared with the Canadian Arctic archipelago which is thought to be entirely of Pacific origin (Jones et al., 2003). Unfortunately there are, as yet, no abiotic time trend data comparing the North American and European Arctic such as ice core or sediment core records. The Canadian ice cap study from Devon Island shows relatively constant PFCA concentrations and slowly declining PFOS concentrations, while sediment cores analysed from lakes in the same region were not analysed with sufficient resolution to show recent trends.

Precursors of PFOS (the perfluorosulfonamido alcohols) and PFCAs (perfluorotelomer alcohols and their oxidation products, fluorotelomer acids) have been detected in Arctic air. As might be expected for remote regions, concentrations in Arctic air are one order of magnitude lower than in more southern, urban regions. These precursors are volatile and studies in mammals and fish indicate that they are rapidly degraded to PFAs. An exception is PFOSA (perfluorooctane-sulfonamide) and N-EtFOSA (the ethyl derivative of PFOSA) which were detected in whales and in marine invertebrates at similar levels to PFOS but were near detection limits or non-detect levels in birds, seals and fish. PFOA and PFOS have also been detected in particle phase air samples and deposition of PFOS and PFCAs has been determined in Canadian Arctic ice caps. Taken together these observations indicate that for terrestrial and freshwater biota, the deposition of PFAs from atmospheric degradation of precursors is the main source of PFOS and PFCAs. However for marine wildlife, oceanic transport contributes additional PFAs to food webs. Comparisons between terrestrial/freshwater and marine biota are limited but generally show lower concentrations in mammals e.g. caribou/reindeer.

Knowledge of sources and trends of PFAs in the Arctic is important particularly for the PFCAs, for which emissions of precursors are known to be increasing globally at least as of 2005. The freshwater and terrestrial ecosystems have had relatively limited study, particularly in terms of spatial trends within the circumpolar Arctic.

Virtually nothing is known about uses and emissions of PFCs in the Russian Arctic which encompasses nearly 50% of the circumpolar area. As a non-signatory of the Stockholm Convention, Russia has not contributed information to UNEP reports on global PFOS use or risk management (UNEP, 2007).

Local sources in the Arctic are not well documented. The presence of relatively high PFOS in sediments and lake water downstream from an airport in the Canadian high Arctic, where it was presumably used as a fire fighting foam, illustrates the potential for local contamination in the circumpolar Arctic. However, it is doubtful if local PFC sources will significantly influence PFC concentrations in the Arctic regional marine environment given very low population densities. Exceptions could be northern Norway and northwestern Russia where there are larger cities and villages relative to other regions of the circumpolar Arctic bordering the Arctic Ocean.

There is great need for additional seawater measurements to validate existing model predictions, to understand sources and pathways both of deposition and bioaccumulation of PFAs. There is also the need for expanded atmospheric monitoring to confirm spatial trends and to assess temporal trends. An opportunity appears to have been missed to follow air concentrations as PFOS precursor production was phased out. New atmospheric monitoring should include recently identified potential PFCA precursors such as the fluorinated olefins, iodides and acrylates.

### 4.3. Polychlorinated naphthalenes

As reviewed by Bidleman et al. (2010-this issue) in this issue, a limited amount of new information has been published on polychlorinated naphthalenes (PCNs) in the Arctic since the last AMAP assessment of POPs (de Wit et al., 2004). PCNs have legacy sources due to volatilization from old products and from soils, while emissions continue from combustion sources. Thus there could be minor sources within the circumpolar region due to combustion and particularly due to waste burning with combustion indicated by the presence of marker congeners such as CN-29, -44 and -54. Both legacy and combustion sources contribute to air concentrations in temperate regions.

The number of measurements of PCNs in Arctic air greatly expanded in the past 5 years due to high volume air sampling at Svalbard, Northern Greenland, Northern Sweden and near Tromsø in northern Norway. Also, passive air sampling for the Global Atmospheric Passive Sampling (GAPS) study (Pozo et al., 2006) showed detectable total PCN concentrations (ΣPCN; 3–8 Cl) at 0.86 to 7.6 pg $m^3$ concentrations at 4 Arctic–subarctic sites. Compared with other POPs, spatial variability of ΣPCNs is high, with 1–2 orders of magnitude difference among Arctic–subarctic stations. PCNs at Alert in the Canadian high Arctic appeared to be derived from mostly evaporation sources, while combustion influence was more evident at Ny Ålesund based on characteristic congeners. The combustion influence at Ny Ålesund is consistent with both local sources and proximity to populated areas of northern Europe, which is also observed for several other POPs at this site. Lack of temporal trends in air or for deposition in snow and in Arctic sediments is a major knowledge gap for PCNs.

Published data on PCNs in Arctic biota are rather limited compared to other POPs and also compared to abiotic measurements. However, the past 5 years have seen completion of several studies, particularly from Greenland and Bjørnøya (Bear Island) in Norway in which a substantial number of seabird and marine mammal samples were analysed. Generally sub-ng/g (lipid weight) concentrations have been reported in marine mammal blubber while seabird eggs contain higher levels (means of 1–10 ng/g lipid). Overall PCN concentrations in biota are much lower than most other major legacy organochlorines in the same samples (e.g. PCBs, DDT, HCHs, CBz, chlordanes, toxaphene). PCNs can be compared with non-ortho and mono-ortho substituted PCBs on a TCDD toxic equivalent (TEQ) basis since information is available on their relative potencies in terms of dioxin-like induction of aryl hydrocarbon

hydrolyase activity. On this basis PCNs make up <1% of TCDD TEQs in seals and in seabird eggs but possibly up to 6–15% in whales (e.g. beluga, long-finned pilot whale blubber) depending on the number of congeners included.

Further measurements of PCNs in Arctic air are needed to verify the large spatial differences observed in previous studies, in particular the high concentrations in the European Arctic. Analysis of archived air sample extracts, or other archives such as lake sediment cores or ice cores, might aid in resolving questions of temporal trends of PCNs. There also is a need for more data on PCNs in cetaceans given that available data suggest that PCNs are important contributors to the ΣTEQ in these animals. PCNs should be assessed with other compounds that have TCDD TEFs available i.e. mono- and non-ortho PCBs and PCDD/Fs so that their significance can be properly evaluated.

### 4.4. Endosulfan

A paper by Weber et al. (2010-this issue) in this special issue focuses solely on endosulfan because it is the most abundant current use pesticide (CUP) in the Arctic environment. Endosulfan is still in use as an insecticide in many parts of the world including in circumpolar countries. While overall global use has remained relatively constant at around 12,000 t/y from the mid-1990s to 2004 quantities produced in China increased over the same period (Jia et al. 2008). However, declining use has apparently occurred in Europe since the mid-1990s (54%). It is therefore interesting to note that no decline has been observed in α-endosulfan in Arctic air at Alert over this period and that this endosulfan isomer showed increasing concentrations in Svalbard and Devon Island ice caps. Also increasing endosulfan concentrations have been seen in lake sediment cores from mid-latitude alpine lakes in the western USA. These trends imply that estimated production and use trends may not be entirely correct and/or that long range transport is occurring from use areas throughout the northern hemisphere rather than just in Europe and mid-latitude North America. Endosulfan is currently under discussion for inclusion under the UN-ECE LRTAP POPs Protocol and the Stockholm Convention.

While α-endosulfan and its oxidation product endosulfan sulfate are predominant chlorinated organics in Arctic abiotic environments, they are much less prominent in biota. The limited information available in wildlife indicates that concentrations of endosulfan and endosulfan sulfate in blubber of marine mammals are an order of magnitude lower than those of major legacy POPs such as DDT and chlordane. Unlike most of the other POPs, there are major challenges of determining low levels of endosulfan isomers in fish and mammals and as a result much of the data available for wildlife samples from Canada and Greenland, where most measurements have been made, are unreliable and need GC-MS confirmation. Weber et al. (2010-this issue) have concluded that the deviations between GC-ECD and GC-MS for α-endosulfan are about 2-fold for fish (Arctic char) and up to 12-fold for beluga blubber. Results in the recent paper by Kelly et al. (2007), which used GC-high resolution MS to quantify α- and β-endosulfan and endosulfan sulfate are thought to be the most reliable because the use of high resolution MS removes the possible interference from chlordane which has similar structure and gas phase, mass spectrometric fragmentation patterns. The results reported by Kelly et al. (2007) confirm the presence of all 3 endosulfan species in beluga and ringed seal, as well as in other Arctic/subarctic samples. Furthermore because there is seawater data of good quality for the same analytes it is possible to estimate bioaccumulation factors (BAFs) for total endosulfan. These range from 1.45 to $6.76\times10^5$ on a lipid weight basis (Weber et al., 2010-this issue). On a wet weight basis, BAFs for Σendosulfan in fish from East Hudson Bay ranged from 1690 to 7280 which is within the range of laboratory BCF values. Biomagnification factors (BMF) >1 were apparent for Σendosulfan for beluga and ringed seals preying on Arctic cod and on salmon, resulting in an overall mean BMF of 1.5 from fish to marine mammals. Thus endosulfan appears to biomagnify in Arctic marine food webs although not to the extent of legacy organochlorines. However, high BMFs mainly result from high β-endosulfan concentrations, particularly, in beluga blubber. The predominance of the β-isomer in marine mammal blubber is particularly interesting, considering that it is not prominent in fish, seawater, or air samples, and deserves further study.

There is currently poor spatial coverage for measurements of endosulfan in Arctic biota with almost all reports from Canada and Greenland. A stronger circumpolar dataset for endosulfan species in biota is needed as a baseline particularly if it is eventually subject to a global ban. Reliable temporal trend data for endosulfan in Arctic biota are also lacking however this could be changed relatively easily by reanalysis of archived samples using GC-MS.

### 4.5. Other current-use pesticides

Previous AMAP assessments have highlighted lindane (γ-HCH) as a CUP that was ubiquitously present in the Arctic and, as discussed, endosulfan, is also ubiquitous at least in the abiotic environment. In their article in this special issue, Hoferkamp et al. (2010-this issue), provide the first review of other current use pesticides in the Arctic environment. This topic has not been addressed by previous AMAP POPs assessments. Several other current use pesticides (including chlorpyrifos, chlorothalonil, dacthal, diazinon, methoxychlor, and trifluralin) have been consistently detected in the Arctic. In 2009, trifluralin, dicofol and pentachlorophenol were proposed to be added to the UNECE list of POPs and are currently under review by the UNECE POPs Task Force (UNECE, 2009). In the case of dicofol this CUP appears to be a concern due to the presence of DDT impurities; there are no direct measurements of it in the Arctic. The European Union recently placed endosulfan and trifluralin on an "excluded" list (European Union 2009).

The levels of these other CUPs are often low, but their presence shows that they can transport over long distances and accumulate in the food web. The results of studies in Alaskan and mid-latitude national parks in the USA showed that CUPs dominated the distribution of semi-volatile organic compounds (Landers et al., 2008). In all parks sampled, including three in the Alaskan Arctic, chlorpyrifos and dacthal were commonly found and chlorpyrifos, dacthal and methoxychlor were identified above MDLs in more than 50% of fish samples. Dacthal and chlorpyrifos also have been detected in Arctic lichen and in conifer needles. Studies of CUPs in Arctic ice cap samples suggest that many more may be present, however the list of target analytes for most studies has been relatively small compared to the number of pesticides currently in commerce. There is also the potential for false positives from GC-low resolution mass spectrometry or GC-electron capture detection of CUPs. This is discussed by Weber et al. (2010-this issue) in connection with analysis of endosulfan but could also apply to other CUPs.

There is very limited data for CUPs in Arctic biota. Apart from the study by Landers et al. (2008) where dacthal and chlorpyrifos were detected most other studies have reported only methoxychlor and pentachloroanisole (PCA; methylated derivative of pentachlorophenol) in fish. Detections in mammals are even less frequent. A more systematic approach is needed to assess whether other CUPs might be accumulating in the Arctic perhaps by screening all registered CUPs by use of modeling using the OECD LRT tool and more complex models which include emissions estimates such as GloboPOP.

## 5. Biological effects

The past 5 years has seen a dramatic increase in the number of publications studying possible biological effects of organohalogen compounds in Arctic biota. In previous assessments, the approach for assessing effects was to use various effects thresholds for some POPs derived mainly from laboratory or captive animal exposures and

compare these to current body concentrations of the same POPs (de Wit et al., 2004). In their review, Letcher et al. (2010-this issue), point out that there are now effects data for populations of several top trophic level species, including seabirds (e.g., glaucous gull (*Larus hyperboreus*)), polar bears (*Ursus maritimus*), polar (Arctic) fox (*Vulpes lagopus*), and Arctic char (*Salvelinus alpinus*), as well as semi-captive studies on sled dogs (*Canis familiaris*).

The indications of effects of organohalogen compound (OHC) exposure are largely based on correlations between biomarker endpoints (e.g., immune and endocrine endpoints, pathological changes in tissues, reproductive and developmental effects) and tissue residue levels of OHCs (e.g., PCBs, DDTs, CHLs, PBDEs and in a few cases PFCAs and PFSAs. While cause and effect cannot be assessed for such studies, semi-field studies with captive Greenland sled dogs have demonstrated that cohorts exposed to a OHC-contaminated (West Greenland minke whale blubber) versus control (commercial pork fat) diets have changes in immune and endocrine endpoints. Also, performance studies mimicking environmentally relevant PCB concentrations in Arctic char have demonstrated biological effects as a result of the PCB exposure. Another aspect of the exposure-effects linkage is that persistent metabolites such as methyl sulfonyl-PCBs and DDEs and hydroxylated-PCBs are frequently correlated with effects endpoints and may be more important than the original POP compounds. The general lack of basic ecological and physiological information for Arctic wildlife makes it difficult to assess potential changes caused by contaminants.

Overall Letcher et al. (2010-this issue) conclude that there remains minimal evidence that OHCs are having widespread effects on the health of Arctic organisms, with the possible exception of East Greenland and Svalbard polar bears and Svalbard glaucous gulls. This is consistent with previous conclusions (de Wit et al., 2004) using much more limited information. However, out of these effects studies has come better appreciation for the effects of other environmental, ecological and physiological stressors (both anthropogenic and natural) such as seasonal changes in food intake and corresponding cycles of fattening and emaciation seen in Arctic animals. These can modify contaminant tissue distribution and toxicokinetics. The impact of climate change, which is bringing seasonal ice and temperature changes, and along with it, diet shifts and nutritional changes, disease, species invasion all need to be considered in the context of biological effects as well. For example will disease resistance be impacted by toxicant exposure?

## 6. Recommendations

### 6.1. Continued measurements of legacy POPs

Firm conclusions about the impact of policy decisions on environmental levels will require continued monitoring of 'legacy POPs' in both abiotic environments and in key biota. AMAP information on temporal trends in the Arctic has contributed to the initial evaluations of the 'effectiveness and sufficiency' of the UN ECE LRTAP Convention Protocol on POPs, and the Stockholm Convention, and are expected to continue to do so in the future.

### 6.2. Measurements of new POPs and related compounds

Data for spatial and temporal trends in the Arctic were crucial information in the assessment of 8 of the 9 new chemicals added to the POPs list in May 2009 for the Stockholm Convention. Only chlordecone had not been measured in the Arctic. The past few years have seen a large increase in the number of new chemicals detected in the Arctic. We encourage the continuation of this measurement activity since it has relevance not only for the Stockholm Convention but also for other national assessments of chemicals such as ChAMP and REACH, and for the assessments of potential health effects on Arctic ecosystems and humans (AMAP, 2009).

### 6.3. Climate change and time trends in biota

There is a need to recognize that climate change in the Arctic may be bringing about diet shifts for top predators typically used for time trend studies. Strategies should be devised such as collection of important ancillary data (e.g. stable isotope ratios, fatty acid profiles) to make future trends in POPs interpretable and thus not dismissed as merely changes in trophic status of the animals.

As the time series get longer and more statistically robust, it may be possible to discern how contaminant trends in biota are affected by climate variability and possible changes in contaminant pathways that may be occurring due to such factors as thinning of Arctic ice and changes in river runoff and precipitation patterns (Macdonald et al., 2005).

Warming of the Arctic climate regime may already be affecting temporal trends of POPs in air (Becker et al., 2009). Increased frequencies of forest fire events due to climate change may result in enhanced input of pollutants to the Arctic; as inferred from results of higher PCB and OCP concentrations measured at Zeppelin and Alert.

### 6.4. Climate change and biological effects

Related to the points raised in Section 6.3, there is a need to further investigate the interrelationships between climate change-mediated ecological changes (diet shifts and nutritional changes, disease, species invasion need to be considered in the context) and how they may change the levels and trends of POPs exposure, and possibly on POPs-mediated effects. For example there is evidence that that earlier ice break-up date over the last 20 years in western Hudson Bay resulted in a temporal shift in the diet of polar bears (McKinney et al., 2009).

### 6.5. Statistical power of time trend studies

There remain uncertainties in the assessment of trends in the Arctic due to a variety of factors related to duration of temporal trend studies and their consistency over time, and possible changes in laboratory capability over time. For example, under the biota temporal trend monitoring programme, the target that has been established is a capability (statistical power of 80%) to detect a 5% annual change with the significance level of 5% (Bignert et al. 2004; Rigét et al., 2010-this issue). Of the large number of time series for legacy POPs in Arctic biota currently available (316 individual series with 6 or more years of data; some as far back as the early 1970s) most still have insufficient number of years to fulfill this target. In addition, possible ecosystem changes that can affect contaminant exposure need to be taken into account. As additional years of monitoring are added to existing time series, their ability to meet the statistical power requirements in order to verify temporal trends is improving and thus such studies need to be continued.

### 6.6. Concerns with respect to atmospheric monitoring

Atmospheric monitoring programmes also need to continue in order to allow examination of the response to efforts to reduce global emissions, to validate global models of emissions and transport, as well as to provide the knowledge basis to interpret POP measurements under the influence of climate change. An expansion of passive air sampling of contaminants to more areas of the circumpolar Arctic presents an opportunity to improve spatial coverage, and if done quarterly (as in GAPS) this would still provide much better resolution that most other abiotic media (e.g. snow, sediment cores). The use of passive samplers might also facilitate increasing the number of analytes determined in air samples (for gas phase type contaminants at least) because these programs are more "nimble" i.e. involve much lower costs for site operation and can be started on a small scale basis. However, some sites with high temporal resolution are needed,

particularly for the transport and deposition modeling, to validate passive sampler measurements, and to monitor contaminants that cannot be monitored by passive samplers, in particular particle-associated POPs.

### 6.7. Regional and global fate and exposure modeling of POPs

There have been significant advances in global modelling of atmospheric and oceanic transport of contaminants to the Arctic. However the models are often limited by the lack of emission information. Greater reconciliation is required between environmental measurements and emission inventories, with a move towards creating spatially resolved emission inventories over a hemispheric or even global scale for new POPs. There is a need for better coordination with chemicals fate and long range transport modelers and with risk/exposure assessors who frequently have prioritized chemicals in commerce using Quantitative Structure Property Relationships but lack measurement data.

### 6.8. Interlaboratory comparisons and circumpolar coordination

AMAP atmospheric and biological monitoring of POPs in the Arctic is based on nationally-established monitoring programmes. Through recommendations of its expert group on POPs, AMAP encourages activities to harmonize these programs to meet circumpolar monitoring objectives. However, ensuring quality assurance and data comparability while at the same time assuring good geographical and temporal coverage, remains a challenge. Building on previous AMAP POPs assessments (de March et al. 1998; de Wit et al. 2004) as well as strong national programs in, in particular Arctic Canada, Greenland, Iceland, northern Norway, Sweden and Finland, there is good cooperation among investigators with most laboratories participating in coordinated QA/QC activities. However, continued and possibly mandatory participation in these activities is of utmost importance to assure the continued strength of the AMAP monitoring programme.

### 6.9. Quality assurance and confirmation of new contaminants

The monitoring programs have generally used relatively low cost, routine equipment such as GC-electron capture detection (GC-ECD) for PCBs and other legacy POPs. Similarly BFRs are typically being analysed by GC-low resolution negative ion MS by monitoring of the characteristic Br ions. These methodologies may be subject to false positives due to the presence of co-eluting components. An example discussed in the endosulfan review (Weber et al., 2010-this issue) is the interference by chlordane-related compounds. PBDE interference can also give rise to mis-identification of other BFR compounds such as HxBBz and PBT (Gouteux et al. 2008; Alaee et al. 2001), while PBB153 interferes with analysis of BDE154. Thus additional confirmation, by use of additional characteristic ions as discussed by Kierkegaard et al. (2009) or by GC-high resolution MS or other high resolution instrumental techniques such as GC or LC-TOF, particularly for new contaminants in Arctic samples, is highly recommended.

### 6.10. Archiving for biological effects as well as contaminant trends

Sample archives should be promoted as sources for materials to assess metabolites, nutrients and biomarkers as well as contaminants in chemical trend monitoring studies. This provides the potential for improving consistency of laboratory analyses (through analysis of all samples using a common technique, or all samples at the same laboratory), analysis of archived materials for 'new' contaminants as laboratory methods are developed or improved, and improved reproducibility of results, particularly for biological effects.

### 6.11. Archiving of data

Assessments of data, in particular at the Arctic wide scale, requires that data from many sources are brought together and handled, if possible, in a consistent manner. For temporal trend studies in particular, maintaining access to consistent datasets over long periods is critical. AMAP has therefore established thematic data centres to ensure that data, at the level of detail required for systematic analysis, are archived and available for future studies (for more information see www.amap.no). Reporting of key Arctic datasets to these data centres should be strongly encouraged and promoted at the national level.

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