AN OVERVIEW OF TEMPORAL TRENDS OF LEGACY AND EMERGING CONTAMINANTS IN THE ARCTIC AND POSSIBLE IMPLICATIONS FOR TOP PREDATORS AND HUMANS

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs), which went into force in May, 2004, states that chemicals may qualify as POPs if they are found far from sources and show evidence of long range transport[1]. This has made the Arctic an important indicator region for assessing persistence and bioaccumulation properties of POPs and for identifying potential new POPs. The Arctic environment is well suited as a region in which to evaluate POPs. Cold conditions favor persistence of POPs relative to temperate or tropical environments. Long food webs that include the presence of fourth level carnivores (i.e. polar bear (*Ursus maritimus*)), and storage of lipid as an energy source, make Arctic food webs vulnerable to bioaccumulative chemicals. This in turn has led to high POP exposures for Arctic top predators and some indigenous human populations, with risks for possible effects. Although many legacy POPs are now regulated and some emerging contaminants are under review for regulation, there are new chemicals being found in the Arctic that are not regulated. Temporal trend monitoring is important to follow the results of regulation as well as for monitoring exposure risks and linking these to possible effects. The Arctic Monitoring and Assessment Programme (AMAP) has previously reported on temporal trends of primarily legacy POPs up to the early 2000s [2,3]. This presentation is an update of temporal trends of legacy POPs as well as including several emerging POPs that have been presented in recent AMAP Assessments.

Temporal trends

Legacy POPs: Riget et al.[4] have recently assessed the time series available for legacy POPs in Arctic biota while Hung et al.[5] have examined the trends in air concentrations. Updated time series are available for 8 groups of legacy POPs in Arctic biota, α-, β- and γ-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[4]. 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 has been carried out since the early 1990s. 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[5]. For human populations in the Arctic, fewer time trend data series are available but include PCB153, p,p-DDE and oxychlordane[6].

In all studies, levels of most of the legacy POPs have declined in the Arctic environment. Declining concentrations of PCBs, DDT- and chlordane-compounds, as well as HCHs and dieldrin in air were observed at one or more Arctic air monitoring stations [5]. 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. Phase-outs of technical HCH use in China have been shown to coincide with declining concentrations in Arctic air previously[7] while the phase out of toxaphene use in the southern USA in the 1980s also was apparent in Arctic air measurements [8].

Declining air concentrations of some legacy POPs are also reflected to some extent in biological time series. Declines were observed in studies of marine and freshwater biota across the Arctic and in reindeer from northern Sweden (the only terrestrial mammal studies)[4]. 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, ringed seals and beluga, particularly in the western Canadian Arctic. This is 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[8]. Σ_{10}PCB and PCB153 have declined significantly in almost all time series studies albeit with relatively low annual % declines (annual decrease of 1.9% (Σ_{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. In contrast, the mean annual change in α-HCH in all biological time series was a decrease of 7.4%. When measured over time, declines of PCB, DDE and oxychlordanes have also been seen in human indigenous and non-indigenous Arctic populations from Canada, Greenland, Iceland, Sweden and Finland[6].

Emerging POPs: 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[9]. It seems likely that the reduced emissions of penta- and octaPBDEs, 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. 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[5]. 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. 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). Analyses of archived human breast milk samples from Arctic Canada and Quebec both show increasing trends of tri-hexaBDEs from 1990 to 2002[6].

Leveling off or decline in PFOS concentrations has generally been observed in Alaska, the Canadian Arctic and northern Norway, but not in Greenland[10]. 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. In temporal trend studies showing PFOS declines/leveling off, concentrations of major 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. However the lack of declining trends of PFOS in Greenland may also 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[11]. Unfortunately there are, as yet, no abiotic time trend data comparing the North America 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. Temporal trends of PFCs in humans from the Arctic have not been performed.

Endosulfan is still in use as an insecticide in many parts of the world including in circumpolar countries and overall global use has remained relatively constant at around 12000 t/y from the mid-1990s to 2004. However, declining use has apparently occurred in the northern hemisphere since 1996 (by 30%) with a large part of this decline coming in Europe (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[12]. It therefore seems likely that the abiotic trends seen in the Arctic are reflecting global use rather than use only in the northern hemisphere. However, it is worth noting that increasing endosulfan concentrations have also been seen in lake sediment cores from mid-latitude alpine lakes in the western USA, which implies that estimated production and use trends may not be entirely correct. Endosulfan is currently under discussion for inclusion under the UN-ECE LRTAP POPs Protocol and the Stockholm Convention. Several other current use pesticides (including chlorpyrifos, chlorothalonil, dacthal, diazinon, methoxychlor, and trifluralin) have been consistently detected in the Arctic, but there are no temporal trend data[13]. No human data are available for current use pesticides in humans in the Arctic.

Conclusions

Long term studies in air, biota and humans show that levels of most legacy POPs (e.g. PCBs, DDTs, HCHs, chlorobenzenes, chlordanes, dieldrin, toxaphene) have declined in the Arctic environment. 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. It is probably too early to say whether the more recent geographically broader bans of the 12 POPs in the UN ECE LRTAP POPs Protocol and particularly under the Stockholm Convention have contributed to the declining trends since most of the studies involve measurements of samples up to 2005 or 2006. Levels of a number of emerging POPs are either leveling off, possibly in response to discontinued use or recent bans, or are still increasing due to continued production and use. Despite the declines, concentrations of PCBs still exceed human health guidelines in some Inuit populations in eastern Canada, on Greenland, and in Russia as well as other indigenous groups in Canada and Russia[6]. Concentrations of several organochlorine POPs in some top predators are also above thresholds for effects[14]. High exposures to organochlorine POPs in some Arctic human populations and in top predators such as polar bears have also been linked to health effects[6,14]. Based on past experience, increasing temporal trends of emerging contaminants and the increasing number of chemicals that are reaching the Arctic raise concern about the potential for increasing exposure of top predators and some indigenous populations to these, as well as possible effects of chemical mixtures.

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