LEVELS AND TRENDS OF PERSISTENT ORGANIC POLLUTANTS IN THE ARCTIC ENVIRONMENT

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Introduction

Arctic biota were demonstrated to contain a range of persistent organic pollutants (POPs), particularly organochlorines (OCs) pesticides and PCBs in the 1970s, however, until the mid-1990s there was limited knowledge on the sources, pathways, levels, spatial and temporal trends and biological effects of these substances in Arctic species[1,2]. Two reports by the Arctic Monitoring and Assessment Program (AMAP) reviewed the data on POPs in Arctic air, seawater, sediments, and terrestrial, freshwater and marine biota, that was available as of 1996[3], with an update until 2002[4]. Some major findings on levels and trends of POPs in air, seawater, fish, in top predators and in marine food web organisms from these assessments along with new data, particularly for "new" contaminants, that has emerged since these were published will be presented here.

Sources and spatial trends

Information on global sources of POPs has improved greatly with the publication of global gridded inventories for hexachlorocyclohexane (HCH)[5] , and PCBs[6]. Harbours in Norway, Svalbard, Canada, and Russia, as well as areas around former military bases in Alaska, Canada and Norway (Jan Mayen; Svalbard) have been shown to have elevated levels of some PCBs in sediments and/or biota. Many of the former military sites in Canada, Alaska, Greenland and Norway have undergone cleanups, which include removal of contaminated equipment and soils. The situation in the Russian Arctic regarding PCB use at military sites is unclear but recent information from abandoned military sites on Franz Josef Land indicate similar problems.

Less is known about sources of dioxin-like PCBs and polychlorinated dibenzo-p-dioxins and –dibenzofurans (PCDD/Fs) in the Arctic. An inventory based on US and Canada per-capita dioxin emissions estimated for 1996, shows most of the Arctic region of North America having emissions of <0.1 ug TEQ/km^2/yr and more populated areas (e.g. southern Alaska, southern Yukon, Labrador) with estimated emissions of 0.1-25 ug TEQ/km^2/yr [7]. This is consistent with the very low population density (total population of North American Arctic of 650,000;land area of 7.5×10^6 km^2). Densely populated regions of North America have emissions of 100-5000 ug TEQ/km^2/yr and higher values for point sources such as municipal waste incinerators. There is also local open, low temperature, burning of municipal garbage in the Canadian Arctic, Alaska and Russia, which probably contributes to loadings of PCDD/Fs to the Arctic atmosphere and local contamination.

Measurements of airborne POPs were carried out at Alert (Nunavut, Canada), Pallas (Finland), Storhofdi (Iceland), and Ny-Ålesund, (Svalbard, Norway) and a new site at Amderma (western Russia) began operation in 1999. Major OCs in Arctic air are α-and γ-HCH, p,p'-DDT, chlordane (CHL) compounds, endosulfan, pentachloro-anisole (PeCA), HCB and PCBs (10 to about 100 congeners)[8,9]. Results suggest uniform average concentrations of most OC compounds. Amderma, in northwest Russia had average Σ10PCB of 4 pg/m^3 in 1999-00 (the first year of operation of this site), similar to Alert and lower than Pallas or Storhofdi. New chemicals detected at several of these sites include polybrominated diphenyl ethers (PBDEs), chlorinated paraffins, chlorinated naphthalenes, PeCA, tetrachloro-veratroles. Air mass back trajectories show that PCBs measured at Alert on northern Ellesmere Island originated primarily from North American sources, however, Central and Eastern Russia were also potential sources based on prevailing air mass movements[10]. In the Yukon and Alaska, Asian sources likely predominate based on known air mass movements[10,11]. Less is known about long range atmospheric transport of PCDD/Fs to the North American Arctic. PCDD/Fs were determined in soils from Alaska, the Yukon and NWT in the Canadian Arctic, western Greenland, and Norway and

northwestern Russia[12, 13]. Fluxes of total PCDD/Fs estimated from the mass of chemical in a 10x10cm (15 cm depth) core ranged from 1.2-143 ng/m^2 yr. The authors concluded that PCDD/Fs did not move appreciably from warm to cold latitudes. Most Arctic soil samples were characterized by high proportions of OCDD although TCDFs were also important contributors to total PCDD/Fs.

Knowledge of levels of persistent OCs in Arctic wildlife has expanded, especially in the case of Alaska, Greenland, Svalbard/Barents Sea, and western Arctic Russia[4]. Species studied for the first time in detail include marine zooplankton (*Calanoid* sp.), mussels (*Mytilus* sp) (Alaska, Faroe Islands, and Canada), soils (Norway, Canada/Russia), lichen and mosses (Russia/Alaska), bowhead whales and Arctic fox (in Alaska and Canada), bearded seals (Alaska and Russia), bald eagles (Alaska/Aleutians), black guillemots (Faroes) and Greenland shark (Canada/Greenland). Measurements continued on many key AMAP species such as Atlantic cod, beluga whales, ringed seals, polar bears, seabird eggs and liver (kittiwake, thick-billed murre, northern fulmar, black guillemots). This work confirmed previous observations that levels of total PCBs (ΣPCB) and total DDT (ΣDDT) compounds in polar bear, ringed seals and seabirds, are highest in the European Arctic and lowest in the western North American Arctic while HCH isomers (ΣHCH) are higher in the North American Arctic. Highest concentrations of PCBs in polar bear were found in samples from the Kara Sea and Franz Josef Land. A surprising finding has been relatively high toxaphene in harp and ringed seals from Svalbard and the White Sea.

A recent review of brominated flame retardants in the Arctic[14] reports that not only lower brominated PBDEs, but also DecaBDE, hexabromocyclododecane (HBCD), PBBs and tetrabromobisphenol A (TBBPA) are found in both abiotic and biotic samples. Spatial trends of PBDEs in marine mammals and seabirds show highest concentrations on East Greenland and Svalbard. Highest HBCD levels are also seen in polar bears from East Greenland and Svalbard. These spatial trends are similar to those seen for OCs indicating source regions in eastern North America and western Europe. DeBDE has been found in polar bears and Arctic seabirds.

The discovery of perfluorinated compounds (PFCs), particularly perfluorooctane sulfonate (PFOS) in polar bears[15] has led to considerable follow-up of a range of PFCs, such as perfluoro-carboxylic acids (PFCAs), -sulfonamides (PFOSAs) and -sulfonamide ethanols (PFOSEs) in Arctic biota. Various PFCs have been found in polar bear, ringed seal, Arctic fox, mink, loons, seabirds and fish in the Canadian Arctic[16], polar bear, ringed seal, minke whale and black guillemot from Greenland[17,18], in long-finned pilot whale and northern fulmar from the Faroe Islands[17], in various organisms in a food web from the eastern Canadian Arctic[19] (zooplankton to marine mammals and seabirds) and in glaucous gull from the Norwegian Arctic[20]. A more circumpolar study of polar bears covering Alaska, Canada, Greenland and Svalbard has also been performed[21]. PFOS is the predominant PFC in most species studied and concentrations are as high or higher than those of single PCB congeners in polar bears. For polar bears, spatial trends indicate highest PFA concentrations in East Greenland, Svalbard and Hudson Bay but that there are differences in PFA profiles from different parts of the Arctic indicating different source regions[21-24].

Transport of POPs in migratory animals may also be a significant pathway, in the Arctic, where many important species such as seabirds, cetaceans (beluga, bowhead, minke) and pinnipeds (harp seals), salmon and Atlantic cod are migratory[4]. Ewald et al.[25] described the entry of PCBs and DDT into the grayling population of the Copper River in Alaska by migrating sockeye salmon. The grayling in a salmon spawning lake had contaminant concentrations more than double those found in grayling from a nearby, but salmon-free, lake. Detailed studies of the food web of Lake Ellasjøen at Bjørnøya (Bear Island) have shown that a biological pathway (seabird guano) is probably responsible for the elevated levels of OCs in Arctic char from this lake[26]. A similar study in several Arctic Canadian ponds showed a direct correlation between contaminant concentrations in sediments and how impacted the ponds were from seabird guano[27].

Temporal trends

Hung et al.[8,9] found significant declines of α-HCH, γ-HCH, PeCA, chlordane-related compounds and PCB 28, 101, 153 and 180 over a 5-year period (1993-1998) as well as increases in endosulfan and p,p'-DDE. Detailed analysis of temporal trends at other air sampling sites has not been carried out.

Temporal trends of POPs in Arctic biota have been extended so that a 25 to 30 year perspective is available for polar bears, seabirds and ringed seals in the Canadian Arctic, as well as for fish in the Swedish Arctic. Studies covering a 10-15 year period are available for polar bear at Svalbard, peregrine falcons in Alaska and Greenland, Atlantic cod in Iceland, glaucous gulls in Svalbard, burbot, lake trout and beluga whales in Canada, ringed seal from East Greenland and walrus in northwestern Greenland. Levels of ΣPCB, ΣDDT, ΣHCH and HCB in pike and Arctic char from the Swedish Arctic have declined significantly since the late 1960s into the 1990s, decreasing at a rate of approximately 4% to 10% per year[4]. However, no significant decline has been observed for the past 10 years for HCH isomers and HCB, while ΣPCB and ΣDDT continue to decline at about the same rate in the 1990s as in the 1980s. ΣDDT and ΣHCH both declined significantly in liver of burbot from 8 Russian north flowing rivers between 1988 and 1994 in parallel to declines of these pesticides in river water[28].

Levels of ΣPCB and ΣDDT decreased significantly in eggs of kittiwake, thick-billed murre, northern fulmar, in the Canadian Arctic archipelago (1975-1998), while ΣCHL, dieldrin and mirex levels decreased in kittiwake eggs only[29]. ΣDDT also declined significantly in female ringed seals from three locations in the Canadian Arctic archipelago, between the early/mid-1970's to late-1990's/2000. ΣDDT had the largest decline of any "legacy" organochlorines – 2.5 x at Ausuittuq, 3.3 x at Ikajutit and 2.0x at Sachs Harbour over 13-30 years[30]. Levels of PCDD/PCDFs and non-ortho PCBs have declined in ringed seals from East Greenland from 1986 to 2003[31]. Temporal trends of PCB 153 concentrations in polar bear blood were studied using annual samples collected between 1990 and 1998[32]. Decreases of ca. 40% occurred in the early 1990s, and stabilized thereafter. This is a more rapid trend than was found for PCB 153 in Hudson Bay polar bears during the same time period.

Ikonomou et al.[33] reported exponential increases in total (Br_2-Br_7)-PBDEs (ΣPBDEs) in male ringed seals aged 0-15 years from Holman in the western Canadian Arctic over the period 1981 to 2000. ΣPBDEs increased 9-fold over this period. Similar increase of PBDEs were found in beluga whales[34]. The doubling time for PBDEs in beluga during the early 1990s (t2=3.0 years) was faster than in Holman ringed seals (t2=4.5 years). Vorkamp et al.[35] found significantly increasing concentrations of penta-, hexa and decaBDE in peregrine falcons from southern Greenland from 1986 to 2003.

Bossi et al.[18] found increasing temporal trends for PFOS and some PFCAs in ringed seals from two sites on Greenland. Archived polar bear liver tissues from two geographic locations in the North American Arctic showed exponential increases for PFOS and PFCAs with carbon chain lengths of C9-C11 between 1972 and 2002[36]. The doubling times ranged from 3.9-5.6 years for PFNA to 9.8-13.1 years for PFOS.

Bioaccumulation/biomagnification

Previous studies of OCs in Arctic food webs have been reviewed to identify factors of importance for bioaccumulation and trophic transfer[37,38]. Diet and trophic level were dominant factors for seabirds and marine mammals, but biotransformation also has influence. Few studies exist, but these indicate that BDE 47, 99, 100 and 153 biomagnify in Arctic marine food webs[14]. This has been seen when comparing concentrations in ringed seal and beluga to polar cod, and polar bears to ringed seal from the same area. For PFAs, PFOS and PFCAs were found in higher concentrations at higher trophic levels in the food web[16], and PFOS has been shown to biomagnify from lower trophic levels to predators in the Arctic marine food web[17,19].

References

1. Muir DCG, Wagemann R,Hargrave BT,Thomas D,Peakall DB,Norstrom RJ. *Sci Total Environ* 1992;122: 75.
2. Barrie LA, Gregor D, Hargrave B, Lake R, Muir DCG, Shearer R, Tracey B, Bidleman T. *Sci Total Environ* 1992;122:1.
3. de March BGE, de Wit CA, Muir DCG (eds). In: *Arctic Assessment Report*, Chapter 6. Arctic Monitoring and Assessment Programme. Oslo. Norway, 1998:183-372.

4. de Wit CA, Fisk AT, Hobbs KE, Muir DCG, Gabrielsen GW, Kallenborn R, Krahn MM, Norstrom RJ, Skaare JU. In: *AMAP Assessment 2002: Persistent Organic Pollutants in the Arctic*, de Wit CA, Fisk AT, Hobbs KE, Muir DCG. (eds), Arctic Monitoring and Assessment Programme. Oslo. Norway, 2004:309 pp.
5. Li YF. *J Geophys Res* 1999;104, D19, 23,785.
6. Breivik K, Sweetman A, Pacyna JM, Jones KC. *Sci Total Environ* 2002;290:199.
7. Cohen MD, Draxler RR, Artz R, Commoner B, Bartlett P, Cooney P, Couchot K, Dickar A., Eisl H, Hill C, Quigley J, Rosenthal JE, Niemi D, Ratte D, Deslauriers M, Laurin R, Mathewson-Brake L, McDonald J. 2002 *Environ Sci Technol* 2002;36: 4831.
8. Hung H, Halsall CJ, Blanchard P, Li HH, Fellin P, Stern G, Rosenberg B. *Environ Sci Technol* 2001;35:1303.
9. Hung H, Halsall CJ, Blanchard P, Li HH, Fellin P, Stern G, Rosenberg B. *Environ Sci Technol* 2002;36: 862.
10. Stern GA, Halsall CJ, Barrie LA, Muir DCG, Fellin P, Rosenberg B, Rovinsky FYa, Kononov Eya, Pastuhov B. *Environ Sci Technol* 1997;31:3619.
11. Bailey R, Barrie LA, Halsall CJ, Fellin P, Muir DCG *J Geophys Res Atmos* 2000;105:11805.
12. Wagrowski DM, Hites RA. *Environ Sci Technol* 2000;34:2952.
13. Brzuzy LP, Hites RA. *Environ Sci Technol* 1996;30:1797.
14. de Wit CA, Alaee M, Muir DCG. *Chemosphere* 2006;63: in press.
15. Giesy JP, Kannan K. *Environ Sci Technol* 2001;35:1339.
16. Martin JW, Smithwick MM, Braune BM, Hoekstra PF, Muir DCG, Mabury SA. *Environ Sci Technol* 2004;38:373.
17. Bossi R, Riget FF, Dietz R, Sonne C, Fauser P, Dam M, Vorkamp K. *Environ Poll* 2005;136:323.
18. Bossi R, Riget FF, Dietz R. *Environ Sci Technol* 2005;39:7416.
19. Tomy GT, Budakowski W, Halldorson T, Helm PA, Stern GA, Friesen K, Pepper K, Tittlemier SA, Fisk AT. *Environ Sci Technol* 2004;38:6475.
20. Verreault J, Houde M, Gabrielsen GW, Berger U, Haukås M, Letcher RJ, Muir DCG. *Environ Sci Technol* 2005;39:7439.
21. Smithwick M, Mabury SA, Solomon KR, Sonne C, Martin JW, Born EW, Dietz R, Derocher AE, Letcher RJ, Evans TJ, Gabrielsen GW, Nagy J, Stirling I, Taylor MK, Muir DCG. *Environ Sci Technol* 2005;39:5517.
22. De Silva AO, Mabury SA. *Environ Sci Technol* 2004;38:6538.
23. Smithwick M, Muir DCG, Mabury SA, Solomon KR, Martin JW, Sonne C, Born EW, Letcher RJ, Dietz R. *Environ Toxicol Chem* 2005;24:981.
24. Kannan K, Yun SH, Evans TJ. *Environ Sci Technol* 2005;39:9057.
25. Ewald G, Larsson P, Linge H, Okla L, Szarzi N. *Arctic* 1998;51:40.
26. Evenset A, Christensen GN, Skotvold T, Fjeld E, Schlabach M, Wartena E, Gregor D. *Sci Total Environ* 2004;318:125.
27. Blais JM, Kimpe LE, McMahon D, Keatley BE, Mallory ML, Douglas MSV, Smol JP. *Science* 2005;309:445.
28. Zhulidov AV, Robarts RD, Headley JV, Liber K, Zhulidov DA, Zhulidova AV, Pavlov DF. *Sci Total Environ* 2002;293: 231.
29. Braune BM, Donaldson GM, Hobson KA. *Environ Pollut* 2001;114:39.
30. Muir D, Fisk A, Kwan M. In: *Synopsis of Research Conducted Under the 2000-2001 Northern Contaminants Program*, Kalhok S. (ed.), Indian and Northern Affairs Canada, Ottawa, Canada, 2001:208-214.
31. Riget F, Vikelsøe J, Dietz R. *Mar Poll Bull* 2005;50:1523.
32. Henriksen EO, Wiig Ø, Skaare JU, Gabrielsen GW, Derocher AE. *J Environ Monit* 2001;3:493.
33. Ikonomou MG, Rayne S, Addison RF. *Environ Sci Technol* 2002;36:1886.
34. Stern GA, Ikonomou M. In: *Synopsis of Research Conducted Under the 1999-2000 Northern Contaminants Program*, Kalhok, S. (ed), Indian and Northern Affairs Canada. Ottawa, ON, 2000:227-232.
35. Vorkamp K,Thomsen M, Falk K, Leslie H, Møller S, Sørensen PB. *Environ Sci Technol* 2005;39:8199.
36. Smithwick M, Norstrom RJ, Mabury SA, Solomon K, Evans TJ, Stirling I, Taylor MK, Muir DCG. *Environ Sci Technol* 2006;40:1139.
37. Borgå K, Fisk AT, Hoekstra PF, Muir DCG. *Environ Toxicol Chem* 2004;23:2367.
38. Borgå K, Gabrielsen GW, Skaare JU, Kleivane L, Norstrom RJ, Fisk AT. *Environ Sci Technol* 2005;39:4343.