Chapter 4

Regional and Circumpolar Levels and Trends in Abiotic and Biotic Media

This section reviews new information on the levels and spatial trends of POPs in Arctic abiotic and biotic media available since 1996. Some earlier data which were omitted from the previous assessment are also included. Most interpretations in this chapter, including comparisons and conclusions about spatial trends, were made by scientists in charge of projects described (most are listed as contributing authors) and by the four editors. In some cases interpretation was not possible due to limited sample numbers. The new data are primarily entered as summary data in the Annex Tables, and interpretations were kept to a minimum. It should also be noted that sample sizes for results given in the Annex Tables vary greatly. Readers should be aware of the risk of spurious conclusions drawn from small data sets. Within the AMAP monitoring program, QA/QC criteria have been defined, and these have been followed by almost all laboratories that have contributed data to the assessment. All laboratories providing data within their national monitoring programs have also taken part in intercalibration exercises. Therefore, the data presented here are comparable across laboratories. The only major exceptions occur when varying numbers of congeners have been analyzed and quantified. This is most prevalent for PCBs and toxaphene, both of which have been reported as differing numbers of congeners as well as total sums based on quantification against a technical product (total PCB, total toxaphene).

Readers are also reminded that concentrations are expressed in several ways in this report. In biological samples concentrations are expressed on a wet weight basis, giving the concentration of OC in the total weight of tissue analyzed; on a lipid weight basis, giving the concentration in the lipids in that particular tissue; or as a body burden, giving the contaminant concentration in the whole organism. OC levels in abiotic samples and some biotic samples, most often plants, are expressed on a dry weight basis. The following abbreviations are used throughout the text to distinguish lipid weight concentrations (that is 'ng/g lw'), from results reported on a wet weight ('ww') or dry weight ('dw') basis. All lipid weight concentrations are calculated from the wet weight concentrations unless otherwise indicated. Concentrations of OCs in air samples expressed as pg/m^3 are presented for gas phase and particle phase separately or are summed to give a total air concentration. Fluxes of OCs in sediments are expressed as $ng/m^2/yr$ (i.e. concentration in $ng/g \times$ sedimentation rate $g/m^2/yr$).

4.1. Atmospheric environment
4.1.1. Air
4.1.1.1. Introduction

Measurements of POPs in Arctic air have continued on a weekly basis at locations in Canada, Iceland, Norway, Finland, and Russia, building on the datasets discussed in the first assessment. In addition, over the past five years, a number of ship-based studies have also measured air concentrations of POPs over shorter time periods to address air–water exchange.
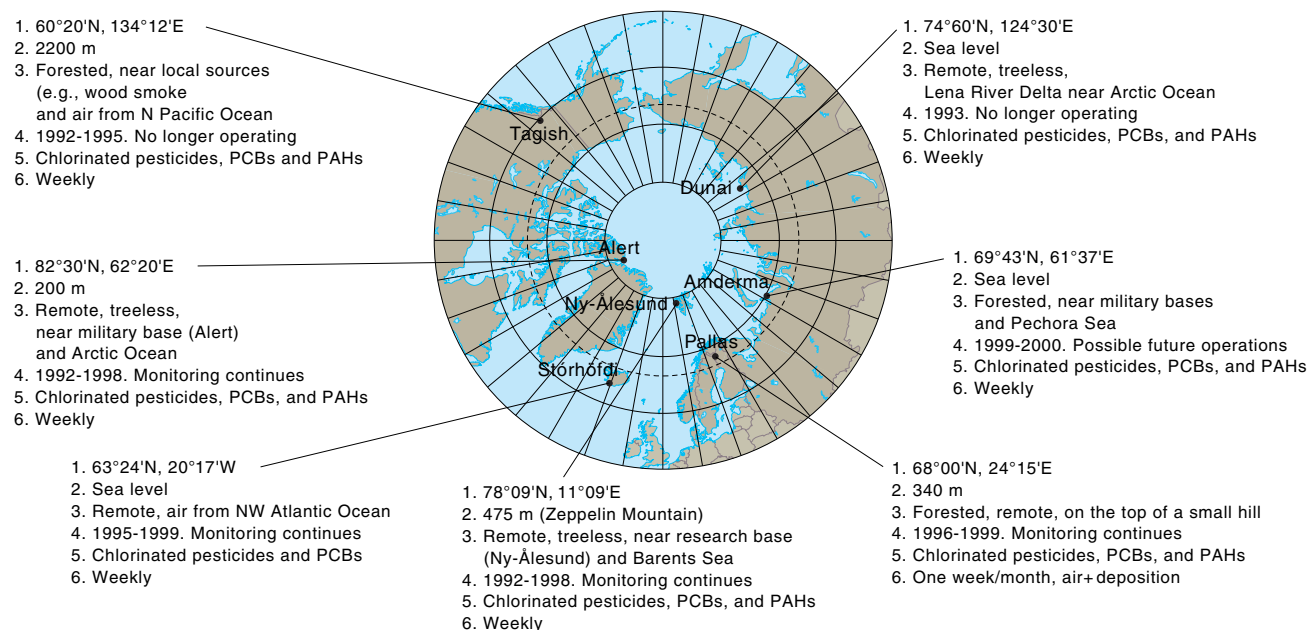

1. 60°20'N, 134°12'E
2. 2200 m
3. Forested, near local sources
   (e.g., wood smoke
   and air from N Pacific Ocean
4. 1992-1995. No longer operating
5. Chlorinated pesticides, PCBs and PAHs
6. Weekly

1. 82°30'N, 62°20'E
2. 200 m
3. Remote, treeless,
   near military base (Alert)
   and Arctic Ocean
4. 1992-1998. Monitoring continues
5. Chlorinated pesticides, and PAHs
6. Weekly

1. 63°24'N, 20°17'W
2. Sea level
3. Remote, air from NW Atlantic Ocean
4. 1995-1999. Monitoring continues
5. Chlorinated pesticides and PCBs
6. Weekly

1. 78°09'N, 11°09'E
2. 475 m (Zeppelin Mountain)
3. Remote, treeless, near research base
   (Ny-Ålesund) and Barents Sea
4. 1992-1998. Monitoring continues
5. Chlorinated pesticides, PCBs, and PAHs
6. Weekly

1. 74°60'N, 124°30'E
2. Sea level
3. Remote, treeless,
   Lena River Delta near Arctic Ocean
4. 1993. No longer operating
5. Chlorinated pesticides, PCBs, and PAHs
6. Weekly

1. 69°43'N, 61°37'E
2. Sea level
3. Forested, near military bases
   and Pechora Sea
4. 1999-2000. Possible future operations
5. Chlorinated pesticides, PCBs, and PAHs
6. Weekly

1. 68°00'N, 24°15'E
2. 340 m
3. Forested, remote, on the top of a small hill
4. 1996-1999. Monitoring continues
5. Chlorinated pesticides, PCBs, and PAHs
6. One week/month, air+ deposition

Tagish • Dunai • Alert • Anderma • Ny-Ålesund • Pallas • Stórhöfdi

Figure 4·1. Locations and site-specific information for each POPs air monitoring station. 1. Latitude/longitude; 2. Elevation; 3. Description; 4. Sampling period and status as of 2002 (this is the total operational period for which data were available for this assessment. Sampling period varies with chemicals measured); 5. POPs monitored; 6. Sampling schedule.
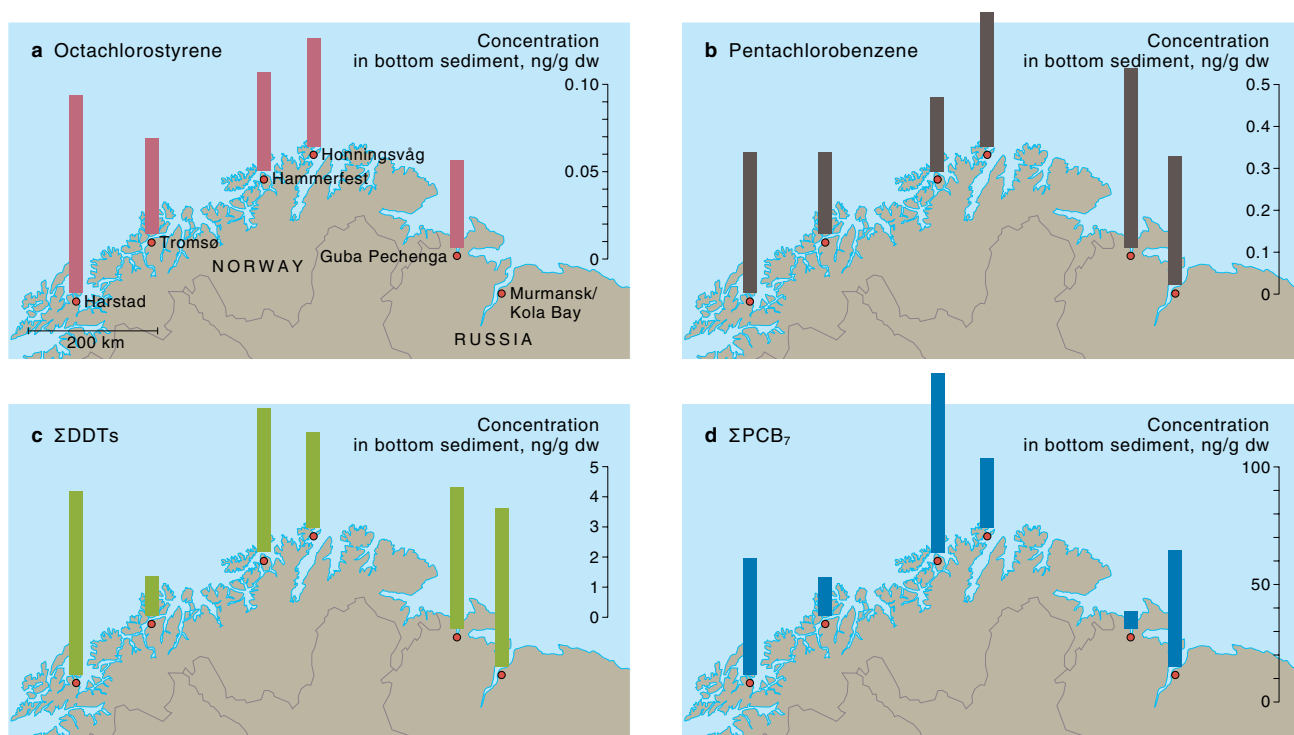
Figure 4·35. Geometric mean concentrations of octachlorostyrene, pentachlorobenzene, ΣDDT, and ΣPCB$_7$ in bottom sediments of some harbors of northern Norway and the Kola Peninsula. ΣDDT = p,p'-DDE + p,p'-DDD + p,p'-DDT; ΣPCB$_7$ = CB28 + CB52 + CB101 + CB118 + CB138 + CB153 + CB180.

The highest concentration of ΣPCB$_7$ was found in the harbors of Harstad, Hammerfest, and the Murmansk area of Kola Bay (Figure 4·35). Detailed results are presented in Annex Table 9. All these harbors had PCB concentrations, which according to guidelines from Norwegian State Pollution Control Authority (SFT) (Molvær *et al.*, 1997) are classified as 'strongly polluted'. In all the harbors, locations were found having ΣDDT concentrations classified as 'strongly polluted'. The concentrations of pentachlorobenzene and OCS were also elevated in all the harbors compared to previous reports for background areas at offshore locations (de March *et al.*, 1998).

There were also statistically significant differences ($p < 0.05$) between the distributions of HCB and ΣHCHs in the six harbors. For OCS, Harstad harbor was significantly different from the four others (no data from Kola Bay), and for pentachlorobenzene, both Harstad and Pechenga were significantly different compared to the other four harbors. For ΣDDTs, Tromsø had a significantly different pattern, and for ΣPCB$_7$, the most polluted harbors (Harstad, Hammerfest, Honningsvåg, and Kola Bay) comprised a homogeneous group different from the two others (Figure 4·35).

In sediments from all these harbors and also from Honningsvåg and Kola Bay areas, the higher chlorinated CBs predominated in samples where the highest ΣPCB$_7$ concentrations were found. Only sediments from Guba Pechenga with maximum ΣPCB$_7$ levels had high percentages of lower chlorinated CBs.

Savinova *et al.* (2000a) analyzed samples collected in 1997 from Kola Bay and Guba Zapadnaya Litsa on the western Kola Peninsula. In general, levels of OCs were similar to those reported by Dahle *et al.* (2000). However, high concentrations of toxaphene were found at locations in Kola Bay (up to 681 ng/g dw) and intermedi-

ate concentrations in Guba Zapadnaya Litsa (19-95 ng/g dw). This was the first report of toxaphene in marine sediments in the European Arctic and it suggests use and/or spills in the harbor area of Polamyy north of Murmansk.

Savinov *et al.* (2003) reported OCs in sediments collected in 1997 in Guba Pechenga and adjacent marine coastal areas: Varangerfjord, Guba Malaya Volokovaya, and Guba Bol'shaya Volokovaya on the western Kola Peninsula. Slightly elevated ΣDDT concentrations (37 ng/g dw) were found in Liinakhamari harbor in Guba Pechenga and a high DDT:DDE ratio (23.4) indicated a possible local DDT source in this area. However, the overall average ΣDDT levels in Guba Pechenga sediments were comparable with those in harbor sediments of northern Norway (Dahle *et al.*, 2000) and outer Kola Bay (Savinova *et al.*, 2000a). PCB concentrations in Guba Pechenga were slightly elevated in Liinakhamari harbor as well. However, overall values was significantly lower in comparison with those found in harbors of the northern Norway and Kola Bay (Dahle *et al.*, 2000; Savinova *et al.*, 2000a)

The studies of harbors in northern Norway and northwestern Russia indicate that harbors may be 'hot spots' for contaminants in the Arctic. Steps need to be taken to understand the extent of the pollution in the harbors, the potential for spreading to adjacent waters including the Barents Sea, and the impact on regional fauna.

Analysis of a sediment core from the profundal area of Kandalashka Bay in the White Sea revealed relatively low levels of persistent OCs (Annex Table 9). Maximum concentrations of most OCs were found in deeper layers indicating greater inputs in the recent past (Muir *et al.*, 2002a). ΣPCB concentrations were higher than back-

ground locations in the southwest Barents Sea (Savinov *et al.*, 2003) but lower than in Kola Bay and Guba Zapadnaya Litsa.

Kara and Laptev Seas

Sericano *et al.* (2001) reported POPs in surficial sediments from the southern Kara Sea adjacent to the Ob and Yenisey. The samples were collected in 1993. However, results were not available for the previous AMAP POPs assessment. ΣDDT and ΣPCB concentrations in sediments ranged from <0.1 to 1.2 ng/g dw and <0.1 to 1.5 ng/g dw, respectively. Chlordane compounds were not detected (<0.1 ng/g dw). Despite the low levels, a distinct distribution pattern was observed with higher concentrations in the lower part of the Yenisey below the salt wedge. The concentrations of ΣDDTs and ΣPCBs in marine sediments were within the range reported previously for the Ob and Yenisey Gulf (0.03-0.8 ng/g dw and 0.01-2.2 ng/g dw, respectively) (Vlasov and Melnikov, 1995, *in* de March *et al.*, 1998).

Relatively high proportions of *p,p'*-DDT and *o,p'*-DDT in sediments suggested local or fresh sources of DDT at the time of sample collection (1993). The PCB homologue profile in the sediments was dominated by Pe- and HxCBs, suggesting local or nearby sources of PCBs to the Kara Sea.

Utschakowski (1998) determined PCBs in surface sediment samples collected in 1993 from the southern Laptev Sea offshore of the Lena River Delta. ΣPCB concentrations averaged 0.53 ng/g dw (range 0.14-1.99 ng/g dw) and were correlated with organic carbon content of the sediments (Annex Table 9).

Canadian Arctic

In 1997 and 1998, sediment cores and grab samples were collected from various regions of the Canadian Arctic Archipelago including northern Baffin Bay (Annex Table 9). A number of these grab samples have been analyzed for OC pesticides, PCBs, and current-use contaminants such as short-chain (C_{10}-C_{13}) chlorinated par-

affins and PBDEs (Stern and Lockhart, 2001). Concentrations of the major OC groups were lower than reported previously for Hudson Bay surface sediments taken from a core (Lockhart, 1997). A generally decreasing trend from south to north and from east to west is apparent from the results, although this could be influenced by variation in sedimentation rates (Figure 4·36).

ΣPCB concentrations in the sediments from the archipelago waters ranged from 0.3 to 2.9 ng/g dw. These are at the low end of the range for marine sediments found in the previous AMAP POPs assessment (de March *et al.*, 1998). DDT and total chlordane-related compounds were present at extremely low levels (0.04-0.44 ng/g dw). SCCP concentrations in the surface sediments ranged from 4.8 to 77.4 ng/g dw and were among the predominant OC compounds in these sediments. As with the OC pesticides and PCBs, a decreasing trend in SCCP concentrations was observed from southern (Barrow Strait) to northern (Peary Channel) and western Arctic (M'Clure Strait/Viscount Melville). Sediment concentrations were lower than in the eastern Arctic (Strathcona Sound/Lancaster Sound) sediments (Annex Table 9; Figure 4·36).

4.4.3. Marine phytoplankton and invertebrates

Marine invertebrates provide a link between phytoplankton and fish/seabirds/mammals in Arctic marine food webs. They are important in the transfer of carbon and nutrients as well as POPs to upper trophic-level organisms. An understanding of the trends and dynamics of POPs in marine invertebrates is a key to understanding the trends of POPs in Arctic marine ecosystems.

A number of studies have been recently carried out to examine OC concentrations in marine invertebrates, an area identified as a knowledge gap in the first AMAP assessment report. These studies covered a wide geographical area and have provided information on spatial trends. There was also a single study on levels of OCs in plankton, predominantly phytoplankton. Many of these stud-
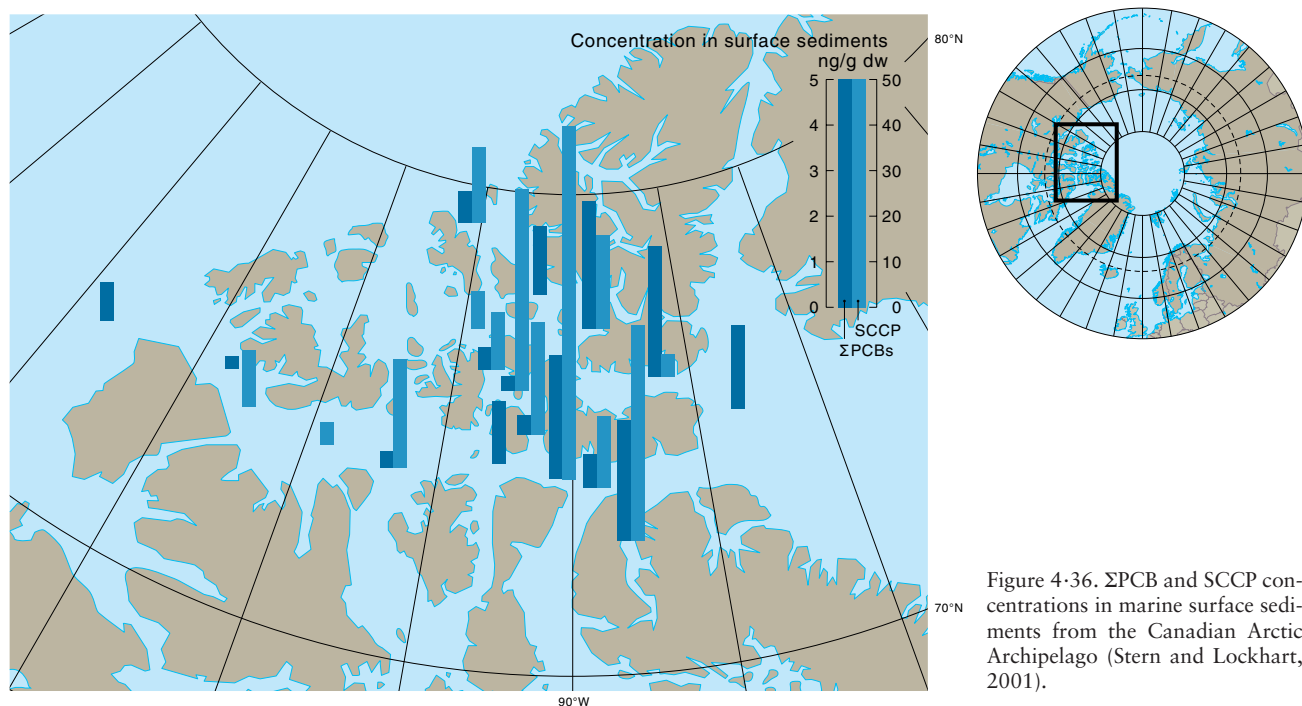

Figure 4·36. ΣPCB and SCCP concentrations in marine surface sediments from the Canadian Arctic Archipelago (Stern and Lockhart, 2001).

ies were designed to examine factors that influence OC concentrations in these lower trophic-level organisms. A large number of samples from single species, particularly in zooplankton, were analyzed for OCs. In a number of cases, these data were used in food web studies, discussed in Section 4.4.9.

In general, OC concentrations in marine phytoplankton and invertebrates are low, consistent with their generally lower trophic levels and smaller body sizes. Invertebrates that are longer-lived, larger-bodied or that scavenge have higher POP levels and are generally benthic.

Phytoplankton
Marine samples were collected to the west of Bjørnøya (74°22'N, 18°55'E) as part of a marine food web study (Evenset *et al*., 2002). This work was part of the larger study examining elevated levels in Ellasjøen (see Section 4.3.5). Twenty-three vertical hauls (net diameter 25 cm, mesh size 5 μm) were taken from 20 m depth to the surface. These samples were predominantly phytoplankton. Low concentrations of PCBs and pesticides (mostly below detection limits for pesticides) were found in the marine phytoplankton sample taken west of Bjørnøya (Annex Table 10).

Zooplankton
A number of studies have examined OCs in pelagic zooplankton. The most common OC compounds in pelagic zooplankton are the more water-soluble compounds, such as the HCH isomers and lower chlorinated PCB congeners. This reflects the smaller size, lower trophic level, and lack of biotransformation capacity generally found in zooplankton as compared to fish, mammals, and birds.

Spatial trends in calanoid copepods
OC concentrations were determined in calanoid copepod samples from a number of studies in the Beaufort Sea and Hudson Bay (Hoekstra *et al*., 2002b), northern Baffin Bay (Fisk *et al*., 2001a), and in the ocean around Svalbard (Borgå *et al*., 2001) (see Figure 4·37 for locations). Calanoid copepods are dominant components, in terms of both number and biomass, in high-latitude marine zooplankton communities, and play an important role in polar food webs, as their high lipid reservoirs and biomass provide organisms at higher trophic levels with a high-energy diet (Springer *et al*., 1996). Concentrations (lipid-normalized) of ΣPCB_{10} (sum of ten congeners) in the Beaufort Sea samples were slightly lower than those in northern Baffin Bay and Hudson Bay, which were similar (Figure 4·37). OC concentrations in the North American copepods were greater than those measured in oceans to the east (Greenland Sea) and north of Svalbard but lower than those observed to the south of Svalbard (Barents Sea) (Figure 4·37). Similar trends were seen with other OC groups including toxaphene, $\Sigma DDTs$, and $\Sigma CHLs$. Levels of OCs were also higher in the northern Baffin Bay predatory amphipod, *Themisto libellula* (Fisk *et al*., 2002a) compared with the same species collected east and north of Svalbard (Borgå *et al*., 2001). These spatial trends do not agree with that observed in marine mammals (Muir *et al*., 2000b) and some seabird species (Fisk *et al*., 2001b). Concentrations of most OCs, excluding HCH, in upper
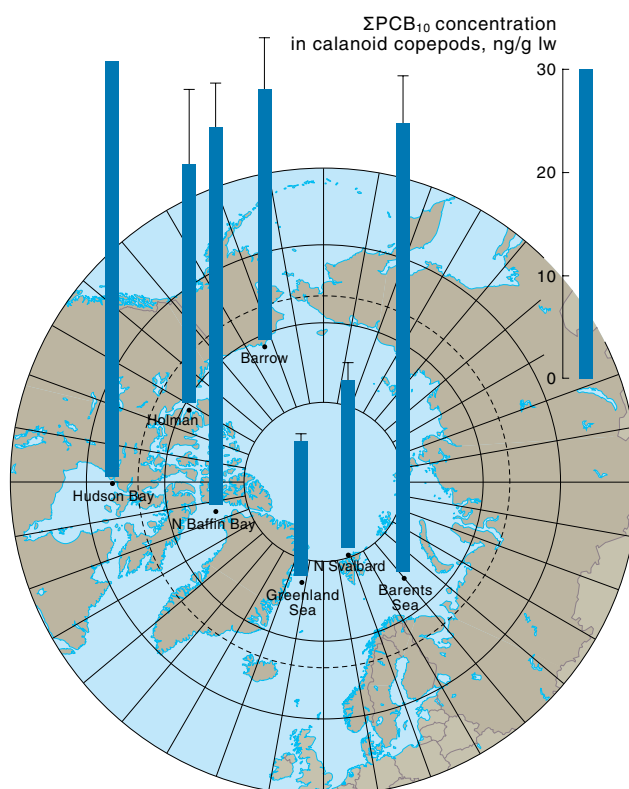

Figure 4·37. Concentrations of ΣPCB_{10} in calanoid copepods from Barrow, Alaska; Holman, NWT and Hudson Bay (Hoekstra *et al*., 2002b); northern Baffin Bay (Fisk *et al*., 2001a); and regions around Svalbard (ΣPCB_9, Borgå *et al*., 2001).

trophic-level organisms are much higher in the European compared to the North American Arctic. Thus, concentrations found at the base of these two food webs cannot explain the high POP levels seen in upper trophic-level organisms in the European Arctic compared to northern Baffin Bay.

The low OC concentrations in the copepods from east (Greenland Sea) and north of Svalbard may be due to timing of the sample collection, seasonal changes in water concentrations of OCs, and/or the source of water in these locations. As a small organism, the copepod could reflect subtle changes of OCs in water that a large organism would not. The source of water for these copepods would come predominantly from under the ice cap to the north, which would explain, in part, the lower concentration of OCs compared to the Barents Sea copepods. The collection of the copepods from the east and north of Svalbard also occurred in September and October after the open-water period. Hargrave *et al*. (2000) found that OC concentrations were highest in Arctic zooplankton during periods of ice cover.

Concentrations of HCB and HCH isomers in the Beaufort Sea copepods were relatively higher than the more easterly sampling locations. The abundance of HCB and $\Sigma HCHs$ in Alaskan and western Canadian zooplankton reflects the long-range atmospheric transport of the chemicals and geographic proximity to areas of recent application in Asia (Li, 1999a; 1999b; Bailey *et al*., 2000). The concentrations of OC compounds in zooplankton samples, including *Calanus hyperboreus*, collected in the late 1980s in the Arctic Ocean were similar to the Beaufort Sea values (Bidleman *et al*., 1989). This suggests that OC concentrations in the western

Arctic zooplankton have remained constant during the 1990s in the Beaufort Sea region.

The ranking of OC group concentrations in the Alaskan and Canadian copepods from highest to lowest were: toxaphene ≥ ΣPCBs > ΣHCHs > ΣDDTs > ΣCHLs > ΣCBz (Fisk *et al*., 2001a; Hoekstra *et al*., 2002b). There are no toxaphene data for the Barents Sea copepods, but the general ranking of OCs is similar, except for lower relative levels of ΣHCHs (Borgå *et al*., 2001). Recent work on mixed zooplankton from the west of Bjørnøya found toxaphene to be the predominant OC although at concentrations lower than PCBs (Annex Table 10) (Evenset *et al*., 2002). The higher abundance of toxaphene congeners relative to other OCs in North American zooplankton is consistent with OC concentrations in zooplankton collected in the Arctic Ocean offshore from Axel Heiberg Island in the Canadian Arctic (Bidleman *et al*., 1989). The α- and γ-HCH isomers and lower chlorinated PCB congeners were the most common OCs found in the Arctic calanoid copepods.

Levels in other zooplankton species
OC data for a number of other pelagic zooplankton have been recently generated in northern Baffin Bay (Fisk *et al*., 2001c; 2002a; Moisey *et al*., 2001) and the Barents Sea region (Borgå *et al*., 2001; 2002b). A majority of these samples were analyzed as part of food web studies, discussed in Section 4.4.9. Seven species of zooplankton were collected in northern Baffin Bay and analyzed for OCs, including: *C. hyperboreus* (herbivorous copepod, discussed above); *Euchaeta glacialis* (omnivorous copepod); *Metridia longa* (omnivorous copepod); *Mysis occulata* (detritus-feeding and predatory mysid); *Themisto libellula* (predatory amphipod); *Sagitta* sp. (predatory arrowworm); and *Pandalus* sp. (predatory shrimp). Lipid content varied between species, ranging from 2.1 to 7.0%. OC concentrations (lipid corrected) varied between species and appeared to be related, in part, to a combination of trophic position (as determined by $\delta^{15}N$) and body size (Figure 4·38). The relative ranking of OC groups also varied with the species.

In general, for these zooplankton species, ΣPCB concentrations were highest and ΣCBz concentrations were lowest. Borgå *et al*. (2001) measured OCs in the herbivorous pelagic copepod *Calanus* sp. (copepods), the herbivorous euphausiid *Thysanoessa* sp., and the predacious pelagic crustacean *Parathemisto libellula* (amphipod). OC concentrations were similar to those observed in the northern Baffin Bay zooplankton.

Concentrations of PCBs (both as sum of 11 congeners and Aroclor 1254) were determined in mixed zooplankton (*Calanus* sp., *T. libellula*, ctenophores, gastropods) and shrimp (*Pandalus borealis*) collected in 1991 from various sites within the Barents Sea region (Joiris *et al*., 1997). ΣPCB levels were not related to lipid levels of the zooplankton. Levels of ΣPCB were higher in the shrimp samples compared to the mixed zooplankton using lipid corrected values, but lower when wet weight concentrations were examined. Concentrations for both sample types did not vary between sites. Concentrations were found to be lower than levels measured in similar species from the Atlantic Ocean but higher than levels observed in the Canadian Arctic.

Factors influencing OC levels in zooplankton
The relative abundance of hydrophobic chemicals such as ΣDDTs and ΣCHLs in copepod samples of Alaska and Canada was greater than that observed in water (Fisk *et al*., 2001a; Hoekstra *et al*., 2002b), and reflects their greater potential for bioaccumulation from the abiotic environment into marine zooplankton near the base of the food chain than less hydrophobic OCs. The relationships observed between the bioconcentration factor (BCF) and K_{ow} for the Beaufort Sea and northern Baffin Bay calanoid copepods were linear and near, but slightly higher than, 1:1 for OCs with a log K_{ow} between 3 and 6, but curvilinear when hydrophobic OCs (log $K_{ow} > 6$) were included (Fisk *et al*., 2001a; Hoekstra *et al*., 2002b). These results suggest that for hydrophobic OCs (log K_{ow} 3.8-6.0) dietary accumulation may play a small role in elevating OC levels above equilibrium in zooplankton.

Studies of OC levels in zooplankton collected to the west of Bjørnøya found that zooplankton size was an important variable in OC concentrations (Evenset *et al*., 2002). The concentrations in zooplankton seemed to increase from small zooplankton (<1 mm, mainly copepods) to larger zooplankton (>1 mm, mainly comb jel-
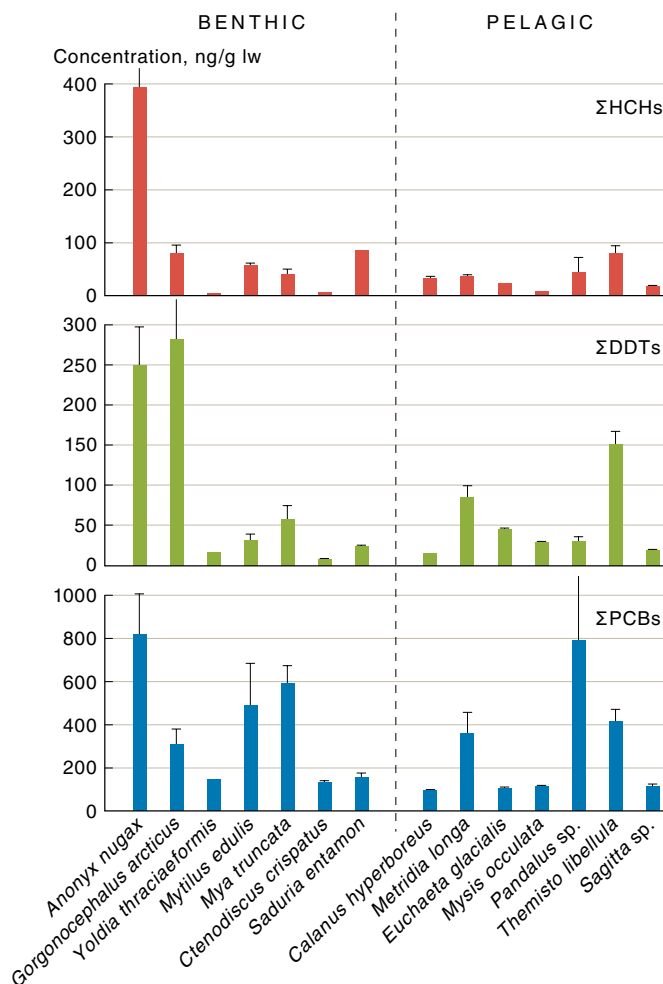

Figure 4·38. Concentrations of ΣHCHs, ΣDDTs, and ΣPCBs in Arctic benthic and pelagic invertebrates. All samples were collected in 1998 in northern Baffin Bay except *M. truncata* (1993 in Iqaluit harbor), *M. edulis* (1998 at seven locations in northern Quebec) and *S. entamon* (1998 in northern Alaska near Barrow). Results of *A. nugax* and *G. arcticus* include samples from Cumberland Sound. All data from Fisk et al. (2002a). Bars are mean ± 1 SE; see Annex Table 10 for sample numbers.

lies, arrow worms, and medusae) to larger crustaceans. The exception was PCBs, concentrations of which were highest in the zooplankton >1 mm.

To investigate the levels of OCs in sympagic (i.e. associated with ice edges) fauna, ice-associated amphipods were collected in the marginal ice zone north of Svalbard and in the Fram Strait in September 1998 and 1999 (Borgå *et al.*, 2002a; 2002b). Amphipods dominate the sympagic fauna (Melnikov, 1997), and represent a direct link between ice-algae and sympagic meiofauna and higher trophic levels (Lønne and Gulliksen, 1989; Lønne and Gabrielsen, 1992). Due to the general sea-ice drift pattern (Colony and Thorndike, 1985) and the possible transport of contaminants by sea ice (Pfirman *et al.*, 1995), the contaminant occurrence in organisms in melting areas, such as the marginal ice zone north of Svalbard and in the Fram Strait, is of special interest and may explain elevated OC concentrations in Svalbard marine mammals and seabirds. Three species of amphipods, representing a number of feeding strategies, were analyzed for OCs (Borgå *et al.*, 2002a; 2002b) including *Apherusa glacialis*, *Onisimus* sp. and *Gammarus wilkitzkii*. OC concentrations increased from the more herbivorous *A. glacialis* to the more carnivorous *G. wilkitzkii* and the more necrophagous *Onisimus* sp. (Borgå *et al.*, 2002a). The composition of compound classes of HCHs, chlordanes, and DDTs was similar between the amphipod families, whereas the profiles of PCBs differed.

Even though marine invertebrates have direct uptake by passive diffusion of contaminants across their gills, these results imply that the species' ecology, such as diet, is important in the bioaccumulation process of OCs. In addition, the results show that the sea-ice drift route influences the concentrations of OC pollutants in sympagic organisms.

In sympagic amphipods, the levels and patterns of OCs differed spatially, with higher α-HCH concentrations in amphipods from the Fram Strait in comparison to amphipods collected north of Svalbard (Borgå *et al.*, 2002c). This could be related to the sea-ice drift route, since sea ice in the Fram Strait had a drift route across the central Arctic Ocean, while the sea ice north of Svalbard had a western drift route to the sampling stations.

The largest and longest-living sympagic amphipod, *G. wilkitzkii*, lives up to five years, reaching a maximum body length of 62 mm (Lønne and Gulliksen, 1991; Poltermann, 1997; 2000). With increasing age and size, *G. wilkitzkii* switches gradually from herbivory to a more carnivorous diet (Werner, 1997; Poltermann, 2000; Scott *et al.*, 2001). The OC burden in *G. wilkitzkii* may increase with age due to bioaccumulation over time, and due to increased biomagnification associated with the amphipod's age and size-related shift in trophic position. In addition, the contaminant burden in gilled organisms may be related to increasing size and body mass due to changes in lipid content, total metabolism, and the surface-to-volume ratio of gills which influences the exchange rate of OCs with water (Landrum, 1988; Walker *et al.*, 1996). The OC concentrations in two size-classes (small <29 mm and large >29 mm) of *G. wilkitzkii* were analyzed. The concentrations of more lipophilic compounds (e.g., PCBs) were lower in the smaller size-class, whereas concentrations of more hydrophobic compounds (e.g., HCHs) did not differ by size-class (Borgå *et al.*, 2002c).

Benthic marine invertebrates

Benthic invertebrates have a larger range of sizes, feeding ecology, and ecological niches than pelagic zooplankton, and therefore, have a greater range of OC concentrations (Fisk *et al.*, 2002a). Scavenging benthic invertebrates have the potential to have very high OC concentrations. PCBs are the OC group with the greatest concentrations in benthic invertebrates, with chlordane and DDT having high concentrations in certain species.

A number of Arctic benthic invertebrates have been analyzed for OCs since the previous AMAP assessment (see Annex Table 10). As with other invertebrates, ΣPCB concentrations were highest in benthic species, but the concentrations of the other OC groups varied with the invertebrates' feeding strategy (Figure 4·38). Scavenging invertebrates, such as the amphipod *Anonyx nugax* and basketstar *Gorgonocephalus arcticus*, have ΣHCH, ΣCHL and ΣDDT concentrations that are within 30-50% of ΣPCB concentrations. In filter-feeding and detritus-feeding invertebrates, such as *Yoldia thraciaeformis* or *Ctenodiscus crispatus*, the concentrations of other OC groups are much lower (approximately 20%) than ΣPCB concentrations. The highest concentrations of OCs in invertebrates are found in *A. nugax*, which have concentrations in the same range as found in Arctic cod and the little auk (seabird) (Fisk *et al.*, 2001c). OC concentrations in filter- and detritus-feeding invertebrates are among the lowest found in any biota in the world and are similar to pelagic zooplankton (Figure 4·38).

The blue mussel is a monitoring species that has been commonly used throughout the world, including the Arctic, to monitor OCs. PCBs and other OCs were present at very low levels in blue mussels from five locations in Nunavik, in the Ungava Bay and Hudson Strait areas, and two locations in Labrador, all from the eastern Canadian Arctic (Fisk *et al.*, 2002a) (see Annex Table 10 for locations). PCBs were present at much higher concentrations (range of means 3.7-46 ng/g ww) in mussel tissues compared to other OCs. HCH isomers were the next most prominent contaminants, with means ranging from 1.1 to 2.9 ng/g ww. The greater sorption of PCBs to sediment particles filtered by mussels, compared to most other OCs, especially HCH, may account for the much higher concentrations of PCBs. Doidge *et al.* (1993) found low ng/g ww levels of PCBs and OC pesticides in a survey of blue mussels from six communities in Nunavik. Levels of PCBs in mussel samples from Kuujjuaq were considerably higher than in the same species at most other locations, suggesting that local contamination sources might be a factor.

Levels of PCBs were determined in mussels (*Mytilus trossulus*) from 39 sites within the Aleutian Islands and five sites from southeast Alaska in 1994/1995 to determine whether high PCB levels in sea otter (*Enhydra lutris*) were due to local sources (Reese, 1998). Very high PCB concentrations were found at Amchitka, Adak, and Unalaska Islands (83, 430, and 2800 ng/g dw, respectively) but low levels were found elsewhere (ranging from 7.1 to 51 ng/g dw). This is a clear example of the influence of point source contamination, probably from military facilities, in the Arctic, which results in concentra-

tions that rank with the most contaminated sites in North America. Spatial patterns of OC pesticides suggest that these compounds come from sources that are more distant.

In 1997, soft parts of blue mussels collected in the Faroe Islands were analyzed for OCs (Larsen and Dam, 1999). The highest concentrations detected were for CB153 and *p,p'*-DDE, both at 0.7 ng/g ww and CB138 and *p,p'*-DDT, both at 0.4 ng/g ww. These concentrations are in the range of those measured in blue mussels in the eastern Canadian Arctic (Fisk *et al.*, 2002a) but are much lower than those measured close to the military sites in southeastern Alaska.

To assess the influence of point sources of pollutants on Svalbard (Spitsbergen), five species of benthic invertebrates were collected at various distances from possible point sources in 1998 and 1999 and analyzed for HCB, PAHs and PCBs (Hop *et al.*, 2001). Stable isotope analysis revealed that these species were all feeding at a low trophic level. Local inputs of PAHs and PCBs seemed to be present in some of the island's harbors and were elevated in benthic fauna compared to samples from Bjørnøya, which has little industry. The PCB profiles were similar to technical PCB, suggesting a local source. Concentrations were higher at sites closer to settlements. HCB did not appear to have local sources. This study provides more evidence that point sources in the Arctic can have a significant influence on the observed OC levels in wildlife.

In a recent study (Evenset *et al.*, 2002), spider crabs (*Hyas araneus*) were collected by diving in the littoral zone off the southwest part of Bjørnøya (late June 2000). Spider crabs had slightly higher PCB and pesticide concentrations than zooplankton collected from the same region. This study produced the first toxaphene results for Arctic benthic invertebrates and showed that toxaphene is present, although at lower concentrations than ΣPCBs, ΣDDTs and ΣHCHs.

4.4.3.1. TBT

TBT received limited attention in the first AMAP POPs assessment, as only a few invertebrates had been analyzed for TBT and its metabolites (DBT, MBT). TBT and its degradation products have now been measured in the blue mussel in Greenland, the Faroe Islands, Norway, and Iceland. Most of the studies dealing with TBT in the western part of the Atlantic are from animals living south of the AMAP area (Chau *et al.*, 1997; St-Jean *et al.*, 1999). In Greenland, TBT levels have only been examined near Nuuk, the largest town (≈13 000 inhabitants) in central western Greenland (Jacobsen and Asmund, 2000). Levels there were quite low (close to 1 ng/g ww) despite the fact that Nuuk harbor hosts several large shrimp trawlers. In the Faroe Islands, TBT was measured in the blue mussel at eight sites in 1996. The levels ranged from 49 to 372 ng Sn/g dw (Følsvik *et al.*, 1998). Highest levels were found near Tórshavn, the capital of the Faroe Islands. In northern Norway, the levels of TBT were generally very high in 1993 and 1994 (Berge *et al.*, 1997), in particular near harbors, where levels as high as 4407 ng/g dw have been reported. In Iceland, the levels of TBT in the blue mussel were on average 122.6 ng/g ww ± 92.5 (SD) near the large harbor

area of Reykjavík. At sites in southwestern, western, and northwestern Iceland, the levels were usually low (14.7 ng/g ww ± 13.2 (SD)) (Skarphéðinsdóttir *et al.*, 1996). High levels of TBT are still found in the blue mussel near larger harbors. Near Reykjavík harbor, the level of TBT was around 4420 ng/g dw in 2000 (Halldórsson, 2002).

TBT levels were examined in the dogwhelk along the Norwegian coast from 1993 to 1995 (Følsvik *et al.*, 1999) and again in 2000 (Green *et al.*, 2002). The concentrations ranged from 8 to 141 ng Sn/g dw at sites within the AMAP area in 1993 to 1995. Out of ten sites north of 65° N, TBT was at or below the detection limits at three of the sites. The most recent studies of TBT levels show that at eight locations in northern Norway, the levels are lower than found in the earlier study (Green *et al.*, 2002). Two sites had less than 7 ng Sn/g dw, while at the rest of the sites, the levels ranged from approximately 35 to 100 ng Sn/g dw.

TBT levels were examined in the limpet, *Patella vulgata,* at eight sites in the Faroe Islands (Følsvik *et al.*, 1998). At only one site, near Tórshavn, were the levels above detection limits (90 ng Sn/g dw). Skarphéðinsdóttir *et al.* (1996) measured TBT levels in the blue mussel and the dogwhelk at a single site near Reykjavík harbor at different times of the year. The levels of TBT in the tissue of the blue mussel and the dogwhelk seem to vary considerably over the year at northern latitudes. High levels (approximately 60 - 70 ng/g ww) were found in the blue mussel from July to January, while from February to April, the levels were less than 15 ng/g ww. In the dogwhelk, the summer and autumn levels were approximately 30 - 40 ng/g ww, while during late winter and early spring the levels were comparable to those found in the blue mussel. Skarphéðinsdóttir *et al.* (1996) concluded that monitoring of TBT in these animals at high latitudes should be confined to late summer or early autumn.

4.4.4. Marine and anadromous fish

Marine and anadromous fish occupy a range of trophic positions in Arctic marine ecosystems, and hence concentrations of OCs are quite variable. The Arctic cod (polar cod, *Boreogadus saida*) is considered a key link in marine food webs between invertebrates and seabirds/marine mammals, including the ringed seal and beluga. A number of these fish species are important components of the traditional human diet (e.g., Arctic char) and several have become important commercially (e.g., Greenland halibut (turbot, *Reinhardtius hippoglossoides*)). There was a somewhat large dataset available for OCs in marine fish in the first AMAP POPs assessment (de March *et al.*, 1998). Less data have been produced on these organisms since that report; however, the data produced recently are of improved quality with a greater range of contaminants measured, particularly PCB congeners. Six marine fish species were recommended for inclusion in the AMAP Phase II monitoring program, including Arctic char, whitefish/cisco (*Coregonus* spp.), Arctic cod, Atlantic cod, sculpin (*Myoxocephalus* spp.) and long rough dab (*Hippoglossoides platessoides*). Data on 'new' POPs have only been produced for a few of these species.

OCs have generally been measured in the liver or muscle tissue of fish. The amount of lipid found in these tissues can vary significantly within and between species and needs to be taken into account when comparing levels of OCs between species. For example, the Atlantic and Arctic cod have high-lipid livers and low-lipid muscle, whereas the Greenland halibut has similar lipid content in liver and muscle. Differences in size, growth rate (Johnston *et al.*, 2002), and trophic position (Fisk *et al.*, 2001c) can all influence observed OC levels in fish and need to be considered when comparing different populations, locations or studies. For most of the OC data produced for Arctic fish, these variables have not been adequately accounted for.

Concentrations of OCs in marine fish are generally higher than those observed in freshwater fish and marine zooplankton. For some larger species of fish, OC levels are similar to ringed seals, likely due to feeding at a higher trophic level (Fisk *et al.*, 2002b).

Sea-run Arctic char

Low levels of OCs were detected in anadromous Arctic char muscle (including skin) from two locations in Labrador and three locations in Nunavik in the Canadian Arctic (Muir *et al.*, 2000c) (Annex Table 10). PCBs were the most prominent contaminants at Labrador sites, with concentrations averaging 30 ng/g ww in samples from Makkovik and 63 ng/g ww in samples from Nain. ΣPCB levels in char muscle samples from the three locations in Nunavik were lower, with means ranging from 13 to 18 ng/g ww. Statistical analysis showed that there were no significant differences in ΣPCB concentrations among locations. Lipid content, length, and age were not significant co-variates. ΣPCB levels were, however, influenced by the sex of the fish, with males having significantly higher levels than females. This may be due to the timing of sampling near the spawning period for the char. Females may have mobilized fat from muscle to reproduce and, subsequently, transferred contaminants to their eggs as the fat is mobilized, thus lowering the concentrations observed in muscle. The next most prominent groups of OCs in char muscle were the HCH and DDT groups, which were present at low ng/g levels. ΣDDT levels were higher at Nain and Lavrentiya than other locations. In general, these levels of persistent OCs are similar to or lower than those reported in char muscle from other locations in the Canadian Arctic (Muir *et al.*, 1999b). Concentrations of all OCs were much lower in muscle samples from sea-run char from Finland.

Arctic (polar) cod

PCBs was the dominant OC group, followed by CHLs in Arctic cod collected in northern Baffin Bay in 1998 (Fisk *et al.*, 2002c), Barrow, Alaska in 1998 and 1999 (Hoekstra *et al.*, 2003a), and the Barents Sea in 1995 (Borgå *et al.*, 2001). For Arctic cod collected around Jan Mayen, ΣDDTs was the next dominant OC group after PCBs (Gabrielsen *et al.*, 1997). Concentrations (lipid corrected) of ΣPCBs were quite similar in cod from the Barents Sea and around Jan Mayen but were somewhat higher in northern Baffin Bay and Alaskan cod (Figure 4·39). ΣDDTs was somewhat higher in the northern Baffin Bay Arctic cod than other locations. ΣHCHs was highest in the Canadian cod, reflecting the higher con-
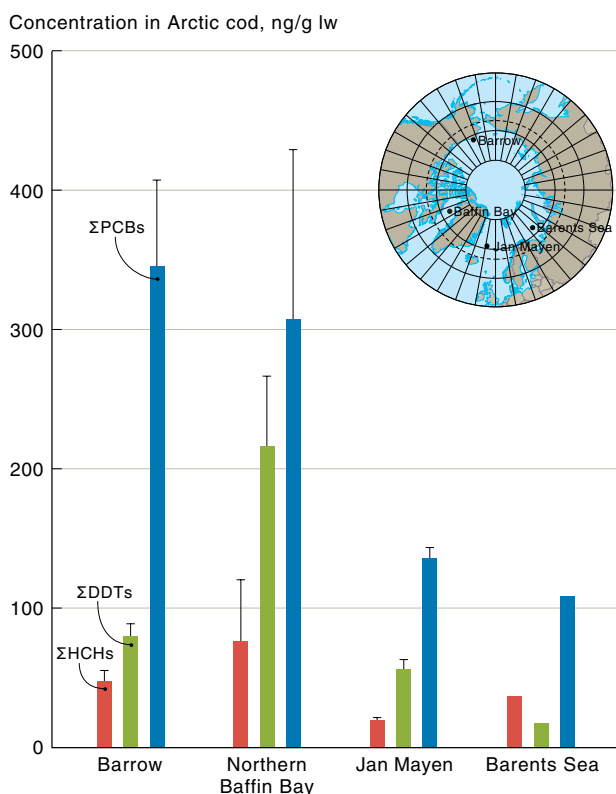

Figure 4·39. Concentrations (±SD) of ΣHCHs, ΣDDTs, and ΣPCBs in Arctic cod collected in Barrow, Alaska (Hoekstra, 2002b), northern Baffin Bay (Fisk *et al.*, 2001c), Jan Mayen (Gabrielsen *et al.*, 1997), and that Barents Sea (Borgå *et al.*, 2001).

centrations also seen in seawater. These spatial trends generally follow those of zooplankton (Section 4.4.3) but are not consistent with spatial trends observed in marine mammals and seabirds at higher trophic levels (Muir *et al.*, 2000b) (Sections 4.4.5 and 4.4.6).

Atlantic cod

OC data were also generated recently (1998-2000) for Atlantic cod from the Barents Sea (Borgå *et al.*, 2001), locations around Iceland (Yngvadóttir and Halldórsdóttir, 2002), and southwestern Greenland (Muir and Johansen, 2001). Concentrations of OCs were consistent at all locations. Concentrations (ng/g lw) of ΣHCHs ranged from 15 (Iceland) to 41 ng/g lw (Barents Sea) and ΣPCB concentrations from 199 (Iceland) to 281 (southwestern Greenland) ng/g lw. In the Barents Sea, concentrations in Atlantic cod were about twice as high as those observed in Arctic cod, and could be due to feeding at a higher trophic level, larger size or longer life span of the Atlantic cod. The Icelandic data were part of a continuing monitoring program in Iceland, which also includes the dab (*Limanda limanda*), and is discussed under temporal trends in Section 5.4.2.

Faroe Islands fish

In the Faroe Islands, livers from shorthorn sculpin sampled in 1999 and 2000 (n = 13 and 15) were analyzed (Hoydal *et al.*, 2001). The single OC occurring in highest mean concentrations was *p,p'*-DDE at 84 and 134 ng/g ww in 1999 and 2000, respectively. The second highest mean concentration was CB153 at 58 and 94 ng/g ww in 1999 and 2000, respectively. The concentrations of chlordanes, toxaphene, and mirex were less by a fac-
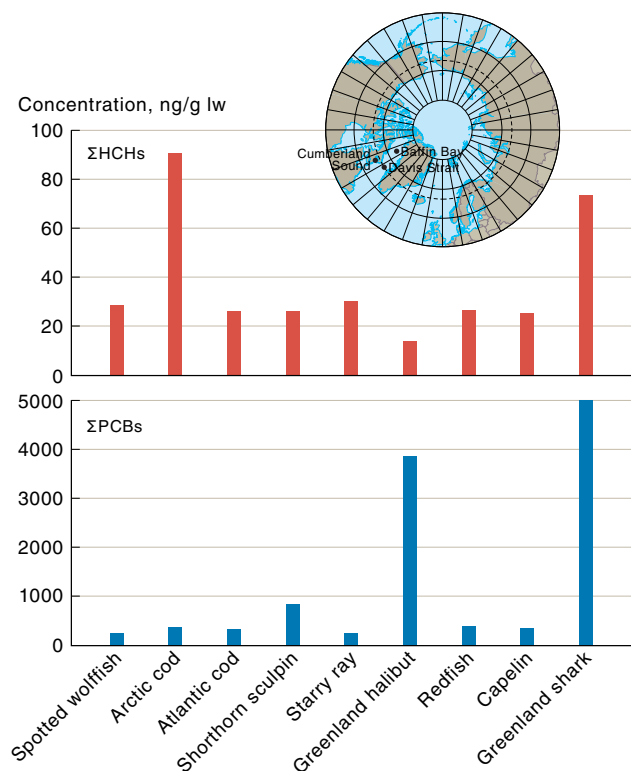
Figure 4·40. Concentrations of ΣHCHs and ΣPCBs in Arctic marine fish collected in Davis Strait and Baffin Bay (all species except Greenland shark, which were collected in Cumberland Sound). Arctic cod data from (Fisk *et al.*, 2001c), Greenland shark data from Fisk *et al.* (2002b), all other data from Denmark (2002).

tor of 8 or more. There was large variability in OC concentrations between individual fish. No significant correlations between length or age and OC concentrations were found. Overall, the concentrations of OCs were higher in the year 2000 samples than in 1999. The reason may be related to the fact that the sampling stations were not in identical locations between years. A local pollution source at one of these sites as an explanation for between-year differences is not likely, due to the similar ratios of concentrations for PCB, toxaphene, DDTs, and mirex.

Results are also available for Atlantic cod sampled in 1997 at the Faroe Islands shelf (Larsen and Dam, 1999). Liver samples from 45 fish were analyzed in two pools with lipid contents of 56.9 and 53.5%. As for sculpin, the single OC occurring in highest concentrations was *p,p'*-DDE, at 40 and 37 ng/g ww, with CB153 having the second highest concentration at 25 and 26 ng/g ww, respectively. In contrast to sculpin, the concentration of *trans*-nonachlor was similar to that of CB153, near 20 ng/g ww and *p,p'*-DDD was almost half the concentration of *p,p'*-DDE in Atlantic cod. In sculpin, the ratio of *p,p'*-DDD to *p,p'*-DDE was close to 1/100.

Greenland marine fish
Concentrations of OCs have been measured in a range of marine fish around Greenland (Figure 4·40 and Annex Table 10). A majority of these were collected as part of a larger study on OCs in foodstuffs. There is a lack of data from other Arctic regions to use for spatial comparisons. Concentrations of OCs were fairly consistent across species with the exception of the Greenland shark (*Somniosus microcephalus*) and Greenland halibut, which

had higher levels. The Greenland halibut is a large, benthic fish, which may account for the higher levels. OC levels in the Greenland shark are discussed below in this section. PCBs were the predominant OCs followed by ΣDDTs and chlordanes in these fish, reflecting their generally higher trophic level, as compared with zooplankton.

Greenland shark and Greenland halibut
Concentrations of OCs in the Greenland sharks collected in the Davis Strait and Cumberland Sound region in 1997 and 1999 (Fisk *et al.*, 2002b) were in the range of other top Arctic marine predators, the polar bear, and glaucous gull (Figure 4·41). The Greenland shark is the only known shark to routinely inhabit Arctic waters, and limited evidence indicates that these animals may be long-lived (>100 years) (see Hansen, 1963) and potentially numerous. Concentrations (lipid basis) of OCs in Greenland sharks in the study of Fisk *et al.* (2002b) were not related to fork length, sex, δ^{13}C or δ^{15}N. Greenland sharks had higher OC concentrations than black dogfish (*Centroscyllium fabricii*), a small (<1 m in length), deepwater shark collected in Davis Strait (see Berg *et al.*, 1997). Lower OC concentrations in the black dogfish were not unexpected because this species feeds lower in the food web, mainly on crustaceans and small fish (Compagno, 1984). Concentrations of OCs (lipid basis) in Greenland sharks were 10-100 and 3-10 times higher than those observed in Greenland halibut and ringed seals, respectively, suggesting a very high trophic position. Marine mammals have been found in the stomachs of Greenland sharks (Fisk *et al.*, 2002b). Concentrations of ΣDDTs in the study samples of Greenland sharks are among the highest in Canadian Arctic biota, which may be related to the low metabolism and long life span of these sharks. Reported concentrations of ΣPCBs and ΣDDTs in Greenland halibut collected in the Davis Strait in 1992 (Berg *et al.*, 1997) were five and ten times higher, respectively, but concentrations of ΣCHL and ΣHCH were very similar to those reported for Greenland halibut in the study of Fisk *et al.* (2002b). The higher PCB and DDT in Greenland halibut reported in Berg *et al.*, (1997) could be due to the larger size and the deeperwater habits of these Greenland halibut.
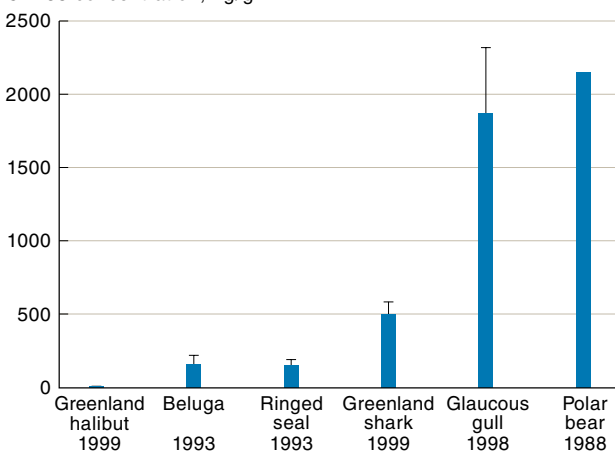

Figure 4·41. Mean (±SE) concentrations of CB153 in Greenland halibut (Fisk *et al.*, 2002b), beluga (Muir *et al.*, 1999b), ringed seal (Muir *et al.*, 1999c), Greenland shark (Fisk *et al.*, 2002b), glaucous gull (collected in northern Baffin Bay, Fisk *et al.*, 2001c), and polar bear (mean only) (Norstrom *et al.*, 1998) from Cumberland Sound.

Jan Mayen fish
Long rough dab, capelin (*Mallotus villosus*), grey gurnard (*Eutrigla gurnardus*), coalfish (*Pollachius virens*), Atlantic poacher (*Leptagonus decagonus*), daubed shanny (*Lumpenus maculates*), and checkered eelpout (*Lycodes vahli*) were collected from around Jan Mayen, and liver samples were analyzed for OCs (Gabrielsen *et al.*, 1997). ΣPCBs were the predominant contaminants followed by ΣDDTs. On a lipid weight basis, the highest OC concentrations were seen in long rough dab and checkered eelpout.

Toxaphene in fish from European waters
Concentrations of three toxaphene congeners (Parlars 26, 50 and 62) were determined in 221 fish samples, covering 23 species from northern European waters (McHugh *et al.*, 2000). Levels of the three congeners were highest in the Barents Sea and Norwegian Sea regions compared with the coast of Iceland, the North Sea, and the Baltic Sea. However, some of the differences between regions could be due to the use of different fish species, which will feed differently and influence exposure levels. Toxaphene concentrations in these fish are in the range reported for other marine fish from this region (see Annex Table 10).

4.4.4.1. 'New' chemicals in marine and anadromous fish

PBDEs in marine fish
PBDEs have been determined in the liver of a few species of marine fish: Atlantic cod and tusk (*Brosme brosme*) from Norway (Herzke, 2002a); and, Atlantic cod (liver and muscle) and Greenland halibut (liver) from Greenland (Muir and Johansen, 2001) (Annex Table 17). ΣPBDE levels in the liver of the Norwegian fish ranged from 24 to 109 and 60 to 300 ng/g lw in the Atlantic cod and tusk, respectively. These concentrations are much higher than levels observed in the fish off southwestern Greenland. Shorthorn sculpin, cod, spotted wolffish, and starry ray were studied during 2000 near the western Greenland villages of Quaqortoq (3500 inhabitants), Igaliko (30 inhabitants), and Usuk (background site 3-5 km from Igaliko) (Christensen *et al.*, 2002; Vorkamp *et al.*, 2002). The highest concentrations of PBDEs were observed in fish from Quaqortoq (46 ng/g lw) followed by Igaliko (18 ng/g lw) and Usuk (12 ng/g lw). The levels of PBDEs were 15-24 times lower than PCB levels measured in the same individuals, except for shorthorn sculpin collected at Quaqortoq, where the level of ΣPCBs was 40 times higher. For all fish, BDE47 dominated the PBDE congener pattern.

4.4.5. Seabirds

There are approximately fifty species of Arctic seabirds (de March *et al.*, 1998). They have a variety of feeding and migration strategies, and accordingly, POP concentrations can vary considerably among species. Species, such as the glaucous gull, great skua (*Stercorarius skua*), and great black-backed gull (*Larus marinus*), that may migrate to more contaminated regions and/or that scavenge, particularly on dead marine mammals, have the highest POP concentrations (Gabrielsen *et al.*, 1997; Borgå *et al.*, 2001; Fisk *et al.*, 2001b; 2001c). Biological

effects related to POP exposure have been seen in highly contaminated glaucous gulls (Bustnes *et al.*, 2000), and concerns about POP effects remain for some other species of Arctic seabirds. Seabirds also have the potential to biologically transport POPs from one region to another (e.g., marine to the freshwater ecosystems) through the production and release of guano (see Section 4.3.5).

There has been a considerable amount of work done on POPs in Arctic seabirds since the first AMAP assessment report, encompassing a wide range of species (Annex Table 11). Continued monitoring of POPs in Canadian Arctic seabird eggs from 1975 to 1998 and beyond, has provided a strong dataset for examining temporal trends between different species (Section 5.4.3). A comprehensive study of OCs in Barents Sea seabird eggs (Barrett *et al.*, 1996) was not included in the first AMAP POPs assessment. A number of studies have also been carried out examining OC concentrations and dynamics in adult seabirds (Henriksen *et al.*, 2000; Borgå *et al.*, 2001; Fisk *et al.*, 2001b), some of which were part of larger studies examining spatial trends (Gabrielsen *et al.*, 1997) or food web dynamics of OCs, discussed in Section 4.4.9. New data on PCDD/Fs, toxaphene, and 'new' POPs have also been generated for Canadian seabirds (Braune *et al.*, 2001a) and on mono-*ortho* and non-*ortho* PCBs, toxaphene, and 'new' POPs in glaucous gulls on Bjørnøya and Svalbard (Daelemans *et al.*, 1992; Burkow *et al.*, 2001; Herzke *et al.*, 2003).

PCBs are the most common OCs measured in Arctic seabirds (see Figure 4·42) (Barrett *et al.*, 1996; Borgå *et al.*, 2001; Braune *et al.*, 2001b; Buckman *et al.*, 2004), although the relative amounts are related to the trophic position of the seabird (Borgå *et al.*, 2001). Higher trophic-level seabirds generally have a larger proportion of PCBs as a percentage of total OCs. This is due to the greater biomagnification potential of PCBs and the ability of seabirds to metabolize other OCs, such as α-HCH (Moisey *et al.*, 2001) and some chlordane components (Fisk *et al.*, 2001b). Other recalcitrant and biomagnifying OCs, such as *p,p'*-DDE and oxychlordane, also become more prevalent (Borgå *et al.*, 2001, Fisk *et al.*, 2001b), although the relative proportions can vary dramatically between species, even within the same family (Fisk *et al.*, 2001b). Of particular note are the relative proportions of HCH isomers, which in seabirds are dominated by β-HCH (Barrett *et al.*, 1996; Moisey *et al.*, 2001). Seabirds are able to efficiently metabolize α- and γ-HCH but not β-HCH (Moisey *et al.*, 2001).

Species comparison
OC concentrations in seabirds were, in general, related to trophic position and secondarily to migration, with the highest concentrations found in great skuas, great black-backed gulls, and glaucous gulls. These are species that scavenge, prey on other seabird species, and migrate to more southerly habitats in the winter (Barrett *et al.*, 1996; Gabrielsen *et al.*, 1997; Borgå *et al.*, 2001; Fisk *et al.*, 2001c). Glaucous gulls, however, do not migrate as far as the other two species. These concentration–trophic level relationships in seabirds hold throughout the Arctic, including the Barents Sea area, and around the Jan Mayen, northern Baffin Bay, and the Iceland regions (Barrett *et al.*, 1996; Gabrielsen *et al.*, 1997; Borgå *et al.*,
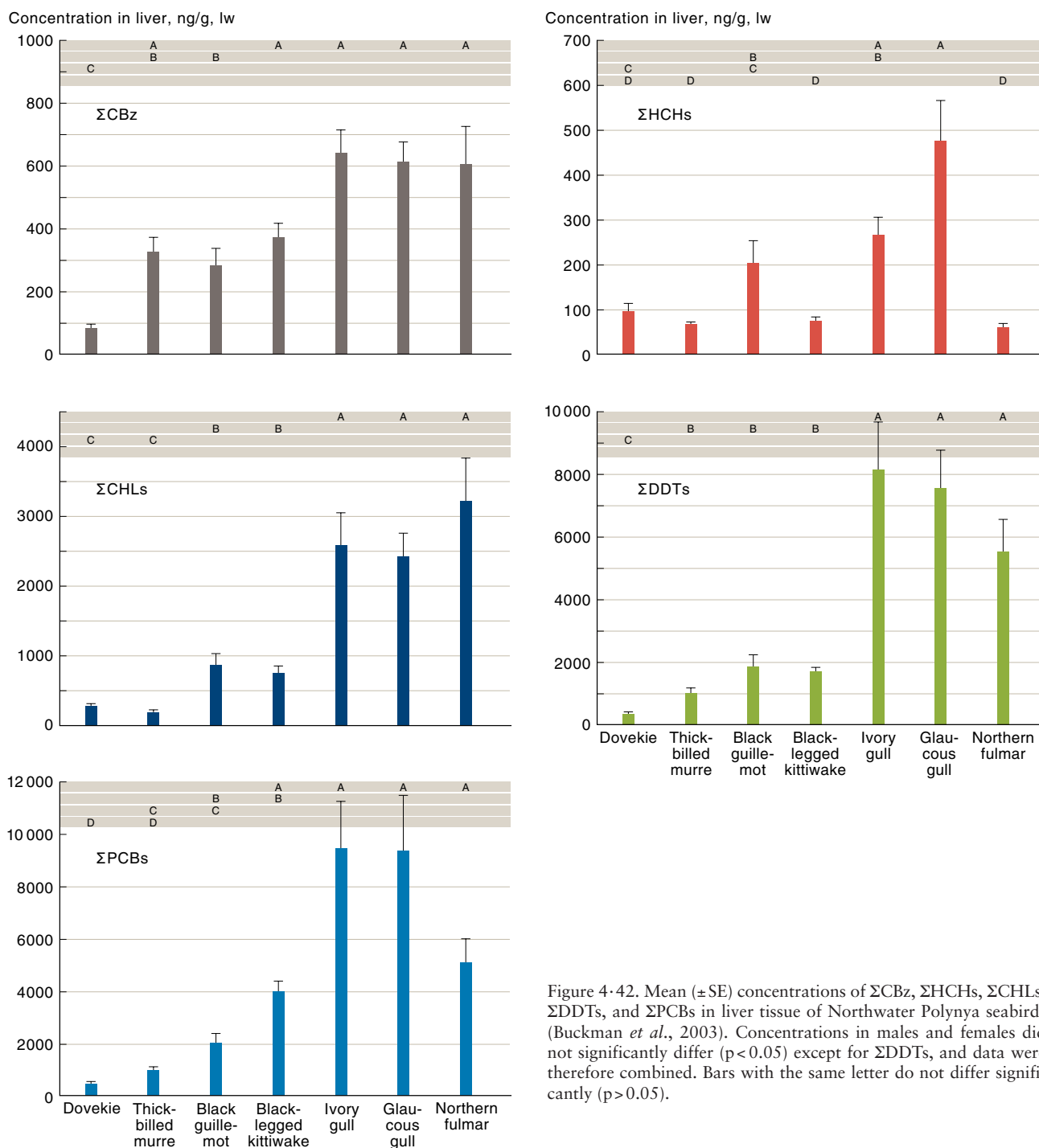
Concentration in liver, ng/g, lw

Concentration in liver, ng/g, lw

Figure 4·42. Mean (± SE) concentrations of ΣCBz, ΣHCHs, ΣCHLs, ΣDDTs, and ΣPCBs in liver tissue of Northwater Polynya seabirds (Buckman *et al.*, 2003). Concentrations in males and females did not significantly differ (p < 0.05) except for ΣDDTs, and data were therefore combined. Bars with the same letter do not differ significantly (p > 0.05).

2001; Fisk *et al.*, 2001c; Ólafsdóttir *et al.*, 2001). In northern Baffin Bay, ivory gull (*Pagophila eburnean*) and northern fulmar (*Fulmarus glacialis*), both of which scavenge, had slightly lower OC concentrations than glaucous gulls from the same area but higher concentrations than other seabirds (Figure 4·42) (Buckman *et al.*, 2004). OC concentrations in black-legged kittiwakes (*Rissa tridactyla*), a non-scavenging species, were lower than scavenging seabird species but were higher than the fish- and zooplankton-eating alcids (guillemots, murres, and little auks) in both Baffin Bay and the Barents Sea area. On Jan Mayen, dovekies had the lowest OC concentrations; black-legged kittiwakes, fulmars, and black guillemots had intermediate concentrations; and, highest concentrations were found in glaucous gulls, great black-backed gulls, and great skuas (Gabrielsen *et al.*, 1997).

Black-legged kittiwakes have been shown to feed at a lower or similar trophic level as the black guillemot (Hobson *et al.*, 2002). Kittiwakes are known to migrate longer distances (e.g., to southern regions) than black guillemot, which probably only move locally during the winter (Anker-Nilssen *et al.*, 2000). Therefore, the higher OC concentrations in black-legged kittiwakes are likely to be a result of uptake at their winter habitat, highlighting the impact, in both the Canadian and European Arctic, of migration to more contaminated regions.

OC concentrations can also vary within a single population of seabirds. Sagerup *et al.* (2002) observed a large range of OC concentrations in the livers of glaucous gulls collected in the western Barents Sea in 1996. For example, ΣPCB concentrations ranged from 16 000 to 292 000 ng/g lw. Concentrations of OCs were signifi-

cantly correlated to $\delta^{15}N$ ($r^2 = 0.18$), and therefore, diet accounted for some of the variation within this population. Bustnes *et al.* (2000) studied two colonies of glaucous gulls on Bjørnøya that nested only a few kilometers from each other but had different food habits. The two colonies had different OC concentrations, with the cliff colony having much higher concentrations than the sea-level colony. The colony that nested on cliffs fed more on other seabird eggs and chicks, whereas indications were that the sea-level colony fed more on fish (i.e. fed at a lower trophic level).

Influence of sex and tissue

Lipid-corrected concentrations of OCs have rarely been found to vary significantly between sexes or tissues of seabirds (Ólafsdóttir *et al.*, 1998; Buckman *et al.*, 2004). For example, concentrations of OCs were found to be similar between liver and muscle, tissues with similar lipid content, of the common eider (*Somateria mollissima*) collected in Iceland (Ólafsdóttir *et al.*, 1998). This is a commonly observed phenomenon and reflects the hydrophobic nature of OCs and accumulation in lipid. Lipid-normalized concentrations of OCs generally did not vary to a large extent between liver and fat in seabirds (Buckman *et al.*, 2004; Fisk *et al.*, 2001b), but lipid-corrected concentrations of chlordane compounds were significantly lower in the liver compared with the fat of little auks collected in Baffin Bay in May/June. At that time, little auks are feeding heavily on low trophic-level zooplankton (e.g., copepods) in anticipation of reproduction and egg production. Ólafsdóttir *et al.* (1998) observed large seasonal changes in OC concentrations in the muscle and liver tissue of the common eider, which were attributed to relocation of OCs to these tissues due to the shrinking of body fat. Therefore, changes in diet, the effects of migration and/or reproduction can, in certain cases, result in differences between tissues and in seasonal changes in OC concentrations in seabirds.

Spatial trends

Spatial trends of OCs in Arctic seabirds varied with the seabird species and the chemical, and generally were in agreement with spatial trends observed previously in seabirds (de March *et al.*, 1998) and marine mammals (Muir and Norstrom, 2000; Muir *et al.*, 2000b). Concentrations of most OCs in seabirds are highest in the Russian part of the Barents Sea and lowest in the North American Arctic, with the exception of HCH, which is higher in the North American Arctic (Annex Table 11). There is a lack of data for the eastern Russian Arctic.

ΣPCB data for four seabird species (thick-billed murre or Brünnich's guillemot, black guillemot, black-legged kittiwake, and glaucous gull) are available from a number of locations, and highlight the geographical trends despite different tissues having been analyzed. The first three of these seabird species are non-scavengers, feeding on zooplankton and fish, although the black guillemot is more of an inshore feeder. Black guillemots do not migrate, but thick-billed murres do. Black-legged kittiwakes migrate long distances, exposing themselves to higher levels of OCs in more southerly habitats. ΣHCH concentrations were highest in the Canadian seabirds (no HCH data are available for the Bering Sea murres), which reflects the higher concentrations of these chemicals in the
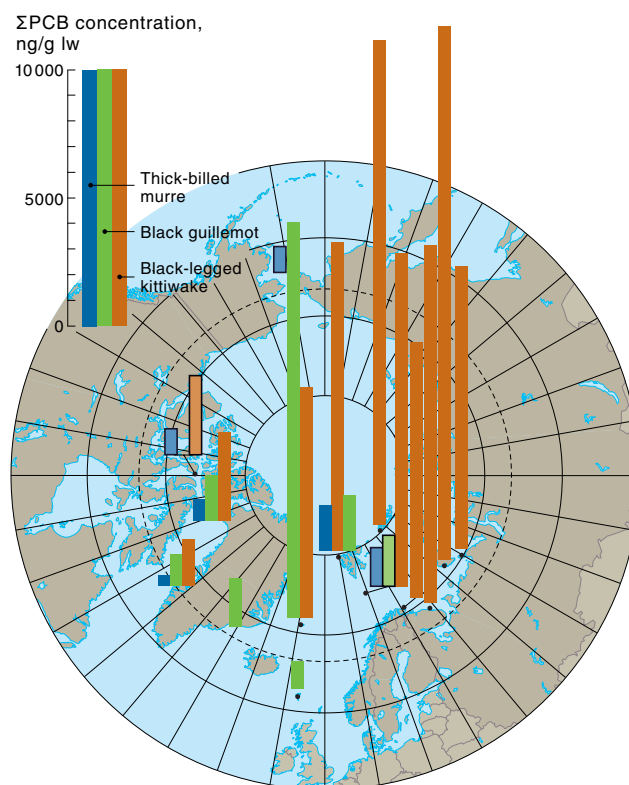

Figure 4·43. Concentrations of PCBs in liver (solid columns) and eggs (lighter-shaded, outlined columns) of thick-billed murre, black guillemot, and black-legged kittiwakes from regions throughout the Arctic. Data for the Bering Sea (year of collection: 2000; Vander Pol *et al.*, 2002), Prince Leopold Island (1998; Braune *et al.*, 2001a), northern Baffin Bay (1998; Buckman *et al.*, 2002), West and East Greenland (1999, 2000; Muir and Johansen, 2001), Barents Sea (1995; Borgå *et al.*, 2001 and; 1995; Gabrielsen *et al.*, 1997), Bjørnøya (1999; Evenset *et al.*, 2002), Faroe Islands (1995/96; Hoydal *et al.*, 2001), and Jan Mayen (1995; Gabrielsen *et al.*, 1997).

Canadian Arctic due to the closer proximity to Asia, where HCH has recently been used. ΣDDT concentrations were similar within and between species in the Canadian and Barents Sea thick-billed murres, black guillemots, and kittiwakes but were lower in the Greenland seabirds. There was much more variation for ΣPCB concentrations (Figure 4·43). For black guillemots, highest ΣPCB concentrations were found on Jan Mayen (15 300 ng/g lw in liver) followed by Iceland (4560 ng/g lw in muscle, not shown in figure). The higher concentrations on Iceland could in part be due to the inclusion of birds collected in 1991 and 1992 and/or due to muscle being analyzed instead of liver. For thick-billed murres, highest ΣPCB concentrations were seen in the Barents Sea area and lowest concentrations in the North American Arctic. Black-legged kittiwakes had the highest ΣPCB concentrations of the three non-scavenger species, with highest concentrations found in the eastern Barents Sea around Novaya Zemlya and Franz Josef Land. ΣPCB (10 000 - 21 000 ng/g lw) and ΣDDT concentrations (500 - 1900 ng/g lw) in the kittiwakes from around the Barents Sea region, including Svalbard, Bjørnøya, Franz Josef Land, Novaya Zemlya, and the Kola Peninsula, were fairly similar and are probably indicative of exposure due to migration more than to local sources.

Concentrations of ΣPCBs and ΣDDTs in glaucous gulls, a high trophic-level scavenging seabird, were higher in the Barents Sea and Jan Mayen than in Baffin Bay,
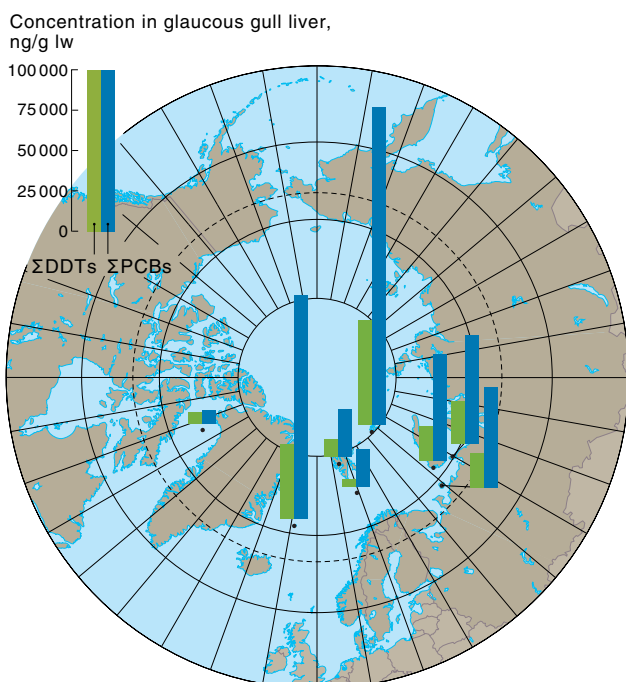
Concentration in glaucous gull liver,
ng/g lw

Figure 4·44. Concentrations of ΣPCBs and ΣDDTs in glaucous gull liver. Data for Baffin Bay are from Fisk *et al.* (2001b), for all other sites data are from Gabrielsen *et al.* (1997).

with highest concentrations around Franz Josef Land (Figure 4·44). Higher ΣPCB and ΣDDT concentrations in seabirds from the Barents Sea region, relative to seabirds from more westerly regions, have been observed previously (de March *et al.*, 1998). OC levels, including ΣPCBs and ΣDDTs in zooplankton and fish from the Barents Sea were within the range of those recorded in similar species in the Canadian Arctic. The low OC levels in selected taxa at lower trophic positions were unexpected, based on the higher levels of ΣPCB and ΣDDT, in particular, in higher trophic-level predators in the Barents Sea compared to the Canadian Arctic (Borgå *et al.*, 2001). Therefore, a diet of pelagic organisms does not seem to explain the elevated concentrations in top predators in the Barents Sea area, here exemplified by glaucous gulls. A diet of ice-associated fauna may, however, be of importance in the bioaccumulation of OCs (Norstrom *et al.*, 1998). As suggested by Pfirman *et al.* (1995), contaminated particles in the sea ice may be released in the melting areas in the Fram Strait and the Barents Sea, followed by bioaccumulation in ice-associated fauna. However, ice-associated fauna from the marginal ice zone near Svalbard have low OC levels (Borgå *et al.*, 2002b; 2002c), which correspond to levels in zooplankton at similar trophic positions from the Barents Sea (Borgå *et al.*, 2001).

Canadian seabird eggs
As part of a continuing temporal-trend study of contaminants in seabird eggs (see Section 5.4.3), thick-billed murre, northern fulmar, and black-legged kittiwake eggs were collected on Prince Leopold Island in Lancaster Sound in 1998 and analyzed for OCs (Braune *et al.*, 2001b). Concentrations and the relative proportions of OC groups were in general agreement with those observed in tissues of adult birds of the same species collected in northern Baffin Bay (Fisk *et al.*, 2001b; Buck-

man *et al.*, 2004). Lipid content in the eggs of the three species was similar, allowing comparisons of wet weight concentration data. PCB was the predominant OC in all three species and was similar in black-legged kittiwakes and northern fulmars (280±20 and 270±20 ng/g ww, respectively) and nearly twice that observed in thick-billed murres (130±10 ng/g ww). This reflects the higher trophic level of northern fulmars and black-legged kittiwakes and migration to more contaminated habitats by the kittiwakes. ΣDDTs was highest in the northern fulmar (210±20 ng/g ww), followed by the thick-billed murre (100±10 ng/g ww) and the black-legged kittiwake (60±10 ng/g ww), and similar trends were observed for ΣCHLs.

Faroe Islands black guillemots
A large study of black guillemots in the Faroe Islands in 1995 and 1996 (Dam, 2000) revealed that the black guillemot had distinctive winter and summer diets, where fish (primarily *Amodytidae* or sandeel type) made up a substantial dietary component in spring and early summer along with *Galathea* spp. crustaceans. In winter, the diet was dominated by *Galathea* spp. and gastropods, in particular the banded chink shell, *Lacuna divericata*. Indications of elevated OC concentrations in liver of adult males and females in spring hints to a possible link to a fish-dominated diet at that time. The single OC occurring in highest concentrations was most often CB153, but the concentration differences between this PCB congener and *p,p'*-DDE were small, and in some samples, nonexistent. In April 1996, the CB153 concentrations in adult females and males were 37 and 42 ng/g ww and *p,p'*-DDE concentrations were 24 and 30 ng/g ww, respectively. In August 1996, the respective CB153 concentrations were 20 ng/g ww and 24 ng/g ww, and *p,p'*-DDE concentrations were 9 ng/g ww and 10 ng/g ww in females and males, respectively.

Grey heron and shag from Norway
ΣPCB concentrations (34 congeners) were measured in the yolk sac of grey heron (*Ardea cinerea*) hatchlings from two populations in Norway, at Frøya (mid-Norway) and Finnfjordøy (northern Norway) (Jenssen *et al.*, 2001). No statistically significant differences were seen in ΣPCB concentrations between the two populations. Mean PCB concentrations were 2070 (Frøya) and 2450 ng/g ww (Finnfjordøy) with ranges of 570-4520 ng/g ww and 1360-4910 ng/g ww, respectively. Similarly, yolk sacs from newly hatched shag chicks (*Phalacrocorax aristotelis*), from the island of Sklinna on the central Norwegian coast were analyzed for 29 PCB congeners (Murvoll *et al.*, 1999). The mean ΣPCB concentration was 1200 ng/g ww.

Alaskan bald eagle eggs
Levels of OCs were measured in the eggs of bald eagles (*Haliaeetus leucocephalus*) from four islands of the Aleutian Archipelago to assess their possible role in low reproductive productivity on one of the islands, Kiska Island (Anthony *et al.*, 1999). Bald eagles are resident on these islands and do not migrate. Samples were collected in 1993 and 1994, and OC pesticides were elevated in eggs from all four islands. No statistically significant differences were seen between the four islands for β-HCH,

dieldrin, HCB or heptachlor epoxide concentrations. *p,p'*-DDE concentrations ranged from 300 to 4100 ng/g ww, but were significantly higher in the eggs collected on Kiska Island (geometric mean of 2750 ng/g ww) as compared to Adak, Tanaga, and Amchitka Islands (geometric means of 750-950 ng/g ww). *Trans*-nonachlor, mirex, oxychlordane, and mercury concentrations followed the same general pattern as DDE, with highest concentrations on Kiska Island. Kiska Island is furthest west, and the authors concluded that the east–west increase in concentrations suggested Asiatic sources of these contaminants. ΣPCB concentrations (as Aroclor 1260) ranged between 100 and 9900 ng/g ww on the four islands and were highest on the three islands (Adak, Kiska, and Amchitka) that had military facilities (geometric means of 2100, 2090, and 1700 ng/g ww, respectively). PCB concentrations on Tanaga Island were much lower (geometric mean of 700 µg/g ww). The Kiska Island bald eagles had a higher percentage of seabirds, such as northern fulmars and glaucous-winged gulls, in their diet, which could explain their higher OC concentrations. This study highlights the potential for local OC contamination from military activities to result in elevated OC concentrations in wildlife.

PCDD/Fs, mono- and non-ortho PCBs,
and toxaphene in seabirds
Recently, compounds such as PCDD/Fs, non-*ortho* PCBs and toxaphene were analyzed in thick-billed murres, northern fulmars, and black-legged kittiwakes collected on Prince Leopold Island in Lancaster Sound (Braune *et al*., 2001a) (Annex Table 16). These compounds have not been measured previously in Canadian Arctic seabirds. Samples included livers from 1975 and 1993 and egg samples from 1993. This study was set up as a pilot study to determine if temporal changes had occurred, and is examined in more detail in Section 5.4.3. PCDD/Fs and non-*ortho* PCBs were found in all Arctic seabird samples analyzed in this study. In particular, concentrations of HxCDDs, PeCDFs and HxCDFs found in Arctic seabird livers exceeded levels reported for marine mammals in the Canadian Arctic (de March *et al*., 1998) by several orders of magnitude. Ringed seals, polar bears, and walrus (*Odobenus rosmarus*) in the Canadian Arctic tend to have congener profiles dominated by higher TCDD and lower PeCDD and PeCDF levels (de March *et al*., 1998), whereas Arctic seabirds show the reverse profile. Concentrations of PCDD/F homologues in the Arctic seabirds are in the range reported for seabirds from temperate North America and Europe (Hebert *et al*., 1994; van den Berg *et al*., 1987). Toxaphene was detected in every seabird sample analyzed, except for the pool of kittiwake livers from 1975, and concentrations were one to two orders of magnitude lower than reported for marine mammals from the Canadian Arctic (Muir *et al*., 1999b).

PCDD/F concentrations in common guillemot eggs from the Faroe Islands sampled in 2000 were 10 pg/g ww (Mikkelsen, 2002). These concentrations were lower than seen in pilot whale blubber from the Faroe Islands, indicating a similar relationship as seen in the Canadian Arctic between seabirds and mammals. However, the difference between the TEQs in pilot whale and guillemot were less pronounced, approximately six times higher on a lipid weight basis (Mikkelsen, 2002).

Yolk sacs from grey heron hatchlings from two sites in Norway (Frøya, Finnfjordøy) had TEQs based on mono-*ortho* PCBs of 79.4 pg/g ww and 93.2 pg/g ww, respectively (Jenssen *et al*., 2001). Ranges were 21-179 and 55-177 pg/g ww, respectively. Yolk sacs from shag hatchlings from Sklinna (central Norwegian coast) had TEQs based on mono-*ortho* PCBs of 44 pg/g ww (Murvoll *et al*., 1999).

Liver samples from glaucous gulls from Longyearbyen on Svalbard were analyzed for PCBs including non- and mono-*ortho* PCBs (Daelemans *et al*., 1992). The TEQ concentration based on these congeners was 2500 pg/g ww. Toxaphene was measured in the liver of eighteen glaucous gulls collected from Bjørnøya and four from Longyearbyen in 1999 (Burkow *et al*., 2001; Herzke *et al*. 2003). Additionally, toxaphene was analyzed in the intestinal contents of fifteen of the glaucous gulls from Bjørnøya. Toxaphene Parlars 50 and 26 had average concentrations of 10 and 19 ng/g ww, respectively, in liver and were the dominant toxaphene congeners. For glaucous gulls from Bjørnøya, total toxaphene concentrations in gut contents were 84 ng/g ww, in posterior colon contents 53 ng/g ww, and in muscle 175 ng/g ww (Evenset *et al*., 2002). Levels of toxaphene were up to 100 times lower than PCBs and some of the legacy OC pesticides.

4.4.5.1. 'New' chemicals in seabirds

A number of very recent studies have examined levels of 'new' chemicals in Arctic seabirds, in particular brominated compounds (Annex Table 17).

Canadian seabirds
A range of 'new' chemicals was measured as part of the PCDD/F and toxaphene analyses in Arctic seabirds described in Section 4.4.5 (Braune *et al*., 2000; 2001a). These include livers (1975 and 1993) and eggs (1993) from thick-billed murres, northern fulmars, and black-legged kittiwakes collected on Prince Leopold Island in Lancaster Sound. These results are discussed in more detail in the temporal-trends section (Section 5.4.3).

PBDEs were present at low ng/g levels in most of the samples analyzed. The highest estimated PBDE levels (3 ng/g ww or about 60-70 ng/g lw) were detected in the 1993 egg and liver samples of kittiwakes, and the 1993 murre and fulmar samples also contained ng/g levels. BDE47 was the major PBDE congener in all the samples. Although the data suggest that exposure to PBDEs has increased from 1975 to 1993, the highest level reported is an order of magnitude lower than levels reported for Swedish common guillemots from the Baltic Sea in 1993 (720 ng/g lw) (Sellström *et al*., 1993; 2003; Sellström, 1999), but is still higher than levels reported for Canadian marine mammals (Stern and Addison, 1999; Stern and Ikonomou, 2000; 2001). However, PBDE concentrations in Baltic Sea guillemots have declined since their peak in the mid-1980s and were lower (143 ng/g lw) in 1999 (Sellström *et al*., 2003). Temporal trends of PBDEs in marine mammals indicate increasing levels in the Canadian Arctic during the period of decline in the Baltic Sea (see Section 5.4.6.1), implying that concentrations in Canadian Arctic seabirds may be approaching those of guillemot in the Baltic Sea.

Halogenated dimethyl bipyrroles (HDBPs), which are naturally-occurring, mixed bromine/chlorine persistent organic compounds, have been shown to bioaccumulate in seabird eggs (Tittlemier *et al.*, 1999). HDBPs were detected in all of the 1993 samples and only one of the liver samples from 1975. The major contaminant found was 1,1'-dimethyl-3,3',4,4'-tetrabromo-5,5'-dichloro-2,2'-bipyrrole (DBP-Br$_4$Cl$_2$). The highest estimated level (a total of 5 ng/g ww) was found in the kittiwake egg sample from 1993. Trace amounts (<2 ng/g ww) of chlorinated terphenyls, hexabrominated biphenyls, and tris(4-chlorophenyl)methane (TCPMe) were also detected in most of the Arctic seabird samples. No chlorinated diphenyl ethers, TCPMe or PCNs were detected in any of these samples (detection limit approximately 2 ng/g ww).

In a separate study, Tittlemier *et al.* (2001) examined levels of HDBPs in four seabird species (dovekie, black guillemot, black-legged kittiwake, and glaucous gull) collected in northern Baffin Bay. This is significant because it represents the first time a naturally produced halogenated compound has been measured in Arctic species. This was part of a larger study on the food web dynamics of these chemicals in marine food webs (Section 4.4.9). HDBPs were detected in all of the samples studied from the Northwater Polynya. Levels of DBP-Br$_4$Cl$_2$ in the seabirds were generally similar to those recorded in seabird samples from Atlantic Canada (Tittlemier *et al.*, 1999). A comparison cannot be made for the other congeners measured since this study contains the first reported concentration data for these congeners. Little auks provide the single clear exception where DBP-Br$_4$Cl$_2$ concentrations (1.76 ng/g ww) were approximately ten times lower than those of the Atlantic puffin (*Fratercula arctica*) (20 ng/g ww), a species that has a similar winter habitat but a more piscivorous diet. The difference in concentrations is likely driven by the little auks feeding at a lower trophic position just prior to their collection in early summer (Fisk *et al.*, 2001b). In the majority of the bird species, DBP-Br$_4$Cl$_2$ was the predominant congener. The exception occurred with black guillemots, where DBP-Br$_6$ was the most abundant congener. This may be due to black guillemots feeding on benthic organisms during part of the year (Gaston and Jones 1998).

Bjørnøya seabirds
Brominated flame retardants were measured in the liver and intestinal contents of fifteen glaucous gulls collected on Bjørnøya in 1999 (Burkow *et al.*, 2001; Herzke *et al.*, 2003). Only two PBDE congeners were detected, BDEs 47 and 99, at concentrations between 2 and 25 ng/g ww (27-450 ng/g lw). Analysis of the samples using gas chromatography/high resolution mass spectroscopy revealed a number of other PBDE and polybrominated biphenyl (PBB) congeners. BDE47 dominates the PBDE congener pattern in seabirds. ΣPBDE levels in most species are approximately 20 times lower than ΣPCB levels, but are up to 1000 times lower for glaucous gulls. For most glaucous gulls, these concentrations are similar to what has been measured in seabird eggs from the Canadian Arctic (Braune, 2000). However, a few individual glaucous gulls had higher PBDE levels (480-560 ng/g lw), which were higher than levels seen in Baltic Sea

guillemots for the same year. Levels of PBDE were up to 100 times lower than levels of PCBs and some of the legacy OC pesticides.

Butyltins have recently been measured in glaucous gulls from Bjørnøya (Table 4·8, page 111). Liver samples were found to contain the TBT metabolites, DBT (detection limit to 51 ng/g ww), and MBT (detection limit to 14 ng/g ww), but no TBT (Berge *et al.*, 2002).

Greenland seabirds
ΣPBDE levels were determined in the liver of thick-billed murre and black guillemot collected from southwestern Greenland in 1999 (Muir and Johansen, 2001). Concentrations of ΣPBDE in the thick-billed murre (1.7±1.6 ng/g ww; 32 ng/g lw) and guillemot (3.0±2.8 ng/g ww; 46 ng/g lw) were similar to levels observed in Canadian Arctic seabird eggs but lower than observed in glaucous gulls from Bjørnøya.

Northern Norway
New data on dioxin-like substances, PCNs, PBDEs, and toxaphene in herring (*Larus argentinus*) and great black-backed gull eggs from northern Norway were recently produced (Gabrielsen, 2002). Eggs were collected in 2001 from four sites: Alta, Kongsfjord (Finmark), Sommarøy, and Vardø. Twenty eggs from each site were pooled into one sample. Concentrations of PCNs, PBDEs, and toxaphene and total TEQs were similar between regions, although levels were somewhat lower in Alta (Annex Tables 15, 16 and 17). TEQ values in these gull eggs are similar to levels measured in Arctic Canadian seabird eggs (Braune, 2001). PBDE and toxaphene levels in these seabirds are slightly higher than measured in Bjørnøya glaucous gulls (Burkow *et al.*, 2001; Herzke *et al.* 2003).

Chiral pesticides
Chiral pollutants exist as two mirror-image forms or optical isomers called enantiomers. Enantiomers have identical physical-chemical properties and abiotic degradation rates, but can have different rates of biotransformation (Buser and Müller, 1992). The chemical manufacturing process results in a mixture containing approximately fifty percent of each chiral compound, called a racemic mixture. Selective biotransformation of one chiral component over another can occur and result in an enantiomeric enrichment (Buser and Müller, 1992). This selective enrichment originates from one enantiomer being more easily biotransformed. The resulting selective accumulation of a single enantiomer can provide information on fate and dynamics of the chemical and may have significant toxicological ramifications. It has been proposed that comparison of enantiomer ratios (ERs) or enantiomer fractions (EFs) may provide information on biotransformation capacity of species and the trophic transfer of contaminants in a food web (Wiberg *et al.*, 2000).

Enantiomeric fractions of chiral chlordane components were examined in the liver and fat of seven Arctic seabird species collected in northern Baffin Bay in 1998 (Fisk *et al.*, 2001b). EFs of chiral components failed to predict concentration or trophic level, but did identify biotransformation differences between species and chlordane components. The relative proportions of chlordane components in seabirds were related to taxonomy and

the magnitude of EF values; the northern fulmar and gulls (black-legged kittiwake, ivory gull, and glaucous gull) had a greater percentage and higher EFs for oxychlordane than the alcids (little auk and black guillemot). The exception was the thick-billed murre, an alcid, where oxychlordane made up a significant percentage of its ΣCHLs. Thick-billed murres appeared to have a greater capacity to metabolize and eliminate chlordane, based on high proportions of oxychlordane and the highest EFs for oxychlordane and heptachlor epoxide.

4.4.6. Marine mammals

There is an extensive database on OCs in Arctic marine mammals. This includes data that were produced before 1997 and summarized in the first AMAP POPs assessment and further studies since that time. The focus on marine mammals comes in part because these animals, in particular seals and whales, are important components of the diet of many Arctic societies. Marine mammals also occupy a range of trophic positions, and a number of species (e.g., polar bears) are apex predators, and thus have high levels of OCs. Therefore, more than for any other group of animals, is concern about OCs greatest in marine mammals, both with respect to effects on the animals themselves and transfer to humans.

All relevant data on OCs and organotin compounds in marine mammals that have become available since the previous AMAP assessment (de March *et al.*, 1998) are reviewed here. It must be emphasized that the spatial trends of persistent OCs discussed below in this section are often qualitative because they are based on evaluations of means and ranges of concentrations from different studies. In the case of the sums of groups of compounds, such as PCBs and chlordanes, some laboratories have included more congeners or components than others in ΣPCB and ΣCHL results. Rigorous comparisons between locations also require information on age, sex, blubber thickness, nutritional status, collection season, and reproductive status of the animals, all of which can have an important influence on contaminant concentrations. This information has been collected for many locations, but used only qualitatively in this assessment of spatial trends between studies.

A considerable body of data has been collected on pinnipeds and cetaceans (both mysticetes and odontocetes) since the previous AMAP POPs assessment (de March *et al.,* 1998). All relevant data that have become available since the previous AMAP assessment are included here for pinnipeds (Annex Table 12) and cetaceans (Annex Table 13). Data for individual toxaphene congeners are reported in Annex Table 15, while data for individual PBDEs are reported in Annex Table 17, and data for PCDD/Fs, non-*ortho* PCBs (nPCBs) and toxic equivalents (TEQs) are reported in Annex Table 16. Although the current assessment primarily includes data and publications since 1996, some reports included here do contain data collected prior to this time, if they were not considered in the previous AMAP assessment.

As in the previous AMAP assessment, by far the most frequently determined OC compounds in marine mammals are still PCBs (as congeners) and DDT-related compounds. Chlordane-related compounds, HCHs and HCB, are somewhat less well represented, while other chloro-

benzenes, toxaphene components, dieldrin, mirex, and PBDEs are not well represented in overall contaminant measurements in marine mammals across the Arctic. PCDD/Fs have also only been quantified to a limited extent across marine mammal species or geographical locations in the Arctic (Annex Table 16).

4.4.6.1. Pinnipeds

Ringed seals
Ringed seals are the most abundant and widely distributed resident Arctic pinniped. Their diet consists of fish, mainly schooling gadids, and crustaceans (amphipods, mysids, and euphausids). They have a broad circumpolar distribution and prefer annual, landfast ice, but are also found in multi-year ice. No clear-cut boundaries are known to separate ringed seal stocks in marine waters. Adults are believed to be relatively sedentary, but subadults sometimes disperse over long distances (Reeves, 1998). Ringed seals are a key component of the diet of polar bears and the Inuit of Canada and Greenland.

Results of studies completed since the previous AMAP POPs assessment are in general agreement with geographical trends reported previously for ringed seals (de March *et al.*, 1998). That is, ΣPCB and ΣDDT concentrations increase from west to east, with levels being lowest in ringed seals from the Chukotka Peninsula (Lavrentiya) (RAIPON/AMAP/GEF Project, 2001) and Alaska (Hoekstra *et al.*, 2003a; Kucklick and Krahn, 2002), intermediate in ringed seals from the eastern Canadian Arctic (Muir *et al.*, 2000b; Fisk *et al.*, 2002d), higher in seals from Svalbard and the White Sea (Wolkers *et al.*, 1998b; Kostamo *et al.*, 2000; Muir *et al.*, 2002b), and highest in seals from the Kara Sea near Dikson (Nakata *et al.*, 1998a) (Figure 4·45). Between Chu-
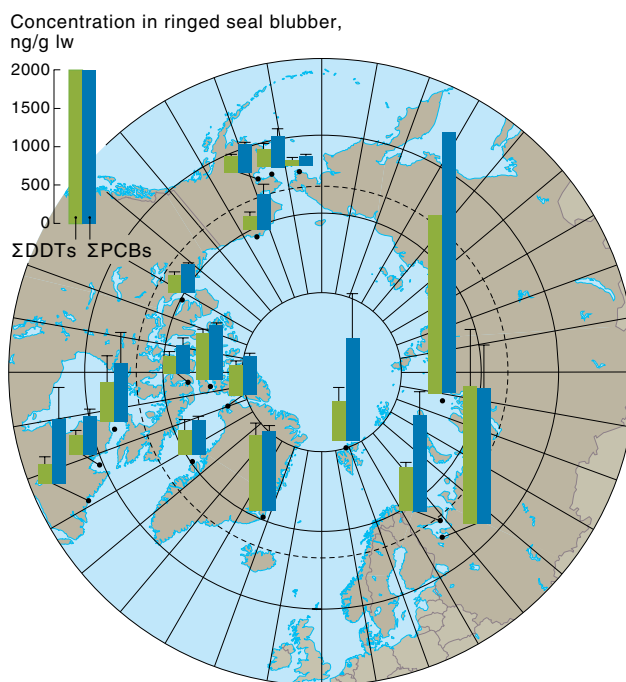

Figure 4·45. Mean (± 95% CI) concentrations of ΣPCBs and ΣDDTs in female ringed seal blubber (Krahn *et al.*, 1997; Muir *et al.*, 1999c; 2001c; 2002c; Muir and Johansen, 2001; Denmark, 2002; Fisk *et al.*, 2002c; Hoekstra, 2003a; Kucklick and Krahn, 2002; Nyman *et al.*, 2002; Nakata *et al.*, 1998a; RAIPON/AMAP/GEF Project, 2001).
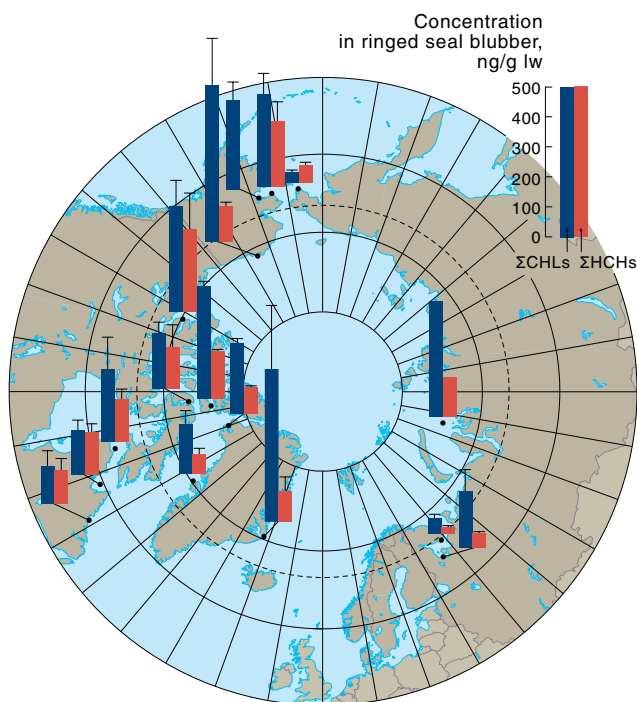
Figure 4·46. Mean (± 95% CI) concentrations of ΣCHLs and ΣHCHs in female ringed seal blubber (Krahn *et al.*, 1997; Muir *et al.*, 1999c; 2001c; 2003; Muir and Johansen, 2001; Denmark, 2002; Fisk *et al.*, 2002c; Hoekstra, 2003a; Kucklick and Krahn, 2002; Nyman *et al.*, 2002; Nakata *et al.*, 1998a; RAIPON/AMAP/GEF Project, 2001).

kotka and the Kara Sea, there are no data for seals in the Russian Arctic, representing a large geographical gap. Levels of ΣCHLs are fairly consistent across the Arctic, while ΣHCH concentrations are highest in Alaska and decrease from west to east (Figure 4·46).

Within Alaska, Kucklick and Krahn (2002) reported that ΣPCB and OC pesticide concentrations measured in ringed seals collected between 1988 and 1998 generally decreased from Barrow to the more westerly site at Nome (Annex Table 12). After adjusting for the effects of age and blubber thickness, females from Barrow were found to have higher concentrations of ΣPCBs, ΣDDTs, ΣCHLs, and dieldrin, while in males, only ΣHCH concentrations were higher in seals from Barrow. Only HCB and mirex were not significantly different between the two locations for either sex. There was general agreement amongst studies between ΣPCB and OC pesticide levels observed in Barrow ringed seals (Hoekstra *et al.*, 2003a; Kucklick and Krahn, 2002), and these levels were comparable to those measured recently in ringed seals from the western Canadian Arctic (de March *et al.*, 1998; Muir *et al.*, 1999b) (Annex Table 12). For example, the geometric mean of ΣDDTs in female seals from Resolute was 340 ng/g ww (range of 163-540 ng/g) (Muir *et al.*, 2000b) versus 408 ng/g ww in the Barrow seals (range of 274-652 ng/g) and 178 ng/g ww (range of 143-387 ng/g) in the seals from Nome.

Further east, ringed seals from Holman, NWT, (Hoekstra *et al.*, 2003a) had levels of PCBs and OC pesticides that were in general agreement with, and intermediate between, levels found in ringed seals from further west (Alaska) (Hoekstra *et al.*, 2003a; Kucklick and Krahn, 2002) and further east (eastern Canadian Arctic) (Muir *et al.*, 2000b; Fisk *et al.*, 2002d). A variety of PCB and

OC pesticides were quantified in the blubber of ringed seals from seven sites within Nunavik and Labrador, in 1998 and 1999 (Muir *et al.*, 1999c; 2000c) (Annex Table 12). For comparison among regions, three sites within Ungava Bay were combined (Kuujjuaq, Kangirsuk and Kangiqsualujjuaq), as were two sites in the Hudson Strait (Salluit and Quaqtaq). The two sites in Labrador (Nain and Makkovik) were treated separately. Average blubber concentrations of ΣPCBs, the major OC contaminants in seals from these four locations, ranged from 572 to 1042 ng/g ww in males, and from 512 to 730 ng/g ww in females (Muir *et al.*, 2000c). The highest levels in males were found in samples from the more westerly locations of Ungava Bay and Hudson Strait, while the highest average levels in females occurred in samples collected at Nain. DDT-related compounds were also prominent contaminants in ringed seal blubber, with average concentrations ranging from 198 to 884 ng/g ww in males. Statistical analysis did not reveal any significant differences in concentrations of ΣPCBs or ΣDDTs among the four locations for females. For males, ΣPCB, ΣDDT, and ΣHCH concentrations were significantly higher in samples from Ungava Bay, after adjusting for age. There was a significant interaction, however, between age and location (i.e. a differing relationship of age with concentrations of the OCs) for males, which may have affected the results. In general, levels of ΣPCBs and ΣDDTs in ringed seal blubber from this study were comparable to those found in ringed seal blubber at other eastern Canadian Arctic locations (Weis and Muir, 1997; Muir, 1998; Muir *et al.*, 1999b), including those from the more northerly region of the Northwater Polynya in northern Baffin Bay (Fisk *et al.*, 2002d). Results for Fisk *et al.* (2002d) were also in the range reported for ringed seals from western-central and northeastern Greenland (Muir and Johansen, 2001; Denmark, 2002) (Annex Table 12). After removing the influence of age, sex, and blubber thickness, ΣPCB and OC pesticide concentrations did not differ in ringed seals from the east and west side of the Northwater Polynya, likely due to the relatively small distance between these two sites (Fisk *et al.*, 2002d). Concentrations of ΣDDTs and ΣPCBs in seals from this region were lower than those reported for this species in Svalbard, Norway (Wolkers *et al.*, 1998b; Kleivane *et al.*, 2000; Severinsen *et al.*, 2000) (Annex Table 12). In contrast, ΣHCH concentrations in Canadian and Alaskan ringed seals were higher than those reported for ringed seals from the European Arctic. These geographical trends are consistent with past compilations of circumpolar data for ringed seals (Muir *et al.*, 2000b) and polar bears (Norstrom *et al*,. 1998).

Levels of ΣPCBs found in Svalbard ringed seals (Wolkers *et al.*, 1998b; Kleivane *et al.*, 2000; Severinsen *et al.*, 2000; Nyman *et al.*, 2002) were in good agreement, and were at least twice as high as those in seals from the Canadian Arctic (Annex Table 12), despite the smaller number of congeners included in ΣPCBs for the Svalbard seals. The predominant PCB congeners in the Kongsfjorden (Svalbard) ringed seals were 153, 138, 99, 180 and 101 (Wolkers *et al.*, 1998b). The observed PCB patterns were very similar to patterns in seals from other studies (Muir *et al.*, 1988; Luckas *et al.*, 1990; Beck *et al.*, 1994), suggesting a similar biotransformation capacity.

Further east, concentrations of ΣPCBs, ΣDDTs, and HCB, quantified in the blubber of ringed seals from the White Sea (Kostamo *et al.*, 2000; Muir *et al.*, 2003) (Annex Table 12), were comparable to or higher than in ringed seals from Svalbard, but lower than reported for this species in the more easterly Kara Sea (Nakata *et al.*, 1998a). Within the White Sea, Muir *et al.* (2003) found higher levels in seals sampled at Dvina Bay, near the city of Archanglesk, in comparison to those from the more northerly and less industrialized region of Gorlo Basin (Annex Table 12). The high levels in the White Sea ringed seals are likely influenced by local point sources, as some parts of the White Sea are heavily industrialized. Levels in White Sea ringed seals were also much lower than levels in two freshwater sub-species of ringed seals living in Lake Saimaa, Finland, (*P. h. saimensis*) and Lake Ladoga, Russia, (*P.h. ladogensis*), (Kostamo *et al.*, 2000). Kostamo *et al.* (2000) found that the PCB congener composition in blubber from the White Sea seals resembled a mixture of Aroclor 1254 and 1260. They also reported that the ΣDDT:ΣPCB ratio in the White Sea ringed seals ranged from 0.96 to 1.49 (Kostamo *et al.*, 2000), which is similar to the results from ringed seals in the east-central Canadian Arctic (Muir *et al.*, 1988). The higher levels found in the Kara Sea seals may be due to OC inputs from the Ob and Yenisey Rivers, which have been shown to be major sources of OCs to the Arctic Ocean via river water and sediments (de March *et al.*, 1998) (Section 4.3.1.1).

Total toxaphene levels in ringed seal blubber were generally lower, moving eastward from Barrow, Alaska, (mid- to high hundreds of ng/g lw) to the Hudson Strait and Ungava Bay (Canada) (low hundreds of ng/g), Greenland and the Barents Sea (tens of ng/g), and then slightly higher (low hundreds of ng/g) in White Sea ringed seals (Annex Table 12) (Wolkers *et al.*, 1998b; Muir and Johansen, 2001; Denmark, 2002; Hoekstra *et al.*, 2003a; Muir *et al.*, 2003). On a congener basis, Parlar 26 levels were highest in ringed seals from Hudson Strait and Ungava Bay in the Canadian Arctic, followed by those in seals from Alaska and the White Sea and then Svalbard, with the lowest levels in seals from western Greenland. Levels of Parlar 50 were highest in seals from Svalbard and Hudson Strait and lower in seals from Ungava Bay and western Greenland (Annex Table 15; Figure 4·47).

In ringed seal blubber from northern Quebec, octa- and nonachlorobornanes were the major homologue groups (Muir *et al.*, 2000d) (Annex Table 15). Toxaphene Parlars 39, 40, and 42 were also identified in the blubber of ringed seals from Arviat, Nunavut (formerly in the NWT) (Loewen *et al.*, 1998), marking the first time that Parlar 42, the most toxic congener in technical toxaphene, has been found in any significant concentrations in a marine mammal. Ringed seals from Kongsfjorden, Svalbard, (Wolkers *et al.*, 1998b) showed no effect of sex, age or total blubber on toxaphene levels. Slightly higher concentrations of toxaphene Parlars 26, 50, and 62 were found in male than female ringed seals from Kongsfjorden (Føreid *et al.*, 2000).

Blubber from ringed seals collected in 1993 near Pangnirtung, Nunavut, were analyzed for non- and mono-*ortho* PCBs (Helm *et al.*, 2002). Total non- and mono-*ortho* PCB concentrations (sum of CBs 77, 81,
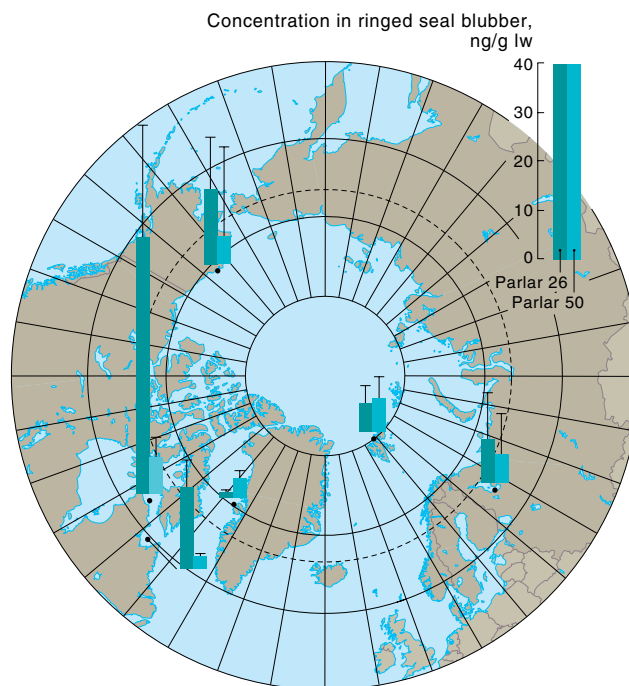

Figure 4·47. Mean (± 95% CI) concentrations of toxaphene Parlar 26 and Parlar 50 in female ringed seal blubber (Wolkers *et al.*, 1998b; Muir *et al.*, 1999c; 2003; Hoekstra, 2003a).

105, 126, 118, 114, 156, and 169) ranged from 14.9 to 32.7 ng/g ww, with congeners 118, 105 and 156 being the most predominant. Mean (± standard deviation) levels of these were lower in female (15.4±0.8 ng/g ww) than male (26.7±8.0 ng/g ww) ringed seals. TEQs for non- and mono-*ortho* PCBs in males and females were 0.624±0.144 pg/g lw and 0.508 ± 0.088 pg/g lw, respectively, most of which was accounted for by congener 126 (Helm *et al.*, 2002) (Annex Table 16). For ringed seals from Holman, TEQs based on non- and mono-*ortho* PCBs in blubber from 2000 ranged from 4.3 to 91 pg/g ww, with the PCBs contributing most to the TEQs (Ikonomou, 2002). Ringed seals from the Kara Sea had total non- and mono-*ortho* PCB concentrations (sum of CBs 77, 105, 118, 126, 156, and 169) of approximately 670 ng/g ww in blubber (Nakata *et al.*, 1998a). The TEQ for these CB congeners was approximately 144 pg/g ww (160 pg/g lw), and CB126 contributed most, followed by CB118. Blubber from ringed seals and spotted seals (*Phoca largha*) collected from the Chukotka Peninsula (Lavrentiya) area were analyzed for PCDD/Fs (RAIPON/AMAP/GEF Project, 2001). TEQs were 1.1 pg/g ww for ringed seals and 1.3 pg/g ww for spotted seals.

Harp seals

Harp seals are an Atlantic species, inhabiting Arctic and subarctic waters. They feed primarily on small marine fish and, secondarily, on crustacean macroplankton. Three separate harp seal populations undergo annual migrations between southerly breeding sites and their northern feeding grounds, both at the edge of the pack ice. Harp seals are not a common dietary item of northern human populations.

Little information has become available on contaminants in harp seals since the previous AMAP assessment. However, recent studies are available for seals

from Svalbard and the White Sea. Data are available for PCBs (Wolkers *et al.*, 1999), DDTs, HCB, HCHs, as well as cyclodiene pesticides such as dieldrin, endrin, and the chlordanes (Wolkers *et al.*, 2000) (Annex Table 12). The levels of PCBs and most pesticides, especially the DDTs, for sub-adult (≤4 years) harp seals from the ice edge, east of Svalbard, were relatively low compared to those reported in other harp seal studies. This was probably, in part, because animals were sampled during the summer, when the total blubber content is high compared to the spring (Wolkers *et al.*, 1999; 2000). In contrast to this, levels of PCBs and OC pesticides quantified in older adult males from the same area (Kleivane *et al.*, 2000) were substantially higher than previously reported in this species (Oehme *et al.*, 1995c; Kleivane *et al.*, 1997).

Levels of PCBs and OC pesticides were quantified in harp seals from the southern ice area located north of the White Sea in 1993 and were also elevated, but to a lesser extent than in the mature Svalbard males. All animals in the Svalbard group were lean specimens in late molt, while those from the White Sea were sampled early in the molt. The Svalbard seals had significantly thinner blubber than the seals sampled outside of the White Sea (Kleivane *et al.*, 2000). Thus, the dramatic decrease in the fat reservoir in adult seals during the molting period, when feeding is at a minimum or non-existent, clearly resulted in a significant concentration of PCBs, DDTs, and chlordanes in the remaining blubber of these seals. To the south, blubber concentrations of PCBs, DDTs, chlordanes, and HCB in harp seals from the Gorlo Basin of the White Sea in 1998 (Muir *et al.*, 2003) were comparable to those reported for harp seals sampled east of Svalbard in 1997 (Wolkers *et al.*, 1999; 2000) and were on the low side of the range of levels reported for this species in the Kleivane *et al.* (2000) study. Mean POP levels in young harp seals sampled in 1992 (Muir *et al.*, 2003) were generally higher compared to those sampled in 1998, and were comparable to those reported for seals north of the White Sea in 1993 (Kleivane *et al.*, 2000). It is not clear if this is an indication of declining levels with time or variability in biological parameters, such as blubber thickness.

Toxaphene levels in juvenile harp seals from eastern Svalbard in 1997 (Wolkers *et al.*, 2000) were comparable to those found in adult females and juveniles from the White Sea in 1998 (Muir *et al.*, 2003). Interestingly, in contrast to results from seals in other areas (Muir *et al.*, 1992a; Wolkers *et al.*, 1998b), toxaphenes were the predominant compounds in young harp seals from eastern Svalbard, exceeding PCB concentrations. Toxaphene concentrations in these young harp seals (Wolkers *et al.*, 2000) were also more than 20 times higher than in juvenile ringed seals from the west coast of Svalbard (Wolkers *et al.*, 1998b). Although there may be species-specific differences, the high toxaphene levels found in the seals from the east coast of Svalbard (Barents Sea) as compared to the seals from the west coast of Svalbard, may indicate that, in spite of a ban on the use and production of these compounds in the western world (Voldner and Li, 1993), the Barents Sea area is continuously exposed to toxaphenes. Thus, in addition to atmospheric long-range transport, another source of toxaphenes may contribute to the high levels found. Furthermore, a study of

harp and ringed seals in the White Sea has demonstrated that levels of toxaphene are higher there than in west Svalbard or Greenland (Savinova *et al.*, 2000b). Studies of sediments in the Kola Bay area have demonstrated that elevated toxaphene is present in sediments in Polamy, a harbor north of Murmansk (Savinova *et al.*, 2000a), possibly associated with past use for insect control on ships.

Harbour and grey seals
Harbour seals are one of the most broadly distributed pinnipeds, inhabiting temperate, subarctic, and in some cases Arctic waters, in the north Atlantic and north Pacific. They are a relatively sedentary species that feed opportunistically on a wide variety of fish, cephalopods, and crustaceans (Bigg, 1981). Grey seals are a more mobile pinniped that occur in Atlantic Canada, around Iceland, the Faroe Islands, Great Britain, Norway, the Kola Peninsula, and the Baltic Sea (Bonner, 1981). They consume a wide variety of fish, as well as some crustaceans and cephalopods, and generally feed further offshore and in deeper waters than do harbour seals.

Blubber concentrations of PCBs, DDTs, chlordanes, dieldrin, and HCB in harbour seals from Prince William Sound (Alaska) in 1993 (Krahn *et al.*, 1997) (Annex Table 12) were similar to corresponding data for this species from the same region in 1989-1990 (Varanasi *et al.*, 1993). Their levels of PCBs and DDTs were about twice those of bearded (*Erignathus barbatus*) and ringed seals from the more northerly region of Norton Sound in the Bering Sea (Alaska) (Krahn *et al.*, 1997). These differences may be explained by the higher trophic position occupied by harbour seals compared to ringed or bearded seals, or by the greater anthropogenic activity in Prince William Sound compared to Norton Sound.

Ruus *et al.* (1999) quantified ΣPCBs, ΣDDTs, ΣCHLs, ΣHCHs, and HCB in harbor and grey seals from Jarfjord, northern Norway (Annex Table 12). Levels of ΣPCBs, ΣDDTs, and ΣCHL levels were up to an order of magnitude higher than in harbour seals from Alaska, while HCB levels were comparable between the two regions (Krahn *et al.*, 1997). Interspecies differences in levels of ΣHCHs and HCB, as well as PCB congener patterns (e.g., CBs 101, 118, 153, and 180) between Norwegian harbor and grey seals, may be explained by different dietary preferences and metabolic capacities. α-HCH was the most abundant of the HCH isomers in both harbor and grey seals from Jarfjord.

Grey seals sampled in 1993-1995 at the Faroe Islands, in connection with a study of their summer diet (Mikkelsen, 1998), were analyzed for OCs in pooled samples initially, and later separately in 30 individuals (Larsen and Dam, 1999; Dam, 2001). The pooled samples were composed of a total of 45 individuals: the pools were composed of adult males (n=4, age >8 yr); adult females (n=20, pregnant individuals); and, juveniles (n=21, 15 females and six males, age >2 yr and <4 yr). As in the Jarfjord study, α-HCH was the dominant HCH isomer, but was pronounced only in the group of juveniles. In the adult female group, the HCH isomers were found in similar or slightly decreasing concentrations in the following order: γ-HCH ≥ α-HCH ≥ β-HCH. The single OC occurring in the highest concentration among the adults was CB153, followed by *p,p'*-
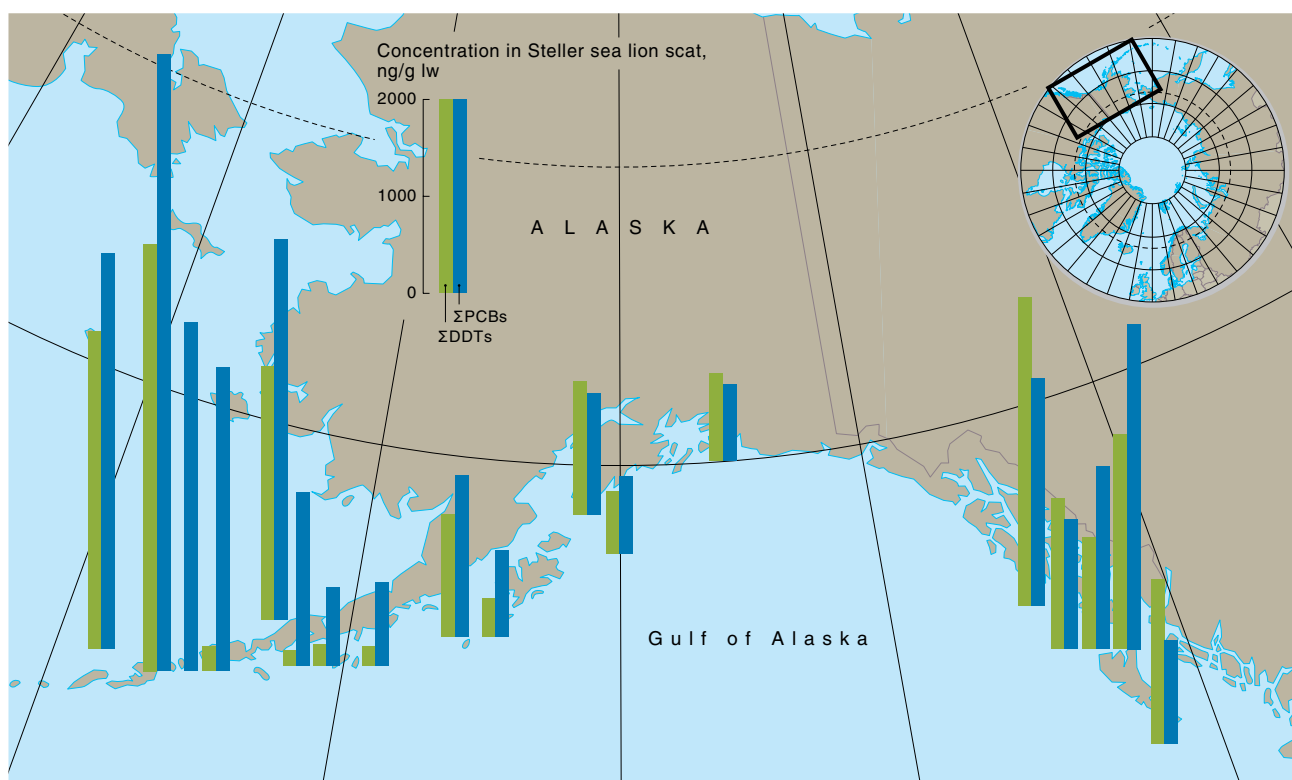
Figure 4·48. Concentrations of ΣPCBs and ΣDDTs in Steller sea lion scat composites collected from rookeries or haulouts in 1998 and 2000 (Beckmen, 2002).

DDE and CB180. CB153 concentrations in blubber were 4900 ng/g ww and 540 ng/g ww in males and females, respectively. In the juveniles, this sequence was different with *p,p'*-DDE > CB153 > CB 138+163, with CB153 at 1200 ng/g ww in blubber. The analyses of the 30 individuals gave the 'typical' pattern of decreasing OC level in females with age and a parallel increase in males. The results further revealed that in the female seals there were significant correlations between toxaphene (as Parlar 50 concentrations) and CB 153 but not among the males. There were, however, highly significant correlations between CB 153 and *p,p'*-DDE and *trans*-nonachlor in both sexes.

Bearded seals

Bearded seals from Norton Sound and Barrow, Alaska had relatively low OC concentrations in blubber compared to other pinniped species from that region and in the broader Arctic context (Krahn *et al.*, 1997; Hoekstra *et al.*, 2003a) (Annex Table 12). This may be primarily because bearded seals remain in the northern Alaskan seas, a region with limited anthropogenic activity, and consume lower trophic-level prey, including a wide variety of invertebrates, such as decapod crustaceans and mollusks (Kelly, 1988; Krahn *et al.*, 1997). Blood samples from bearded seals from Svalbard had comparable OC concentrations on a lipid weight basis to the Alaskan seals, except for HCH, but on the Chukotka Peninsula (Lavrentiya), blubber samples had generally lower OC concentrations compared to Alaska and Svalbard (RAIPON/GEF/AMAP Project, 2001). In contrast to bearded seals from Alaska, Chukotka, and Svalbard, those from the White Sea (Muir *et al.*, 2003) had very high ΣPCB and ΣDDT levels (approximately 3000 ng/g

ww), which is an order of magnitude higher than the other regions. ΣCHL and mirex concentrations were similar in seals from all regions. HCB and HCH concentrations were highest in seals from Barrow, Alaska. HCB levels were comparable in seals from Chukotka, Svalbard, White Sea, and Norton Sound (Annex Table 12). Toxaphene levels in White Sea bearded seals were comparable to those in ringed and harp seals from the same region, as well as levels in northwestern Greenland walrus, Barents Sea harp seals, and ringed seals from Barrow, Alaska (Muir *et al.*, 2000d; 2003; Wolkers *et al.*, 2000; Hoekstra *et al.*, 2003a). The high levels in the White Sea bearded seals are an example of the effects of point sources in the Arctic, as some parts of the White Sea are heavily industrialized. Blubber from bearded seals collected from the Chukotka Peninsula (Lavrentiya) area was analyzed for PCDD/Fs; the TEQ was 0.97 pg/g ww (RAIPON/AMAP/GEF Project, 2001) (Annex Table 16).

Steller sea lions

Based on samples from eighteen rookeries in 1998 and 2000, Beckmen (2002) determined that Steller sea lions sampled from the eastern Aleutian Islands (part of the endangered western Alaskan stock) excrete significantly higher levels of PCBs and DDTs in their feces (mainly adult females) compared to Steller sea lions in southeast Alaska (Figure 4·48). Levels of POPs in blubber biopsies were not significantly different between pups and juveniles in southeast Alaska and Prince William Sound in the Gulf of Alaska (Annex Table 12). Unfortunately, no blubber biopsies were available from the eastern Aleutian Islands or further west in the range. These findings indicate that PCBs are present in the food web ex-

ploited by Steller sea lions in Alaska, at least as far west as the eastern Aleutian Islands. In southeast Alaska where ΣPCB levels were intermediate, the population has increased in recent years. The relatively high levels for the eastern Aleutian Islands, in comparison to the nearby Gulf of Alaska, are of interest, as they suggest either a local source or a strong influence from the Bering Sea.

Northern fur seals

Breeding rookeries for more than 72% of the world's population of northern fur seals are located on the two largest Pribilof Islands, St. Paul and St. George (Alaska) in the Bering Sea (Loughlin *et al*., 1994). A preliminary study demonstrated that young northern fur seal dams (presumably primiparous) in the early post-partum period on St. George and St. Paul Islands, had significantly higher OC levels in their milk and blood than old (multiparous) dams (Beckmen *et al*., 1999). Higher milk OC exposure to the suckling pups was correlated with significantly higher OC levels in blood of the neonatal pups (Beckmen *et al*., 1999). In 1996, 50 perinatal pups were captured for blood sample collection (during the ten-day perinatal period and referred to as neonates), and 43 were re-sampled 29 to 51 days later ('pups'). Mean blood OC levels were higher in neonates than at recapture, and again, neonates of young dams had higher mean blood OC levels than neonates of older dams (Annex Table 12). The traditionally harvested and consumed subadult males have lower concentrations of PCBs and DDTs than do adult females or pups (Annex Table 12). PCB and DDT concentrations in subadult males from another study (Krahn *et al*., 1997) were comparable to levels reported by Beckmen *et al*. (1999). OC concentrations are lowest in fetal blubber but data were only available from two individuals. Pups showed some remarkably high OC concentrations in blubber, especially *p,p'*-DDE, but there is a large variance in blubber lipid content due to nutritional status.

PCB, DDT, chlordane, HCB, and dieldrin levels in subadult northern fur seals from St. Paul Island were comparable to, or higher than, concentrations in ringed and bearded seals from the Bering Sea and harbour seals from Prince William Sound (Gulf of Alaska) (Krahn *et al*., 1997). This can be partially explained by the fur seals' consumption of higher trophic-level prey such as pollock, herring, and squid (Wynne, 1993; Krahn *et al*., 1997), and, perhaps more importantly, by their extensive annual migration. This species migrates as far south as California and through the eastern Pacific as far as Japan, where these animals potentially feed on prey that are much more highly contaminated than prey in the waters of the southern Bering Sea or the Gulf of Alaska.

Concentrations of non- and mono-*ortho* PCBs followed the general pattern for PCBs with highest TEQs found in pups (32 pg/g ww) as compared to adults and subadults (17-21 pg/g ww) (Beckmen, 1999) (Annex Table 16).

Walrus

Walrus are long-lived benthic feeders and, as such, an important indicator species for bioaccumulating contaminants in benthic marine food webs. Although they have an important role in native traditional hunts, rela-

tively little is known about levels of OCs in walrus compared to seals and beluga. The previous AMAP report noted that although walrus generally have low OC concentrations in blubber, some individuals feed at higher trophic levels than others and, as a result, have much higher contaminant concentrations (de March *et al*., 1998). These walrus are believed to be including ringed seals in their diet (Muir *et al*., 1995b). Since then, studies have examined levels of OCs in walrus from the Russian and Alaskan Bering Sea, eastern Hudson Bay, and eastern and western Greenland (Muir and Kwan, 2000; Muir *et al*., 2000e; Seagars and Garlich-Miller, 2001; Kucklick and Struntz, 2002;).

Levels of PCBs and OC pesticides such as DDTs, HCHs, and chlordanes in the blubber of Pacific walrus (*Odobenus rosmarus divergens*) sampled across the Russian and the Alaskan Bering Sea (Seagars and Garlich-Miller, 2001; Kucklick and Struntz, 2002) were comparable to the relatively low levels previously reported in Bering Sea walrus (Galster and Burns, 1972; Taylor *et al*., 1989) (Annex Table 12). As in earlier studies, DDT compounds were essentially absent from walrus blubber in this region, while heptachlor epoxide was detected for the first time at low ng/g levels. In the Bering Sea walrus, oxychlordane dominated ΣCHLs, while β-HCH dominated ΣHCHs (Kucklick and Struntz, 2002). Additionally, significantly higher levels of ΣPCBs occurred in adult males (450 ng/g ww) than females (160 ng/g ww), and significantly higher oxychlordane levels occurred in males than females of any age. No differences were detected between sexes for ΣHCH and dieldrin (Seagars and Garlich-Miller, 2001).

OC levels in walrus from eastern Hudson Bay (northern Quebec) (Atlantic walrus, *O. r. rosmarus*) were much lower than those found in earlier studies from the same area (Muir and Kwan, 2000; Annex Table 12), most likely because the earlier studies sampled walrus that were seal-eaters (Muir *et al*., 1995b). Nonetheless, concentrations of many OCs were comparable to those in recent reports for walrus from other nearby regions such as Foxe Basin (Muir *et al*., 1995b). Levels of ΣPCBs were similar to those in walrus from the Bering Sea and northwestern Greenland, while ΣDDT levels were similar to those in walrus from northwestern Greenland (Muir *et al*., 2000e). ΣHCHs and HCB were also detected in concentrations similar to those in walrus from the Bering Sea and eastern and northwestern Greenland (Muir *et al*., 2000e) (Annex Table 12). In the case of ΣCHLs, levels in eastern Hudson Bay walrus were higher than those in the Bering Sea and northwestern Greenland, but lower than in eastern Greenland walrus (Muir *et al*., 2000e).

An examination of spatial trends in levels of OC compounds in two separate stocks of walrus from Greenland found lower concentrations in the northwestern Greenland animals, and much higher levels of all OCs, except HCH isomers and mono/dichlorobiphenyls in samples from eastern Greenland (Muir *et al*., 2000e) (Annex Table 12). ΣPCB levels averaged 246 ng/g ww in male walrus from northwestern Greenland, and 2860 ng/g ww in samples from eastern Greenland. However, DDT isomers showed the most difference between the two sites, with *p,p'*-DDE and *p,p'*-DDT being 50 and 69 times higher, respectively, in the eastern Greenland

walrus. Toxaphene levels in walrus in northwestern Greenland were lower than those from eastern Greenland, but were consistent with levels reported in ringed seals from Barrow, Alaska, ringed, harp, and bearded seals from the White Sea, and harp seals from the Barents Sea (Wolkers *et al.*, 2000; Hoekstra *et al.*, 2003a; Muir *et al.*, 2003). The eastern Greenland walrus showed a pattern of OCs characteristic of seal-eating animals, although they may have been consuming other prey as well. Despite the apparent differences in prey, the higher levels of OCs in eastern Greenland compared to the northwestern Greenland animals are consistent with results for polar bears, seals and gulls from the same regions.

Butyltins in pinnipeds

Mean butyltin (ΣBTs) concentrations of 17 ng/g ww were found in liver tissue from Steller sea lions sampled at the Aleutian Islands (Alaska) between 1976 and 1985 (Kim *et al.*, 1996a). In these animals, TBT concentrations ranged from 1.9 to 5.6 ng/g ww, while DBT and MBT concentrations ranged from below detection limits to 20 ng/g ww and 7.1 ng/g ww, respectively. DBT was the dominant component in the liver samples, which is in contrast to fish (their prey), in which TBT levels are highest, irrespective of the species and sampling site (e.g., Suzuki *et al.*, 1992; Takayama *et al.*, 1995). This implies that Steller sea lions are capable of metabolically transforming at least some of the TBT residues they consume into DBT and MBT (Kim *et al.*, 1996a). There was no evidence of age- or sex-dependent accumulation of butyltin residues in Steller sea lions, and no evidence of increasing concentrations of DBT and TBT between 1976 and 1985 (Kim *et al.*, 1996a). Butyltin concentrations in Svalbard ringed seals were 1.5 ng/g ww for MBT, 3.1 ng/g ww for DBT, and TBT was not detected (Berge *et al.*, 2002). TBT and its metabolites, DBT and MBT, were non-detectable (sub ng/g) in ringed seal blubber and liver from Labrador and northern Quebec (Muir *et al.*, 1999c; 2000c).

4.4.6.2. Cetaceans
4.4.6.2.1. Mysticetes

Minke whales

North Atlantic minke whales are trans-Atlantic, as well as polar to north temperate in range, and are capable of large-scale migrations. They feed at a lower trophic level than polar bears, odontocetes, and some seals, eating primarily capelin, herring, Atlantic cod, and krill (Larsen and Kapel, 1981; Nordøy and Blix, 1992; Skaug *et al.*, 1997).

Concentrations of PCBs and major OC pesticides quantified in the blubber of minke whales from seven regions across the north Atlantic and European Arctic ranged widely, but generally increased from west to east (Hobbs *et al.*, 2003) (Annex Table 13, Figure 4·49). Contaminant concentrations suggested that western and southeastern Greenland minke whales represent one group of whales, which are distinct from both Jan Mayen minkes and those from other more easterly regions. Although some differences were detected in PCB and OC pesticide concentrations between Jan Mayen whales and those from other regions, overall,
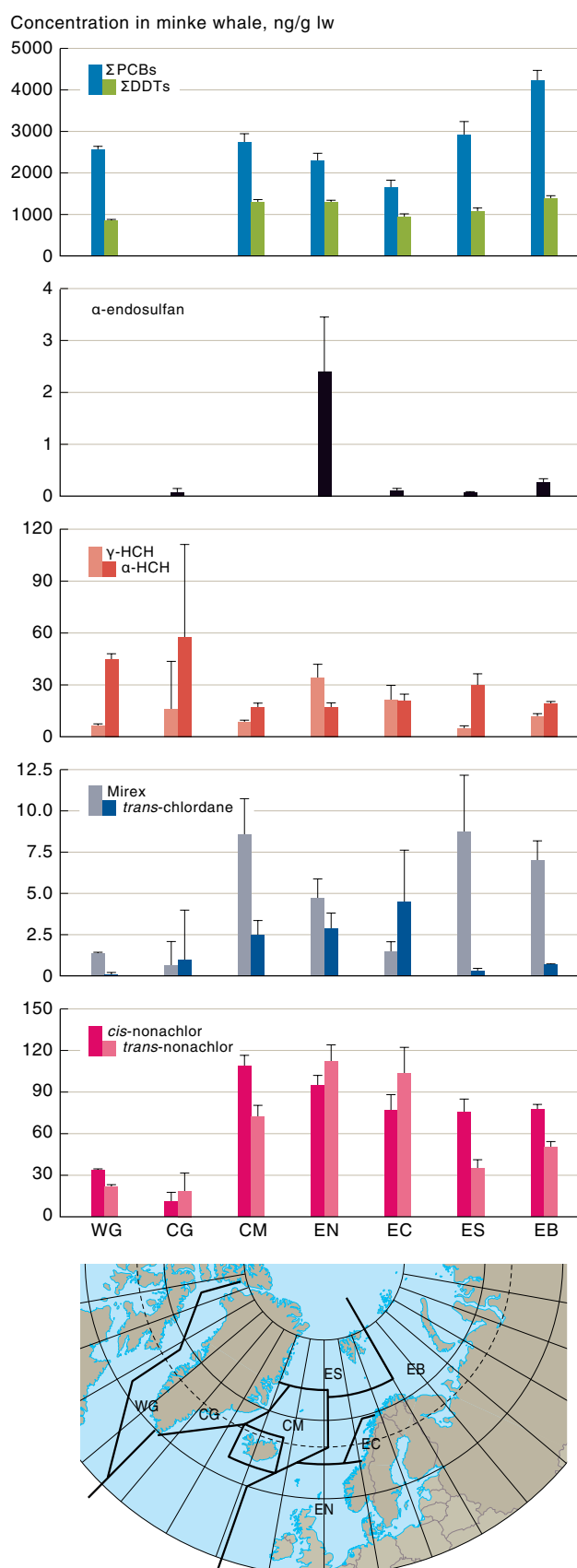

Figure 4·49. Sex-adjusted, geometric mean (± 95% CI) concentrations of ΣPCBs, ΣDDTs, and geometric mean concentrations of α-endosulfan, α-HCH, γ-HCH, mirex, *trans*-chlordane, *cis*-nonachlor, and *trans*-nonachlor in minke whales from several areas in the North Atlantic region. Areas are IWC 'small areas' (WG: west Greenland, CG: southeast Greenland, CM: Jan Mayen, EN: North Sea, EC: Vestfjorden/Lofoten, ES: Svalbard, EB: eastern Barents Sea) (Hobbs *et al.*, 2002a).

Jan Mayen whales were more similar to minke whales from the easterly regions, and generally appeared to be most similar to those from Svalbard and Vestfjorden/Lofoten.

Contaminant levels in minke whales from the North Sea and the Kola Peninsula region of the Barents Sea were relatively distinct from other groups of whales, and were often higher compared to other areas. For example, North Sea minkes had higher concentrations of the current-use pesticides, lindane (γ-HCH), α-endosulfan, and *trans*-nonachlor, compared to Svalbard whales. Minkes from the Kola Peninsula region of the Barents Sea had higher concentrations of PCBs, and a lower ΣDDT:ΣPCB ratio compared to those from Vestfjorden/Lofoten, as well as marginally higher ΣPCB concentrations compared to the North Sea and Svalbard whales. Therefore, although some mixing probably occurs between whales from the Kola Peninsula and Svalbard and between whales from North Sea and Vestfjorden/Lofoten, there appears to be some separation between whales from these two sets of regions. Furthermore, Skaare *et al.* (2001c) found significantly lower concentrations of PCBs in the dorsal blubber of adult female minkes sampled near Spitsbergen (461 ng/g ww) compared to adult females sampled in the North Sea (2190 ng/g ww) (Annex Table 13). Despite these distinctions, there was a general blurring in levels and patterns of PCBs and OC pesticides in minkes from Jan Mayen, Svalbard, Vestfjorden/Lofoten, the North Sea, and the Kola Peninsula region of the Barents Sea, suggesting that minke whales are quite mobile and feed in multiple areas (Hobbs *et al.*, 2003).

Mean ΣPCB, ΣDDT, ΣCHL, ΣHCH, and HCB concentrations reported in minke whales from the northeast Atlantic (western Spitsbergen, Lofoten/Vesteralen, Finmark, Bjørnøya, and the Kola Peninsula) in 1992 (Kleivane and Skaare, 1998) were about two to three times higher than mean levels reported in the same general regions by Hobbs *et al.* (2003). The lower contaminant levels in more recent minke samples (Hobbs *et al.*, 2003) may be attributable to changes in the availability of northeast Atlantic minke whale prey species. For example, in 1992, the diet of Svalbard minke whales was dominated by capelin, while in subsequent years, following the collapse of the capelin stocks in 1992/1993, their diet was almost 100% krill (Haug *et al.*, 2002).

Concentrations of PCDD/Fs and non- and mono-*ortho* PCBs were also analyzed in dorsal blubber of female minkes sampled near Svalbard and in the North Sea (Annex Table 16). Total mean TEQs based on these compounds were 24 pg/g ww (range 10-37 pg/g ww) for Svalbard and 67 pg/g ww (range 25-103 pg/g ww) for the North Sea whales (Skaare *et al.*, 2001c). The major contribution to the TEQs came from the non- and mono-*ortho* PCBs.

Levels of total toxaphene showed considerably more geographic variability than ΣPCBs (Hobbs *et al.*, 2002a). Levels were highest in the North Sea whales, followed by those from Jan Mayen and west Svalbard. The lowest levels occurred in whales from either side of Greenland and from the Vestfjorden/Lofoten region of Norway. Total toxaphene levels in minkes from the Kola Peninsula region of the Barents Sea were intermediate in comparison to the other sites (Hobbs *et al.*, 2002a).

Grey whales (Eschrichtius robustus)

The eastern grey whale stock makes an annual round-trip migration between their breeding grounds in subtropical waters (e.g., off Baja California and the southern Gulf of California) and their predominant feeding grounds in the northern Pacific Ocean. Although the majority of feeding occurs in the Bering and Chukchi Seas around Alaska (Highsmith and Coyle, 1992; Moore *et al.*, 2000), some animals spend extended periods in the spring and summer opportunistically feeding in the coastal waters of Washington, California, Oregon, and British Columbia. Grey whales feed primarily on benthic prey, such as ampeliscid amphipods, using suction to engulf sediments and prey from the bottom, then filtering out water and sediment through their baleen plates and ingesting the remaining prey. This unique feeding method often results in the ingestion of sediment and other bottom materials. Thus, exposure to sediment-associated contaminants is possible if they feed in areas containing contaminated sediments and benthic invertebrates.

ΣPCB and ΣDDT blubber concentrations of 17 grey whales sampled from the Chirikov Basin of the Russian Bering Sea in October 1994 ranged from 110 to 1300 and 30 to 540 ng/g ww, respectively (Krahn *et al.*, 2001; Tilbury *et al.*, 2002) (Annex Table 13). All of the whales sampled were juveniles, thus minimizing the influence of length (i.e. related to age and developmental stage) on contaminant concentrations. Futhermore, no significant differences in concentrations (lw) occurred by sex within each group of whales sampled. Blubber from one grey whale from the Chukotka Peninsula (Lavrentiya) was analyzed for OCs including PCDD/Fs. ΣPCB and ΣDDT concentrations were 196 ng/g ww and 93 ng/g ww, respectively, and TEQ based on PCDD/F was 1.8 pg/g ww (Annex Table 16) (RAIPON/AMAP/GEF Project, 2001). No other grey whale data are available for comparison. However, on a wet weight basis, these levels are similar to ΣPCB and ΣDDT levels in other mysticetes. For example, mean concentrations of ΣPCBs in blubber of bowhead whales (*Balaena mysticetus*) from Alaska (Hoekstra *et al.*, 2002c), fin whales (*Balaena physalus*) from the north Atlantic (Aguilar and Borrell, 1994), and minke whales from western Greenland (Hobbs *et al.*, 2003) were 359, 732, and 2290 ng/g ww, respectively. Similarly, mean concentrations of ΣDDTs in bowhead-, fin-, and minke whales were 331, 633, and 650 ng/g ww, respectively.

Bowhead whales

The bowhead whale is a large mysticete found in Arctic waters. The largest population, the Bering Sea stock, migrates annually between the eastern Beaufort Sea-Amundsen Gulf in summer and the Chukchi and northern Bering Sea in the winter (Schell *et al.*, 1989; Lowry, 1993; Moore and Reeves, 1993). Blubber and liver tissue were collected during the Native subsistence harvest of this species, which coincides with the migration between the Beaufort and Bering Seas.

OC concentrations in Alaskan bowhead whales reported by Hoekstra *et al.* (2002c) (Annex Table 13) were similar to values reported by Mössner and Ballschmiter (1997) and O'Hara *et al.* (1999). Hoekstra *et al.* (2002c) also reported mean concentrations of toxaphene in bow-

head whales for the first time. The bioaccumulation of PCBs and OC pesticides in bowhead whale blubber appeared to change seasonally and was characterized by differences in analyte metabolism. The proportions of individual OCs in bowhead blubber samples were related to the harvest season. Principal components analysis showed that whales harvested in the autumn of 1997-2000 had higher loadings for less chlorinated PCBs, toxaphene, and chlorobenzene congeners, which distinguished them from spring harvest specimens collected during 1998-2000 that had higher proportions of the more recalcitrant PCBs (CBs 153 and 180), *p,p'*-DDE, HCB and β-HCH. The patterns of OC loadings found in bowhead whale blubber generally reflect the different levels of persistent OCs in the surface waters of the Bering and Beaufort Seas (Iwata *et al.*, 1993; Hoekstra *et al.*, 2002c). Toxaphene levels in the Beaufort Sea bowheads were comparable to those measured in minke whales from western Greenland and the Norwegian Sea (Hobbs *et al.*, 2002a). Results reported by Hoekstra *et al.* (2002c) demonstrate that bowhead whales are exposed to a variety of OC pollutants from lower trophic-level prey items, and that seasonal variation in OC profiles coincides with the annual migration between the Beaufort and Bering Seas. The influence of collection season on OC bioaccumulation in blubber seen in their study suggests that OC concentrations change annually in the whales, and that spatial differences in contaminant levels within the Bering-Chukchi-Beaufort region may be reflected in marine biota.

4.4.6.2.2. Odontocetes

Belugas

The beluga or white whale is a small (up to 4.5 m long) toothed cetacean (odontocete) that is circumpolar in distribution in the Arctic. Belugas feed near the top of the marine food web on a variety of fish and invertebrates, such as cephalopods and shrimp (Banfield, 1974), and are relatively long lived (>35 yr). They have a nearly continuous distribution across the Russian Arctic coast, but in the NE Atlantic Ocean they are limited to the north coast of Norway, and in the Pacific Ocean, to the Okhotsk Sea (Kleinenberg *et al.*, 1964). They are present along the east and west coasts of Greenland and in North America, from Alaska across the Canadian western Arctic to a large population in Hudson Bay, and among islands in the eastern Canadian Arctic. Beluga movements are extensive, seasonal and generally predictable. They come into coastal waters and estuaries in mid-summer, and spend the winter offshore in pack ice and polynyas (Brodie, 1989).

In a recent study by Krahn *et al.* (2000), samples of beluga blubber from three of the five different Alaskan stocks (eastern Beaufort Sea, eastern Chukchi Sea and Cook Inlet) were analyzed for concentrations and patterns of OC contaminants. ΣPCBs, ΣDDTs, ΣCHLs and HCB levels in Point Lay (eastern Chukchi Sea) beluga blubber (Wade *et al.*, 1997; Hoekstra *et al.*, 2003a) (Annex Table 13) were in good agreement with those reported for the same region by Krahn *et al.* (2000). Blubber of Alaskan belugas contained PCBs and OC pesticides in ranges similar to those found in belugas from the Canadian Arctic (Annex Table 13) (Sang *et al.*, 2000). The Cook Inlet stock generally had the lowest concentrations, while the eastern Beaufort Sea stock had the highest concentrations. This is somewhat surprising given that whales from the Cook Inlet stock reside in one of the most 'urban' areas of Alaska, where anthropogenic contamination results from relatively higher density of human residents and commercial activities. The eastern Chukchi Sea and eastern Beaufort Sea stocks could clearly be distinguished from the Cook Inlet stock by patterns of individual OC analytes, and although there was some overlap between the males and females of the Cook Inlet stock, these groups were also generally separated (Krahn *et al.*, 2000). These differences in contaminant patterns are indicative of differences in contaminant accumulation, which likely reflects differences in habitat use and prey forage among the stocks.

In the Canadian Arctic, PCBs were quantitatively the most predominant POPs in the blubber of eastern Hudson Bay belugas, followed by DDT and chlordane-related compounds (Sang *et al.*, 2000) (Annex Table 13). Higher concentrations of all major groups of OCs, except for ΣHCHs, were observed in blubber of males (n = 8) as compared to females (n = 2). Data were too limited to evaluate effects of age or animal condition on contaminant levels. No other contaminant data for beluga blubber samples from the Hudson Strait area (Kangiqsujuaq) have been analyzed for comparison. Levels of major OC groups in male beluga blubber sampled by Sang *et al.* (2000) were, however, similar to previous reports for male beluga from eastern Hudson Bay (Nastapoka River) in the mid-1980s (Muir *et al.*, 1990b), and much lower than levels in beluga from the southeast Baffin beluga stock. Muir *et al.* (1990b) concluded that belugas sampled from the Kangiqsujuaq area of the Hudson Strait are from a population that inhabits eastern Hudson Bay and southern Hudson Strait, and not the southeast Baffin Island area. Innes *et al.* (2001) also concluded that there are distinct differences in the OC signature of southeast Baffin and Hudson Bay belugas. Comparisons between east Hudson Bay and west Hudson Bay beluga are complicated by missing age estimates and lipid content data for these whales (Hobbs *et al.*, 2002b) (Annex Table 13). With this in mind, it seems that the western Hudson Bay beluga may generally have had higher PCB and OC pesticide concentrations than the east Hudson Bay whales. This may be at least partially a result of the west Hudson Bay beluga having been sampled six years before the east Hudson Bay whales. OC levels for beluga from Kimmirut, Baffin Island were similar to, but somewhat higher than, levels in the east Hudson Bay beluga (Annex Table 13). Non- and mono-*ortho* PCBs in beluga from the same region were analyzed by Helm *et al.* (2002), and levels ranged from 14.4 to 294 ng/g ww, with CBs 118, 105, and 156 being the most dominant congeners. Total non- and mono-*ortho* PCBs were lower in females (60.2 ± 40.3 ng/g ww) than males (228 ± 113 ng/g ww). TEQs in males and females were 1.73 ± 0.627 pg/g lw and 1.32 ± 0.909 pg/g lw respectively, most of which was accounted for by congener 126 (Helm *et al.*, 2002) (Annex Table 16). Stern and Addison (1999) analyzed non-*ortho* PCBs (CBs 77, 126, and 169) in beluga from Cumberland Sound. The TEQ in blubber from 1997 was 6.1 pg/g lw.
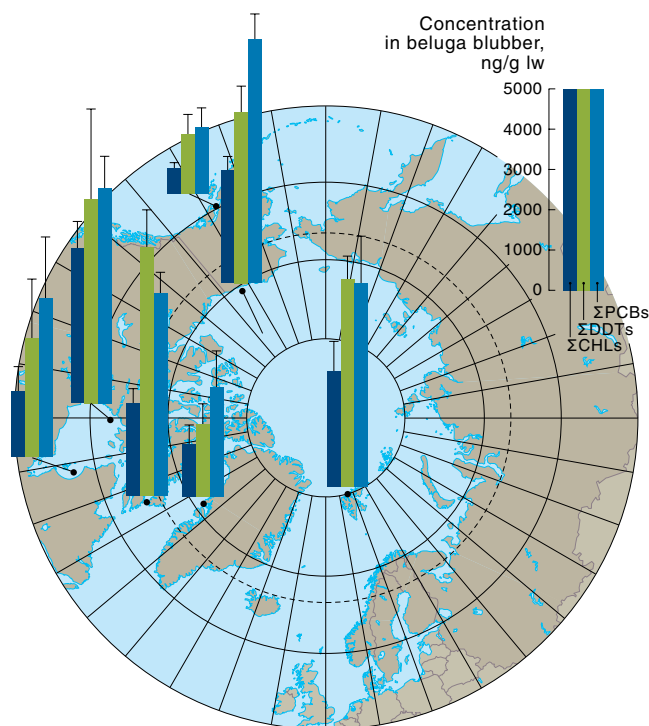
Figure 4·50. Mean (± 95% CI) concentrations (ng/g lw) of ΣPCBs, ΣDDTs and ΣCHLs in male beluga whale blubber (Stern and Addison, 1999; Krahn *et al*., 2000; Sang *et al*., 2000; Andersen *et al.*, 2001a; Muir and Johansen, 2001; Hobbs *et al*., 2002b).

Further east, Andersen *et al*. (2001a) and Wolkers (2002) reported levels and patterns of OC pollutants in blubber biopsies taken from belugas from western Svalbard (Annex Table 13). Levels reported in the two studies were comparable, and the slightly lower levels in whales examined by Wolkers (2002) were consistent with their younger age (immature) compared with those reported in Andersen *et al*. (2001a). Andersen *et al*. (2002) also reported high levels of toxaphene (11 400 ± 4210 ng/g lw) in the same ten Svalbard belugas they examined for OC pollutants (Annex Table 13). Overall, levels of ΣPCBs, ΣDDTs and ΣCHLs in belugas from the Arctic are generally highest in the Beaufort and Barents Seas and western Hudson Bay, somewhat lower in the rest of the Canadian Arctic, and lowest in Cook Inlet, southern Alaska (Figure 4·50).

As is typical of top predators in Arctic marine food chains (Borgå *et al*., 2001; Fisk *et al*., 2001c), the major compounds detected in beluga blubber were ΣPCBs, ΣDDTs, toxaphene, and ΣCHLs. OC levels in the Svalbard belugas were generally similar to, or slightly higher than, values in other more westerly Arctic beluga stocks (Annex Table 13) (Muir *et al*., 1990b; Stern *et al*., 1994; Muir *et al*., 1999b), but were lower than in those from the St. Lawrence River (Canada) (Muir *et al*., 1990b; Muir *et al*., 1996b). In whales examined by Andersen *et al*. (2001a), ΣHCHs was dominated by β-HCH in contrast to reports for belugas from the Canadian Arctic (Muir *et al*., 1990b). Patterns in relative prevalence of various OC compounds to their compound groups were consistent with what is seen in other marine mammals in the Arctic.

Toxaphene levels in beluga from Alaska and Svalbard were quite variable, with mean values ranging from roughly 1000 to 10 000 ng/g ww (Wade *et al*., 1997;

Hoekstra *et al*., 2003a), while levels in Pangnirtung beluga were consistently on the high end of this range (Stern, 1999; Stern and Addison, 1999) (Annex Table 13).

Long-finned pilot whales (Globicephala melas)
Screening for OCs was performed on blubber samples from 420 long-finned pilot whales sampled in 1997 at the Faroe Islands (Dam and Bloch, 2000). The analyses were done on pooled samples of whales from nine separate schools with each school represented by a subsample of 50 individuals randomly sampled from a total of 805 individuals. In general, concentrations of all OCs were of similar magnitude in the juveniles and adult males, but were approximately half as high in adult females. *p,p*'-DDE dominated the DDT group, accounting for 60 ± 6%, 57 ± 7%, and 65 ± 3% of the ΣDDTs in the young, females and males, respectively. Chlordane was dominated by *trans*-nonachlor, which accounted for approximately 50% of ΣCHLs. There is a general scarcity of data on these compounds, but it may be noted that in a study of five male and nine female long-finned pilot whales stranded in Newfoundland in 1980 (Muir *et al*., 1988), concentrations of *trans*-nonachlor and ΣCHLs were half of what was found in the Faroese study. The concentrations of HCB in the Newfoundland study (Muir *et al*., 1988) were very similar to what was found in the Faroese study (Dam and Bloch, 2000). The much higher PCB concentrations found in pilot whales of the Faroe Islands compared to stranded individuals in New Zealand (Schröder, 1998) is noteworthy, and in agreement with what is seen for baleen whales (O´Shea and Brownell, 1994). In the Faroese study, the mean ΣPCBs for all 417 individuals was 11 900 ng/g ww, whereas the mean for the 61 individuals from New Zealand was 310 ng/g ww.

In the Faroe Islands, samples from 100 individuals from two pilot whale schools (Sandavágur, August 26, 1997 and Tórshavn, September 24, 1997) were analyzed in order to determine the variability in pollutant load within the groups of adult males and females, and juveniles (Dam, 2001). No strong relationships between ΣPCB$_7$ and *p,p*'-DDE and pilot whale length were found although older males tended to have higher concentrations. Toxaphene was also determined in these samples including Parlars 26, 32, 50, 62, and 69, but of these, Parlars 32 and 69 were not detected in any sample. Juvenile males had the highest concentrations of toxaphene and levels were lower in adults.

Killer whales (Orcinus orca)
Killer whale populations that inhabit Washington's Puget Sound (U.S.), the inside waters of British Columbia, southeast Alaska, and Kenai Fjords/Prince William Sound, Alaska, have been extensively studied over the past 30 years. Two eco-types of killer whales, 'transient' and 'resident', occur in all of these regions. These eco-types are genetically distinct and differ in various aspects of morphology, vocalization patterns, diet, and habitat use. For example, transient killer whales feed on marine mammals, while resident killer whales are fish-eaters. Various genetic and photo-identification studies of eastern North Pacific killer whales have provided information on the male-female composition of most of these resident pods and transient groups, as well as the ap-

proximate age, reproductive status, and putative recruitment order (birth order) of the individual whales.

Concentrations of PCBs and OC pesticides, including dioxin-like PCB congeners and DDTs, in blubber biopsies from free-ranging transient killer whales were much higher than those found in resident animals sampled from the Kenai Fjords/Prince William Sound areas between 1994 and 1999 (Annex Table 13). Mean blubber ΣPCB concentrations were 3900 ng/g ww in residents (range 270-27 000 ng/g ww) and 59 000 ng/g ww (range 4900-140 000 ng/g ww) in transients. These differences are apparently due to the differences in diets of these two killer whale eco-types (Ylitalo *et al.*, 2001). The concentrations of PCBs and DDTs that were measured in blubber of the Alaskan killer whales were much higher than the concentrations in blubber of various other cetaceans and pinnipeds that reside and feed in Alaskan waters (Annex Tables 12 and 13) (de March *et al.*, 1998). The ΣPCB levels measured in these Alaskan transient killer whales are similar to those recently reported in biopsy blubber samples of transient killer whales from the more contaminated coastal waters of British Columbia (Ross *et al.*, 2000). Mean mono-*ortho* PCB TEQs in residents were 29 pg/g ww (range 1.5-150 pg/g), and in transients, 220 pg/g ww (range 14-580 pg/g) in blubber (Annex Table 16).

Harbour porpoises
Concentrations of PCBs, HCB, *p,p'*-DDD, *p,p'*-DDE, γ-HCH, and PCDD/Fs were lower in immature harbour porpoises from southwestern Greenland in comparison with levels in immature, non-Arctic dwelling porpoises from the North and Baltic Seas (Bruhn *et al.*, 1999). α-HCH values were highest in porpoises from southwestern Greenland. *p,p'*-DDT was only detected in the Greenland porpoises, possibly due to a higher degree of metabolic induction in the non-Arctic animals. The higher proportion of lower chlorinated PCBs in the Arctic samples is likely associated with a predominance of these more volatile compounds in the atmosphere, or perhaps to a lesser degree, metabolic induction, and subsequent excretion of these compounds, relative to the non-Arctic animals. The concentrations of PCDD/Fs, given as TEQs in the Arctic porpoises, ranged from 0.2 to 0.9 pg/g lw with a median of 0.41 pg/g lw (Annex Table 16). Mono-*ortho* PCBs were also determined, and TEQs based on these were stated to be 40-70 times higher than for PCDD/F TEQs in the three populations, but actual TEQ values were not given in the publication. CB 118 contributed most to the total TEQs.

Further east, Berggren *et al.* (1999) found that PCB and DDT levels in blubber sampled from mature male harbour porpoises from the Norwegian west coast were relatively high compared to other Arctic-dwelling cetaceans, and were comparable to levels in samples taken from the Baltic and Kattegat-Skagerak Seas (Annex Table 13). They were an order of magnitude higher than in porpoises from southwestern Greenland (Bruhn *et al.*, 1999). Porpoises from the west coast of Norway had the most variability in non-*ortho* PCB concentrations (96-7624 pg/g lw) compared to the other more southerly sites, which may be caused by exposure of some porpoises to a local contaminant source. Their ΣPCDD/F concentrations ranged from 7.3 to 19 pg/g lw, lower than in mature porpoises from the more southerly locations. The mean TEQ based on PCDD/Fs, non- and mono-*ortho* PCBs was 111 pg/g lw (Annex Table 16).

Narwhal (Monodon monoceros)
Narwhal are deep-water, benthic feeders and are an important Arctic species that has received little attention in terms of contaminants studies. In the Canadian Arctic, levels of PCBs, DDTs and chlordanes (not corrected for age) were generally higher in male narwhal from Pond Inlet (northeastern Baffin Island), than those from Broughton Island (eastern Baffin Island), or Grise Fjord (southern Ellesmere Island). Similar trends occurred for toxaphene in narwhal from these sites (Stern, 2001) (Annex Table 13). Concentrations of PCBs, DDTs, and chlordanes were generally higher in narwhal from Svalbard (Wolkers, 2002) as compared to those from Greenland (Denmark, 2002), while HCHs, HCB, and toxaphene levels were comparable between these regions (Annex Table 13). Overall, levels of POPs in narwhal were quite similar in the Canadian Arctic and western Greenland, while levels of PCBs, DDTs and chlordanes were considerably higher in the Svalbard narwhal. Levels of ΣHCHs, HCB and toxaphene were relatively consistent across the sites sampled.

Organotins in cetaceans
Studies indicate that marine mammals are exposed to organotins but data from the Arctic area are lacking. Harbour porpoise, harbour seal, and ringed seal are species that have been analyzed for organotins in Norwegian territories (Berge *et al.*, 2002). Relatively high concentrations were observed in liver from harbour porpoises caught in 1988 (Table 4·8), just before restrictions on the use of TBT (mainly on small boats) were introduced in several other European countries. The concentrations were significantly reduced 11 years later (Table 4·8), possibly as a consequence of the introduced restrictions. Mean concentrations in porpoise from the west coast of Norway in 1998/1999 were higher than in samples collected further north in the Barents Sea. Considerably lower concentrations were observed in seals compared to porpoises. The lowest concentrations were found in seals from Spitsbergen, where only traces of DBT and MBT (degradation products of TBT) were found. The degradation products in all samples were generally more predominant than TBT itself, and probably indicated metabolic capacity to degrade TBT. Triphenyltin (TPhT) was observed in all porpoise samples and in common seals but not in ringed seals. The limited data available indicate low to moderate exposure to organotins in Arctic areas like Spitsbergen and Bjørnøya. Marine mammals are more exposed, however, along the Norwegian coast. It is anticipated that exposure will decline further as a consequence of additional restrictions on the use of organotin in antifouling paint for ships.

Butyltin levels were quantified in liver tissue from male Dall's porpoises sampled from the Aleutian Islands chain, the Bering Sea, and the northwestern North Pacific between 1979 and 1984 (Tanabe *et al.*, 1998). Low levels (ΣBTs = 41-180 ng/g ww) were found in Dall's porpoises from these sites, compared with cetaceans and pinnipeds examined in other regions, including Japan, China, the Philippines, the west Pacific and India (17-

Table 4·8. Concentrations of mono-, di- and tributyltin and triphenyltin (in ng Sn/g ww) in marine mammals and seabirds from Norway and the Faroe Islands.

Species/year	Location	dw %	MBT	DBT	TBT	TPhT	Reference [a]
Harbour porpoise, 1988	Norwegian coast of the Barents Sea	–	35	285	98	27	1
Harbour porpoise 1999	Norwegian coast of the Barents Sea	–	11	67	34	6	1
Harbour porpoise, 1999	West coast of Norway	–	19	122	40	10	1
Common seal ,1998/1999	West coast of Norway	–	11.7	8.6	1.2	3.3	1
Ringed seal, 2000	Spitsbergen (Ny-Ålesund)	–	1	1.6	<1	<1	1
Glaucous gull, 1998	Bjørnøya	–	<1	11.7	<3	<3	1
Pilot whale, adult male, 2000	Faroe Islands	36	<0.1	1.3	3.0	<0.1	2
Pilot whale, adult female, 2000	Faroe Islands	22	<0.1	1.4	1.8	<0.1	2
Pilot whale, adult female, 2000	Faroe Islands	29	<0.1	1.8	2.2	<0.1	2
Pilot whale, fetus, 2000	Faroe Islands	19	<0.1	1.8	1.2	<0.1	2
Pilot whale, fetus, 2000	Faroe Islands	21	<0.1	<0.1	<0.1	<0.1	2
Pilot whale, fetus, 2000	Faroe Islands	14	<0.1	<0.1	<0.1	<0.1	2

[a] 1: Berge *et al.* (2002); 2: Mikkelsen (2002).

3000 ng/g ww). DBTs were predominant among the butyltins. MBT, DBT and TBT concentrations in the Dall's porpoises ranged from 22 to 33, 29 to 59, and 12 to 26 ng/g ww, respectively. Further east, butyltin (MBT, DBT, and TBT) was not detectable in livers from five Hudson Strait (Canada) belugas sampled in the summer of 1998 (de Mora *et al.*, 1999). The authors concluded that the limited maritime shipping activities in northern Quebec were not sufficient to provide an appreciable input of TBT into the marine environment of northern Quebec, and that since these same whales were contaminated with OCs but not butyltins, it was unlikely that aerial input could be a source of organotin compounds to Arctic whale populations. In contrast to this, butyltins were detected in all 21 samples examined from the more southerly St. Lawrence River population of beluga whales located in eastern Canada (de Mora *et al.*, 1999).

Organotins, such as mono-, di- and tri-substituted butyl- and phenyltin compounds, were analyzed in pilot whale kidney and blubber from three adults (two females, one male) and three fetuses sampled in the Faroe Islands in 2000 (Mikkelsen, 2002). The results showed no detectable concentrations of organotins in blubber tissue and kidney (detection limit 0.1 ng Sn/g ww) except some low concentrations of DBT and TBT near the detection limit in the adults and in one of the fetuses (Table 4·8).

4.4.6.3. 'New' chemicals in pinnipeds and cetaceans

Of the data produced on 'new' chemicals in the Arctic, the greatest amount has been generated for marine mammals, in particular seals and whales. These are logical animals in which to check for 'new' chemicals, as seals and whales have among the highest levels of OCs in the Arctic.

PBDEs
PBDE data have been produced for seals and whales from the Canadian and European Arctic (Annex Table 17). There have been two temporal trends studies of PBDEs, in beluga (Stern and Ikonomou, 2000; 2001) and ringed seals (Ikonomou *et al.*, 2002), which have shown that the concentrations of these compounds are increasing in Arctic marine mammals (see Section 5.4.6.1). In general, concentrations of PBDEs are orders of magnitude less than legacy OCs such as PCBs and

DDTs. However, PBDEs consist of a much smaller number of individual compounds, so the difference between individual PBDE and individual PCB congeners is less. BDE47 is the most common congener measured, followed by BDE congeners 99 and 153. Other BDE congeners, such as 100 and 49 have been measured in Canadian Arctic beluga (Stern and Ikonomou, 2000; 2001), but others, such as BDEs 85 and 138, have been reported as non-detectable in Svalbard beluga and Faroe Islands pilot whales (van Bavel *et al.*, 2001). These congeners are found at lower concentrations in the technical PBDE products, but may also be less prevalent due to biotransformation.

Although it is too early to draw conclusions about spatial trends of PBDEs in Arctic marine mammals, there are sufficient data to suggest that concentrations are higher in the European Arctic compared with the North American Arctic. Concentrations of ΣPBDEs were 92.9 ± 56.5 ng/g ww in Svalbard beluga blubber collected in 1998 (van Bavel *et al.*, 2001) and were higher, compared to concentrations of 15.5 ng/g ww in beluga from the western Canadian Arctic (Stern and Ikomonou, 2000; 2001). ΣPBDE concentrations in the blubber of ringed seals from northeastern Greenland (58 ± 23 ng/g ww) were an order of magnitude higher than levels reported from western Greenland (3.6 ± 1.1 ng/g ww) (Muir and Johansen, 2001) and the western Canadian Arctic (4.6 ng/g, ww) (Ikonomou *et al.*, 2002).

Minke whales from the Barents Sea had ΣPBDE levels of 0.15-0.45 ng/g ww in muscle, while minke whales from the Norwegian Sea had higher levels at 3.1-15 ng/g ww in muscle (Herzke, 2002b).

The greatest concentrations of PBDEs measured in the Arctic are those observed in Faroe Islands long-finned pilot whales (144-1620 ng/g ww) (Annex Table 17) (van Bavel *et al.*, 2001). Concentrations are an order of magnitude greater than in any other Arctic marine mammal examined to date. Due to a general lack of PBDE data in the Arctic, it is difficult to determine if these high levels are due to spatial trends or the behavior of the pilot whales (i.e. trophic level). Additionally, as in beluga whales from Svalbard (van Bavel *et al.*, 2001), surprisingly high levels of methoxylated PBDE (Me-O-PBDE), almost comparable to the most abundant BDE47, were found in the pilot whale. Results for long-finned pilot whales from Tórshavn, Faroe Islands, also revealed large differences between PBDE concentrations with age
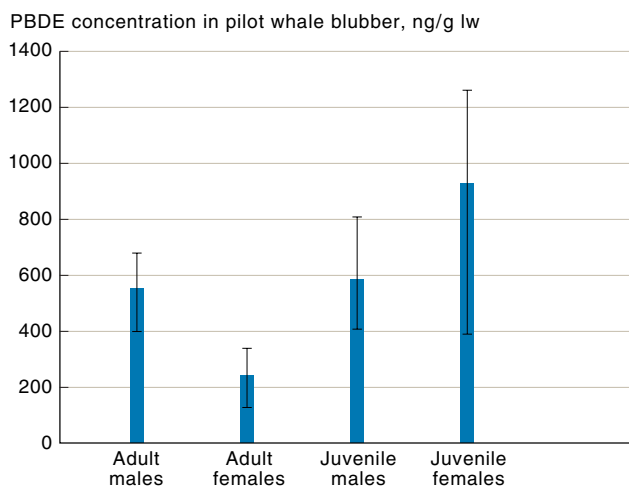
PBDE concentration in pilot whale blubber, ng/g lw

Figure 4·51. Mean (and range) of concentrations of PBDEs in long-finned pilot whales (adult males and females compared to juvenile males and females) caught at the Faroe Islands (van Bavel *et al.*, 2001).

and sex (van Bavel *et al.*, 1999). However, the highest levels were found in juveniles (402-1246 ng/g lw), with somewhat lower values in adult males (397-669 ng/g lw) and the lowest values in adult females (126-326 ng/g lw) (Figure 4·51) (van Bavel *et al.*, 1999). This indicates transfer of the PBDEs from mother to calf by lactation. Results from a mother and fetus also indicated the presence of a partial transplacental barrier, as the level in the fetus was generally half the amount of the mother (van Bavel *et al.*, 2001).

Other 'new' chemicals
In addition to the PBDEs, a number of studies have also examined several other 'new' OCs, including PFOS, tris(4-chlorophenyl) methanol (TCPM-OH), SCCPs, PCNs, endosulfan sulfate, and a number of chiral compounds.

PFOS was detected in the blood of ringed seals, and blood and liver of northern fur seals (Table 4·9) (Giesy and Kannan, 2001; Kannan *et al.*, 2001a). Concentrations were greater in liver compared to blood. No obvious trends between the Canadian and European Arctic in PFOS in ringed seals were observed, although this is a very small dataset.

Lower chlorinated CBz have been detected in Arctic seawater and in lower trophic organisms from northern Quebec (Muir *et al.*, 2000c; Muir *et al.*, 2000f).

Hexachlorobutadiene (HCBD) is mainly created as a by-product in the manufacture of chlorinated hydrocarbons like tri- and tetrachloroethene. This hydrophobic (log K_{ow} 4.78) and volatile product (vapor pressure = 19.96-20.00 Pa (20-25°C)) (Mackay *et al.*, 2000) has been detected at low levels in Arctic biota (Muir *et al.*, 2000f) and in the north Atlantic Ocean (WHO/IPCS, 1994).

TCPM-OH was measured in five ringed seals from northern Russia, near the Yenisey River, and had a mean concentration of about 47 ng/g lw, in 1995 (Watanabe *et al.*, 1999).

Blubber from beluga whales collected in 1994 near Kimmirut, Nunavut, was analyzed for PCNs and non- and mono-*ortho* PCBs (Helm *et al.*, 2002). ΣPCN concentrations ranged from 40 to 384 pg/g (n=6), on a wet weight basis (approximately 90% lipid), and were dominated by PeCNs. ΣPCN levels were lower in female belugas (n=3) than in males (n=3). Total non- and mono-*ortho* PCB concentrations were much higher than ΣPCNs, ranging from 14.4-294 ng/g ww in beluga whale blubber with the CBs 118, 105, and 156 having the highest concentrations. PCNs contributed an extra 11% (0.026-0.40 pg TEQ/g ww) to total TEQs (0.30-2.6 pg TEQ/g ww) calculated using non- and mono-*ortho* PCBs and PCNs. Most of the TEQs in beluga were accounted for by CB 126.

Blubber from ringed seals from Pangnirtung, Nunavut, collected in 1993 also contained PCNs (Helm *et al.*, 2002), but concentrations were lower than in beluga, ranging from 29-63 pg/g ww. The PCNs added insignificantly to the total TEQs.

Endosulfan sulfate was found in blubber of beluga from Pangnirtung collected in 1996/1997, with approximate mean concentrations of 13.5 ng/g lw (Stern and Addison, 1999).

Chiral contaminants
As discussed in the seabird section (Section 4.4.5.1), chiral pollutants exist in two forms as optical isomers called enantiomers. Enantiomers have identical physical-chemical properties and abiotic degradation rates, but can

Table 4·9. Concentrations of PFOS in liver and/or blood of Arctic marine mammals (ng/g ww or ng/mL) from Kannan *et al.* (2001a) and Giesy and Kannan (2001).

Species/tissue	Location	n	Collection year	Sex	Age class	PFOS[a]
Ringed seal blood plasma	Cumberland Sound	24	1998	M and F		<3-12
Ringed seal blood plasma	Spitsbergen	10	1996	4 M; 6 F	3.0-20 yr	8.1±2.5
Ringed seal blood plasma	Spitsbergen	8	1998	3 M; 5 F	2.0-12 yr	10.1±2.7
Northern fur seal liver	Pribilof Islands (Bering Sea)	13	1995 and 1998	11 M; 2 F	3 pups (<4 m); 10 subadults (2-4 yr)	<10-122 [38]
Northern fur seal blood	Pribilof Islands (Bering Sea)	10	1995	10 F	adult (>3 yr)	<6
Northern fur seal blood	Pribilof Islands (Bering Sea)	7	1995	7 M	subadult (2-4 yr)	<6
Polar bear liver	Northwestern Alaska (Barrow; Nuiqsut; Point Lay; Gambell; Shishmaref; Little Diomede; Savoonga)	17	13 Dec.1997-15 Jun.1999	14 M; 3 F	13 adults (>5 yr); 4 subadults (3-4 yr)	175-678 (350)
Polar bear blood	Beaufort Sea	14	1999	7 M; 7 F	n.a.	26-52 (34)

[a] Values in brackets [ ] indicate the percentage of detectable observations. Values in parentheses ( ) indicate the mean.

have different rates of biotransformation, providing information on the ability of species to biotransform OCs.

Wiberg *et al.* (2000) examined ERs of α-HCH and several chlordane compounds in the blubber and liver of ringed seals from Resolute Bay in the Canadian Arctic. The ERs in ringed seals were frequently nonracemic (ER ≠1), due to enantiomer-specific biotransformation; however, cod from the same region showed near-racemic mixtures (ER =1) for most compounds. (+)-α-HCH was more abundant than (–)-α-HCH in ringed seals. There was no uniform trend for the ER changes in the various chlordane compounds examined. It was also determined that oxychlordane was formed in ringed seals and metabolized by polar bears that preyed on them, and the ER had an important role in the class separation of male/female seals and fat/liver tissues.

EFs of α-HCH and other chiral contaminants in seal blubber may not reflect the metabolic capability of seals. Wiberg *et al.* (1998; 2000) noted near racemic α-HCH (EFs = approximately 0.52) in blubber of ringed seals but non-racemic values in liver (EFs = approximately 0.6). This phenomenon was observed with other chiral pollutants, such as *trans*-chlordane, but in some cases, the EF was greater in blubber (Wiberg *et al.,* 2000). Wiberg *et al.* (1998) attributed this difference to greater metabolic activity in the liver as compared to the blubber. This would imply that the proportion of the α-HCH body burden that is transformed is small, and consequently, the EF in ringed seal blubber is closer to that in the diet than in the liver. This is not always the case, since EFs of many chiral OCs in ringed seal blubber have been found that do not match their main prey item, Arctic cod (Wiberg *et al.*, 2000; Moisey *et al.*, 2001). In seabirds, which do not retain as large a reserve of fat as found in ringed seals, there were no differences in EFs of chiral chlordanes between liver and fat (Fisk *et al.,* 2001b). Differences in EFs of chiral pollutants between tissues of seals, and potentially other marine mammals, require further study.

Harbour and grey seals from Iceland showed an α-HCH ER >1 (Klobes *et al.*, 1998a). The ER of CB149 was comparable in the two species, but for oxychlordane, ER < 1 was observed in harbour seals, while the oxychlordane ER in grey seals was >1. The differing ER for oxychlordane was consistent with results for blubber from two harbour seals from the German North Sea coast (König *et al.*, 1994) and a Baltic Sea grey seal (Müller and Buser, 1994). An excess of (+) α-HCH (EFs = 0.58) was found in the blubber of harbour and grey seals, although no data were provided for their food.

EFs of chiral contaminants and stable isotopes of nitrogen (δ^{15}N) and carbon (δ^{13}C) were measured along with OCs in ringed seals collected from the east and west side of the Northwater Polynya in northern Baffin Bay (Fisk *et al.*, 2002d). *Cis*- and *trans*-chlordane, oxychlordane, and heptachlor epoxide were all non-racemic in the ringed seal blubber but did not vary with age, sex or collection site. α-HCH appeared racemic (EF = 0.50 ± 0.01) in the seals, although this EF is different from those previously observed in their prey species, and was found to vary significantly with age. An overall food web assessment of α-HCH in the Northwater Polynya, which included the ringed seal data of the study by Fisk *et al.* (2002d), concluded that ringed seals do not metabolize α-HCH efficiently (Moisey *et al.,* 2001). EF values in the ringed seals varied considerably from other Arctic marine mammals and seabirds, providing additional evidence that the type(s) and characteristic(s) of the enzymes involved in biotransformation of chiral OCs vary between these organisms.

4.4.6.4. Persistent OCs in other pinniped and cetacean tissues

Compared to blubber, fewer analyses of brain, liver, kidney, muscle, and blood have been made in pinnipeds and cetaceans. However, in all these tissues, OC concentrations are generally lower than in blubber because of their lower lipid content. Low ng/g ww levels of PCBs and OC pesticides were found in liver, kidney, and muscle from ringed seals sampled from Greenland (Muir and Johansen, 2001) and in blood sampled from ringed and bearded seals from Svalbard, Norway, and Alaskan northern fur seals (Bang *et al.*, 2001; Beckmen, 2002) (Annex Table 12). Similarly, low ng/g ww levels of PCBs and OC pesticides were found in brain, liver, and muscle from beluga from Hendrickson Island in the western Canadian Arctic (Metcalfe *et al.*, 1999) and in bowhead whales from the Bering-Chukchi-Beaufort Seas (Hoekstra *et al.*, 2002c) (Annex Table 13). When lipid concentrations were compared to wet weight concentrations of OCs in brain, liver, kidney, and muscle from grey whales sampled from the Chirikov Basin of the Russian Bering Sea, lipid levels were significantly correlated to ΣPCBs, ΣDDTs, ΣCHLs, and HCB (Krahn *et al.*, 2001; Tilbury *et al.*, 2002). This relationship is consistent with a study by Aguilar and Borrell (1985) reporting that lipid content is an important factor in controlling accumulation of lipophilic OCs in marine mammals. In both beluga and grey whales, concentrations of OCs in these tissues, with the exception of brain, were generally more comparable when the values were calculated on a lipid weight rather than on a wet weight basis (Krahn *et al.*, 2001; Tilbury *et al.*, 2002).

In brain tissue, total lipid-normalized concentrations were significantly lower than in all other tissues. This is in agreement with previous reports that the blood–brain barrier controls the transport of certain contaminants to brain tissue (Norton, 1980). Beluga brain samples could be distinguished from other tissues by differences in PCB congener patterns and higher concentrations of ΣHCHs (primarily α-HCH), as was reported in an earlier study for northern fur seals and harbour porpoises (Mössner *et al.*, 1992). In addition, the lipids in the brain of marine mammals consist of high proportions of polar lipids (i.e. phospholipids and cholesterol) (Fukushima and Kawai, 1980; Aguilar and Borrell, 1985; Tilbury *et al.*, 1997) that have a lower affinity for OCs than neutral lipids. Thus, the greater proportion of neutral lipids (i.e. triglycerides and non-esterified fatty acids) found in tissues other than the brain favors the accumulation of OC compounds in these tissues (Kawai *et al.*, 1988). These variations in patterns of POPs in the different tissues may also be influenced by differences in contaminant metabolism or the degree of blood perfusion in the various tissues (Kiceniuk *et al.*, 1997; Jenssen *et al.*, 1996; Metcalfe *et al.*, 1999). The need for caution in interpreting OC concentration data from different tissues is

further demonstrated by findings reported for a study examining how concentrations of OCs in blood and blubber vary with nutritional condition in captive and wild, fasting ringed seals (Lydersen *et al.*, 2002). The study demonstrated that extreme variability occurs in the concentrations of OCs in seal blood in response to change in body condition as a result of fasting, and that the responses of blubber OC concentrations are also very different compared to those in blood. The authors concluded by recommending that, since the natural variation in body condition is extreme during annual cycles of phocid seals, blood should not be used in studies of OCs, where the aim of the study is to monitor OC levels for comparative purposes or time-trend analyses.

4.4.6.5. Effects of age and sex on OC levels in pinnipeds and cetaceans

As mentioned previously, age and sex are important factors that must be taken into account to ensure accurate comparisons of contaminant levels in pinnipeds and cetaceans. Results of recent studies are consistent with previously recorded trends showing that most OCs occur at lower levels in juveniles than adults, and lower in adult females than in adult males (Krahn *et al.*, 1997; Wade *et al.*, 1997; Kleivane and Skaare, 1998; Severinsen *et al.*, 2000; Bang *et al.*, 2001; Ylitalo *et al.*, 2001; Fisk *et al.* 2002d; Hoekstra *et al.*, 2002c; Krahn *et al.*, 2001). PCB and OC pesticide concentrations also increase with age in males, and may either decrease, remain relatively constant or increase with age in females, although in the latter case, generally at a slower rate than in males (Wolkers *et al.*, 1998b; Muir *et al.*, 2000b; Fisk *et al.*, 2002d; Hoekstra *et al.*, 2002c). Lower levels of contaminants in females are normally primarily attributable to the transfer of compounds to offspring during gestation and lactation. Whether or not females experience age-related changes in contaminant levels is variable, and regardless of the rate of change, this age–concentration relationship likely depends largely on their level of contaminant exposure, as well as how often they successfully produce and wean offspring. Nonetheless, it is important to remember that age- and sex-related trends in contaminant concentrations may vary both within and between species, depending on the compound being examined.

Concentrations of ΣPCBs, ΣDDTs, and ΣCHL compounds often increase with age in marine mammals. This was the case in both sexes of ringed seals from the northern Baffin Bay region (Fisk *et al.*, 2002d), and in male, but not female, ringed seals from Alaska (Kucklick and Krahn, 2002), as well as those in a circumpolar study that statistically examined ringed seal data from the previous AMAP assessment (Muir *et al.*, 2000b). The significant relationships observed in the female ringed seals from northern Baffin Bay are likely due to the inclusion of very old female seals (>40 years) that have probably stopped reproducing (Fisk *et al.*, 2002d). Wolkers *et al.* (1998b) found PCBs increased with age in Svalbard ringed seals, but that sex was not an important variable, and suggested that in the Svalbard seals, continued feeding by females during lactation may compensate for loss of OCs during lactation. The authors also
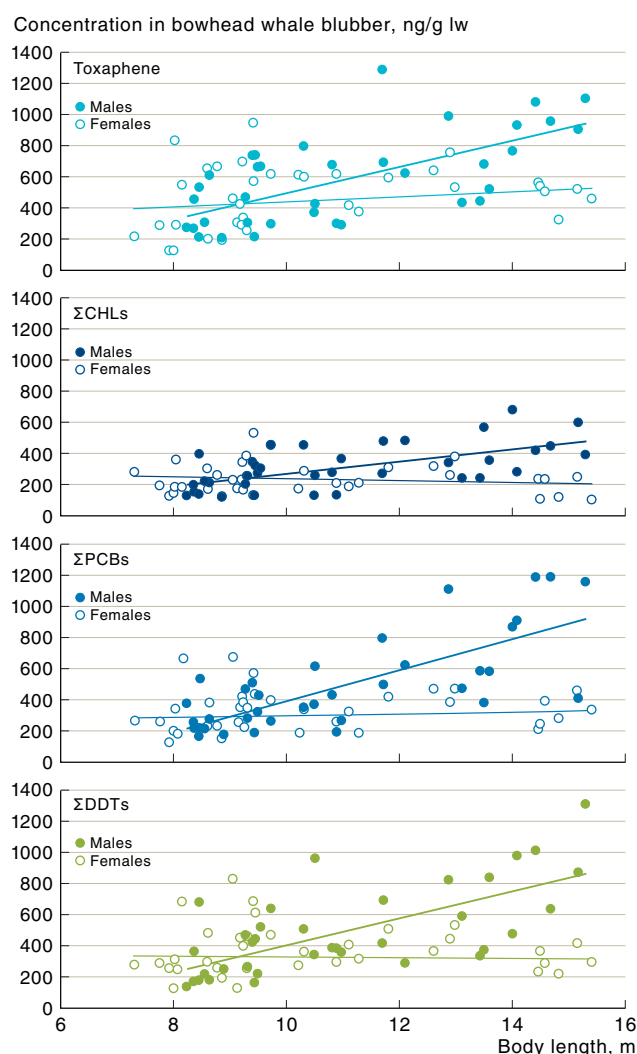

Figure 4·52. Body length versus ΣOC concentrations in blubber samples from male and female bowhead whales. Significant relationships between increasing body length and ΣOC concentrations (p < 0.05 for all comparisons) were found for male bowhead whales (Toxaphene, $r^2 = 0.44$; ΣCHLs, $r^2 = 0.38$; ΣPCBs, $r^2 = 0.56$; ΣDDTs, $r^2 = 0.45$). Source: Hoekstra *et al.*, 2002c.

found no difference in PCB congener pattern, relative to CB153, between the sexes in adults, while juveniles showed significantly higher relative concentrations of the lower chlorinated PCBs (28, 52, 74, 99, 101, and 118) and lower relative concentrations of the higher chlorinated PCBs (170 and 180) as compared to the adults (Wolkers *et al.*, 1998b).

In male Alaskan bowhead whales, levels of ΣPCBs, ΣDDTs, ΣCHLs, and toxaphene significantly increased with body length, and thus presumably with age (Figure 4·52) (Hoekstra *et al.*, 2002c). In female bowheads, this relationship applied until they reached approximately 13 m in length, while those longer than 13 m had generally lower concentrations of these compounds than shorter, younger females. Similar decreasing OC concentrations with age occurred in female belugas from Point Lay, Alaska (Wade *et al.*, 1997). However, in contrast to this, concentrations of ΣHCHs and HCB or ΣCBz often do not show sex- or age-related differences in pinnipeds and cetaceans. For example, no sex-related differences were observed for HCB or dieldrin concentrations in Alaskan ringed seals of comparable ages (Kucklick and Krahn, 2002), or for ΣCBz and ΣHCHs in seals from the

Nunavut region (Fisk *et al*., 2002d). Similarly, ΣHCH and ΣCBz or HCB levels were independent of age and sex in Alaskan bowhead whales and Barents Sea minke whales (Kleivane and Skaare, 1998; O'Hara *et al*., 1999; Hoekstra *et al*., 2002c). Notably, much lower levels of OCs occurred in reproductive female Alaskan killer whales than sexually immature whales or mature male animals of the same age class (Ylitalo *et al*., 2001), and a single beluga fetus from Point Lay, Alaska, had about 10% higher concentrations for all OCs compared to its mother (Wade *et al*., 1997).

Recruitment order (birth order) can also influence the concentrations of OCs in pinnipeds and cetaceans. For example, in northern fur seals from St. George Island, Alaska, pups of young (presumably primiparous) dams had significantly elevated levels of PCBs in their blood as compared with pups of older (multiparous) dams (Beckmen *et al*., 1999). Similarly, in adult male resident Alaskan killer whales, first-recruit whales contained much higher OC concentrations than those measured in non-first-recruited (e.g., second-recruited, third-recruited) resident animals from the same age group (Ylitalo *et al*., 2001).

Faroe Islands study
A recent study in the Faroe Islands examined the relationship between OC concentrations and length in pilot whales (1997), white-sided dolphins (*Lagenorhynchus acutus*) (1997), and grey seals (1993-1995) (Dam, 2001). The following comparisons of the OC concentrations in the three species are based on females because they maintain constant OC concentrations that are not dependent on age, and because there were a greater number of females to sample, especially in pilot whale pods. Overall, the single OC occurring at the highest concentration was *p,p'*-DDE, which was found at 10 800 ng/g lw in the juvenile females of one pod of pilot whales, with decreasing concentrations among juveniles in the other pilot whale pod, followed by white-sided dolphins and grey seals. The OCs occurring in the next highest concentration were Parlar 50 (a component of toxaphene) at 3900 ng/g lw and CB 153 at 3600 ng/g lw in the same group of juvenile pilot whales that had the highest *p,p'*-DDE concentrations. *p,p'*-DDT and *trans*-nonachlor were both found at similar concentrations in the odontocete juveniles, but were markedly lower in grey seals.

When comparing the juvenile and adult female grey seals, white-sided dolphins, and pilot whales, it appeared that the difference in OC burden between the two age groups was highest for white-sided dolphins and lowest for grey seals. This could be a consequence of different criteria used to sort individuals into the age groups for each species. Only grey seals were sorted based on actual inspection of reproductive state, and the odontocetes were sorted according to body length. The difference between ΣPCBs in the juvenile and adult white-sided dolphins was less than the average seen for the other OCs. Some of the chlordanes and β-HCH exhibited a similar pattern. This generally occurred for the two other species. The OC with greatest difference amongst the two age groups was oxychlordane, which occurred at an exceptionally low concentration (27 ng/g lw) in adult female white-sided dolphins. Similarly, the

mean value for sum toxaphene for the adult female white-sided dolphins was only one tenth that of the juveniles (Parlar 50 at 1872 ng/g lw, n = 7 juveniles).

4.4.7. Polar bear

Polar bears (*Ursus maritimus*) are widely distributed throughout the Arctic, including some subarctic regions, and range over large areas in search of food. They move south with the ice in the autumn and winter and then north as the pack ice melts in the spring and summer. These seasonal movements of the sea ice also influence the distribution and concentration of their primary prey, ringed and bearded seals (Stirling *et al*., 1982; Kingsley *et al*., 1985). Polar bears are top Arctic predators, and often eat only the blubber from a seal (Stirling and McEwan, 1975), where the highest concentrations of OCs are found. Polar bears have superior biotransformation capacity and have high levels of OC metabolites.

OC levels in polar bears were covered extensively in the previous AMAP assessment (de March *et al*., 1998) with good spatial coverage. Much like other marine mammals, OCs in polar bears were found to be generally highest in the European and lower in the North American Arctic (de March *et al*., 1998). Some spatial trends were also observed within the Canadian Arctic (Norstrom *et al*., 1998).

Since the first AMAP assessment, monitoring of OCs in polar bears has continued in western Hudson Bay (Norstrom 2000; 2001), Alaska, Svalbard, and Greenland. There have also been studies on OC levels in polar bear plasma from the Russian Arctic (Andersen *et al*., 2001b; Lie *et al*., 2003). Temporal-trend studies have been carried out in western Hudson Bay and Svalbard polar bears and are discussed in detail in Section 5.4.5.2.

Alaska polar bears
Although elevated OC concentrations have been documented in Canadian, eastern Greenland and Norwegian polar bear populations, relatively little information is available for populations in Alaska. Lentfer (1976) documented elevated OC concentrations in polar bears prior to the major oil and gas development on the North Slope. Data collected through satellite telemetry indicate that there are two distinct polar bear population stocks in Alaska: one in the southern Beaufort Sea and the other in the Chukchi/Bering Seas (Amstrup, 1995), with an area of overlap from Point Barrow to Point Hope. Differences in the feeding ecology of polar bears between the Beaufort and the Chukchi/Bering Seas may affect OC concentrations found in the two stocks. Specifically, polar bears in the Chukchi/Bering Seas feed more heavily on Pacific walrus carcasses.

Levels of ΣPCB, ΣDDT, ΣCHL, and ΣHCH determined in adult male polar bears sampled from the Barrow and St. Lawrence Island regions of Alaska between 1996 and 1998 (Krahn *et al*., 2002), were consistent with levels in adult males from the southern Beaufort Sea population in northern Alaska and the Chukchi/Bering Sea population in western Alaska (Evans, 2001) around the same time (Annex Table 14). These data provide an important addition to contaminant level data in Alaska. Levels of PCBs in these Alaskan bears are relatively low compared to levels found in polar bears in
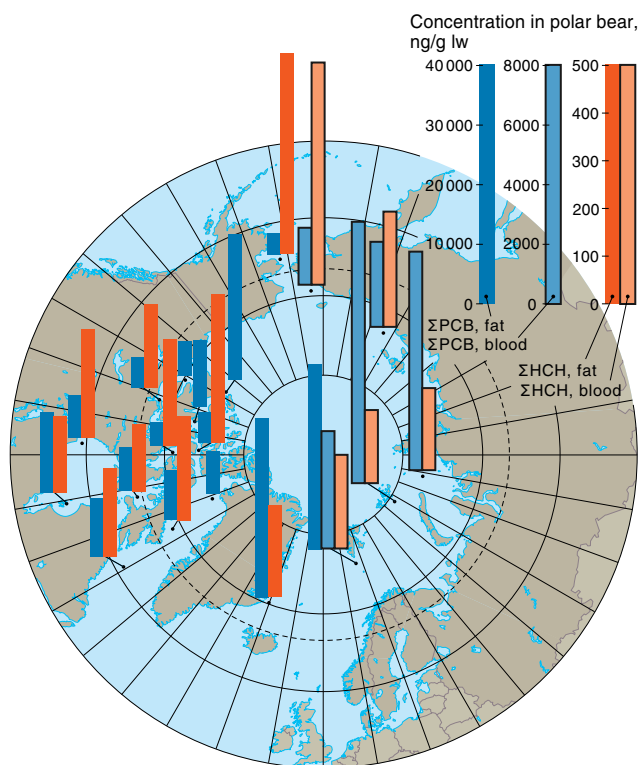
Figure 4·53. Concentrations (of ΣPCBs and ΣHCHs in blood from adult female polar bears (age 5-28 yr) from Svalbard and the Russian Arctic (Andersen *et al.* 2001b), and in fat from polar bears (adjusted to levels expected in 11-year-old males after correction for age and sex) from the Bering Sea, Canada, eastern Greenland, and Svalbard (de March *et al.*, 1998). At Svalbard, lipid-weight PCB concentrations measured in fat are approximately five times higher than in blood from the same animals. Assuming that this relationship is the same in other areas, high fat PCB concentrations can be expected in bears in the Russian Arctic.

eastern Hudson Bay, Canada, eastern Greenland, and Svalbard, Norway (Figure 4·53). ΣPCB levels for males from Alaska were higher than those reported by Norstrom *et al.* (1998) for three bears taken west of Barrow, Alaska. Significantly higher levels of ΣPCBs were found in bears from the southern Beaufort Sea population than in the Chukchi/Bering Seas population. Average ΣHCH levels in bears sampled by Evans (2001) (Annex Table 14) are among the highest levels reported in the Arctic, and were similar to the high levels reported for the Chukchi and Bering Seas by Norstrom *et al.* (1998). There were no significant differences between ΣHCH levels in the Chukchi/Bering Seas and southern Beaufort Sea populations. β-HCH, the most persistent HCH isomer, constituted about 93% of ΣHCHs. Although α-HCH contributed only a small fraction of the ΣHCHs in fat, unlike β-HCH, it occurred in significantly greater concentrations in bears from the southern Beaufort Sea region. The chlordane compounds in these bears were the next most abundant compounds, and although, the levels were not significantly different between the two populations (p<0.07), there was a trend suggesting higher levels in the southern Beaufort Sea population.

Greenland polar bears
OC levels were recently determined in the fat of Greenland polar bears collected in 1999/2000 (Sonne-Hansen, 2002; Dietz *et al.*, 2003) (Annex Table 14). These bears ranged in age from two to ten years. As observed in

other polar bears, ΣPCBs dominated the OC loads with concentrations that were an order of magnitude greater than any other OC group. Concentrations of OCs were greater in the males except for chlordanes, which have been observed in polar bears from other regions (Norstrom *et al.* 1998). Concentrations of ΣPCBs were much lower than previously reported for East Greenland bears whilst levels of DDE were within the range previously reported (see Section 5.4.5).

Iceland polar bears
Although polar bears are not naturally occurring in Iceland, they do appear occasionally on drifting pack ice. Klobes *et al.* (1998b) analyzed PCB and OC pesticide levels in the adipose tissue and liver of one such polar bear. They found distinctly different contaminant profiles in the two tissues, where the liver had patterns similar to those found in the Icelandic Arctic fox, with oxychlordane as the predominant compound. In the adipose tissue, CB 153 predominated, followed by C180 and oxychlordane. Oxychlordane and *p,p'*-DDD were the only compounds found to be more abundant in liver than in adipose tissue, and toxaphene Parlars 26 and 50 were present in the adipose, but not the liver tissue. The sum concentration of Parlars 26 and 50 found in adipose tissue was within the range of the levels of toxaphene Parlars (26, 52, and 62) quantified in the adipose tissue of polar bears from Svalbard in an earlier study (Bernhoft *et al.*, 1997). Due to the high levels of oxychlordane relative to PCBs, the authors concluded that it was likely that the bear originated from Greenland, not Svalbard.

OCs in Norwegian and Russian polar bear plasma
Geographical variations in PCB (Andersen *et al.*, 2001b) and OC pesticide concentrations (Lie *et al.*, 2003) were studied in blood samples from ninety adult female polar bears from Svalbard, Franz Josef Land, Kara Sea, East Siberian Sea and Chukchi Sea, between 1987 and 1995 (Annex Table 14). Regional differences in levels and patterns of PCBs, oxychlordane, *trans*-nonachlor, α-HCH, β-HCH, and *p,p'*-DDE were found. Bears from Franz Josef Land and the Kara Sea had similar ΣPCB levels and these were higher than all other populations (Figure 4·53). Svalbard polar bear PCB levels were similar to those from the East Siberian Sea, but higher than those from the Chukchi Sea. Svalbard polar bears had relatively lower proportions of CB99 and higher proportions of CB194 than bears from other regions. Bears from Franz Josef Land had higher proportions of CB180, but lower CB153 levels compared to all other regions. Of the PCB congeners investigated by Andersen *et al.* (2001b), the lower chlorinated CBs increased, and the higher chlorinated CBs decreased from Svalbard eastward to the Chukchi Sea. In all regions, oxychlordane was the dominant OC pesticide, and the highest levels of oxychlordane, *trans*-nonachlor, and DDE were found in bears from Franz Josef Land and the Kara Sea. Polar bears from the Chukchi Sea had the highest levels of α- and β-HCH. The lowest α-HCH concentration was found in bears from the Kara Sea and was lower than in bears from all the other circumpolar regions. In all the bears, ΣHCHs was dominated by β-HCH. HCB levels did not differ between regions.

Results from Andersen *et al.* (2001b) and Lie *et al.* (2003) combined with earlier findings (Bernhoft *et al.*,

1997; Norstrom *et al.*, 1998), indicate that polar bears from Franz Josef Land and the Kara Sea have the highest ΣPCB, ΣCHL and ΣDDT levels in the Arctic. Decreasing trends were seen eastward and westward from these regions, and may imply the presence of significant pollution sources in the Russian Arctic area. Regional differences in pollution sources, contaminant transport, and prey preferences could also explain the variation in PCB and OC pesticide levels and patterns between regions.

Ringed seals are assumed to be the most important and common prey of polar bears. However, Kleivane *et al.* (2000) found an unexpectedly high number of bears on the ice east of Svalbard feeding on harp seals in June 1995. Significantly higher OC concentrations were found in blubber samples from adult male harp seals from this area during their June 1995 molt (when they fast and live off their blubber), as compared to ringed seals sampled at the same time, which marks the very beginning of their molting season (Kleivane *et al.*, 2000). Significant species-specific differences were, however, detected only for ΣHCHs and HCB, while differences in ΣPCBs, ΣDDTs, and ΣCHLs were ascribed to age, xiphosternal blubber thickness, and possible differences in xenobiotic metabolizing capacity (Boon *et al.*, 1992; Wolkers *et al.*, 1999). These results indicate that it is not necessarily the species, but the time, availability, and biological condition of polar bear prey that may play a major role in the biomagnification of OCs at the top of the Arctic ecosystem (Kleivane *et al.*, 2000).

OCs in Canadian polar bear plasma

Concentrations of OCs were determined in the plasma of Resolute Bay polar bears (Norstrom, 2000; Sandau, 2000) (Annex Table 14). This work also included plasma samples from Svalbard polar bears. ΣCHLs and ΣPCBs were the dominant OC groups found in the plasma of polar bears from both regions. OC concentrations were two times higher in subadults than adults except for ΣDDT concentrations, which were similar. These results were in line with previous findings in polar bear adipose tissue. The exceptions were chlordanes, which were 30-60% lower in males, but concentrations were similar comparing the same sex in both areas. ΣPCB concentrations were similar in males and females from both areas, and two to three times higher in the Svalbard bears, in line with previous analyses of adipose tissue from these areas (Norstrom, *et al.* 1998).

Influence of age and sex on OC levels in polar bears

The effects of age and sex are also important considerations with respect to PCBs and OC pesticides in polar bears. In 1995, Norstrom (1999a) examined concentrations of OCs in male and female polar bears from Hudson Bay to test the effect of sex over a single year. Concentrations of OCs in males were similar to those in females; however, there was a (generally non-significant) tendency for most residues to be lower in males, except PCBs and DDTs, which were slightly higher in males. The difference in PCBs between males and females was not as large as observed in more extensive data sets. Norstrom *et al.* (1998) showed that males had 40% higher ΣPCB concentrations than females on average. Younger male bears have ΣPCB concentrations closer to those in females, which may explain the similarity be-

tween males and females in 1995. Males had 30% lower levels of chlordanes than females, which is the same as that found by Norstrom *et al.* (1998). Polischuk *et al.* (2002) showed that males are capable of metabolizing chlordanes during a seasonal fast, while females are not. The enhanced metabolic capability of males therefore, explains the lower levels of chlordanes and possibly some of the other compound groups in males. Lower levels of ΣPCBs and lack of an age effect in females are presumed to be due to the additional losses from lactation.

Influence of reproduction on OC levels in polar bears

To study the effect of fasting, gestation and lactation on toxicokinetics, POP concentrations were determined in adipose tissue, plasma, and milk samples from seven female polar bears and their cubs near Cape Churchill, Hudson Bay, between 1992 and 1996 (Polischuk, 1999; Norstrom, 2000). Pregnant females were captured from August 7 to October 7, and the same females with cubs were captured from March 2 to March 17 of the following year before they had moved onto the ice to begin hunting seals. All females had therefore been fasting five to seven months by the time of their second capture. Body composition of females was determined from ^{2}H dilution in blood, and body weight. The total body mass of females declined by $43 \pm 5\%$, and total fat mass declined by $42 \pm 3\%$. The proportion of mass lost as fat, ranged between 55 and 66%.

During gestation and early lactation, the mean concentrations of ΣPCBs, ΣCHLs, and ΣCBz in female adipose tissue increased significantly by 2096 ± 1292 ng/g ww, 1600 ± 1349 ng/g ww, and 49 ± 23 ng/g ww, respectively. Adipose tissue concentrations of ΣDDT declined by 91 ± 82 ng/g ww, while concentrations of ΣHCH remained the same. Despite these increases in concentration, POP body burdens in female polar bears declined during gestation and the early lactation period due to loss of fat mass (Figure 4·54). In descending order, the mean proportional decrease in body burdens was
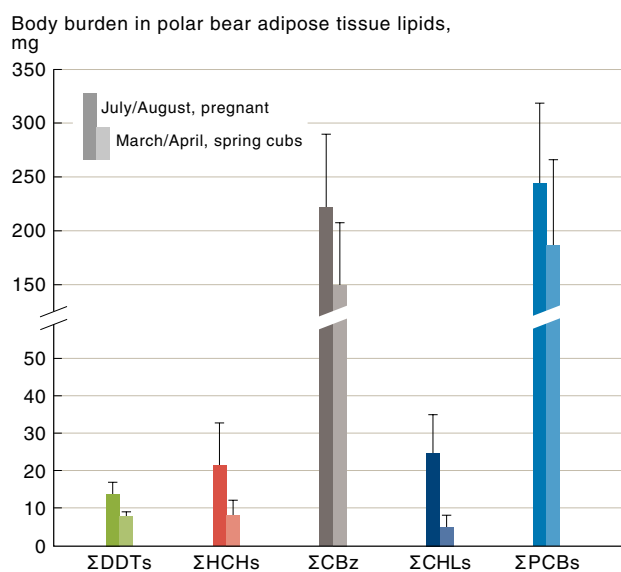
Body burden in polar bear adipose tissue lipids, mg

Figure 4·54. Mean (± SD) body burden (mg) of major POPs in adipose tissue lipids of polar bear females on land, in the summer (pregnant) and the following March (with cubs-of-the-year, COYs) in the Cape Churchill area, Hudson Bay (1992-1996). In all cases, the difference in body burden between the two periods was statistically significant.
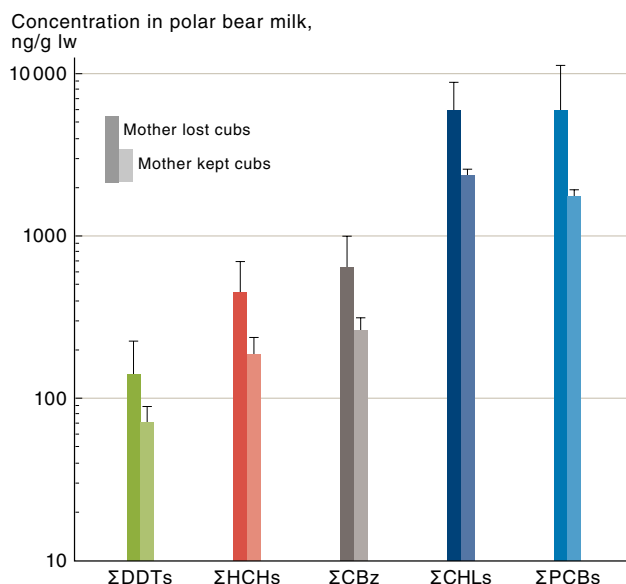
Concentration in polar bear milk,
ng/g lw

Figure 4·55. Mean (± SD) concentrations of major POPs in milk of female polar bear with cubs, after emerging in March from dens in the Cape Churchill area, Hudson Bay (1992-1996). The data are grouped according to whether the female still had her cubs the following fall, or had lost them. In all cases, the difference in concentrations between the two groups was statistically significant.

ΣDDTs (75±8%) > ΣHCHs (61±8%) > ΣCBz (45±12%) > ΣCHLs (29±20%) ≈ ΣPCB (24±16%), while the mean mass of POPs lost was ΣCHLs (71±57 mg) > ΣPCBs (56±34 mg) > ΣDDTs (20±8 mg) > ΣHCHs (14±7 mg) > ΣCBz (7±2 mg). Biotransformation during gestation and lactation probably accounts for the greater proportional decrease in ΣCBz, ΣHCHs, and ΣDDTs compared to ΣPCBs and ΣCHLs.

The mean period between first and second capture (mostly in their dens) was 188±22 days, and the mean number of days of lactation prior to sampling was approximately 79±4 days. It is likely that the toxicokinetics of OCs during the first 100 days were similar to that during the subsequent summer fast. The polar bear cub weighs only about 0.7 kg at birth (I. Stirling, pers. comm., Canadian Wildlife Service, Environment Canada, Edmonton AB) and two newborn cubs represent about 0.4% of the mother's weight. Therefore OC transfer to the fetus is unlikely to be a significant part of the mother's body burden. Thus, most of the 24-29% loss of body burdens of the poorly biotransformed ΣCHLs and ΣPCBs from the mother during the 188-day fast must have been transferred to the cub in milk during the 79-day lactation period prior to capture, at which time the cubs weighed 12.7 ± 0.9 kg. However, on average, only about 25-50% of this body-burden loss could be accounted for by ΣCHL and ΣPCB burdens in the cubs. Furthermore, a crude estimate of lactational transfer based on cub growth rates could only account for half of the body-burden loss from the females. These discrepancies are difficult to reconcile and require further study.

Mothers that were recaptured in the autumn without cubs had higher OC concentrations in their milk when emerging from their dens in spring. By comparison, mothers recaptured in the autumn and still accompanied by cubs had lower OC concentrations in their milk the previous spring (Figure 4·55). The differences in concentrations were significant for all residue classes. For example, PCBs were approximately three times higher

(5780 ng/g lw) in females that lost their cubs than in females that kept their cubs (1830 ng/g lw). It is not known how much significance can be attached to this finding in terms of reproductive performance, but it is suggestive, at least, that cub survival may be dependent on the degree of exposure to OCs in milk.

In a study on Svalbard, 35 mother/cub pairs were sampled during late March to mid-May in 1995-1998 (Lie *et al.*, 2000). Blood plasma samples were analyzed for six CBs (99, 118, 153, 156, 180, and 194), which make up 78% of total PCB concentrations in polar bears based on 28 congeners. Samples were grouped according to age and reproductive status: cubs (cubs-of-the-year); yearlings; females with cubs; and, females with yearlings. Geometric mean ΣPCB concentrations in plasma were 12 300 ng/g lw in cubs, 5820 ng/g lw in females with cubs, 6820 ng/g lw in yearlings, and 2945 ng/g lw in females with yearlings (Annex Table 14, Figure 4·56). Cub ΣPCB concentrations were significantly higher than the other three groups, and ΣPCB concentrations in fe-
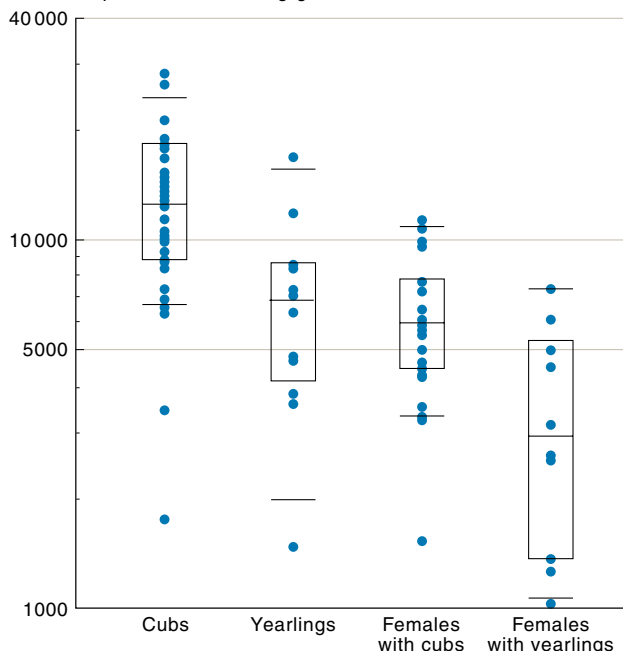
ΣPCBs in polar bear blood, ng/g lw

Figure 4·56. ΣPCB concentrations in blood plasma of polar bears: cubs (three to four months old), yearlings, females with cubs, and females with yearlings (Lie *et al.*, 2000). Dots represent individual values.

males with yearlings were significantly lower than the other three groups ($p < 0.05$).

The ΣPCB concentrations found in the adult bears and yearlings were comparable to those found in earlier studies on Svalbard (Bernhoft *et al.*, 1997; 2000). No previous studies of 3-4 month old cubs on Svalbard have been done. The results show that cubs and yearlings have higher ΣPCB concentrations than their mothers, probably due to lactational transfer. This has also been seen previously in Canadian polar bears (Polischuk *et al.*, 1995; Polischuk, 1999). Cub survival in the Svalbard population is lower than in other populations, and the high ΣPCB concentrations found in cubs compared to older bears could be a possible explanation. There may be other causes, however, such as high population density.

Tissue distributions of OCs in female polar bears

In the vicinity of Cape Churchill, Hudson Bay, between 1992-1996, distribution of POPs in plasma relative to adipose tissue was determined in the following stages: pregnant females in the summer at the beginning of the on-land fast; females with cubs emerging from the den; females with cubs in summer; and, females with cubs after 1-2 months fasting (Polischuk, 1999; Norstrom, 2000). At all of these stages, the ratio of concentrations of ΣCHLs and ΣPCBs in whole plasma to adipose tissue lipids was the same as the fraction of lipids determined in plasma, 0.01. That is, these POPs were equally distributed in adipose and plasma lipids. Plasma : adipose tissue ratios of ΣCBz in pregnant females in summer and in females the following spring with cubs, and ΣHCHs in pregnant females were also distributed according to lipid content. The plasma : adipose tissue ratios of ΣCBz and ΣHCHs were two to three times higher in plasma of females with cubs in the summer and autumn than predicted by lipid content, suggesting that components of the plasma other than extractable lipids were responsible for some of the carrying capacity of plasma at these times. The plasma : adipose tissue ratio of ΣDDT was close to two times that of the lipid fraction in female plasma at all times. This is probably indicative of binding to proteins in plasma, as well as lipids. There was no indication that physical-chemical properties, such as water solubility or log K_{ow}, were governing the partitioning of POPs between plasma and adipose tissue.

Ratios of POP concentrations in milk lipids : female adipose tissue lipids were determined in spring, summer and autumn. The ratio was greatest for ΣHCHs and lowest for ΣDDTs and ΣPCBs. On a lipid weight basis, the ratio ranged from close to 1 : 1 for ΣPCBs and ΣCHLs to approximately 2 : 1 for ΣCBz and ΣHCHs, indicating that milk lipids were not at equilibrium with adipose tissue lipids for these compounds. The milk : adipose ratios for ΣCBz were significantly greater than ΣCHLs, ΣDDTs, and ΣPCBs. Similarly, ratios for ΣCHLs were significantly greater than ΣDDTs and ΣPCBs.

The ranking of the milk : adipose ratios for the chemical groups was similar to that of the K_{ow}s for the chemicals (Hawker and Connell, 1988; Mackay *et al.*, 1992), unlike what was seen for plasma. Since it is improbable that concentrations in extractable milk lipids would be higher than those in adipose tissue on a thermodynamic basis, low K_{ow} OCs must partition from adipose tissue to constituents of milk other than extractable lipids, such as lipoproteins.

Effect of seasonal fasting on whole-body toxicokinetics in Hudson Bay polar bears

POP concentrations were determined in adipose tissue from 47 fasting polar bears in the Cape Churchill area of western Hudson Bay during the summer to autumn of 1992-1995 (Polischuk, 1999; Norstrom, 2000). Body burdens (mg/animal) were also determined based on body composition determined from ^{2}H dilution in blood and body weight. Adipose tissue, milk, and blood samples were taken when the bears came on land in July/August. The same bears were recaptured and sampled in September/October (47-68 days apart) during the fasting period. Five categories of bears were defined: cubs-of-the-year (COYs); yearlings (YRLGs); females with COYs

(Fem/COYs); females with yearlings (Fem/YRLG); and, males. There were no single females sampled.

Concentrations of ΣCBz, ΣCHLs, and ΣPCBs in adipose tissue lipid increased, and concentrations of ΣDDTs decreased in all bears during the 47-68 day fast. The changes in concentration of ΣCHLs and ΣPCBs in adults were mostly significant. In COYs, the concentrations of ΣCHLs and ΣPCBs increased 30%, while those of ΣHCHs and ΣDDTs decreased by 20% and 34%, respectively, during the fasting period. Increases in concentration in adipose tissue in adults were entirely due to utilization of lipids by the bears. Most of the increases in concentration in COYs were due to decreased adipose tissue, not uptake from nursing. The body burden of ΣCHLs and ΣPCBs in females with COYs did not decrease during fasting. Taken together, these data suggest that the COYs were nursing very little during the 47-68 day period.

Biotransformation of *p,p'*-DDE and HCHs occurred in all bears during the fast, as did biotransformation of oxychlordane and some other chlordane compounds in adult males. Chlorobenzenes, oxychlordane (except males), and the major PCB congeners (CBs 60, 99, 138, 153, 156, 170, 180, and 194) were not metabolized or cleared by any other mechanism at a measurable rate over 47-68 days of fasting.

In males, no age-related increases were found in concentrations of the compounds with slow biotransformation rates during fasting, except highly chlorinated PCBs (CBs 180 and 194). That is, average annual rate of intake and excretion of the POPs are balanced. Clearance of all POPs by a mechanism other than biotransformation is, therefore, occurring for at least part of the year. For most of the POPs, there was no significant difference in concentrations or trends in males and females. Therefore, lactation is not governing the rate of excretion in females, except perhaps for octa- and nonachlorinated PCBs. The only clearance mechanism for slowly biotransformed POPs that remains available to both sexes, is partitioning to gut contents and excretion in feces during periods when they are feeding.

Toxicokinetics of POPs in polar bears are therefore likely to be variable with season, sex/reproductive status, and area. Slowly biotransformed PCBs, oxychlordane (except in adult males), and chlorobenzenes will be taken up and excreted in feces only during periods of active feeding. On the other hand, oxychlordane in males and HCHs and *p,p'*-DDE in all bears are taken up during feeding periods, but biotransformed throughout the year regardless of whether the bear is feeding or not. Due to lack of ice from which to hunt seals during summer and autumn in southwestern Hudson Bay, feeding may be restricted to 7-8 months of the year for males, solitary females and females with cubs or yearlings, and as short as 4 months for pregnant females. In more northerly areas, polar bears (except pregnant females) may not fast at all, if they can remain on the ice to hunt ringed seal or have marine mammal carcasses to scavenge. In this case, uptake and clearance will occur year-round.

4.4.7.1. 'New' chemicals in polar bears

A number of 'new' chemicals have been measured in polar bears. As an apex predator, the polar bear has among the highest levels of POPs and is a logical organism to

utilize when searching for 'new' chemicals. However, the superior biotransformation capacity of polar bears may also reduce levels of some chemicals below detection limits.

Perfluorinated compounds
PFOS has been detected in liver of polar bears from northern Alaska and in blood plasma of ringed seals from Pangnirtung (Nunavut) and Svalbard (Giesy and Kannan, 2001; Kannan *et al.*, 2001a). Other PFAs were detected at lower levels but not reported (Kannan *et al.*, 2001a; K. Kannan, pers. comm.). The levels of PFOS in polar bear liver are in the hundreds of ng/g ww range, suggesting that this compound is one of the most prominent individual organohalogen chemicals in polar bear, when considering levels of PCBs, chlordane, and HCH-related chemicals (Norstrom *et al.*, 1998). Levels in the polar bear were higher than levels found in ringed seals suggesting that PFOS can biomagify (Table 4·9).

PBDEs
Mean ΣPBDE concentrations in polar bears from Svalbard are 17.5 ng/g ww (14-144 ng/g lw), in the same range as minke whales and beluga from the Barents Sea area (Annex Table 17). ΣPBDE concentrations are more than 100 times lower than ΣPCB levels. The congener pattern was dominated by BDE47 and a methoxy-TeBDE (van Bavel *et al.*, 2001). This indicates that polar bears may metabolize PBDEs, and therefore, the concentrations of parent compounds may not give an accurate picture of total exposure. No other data on PBDEs in polar bears could be found in the literature for comparison.

Chiral compounds
ERs of α-HCH and several chlordane compounds were examined in the fat and liver of polar bears and the ringed seals that they preyed on (Wiberg *et al.*, 2000). The authors found that polar bears frequently showed non-racemic (ER ≠ 1) mixtures of most compounds due to enantiomer-specific biotransformation. As (+)-α-HCH was transferred up the food chain from ringed seals to polar bears, it became more abundant relative to (−)-α-HCH. There was no uniform trend for the ER changes in the various chlordane compounds examined. It was also determined that oxychlordane was formed in ringed seals and metabolized by polar bears. In addition, the ERs of some highly recalcitrant chlordanes in polar bear fat showed linear relationships with age (Wiberg *et al.*, 2000).

Metabolites of OCs in polar bears
There have been a number of comprehensive studies on OC metabolite formation, mainly MeSO$_2$- and OH-PCBs, in polar bears (Letcher *et al.*, 1996; Norstrom, 1997; Sandau *et al.*, 2000). Polar bears have superior ability to biotransform OCs. For example, the PCB burden in polar bears is dominated by a small number of congeners, much less than that observed in their major prey item the ringed seal (Muir *et al.*, 1988).

MeSO$_2$-PCB and -*p,p'*-DDE metabolites were examined in the tissues of polar bears shot in 1993 in Resolute Bay (Letcher *et al.*, 1996; Norstrom, 1997). Concentrations of the ΣMeSO$_2$-PCB were highest in liver (3049 ± 1290 ng/g lw) and represented 11% of the concentrations of ΣPCBs. In fat, testes, lung, and brain,

ΣMeSO$_2$-PCB had, respectively, 2, 9, 13, and 60 times lower levels than liver on a lipid weight basis. The major congeners in all tissues were 3- and 4-MeSO$_2$-CB87 and 3- and 4-MeSO$_2$-CB 101. MeSO$_2$-PCB uptake from seal appears to be the most important source of MeSO$_2$-PCBs in bears.

3-MeSO$_2$-*p,p'*-DDE concentrations (303 ± 85 ng/g lw) in liver were nearly half those of DDE and were 126 to 337 times higher than found in testes, adipose, and lung tissues. The highly asymmetric tissue distribution of ΣMeSO$_2$-*p,p'*-DDEs may be due to several factors, such as the liver being the site of its formation or because of its highly selective binding in liver cells. It is not possible to resolve the relative importance of MeSO$_2$-DDE bio-accumulation versus formation in the polar bear based on adipose tissue concentrations.

MeSO$_2$-PCBs are efficiently transferred from polar bear females to cubs via milk, resulting in concentrations that are approximately three times higher in the cubs than their mothers, compared to approximately two times higher for PCBs. 3-MeSO$_2$-*p,p'*-DDE was not preferentially transferred to cubs. Decreased cub survival is emerging as one of the major issues in eco-toxicology of polar bears. It is assumed that PCBs are the cause. However, ΣMeSO$_2$-PCBs are present at 8-10% of ΣPCBs in cubs, and their involvement in possible effects should be considered in any future studies.

Phenolic compounds and neutral POPs were identified and determined in polar bear blood plasma from the Resolute Bay area in the Canadian Arctic and Svalbard (Figure 4·57) (Norstrom, 2000; Sandau *et al.*, 2000). Thirty-five compounds in the phenolic fraction were identified as hydroxy-PCBs (OH-PCBs) in the two polar bear populations. The OH-PCB identity number system follows that of the PCB system with the same chlorine substitution pattern, with addition of the OH-group. Note that the precursor PCBs to the OH-PCBs frequently do not have the same chlorine substitution pattern, since chlorines shift on the ring during metabolism. In addition to OH-PCBs, a previously unidentified phenolic metabolite of OCS, 4-hydroxyheptachlorostyrene (4-OH-HpCS) was identified in polar bear plasma (Sandau *et al.*, 2000). The compound was synthesized, and the binding affinity to human TTR was determined to be about 1.1 times that of T4. Therefore, it is most likely that 4-OH-HpCS is present in polar bear plasma bound to TTR. Traces of pentachlorophenol at approximately 0.2 ng/g ww were also found.

Mean concentrations of ΣOH-PCBs in polar bear plasma ranged from 57 ng/g ww in males from Resolute to 218 ng/g ww in females from Svalbard. Females had significantly higher concentrations of ΣOH-PCBs than males. The ratio of ΣOH-PCBs/ΣPCBs in plasma was also significantly lower in females (mean 1.49) than males (mean 4.08). It appears that females either have a higher binding capacity for OH-PCBs in plasma (i.e. higher TTR concentration) than males, or a higher capacity to form OH-PCBs. The concentration of ΣOH-PCBs was two to three times higher than any other residue class in female polar bear plasma. In the other age groups and males, the concentration of ΣOH-PCBs was equal to, or higher than, the concentration of the next highest residue class, ΣPCBs. The concentration of ΣOH-PCBs in subadults was the same as that in females.
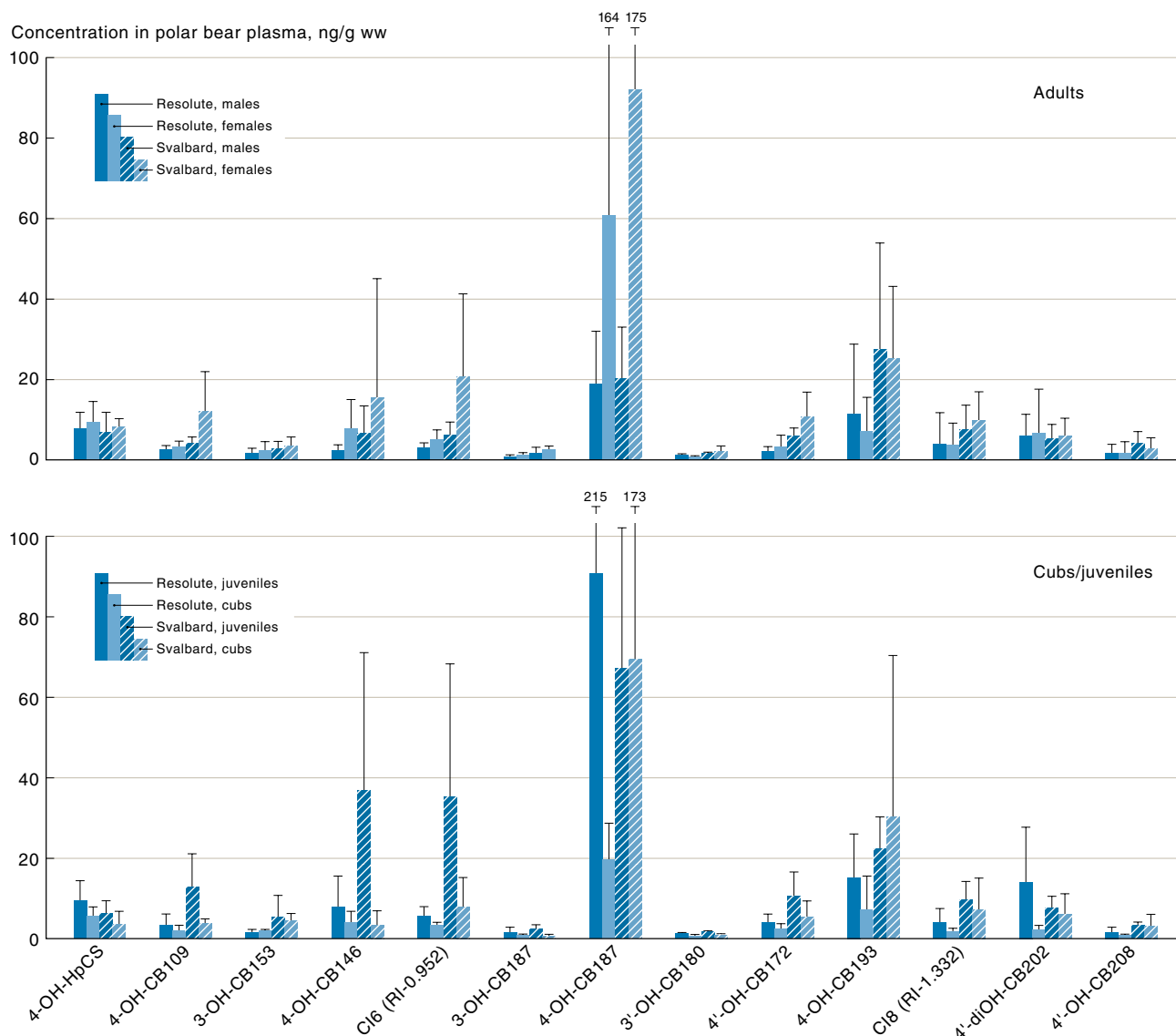
Figure 4·57. Mean (± SD) concentrations of major OH-PCB congeners and OH-HpCS in plasma from polar bears from Resolute Bay in the Canadian Arctic, collected in April-May 1997, and from Svalbard, collected in April-May 1998. Adult males and females, n = 12-15 in each category; cubs (0-2 yr) and juveniles (3-4 yr), n = 2-5 in each category.

Thus, it appears that there is no selective transfer of OH-PCBs in polar bear milk, unlike MeSO$_2$-PCBs.

To put the importance of OH-PCBs and other phenolic compounds in polar bear plasma into context, the ranking of concentrations of the first 50 individual POPs, both neutral and phenolic, was determined in the combined Resolute Bay/Svalbard data set. Out of the ten highest POPs in plasma, six are phenolic compounds, three are PCBs, and the last one is oxychlordane. These six phenolic compounds, including 4-OH-HpCS, constituted 42% by weight of all POPs in polar bear plasma. Of the remaining forty compounds, nine are chlordane-related compounds, seventeen are PCBs, five are OH-PCBs, and the rest are chlorobenzenes, DDTs, HCHs, and pentachlorophenol (PCP).

In order to determine the potential for bioaccumulation of hydroxy metabolites of PCBs and OCS, patterns of accumulation of these metabolites and their precursors were studied in ringed seal and compared to those in polar bear. Concentrations of ΣOH-PCBs were 1000 times lower in ringed seal than in polar bear plasma, whereas ΣPCBs were only two times lower. Considering that most of the hydroxy metabolites in ringed seal are probably in blood, and at low concentrations, it would seem that the potential for the polar bear to bioaccumulate OH-PCBs and 4-OH-HpCS is very low.

4.4.8. Arctic fox and sea otter

Arctic fox (Alopex lagopus)
The Arctic fox is one of the few species that constitutes an important component of both the terrestrial and marine ecosystems (Hiruki and Stirling, 1989). On land, Arctic foxes feed mainly on lemmings, birds, and their eggs, as well as scavenging on caribou remains (Kennedy, 1980; Stickney, 1991; Kapel, 1999) whereas coastal foxes will also eat marine invertebrates (Fay and Stephenson, 1989; Kapel, 1999) and fish (Banfield, 1987) in summer. In winter and spring on the sea ice, Arctic foxes scavenge the remains of ringed seals and bearded seals killed by polar bears (Stirling and Smith, 1977; Andriashek *et al.*, 1985; Fay and Stephenson, 1989; Hiruki and Stirling, 1989; Kapel, 1999), and they will also actively prey on newborn seal pups and eat placental remnants (Smith, 1976; Andriashek *et al.*, 1985; Lydersen and Gjertz, 1986). Populations feeding at dif-

ferent trophic levels (Peterson and Fry, 1987; Hobson and Welch, 1992) and in marine or terrestrial/freshwater environments (reviewed by Hobson *et al.*, 1997) can be distinguished using stable isotope analyses. The $^{15}N:^{14}N$ isotope ratio, often reported as $\delta^{15}N$, increases in a predictable manner between trophic levels (Kelly, 2000), allowing trophic positions and OC concentrations to be interpreted along a continuous variable. Carbon isotopes ($^{13}C/^{12}C$) are not enriched significantly between trophic positions and can be used to evaluate energetic pathways between regions with differing carbon sources. As a result, stable carbon isotope signatures can differentiate an organism's dependence on inshore/benthic and offshore/pelagic regions (Hobson *et al.*, 1995).

Arctic fox muscle and liver tissues were collected at Barrow, Alaska, (n = 18) and Holman, NWT, (n = 20) from 1998 to 2000, to elucidate the feeding ecology of this species, and relate these findings to body residue patterns of OC contaminants (Braune *et al.,* 2001d; Hoekstra *et al.*, 2003b) (Annex Table 14). At both sites, PCBs and chlordane-related compounds were the predominant OCs present in muscle, while in liver, chlordanes were the predominant group, followed by PCBs. The most abundant OC analytes extracted from Arctic fox muscle and liver were oxychlordane, the principal metabolite of chlordane-related compounds, CB153 and CB180. While mean concentrations of all major OC groups were less than 250 ng/g ww, a few individuals had very high levels of total PCBs and oxychlordane. The concentrations of OCs were relatively elevated on a lipid basis. For example, ΣPCBs ranged from 110 to 14 600 ng/g lw in liver and from 76 to 8047 ng/g lw in muscle in the Holman foxes. The mean, lipid-adjusted ΣPCB concentrations in foxes from Holman and Barrow (1853±730 ng/g lw and 1516±370 ng/g lw, respectively) are lower than ΣPCBs in Arctic fox liver from Svalbard, the Norwegian mainland, and Iceland (Norheim, 1978; Wang-Andersen *et al.*, 1993; Skaare, 1996; Klobes *et al.*, 1998b;), which is consistent with the west–east gradient of ΣPCB concentrations in ringed seals (Muir *et al.*, 2000b). The OC profile in the Arctic fox suggests a similarity in metabolism with the polar bear, and that the capacity of this species to biotransform OCs dramatically influences accumulation profiles.

PCB, DDT, and chlordane levels measured in fat of young Arctic foxes from the Pribilof Islands, Alaska, (Krahn *et al.* 2002) (Annex Table 14) were higher, on a wet weight basis, than liver and muscle concentrations in Canadian foxes from Holman, NWT. On a lipid weight basis, OC concentrations in the foxes from the Pribilof Islands were also slightly higher than concentrations in the Holman foxes (Hoekstra *et al.*, 2003b). TEQs based on mono-*ortho* PCB concentrations range from 3.4 to 146 pg/g ww, with means of 22.7 and 69.5 pg/g ww for females and males, respectively.

Concentrations of several OC groups in both liver and muscle samples were not significantly correlated with increasing trophic position based on stable nitrogen isotope ($^{15}N/^{14}N$) values from the Holman and Barrow foxes (Hoekstra *et al.*, 2003b). ΣHCHs had the strongest positive relationship with trophic position (Figure 4·58). The stable isotope data suggest that as the Hol-
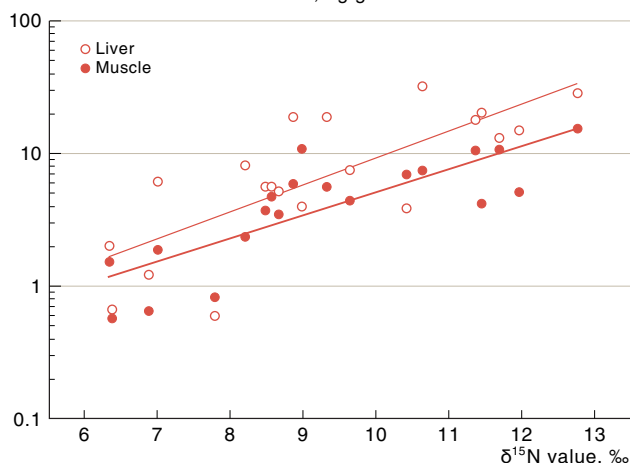

Figure 4·58. $\delta^{15}N$ isotope ratio versus ΣHCH concentrations in liver and muscle tissue of Arctic fox (Hoekstra *et al.*, 2003b). Relationship for muscle and liver samples are: log ΣHCH = 0.175 $\delta^{15}N$ – 1.04 ($r^2 = 0.67$), and log ΣHCH = 0.204 $\delta^{15}N$ – 1.07 ($r^2 = 0.59$), respectively.

man Arctic fox population shifts its feeding from the terrestrial/freshwater systems to the marine environment, its relative trophic position significantly increases. However, most OC concentrations were not strongly correlated to trophic position. The comparison of $\delta^{15}N$ with OC concentrations indicated that trophic position does not serve as an accurate predictor for OC bioaccumulation in the Arctic fox, possibly due to different turnover rates of OCs and stable isotopes in metabolically active tissues, and/or the capacity of the Arctic fox to readily biotransform OCs.
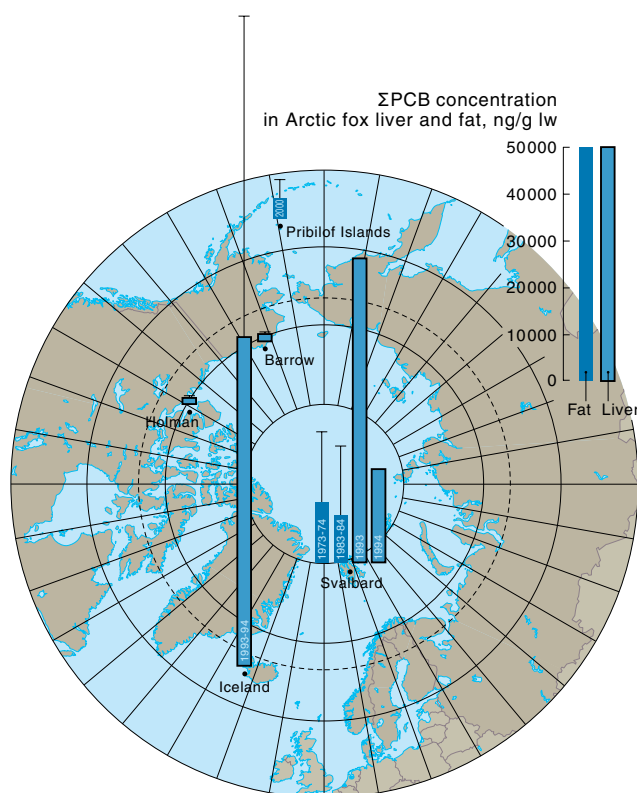

Figure 4·59. Concentrations of ΣPCBs in Arctic fox liver and fat from Pribilof Islands, Barrow, Holman, Iceland, and Svalbard (previous AAR data).

Concentrations of PCBs and a variety of OC pesticides were measured in the livers of foxes from an inland and coastal region of Iceland (Klobes *et al.*, 1998b) (Annex Table 14). In both regions, the foxes' OC patterns were dominated by oxychlordane. PCB was dominated by CB 180, *p,p'*-DDE was dominant in the DDT group of contaminants, and γ-HCH and β-HCH were the only detectable HCH compounds. ΣPCB levels were much higher in the coastal foxes (approximately 72 500 ng/g lw) than in inland foxes (approximately 1000 ng/g lw). The ΣPCB concentrations in coastal foxes are comparable to concentrations previously seen on Svalbard (20 000-64 000 ng/g lw) (Skaare, 1996). This was explained by the significant differences in trophic levels of the two groups of foxes, where the coastal foxes consume prey items such as piscivorous birds and carcasses of seals, and the inland foxes consume relatively more herbivorous species such as ptarmigan and geese. This is consistent with the findings of Hoekstra *et al.* (2003b) for foxes from Alaska and the western Canadian Arctic. ΣPCB concentrations for all Arctic foxes, including those studied previously on Svalbard, are presented in Figure 4·59.

Sea otter (Enhydra lutris)

Sea otters are an endangered marine mammal that inhabits the north Pacific Rim. These non-migratory animals are part of the mink family feeding on marine shellfish, and therefore, may be particularly sensitive to the effects of OCs. Members of the mink family have been shown to be highly sensitive to the effects of OCs (Hornshaw *et al.*, 1983). OCs were measured in the liver of sea otters collected in southeastern Alaska, the Aleutian Islands, and California between 1988 and 1992 (Bacon *et al.*, 1999). OC concentrations were much lower in the Alaskan otters compared with the Californian otters with the exception of PCBs in the Aleutian otters (Bacon *et al.*, 1999). ΣPCB levels in the Aleutian otters were 310 ng/g ww, 1.7 and 38 times higher than those measured in the California (180 ng/g ww) and southeastern Alaska otters (8 ng/g ww), respectively. PCDD and PCDF levels were very low in all otter populations. The source of the high levels of PCBs in the Aleutian islands is unknown and remains a concern for the health of the sea otter population in this region. As a non-migratory animal, the source of these high PCBs is likely local (Estes *et al.*, 1997).

4.4.9. Food web studies

A number of studies examining the food web transfer of OCs in marine food webs have been carried out since 1997, filling a knowledge gap identified in the previous AMAP POPs assessment (de March *et al.*, 1998). These studies incorporated a larger number of species and trophic levels than was previously available for a single Arctic marine food web, and also incorporated stable isotopes of nitrogen to discern trophic positions. They provide an advantage over relationships developed for the original AMAP POPs assessment, in that all samples were collected at the same time and in the same region, and the analytical methods were consistent for all samples.

Barents Sea food web study

To study the bioaccumulation of OCs in the Barents Sea food web, and to examine whether biomagnification could partially explain the high burden of contaminants in top predators near Svalbard (Wang-Andersen *et al.*, 1993; Gabrielsen *et al.*, 1995; Andersen *et al.*, 2001b), selected taxa of zooplankton, fish, and seabirds were collected in the Barents Sea near Bjørnøya in June 1995 (Borgå *et al.*, 2001). OC concentrations increased along the food web in a manner that mainly reflected the organisms' trophic position in the food web, as predicted by previous dietary studies. The concentrations of OCs (ΣHCHs, HCB, ΣCHLs, ΣDDTs, and ΣPCBs) were low in zooplankton and fish, but biomagnified by one to three orders of magnitude in seabirds, with the highest concentrations being found in glaucous gulls. The low OC levels in selected taxa at lower trophic positions were unexpected considering the high concentrations of particularly ΣDDTs and ΣPCBs in top predators. Since a diet of pelagic organisms does not seem to explain the elevated concentrations found in top predators near Svalbard, in this case exemplified by glaucous gulls, a diet of ice-associated fauna may be of importance in the bioaccumulation of OCs instead (Norstrom *et al.*, 1998). As suggested by Pfirman *et al.* (1995), contaminated particles in the sea ice may be released in the melting areas of the Fram Strait and the Barents Sea, followed by bioaccumulation in ice-associated fauna.

Northern Norway food web study

Biomagnification of OCs was studied in the marine food web of Jarfjord, Norway (69°48'N, 30°25'E) (Ruus *et al.*, 1999). Samples included two species of fish (lesser sandeel (*Ammodytes marinus*) and cod) and seal (harbour/grey seals) collected in 1989 and 1990. Most OCs were found to biomagnify. The trophic level with the greatest biomagnification for ΣDDTs was identified from sandeel to harbour seal. The proportions of highly chlorinated PCBs, DDE and oxychlordane increased with trophic level, whereas PCBs that were mono-*ortho* substituted or *meta-para*-unsubstituted and DDD decreased from fish to seal, reflecting the influence of biotransformation. The study demonstrated the influence of physical-chemical properties and biotransformation on food web dynamics of OCs in Artic marine food webs.

Northwater Polynya food web study

OCs and stable isotopes of nitrogen (δ¹⁵N) were measured in zooplankton (six species), a benthic invertebrate (*Anonyx nugax*), Arctic cod, seabirds (six species), and ringed seals collected in 1998 in the Northwater Polynya. The purpose was to examine the effects of biological and chemical factors on trophic transfer of OCs in an Arctic marine food web (Fisk *et al.*, 2001c). The Northwater Polynya is located in northern Baffin Bay and is the largest and most productive polynya (area of open water in ice-covered sea) in the Canadian Arctic. The trophic relationships derived from stable isotope analysis for the Northwater Polynya food web fell into the range expected based on stable isotope results for another Arctic polynya food web (Hobson *et al.*, 1995), with seabirds and ringed seal at the top level, and zooplankton species occupying lower trophic levels. Strong positive relationships were found between recalcitrant
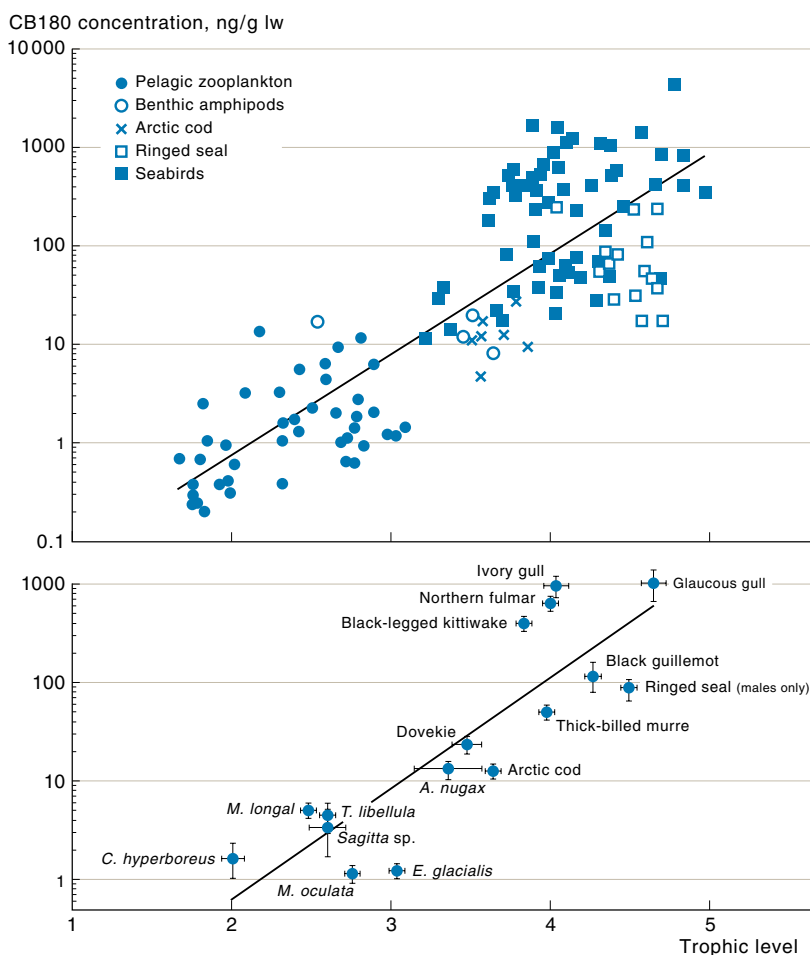
Figure 4·60. CB180 concentrations versus trophic level relationships for the Northwater Polynya marine food web (Fisk *et al.*, 2001c). The top graph shows all data points and the bottom graph shows mean (± 1 SE) values for each species. Lines are log-linear regressions. Trophic level is based on $\delta^{15}N$.

OC concentrations (lipid corrected) and trophic level based on stable isotopes of nitrogen, providing clear evidence of OC biomagnification in Arctic marine food webs (Figure 4·60). Food web magnification factors (FWMF), determined from the slope of OC concentration/trophic level relationships in this work, are in good agreement with values obtained for food webs from temperate and Arctic ecosystems involving marine birds and mammals (Norstrom, 1994; Jarman *et al.*, 1996).

Biomagnification

Biomagnification factors (BMFs, the ratio of lipid-adjusted concentration in predator to lipid-adjusted concentration in prey) values for the Barents Sea and Northwater Polynya food webs are summarized in Table 4·10. BMFs determined for the Northwater Polynya food web were corrected for trophic level differences based on stable isotopes because many of these species have varied diets, and for many of these comparisons the predator was not a full trophic level above the prey based on $\delta^{15}N$ values (Fisk *et al.*, 2001c). Since BMFs reflect concentrations throughout the food web, the lowest BMFs were found in trophic interactions with carnivorous zooplankton (*Parathemisto libellula*) as predators on copepods. The BMFs were higher with fish as predators, and much higher when seabirds were the predators on zooplankton and fish. In amphipods, Arctic cod, and cod, the low OC concentrations and biomagnification factors may be explained by their abilities to excrete contaminants through the respiratory surface into water. The seabirds' higher trophic position and energy requirements, and their lack of direct diffusion of contaminants can explain the high biomagnification factors in seabirds compared to fish. Generally, PCBs and *p,p'*-DDE had the highest BMFs, followed by HCB and chlordanes. Compared to other compound classes, the BMFs for HCHs were low, reflecting the low K_{ow} of HCHs. In general, there was good agreement between BMFs for the two studies, although there were some notable exceptions.

BMFs determined for amphipods, using copepods as the prey item, were one to two orders of magnitude higher in the Northwater Polynya food web versus the Barents Sea food web. Fisk *et al.* (2001c) suggested, however, that the Northwater Polynya BMFs for zooplankton were not realistic because concentrations of OCs in zooplankton may be controlled by OC concentrations in water and not prey (Fisk *et al.*, 2001a). In addition, the higher concentrations in the amphipods may be driven by their larger size (Fisk *et al.*, 2002a). Other variables, such as season, may influence invertebrate OC levels, and this requires more research. BMFs for Arctic cod/amphipods were around 1, but are in the range of BMFs reported for similar-sized fish in laboratory experiments (Fisk *et al.*, 1998) and field observations (Rasmussen *et al.*, 1990). BMFs calculated for Northwater Polynya ringed seals (Table 4·10) were slightly lower, but within the range of those reported for male ringed seals from the east central Canadian Arctic (Muir *et al.*, 1988).

The BMFs of seabirds, which used Arctic cod as the prey item, varied between species and food webs (Table 4·10) and appear to be related to scavenging of marine mammals and/or migration to more contaminated regions. The higher BMFs in the Barents Sea food web suggest that the diet of these seabirds includes a larger

Table 4·10. Biomagnification factors determined for key fauna in the marine food webs of the Barents Sea and northern Baffin Bay. Biomagnification factors are based on lipid corrected concentrations. Biomagnification factors for Baffin Bay were corrected to one full trophic level based on trophic levels derived from stable nitrogen isotopes.

Predator/prey	Site	HCB	ΣHCHs	ΣCHLs	*p',p'*-DDE	ΣPCBs
Amphipod/copepod	Barents Sea	1.5	1.3	1.9	0.4	1.1
	Baffin Bay	3.8	4.5	26.5	16	4.6
Arctic cod/amphipod	Barents Sea	2.0	1.2	3.5	1.7	2.2
	Baffin Bay	6.1	1.1	1.6	3.1	0.9
Thick-billed murre/Arctic cod	Barents Sea	15	1.3	2.6	62	17
	Baffin Bay	10.9	2.1	1.8	19	8.2
Black guillemot/Arctic cod	Barents Sea	8.6	1.1	3.9	40	19
	Baffin Bay	5.0	3.5	4.0	18.5	8.9
Black-legged kittiwake/Arctic cod	Barents Sea	22	1.2	5.9	70	164
	Baffin Bay	21.6	4.2	11.6	56	60.5
Glaucous gull/Arctic cod	Barents Sea	105	6.8	73	2299	1144
	Baffin Bay	6.7	5.2	80	49	28
Ringed seal/Arctic cod	Baffin Bay	0.5	2.0	2.4	7.0	5.5
Food web biomagnification factor (BMF)		4.1	2.7	7.0	14	4.6

percentage of higher trophic-level organisms than does the Northwater Polynya food web. BMFs were highest in black-legged kittiwakes and glaucous gulls, which reflect the migration of the kittiwakes to more contaminated regions and the scavenging of marine mammals and predation on other birds by glaucous gulls. The extremely high BMFs for the Barents Sea glaucous gulls suggest that scavenging and predation may be more prevalent in this population. BMFs reported for Arctic seabirds are in the range reported for other fish-eating birds (Braune and Norstrom, 1989; Hendriks, 1995). Braune and Norstrom (1989) reported whole-body BMFs for a range of OCs, including PCBs in Lake Ontario herring gulls that ranged from 18 to 59 for persistent POPs, and

from 1 to 9 for readily metabolized OCs. These are slightly lower than those calculated for glaucous gulls, which is likely due to scavenging highly contaminated marine mammals by the glaucous gulls and/or from having a higher burden of POPs due to accumulation from more polluted winter habitats, as discussed above.

Results of these studies provided insights into the fate and dynamics of OCs in marine food webs. The OC pattern in the Barents Sea food web changed from zooplankton and fish to seabirds, with decreasing relative contributions of HCHs, HCB, and chlordanes to total OC concentrations, and increasing relative contribution of DDTs, PCBs, persistent compounds, and metabolites (Figure 4·61). This corresponded to previous studies from
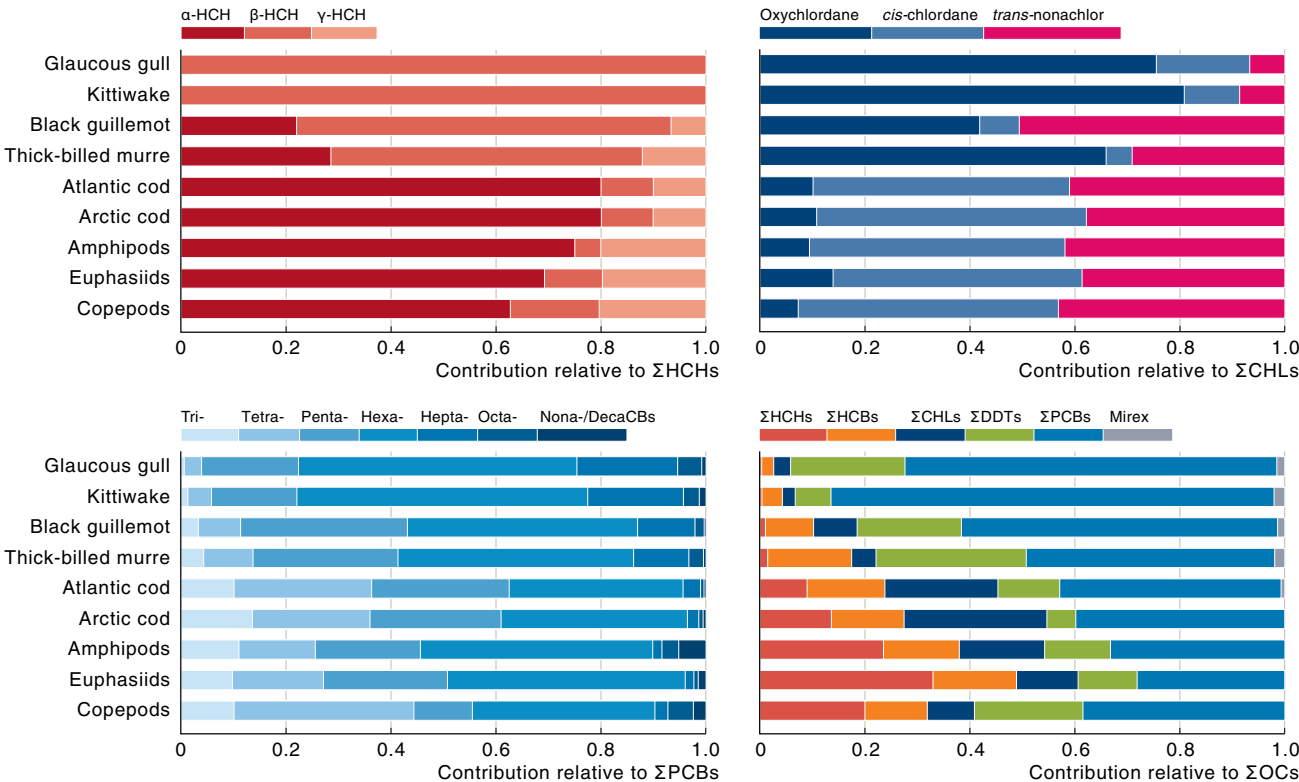

Figure 4·61. Relative proportions of individual OC compounds in the Barents Sea food web (Borgå *et al.*, 2001).

other areas (Tanabe *et al.*, 1984; Hargrave *et al.*, 1992; Ray *et al.*, 1999). The high contribution of compounds from the technical mixture of HCH (α-HCH and γ-HCH) and chlordanes (*cis*-chlordane and *trans*-nonachlor) to ΣHCHs and ΣCHLs in zooplankton and fish is consistent with limited metabolic capacities of these organisms. In contrast, high relative contributions of the most persistent compounds and metabolites of HCHs (β-HCH) and chlordanes (oxychlordane) in seabirds are consistent with their higher ability to metabolize and excrete the other HCHs and chlordanes. The PCB congener pattern, showing increased influence of higher chlorinated congeners with trophic position of the organism (Figure 4·61), is consistent with the tendency of higher chlorinated congeners to biomagnify, since they are not readily metabolized and excreted (Oliver and Niimi, 1988).

One of the most striking differences in BMFs was between poikilotherms (fish) and homeotherms (seabirds and mammals) (Table 4·10). Large differences in BMFs between poikilotherms and homeotherms were first demonstrated in herring gulls and salmon for Lake Ontario (Braune and Norstrom, 1989). Greater BMFs, and hence, exposure to OCs in homeotherms, has been attributed to their greater energy requirements and feeding rates (Braune and Norstrom, 1989; Fisk *et al.*, 2001c). A similar relationship was also seen in the Jarfjord study, with BMFs for the cod-sandeel predator-prey relationship being lower (2-3 for recalcitrant POPs) than for the seal-cod relationship (8-10 for recalcitrant POPs) (Ruus *et al.*, 1999).

A strong relationship between FWMFs, determined from concentration-trophic level relationships, and log K$_{ow}$ was found for recalcitrant OCs (Figure 4·62). It is clear that increasing log K$_{ow}$ results in greater trophic transfer of recalcitrant POPs in Arctic marine food webs. This relationship provides insight into the behavior of a
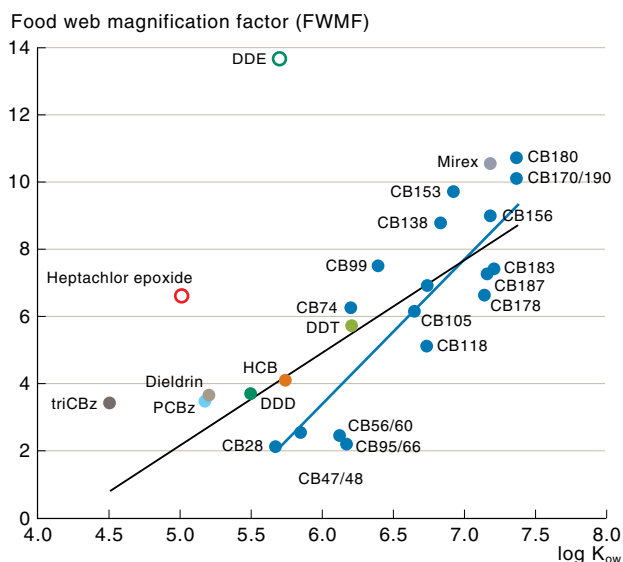
number of POPs. For example, DDE and heptachlor epoxide have values of FWMFs that are much greater than predicted based on the FWMF-log K$_{ow}$ relationships. DDE has been well established as a metabolite of DDT formed in animals. These results suggest that a large percentage of the high concentrations of DDE in upper trophic-level Arctic organisms are due to metabolic formation. Heptachlor epoxide, which is not in technical mixtures, is formed from heptachlor by photo-oxidation or in the liver of mammals (Buser and Müller, 1993). Results from this study suggest that heptachlor epoxide is formed in upper trophic-level Arctic organisms, and may account for a large percentage of concentrations in these animals.

4.4.9.1. Trophic transfer of 'new' and chiral chemicals in marine food webs

Concentrations of four organohalogens, that are possibly naturally produced (collectively termed HDBPs), 1,1'-dimethyl-3,3',4-tribromo-4,5,5'-trichloro-2,2'-bipyrrole (DBP-Br$_3$Cl$_3$), 1,1'-dimethyl-3,3',4,4'-tetrabromo-5,5'-dichloro-2,2'-bipyrrole (DBP-Br$_4$Cl$_2$), 1,1'-dimethyl-3,3',4,4',5-pentabromo-5'-chloro-2,2'-bipyrrole (DBP-Br$_5$Cl), and 1,1'-dimethyl-3,3',4,4',5,5'-hexabromo-2,2'-bipyrrole (DBP-Br$_6$), were quantified in the Arctic marine food web of northern Baffin Bay (Tittlemier *et al.*, 2001). The extracts used for this analysis were also used for the OC analysis of the Northwater Polynya food web discussed in Section 4.4.9 but with fewer species. All HDBP congeners were found to significantly biomagnify, or increase in concentration with trophic level in the invertebrate→fish→seabird food web. None of the four HDBP congeners in ringed seals followed the general trend of increasing concentration with trophic level, which was likely due to an ability of the seals to metabolize HDBPs.

Metabolism of chiral contaminants can identify differences in species biotransformation ability and provide insights into the fate of OCs in food webs. Concentrations of HCH isomers (α, β, and γ) and EFs of α-HCH were determined in the northern Baffin Bay marine food web (Moisey *et al.*, 2001), also discussed in Section 4.4.9. For invertebrates and fish, the BMFs of the three isomers were >1, and the proportion of each isomer and the EFs of α-HCH were similar to those found in water, suggesting minimal biotransformation. Seabirds appear to readily metabolize γ- and α-HCH, based on low BMFs for these isomers, high proportions of β-HCH (62-96%), and high EFs (0.65 to 0.97) for α-HCH. The α- and β-HCH isomers appear to be recalcitrant in ringed seals based on BMFs >1, with this species having near racemic EFs for α-HCH. The β-isomer appears to be recalcitrant in all species examined and had an overall FWMF of 3.9. EFs of α-HCH provided conclusive evidence that biotransformation was accounting for much of the HCH isomer patterns observed in the northern Baffin Bay food web.

4.4.9.2. Trophic transfer of metabolites in polar bear food web

Concentrations of MeSO$_2$-PCBs and -p,p'-DDEs and their precursor PCBs and p,p'-DDE were compared in the Arctic cod→ringed seal→polar bear food chain

Figure 4·62. Relationship between food web magnification factors (FWMFs) and log K$_{ow}$ of recalcitrant POPs in the Northwater Polynya marine food web (Fisk *et al.*, 2001c). FWMFs were determined from the relationship between concentration (on a lipid weight basis) and trophic level. Log K$_{ow}$s of PCBs are from Hawker and Connell (1988), and for all other POPs are from Mackay *et al.* (2000). Regression lines are shown for PCBs (BMF = −22.7 + 4.4 logK$_{ow}$, r^2=0.72) and for 'all' compounds (including PCBs, but excluding DDE and heptachlor epoxide (HE)) (BMF = −11.8 + 2.8 logK$_{ow}$, r^2=0.64).
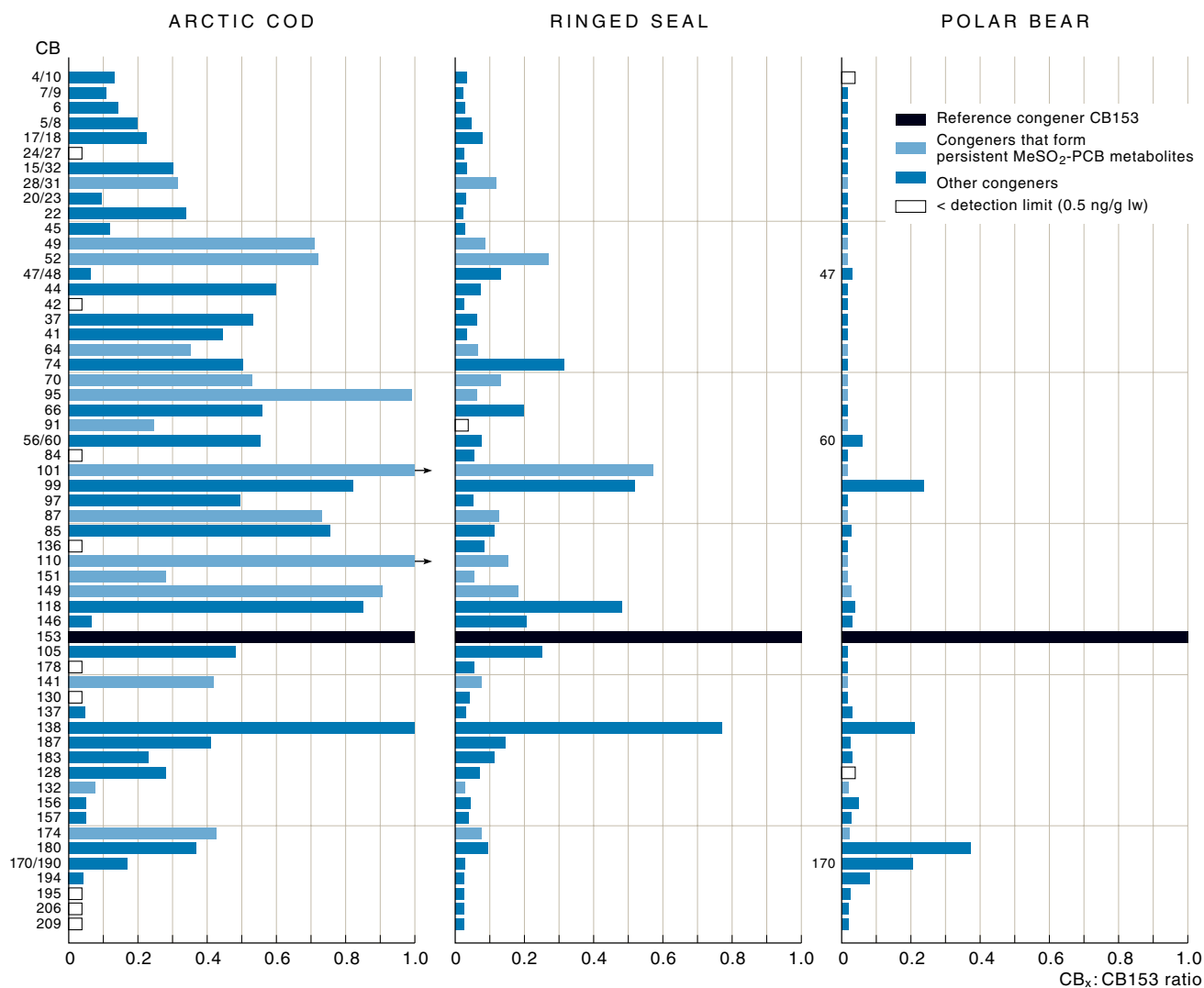
Figure 4·63. Ratios of CB congener concentration to CB153 concentration in whole Arctic cod, ringed seal blubber, and polar bear adipose tissue from the Resolute Bay area in the Canadian Arctic, in 1993 (Letcher *et al.*, 1998).

from Resolute Bay to determine the relative importance of bioaccumulation from the food chain and formation by metabolism of precursors in polar bear (Letcher *et al.*, 1996; Norstrom, 1997).

Overall, there was little difference in the PCB pattern in cod relative to the Aroclor standard (1242:1254:1260, 1:1:1). However, the PCB patterns changed noticeably in seal and bear, especially PCB congeners possessing hydrogens at the *meta-para* (3,4) position on one or more ring (Figure 4·63). *Meta-para* PCBs were present in seal blubber but notably absent in polar bear (<0.05 ng/g lw). These PCBs included CBs 31, 49, 64, 70, 91, 101, 110, 141, 132, and 174, all of which were also present in the form of their 3- and 4-MeSO$_2$-PCB metabolites in seal and bear. Metabolites of CBs 52 and 95 were not found in the polar bear. These PCB congeners possess hydrogens at both *meta-para* positions, and may metabolize to *bis*-MeSO$_2$-PCBs or to OH-PCBs.

4.4.10. Summary and conclusions – marine environment

The greatest amount of research on OCs in the Arctic since the previous AMAP assessment, post-1996, has been in the marine environment. As might be expected, circumpolar coverage of information on OCs in the Arctic is greatest in the marine environment. Research has focused on this environment because OC levels are elevated in top predators due to long food chains; the fact that the marine environment accounts for a large percentage of the area of the Arctic; and, the fact that many marine organisms are important components of the human diet.

A number of studies have examined OCs in marine zooplankton, filling a knowledge gap identified in the first AMAP POPs assessment. As expected, levels of OCs are low in marine zooplankton, reflecting their lower trophic levels. Data are available for similar species from Alaskan, Canadian, and European Arctic waters, providing almost circumpolar coverage; very limited data are however available for Russian seas. In addition, there is no information on 'new' chemicals in Arctic marine zooplankton, which is necessary to assess the trophic transfer of these chemicals to higher trophic levels. The circumpolar trends of OCs in zooplankton differ from those observed in higher trophic-level organisms, in that there are no large differences between the North American Arctic and the European Arctic. In calanoid copepods from the Barents Sea and northern Baffin Bay, OC levels, with the exception of HCH and CBz, were

also similar. OC concentrations observed in copepods from the Greenland Sea region were lower than those observed in the North American Arctic, which differs from the pattern of levels found in marine mammals from these areas. This could be due to a number of factors related to the season of collection, which varied with these studies. HCH levels were found to be greatest in Alaskan zooplankton, reflecting the proximity to Asian sources of these compounds. Ice-associated fauna from the marginal ice zone near Svalbard have low OC levels, comparable with levels in zooplankton at similar trophic positions from the Barents Sea.

OC levels in benthic invertebrates varied to a greater extent than in zooplankton. Benthic invertebrates that scavenge can accumulate OCs at levels similar to marine fish and lower trophic-level birds. There are currently insufficient data to examine temporal trends in these organisms. Toxaphene was measured in spider crabs collected north of Norway, demonstrating that this contaminant is present in invertebrates throughout the European as well as the North American Arctic. Data for benthic invertebrates are lacking from Russia.

OC data for a number of marine fish species have been generated since the previous AMAP assessment, mainly in Greenland and Canada but also for Arctic cod from a number of regions. Very little new data are available for Russian marine fish. OC concentrations are higher in marine than in freshwater fish, and for some species, are very high. PBDEs have been measured in a small number of species from Greenland and Norway at levels much lower than those of legacy OCs. Levels of OCs in Arctic cod in the Barents Sea were similar to those in northern Baffin Bay and Barrow, Alaska. OC concentrations were found to be very high in the Greenland shark, a large long-lived fish that feeds at a high trophic level.

A fair amount of new data has been produced for Arctic seabirds since the previous AMAP assessment. OC concentrations in seabirds vary dramatically between species, reflecting the large range in trophic levels at which they feed. Highest OC concentrations are observed in the scavenging seabirds, in particular, great skuas, great black-backed gulls, and glaucous gulls, which also prey on other seabirds, but migrating species such as black-legged kittiwakes can also accumulate high OC levels from southern habitats. Circumpolar trends of OCs in seabirds, particularly ΣPCBs and ΣDDTs, show highest levels in the Russian Barents Sea (Franz Josef Land, Novaya Zemlya) and lowest concentrations in the Canadian and Alaskan Arctic, with the exception of HCH. This is similar to what has previously been observed. Data are limited for the central and eastern Russian Arctic. Various combinations of non- and mono-*ortho* PCBs and PCDD/Fs have been determined in several seabird species from the Canadian and Norwegian Arctic, and the Faroe Islands. Highest TEQ levels are found for glaucous gulls on Svalbard. Data for 'new' chemicals, including PCNs, PBDEs, and butyltins, are also available.

There is wide coverage of POP concentration data in a diverse group of pinniped species, both those that are typical Arctic species (ringed, harp, and bearded seals, walrus), and those that are not typically Arctic (harbour, grey, and northern fur seals, Steller sea lions). There is good geographical coverage for ringed seals, but limited

spatial coverage for other Arctic species, some of which play an important role in Inuit diets. As was reported in the previous AMAP assessment, levels of OCs in ringed seals are greatest in the European and western Russian Arctic, in particular the Kara Sea, lower in the Canadian Arctic, and lowest in the Alaskan Arctic and the Chukotka Peninsula of eastern Russia. The exceptions are for chlorobenzene concentrations, which have a uniform circumpolar distribution, and HCH concentrations, which are higher in the Alaskan and western Canadian Arctic. OC concentrations in harp seal are much higher during their molt, when they live off their blubber reserves. Higher PCB concentrations are also indicated in Steller sea lions from the Aleutian Islands compared to the Gulf of Alaska and southeast Alaska. Non- and mono-*ortho* PCB and PCDD/Fs were determined in a few species at a few sites. PCDD/Fs were fairly insignificant contributors to the TEQs compared to the PCBs. Concentrations, as TEQs, were highest in ringed seals from the Kara Sea followed by the Canadian Arctic and Chukotka Peninsula. Northern fur seals had TEQs similar to Canadian ringed seals. Data for 'new' chemicals have also been produced for ringed seals, including PCNs, PBDEs, PFOS, and butyltins. From the limited data available, it appears that PBDE levels are higher in European ringed seals compared with Canadian ringed seals.

Coverage of mysticete whale species has been improved compared with the previous AMAP assessment. In particular, a large amount of data has been produced for minke whales, providing good spatial coverage in the North Atlantic region. Spatial trends of OCs in minke whale are similar to other marine mammals, with the highest OCs levels in the Kara Sea region of Russia and decreasing concentrations to the west and to the south (e.g., the North Sea). PCDD/Fs, non- and mono-*ortho* PCBs and PBDEs have also been analyzed in minke whales around Svalbard. In addition, comprehensive data have been produced for the bowhead whale in Alaskan waters. In general, OC concentrations are lower in the mysticetes (filter-feeding whales) compared to odontocetes (toothed whales). There are limited 'new' chemical data for these organisms.

New data on odontocetes are available, and the beluga is the most widely studied. Data for Russia continues to be limited. There has also been improved coverage of other odontocetes compared to the previous AMAP assessment, but further improvement is still warranted (e.g., for narwhal, which have POP levels as high as in beluga and are also important to native communities). Comparison of OC levels in odontocetes from different regions shows a similar pattern as that seen in ringed seals. Highest levels are found in Svalbard animals, and lowest levels are found in Alaskan animals. HCH levels are again higher in belugas from Alaska. Highest OC concentrations are found in transient killer whales, followed by resident killer whales in Alaska, long-finned pilot whales from the Faroe Islands, and harbour porpoises from northern Norway. PCDD/Fs, non- and mono-*ortho* PCBs have also been analyzed in several species of odontocetes including beluga, harbour porpoise, and killer whale. A reasonable amount of data are available on 'new' chemicals in odontocetes. PCNs, PBDEs and endosulfan sulfate were found in beluga. PBDE levels in these whales follow those found in ringed

seals, with levels higher in and around Svalbard. Highest levels of PBDEs were seen in long-finned pilot whales from the Faroe Islands region. Low concentrations of butyltins were found in Norwegian harbour porpoise and Faroe Islands long-finned pilot whale, but were not detected in Canadian belugas.

A large amount of OC data has been produced for polar bears, including studies on levels in plasma from Russian polar bears. This is an important dataset because it provides the most comprehensive spatial trends coverage that includes Russia. The results clearly indicate that the Russian Arctic around the Kara Sea is the most contaminated marine area of the Arctic, particularly for PCBs and DDTs. Levels decrease to the east and west of the Kara Sea, with the lowest levels seen in Alaska and the western Canadian Arctic. A number of 'new' chemicals have also been measured in polar bears, including PBDEs and PFOS. PFOS levels are high in the polar bear and require more study. There have also been a number of studies that have examined factors that influence OC levels in bears, including reproduction, sex, and fasting. Concentrations of MeSO$_2$-PCB and *-p,p'*-DDE metabolites, OH-PCBs and a previously unidentified phenolic metabolite of OCS, 4-hydroxyheptachlorostyrene (4-OH-HpCS), have been determined in polar bears and found to be high.

New data for OCs have been generated for Arctic fox from sites in Alaska, Canada, and Iceland. Concentrations are related to food habits, with highest OC concentrations in foxes that feed in the marine food web. Mean PCB concentrations were lowest in Arctic fox from Canada, Barrow, Alaska, and inland Iceland, and higher in foxes from the Pribilof Islands, Alaska. The highest concentrations were found in foxes from coastal Iceland, and these are comparable to those found previously on Svalbard.

Within Alaska, OC concentrations (except for HCHs) were considerably higher in sea otters from the Aleutian Islands than from southeast Alaska, indicating possible local sources.

High levels of PCBs observed in blue mussels, sea otters, and bald eagles from the Aleutian Archipelago in Alaska appear to be due to local contamination. All of these species are non-migratory and would be exposed to contaminants from the local area. In the case of the bald eagles, high levels were observed in eagles nesting on islands that previously had military facilities. High *p,p'*-DDE levels in the bald eagles are correlated to reduced reproductive productivity. A similar situation has been found at Saglek Bay, Labrador, Canada, where local PCB contamination from a military radar site has led to higher PCB levels in marine sediments, invertebrates, fish, black guillemot, and ringed seals. Local sources of contamination in the Arctic warrant further consideration and monitoring. Steller sea lions from the Aleutian Islands also have higher PCB concentrations in their scat, indicating higher exposure there than in the Gulf of Alaska and southeast Alaska. Whether this is also due to exposure from local sources remains to be determined.

In addition to regional influences, age, sex, and trophic level all play an important role in the accumulation of OCs in marine mammals. Although there are exceptions, most commonly concentrations increase with age in males. In females, changing contaminant levels with age, and the rate of that change, are more variable and probably depend not only on the female's level of exposure to contaminants, but also how often they successfully produce and how long they nurse their offspring. Lipid content of tissues also plays a significant role in contaminant accumulation, with OCs increasing with the lipid content of the tissue.

Although some new data have become available since the previous AMAP assessment, there is still a lack of contaminant data on marine mammals from the Russian Arctic. This is particularly significant given that available data indicate that the highest levels of many compounds in the marine environment occur in some of the Russian seas.

A number of comprehensive food web studies have been carried out since the previous AMAP POPs assessment. These studies have increased our understanding of how OCs move through marine food webs. The studies also show that OC levels, generally, are similar in lower trophic-level organisms (zooplankton, copepods, and Arctic cod) in northern Baffin Bay and the Barents Sea, with the exception of HCH, which is higher in the North American Arctic. However, in seabirds, ringed seal, and polar bear, there are clear spatial differences, with higher concentrations of DDT and PCB, in particular, in the Barents Sea region as compared to the northern Baffin Bay area. Thus, on its own, a diet of pelagic organisms does not appear to explain the elevated concentrations in top predators in the Barents Sea area. The full explanation for these spatial differences is, therefore, still unclear. All spatial trends that include the Russian Arctic clearly show, however, that PCB and DDT concentrations are highest in the eastern Barents Sea and Kara Sea area, indicating significant local sources of DDTs and PCBs to the Russian Arctic. This is also indicated by high OC inputs from the Ob, Taz, Nadym, Pur, and Yenisey Rivers, which have been shown to be major sources of OCs to the Kara Sea/Arctic Ocean via river water and sediments.

Toxaphene congeners are being measured more often, but there is still a need for a broader inclusion of these compounds in research programs, both as single congener data, and as sum of congeners. Existing data indicate that levels vary significantly between species, but recent data indicate that the highest levels are in the thousands of ng/g range in cetaceans. Toxaphenes have also been shown to be an important contaminant in the European Arctic.

Data for brominated flame retardants, such as PBDEs are not widely available, and are needed, both for individual compounds and sums. The highest reported levels are in the thousands of ng/g range in pilot whales, but otherwise, are in the low ng/g range. Although PBDE concentrations are much lower than for legacy OCs, their rapidly increasing concentrations over time warrant additional research and continued monitoring.

Problems remain with the number of individual components examined within a family of contaminants (e.g., PCBs, chlordanes, DDTs, and toxaphene) with laboratories continuing to report different numbers of compounds, especially in the case of PCBs and chlordane. This continues to make it a challenge to compare results from studies within the Arctic as well as with those in the temperate and tropical marine environments.

Data were available for this assessment from the six land-based stations: Tagish (Yukon, Canada); Alert (Nunavut, Canada); Pallas (Finland); Stórhöfði (Iceland); Dunai (eastern Russia); and, Ny-Ålesund (Svalbard, Norway). The data from the Norwegian, Icelandic, Finnish and Canadian stations were made available from the AMAP Thematic Data Center for atmospheric contaminants at the Norwegian Institute for Air Research (Kjeller, Norway). In addition, selected results from the air monitoring station at Amderma in northwest Russia, jointly operated (since March 1999) by Russia and Canada, were available for the assessment.

The locations of these stations relative to possible local, as well as long-range transported POPs, constitute an important consideration when evaluating spatial trends (Figure 4·1). Most stations are at remote but well-established research stations. Some are influenced by local events such as forest fires, wood burning for domestic heating, and garbage burning. This may be the case for the Tagish site in particular, as discussed further in Section 4.1.2.5.3. Samplers at Alert and Ny-Ålesund have experienced contamination due to presence of OC pesticides in building materials (Alert) and PCBs (Ny-Ålesund). Altitude may also be a factor. Tagish is much higher than all other sites and receives air from the northeast Pacific Ocean

Alert, Tagish, Dunai, Amderma, and Ny-Ålesund operate on a weekly sampling basis, while at Pallas sampling is conducted one week per month, and Stórhöfði reports data from samples collected over a two- to three-week period. In order to compare results with the weekly samples from the rest of the stations, the week of the sampling period was chosen for the comparison and the other weeks omitted. Using this approach, it was possible to compare the data from all stations; however, the resolution of the Icelandic data is reduced and of limited use for the elucidation of long-range transboundary events.

In the discussion that follows, average annual concentrations of selected POPs are compared among the stations to examine prevailing spatial trends in the late 1990s. Results from shipboard measurements in the late 1990s are also discussed. An assessment of long-term temporal trends in air from many of the same stations is presented in Section 5.1.1.

4.1.2. Air concentrations – spatial trends
4.1.2.1. OC pesticides

A full list of the OC chemicals monitored is given in Annex Table 2. Major OC pesticides in Arctic air are α- and γ-HCH, p,p'-DDT, chlordane compounds, endosulfan, pentachloroanisole, as well as HCB (a multisource chemical) (Halsall et al., 1998; Hung et al., 2002b). Unfortunately, not all of these compounds are measured at all locations. HCH and DDT-related compounds are compared in Figure 4·2 at five locations using average, minimum and maximum concentrations in the gas + particle phase (pg/m^3) for different years. Results suggest rather uniform average concentrations of γ-HCH isomers and greater regional variation of α-HCH. In all Arctic samples, γ-HCH represents about 15-20% of the total α- and γ-HCH burden. This distribution seems to be independent of the geographic location of the station. The lowest ΣHCH average concentrations were measured in the Stórhöfði and Amderma samples. The highest average values were found at Ny-Ålesund and Alert in 1996 (73 and 62 pg/m^3 ΣHCHs, respectively).

Highest average and maximum values of DDT-related compounds were found at Stórhöfði. The contribution of the parent compounds o,p'- and p,p'-DDT, accounts for more than 60% of the total DDT burden suggesting fresh sources. The DDT group pattern at Amderma also had a high proportion of p,p'-DDTs (50% of ΣDDTs). However, overall levels of ΣDDTs at Amderma were lower than Stórhöfði and similar to the other sites (Figure 4·2). At Alert, summertime DDT/DDE ratios of the order of 1-1.5 have been observed, whereas for Amderma, the DDT/DDE ratios were about 3. A larger DDT/DDE ratio has also been observed at Tagish in western Canada and is linked to trans-Pacific transport from Asia (Bailey et al., 2000). Higher DDT/DDE ratios are indicative of fresh sources.

Elevated maximum concentrations, indicating incursions of southern air with higher levels of γ-HCH and DDT compounds, occurred in spring and summer months particularly at Ny-Ålesund, Alert, and Stórhöfði. Halsall et al. (1998) also reported relatively uniform mean annual concentrations of HCH and DDT isomers in Arctic air collected in 1993 from Alert, Dunai, Tagish, and Ny-Ålesund. Back-trajectory results for the 1996 and 1998
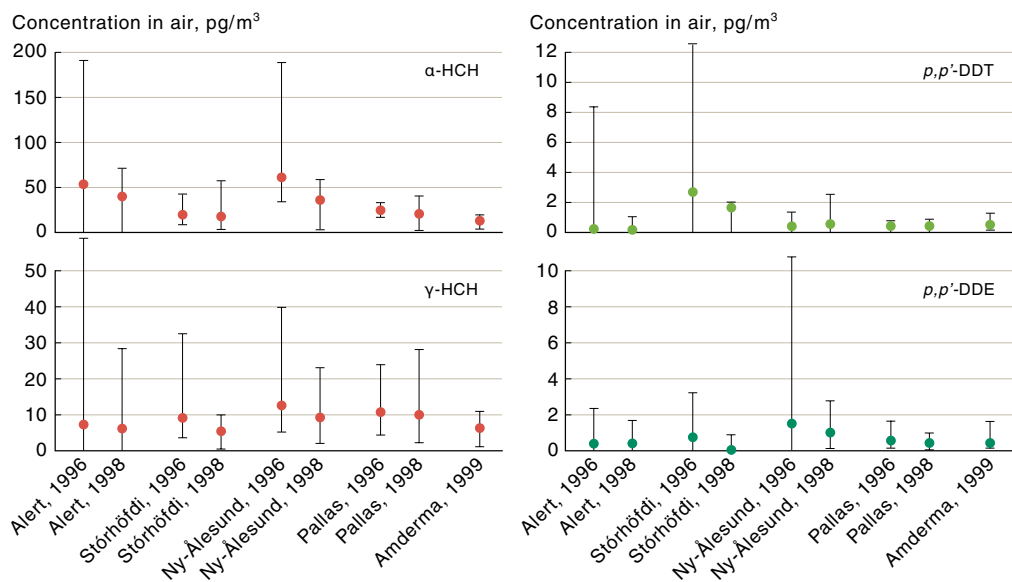

Figure 4·2. Comparison of average annual concentrations of major HCH- and DDT-related compounds in air (gas + particle phase) at monitoring stations in Canada (Alert), Iceland (Stórhöfði), Norway (Ny-Ålesund, Zeppelin Mountain), Finland (Pallas), (all 1996 and 1998), and western Russia (Amderma) (1999). Bars represent the ranges.
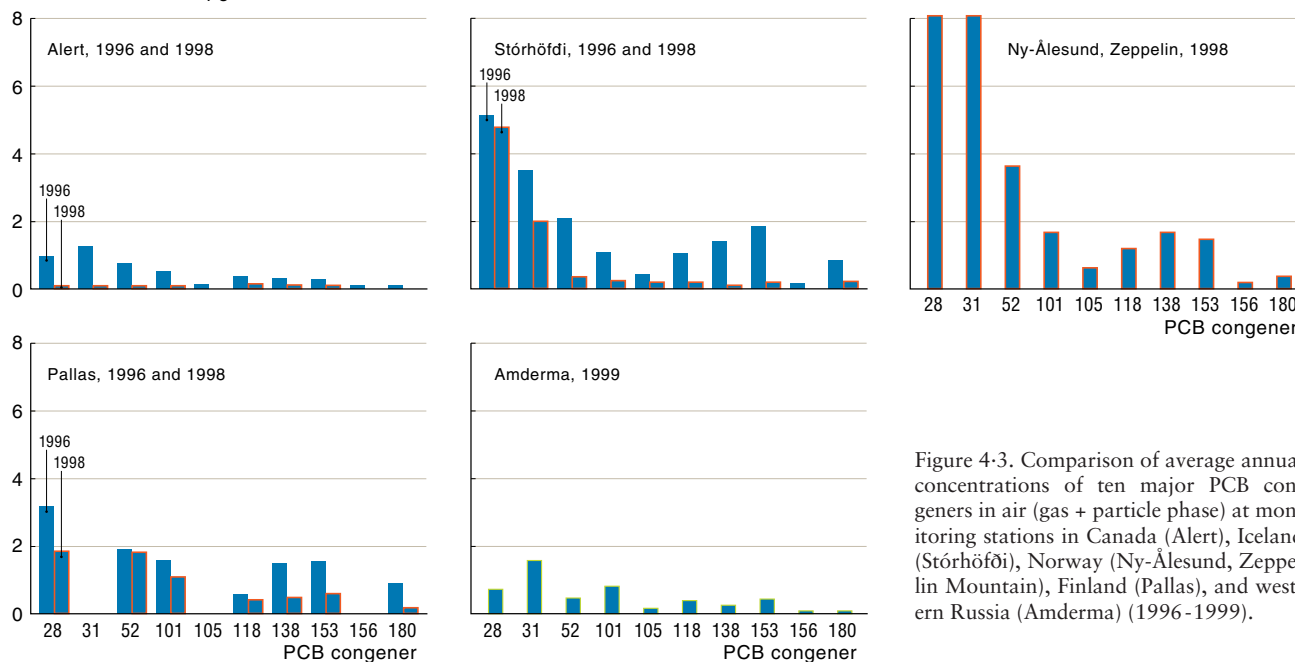
Concentration in air, pg/m³

Figure 4·3. Comparison of average annual concentrations of ten major PCB congeners in air (gas + particle phase) at monitoring stations in Canada (Alert), Iceland (Stórhöfði), Norway (Ny-Ålesund, Zeppelin Mountain), Finland (Pallas), and western Russia (Amderma) (1996-1999).

data shown in Figure 4·2 are not available. Harner *et al*. (1999), however, measured HCH isomers during a cruise in the Barents Sea and the eastern Arctic Ocean in July-September 1996 and found that concentrations and proportions of γ-HCH increased in air masses that had passed over central Europe. This is consistent with similar observations at Lista, Norway (Haugen *et al*., 1998) and the southern Baltic Sea (Wiberg *et al*., 2001). In the Barents Sea and eastern Arctic Ocean, summertime, above-ocean concentrations of α-HCH (11-68 pg/m³) and γ-HCH (6-68 pg/m³) measured by Harner *et al*. (1999) were within the range observed at Alert and Ny-Ålesund at the same time of year, but higher than at Pallas and Stórhöfði.

4.1.2.2. PCBs

Figure 4·3 presents the distribution of ten PCB congeners (PCB$_{10}$) (seven congeners for Pallas) measured at five stations in 1996 and/or 1998 or 1999. Results were not available from all stations for all years. In particular, there were blank problems at the Ny-Ålesund site so that the 1996 data could not be used. Earlier measurements of PCBs in air (1993-94) from Alert, Tagish, and Dunai have been published (Fellin *et al*., 1996; Stern *et al*., 1997) and, along with results from Ny-Ålesund and Stórhöfði (Heimaey Island, Iceland), were discussed in the previous AMAP assessment (de March *et al*., 1998). The congener distribution is derived from annual average concentrations. In general, PCBs 28, 31, and 52 form the majority of the ΣPCB$_{10}$ burden. Reporting of only ten PCB congeners seriously underestimates the total PCBs in air and makes source identification problematic. For example, ΣPCB$_{10}$ represented only 11-27% of total PCB (based on 88 congeners) at Alert (1994), Dunai, and Tagish (Stern *et al*., 1997). Major contributors to total PCBs at Alert, and probably at all Arctic sites, are the mono- and dichlorobiphenyls (CBs 3, 4, 5, 6, 8, 16, 18). Nevertheless, ΣPCB$_{10}$ was highly correlated (r^2 = 0.80) with total PCBs at Alert, which suggests that overall trends can be assessed.

Highest ΣPCB$_{10}$ concentrations were found at Ny-Ålesund compared to other sites (Figure 4·3). Results for Alert were consistently lower than other sites. Amderma, in northwest Russia, had average ΣPCB$_{10}$ of 4 pg/m³ in 1999-2000 (the first year of site operations), similar to Alert and lower than Pallas or Stórhöfði. Homologues at Amderma were more evenly distributed than at sites such as Alert and Tagish. There were similarities between Amderma and Dunai, another Russian site operated in the mid-1990s. The concentration range of 5 to 30 pg/m³ for ΣPCB$_{10}$, or about 20-100 pg/m³ for total PCBs, probably represents background levels independent of the station location. Air mass back-trajectories for Alert and Dunai, reported by Stern *et al*. (1997), showed that the PCB profile of air masses passing over Russia differed from air masses from the North American sector by having higher proportions and concentrations of penta- and hexachlorobiphenyls. Samples originating over the northern Pacific had higher proportions of trichlorobiphenyls.

4.1.2.3. PCDD/Fs

During the winter of 2000/2001, 15 weekly filter samples from Alert (particulate phase) were analyzed for PCDD/Fs (Hung *et al*., 2002a). The sampling period coincided with the occurrence of Arctic haze, when airborne particulate levels are high. Since PCDD/Fs have similar properties to PAHs (e.g., both originate from combustion sources and have low volatility with high tendencies to partition to aerosols), they are expected to follow similar seasonal cycles, and thus maximum concentrations of PCDD/Fs were anticipated during winter months. Table 4·1 (next page) compares the atmospheric concentrations observed at Alert (week 49 of 2000, weeks 3 and 7 of 2001) with those found at other locations. The concentrations of both ΣPCDDs and ΣPCDFs observed were lower than those found at Ny-Ålesund in the mid-1990s (Schlabach *et al.,* 1996) and lower than most other locations worldwide except the

Table 4·1. Comparison of reported concentrations of PCDD/Fs in Arctic and temperate air samples.

Location/dates	Total PCDD (fg/m^3)	Total PCDF (fg/m^3)
Alert, filter only (11/00-02/01)	2.1-13	2.4-46
Ny-Ålesund (21/4-17/5/95)[a]	28	76
Ny-Ålesund (21/7-23/8/95)[a]	16	51
Trout Lake, Wisconsin (mid-1990s)[b]	240	180
Bloomington, Indiana – suburban[b]	2500	2600
Nordrhein-Westfalen, Germany – urban and industrial[b]	3200	5500
Barbados (18/3/96-13/8/97)[c]	6.8	12
Bermuda (4/6/96-20/8/97)[c]	25	16

[a] Schlabach *et al.* (1996).
[b] Adapted from Table 3 of Luger *et al.* (1996).
[c] Calculated from supplementary material of Baker and Hites (1999).

ocean island locations of Bermuda and Barbados. The low PCDD/F levels are attributable to the remoteness of Alert and the absence of anthropogenic activities nearby. At the time of sampling, during the first week of 2001, Alert was mainly affected by air originating from the North Atlantic and North America. During the second and third weeks, when the air concentrations of PCDD/Fs peaked at Alert, the origin of the air mass shifted eastward further into Russia and Eurasia. After that time, the influence from Eurasia decreased while the North Atlantic sector regained dominance when the concentrations tapered off during the fourth and fifth weeks.

4.1.2.4. PAHs

All stations reported up to 25 PAH compounds in atmospheric samples to the AMAP database (see list in Annex Table 2); however, only 11 PAH compounds (PAH$_{11}$) were reported from all stations. Thus, a level comparison for the compounds anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b,j,k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, indeno[c,d]pyrene, phenanthrene, and pyrene was performed (Figure 4·4). Airborne PAHs were not reported in the previous assessment of POPs or petroleum hydrocarbons (Robertson, 1998). Results from Alert, Dunai, and Tagish from 1993-1994 were, however, reported by Halsall *et al.* (1997). Therefore, results
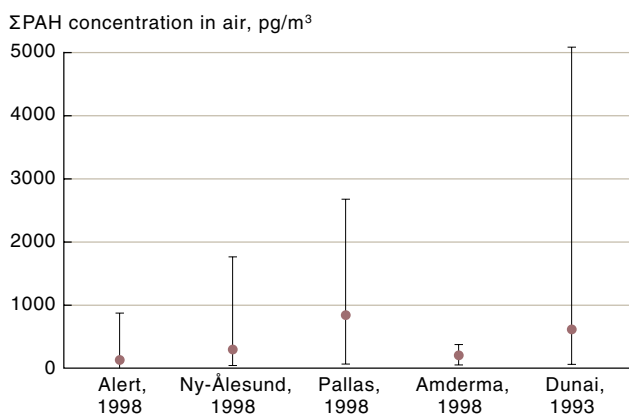
from 1993 for Dunai were included in Figure 4·4 for comparison with more recent results from Alert, Ny-Ålesund, Pallas, and Amderma to give a broader perspective of prevailing levels in air. Temporal trends of PAHs in air, using the long-term data, are presented in Section 5.1.1.3.

All stations reported wide ranges of air concentrations of ΣPAH$_{11}$, ranging from less than 10 pg/m^3 (the approximate reporting limit) to 5000 pg/m^3 (vapor phase and particles). Highest average annual concentrations of airborne ΣPAH$_{11}$ were found at Pallas and lowest at Alert (Figure 4·4). PAH concentrations in air from the Ny-Ålesund station were similar overall to those at Alert and Pallas, although some high maxima have been recorded (maximum value of 5800 pg/m^3 in 1997). The data from Amderma were missing results from winter time and therefore, were not suitable for comparison.

Halsall *et al.* (1997) found clear seasonality in the PAH concentrations at Alert, Dunai, and Tagish (1993-94), with highest concentrations occurring during the colder months. Highest concentrations of ΣPAHs (18 unsubstituted PAH) were found at Dunai (2580 ± 2230 pg/m^3) during the winter period (November-March) compared to Alert (714 ± 579 pg/m^3) and Tagish (312 ± 236 pg/m^3). Air mass back-trajectories revealed that long-range transport from Eurasian sources gave rise to elevated PAH concentrations at Dunai and Alert. These elevated concentrations were also characterized by high levels of dibenzothiophene, a marker of coal and oil combustion, and by high ratios of benzo[a]pyrene (B[a]P) to benzo[e]pyrene (B[e]P) (0.6-0.8) which resemble urban air sources. Air at Ny-Ålesund was also characterized by high B[a]P/B[e]P ratios (average 2.7) suggesting long-range transport, as well as possible influences from local combustion on Svalbard. This suggests very limited breakdown of B[a]P in the troposphere during the winter months. The B[a]P was 100% in the particulate phase during the winter period at all locations.

Halsall *et al.* (2000) developed a simple model to describe the removal processes for four PAHs: fluorene, phenanthrene, fluoranthene and benzo[a]pyrene, transported over a five-day period from the U.K. to the Arctic. They noted that U.K. urban air was dominated by phenanthrene (52% of the sum of four compounds) and had a relatively high proportion of B[a]P (3%). By contrast, air at Dunai had much higher fractions of fluorene. The more rapid degradation of phenanthrene by

ΣPAH concentration in air, pg/m^3

Figure 4·4. Average and range of concentrations of PAHs in air (gas + particle phase) from five Arctic air monitoring stations during the 1990s. Results are based on 11 PAH compounds that are monitored at all stations.

Table 4·2. Current-use pesticides and other semi-volatile organochlorine compounds that are now being measured in Arctic air (gas phase) during 1993-1994, pg/m^3 (Halsall *et al.*, 1998; Bidleman *et al.*, 1999; 2000; 2001; Helm and Bidleman, 2003).

Compound	Alert			Tagish			Dunai		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Current-use pesticides									
Endosulfan	4.22	0.02	16.2	7.05	0.08	88.6	2.99	0.05	7.18
Methoxychlor	0.27	0.07	1.43	0.36	0.09	6.53	0.41	0.22	0.73
Trifluralin	0.12	0.03	0.64	0.16	0.04	2.92	0.18	0.09	0.13
Pentachloroanisole	3.03	0.1	20.5	3.28	0.04	73.4	2.92	0.95	6.92
By-products									
Trichloroveratrole	0.93	0.05	10.1	1.85	0.07	20.6	1.49	0.15	3.65
Tetrachloroveratrole	0.19	0.05	0.99	0.25	0.07	4.52	0.44	0.15	2.19
Octachlorostyrene	0.79	0.04	2.96	0.67	0.07	11.9	0.60	0.11	1.74
Other halogenated compounds [a]									
Polychlorinated naphthalenes	0.50	<0.01	1.00	0.30	<0.01	1.40	0.79	<0.01	2.60
Coplanar PCBs [b]	0.085	0.03	0.20	0.047	<0.01	0.11	0.41	0.19	0.82
Polybrominated diphenyl ethers	282	10	868	424	27	2127	14	0	62
Chlorinated paraffins (C10-C13)	2.0	<0.4	7.3	–	–	–	–	–	–

[a] Based on retrospective analysis of 28-day composite samples from 1994 and January 1995 only.
[b] Coplanar PCB = Sum of CBs 81, 77, 118, 114, 105, 126, 156, and 169.

OH radicals, combined with a shift to the particulate phase as air masses pass into the polar region, probably accounted for the removal of phenanthrene and other higher molecular weight PAHs.

4.1.2.5. 'New' chemicals in the Arctic atmosphere
4.1.2.5.1. Current-use pesticides and chlorinated by-products

Halsall *et al.* (1998) reported the presence of the current-use pesticides endosulfan, methoxychlor, and trifluralin, as well as the pentachlorophenol metabolite, pentachloroanisole (PeCA), in air at Alert, Tagish, and Dunai during 1993-94. PeCA and endosulfan were among the top five pesticide-related compounds at all three sites, exceeded in concentration only by total PCBs, HCB, and α- and γ-HCH (itself a current-use pesticide). Methoxychlor and trifluralin were also detected at sub-pg/m^3 concentrations at all three sites (Table 4·2). Trifluralin volatilization from agricultural soils has been well documented (Majewski *et al.*, 1998), and it has a very short atmospheric half-life (Mackay *et al.*, 1997). Its appearance in Arctic air is therefore, surprising, especially at all three locations. However, more than 5×10^6 kg was applied annually in western Canada and U.S. in the mid-1990s for weed control in soybean, cotton, and cereal crops (NCFAP, 2001). Concentrations at Alert in 1994 (Halsall *et al.*, 1998) were more than 1000 times lower than observed over the Mississippi River by Majewski *et al.* (1998).

Methoxychlor had limited agricultural use on fruit crops (NCFAP, 2001) as well as in home-gardening products. Methoxchlor is more stable to sunlight photolysis than its chlorinated analog DDT, and thus may have a relatively long atmospheric half-life (Zepp *et al.*, 1977).

Two other methylated chlorophenolics, trichloroveratrole and tetrachloroveratrole, were reported by Halsall *et al.* (1998) in air from all three sampling locations at sub-pg/m^3 concentrations (Table 4·2). These compounds may originate from bleaching of wood pulp and chlorination of wastewaters. However, their widespread detection at all three locations suggests other unknown sources. Führer *et al.* (1996) have reported a series of chlorinated

anisoles and tetrachlorodimethoxybenzene in air from waste treatment plants and in marine air over the tropical Atlantic Ocean, suggesting that these chlorinated methoxylated aromatics are widespread in the troposphere.

OCS, a semi-volatile by-product of magnesium and chlorine manufacturing, was detectable at the three Arctic stations studied by Halsall *et al.* (1998). While mean concentrations of OCS were low relative to many OC pesticides, maximum concentrations were up to 15 times higher, especially at Tagish, illustrating that long-range transport events from source regions are contributing to the presence of OCS. Actual source regions have not been identified for OCS.

4.1.2.5.2. PCNs and coplanar PCBs

Polychlorinated naphthalenes, mono- and non-*ortho* substituted (coplanar) PCBs, polybrominated diphenyl ethers, and chlorinated paraffins were determined in retrospective analyses of pooled archived extracts from Alert and Dunai stations from 1994, and reported by Bidleman *et al.* (1999; 2000; 2001), Harner *et al.* (1998), and Helm and Bidleman (2003). The extracts represented 28-day composites (based on four weekly samples). Although use of the archived extracts meant that extraction conditions for these compounds were not optimized, the study nevertheless provided the first look at their presence in the Arctic as well as some information on seasonal variation.

The ΣPCN concentrations in 1994-1995 ranged from <0.01 to 1.00 pg/m^3 at Alert, <0.01 to 1.4 pg/m^3 at Tagish (both Canadian sites), and from <0.01 to 2.60 pg/m^3 at Dunai, Russia (Figure 4·5). The ΣPCN levels at Alert were within the range reported for 1993 (0.003-0.077 pg/m^3), while those at Dunai (0.001-0.009 pg/m^3) were comparable (Harner *et al.*, 1998). ΣPCN concentrations at these High Arctic sites were lower than ΣPCNs observed at lower latitudes over the eastern Arctic Ocean, Norwegian Sea, and Barents Sea (Harner *et al.*, 1998). Elevated ΣPCNs over the Barents Sea were associated with air trajectories from the North Sea – central Europe region, and, in subsequent work, Harner *et al.* (2000) found especially high ΣPCNs in urban air
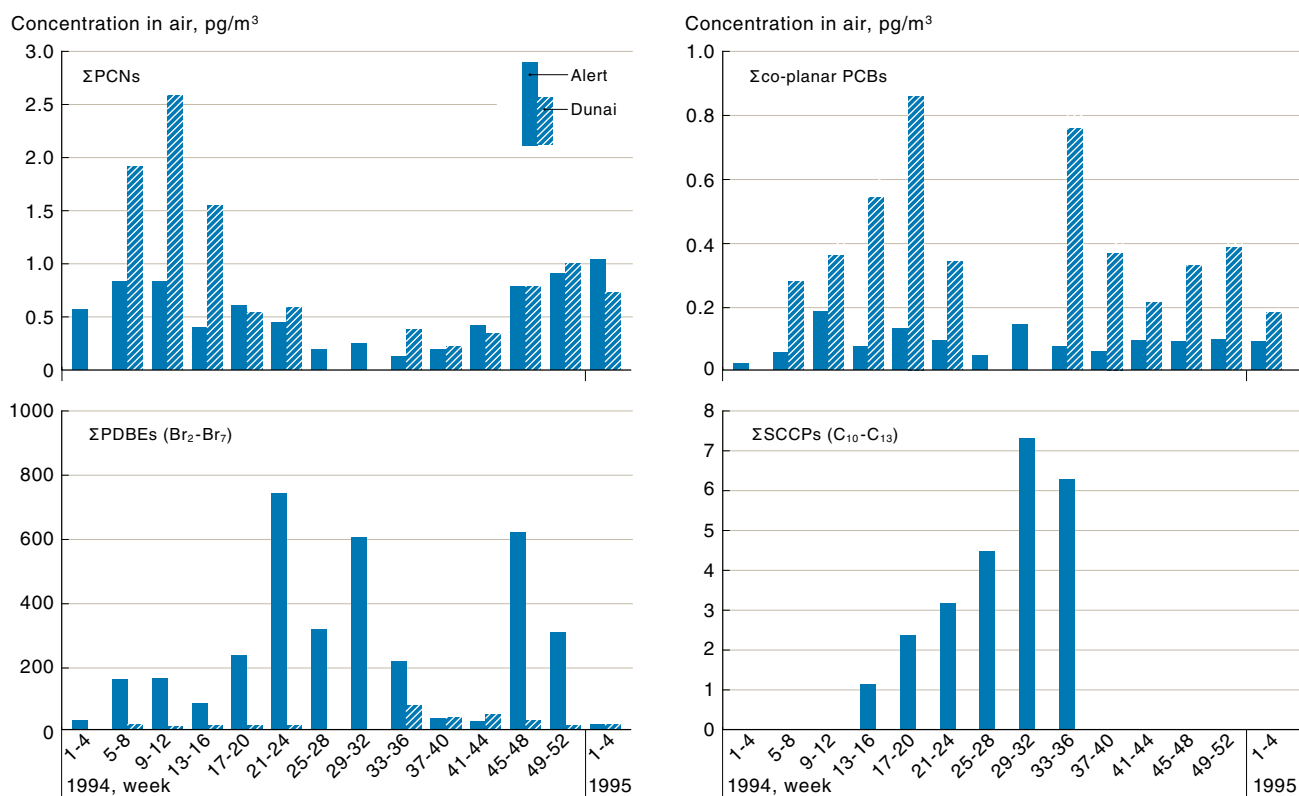
Figure 4·5. Concentrations of PCNs, co-planar PCBs, PBDEs and SCCPs in archived air samples (4-week composite samples from 1994 and early 1995).

from the U.K. Higher ΣPCN concentrations were found at Alert, Tagish, and Dunai in winter months (October-April) than in summer months (May-September) (Figure 4·5). This is similar to the seasonality observed for PAHs (Halsall *et al*., 1997), and suggests that PCNs, like PAHs, may be combustion-related and associated with Arctic haze during winter/spring, or lost due to effects of photolysis in summer. In support of the former explanation, certain PCN congeners associated with combustion (e.g., CNs 13, 26, 29, 44, and 54) were enriched in the winter air samples (Helm and Bidleman, 2003).

The coplanar PCBs (non-*ortho* and mono-*ortho* substituted PCBs: CBs 81, 77, 118, 114, 105, 126, 156, and 169) were also measured in the archived samples from 1994 to early 1995 (Helm and Bidleman, 2003) and in an earlier set from 1993 (Harner *et al*., 1998). With the exception of CBs 105, 118, and 156, these congeners have not been determined previously in Arctic air. The sum of these five congeners averaged 0.085 pg/m³ at Alert, 0.047 pg/m³ at Tagish, and 0.41 pg/m³ at Dunai for the 1994-95 set. Pentachlorobiphenyl congeners 118 and 105 were the dominant congeners at all sites. Seasonal variation was observed at the Dunai site with higher coplanar PCB concentrations during the summer months, while no trend was evident at Alert and Tagish. This agrees with the findings of Stern *et al*. (1997) that the contribution of PeCB congeners to ΣPCBs increased in the summer, particularly at Dunai. The authors suggested that emissions of Russian PCB mixtures with higher percentages of pentaCBs (PeCBs) could account for this observation. Coplanar PCB concentrations were elevated in shipboard samples collected from the Barents Sea in 1996 and, like PCNs, were associated with air transport from Europe (Harner *et al*., 1998).

The contribution to dioxin TEQs in air samples was calculated for PCNs and coplanar PCBs using relative potencies or toxic equivalency factors determined by H-II-4 E bioassays for both PCNs (Blankenship *et al*., 2000; Villeneuve *et al*., 2000; Kannan *et al*., 2001b) and PCBs (Giesy *et al*., 1997). Average ΣTEQs (sum of TEQs for PCNs, mono- and non-*ortho* PCBs) during the cold season of 1994-1995 were 0.022 fg/m³ at Alert, 0.0075 fg/m³ at Tagish, and 0.061 fg/m³ at Dunai. PCNs contributed approximately 70-74% of TEQs relative to the PCBs in air at Alert and Dunai and 31% at Tagish. PCN congeners 66/67, 64/68, and 73 contributed most of the TEQs due to PCNs, while PCB congener 126 was by far the dominant contributor to coplanar PCB TEQ.

4.1.2.5.3. PBDEs

PBDEs have been determined in archived air samples from the Canadian Arctic (Bidleman *et al*., 2001) and in a short air monitoring campaign on Bjørnøya (Norway) in 1999-2000 (Kallenborn, 2002a). In the Canadian study, PBDEs were measured in the same archived extracts as the PCNs and coplanar PCBs (Bidleman *et al*., 2001) (Table 4·2). Results for Dunai and Alert are shown in Figure 4·5. A significant fraction of the PBDEs (10-25% for BDE47; 10-90% for BDE99) were present in the particulate phase during the winter months. Levels of PBDEs in air samples from Dunai were much lower than at Alert. Much higher concentrations of PBDEs were found in air samples from Tagish (Table 4·2). The concentrations at Alert and Tagish were higher than air concentrations reported by Strandberg *et al*. (2001) for the city of Chicago (mean of 52 pg/m³ for 1997-1999) and much higher than concentrations at air monitoring sites

in the Great Lakes (means of 5-23 pg/m³ at three sites). In the case of Tagish, there is the possibility that incineration of household items in the region could contribute PBDEs to the air at the sampling site. At Alert, the source has not been identified.

In contrast, the air concentrations of total PBDEs observed at Bjørnøya ranged from 3-10 pg/m³ for the period of mid-December 1999 to mid-April 2000. The same suite of PBDE congeners as Alert were detected, with BDE47 predominating. Di- and TrBDEs (BDEs 13, 15, and 33) also were prominent. While no summertime concentrations are available from Bjørnøya, the results suggest that levels are much lower than at Alert or Tagish but similar to levels in rural areas of the Great Lakes. Thus, the reported results for Alert are probably not typical of concentrations of PBDEs in Arctic air, although they could be typical of low-temperature burning which is common in Arctic communities in Canada and Alaska. Further measurements are being conducted in an effort to better understand the levels and potential sources at Alert. The main PBDE congeners observed at all sites were BDEs 47, 99, 100, 153, and 154 with BDE99 having the highest concentrations. BDE47 predominated in all Great Lakes samples (Strandberg *et al.*, 2001), as well as in air samples in Sweden (Bergander *et al.*, 1995; de Wit, 2002). Mono-, di- and triBDEs were found in air samples from Alert, which may indicate photodegradation (debromination) of PBDEs during long-range atmospheric transport. The PBDE results, if typical, imply significant air contamination by these compounds. Air concentrations are higher than for ΣPCBs at the same sites.

4.1.2.5.4. SCCPs

SCCPs were analyzed in the same archived extracts from Alert that were analyzed for PCBs, coplanar PCBs, and PBDEs. SCCPs were above method detection limits only in samples from the summer months, and were highest in August. Individual homologue concentrations indicated that the chlorododecanes (C_{12}), accounted for approximately 50% of the total, the bulk being from the hexa- and heptachlorododecanes. Levels of SCCPs were below detection limits in polyurethane foam plugs (PUFs) for periods other than summer months and also in all filters (Bidleman *et al.*, 2001).

4.1.3. Air and fog water measurements at Bjørnøya

In 1994, very high levels of PCBs in Arctic char and sediment from the lake Ellasjøen on Bjørnøya (Bear Island, 74°N, 19°E), situated about 500 km southwest of Svalbard (Skotvold *et al.*, 1999), prompted a comprehensive research study which was started in 1999 (Evenset *et al.* 2002; Kallenborn, 2002a; 2002b). The studies included investigation of the influence of atmospheric long-range transport on POPs at the Ellasjøen area on Bjørnøya. This included the measurement of POPs in ambient air, snow, and fog water (Annex Table 3). Fog water was included based on information provided by the Norwegian Meteorological Institute that, on average, fog events were occurring more than 30% of the time in summer, and to assess fog as medium for transport and deposition pathways at Bjørnøya. A total of 20 air samples (average volume: 1000 m³) were collected every second week in 1999 and spring 2000. In the Ellasjøen catchment area and at the meteorological station on Bjørnøya, four fog water samples (approximately 50 L) were collected during the 2000 summer sampling campaign.

Continuous POP monitoring in ambient air at the 'Zeppelin Mountain' atmospheric research station (Ny-Ålesund, Svalbard) provided an excellent comparison for the Bjørnøya air samples. Typical POP distributions in air samples from Bjørnøya (meteorological station) and the Ny-Ålesund measuring station are presented in Figure 4·6. In general, the air concentrations of
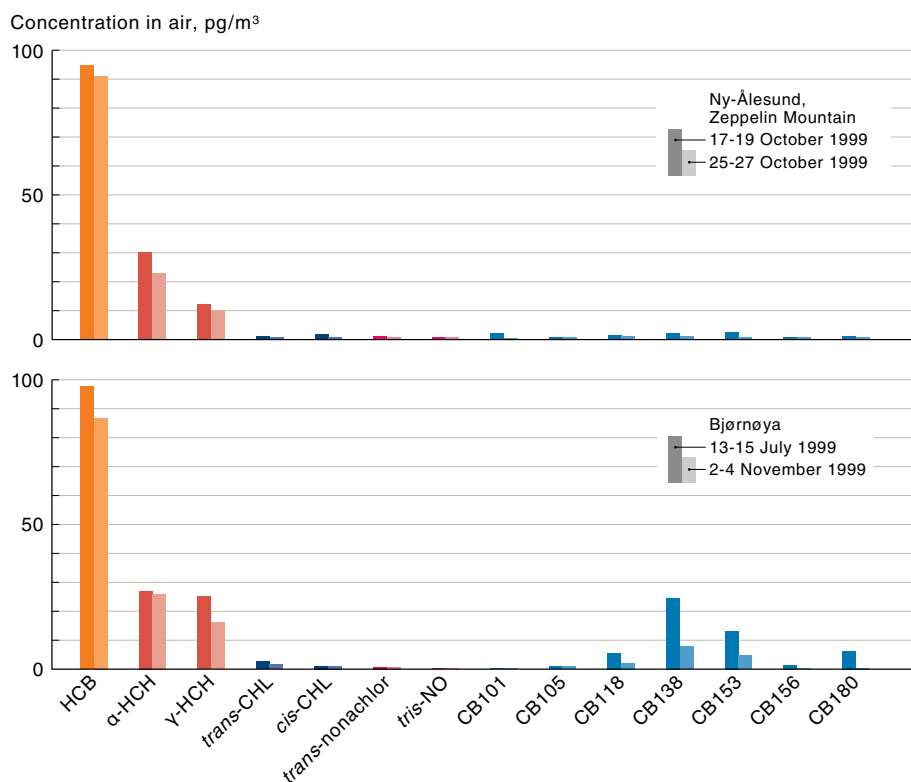

Figure 4·6. POP concentrations in ambient air from the Bjørnøya (Bear Island) meteorological station and the 'Zeppelin Mountain' atmospheric research station at Ny-Ålesund (Svalbard) in 1999.
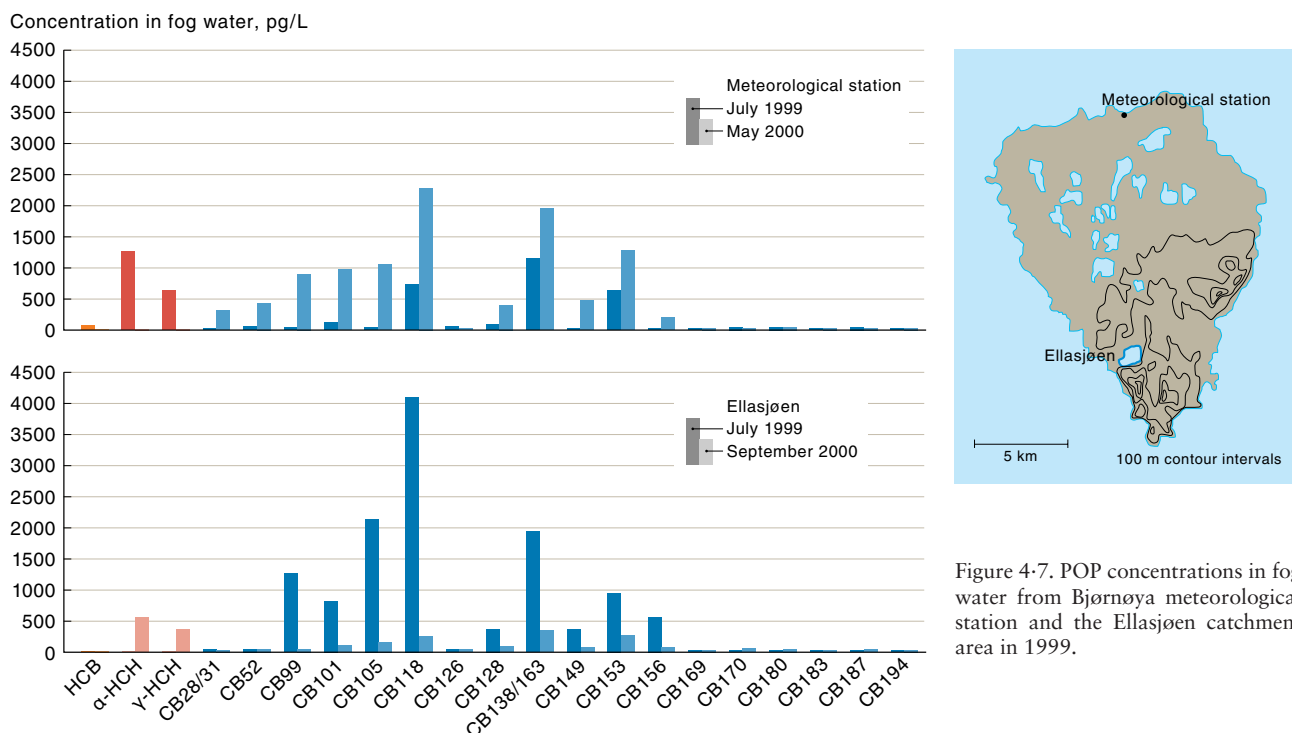
Concentration in fog water, pg/L

Figure 4·7. POP concentrations in fog water from Bjørnøya meteorological station and the Ellasjøen catchment area in 1999.

POPs were similar in ambient air collected at the Ny-Ålesund station and at Bjørnøya, with HCB dominating in all air samples from both stations. The comparison of the PCB patterns, however, reveals remarkable differences.

PCB concentrations in air samples from Ny-Ålesund are dominated by the lower chlorinated congeners. However, the medium chlorinated PCB congeners dominate the Bjørnøya air samples. Usually, the latter PCB pattern is characteristic for biological samples. The dominance of the medium chlorinated PCBs (CBs 153 and 138) is particularly evident in the sample taken in summer (13-15 July 1999). During this period of the year, the cliffs, mainly south of Ellasjøen, are populated by thousands of nesting seabirds. Therefore, one hypothesis for the unusual POP pattern is that the guano of seabirds redistributes into the air around Bjørnøya, and contributes significantly to the elevated POP air levels at Bjørnøya as the dominating local source during summer time.

Medium chlorinated PCB congeners also predominated in fog water samples collected at Bjørnøya, indicating the strong influence of local biological sources (e.g., seabird guano) on POP patterns (Figure 4·7). The influence of possible biological sources is also supported by the predominance of α-HCH in Bjørnøya fog. Seasonal differences are even more pronounced in fog samples compared to ambient air, probably due to the proximity of seabird cliffs and hatching areas in the Ellasjøen catchment area. The September sample from Ellasjøen (2000) showed low PCB concentration levels, whereas fog samples collected in July 1999 at the end of the nesting season at Bjørnøya had concentrations of PCBs (e.g., CB118) that were approximately ten times higher.

Comparable seasonal differences could not be found in the fog water samples from the meteorological station (16 km north of Ellasjøen), probably due to the absence of large seabird colonies.

4.1.4. Passive sampler measurements

Airborne concentrations of PCBs and HCB were measured by passive air samplers (semipermeable membrane devices, SPMDs) along a latitudinal transect from the south of the U.K. to the north of Norway during 1998-2000 (Meijer et al., 2003b). This work is part of an ongoing air sampling campaign in which data were previously gathered for 1994-96 (Ockenden et al., 1998). The SPMDs were exposed for two years in Stevenson screen boxes at remote sites in the U.K. and Norway. Sequestered amounts generally decreased between the two sampling periods by a factor 2-5 over four years, suggesting half-lives of 1.7-4 years. Spatial trends of the 1998-2000 data show a decrease in absolute sequestered amounts of the heavier PCBs with increasing latitude/distance from the source area, whereas the lighter PCBs were more equally distributed along the transect (Figure 4·8). However, relative sequestered amounts (expressed as a ratio to PeCBs)) show a clear latitudinal trend with the relative contribution of the lighter congeners increasing with increasing latitude, providing evidence of latitudinal fractionation. Absolute amounts of HCB were found to increase with increasing latitude, suggesting that this compound is undergoing cold condensation and global fractionation (Meijer et al., 2003a).

4.1.5. Precipitation
4.1.5.1. Background

It is well known that snow and ice play an important role in the hydrological cycle of the Arctic, but they also play a strong role in the behavior of POPs in the environment by modifying chemical cycling between the atmosphere and the Earth's surface. Snow deposition was studied extensively in the Canadian Arctic in the early 1990s and results were reviewed in the previous AMAP
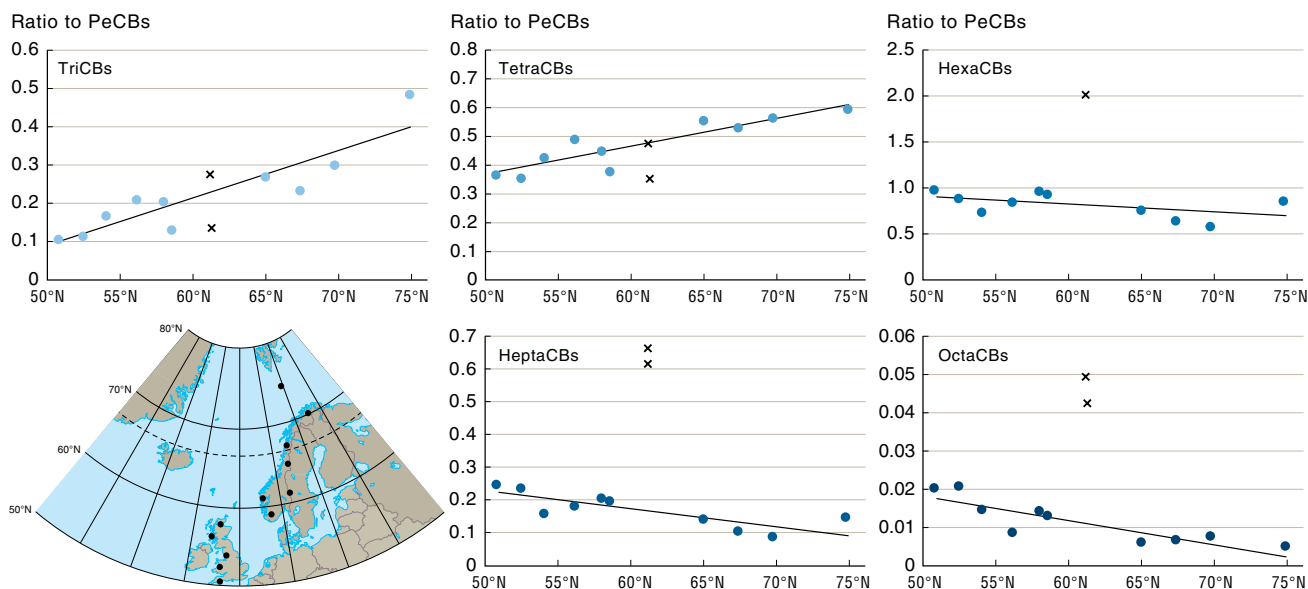
Figure 4·8. Latitudinal trends of PCB homologues in air in northwestern Europe determined using semi-permeable membrane devices (SPMDs) (Meijer *et al.*, 2003b). Results are expressed as ratio to PeCBs. Sites 7 and 8 (crosses) represent outliers omitted from the regression.

POPs assessment (de March *et al.*, 1998) and in Macdonald *et al.* (2000). Studies of POPs in snow on sea ice in the Russian Arctic were also assessed in the previous AMAP assessment report. No additional work, however, appears to have been conducted on POPs in snow in the Canadian or Russian Arctic during the second phase of AMAP. However, sampling and analysis of snow was conducted in northern Alaska, Svalbard and northern Norway.

4.1.5.2. Wet deposition

Bulk deposition of PAHs (31 congeners), PCBs (seven congeners) and HCHs (three congeners) was studied at a site in northern Finland (Pallas and Oulanka) and southern Finland (Evo) in the summers 1993-2001 (Figure 4·9) (Korhonen *et al.*, 1998; Korhonen *et al.*, 2002). In 1993-1994, the sampling in northern Finland was conducted at Oulanka, approximately 100 km south of Pal-
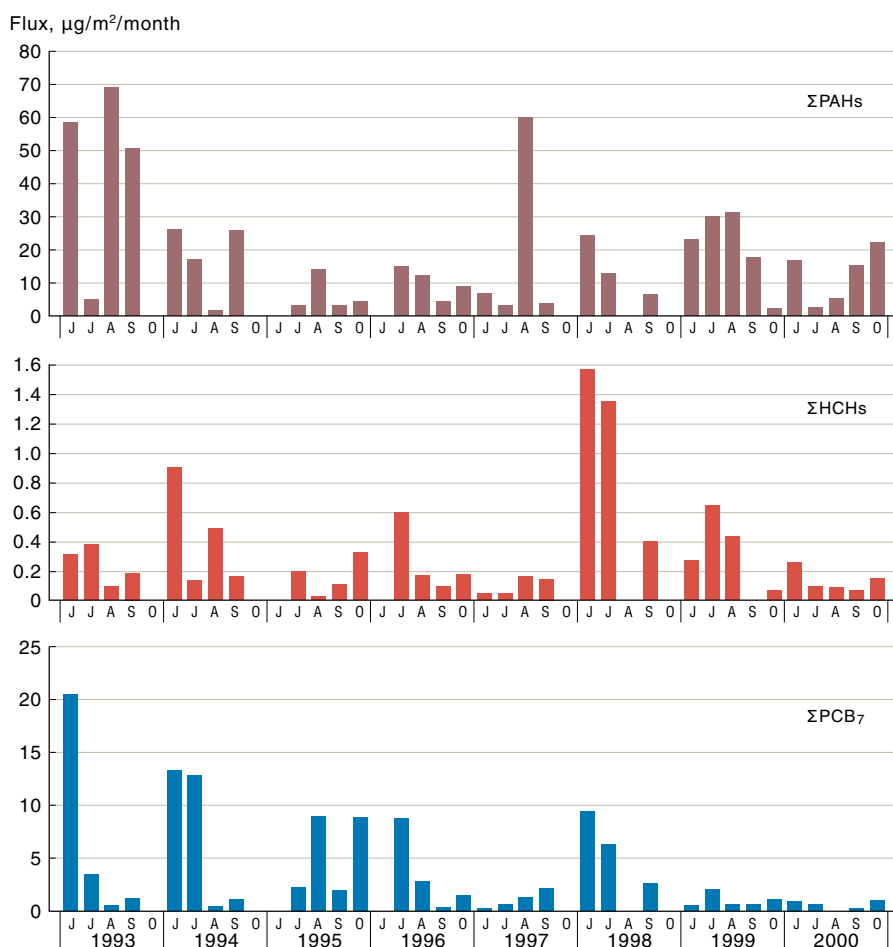

Figure 4·9. Fluxes of PAHs (sum of 31 compounds), ΣHCHs, and total PCB (estimated from analysis of seven congeners) from rainfall at Oulanka (1993-1994) and Pallas (1995-) in northern Finland during the summer months (June-October), 1993-2000.

las. This program represents the longest continuous precipitation monitoring program within the Arctic. Rainfall was collected using a glass funnel bulk sampler (30 cm in diameter) (Korhonen and Kiviranta, 2002). The mean deposition values of PAHs were 27.7 µg/m²/month in southern Finland and 17.9 µg/m²/month in northern Finland. The main PAH components in both southern and northern Finland were phenanthrene, fluoranthrene, and pyrene. PCBs averaged 1.6 µg/m²/month in the south and 1.1 µg/m²/month in the north. CBs 153 and 138 predominated among the seven congeners measured. Mean ΣHCH fluxes were 0.5 µg/m²/month and 0.3 µg/m²/month in the south and north respectively, and γ-HCH was the predominant isomer reflecting lindane use in the Baltic region (HELCOM, 2001). Overall, the deposition of all chemical groups was about 30% higher in southern Finland than in northern Finland. The temporal trends of PCBs in wet deposition at Pallas are discussed in more detail in Section 5.1.2.

4.1.5.3. Fluxes of POPs in surface snow

Garbarino et al. (2002) analyzed snow cores taken over the sea ice from two northwestern Alaska estuaries, Kasegaluk Lagoon, and Admiralty Bay, in 1994-95. They found non-detectable levels of most persistent OC pesticides. However, quantitation limits in the study were high (e.g., 4 ng/L for α-HCH) which precluded detection of most compounds. POPs were measured in surface snows and snow cores (see Section 5.1.3) from Summit (Greenland) and on the Lomonosovfonna and Austfonna glaciers in Svalbard, for 'legacy' OC pesticides and PCBs, by Hermanson et al. (2002) and Matthews (2001) (Table 4·3). Lomonosovfonna is the highest ice sheet on Svalbard at approximately 1250 m above sea level (asl). It is about 35 km from Pyramiden, 75 km from Longyearbyen and 110 km from Barentsburg, all coal-mining towns on western Svalbard. Austfonna is approximately 600 m asl, and is located 180 km northeast of Lomonosovfonna. Summit (3230 m asl), the highest point on Greenland, is roughly 1300 km westsouthwest of Svalbard.

The PCB profile in near-surface snow layers from Lomonosovfonna is shown in Figure 4·10. The volatility of PCB declines with increasing chlorine substitution (from left to right in the diagram). The homologue distribution of PCBs suggests that the more volatile Di- and TrCBs remain largely in the atmosphere or are revola-

tilized and accumulate in small amounts in snow. The less volatile Te- and PeCB homologues accumulate in relatively large amounts in the upper meter of snow, but significant amounts of them may evaporate back into the atmosphere before final burial, resulting in larger proportions of Hp- and OcCB homologues in the deeper snow layers. The high snow surface percentage of the Te- and PeCB homologues, and the lower percentages of Hp- through NoCB homologues suggests that some post-depositional volatilization may be occurring. This is plausible if the homologue distribution of PCB deposited to Lomonosovfonna has not changed. The overall pattern of homologues at the Lomonosovfonna Ice Cap shows a higher proportion of more highly chlorinated PCBs than observed by Gregor et al. (1995) on the Agassiz Ice Cap on Ellesmere Island.

The snow accumulation rate at Austfonna is nearly twice as high as Lomonosovfonna, and is more than twice as high as Summit. Thus, fluxes are the most appropriate way to compare among sites. The proximity of Lomonosovfonna to population centers on Svalbard makes it more likely to accumulate local contaminants than Austfonna, as indicated by the pesticide data. The high flux of ΣDDTs at Lomonosovfonna, nearly nine times greater than Summit, suggests a significant, possibly local source. Other pesticides (ΣHCHs, dieldrin, and endosulfan (α- and β-isomers)) are all higher at Lomonosovfonna than at Austfonna and Summit. Samples from Summit show the highest flux of ΣPCBs, about 25% greater than Lomonosovfonna. The flux of HCB is the lowest of any observed compound, but is 70% greater at Summit than at Lomonosovfonna. By comparison, surface fluxes for ΣPCBs on the Agassiz Ice Cap were about 200 ng/m²/yr in 1992/1993, and ranged from 50 to 650 ng/m²/yr in lower layers (Gregor et al. 1995). PCB deposition at Mould Bay in the Canadian High Arctic ranged from 400 ± 300 to 600 ± 500 ng/m²/yr in 1990-1991 and 1992-1993, respectively (Franz et al., 1997).

Although flux measurements for PCBs in snow from mainland Norway are not available for comparison, Carrera et al. (2001) reported concentrations of ΣPCBs at Ovre in western Norway (63°N, 7°E) of 730 ng/L. ΣDDTs and ΣHCHs were below detection limits in the same samples. In northern Norway at a site near Tromsø, Enge et al. (1998) collected snow in stainless steel lysimeters and reported ΣPCB (eight congeners) concentrations ranging from 1500 to 3600 pg/L sam-

Table 4·3. Concentrations (pg/L) and fluxes (ng/m²/yr) of chlorinated pesticides and PCBs in Arctic glacial snow from Lomonosovfonna and Austfonna (on Svalbard) and Summit (Greenland). (Matthews, 2001; Hermanson et al., 2002).

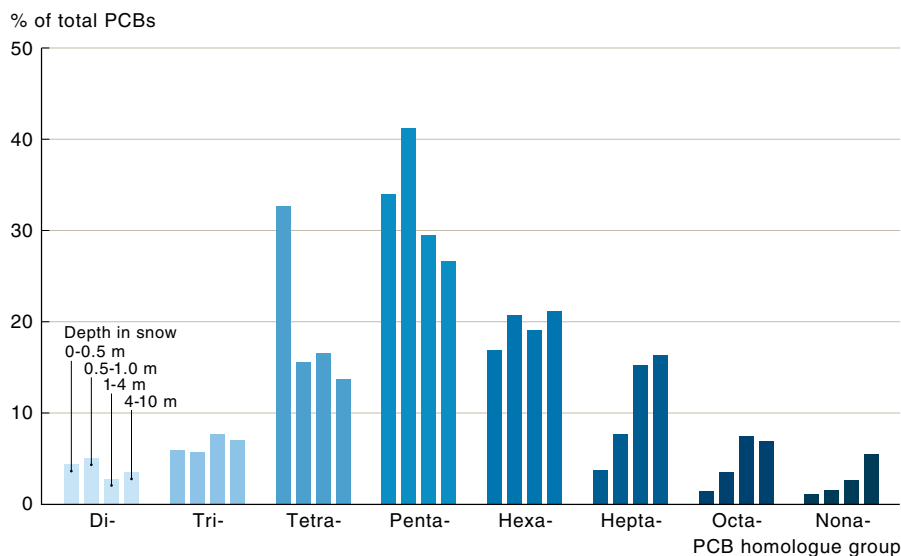| Site	Snow accumulation L/m²/yr	Collection year	HCB	ΣHCHs	ΣCHLs	ΣDDTs	Dieldrin	Endo sulfan	ΣPCBs
			pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
Lomonosovfonna	340	2000	3.4	169	137	550	87.7	85.2	575
Austfonna	657	1998	n.m.	14.1	n.m.	n.m.	11.4	13.2	n.m.
Summit	293	2000	8.2	36.2	105	83.6	94.2	25.2	994
			ng/m²/yr	ng/m²/yr	ng/m²/yr	ng/m²/yr	ng/m²/yr	ng/m²/yr	ng/m²/yr
Lomonosovfonna	340	2000	1.2	57.4	46.6	187	29.8	29.0	195
Austfonna	657	1998		9.3			7.5	8.7	
Summit	293	2000	2.4	10.6	30.7	24.5	27.6	7.4	291

n.m. = not measured.

% of total PCBs

Figure 4·10. PCB homologue distribution at various near-surface depths in snow cores from the Lomonosovfonna glacier on Svalbard (Hermanson *et al.*, 2002).

pled over a three-month period. PCB concentrations in surface snow from the same site were 1040 pg/L, reflecting volatilization from the snow pack.

PAHs

Summit, at the centre of the Greenland Ice Cap (3230 m asl), has been the main location for investigations of PAHs in Arctic glacial snow cores. Jaffrezo *et al.* (1994) determined dissolved and particulate bound PAHs in a snow core from Summit, collected in 1991, representing four years of deposition. They observed a strong correlation between sulfate and total PAH in the snow with maxima in winter/spring and summer minima. Total PAH averaged 1360 ng/g (range 600-2370 ng/g) in the combined dissolved and particulate phases. The pattern of PAH compounds in the surface snow indicated that fossil fuel combustion was the major source as well as biomass burning. Major PAH compounds were naphthalene, phenanthrene, fluoranthene, pyrene, benzo[a]pyrene and benzo[g,h,i]perylene. The latter compound comes mainly from combustion of coal and petroleum (Mascelet *et al.*, 1986). Peters *et al.* (1995) analyzed snow collected from the Agassiz Ice Cap in 1993 as part of a study of a snow core. They found naphthalene (NAP) was by far the major PAH present, representing 88% of ΣPAHs (16 compounds). Similar to the observations of Jaffrezo *et al.* (1994), phenanthrene, fluoranthene and pyrene were the major 3- and 4-ring PAHs present. Excluding NAP, ΣPAH concentrations at Agassiz were 19 ng/L, significantly higher than at Summit. Peters *et al.* (1995) estimated an annual deposition of ΣPAHs (16 unsubstituted PAH compounds) to the Canadian Arctic and subarctic of 37 t per year in the 1980-1990s, based on a deposition flux of 11 μg/m^2/yr. Masclet *et al.* (2000) found PAH concentrations of 1.2 ng/g in particulate matter filtered from melted snow (5-12 L volumes) in surface snows from the Greenland Ice Cap. The PAH levels had pronounced seasonal trends coinciding with Arctic haze events (see Section 5.1.3.2). Measurements of PAHs were performed on a 122 m ice core record from the Lomonosovfonna glacier on Svalbard, but only NAP was detectable (Vehviläinen *et al.*, 2002). This was attributed to the very small (average 56 g) sample sizes. The results suggested that prior to the 1930s, NAP concentrations were below the detection

limit, but increased until the 1980s. In general, NAP concentrations (5000-53 000 ng/g) at Lomonosovfonna were six times lower than in the Agassiz Ice Cap (Peters *et al.*, 1995), but are about fifty times higher than in Greenland (Jaffrezo *et al.*, 1994).

4.1.5.4. 'New' chemicals in snow and ice

Garbarino *et al.* (2002) reported detection of the insecticide chlorpyrifos in snow from two northwestern Alaska estuaries at concentrations ranging from <10 to 80 ng/L as well as the herbicide dacthal (detectable near the quantitation limit of 4 ng/L). Chernyak *et al.* (1996) had previously reported chloropyrifos at 0.17 ng/L in melted sea ice samples from the Bering Sea. Dacthal has not been reported previously in Arctic samples but has been shown to be transported regionally in North America (Rawn et al. 1999).

Laniewski *et al.* (1998) analyzed ice samples from the Mårma glacier in the Swedish Arctic (68°10'N, 18°40'E) and detected a number of chlorinated organics not previously reported in snow or wet deposition in the Arctic. The tri(chloroalkyl)phosphates (TCAPs) were present in the ice sample from the Mårma glacier and snow from southern Sweden and Poland, but were not present in ice from Queen Maud's Land in Antarctica. The isomers detected were tris(2-chloroethyl)phosphate, tris(1-chloro-2-propyl)phosphate, and bis(1-chloro-2-propyl)(3-chloro-1-propyl)phosphate. These compounds are semivolatile (vapor pressures 1-10 Pa at 25°C; (WHO/IPCS, 1998)) and have come into increasing use during the 1990s for use as flame retardants in plastics. Also detected in the glacier were dichlorobenzenes and tetrachlorobenzene (Laniewski *et al.,* 1998).

4.1.5.5. Snow and rain deposition at Bjørnøya

Snow and meltwater were collected in 1999/2000 in order to assess transport and deposition pathways of POPs within the Bjørnøya ecosystem (Evenset *et al.,* 2002; Kallenborn, 2002a). This was in connection with the measurement of POPs in ambient air and fog (see Section 4.1.3) in a study addressing high POP levels in sediment and Arctic char. During a first, preliminary sampling campaign in 1999/2000, two meltwater samples and one deposition snow sample were collected for

Table 4·4. POP levels in snow deposition and meltwater samples from Bjørnøya (pg/L)[a]

Sampling Period	Meteorological station				Ellasjøen				
	Sample type	ΣPCBs	ΣHCHs	HCB	Sampling period	Sample type	ΣPCBs	ΣHCHs	HCB
May 2000	Snow	7220	78	2	Summer 2000	Snow	3200	32	1
July-Sept. 2000	Meltwater 1[b]	1180	490	i.c.	June-Sept. 2000	Meltwater 4[b]	391	921	i.c.
Sept.-Nov. 2000	Meltwater 2[b]	845	1800	i.c.	July 1999	Meltwater 3[b]	3740	740	n.a.

[a] ΣPCBs = 17 congeners, ΣHCHs = α- and γ-HCH, HCB = hexachlorobenzene.
[b] During the summer period of the year, a substantial amount of rain deposition was collected in addition to snow.
i.c. = interference in the chromatogram, n.a. = not analyzed.

POP analyses at the meteorological station. At the lake Ellasjøen, two meltwater and three snow deposition samples were quantified. Meltwater was sampled at the meteorological station and Ellasjøen using a 1-m² meltwater collector. Surface snow was collected over a long period of time (1-2 months) and allowed to melt under natural conditions. Thus, the meltwater sample represented an integrated sample over a long period of time. The POP pattern of the meltwater sample was influenced by remobilization and volatilization processes.

PCBs were the dominant OC contaminants in snow (Table 4·4), while HCHs were the main contributors for the chlorinated pesticides in snow and meltwater from Bjørnøya. In two meltwater samples (Meltwater 2 and Meltwater 4), HCH was the predominant compound class (Table 4·4). Due to relatively high volatility, HCB probably re-volatilizes into the atmosphere and therefore dominated in Bjørnøya ambient air samples but not in meltwater and snow. The highest PCB concentrations were found for snow deposition, collected close to the meteorological station.

These findings indicate characteristic differences found for the distribution of HCHs and PCBs in snow deposition and meltwater. In all snow deposition samples, only minor contribution from HCHs was found. However, the contribution of HCH to the overall contamination is significantly higher in meltwater samples (Figure 4·11). This may partly be caused by re-evaporation of lower chlorinated PCBs into the atmosphere and the parallel continuous uptake of water soluble α- and γ-HCH from the atmosphere. However, the number of samples analyzed is too small to draw final conclusions about this hypothesis regarding snow surface/atmosphere exchange processes. It should be noted that during the summer season, both rain and snow deposition were collected and therefore, a direct correlation between meltwater properties and POP contamination is difficult.
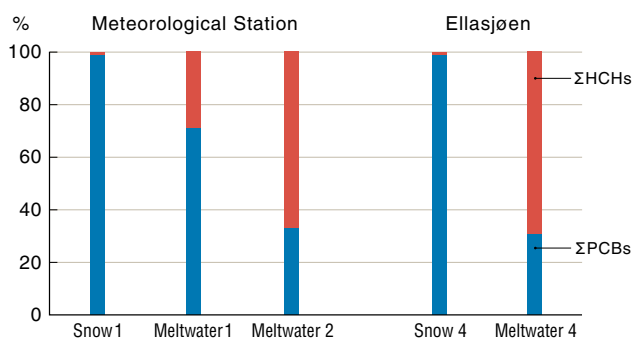

Figure 4·11. Percentage distribution of ΣHCHs and ΣPCBs in snow and meltwater samples from Bjørnøya (Bear Island).

The same analytical method was used for meltwater samples collected at the valley Dividalen in Norway and at Bjørnøya (Ellasjøen and meteorological station). Concentrations of ΣHCHs and ΣPCBs in Bjørnøya meltwater were comparable with those from the Norwegian mainland site. ΣPCB levels of 3600 and 1500 pg/L were found in two meltwater samples from Dividalen. The two meltwater samples taken at the Bjørnøya meteorological station had slightly lower levels of PCBs than the Ellasjøen and the Dividalen samples. No distinct difference in the PCB levels between the Bjørnøya samples and the meltwater taken at the Norwegian mainland was found. This is a rather surprising result, since no local PCB source is known at Bjørnøya, whereas possible sources close to the Dividalen sampling site are known. The extent to which biological sources such as seabird guano, influence the PCB levels, patterns, and distribution of other POPs in snow remains to be determined, however.

4.1.6. Summary and conclusions – air and precipitation

Measurements of POPs in Arctic air have continued on a weekly basis at locations in Canada, Iceland, Norway, Finland, and Russia. A large temporal-trend dataset is being developed as discussed in Section 5.1. With six stations reporting results during the 1990s (although not all operational in all years), it is possible to examine geographical differences in concentrations of major OCs and PAHs among sites and to compare these with results from monitoring stations in southern Canada/U.S. and Sweden. At three stations, results were also available for some current-use pesticides and flame retardants.

In this assessment, spatial comparisons were limited to a relatively small suite of OCs that have been measured at all stations and reported to the AMAP data center. Thus, only ΣPCB₁₀ congeners have been measured at all stations, although data are available for up to 102 congeners at some sites. The reporting of ΣPCB₁₀ underestimates total PCBs in air by four to five times because mono- and dichlorobiphenyls, which predominate in Arctic air, are underrepresented in the list.

Results for ΣHCHs, chlordane, and DDT-related compounds suggest uniformly low concentrations of these pesticides in Arctic air during the mid- to late 1990s. This is expected because, with the exception of γ-HCH, all others have been banned for at least ten years or more in circumpolar countries, although there may be some use of DDT continuing in Russia (see AMAP, 2003). The concentrations of these three OC pesticides in Arctic air were lower than in air at a rural site in the Great

Table 4·5. Comparison of average concentrations of persistent OCs and PAHs in the Great Lakes and at several Arctic locations for approximately the same time period. Concentrations (pg/m^3) represent combined gas and particulate (filter) phases.

	Great Lakes rural[a,c] 1996-98		Great Lakes urban[b,c] 1996-98		Alert 1996-98		Ny-Ålesund 1996-98		Stórhöfði 1996-98		Amderma 1999-2000
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean
ΣPAHs	1160	100	113000	15500	274	34.3	2750	320			
ΣHCHs	97	7.2	131	10	37.2	3.1	55.7	2.8	22.2	1.3	
ΣCHLs	9.4	1.1	151	15	2.0	0.2	1.9	0.1	0.5	0.01	
ΣDDTs	4.5	0.66	80.2	7.9	0.8	0.1	2.1	0.2	2.6	1.2	
HCB	68	2	110	6	40.8	3.2	94.0	6.6	9.8	1.2	
ΣPCBs[d]	63	6	1800	170	7.3	0.6	125.0	35.9	67.4	19.1	4.1

[a] Eagle Harbor – western Lake Superior.
[b] Chicago (downtown).
[c] In the Great Lakes samples, HCH represents the sum of α- and γ-HCH. ΣCHLs represents the sum of *cis*- and *trans*-chlordane and *trans*-nonachlor. ΣDDTs represents the sum of the *p,p'*-isomers of DDT and its two metabolites, DDE and DDD.
[d] Sum of 100 PCB congeners in Great Lakes samples and $ΣPCB_{10}×4$ for Alert, Ny-Ålesund, Stórhöfði, and Amderma.

Lakes region near the shore of Lake Superior (Eagle Harbor) during the same time period (Table 4·5). However, the differences between this temperate North American site and the Arctic stations were less than a factor of 2 for ΣDDTs at Ny-Ålesund, Stórhöfði, and Amderma.

Concentrations of PCBs and HCB at Ny-Ålesund are higher than in rural air in the Great Lakes (Buehler *et al.*, 2001). All other Arctic sites have lower average levels than the rural Great Lakes. The air sampling building at Ny-Ålesund was replaced in 1998 (completed by August 1998) and the elevated CB28 and 31 concentrations observed during the remainder of 1998 may be related to contamination during startup of the new location, although similar concentrations were found in 1999 and 2000 (see Section 5.1). Urban air (Chicago) has much higher concentrations of PCBs and PAHs than any Arctic sites as expected (Table 4·5). Combined with results from Dunai and Stórhöfði, where ΣPCB concentrations were also higher than at Alert and in the upper Great Lakes, the results suggest that, during the period of 1996-1998, the European Arctic continued to receive air with elevated PCB concentrations compared to the North American Arctic.

Although there are fewer data for PAH, higher PAH levels are seen at Dunai and Svalbard than at Alert, Tagish (Halsall *et al.*, 1997) or Lake Superior (Buehler *et al.*, 2001), which also suggests that the European Arctic is receiving elevated atmospheric inputs in comparison to the western Canadian and High Arctic archipelago. Further assessment of the importance of European and particularly Russian sources of PAHs for air concentrations over the Barents Sea awaits more complete datasets from the station at Amderma in northwestern Russia and Pallas in northern Finland.

Concentrations of pesticides and PCBs in Table 4·5 can also be compared with those found at Tenerife (Canary Islands) (28°N, 16°W) during 1999-2000 (Van Drooge *et al.*, 2002). Samples were taken in the free troposphere at 2367 m asl altitude and near sea level at 47 m asl. Concentrations of all substances were higher within the marine boundary layer than at high altitude, except for HCB, which appears to be very well mixed throughout the troposphere. The free tropospheric concentrations were similar to those found at Arctic stations for HCB (51 pg/m^3), ΣHCHs (17 pg/m^3) and ΣDDTs (5 pg/m^3). ΣPCB concentrations (sum of 19 congeners) at

Tenerife were similar to levels measured at Ny-Ålesund and Stórhöfði (78 pg/m^3 at 2367 m and 190 pg/m^3 at sea level), taking into account the difference in the number of congeners.

The past five years has seen a major increase in the number of halogenated organic chemicals detected in Arctic air. Among the current-use pesticides, the presence of trifluralin is surprising because of its short atmospheric half-life. Trifluralin is a common air contaminant in agricultural areas of the U.S. and Canada and is present at ng/m^3 concentrations during application periods in May-June (Grover *et al.*, 1988; Hoff *et al.*, 1992; Majewski *et al.*, 1998). Thus, the high volume of trifluralin use results in detectable levels of this pesticide, and possibly others such as methoxychlor, even though removal processes in the atmosphere are quite rapid. The presence of similar levels of trifluralin at Dunai implies Asian and Russian uses of this pesticide.

The presence of PCNs in air at Alert and over the Barents/Kara Seas found by Harner *et al.* (1998) is an important new finding. The PCNs contribute significantly to total TEQs in air and are correlated with PAHs, suggesting that they are combustion by-products associated with Arctic haze. The Arctic haze association is important because the annual PCN profiles seem to be meteorologically driven, with maxima in winter. A full evaluation of their importance requires concurrent measurements of PCDD/Fs as well as coplanar PCBs. These compounds have not yet been routinely measured and to do so may require modification of sample extraction methodology to optimize their recovery from the particulate phase, as well as increased air volumes for some sampling stations.

A pilot study conducted at Alert revealed that although levels of PCDD/Fs found in air were low, there are still possibilities of significant accumulation of these compounds in other Arctic environmental media due to the low temperatures in the Arctic and slower degradation processes. The PCDD/Fs also have to be considered in the context of coplanar PCBs and PCNs. Further measurements of PCDD/Fs are needed in order to gain more insight into the fate of these compounds in the Arctic given predictions of significant deposition in Nunavut. A report by Commoner *et al.* (2000) has focused attention on the current levels, pathways, and sources of PCDDs and PCDFs in the Canadian Arctic.

In their study, Commoner *et al.* (2000) predicted dioxin TEQ deposition of about 4 to 53 pg TEQ/m²/yr to terrestrial surfaces near eight communities in Nunavut. Highest deposition in the south and east was predicted because of the preponderance of dioxin sources in the eastern U.S. and Canada. Russian and northern European sources were regarded as insignificant for Nunavut in comparison to those in the mid-west U.S. and Ontario and Quebec (Commoner *et al.*, 2000).

The presence of PBDEs in Arctic air has been demonstrated at Alert and Tagish, as well as Dunai in the Russian Arctic and at Bjørnøya in the European Arctic. The elevated levels of PBDEs found at Alert and Tagish must be viewed with caution given that they are far higher than levels found in the Great Lakes region, including within the city of Chicago, and higher than levels found at Bjørnøya during winter time. The results for PBDEs illustrate a general problem with all air sampling for widely used products such as flame retardants, surfactants, and plasticizers (including chlorinated paraffins, perfluorinated acids, and phthalates), which is that sampling media or emissions from building materials or use of materials near the site could inadvertently contaminate the samples. Further work is urgently needed to confirm the levels of PBDEs in air given their increasing presence in Arctic biota (Section 5.4.6.1).

Toxaphene, a major contaminant in Arctic biota, which has also been widely measured in Arctic seawater during the period of 1996-2001, remains relatively unstudied in Arctic air. No new measurements have been reported from any of the monitoring stations. Given the importance of this contaminant in both the North American and European Arctic, additional data are needed in order to examine levels and sources.

The very limited data for PCBs and OC pesticides in snow and precipitation, with the exception of detailed studies at Bjørnøya, illustrates a key knowledge gap about the fate of airborne OCs. For example, the proportion of the contaminants measured in air that is actually entering the snow or soil environment and then re-volatilized is not known. A full understanding of the pathways is essential for predicting future trends and also for evaluating other chemicals that have been detected in Arctic air.

The concentrations of PCBs in snow at Bjørnøya were similar to those in northern Norway (Enge *et al.*, 1998) and much higher than on the Lomonosovfonna and Austfonna glaciers in Svalbard or at Summit, on the Greenland Ice Cap. Air concentrations of PCBs were also higher at Bjørnøya than at Ny-Ålesund. These results suggest a strong influence of local biological sources (e.g., seabird guano) on the POP patterns. This is a surprising new finding which may also be the case on other islands colonized by seabirds.

4.2. Terrestrial environment

Levels of OCs have been shown to be generally lower in the terrestrial Arctic ecosystem than in the aquatic ecosystem (de March *et al.*, 1998). For this reason, the amount of research focused on, and the available data for, the terrestrial Arctic is much more limited, both historically (see Thomas *et al.*, 1992; de March *et al.*, 1998) and in recent years. A number of terrestrial mammals and birds are however important as food species (e.g., caribou), and levels of OCs could be an issue for human consumption. Temporal trends in birds of prey remain an important data set but temporal trend studies in other species, such as lichen or caribou, have not been carried out or continued. More volatile, less bioaccumulative OCs, in particular HCH, are the most common individual compounds found in soil and lower trophic-level terrestrial organisms. At higher trophic levels, such as in wolf and birds of prey, the more bioaccumulative OCs, in particular DDTs and PCBs, become more prevalent.

4.2.1. Soils and plants

There has been a significant amount of new work on concentrations of POPs in soils and plants since the previous AMAP POPs assessment. Global surveys of PCDD/Fs in soils and tree bark by Wagrowski and Hites (2000), and PCBs in soils (Ockenden *et al.*, 2002), have included Arctic sites. An extensive survey of OCs in soil and plants in Russia has also been carried out (RAIPON/AMAP/GEF Project, 2001). This latter study is important because the Russian Arctic was previously identified as a knowledge and data gap for assessment of circumpolar trends of OCs. A project that examined levels of OCs in vegetation and soil from Alaska and Siberia during the years 1991-1993 (Ford *et al.*, 2000) that was not available for the first AMAP report is also considered.

4.2.1.1. PCBs and OC pesticides in vegetation

Samples of vegetation were collected from four regions of the Russian Arctic: Kola Peninsula; Pechora Basin; Taymir Peninsula (Dudinka and Khatanga); and, Chukotka (Kanchalan and Lavrentiya) in 2000/2001 for analysis of OCs (RAIPON/AMAP/GEF Project, 2001). The four regions cover a wide geographical area (Figure 4·12). Pooled samples of three types of vegetation were collected, including berries, lichens, and mosses; the species included for each type of vegetation varied with the region (see Annex Table 4 for species). PCBs were the predominant OC in vegetation, followed by DDT, HCH, and chlorobenzenes. Toxaphene (sum of Parlars 26, 52, and 60; detection limits approximately 0.2 ng/g in biota) and PBDEs (detection limits approximately 0.5 ng/g in biota) were not detected in any vegetation samples, but the detection limits of this study are above the levels normally found for these compounds in vegetation in the Arctic.

Across all regions, OC concentrations were greatest in mosses, followed by lichens and then berries, which had very low concentrations. In general, strong geographical trends in OC concentrations were not observed between regions for any of the three vegetation groups (Figure 4·12 and Annex Table 4). PCB concentrations (3.1-3.9 ng/g dw) in lichens are in the same range reported previously for lichens in the Russian Arctic, collected in 1994 (Melnikov *et al.*, 1995), but are an order of magnitude higher than levels reported for lichen from the Canadian Arctic in 1992-1993 (de March *et al.*, 1998). HCHs were the only OC group with higher concentrations in Canadian Arctic lichens compared to the Russian Arctic. The fact that the Canadian lichens were collected in the early 1990s, and that ΣHCH levels have
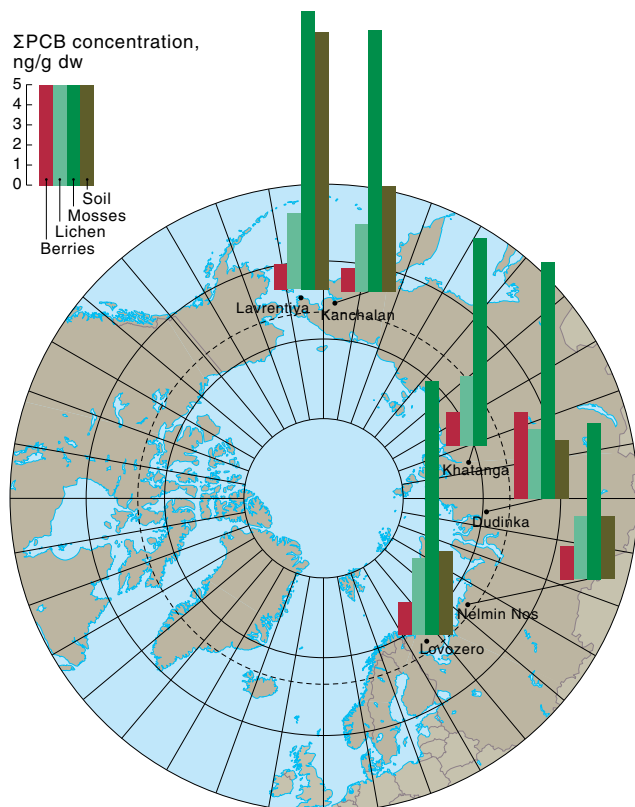
Figure 4·12. Concentrations of ΣPCBs in berries, lichens, mosses, and soils from regions in Arctic Russia (RAIPON/AMAP/GEF Project, 2001). All samples are pools of numerous samples collected in 2000-2001. Species included in each vegetation group are given in Annex Table 4.

decreased in the atmospheric environment may explain part of this trend.

In an older study, a total of 209 vegetation samples (11 species across all sites) were collected from Alaska and Russia in 1991-93 and analyzed for 51 OC pesticides, industrial compounds, and PCB congeners (see Figure 4·13 for locations, and Annex Table 4 for species names and concentrations) (Ford *et al.*, 2000). Vegetation samples were primarily two species of ground-dwelling lichens (*Masonhalea richardsonii* and *Cetraria cucullata*) and two mosses (*Racomitrium lanuginosum* and *Hylocomium splendens*). All four of these species were collected in Alaska but only *C. cucullata* was commonly found at the Russian study sites. Samples of other taxa, most notably blueberries (*Vaccinium uliginosum*), were also taken opportunistically and predominantly in Alaska. Concentrations of OCs in lichens and mosses from all Alaskan and Russian locations were low (low ng/g dw) and in the range reported for Russian lichens, mosses and berries recently collected and discussed above (RAIPON/AMAP/GEF Project, 2001), and previously for Arctic plants (de March *et al.*, 1998).

Analysis of the Alaskan data set demonstrated that concentrations for commonly encountered OCs were generally highest in the lichen *C. cucullata*, followed by the other lichens and mosses (Annex Table 4). This differs from the results of the recent Russian study where the highest OC concentrations were found in mosses. Concentrations of OCs in other Alaskan vegetation, such as blueberries, were very low, and for many species OCs were not detected, consistent with the Russian study. α-HCH and PeCA were the individual OCs with the highest concentrations; ΣPCB concentrations were the highest among OC groups.

OC concentrations in *C. cucullata* collected on the Kola Peninsula/northern Urals (where sampling sites were close to industrial centers) were similar to those measured in the same species from Alaska and Taymir (Figure 4·13). However, PCB concentrations in *C. cucullata* from the Taymir Peninsula were approximately twice as high as those observed at other sites. This is
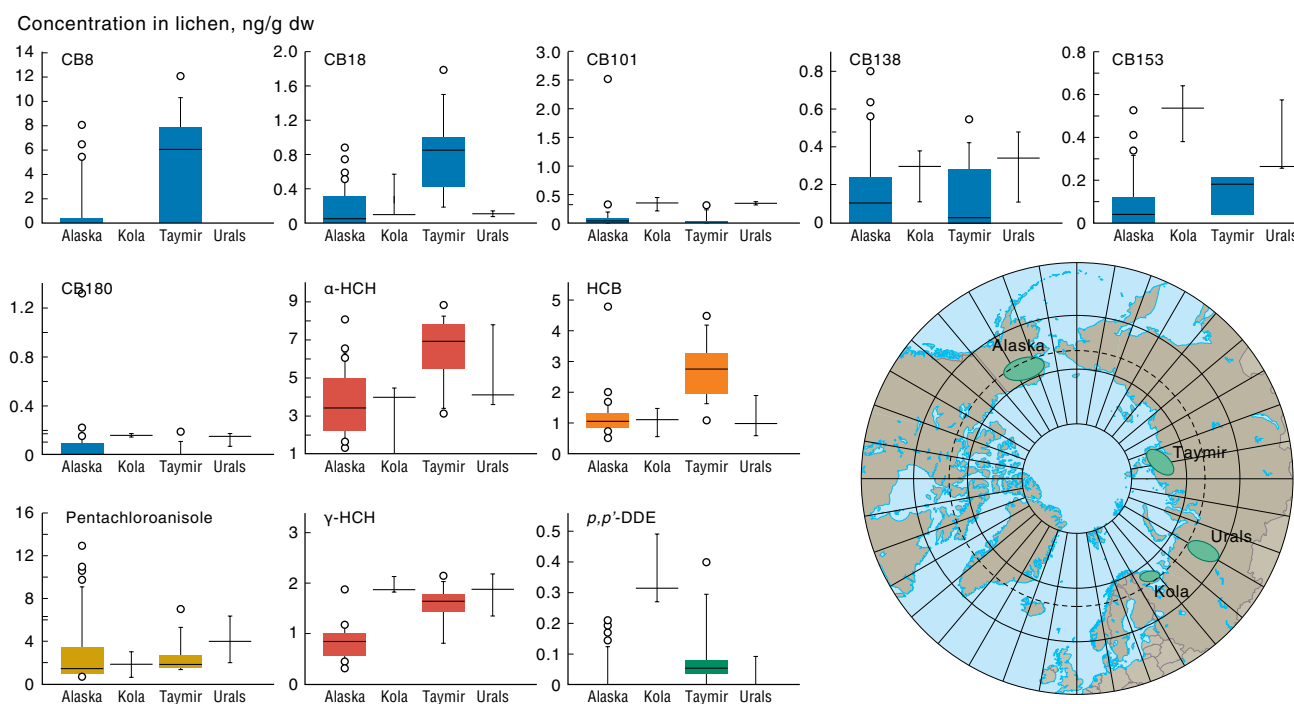

Figure 4·13. Areas where lichens, mosses and soils were sampled in Alaska and Russia between 1991 and 1993, and concentrations of selected OCs in lichen (*Cetraria cucullata*) from Alaskan and Russian locations (Ford *et al.*, 2000).

due, in part, to much higher concentrations of lower chlorinated congeners, in particular CB8. Concentrations of higher chlorinated congeners show less spatial differences, which is consistent with the recent Russian study (RAIPON/AMAP/GEF Project, 2001).

Comparison of individual OC concentrations in *C. cucullata* from the Kola Peninsula/northern Urals, with regionally dispersed samples from Alaska and the Taymir Peninsula, show a diversity of patterns (Figure 4·13). Several analytes (aldrin, endrin, heptachlor and mirex) were not detected in Russian samples but sporadically encountered in Alaskan samples. Lower chlorinated PCBs (CBs 8 and 18) and semi-volatile OCs (α-HCH, HCB) were present in higher concentrations on the Taymir Peninsula (Figure 4·13). Taymir is considerably further north than the sites in the other regions and, this finding is consistent with the predicted global fractionation of semi-volatile persistent organics (Wania and Mackay, 1996). In contrast, higher chlorinated PCBs and several pesticides were present at higher concentrations in samples from Kola/Urals sites than in those from Alaskan and Taymir sites (Figure 4·13). No regional differences were evident for PeCA, *cis*-nonachlor, and CBs 29, 187, and 206 (although outliers were present for some of these analytes in a few Alaskan samples).

4.2.1.2. PCDD/Fs in tree bark

Tree bark was used by Wagrowski and Hites (2000) to study the global distribution of PCDD/Fs. The bark samples (collected at 1 m height) were from locally important tree species from sites in Alaska (1 site), Yukon/Northwest Territories (7 sites) and Norway (1 site), along with samples from 54 other sites in the northern and southern hemisphere. Concentrations of total PCDD/Fs in bark were low in the Arctic, ranging from not-detected (approximately 1 ng/g lw) to 685 pg/g lw with a median of 131 pg/g lw (Annex Table 4). No geographical differences were discernible among the Arctic samples. These concentrations were, however, at the low end of the range found globally in tree bark from temperate zones (approximately 100-227 000 pg/g lw). Most tree bark samples from the Arctic were characterized by high proportions of tetrachlorodibenzofurans. Octachlorodibenzo-*p*-dioxin, which predominated in Arctic soils, was near detection limits in bark. This pattern is consistent with the bark absorbing primarily lower chlorinated PCDD/Fs from the gas phase in areas remote from major sources.

4.2.1.3. OC pesticides and PCBs in soils

Arctic soils in a global survey
Ockenden *et al.* (2002) conducted a global survey of soils from rural and remote locations, which included 22 sites in the Arctic (Canada, eastern Greenland, northern Norway, and northwestern Russia). Samples (0-5 cm depth) were collected from 208 undisturbed sites throughout the world. Sites were more than 2 km from the nearest town/city/busy road and more than 500 m from small dwellings or tracks. The global latitudinal distribution of PCBs in soils is plotted in Figure 2·4. The Arctic soil results are presented in Annex Table 4. ΣPCB

concentrations (27 congeners) in the 22 Arctic samples ranged from 0.004 to 48 ng/g dw with highest concentrations in or near urban areas in northwestern Russia (Monchegorsk) and lowest concentrations in Greenland. After adjusting for soil organic matter (SOM), the range of concentrations was somewhat narrower (0.1-81 ng/g SOM). Ockenden *et al.* (2002) concluded that the SOM content and turnover governs PCB behavior because of their strong affinity for organic carbon. Degradation of POPs in soil is slow, of the order of tens of years (or more) for many compounds (Mackay *et al.*, 2000). As such, physical processes, bioturbation/ploughing, and carbon burial/sequestration in forest soils/peat become key factors. These processes, together with physical occlusion/partitioning into the SOM (Luthy *et al.*, 1997), physically remove the bulk of the atmospherically-derived POPs available for air–surface exchange by taking it below the all-important surface 'skin' of soil which is in active exchange with the atmosphere (Harner *et al.*, 2001).

Russian and Alaskan soils
Samples of surface soil were collected from four regions of the Russian Arctic: Kola Peninsula; Pechora Basin; Taymir Peninsula (Dudinka); and, Chukotka (Kanchalan and Lavrentiya), in 2000-2001 for the analysis of OCs (RAIPON/AMAP/GEF Project, 2001). Samples were collected in the same locations as plants and terrestrial mammals, and covered a wide geographical area. Each sample analyzed comprised a pool of the samples collected. PCBs were the dominant OC measured in soils at all locations. Similar to results for vegetation from these regions, there were no strong geographical trends in OC concentrations in Russian soils (Figure 4·12), and OC concentrations were within a factor of two (Annex Table 4). A single soil sample from Lavrentiya in Chukotka had higher concentrations of ΣPCBs (5.2 ± 3.5 ng/g dw) but, since this is a single sample, caution is warranted about interpreting this as a hot spot. PCB concentrations reported by the RAIPON/AMAP/GEF Project (2001) were generally lower than reported by Ockenden *et al.* (2002); however, the latter soils were generally collected close to urban areas while the former study focused on background levels in remote areas. Concentrations of the OCs are in the range previously reported for Russian soils (Melnikov *et al.*, 1995). Toxaphene (sum of Parlars 26, 52 and 60, detection limits approximately 0.1 ng/g in soil) was not detected in any soil sample, but low concentrations (0.16 to 0.23 ng/g dw) of PBDEs were observed in three soil samples.

In an earlier study, concentrations of OCs in the surface soils of Alaska and Russia, collected between 1991 and 1993, were low (low ng/g dw) (Annex Table 4) (Ford *et al.*, 2000) and in the range of levels reported for Arctic soil in the first AMAP assessment report (de March *et al.*, 1998). ΣPCBs and ΣDDTs were the predominant OCs found, with concentrations of ΣCBz and ΣHCHs being similar to ΣPCB and ΣDDT concentrations in the Alaskan soil only. PeCA, CB28, HCB, and α-HCH were among the more common individual OCs found. Concentrations were much higher in Alaska than on Kola and Taymir Peninsulas in Russia. However, the Alaskan and Taymir samples included both surface vegetation and litter, whereas Kola soils only included the

A-horizons (no vegetation or litter), making comparisons with the Kola samples difficult. OC concentrations in the Alaskan soils are similar, but the older Taymir samples have much lower concentrations than the recently collected Russian soils (RAIPON/AMAP/GEF Project, 2001). Differences in the collection methods and the organic content of the soils may explain some of the differences between the Russian data, but this information is not currently available.

Concentrations of individual OCs in the Kola Peninsula samples, which had no vegetation or litter, rarely exceeded 1 ng/g dw. Due to the removal of vegetation and litter, it is not possible to compare these results with recent results from Russian soil samples. Concentrations of *p,p'*-DDT in Kola soils were one to two orders of magnitude higher than most other analytes, suggesting recent DDT use in this area at the time of collection (1991-1993).

Specific information on A-horizon soils is not available for Alaska and the Taymir Peninsula, although several soil cores from both those regions were taken. When A-horizon and 0-5 cm increment samples are collectively compared to the results for *C. cucullata* lichen, some results were similar and some surprisingly dissimilar. As with the lichen results, endrin, heptachlor, and mirex were found only in Alaskan soils. Surprisingly, concentrations of HCB, α-HCH and CB18 were quite low in the Taymir soil relative to the Kola and even Alaskan soils, although concentrations of CB8 were high. Concentrations of PeCA were high only in Taymir and Alaska, where they reached concentrations that exceeded those of most other analytes by one to two orders of magnitude. Also as with the lichens, the Kola signals for *p,p'*-DDE and CBs 101 and 138 were high relative to Alaska and Taymir. Five of the six DDTs (except *o,p'*-DDE), as well as CB153, were routinely found in Kola/Urals soils, but not in Alaska or Taymir soils.

Inorganic, cryogenically exposed surface soils were collected only in Alaska and the Taymir, and POPs concentrations rarely exceeded 1 ng/g dw in this matrix. Where QA considerations permitted comparison, Alaskan samples of surface inorganic soils had higher analyte concentrations than those from the Taymir, which is opposite to the pattern found for heavy metals and trace elements (Ford *et al.*, 2002).

4.2.1.4. PCDD/Fs in Arctic soils

As part of a global survey of PCDD/Fs in soils and tree bark, Wagrowski and Hites (2000) reported PCDD/Fs in soils from Alaska, the Yukon and NWT in the Canadian Arctic, western Greenland, and Norway. For this assessment, these data were combined with results from Brzuzy and Hites (1996) who conducted an earlier, smaller-scale soil survey that included samples in Alaska and northwestern Russia (Annex Table 4). Fluxes of total PCDD/Fs estimated from the mass of chemicals in a 10×10 cm (15 cm depth) core ranged from 1.2 to 143 ng/m²/yr. There was no consistent geographical trend in the 12 samples; however, higher fluxes were seen in samples from Alaska and western Greenland. By comparison, the range of fluxes of total PCDD/Fs for sites in the mid-latitudes and tropics was 5-8100 ng/m²/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 octachlorodibenzo-*p*-dioxin, although tetrachlorodibenzofurans were also important contributors to total PCDD/Fs.

Using the PCDD/F emission inventory for Canada and the U.S., Commoner *et al*. (2000) predicted 'dioxin' TEQ deposition of about 4-53 pg TEQ/m²/yr for terrestrial surfaces near eight communities in Nunavut. Highest deposition was predicted for the most southerly location (Sanikiluaq, 53 TEQ/m²/yr). Eastern locations such as Broughton Island (9 TEQ/m²/yr) had higher deposition than western locations (Ikaluktutiak, 4 TEQ/m² year). Highest depositions were predicted to occur in the southern and eastern Arctic because of the preponderance of dioxin sources in the eastern U.S. and Canada. Russian and northern European sources were regarded as insignificant in comparison to those in the mid-west U.S., Ontario, and Quebec (Commoner *et al.*, 2000). A direct comparison with the PCDD/F results from Wagrowski and Hites (2000) was not possible because of differences in geographical area and lack of data for specific 2,3,7,8-substituted PCDD/Fs in the soil survey.

4.2.1.5. Simulation of the global fate of PCBs in soils

The Globo-POP model has been used to describe the global fate of PCBs over a time scale of several decades (Wania *et al.*, 1999c; 2000). PCBs have been used as mixtures consisting of individual substances which differ substantially in their physical-chemical characteristics and persistence. It is also likely that the temporal and spatial pattern of release into the environment has been different for different congeners (Breivik *et al.*, 2002b). Large differences in the simulated fate of the various PCB congeners reaffirm the need to perform calculations for individual chemicals rather than chemical mixtures. Thus, calculations were performed for a selection of congeners that vary in the number of chlorine substitutions.

One of the motivations for modeling PCBs globally is to identify the major global-loss processes in order to assess the likely rate of future concentration decline in the Arctic environment and elsewhere (Wania *et al.*, 1999c). The model calculations showed that, historically, atmospheric degradation and transfer to the deep sea contributed most to the loss of PCBs from the global environment, whereas burial in freshwater sediments was of little significance on a global scale. Reaction of the gaseous compounds with OH radicals is the loss process of primary importance for the lighter congeners, whereas the deep-sea transfer process increases in relevance with the degree of chlorination. The model further predicts that the relative importance of the various loss processes has been changing over time, with degradation in soils taking over as the major loss process in the past twenty years. As primary emissions decreased, the concentrations (and thus, loss rates) of PCBs in the atmosphere and ocean water have declined quickly, whereas soils have retained a high pollutant load due to their slow response time (large capacity, but slow evaporation and degradation). Unfortunately, this implies that the future rate of purification of the global environment will be determined by the slow and poorly quantified degra-

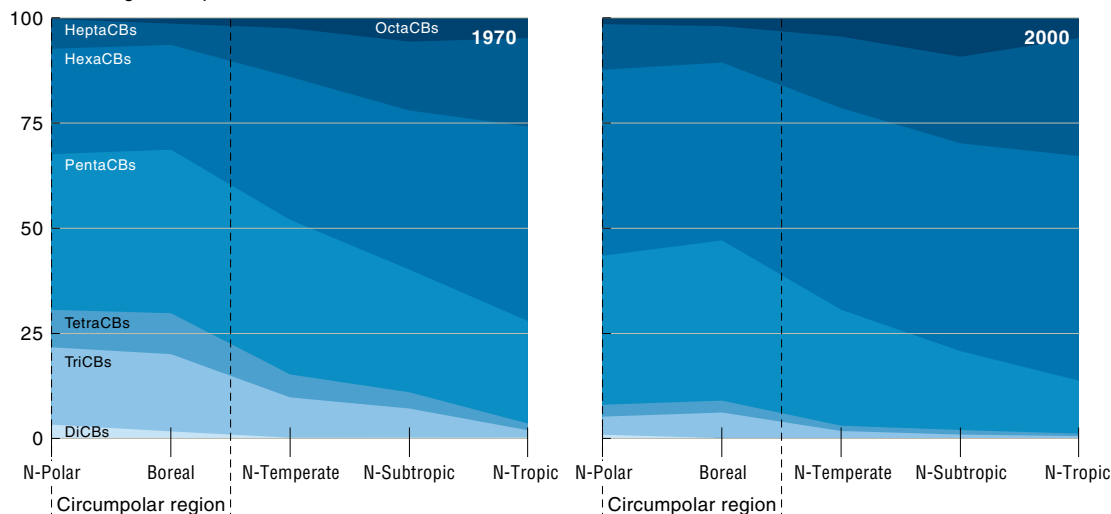PCB homologue composition in soil, %

Figure 4·14. Modeled PCB homologue composition in soil in 1970 and 2000 in different zones of the northern hemisphere. The model predicts a shift to increasingly more volatile homologues with increasing latitude, and increased importance of the less volatile homologues over time, as the lighter homologues are more readily degraded (Wania, 1999).

dation rate in the soil environment. Figure 4·14 shows the homologue composition of PCBs in soil in 1970 and 2000 predicted by the Globo-POP model. The composition shifts to increasingly more volatile homologues with increasing latitude. In the past thirty years of steadily declining PCB emissions, the less volatile congeners have increased in relative importance as the lighter homologues are degraded more readily.

The global distribution model can also be used to investigate compositional shifts among the PCB congeners between compartments, zones and different time periods. Due to their wide range of physical-chemical properties, PCBs have played an important role in the derivation of the concept of global fractionation, which results in compositional shifts of compound mixtures with latitude (Wania and Mackay, 1993; 1996). The model succeeded in reproducing observed shifts toward lighter (lower chlorinated) PCB congeners with increasing latitude (Figure 4·15) found in various measurement cam-

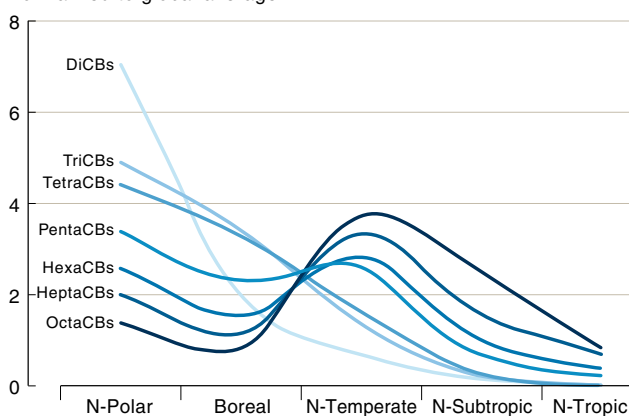PCB homologue concentration in soil, normalized to global average

Figure 4·15. Soil concentrations of various PCB homologues as a function of (northern hemisphere) climate zone for the year 2000, predicted using the 'Globo-POPs' model of Wania and Mackay (2000). The soil concentrations are normalized to the global average concentration of a particular homologue. The concentrations of the lighter homologues, with up to four chlorines, increase steadily with latitude.
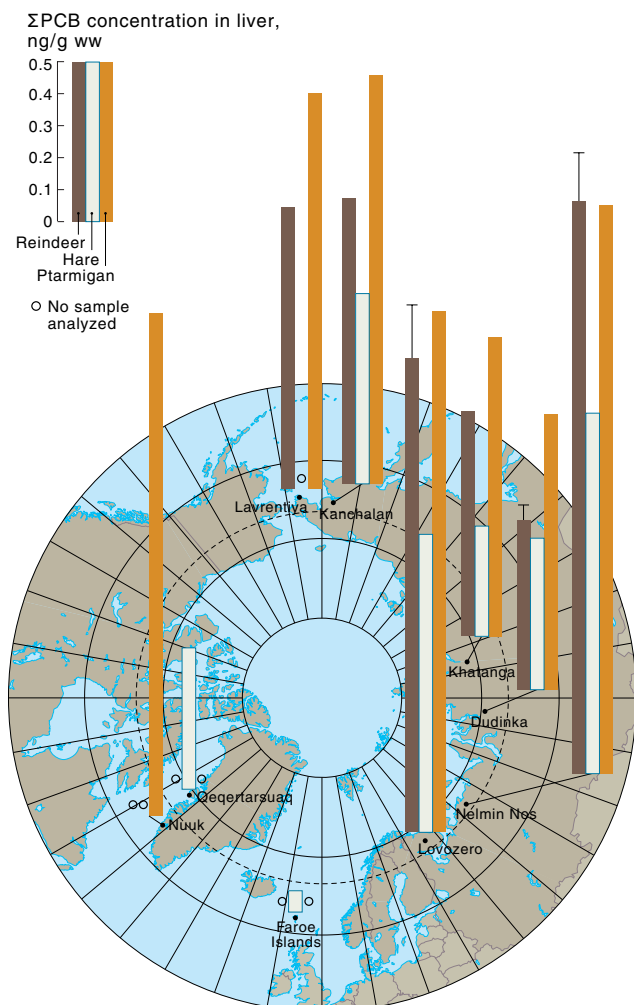
paigns (Muir *et al.*, 1996a; Ockenden *et al.*, 1998; 2002). The model further suggests that these shifts differ between various environmental media, change over time and are rather complex.

4.2.2. Terrestrial herbivores

The previous AMAP assessment reported a large amount of OC data on caribou/reindeer (*Rangifer tarandus*). This species is an important food item in most northern societies and represents an excellent species to monitor terrestrial contamination, due to their diet of plants and lichen. Geographical differences were observed previously in OC concentrations in caribou/reindeer (de March *et al.*, 1998) but, in general, levels were low compared to Arctic marine mammals. For this reason, there are few new data on OC levels in caribou/reindeer and studies of terrestrial species have mainly focused on concentrations of radionuclides and heavy metals. Since 1997, there have been new studies on OCs in terrestrial mammals from Greenland (Muir and Johansen, 2001), Faroe Islands (Larsen and Dam, 1999) and Russia (RAIPON/AMAP/GEF Project, 2001), and a study on OC levels in reindeer from Finland (Hirvi and Henttonen, 2002).

Russian terrestrial herbivores
OC analyses were conducted on samples of various tissues (kidney, liver, and muscle) from four species of terrestrial herbivores (reindeer, mountain hare (*Lepus timidus*), ptarmigan (*Lagopus mutus*), and willow grouse (*Lagopus lagopus*)) collected in 2000-2001 from four regions of the Russian Arctic: Kola Peninsula (Lovozero); Pechora Basin (Nelmin Nos); the Taymir Peninsula (Dudinka and Khatanga); and, Chukotka (Kanchalan and Lavrentiya) (RAIPON/AMAP/GEF Project, 2001). Samples were collected in the same regions as the vegetation and soil samples (see Sections 4.2.1.1 and 4.2.1.3). Across all species, OC concentrations were highest in liver followed by kidney and muscle, which is likely due to higher lipid content of the liver, although no lipid data are currently available for these samples. Across all re-

Figure 4·16. Concentrations of ΣPCBs in reindeer, Arctic hare and ptarmigans/willow grouse from regions within Russia (RAIPON/AMAP/GEF Project, 2001), and from Greenland and the Faroe Islands. Bars are means (with ± 1 SE indicated when more than two pooled samples are available). All samples are pools of numerous samples collected in 2000-2001.

gions and OC groups, OC concentrations were similar in the reindeer, ptarmigan, and willow grouse but lower in the mountain hares (Figure 4·16 and Annex Table 5). Some geographical trends were found. OC concentrations were higher in the regions of Lovozero (Kola Peninsula) and Nelmin Nos (Pechora Basin), but for each species, OC concentrations were within a factor of four across all regions. OC concentrations in these Russian terrestrial herbivores are in the same range as those observed recently in Greenland terrestrial herbivorous mammals (Muir and Johansen, 2001), and reported for Russian reindeer collected in 1994 (Melnikov *et al.*, 1995). Toxaphene (sum of Parlars 26, 52 and 60; detection limits approximately 0.2 ng/g in biota) and PBDEs (detection limits approximately 0.5 ng/g in biota) were not detected in any terrestrial herbivore samples, but the detection limits of this study are above the levels normally found for these compounds in Arctic biota.

Concentrations of ΣPCDDs, ΣPCDFs, and ΣTEQs were reported for muscle of reindeer, hares, ptarmigan and willow grouse collected in 2000-2001 from four regions of the Russian Arctic (RAIPON/AMAP/GEF Project, 2001) (Annex Table 16). Liver was also analyzed in reindeer and hares (the same samples analyzed for OCs,

discussed above). Liver concentrations were higher than muscle for ΣPCDDs, ΣPCDFs, and ΣTEQs and ΣPCDFs were greater than ΣPCDDs. Concentrations of ΣPCDDs, ΣPCDFs, and ΣTEQ were generally below 0.5 pg/g ww, with the exception of reindeer liver from the western sites Kola Peninsula (6.5 pg/g ww), Pechora Basin (2.5 pg/g ww), and the Taymir Peninsula (0.7 pg/g ww). These locations are downwind of large cities (Murmansk, Monchegorsk, Norilsk) which have non-ferrous smelters, a known source of airborne PCDFs.

Greenland terrestrial herbivores
Levels of OCs were assessed in a variety of tissues (liver, kidney, muscle, and fat) of terrestrial mammals (mountain hare, domestic lambs (*Ovis* spp.), and musk-ox (*Ovibos moschatus*)), and ptarmigan of Greenland (Annex Table 5). These species are important foodstuffs (Muir and Johansen, 2001). PCBs (concentration range of 0.5-7.5 ng/g ww) were by far the predominant OCs in all species across all tissues. The ranking of the other OCs varied with the tissue, but, in general, DDT and chlordanes were the next most common OC. Wet weight concentrations were greatest in fat, but lipid-corrected concentrations were often highest in liver or kidney. OC concentrations were similar between species, reflecting similar diets. These concentrations are in the range reported previously for herbivorous terrestrial mammals from the Canadian and European Arctic, but are orders of magnitude less than those observed in marine mammals such as the ringed seal (de March *et al.*, 1998). Compared to the Russian data, PCB concentrations in hares are similar (Figure 4·16) but ptarmigan have much higher concentrations. Interestingly, concentrations of chlorobenzenes observed in these terrestrial samples are similar to those in marine mammals.

Faroe Islands herbivores
Levels of OCs were determined in Faroe Islands terrestrial mammals, sheep, and mountain hare, which are part of the human diet (Larsen and Dam, 1999). In hare liver (n = 13), the predominant OCs were HCB and oxychlordane, both occurring at mean concentrations near 30 ng/g lw. The concentrations of HCB are similar to those found in sculpin from the Faroe Islands, but are one fifth of those detected in other marine species such as black guillemot eggs and pilot whale tissues. The concentration of PCB (as CB153) was low and near the detection limit (approximately 4 ng/g lw), and other congeners were rarely detected. Of the six DDT isomers, only *p,p'*-DDE was regularly detected with a mean concentration of 7 ng/g lw. Toxaphene, mirex, and the other chlordanes were normally not detected. Liver and tallow taken from around the kidney of eight sheep and 17 lambs at each site were sampled from two locations in 1997. In most cases, PCB congeners, chlordanes, toxaphene, and *p,p'*-DDT were not detected. In lamb and sheep liver, the concentration of CB153 and CB138 were approximately 5 ng/g lw and 2 ng/g lw, respectively, with slightly lower concentrations in tallow, especially in sheep. The concentrations of *p,p'*-DDE in sheep and lamb liver were approximately 6 ng/g lw and 3 ng/g lw, respectively. Concentrations of OCs in the Faroe Islands terrestrial herbivores are similar to values reported in similar species from Greenland.

Finland reindeer
OCs were found to be very low in the fat of reindeer collected in northern Finland in 2000, with most OCs below the detection limits (< 5 ng/g) (Hirvi and Hentonen, 2002). However, these detection limits are high and above OC levels normally seen in Arctic terrestrial animals (Annex Table 5). Chlorobenzenes were found at the highest concentration (ΣCBz 14.3 ± 4.4 ng/g ww), followed by ΣDDTs (6.1 ± 1.9 ng/g ww) and ΣPCBs (3.5 ± 8.8 ng/g ww). These concentrations are at the low end of those reported previously for Arctic caribou/reindeer (de March *et al.*, 1998). High levels of chlorobenzenes, relative to other OCs, are often found in caribou/reindeer (de March *et al.*, 1998).

4.2.3. Birds of prey

Birds of prey have been of particular importance in the study of OCs in the Arctic due to their susceptibility to the effects of OCs and the potential for accumulation of OCs from winter habitats. A number of species were examined in the past (see de March *et al.*, 1998) but most recent work has focused on peregrine falcons (*Falco peregrinus*).

4.2.3.1. North American peregrine falcon

Subspecies in Alaska are: the Arctic peregrine (*F. p. tundrius*), which nest in northern tundra; the American peregrine (*F. p. anatum*), which nests in the forested interior; and, the Peale's peregrine (*F. p. pealei*), which nests along the southern coast from the Aleutian Islands to southeast Alaska.

Persistent OC contaminants were measured in American and Arctic peregrine falcon eggs from Alaska during the period of 1979-1995 (Ambrose *et al.*, 2000) (Annex Table 5). This dataset was not included in the first AMAP POPs assessment, and a more detailed discussion of the data is provided in the temporal trends section (Section 5.2). Dieldrin, *p,p'*-DDE, heptachlor epoxide, oxychlordane, mirex, and total (Aroclor) PCBs were consistently detected and measured in all samples. HCB, *p,p'*-dichlorodiphenyldichloroethane (DDD), *p,p'*-DDT, β-HCH, and *trans*-nonachlor were detected in more than 50% of samples, and α-HCH, γ-HCH, *trans*-chlordane, *cis*-chlordane, *o,p'*-DDD, *o,p'*-DDE, *o,p'*-DDT, endosulfan II, and endrin were detected in less than 50% of samples.

4.2.3.2. European Arctic birds of prey

To assess the current level of OCs in Arctic European birds of prey, 44 egg samples from eight different raptor species (Table 4·6) were collected from throughout Norway, including northern parts, during the period 1991-1997 and analyzed for OCs, including toxaphene (Herzke *et al.*, 2002). The DDT-transformation product *p,p'*-DDE still dominates the pesticide burden in all predatory bird eggs (70-90% of the pesticide burden) 30 years after the ban of these chemicals in western countries. PCBs accounted for 70-80% of the total OC burden in predatory birds, confirming the high ecotoxicological potential of this type of contaminant for birds of prey. The highest average concentrations for PCBs were found in eggs from white-tailed sea eagle (*Haliaeetus albicilla*) and peregrine falcon (average ΣPCB concentration: 8.9 µg/g ww and 9.1 µg/g ww, respectively). Merlin (*Falco columbarius*) and sparrowhawk (*Accipiter nisus*) eggs had the highest concentrations of chlorinated pesticides (average sum pesticide concentration: 3.0 µg/g ww and 4.3 µg/g ww, respectively). Toxaphenes were determined, and concentrations were low compared to PCBs and OCs. The highest toxaphene levels were found for bird species feeding on fish or migratory passerines. The highest toxaphene concentration was found in white-tailed sea eagle eggs (0.09 µg/g ww). No toxaphene was found in osprey (*Pandion haliaetus*) and merlin eggs. No spatial or regional specific trends or patterns in OCs were found for the egg samples analyzed.

Osprey, merlin, sparrowhawk and peregrine falcon migrate to southern winter habitats where many pesticides are in use, and feed on local prey available in these regions. Gyrfalcon (*Falco rusticolus*), goshawk (*Accipiter gentiles*), golden eagle (*Aquila chrysaetos*), and white-tailed sea eagle are usually more confined to a specific habitat, and not as apt to migrate. The high pesticide levels found in merlin, sparrowhawk, and peregrine falcon may thus, in part, be explained by their migratory habits.

4.2.3.3. 'New' chemicals in European Arctic birds of prey

High ΣPBDE concentrations have been found in predatory birds feeding on terrestrial mammals and birds, particularly peregrine falcons in northern Sweden (Sellström *et al.,* 2001; Lindberg *et al.*, 2004) and Norway (Herzke *et al.*, 2001a). The mean ΣPBDEs (BDEs 47, 99, 100, 153, and 154) in the two populations are 224 and 260 ng/g ww (4500 and 4700 ng/g lw), respectively, with levels ranging from 43 to 1580 ng/g ww (680-39000 ng/g lw) in the Swedish population. The ΣPBDE levels in Norwegian golden eagles, gyrfalcons, and merlins were 7, 18, and 36 ng/g ww (approximately 140, 360, and 720 ng/g lw). The congener pattern in all these bird species is quite different from that seen in fish and fish-eating birds and mammals, dominated by BDE153 and

Table 4·6. Habitat and diet information for Norwegian bird of prey species from which eggs were collected between 1991 and 1997 for OC analyses (Herzke *et al.*, 2002).

Species	Habitat description	Main food objects
Merlin	Terrestrial	Passerines and waders
White-tailed sea eagle	Marine	Fish and seabirds
Goshawk	Terrestrial	Medium-sized birds, small mammals
Golden eagle	Terrestrial	Mammals and game birds
Peregrine falcon	Terrestrial/marine	Medium-sized birds
Osprey	Limnic	Freshwater fish
Gyrfalcon	Terrestrial	Medium-sized birds
Sparrowhawk	Terrestrial	Passerines

99. The Swedish peregrine falcons also had measurable levels of BDE183 (HpBDE) and BDE209 (DeBDE). ΣPBDE levels are only 3-4 times less than ΣPCB levels in Swedish peregrine falcons. HBCD concentrations ranged from 2.2 to 28 ng/g ww (34-2400 ng/g lw) in the Swedish peregrine falcons. The burden of PBDEs in peregrine falcons may be linked to their migratory habits as the northern population in Sweden overwinters along the coast and estuaries of central and southern Europe. In addition, many of the birds that they prey on when in the Arctic are also migratory and may have PBDE burdens from their overwintering sites further south.

4.2.4. Other carnivores

There are a number of terrestrial mammalian carnivores in the Arctic including the mink, wolf (*Canis lupus*), and wolverine (*Gulo gulo*). The Arctic fox is often considered a terrestrial carnivore but has been included in the marine mammal section of this report (Section 4.4.8). Through the process of biomagnification, these organisms generally have higher concentrations of OCs than terrestrial herbivores (de March *et al.*, 1998). However, the generally lower levels of OCs in the Arctic terrestrial environment results in OC concentrations in terrestrial carnivores that are much lower than in their marine counterparts. Some terrestrial mammals (e.g., the wolf) are also considered to have more efficient biotransformation ability based on the very small numbers of PCB congeners found in their tissues (Gamberg and Braune, 1999; Shore *et al.*, 2001). There have been few studies on OCs in terrestrial carnivores since the original AMAP report, in part because of low concern based on low levels in the terrestrial Arctic environment, and because few terrestrial carnivores are included in the diet of humans.

Wolves

There have been two studies on OC levels and patterns in wolves collected in the subarctic and Arctic in the past five years. Levels of OCs were measured in the liver of 58 wolves collected in northwest Russia (Shore *et al.*, 2001) and in the liver of wolves collected in the Canadian Yukon (Gamberg and Braune, 1999). Both studies found concentrations to be very low (mean or median below 50 ng/g ww) but were slightly higher in the Russian wolves (Annex Table 5). For many samples, common OCs, such as *p,p'*-DDE, were not detected, likely due to a combination of low levels and efficient biotransformation. A small number of highly chlorinated PCB congeners dominated the PCB load in both studies. OC concentrations were not found to vary between sexes and, with the exception of PCBs, did not vary with age. Both studies concluded that the levels of OCs do not pose a threat to the health of wolf populations.

Wolverines

Wolverines are omnivorous terrestrial mammals that live throughout the alpine and Arctic tundra of Canada and Scandinavia. Livers from 12 wolverines were collected at Kugluktuk, Nunavut, in the western Canadian Arctic to determine, for the first time, the residue patterns of OCs in this species (Hoekstra *et al.*, 2002a). The ranking of hepatic concentrations for sum (Σ) OC groups in wolverines was ΣPCBs > ΣCHLs > ΣDDTs > ΣHCHs > ΣCBz.

The most abundant OC analytes detected in wolverine liver (in order from highest to lowest) were CB153, CB180, oxychlordane, CB138, *p,p'*-DDE, CBs 170/190, CB99, CB118, and dieldrin. These OCs are among the most recalcitrant and are also the predominant OCs in other terrestrial Arctic mammalian predators, such as wolves (Gamberg and Braune 1999). Wolverine age and sex did not influence OC concentrations.

Levels of chlordane and HCHs were much lower in the wolverines compared to the Arctic fox collected to the north in Ulukhaqtuuq (Hoekstra *et al.*, 2002a) but are in the range of levels in other Arctic terrestrial mammals. This was expected because coastal populations of Arctic fox are known to scavenge marine mammals, resulting in elevated OCs (Klobes *et al.*, 1998a). However, levels of PCBs and DDTs were similar or higher in the wolverine compared to the Arctic fox. Concentrations of these OCs in the wolverine are much higher than other Arctic terrestrial mammals (Annex Table 5). Although these PCB and DDT levels are below most threshold effects levels (Hoekstra *et al.*, 2002a) an explanation for these unexpected high levels is not evident and merits further research.

Common shrew

OCs were measured in the common shrew (*Sorex araneus*) liver collected in 1999 and 2000 in the area of Pallas, northern Finland (Hirvi and Henttonen, 2002). This small mammal feeds on insects, worms, and other similar small animals. The mean levels of OC pesticides in immature shrews were 0.2-13.0 ng/g ww and in adults 0.5-25.0 ng/g ww, which are similar but slightly higher than levels observed in reindeer from the same region of Finland. ΣPCB concentrations were 0.3-5.0 ng/g ww. The highest levels were measured for oxychlordane followed by α-HCH, γ-HCH and *trans*-nonachlor. The concentrations of these contaminants were 10-20 times higher in shrews than in the humus layers, reflecting biomagnification up this short food web.

4.2.5. Summary and conclusions – terrestrial environment

The first AMAP POPs assessment concluded that there had been a significant amount of research on OC levels in the Arctic terrestrial environment, although it found that there was insufficient spatial coverage of media other than in caribou and reindeer (de March *et al.*, 1998). Since that report (1997 to 2001), studies on the global distribution of PCBs and PCDD/Fs in soils have included sites in the Arctic, thus providing a much clearer perspective of the levels of these contaminants in Arctic soils. With the exception of work in Russia, these studies were not conducted as part of the AMAP implementation programs of various circumpolar countries. While the global survey results show that levels of PCBs and PCDD/Fs are much lower in the Arctic than in the northern temperate zone, there are urban areas within the Arctic, especially in Russia, with elevated PCB levels. The results of global modeling and soil measurements of PCBs imply that the future rate of purification of the global environment will be determined by the slow and poorly quantified degradation rate in the soil environment. Thus, despite low levels, future surveys of Arctic

soils will be important for tracking long-term trends in the elimination of PCBs and related POPs.

The limited amount of research that has been carried out in the terrestrial Arctic confirms what was reported in the first AMAP POPs assessment. It is apparent that Arctic terrestrial biota, with the exception of predatory birds and animals near local sources, have among the lowest OC concentrations of any biota in the world. Concentrations of OCs in this environment are orders of magnitude less than what is observed in the freshwater and marine environments. In soil and lower trophic-level organisms, HCB and HCHs are the most prevalent OCs, but PCBs, chlordane, and DDTs become more prevalent at higher trophic levels. ΣCBz concentrations in caribou/reindeer are similar to ΣPCBs and ΣDDTs.

The extensive spatial survey of OCs in soil, vegetation and terrestrial herbivores carried out very recently in the Russian Arctic (2000 and 2001), provided data that fill a knowledge gap identified in the first AMAP POPs assessment (de March *et al.*, 1998). ΣPCB concentrations were the highest of any OC group, followed by ΣDDTs and ΣHCHs. Toxaphene and PBDEs were rarely detected and only in soil; however, the detection limits in this study are above the levels normally found for these compounds in the Arctic. This survey found that there were minor geographical trends in OC concentrations across Russia in the terrestrial environment, although slightly elevated levels of OCs were observed in terrestrial herbivores from two regions and PCDD/F concentrations were high in reindeer in areas near smelters. The concentrations found were similar to those found in Russian Arctic samples collected in the mid-1990s and in Greenland terrestrial herbivorous mammals, but were slightly higher than those observed in older Canadian Arctic terrestrial studies. There have been no recent studies on OCs in terrestrial herbivores in the Canadian or Alaskan Arctic. Two independent studies on wolves in Canada and Russia found similar levels of OCs.

Contamination of the terrestrial environment by OCs appears to be close to uniform across the circumpolar Arctic, with slightly lower (2-3 times) concentrations in Canada. Lower OC concentrations in the Canadian terrestrial Arctic conform to spatial trends of OCs observed in Arctic air and aquatic biota. However, there has been no recent extensive circumpolar survey of OCs in any one matrix or biota species and therefore, conclusions about spatial trends of OCs in the terrestrial Arctic are difficult and should be made with caution. Although this represents a knowledge gap, the generally low OC levels found in the Arctic terrestrial environment indicate that this not a major issue.

High levels of PBDEs were found in Arctic terrestrial-feeding birds of prey. Congener patterns were quite different from those observed in biota feeding within the aquatic environment. There is very little data for other 'new' chemicals, such as PFOS, in the terrestrial environment. There is a need to assess the levels and spatial trends of 'new' chemicals, particularly in birds of prey.

4.3. Freshwater environment

A fairly substantial dataset on OCs in Arctic freshwater ecosystems was summarized in the first AMAP POPs assessment (de March *et al.*, 1998). That report concluded that 'With the exception of river and lake waters, the original minimum monitoring objectives of AMAP for POPs in freshwater matrices have been met in all circumpolar countries.' The freshwater ecosystems of the Arctic are contaminated almost exclusively by atmospherically transported POPs. There are exceptions to this, such as rivers and the systems fed by these rivers, which flow through northern cities and/or drain more southerly agricultural watersheds.

OC concentrations in Russian Arctic river waters collected in the mid-1990s were found to be approximately ten times higher than levels observed in Canada and Norway (de March *et al.*, 1998). These results were originally questioned but have since been verified as discussed in Section 4.3.1. There were insufficient data to examine circumpolar trends of POPs in freshwaters in detail in the first AMAP assessment report. There was however moderately comprehensive coverage for surface sediments. With the exception of ΣPCB concentrations in water from a few Canadian lakes, levels of OCs in water and sediment did not exceed guideline levels for protecting aquatic wildlife (de March *et al.*, 1998) (see also Table 6.1). OC levels in freshwater biota were found to be higher than in terrestrial biota, but lower than in comparable trophic levels of marine biota (de March *et al.*, 1998). Good circumpolar coverage of OCs was available for Arctic char, which showed similar levels throughout the Arctic except in lakes where some char had become cannibalistic. PCBs were the most common OC group, although toxaphene was shown to be a major OC in Canadian freshwater biota.

Since the first AMAP POPs assessment, there have been a number of studies on POPs (specifically PCBs and OC pesticides) in the freshwater environment, but the amount of data produced is small compared to that produced for the marine environment. As with the terrestrial environment, concentrations of OC contaminants are relatively low in most freshwater biota. Nevertheless, studies of OCs in freshwater fish in Alaska, Canada, Greenland, and Russia have continued, in part because they are important dietary items. Extensive studies on OCs in the food webs of Bjørnøya have also been carried out, and long-term temporal trends studies of freshwater fish in Sweden have continued (Section 5.3.2).

4.3.1. Concentrations and loadings in surface waters
4.3.1.1. Verification of older Russian river water data
Background
The previous AMAP POPs assessment compared concentrations of the OC pesticides HCH and DDT in major north-flowing rivers in Russia to results from Canada and Norway from sampling and analysis campaigns conducted in the mid-1990s. In the past five years, there have been no new studies of POPs in river waters in the Canadian Arctic, northern Norway or in northern Russia. A project was conducted in Russia in 2001-2002 to study contaminants in the Yenisey and Pechora rivers (RAIPON/AMAP/GEF Project, 2001), however the results were not available in time for this assessment. The data from Russian rivers reported in de March *et al.* (1998) were received late in the assessment process and not thoroughly evaluated. Since then, several papers have been published which give a more com-

prehensive description of the quality assurance program followed, as well as the levels and trends of OC pesticides in major Russian rivers (Zhulidov *et al.*, 1998; Alexeeva *et al.*, 2001). Therefore, the available results are re-examined here. Zhulidov *et al.* (2002) have also reported temporal trends of HCH and DDT isomers from the late 1980s to early 1990s in major rivers and these are discussed in Section 5.3.1.

All sampling and analyses of POPs in Russian rivers during the period 1990-1996 were carried out by regional laboratories of ROSHYDROMET (Federal Service of Russia on Hydrometeorology and Environment) with method development and quality assurance carried out by a central co-ordinator (the Hydrochemical Institute, located in Rostov-on-Don). Methods used for the OC pesticides involved solvent extraction (hexane) of 1 L of unfiltered water and gas chromatographic determination. An improved clean-up method involving H_2SO_4 became available in 1995 and was in use in 1996 in all UGMS labs. The internal UGMS results for both precision and accuracy for all contaminants were very good (<30% deviation) for the six OC compounds determined. These six compounds were α-HCH, β-HCH, γ-HCH, *p,p'*-DDE, *p,p'*-DDT, and dihydroheptachlor (DHH; a heptachlor analog not determined in European or North American studies of OC pesticides).

Sampling program
Sampling took place at stations along major Russian rivers that are tributaries to the Arctic Ocean. Most attention was focused on the stations located further downstream in each large river in order to estimate loadings to the Arctic Ocean. Some of the stations were several hundred kilometers upstream of the geographical river mouth, as defined by headlands on the mainland. In some cases, this was because the tidal/saline characteristics of the river extend many kilometers upstream; in others, it was a matter of logistical convenience for sample collection. In some cases, there are cities with significant populations located upstream of the river mouth monitoring stations. Such cities and rivers include: Onega on the Onega River; Novodvinsk and Archangelsk on the Severnaya Dvina River; Naryan-Mar on the Pechora river; and, Dudinka on the Yenisey River.

Estimation of OC pesticide loadings was made difficult by the presence of many non-detect (nd) values. This does not mean that the OCs were not present, only that they were less than the detection limit. In the data sets evaluated, a zero was substituted for 'nd' for spreadsheet purposes whenever, e.g., the mean for an analyte was calculated. This biases the mean result toward a low value; however, substitution of the detection limit would bias the results toward a high value. During examination of the data, it was seen that an occasional maximum value (outlier) represented the determining value in the mean, usually when there were only a small number of data points. Where a reason to reject such points was determined by the group responsible for this study, the mean was recalculated; where there was no reason for rejection, the data were included. All data presented have been 'vetted' in this manner. The extent of the 'nd' values in the data reported in their study is unknown, but it is believed to be extensive so the means and loadings presented here are considered conservative.

Table 4·7. Seven-year weighted mean concentrations (µg/L) of contaminants in Russian northern rivers: 1990-1996[a].

River	α-HCH	γ-HCH	*p,p'*-DDT	*p,p'*-DDE
Kola	0.003	0.003	<0.001	<0.001
Onega	0.003	0.003	<0.001	<0.001
Sev. Dvina	0.001	0.001	<0.001	<0.001
Mezen	0.004	0.004	0.004	<0.001
Pechora	0.002	0.012	0.001	0.001
Ob	0.030	0.053	0.020	0.002
Nadym	0.029	0.065	0.020	0.007
Pur	0.069	0.107	0.027	0.006
Taz	0.058	0.114	0.038	<0.001
Yenisey	0.009	0.016	<0.001	<0.001
Anabar	<0.001	<0.001	<0.001	<0.001
Olenek	0.001	<0.001	<0.001	<0.001
Lena	<0.001	0.001	<0.001	0.008
Kolyma	<0.001	0.003	<0.001	<0.001

[a] Weighted average calculated for all data for the study period, weighted for the number of contributing samples for each annual mean.

Comparability of OC pesticide concentrations for the rivers Ob, Yenisey, Lena, and Kolyma were assessed by Alexeeva *et al.* (2001) using independent data reported by Zhulidov *et al.* (1998). The mid-range of the data from the 'independent specialists' part of that report was employed for comparison since means were not presented. The mid-range values from the independent specialists and the concentration means in this section (Table 4·7) gave inconsistent ratios. In the Ob, values from the specialists were 3-6 times higher than those reported by UGMS laboratories for both α-HCH and γ-HCH; for the Yenisey, the concentrations given in both reports were similar (within 20%), while levels for the Lena and Kolyma were below those of the specialists.

OC pesticide levels and spatial trends
The available concentration data were limited to annual arithmetic means, ranges, and the number of samples (log normal distributions were reported for the larger data sets). This data set for 15 rivers and six regularly monitored OC contaminants over seven years, was examined for each river to assess whether temporal or geographic pattern(s) existed. A significant temporal trend was apparent only for γ-HCH concentrations in the Pechora River (1990-1996), but not for any other pesticide or river. In the case of γ-HCH in the Pechora, the origin of the contaminant must be relatively local because similar patterns were not observed in other nearby rivers. There has, however, been no reported agricultural use of γ-HCH in this basin during the years reported. It may be that the source is from urban waste waters due to domestic uses in towns and cities within the watershed, or from use for biting-fly control in urban and other non-agricultural settings. As a consequence of there being no consistent temporal patterns, the concentration data for the rivers were averaged for the study period, and weighted for the number of contributing samples for each annual mean (Table 4·7)

The α-HCH and γ-HCH concentrations in the rivers draining into the White/Barents Seas (Table 4·7) were in the low µg/L range (means 0.0023 and 0.0041 µg/L, respectively). DDT and DDE were non-detectable except for the Pechora in 1993 and 1996. Even the maximum contaminant levels for the rivers do not appear to change

in any consistent fashion over the reporting period. γ-HCH in the Pechora seemed to display higher mean and maximum levels in the 1990-1994 time period, but these were only 2-3 times those found elsewhere in the same region. DDT and DDE detection limits were high and, therefore, it is not surprising that almost no residues were found to be above the low µg/L range.

Four of the five monitored rivers flowing to the Kara Sea (the Ob, Nadym, Pur, and Taz) were characterized by much higher levels of reported OC pesticides than were rivers flowing to the White and Barents Seas. The fifth, the Yenisey River, is significant for loadings but less so for concentrations. The averages of the annual means for α-HCH, γ-HCH, *p,p'*-DDT, and *p,p'*-DDE in these four rivers were, respectively: 0.028; 0.050; 0.015; and, 0.0022 µg/L, although the contributing means had a high level of variability, and the Ob had more samples contributing to its annual means than did the other rivers. Babkina (1999) reported that agricultural usage and soil concentrations of γ-HCH in the river basins and sub-basins studied here were significant only in the upper Ob-Irtysh Basin, and to a lesser extent, in the upper Yenisey Basin. The Ob River (and its tributary, the Irtysh River) drain agricultural areas in the south of Russia and in Kazakhstan, which have received high pesticide applications including γ-HCH. The observation that the shorter, non-agricultural Nadym, Pur and Taz rivers exhibited γ-HCH levels as high as or higher than those of the Ob lends weight to the premise that forestry, mining or other usage was significant in those basins.

For the HCHs in the Ob, there appears to be a transition around 1993-1994 as concentrations before this period are much higher than those after. Alexeeva *et al.* (1997) reported total HCH usage in Russia at roughly 5000 t/yr for the period 1970 to the mid-1980s, and falling to 600-700 t/yr by the late 1980s. HELCOM (2001) reports lindane use in Russia at 13.7 t in 1990 and 5.9 t in 1996. Unpublished data (Babkina, 1999) show that there was a further sharp reduction in use of HCH in the upper Ob-Irtysh Basin around 1992 and that collectively, the usage in this basin before this time was a significant fraction (approximately 1/3) of the amounts reported for all of the former Soviet Union (fSU) in the late 1980s. The reductions in HCH usage in these upper reaches of the river are roughly reflected in the water concentrations at the river mouth, indicating a fairly rapid system response time.

There were few observations of OC pesticides above the detection limits for any of the rivers flowing into the Laptev and East Siberian Seas (only for HCHs; mainly in 1990). This part of Russia is characterized by tundra over much of these basins, and there is less reason to expect the use of γ-HCH in these regions. It is noted that the 1990 observations were during the period when HCH usage for agriculture was still high. While there are no significant agricultural activities in the region, mining is extensive, and the extent of pesticide use in support of such activities, as with forestry, is unknown.

Other chlorinated pesticides in Russian Arctic rivers
β-HCH was analyzed in water from northern Russian rivers but was not detected at any site. The lack of observations was expected given that the α- and γ-HCH isomer levels are near their limits of detection. In Canadian Arctic rivers, the levels of β-HCH were also less than detection limits (approximately 0.00002 µg/L) (Jeffries *et al.*, 1996). In Norway, they were not reported (Holtan *et al.*, 1994).

The rivers flowing to the Kara Sea were the only ones in which the insecticide degradation product DHH was investigated. This compound may have been used in forests against biting insects, as well as in the agricultural industry. The overall mean of the reported years/rivers was 0.0042 µg/L and, at least for the Ob, the sample numbers were considerable. For all of fSU/Russia, 580 and 520 t/yr of DHH were used in 1990 and 1991, respectively (Alexeeva *et al.*, 1997), and the Ob Basin accounted for 12% of these amounts in both years. Data for later years are not available. This pesticide has not been investigated in Canadian or Norwegian rivers.

Loadings of OC pesticides in the northern Russian seas
The loadings of ΣHCHs and ΣDDTs (1990-1996) are illustrated in Figure 4·17. The Kara Sea received, by far, the largest fraction of OC pesticide discharges going to the northern seas; well over 90% of the totals for three of the four measured organics. α- and γ-HCHs and *p,p'*-DDT flowed to the Arctic largely via the Ob River (α-HCH 50%, γ-HCH 53%, *p,p'*-DDT 72%); DDE largely (76%) entered the Laptev Sea via the Lena River in 1990. Since DDT has been banned for more than 25 years, this material may be partly from soil and deposited material applied earlier (Harner *et al.*, 1998),
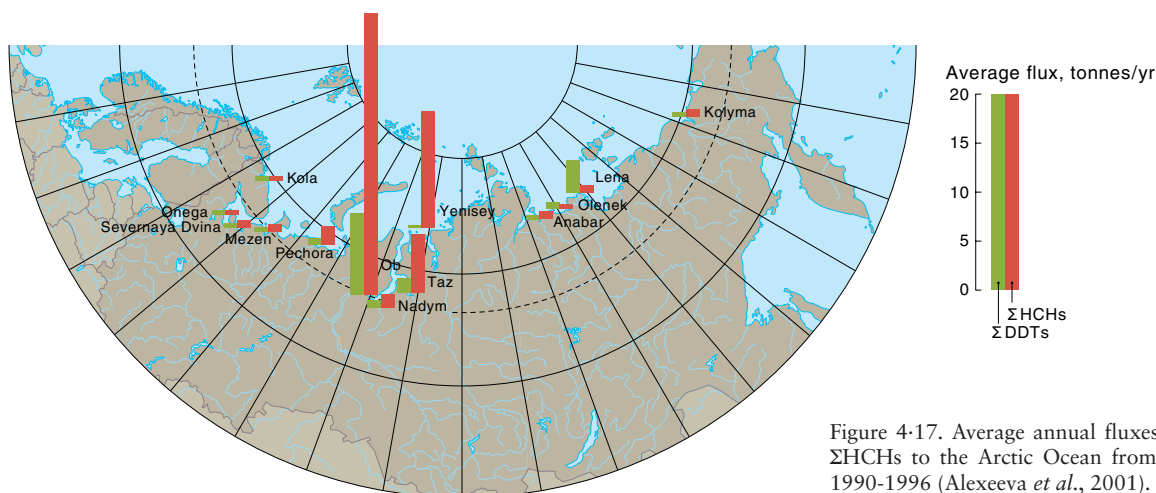

Figure 4·17. Average annual fluxes of ΣDDTs and ΣHCHs to the Arctic Ocean from Russian rivers, 1990-1996 (Alexeeva *et al.*, 2001).

although a higher proportion of DDE would be expected than was observed. The loadings of HCHs were greater than those of DDT and DDE, except for DDE in the Lena in 1990, for which there is no known explanation.

The Ob carried the major loadings of α- and γ-HCHs which, in the case of α-HCH, was 50% of the total for all of the rivers studied. The Yenisey was responsible for a further 24% of the total. The Ob carried 53% of the γ-HCH to the Kara Sea, while the Yenisey carried 18% of this isomer. A major fraction (⅓ based on data for pre-1990 use) of Russia's agricultural use of HCH occurred in the upper reaches of these two rivers (and these are the only reported uses in the northern river basins). The observation that the Nadym, Pur, and Taz rivers also have significant loadings (and high concentrations) of both of these isomers relative even to the Ob, indicates other anthropogenic sources in these non-agricultural watersheds. Forestry and mining are prominent industries in the area, and both use significant quantities of pesticides to provide better working conditions in the region.

These rivers represent the major loadings from the northern flows, but data are incomplete. Using the AMAP data for total flows to the various seas (Gregor *et al*., 1998), the basin loadings from the monitored rivers in each northern sea were scaled up to account for the rivers not monitored (those measured represented 58-80 % of the combined basin flows). The total annual loadings of the OCs were estimated to be 25 t for α-HCH, 44 t for γ-HCH, 13 t for *p,p'*-DDT, and 6 t for *p,p'*-DDE. The HCH values can be compared with the various flux estimates previously reported for the Arctic (Macdonald *et al*., 2000). Ocean current delivery via the Bering Strait was 52 and 12 t/yr for α-HCH and γ-HCH, respectively and, via the atmosphere, 53 and 10 t/yr.

4.3.1.2. Recent studies of OCs in Russian lake and river waters

Samples of freshwater (15-45 L) were collected from lakes and rivers in four regions of the Russian Arctic: Kola Peninsula (Lake Lovozero); Pechora River mouth at Nelmin Nos; Taymir Peninsula (Yenisey River at Dudinka and Khatanga River at Khatanga), and at Kanchalan on the Kanchalan River in Chukotka, in 2000-2001 for analysis of POPs (RAIPON/AMAP/GEF Project, 2001). Samples from Lake Lovozero were collected at various depths (0-30 m). There did not appear to be trends in OC concentrations with depth, and therefore, these data have been combined. Samples from all others sites were collected from rivers near the surface. PCBs were the predominant OC followed by DDTs and chlorobenzenes (Figure 4·18 and Annex Table 6). Toxaphene (sum of Parlars 26, 52, and 60; detection limits approximately 0.1 ng/L) and PBDEs (detection limits approximately 0.5 ng/L) were not detected in any water sample but the detection limits of this study are above the levels that would normally be anticipated for these compounds in the water column.

Except for HCHs, no geographical trends were obvious for any OC group, although levels were slightly higher in Lake Lovozero (Figure 4·18). Whether this is due to these being lake, versus river, samples cannot be
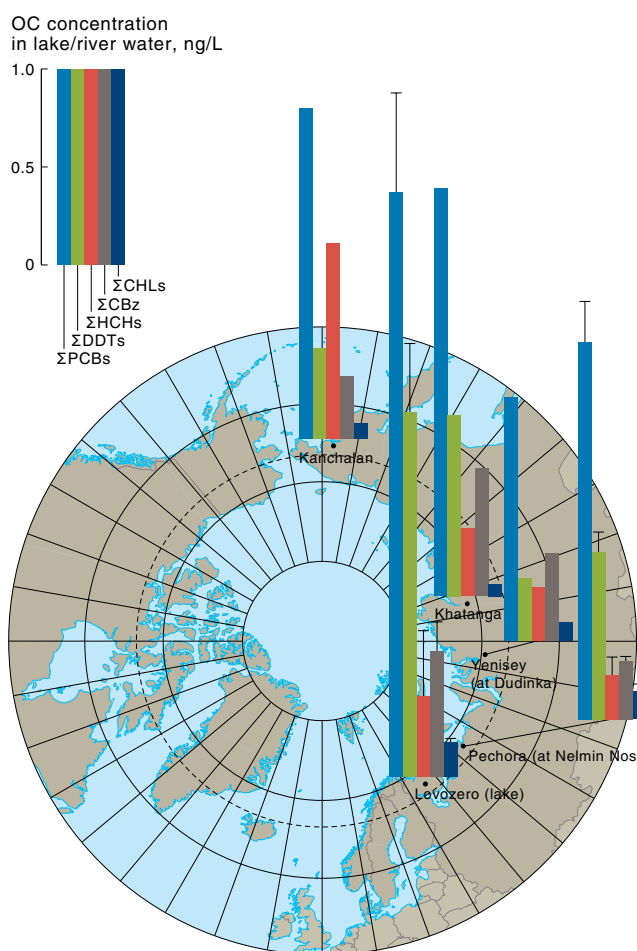

Figure 4·18. Concentrations of OCs in lake (Lovozero) and river water in northern Russia (RAIPON/AMAP/GEF Project, 2001). Bars are means (with ± 1 SE indicated when more than two pooled samples are available). All samples are pools of numerous samples collected in 2000-2001. Samples from Lovozero included surface and depth samples. OC concentrations varied little with depth in Lake Lovozero.

assessed from the information available. OC concentrations are in the same range as levels reported previously for Russian rivers.

4.3.1.3. OCs in Canadian Arctic lake waters

A very limited number of new measurements of POPs in freshwater have been carried out in the Canadian Arctic since the previous AMAP POPs assessment. Law *et al*. (2001) summarized results for α- and γ-HCH in lakes from Cornwallis Island (central Canadian Arctic Archipelago) and the Yukon, and compared the results for Arctic lakes with the Great Lakes and small lakes in south-central Ontario. Concentrations of α-HCH ranged from 0.64 to 1.7 ng/L and γ-HCH ranged from 0.13 to 1.3 ng/L. Sampling dates for the lake waters ranged from 1993 (Yukon) to 1998 (Cornwallis Island). Declining airborne levels of α-HCH over this time period (Li *et al*., 1998a) may have influenced the observed levels in surface waters. Highest concentrations of α-HCH were found in large, cold and oligotrophic lakes, such as those in the Arctic, subarctic, and the upper Great Lakes, and this was attributed to greater inputs from atmospheric deposition and slower loss rates relative to warmer, temperate lakes.

Helm *et al.* (2000) analyzed water from Amituk, Char, and Meretta Lakes for enantiomers and concentrations of α-HCH to estimate the extent of biodegradation in watersheds in the Canadian High Arctic. α-HCH concentrations ranged from 0.839-1.021 ng/L in Char Lake and 1.205-1.264 ng/L in Merreta Lake. By comparison, α-HCH was present at concentrations of 0.520-0.688 ng/L in the water column of Amituk Lake (Falconer *et al.*, 1995) and at 0.119-0.529 ng/L in inflowing streams. The α-HCH ERs declined with increasing stream temperatures indicating greater rates of biodegradation of α-HCH. As stream flows declined during the summer so too did stream volume-to-surface ratios, resulting in greater contact time between water and bed surfaces. The results suggest that enantioselective degradation was enhanced by the greater contact time between the chemical in the water and stream or slope substrates, the presumed site of microbial communities. Approximately 7% of α-HCH in the Amituk Lake Basin was enantioselectively degraded prior to entering the lake. ERs within Amituk Lake were controlled by meltwater inputs rather than within-lake degradation, and clearly illustrate the riverine-like nature of High Arctic lakes.

Differences in the lake α-HCH inventory from the end of summer 1993 to spring 1994 indicate that from 33 to 61% of α-HCH within the lake may have been lost via non-enantioselective microbial degradation at a rate ranging from 0.48 to 1.13/yr. In comparison to the average ER of 0.75 in Amituk Lake, the average ERs in the oligotrophic Char Lake and the more productive Meretta Lake were 0.65 (range 0.62-0.69) and 0.88 (range 0.84-0.90), respectively. These differences are likely attributable to within-lake degradation that is a function of lake water residence times, which are 9-14 yr for Char Lake, 3 yr for Amituk Lake, and <3 yr for Meretta Lake, rather than degradation within streams or lake productivity. Law *et al.* (2001), in a survey of 24 lakes, including the lakes studied by Helm *et al.* (2000), also noted an inverse relationship between enantioselective degradation and lake trophic status inferred by phosphorus and nitrogen concentrations.

4.3.2. Levels and fluxes of OCs in lake and river sediments

A significant number of studies on OCs in sediment were carried out prior to, and summarized in, the original AMAP POPs assessment, allowing for examination of circumpolar trends (de March *et al.*, 1998). A limited number of studies of POPs in freshwater sediments have been conducted since the previous AMAP POPs assessment. In this section, we examine studies of concentrations and fluxes in surface sediments and their spatial variation. Historical profiles are examined in Section 5.3.1. Most of the studies in this assessment involved lakes and rivers that are remote and where POPs inputs are likely due to long-range transport and deposition. Urban/industrial sources of contamination, however, may be important in rivers in Russia as well as in the Northwest Territories and Yukon in Canada and are also considered. The first AMAP assessment concluded that there were no global latitudinal or longitudinal trends of OCs in Arctic lake sediment, although fluxes of OCs declined with latitude if temperate lakes were included.

4.3.2.1. Russian river and lake sediments

Sediment samples were collected from the same sites as surface waters in four regions of the Russian Arctic (Kola Peninsula (Lake Lovozero); Pechora River mouth; on the Taymir Peninsula, the Yenisey River at Dudinka and Khatanga River at Khatanga; and, at Kanchalan on the Kanchalan River in Chukotka) in 2000/2001 and were analyzed for POPs (RAIPON/AMAP/GEF Project, 2001). A single pooled sample was analyzed from each region based on samples collected at either 0-2 cm (Lovozero) or 0-5 cm depth (all others). PCBs were the dominant OCs in the freshwater sediments followed by DDT (Annex Table 6). Toxaphene (sum of Parlars 26, 52, and 60; detection limits approximately 0.1 ng/L) and PBDEs (detection limits approximately 0.5 ng/L) were not detected in any freshwater sediment sample.

OC concentrations were similar in all regions of Russia with the exception of DDT concentrations in Pechora sediment (Annex Table 6). Concentrations of DDT in this region were 70 times higher than the other regions. This sample was a pool of ten subsamples from the Nelmin Nos area of the river. The ratio of DDT isomers to ΣDDT in the Nelmin Nos sediment is 0.67 compared to 0.2-0.24 in the other sediments analyzed in the RAIPON/AMAP/GEF Project. DDT isomers predominate in newly synthesized DDT, but are converted to DDE and DDD isomers in the environment. The high concentrations of ΣDDTs and the high ratio of DDT to ΣDDTs in the Pechora sediment suggest recent use of DDT in this region.

Skotvold and Savinov (2003) reported ΣPCB₁₀ (sum of ten major congeners) in surface (0-2 cm) sediment samples from 11 coastal tundra ponds collected along the Russian Arctic coast from the southeastern Barents Sea to the East Siberian Sea in 1994-95. Most of these data were previously reported in the AMAP POPs assessment (de March *et al.* 1998) but not discussed in detail. Mean ΣPCB concentrations ranged from 0.38 ± 0.22 ng/g dw for three ponds on the Laptev Sea coast to 7.9 ± 9.9 ng/g dw for three ponds on the Kara Sea coast. Only one sample collected in a pond located on Baydaratskaya Bay coast had a relatively high ΣPCB₁₀ concentration (19.3 ng/g).

Overall the ΣPCB concentrations in Russian freshwater lake/river sediments analyzed by the recent RAIPON/AMAP/GEF Project are at similar low ng/g (dw) levels when compared to results from the major north-flowing rivers in Russia reported in the first AMAP POPs assessment (de March *et al.*, 1998). Concentrations in Lake Lovozero sediments were similar to those reported by Skotvold and Savinov (2003) for lakes in northern Finnmark and on the southeastern Barents Sea coast. However, the ΣDDT concentrations in the pooled sediment sample from the Pechora mouth exceeded concentrations previously reported in the first AMAP POPs assessment for the major north-flowing rivers in Russia (de March *et al.*, 1998). In the present dataset (Annex Table 6) one site, Watson Lake, in the Yukon in the Western Canadian Arctic had higher ΣDDTs than the sample from the Pechora. The Watson Lake area was known to have received DDT applications for biting-fly control in the 1950's (Rawn *et al.*, 2001) and use of DDT for this purpose may be the source of the DDT in the Pechora as well.

4.3.2.2. Lake sediments in northern Norway and Sweden

Skotvold and Savinov (2003) determined ΣPCB_{10} in surface bottom sediments (0-2 cm depth) collected from 26 remote lakes in northern Norway in 1994 and 1995 and previously reported, but not discussed in detail, in the AMAP POPs assessment (de March *et al.*, 1998). ΣPCB_{10} levels in sediments from one lake on Svalbard (Barentsvann) and four in Nordland (northern/central Norway) were significantly higher compared to other areas to the east. Significantly lower ΣPCB_{10} levels were found in southwestern and northern Finnmark and the coast of the East Siberian and southeastern Barents Seas compared to the lakes in Nordland, Svalbard, and Bjørnøya. The highest PCB concentrations were found in the lake Ellasjøen on Bjørnøya as discussed in Section 4.3.2.3.

Rose *et al.* (2003) found ΣPCB_{10} concentrations for surface sediments from five lakes along the west coast of Svalbard sampled in 1997 that ranged between 2.5 and 13.5 ng/g (Annex Table 6). This study involved the analysis of surface (0-1 cm) and pre-industrial sediments from dated cores. Highest concentrations and fluxes were recorded in the surface slice of a core from the lake Tenndammen located near the coal mining towns of Barentsburg and Longyearbyen. This lake also showed elevated spherical carbonaceous particles and PAHs in surface slices compared to the other lakes on Svalbard, although levels of contamination were low compared to European sites (Rose *et al.*, 2003).

A latitudinal study of organochlorine contamination in bottom sediments of 100 Swedish lakes, many of which were part of the National Swedish Environmental Monitoring program (Swedish Monitoring Program, 2002), included two lakes from the Swedish Arctic mountains and other other high latitude lakes (Söderström *et al.*, 2002). This study compared concentrations of PCBs (seven congeners), three DDT-related compounds, HCB, and three HCH-isomers in surface (0-2 cm) samples of each lake. The six Swedish Arctic lakes had significantly lower mean concentrations of ΣPCB (0.9 ± 0.5 ng/g dw), $\Sigma DDTs$ (1.0 ± 1.0 ng/g dw), and ΣHCH (0.1 ± 0.05 ng/g dw) than southern lakes (9.2 ± 6.3 ng/g dw, 14.6 ± 12.1 ng/g dw, and 1.3 ± 1.5 ng/g dw, respectively). For HCB the six northern lakes had about three-fold lower concentrations than the 60 southern lakes in the study, reflecting the longer atmospheric half-life of HCB than the other compounds and lack of major past local uses in the south.

These studies in Sweden and the Norwegian and Russian Arctic illustrate how a large array of lakes can be used to assess broad geographical trends in deposition of POPs. Similar approaches have been used in North America (e.g., Muir *et al.*, 1995a; 1996a), but with far fewer and less well characterized lakes than in Sweden or Norway. A limitation of this approach is that, generally, the sediment cores were not dated, thus sedimentation rates and the degree of particle focusing are not known. Given generally lower sedimentation rates, especially in the Arctic mountain lakes and in other lakes above the tree line, it is reasonable to assume that a much longer period of deposition was represented by the 2-cm layer in the high latitude lakes than in those from southern Sweden or northern/central Norway. This complicates the geographical comparison since only recent deposition may be measured in high sedimentation sites versus longer-term deposition at low sedimentation sites.

4.3.2.3. Sediments from lakes on Bjørnøya

Sediment cores were taken from two small lakes (Ellasjøen and Øyangen) on Bjørnøya in 1996 for OC analysis as part of a larger study (Section 4.3.5). Concentrations of all OCs were much higher in Ellasjøen compared to Øyangen. The concentration of PCBs in surface sediment from Ellasjøen ($\Sigma PCB_7 = 60$ ng/g dw) was an order of magnitude higher than in Øyangen ($\Sigma PCB_7 = 4.4$ ng/g dw). As previously noted, the concentrations found in the sediments of Ellasjøen are the highest found for a remote lake in the Arctic. In Ellasjøen, guano from seabirds was identified as a potential source of contaminants (Evenset *et al.*, 2002). Levels reported for Øyangen are in the range generally reported for lakes in northern Norway and Sweden (Skotvold and Savinov, 2003).

DDT isomers make up a small percentage of the total $\Sigma DDTs$ in lake sediments from Bjørnøya indicating that atmopheric input (and/or guano inputs in the case of Ellasjøen) was the primary source.

The only chlordanes with concentrations above the detection limit in the surface sediment from Øyangen were *cis*-chlordane and *trans*- and *cis*-nonachlor at 0.08, 0.06, and 0.03 ng/g dw, respectively. These same compounds were present at concentrations two to four times higher (0.17, 0.22, and 0.10 ng/g dw, respectively) in surface sediments from Ellasjøen. Oxychlordane, *trans*-chlordane, and *cis*-chlordane were also detected in Ellasjøen (0.11, 0.05 and 0.04 ng/g dw, respectively). Heptachlor and its oxidation product, heptachlor epoxide, were below the detection limit in all sediment samples. Concentrations of γ-HCH and α-HCH in the surface sediments from Ellasjøen and Øyangen were relatively low (<0.2 and <0.4 ng/g dw, respectively), as were the concentrations of HCB (<0.8 ng/g dw). Dieldrin was present at 0.51 ng/g dw in the surface sediment in Ellasjøen. None of these pesticides could be detected in the sediment from Øyangen.

4.3.2.4. North American Arctic lake sediments

Concentrations and fluxes of POPs in lake sediments have been recently reported for about 14 lakes in the North American Arctic (Cleverly *et al.*, 1996; Lockhart, 1996; 1997; Macdonald *et al.*, 2000; Muir *et al.,* 2002b; Rawn *et al.,* 2001; Stern and Evans, 2003). When combined with previous studies in Alaska and northern Canada that were reviewed in the AMAP POPs assessment (de March *et al.*, 1998) results are available for about 30 lakes. Similar to the approach used in studies in Norway and Sweden, sediment cores from the deepest point in each lake have been used in almost all studies in the North American Arctic. However, most of the sediment cores have also been dated using the ^{210}Pb or ^{137}Cs techniques (Oldfield and Appleby, 1984) which yields an estimate of sedimentation rates and particle focusing factors. Thus fluxes (concentration $\times$ sedimentation
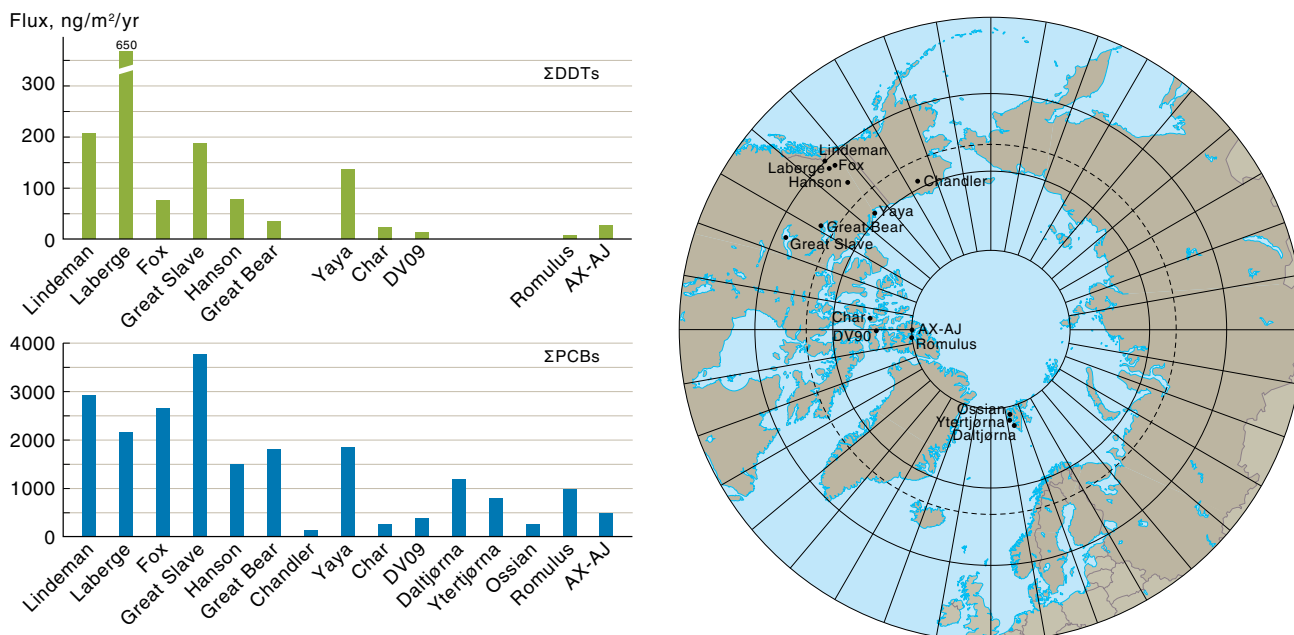
Figure 4·19. Fluxes of ΣDDTs and ΣPCBs in lake sediment cores (averages for slices dated to the 1990s) from the Canadian Arctic and Svalbard. Lakes are arranged by increasing latitude from left to right. A significant decline with increasing north latitude was observed for both DDT and PCB. Lakes with significant influence of local inputs are omitted.

rate) of POPs to lake sediments can be calculated over a wide geographic area in the North American Arctic. Fluxes (post-1990) of ΣDDTs and ΣPCBs reported recently in 14 lakes in the North American Arctic and, for PCBs, in three lakes on Svalbard (Rose et al., 2003) are shown in Figure 4·19.

Alaska
Cleverly *et al*. (1996) measured fluxes of PCBs, including coplanar PCBs, as well as PCDD/Fs in a dated sediment core from Chandler Lake in northern Alaska. These data were not included in the previous AMAP POPs assessment. Very low concentrations of PCBs were detected (Annex Table 6) and fluxes were among the lowest observed in Arctic lake sediments (Figure 4·19). Gubala *et al*. (1995) found similar low fluxes of PCBs and OC pesticides in a sediment core from Wonder Lake and lower fluxes in Schrader Lake in northern Alaska. Overall, knowledge of fluxes of PCBs and OC pesticides to lakes in Alaska is very limited.

Canadian Arctic lakes
Rawn *et al*. (2001) reported fluxes and historical profiles of PCBs and OC pesticides in sediment cores from six lakes and from one alpine lake in northern British Columbia within the Yukon River watershed. Surface concentrations and maximum concentrations in the core are presented in Annex Table 6. Several lakes showed evidence of local contamination. The highest ΣPCB and ΣDDT levels were measured in deep sediments from Watson Lake, although levels were much lower in surface sediments. Both chemicals showed increases in the mid-1940s consistent with the use of pesticides for biting-fly control during the building of the Alaska Highway. Hanson Lake was treated with toxaphene, and Lockhart *et al*. (1997) and Vetter *et al*. (1999) have reported the profile of toxaphene congeners in sediments from this lake. Sediment cores also revealed evidence for past use of DDT in the region, especially in Lake

Laberge (Rawn *et al*., 2001). ΣPCB concentrations in Lindeman and Kusawa Lake surface sediments, both very remote from urban areas in the Yukon, were low relative to the other Yukon lakes that were studied (Annex Table 6).

Concentrations of ΣHCHs and ΣCHLs in surface sediments of the seven lakes studied by Rawn *et al*. (2001) were generally in the low ng/g range, consistent with a predominantly atmospheric input source (Annex Table 6). Subsurface maximum ΣHCH concentrations were observed in all but Lindeman Lake. α- and γ-HCH were the dominant isomers contributing on average, 39 and 52%, respectively, to ΣHCHs. Elevated levels of ΣCHLs were observed in slices dated to the 1970s and early 1980s in Fox, Kusawa, Hanson, and Lindeman Lakes. Peak concentrations were measured in the surface sediment from Atlin Lake (3.87 ng/g dw).

Evans *et al*. (1996) examined concentrations and fluxes of PCBs, OC pesticides, and PCDD/Fs in Great Slave Lake. This study was not reported in the previous AMAP POPs assessment. Great Slave Lake, which is the fourth largest lake in Canada in terms of both surface area (27 000 km^2) and volume (2088 km^3), is a relatively pristine ecosystem with low concentrations of organic contaminants in all but the most industrialized areas (Mudroch *et al*., 1992). Greater than 50% of the population in the Northwest Territories resides along the shores of Great Slave Lake. The Slave River, which receives the majority of its water from the Peace and Athabasca rivers, is the major river entering Great Slave Lake and contributes some 87% of the total annual inflow of 135 km^3 (Evans *et al*., 1996).

Sedimentation rates were highest near the mouth of the Slave River and decreased with increasing distance from the river mouth (Figure 4·20 a). Sedimentation rates were very low at the westernmost sampled station and roughly comparable to that in the East Arm of Great Slave Lake. Most sediments (and associated contaminants), therefore, are likely to be deposited in the
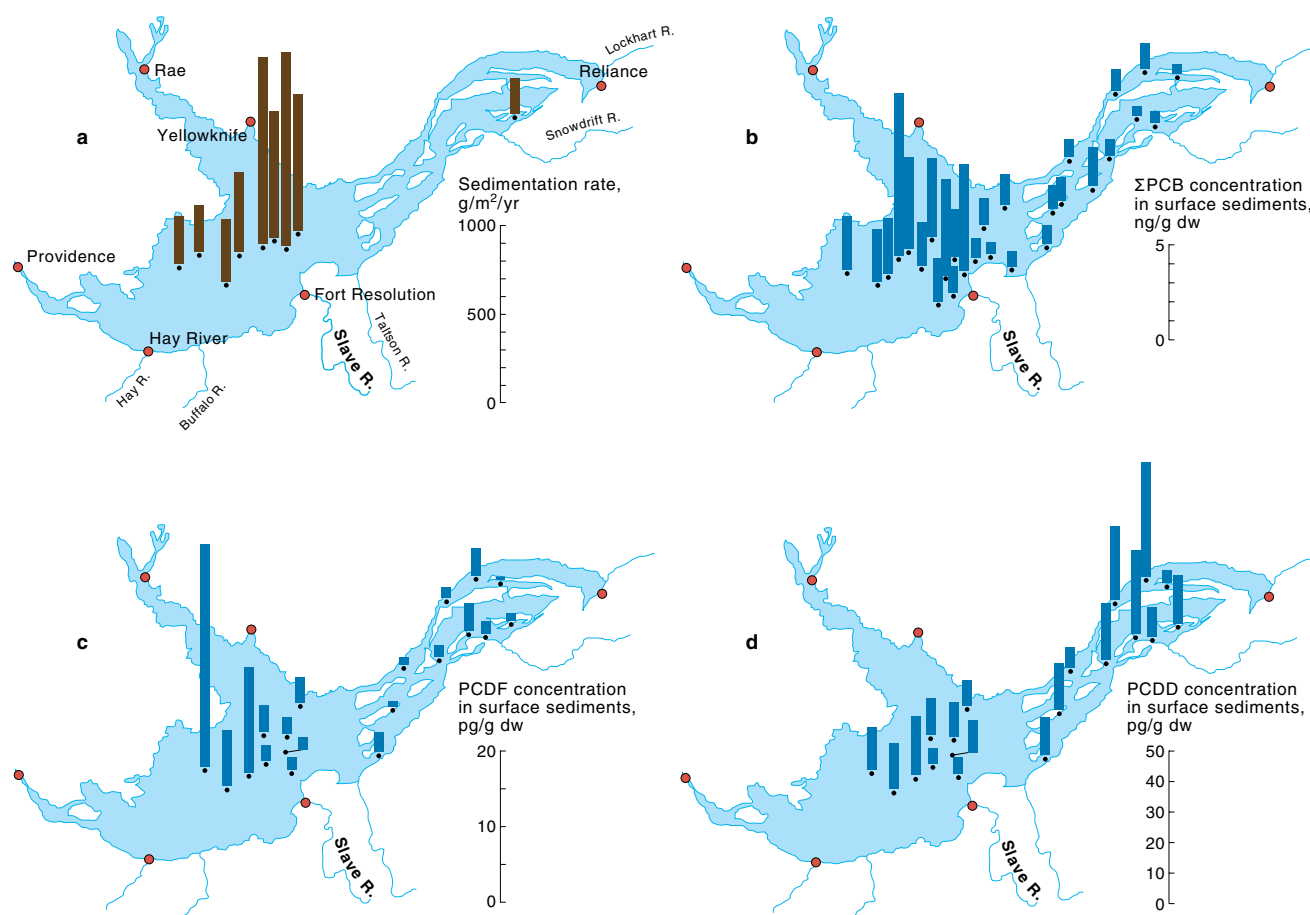
Figure 4·20. a) Sedimentation rates, b) ΣPCB concentrations, c) PCDF concentrations, and d) PCDD concentrations in surface sediments of Great Slave Lake (Northwest Territories, Canada).

deeper regions immediately offshore of the mouth of the Slave River.

ΣPCB (70 congeners) and PCDDFs (major 2,3,7,8-substituted tetra- to octachlorinated congeners) were highest in sediments offshore of the river mouth and decreased with increasing distance from the river mouth (Figure 4·20 b,c,d). This, combined with the higher sedimentation rates in this region, indicates that contaminant fluxes of these compounds to the sediments were substantially greater offshore of the river than with increasing distance away from the river mouth. The converse pattern was observed for PCDFs, which tended to occur in high concentrations in the East Arm of Great Slave Lake.

Lockhart (1997) analyzed a sediment core from Yaya Lake, an isolated lake in the Mackenzie Delta (Annex Table 6). Surface concentrations of major OC pesticides and ΣPCBs in this core were very low, consistent with its isolated location relative to Great Slave Lake (Figure 4·19). Graf Pannatier (1997) examined concentrations and fluxes of PCBs and OC pesticides in a series of 'closure' lakes (connected to the Mackenzie River and flooded annually in the spring freshet) in the Mackenzie Delta. These lakes were characterized by very high sedimentation rates of 2300-12 200 g/m²/yr due to annual sediment deposition from flooding. This was much higher than nearby Yaya Lake (480 g/m²/yr) which is not flooded as frequently (Lockhart, 1997). Concentrations of ΣPCBs and major OC pesticides in sediment cores from Lakes 6 and 7, two middle delta lakes, were low and similar to those in Yaya Lake (Annex Table 6).

Surface and maximum concentrations of major OC pesticides and PCBs in sediment cores from five isolated lakes in the Canadian Arctic Archipelago (Stern and Evans, 2003; Muir *et al.*, 2002b) are presented in Annex Table 6. Surface ΣPCB concentrations (0.5 cm depth) were relatively similar in all lakes ranging from 0.96 to 3.7 ng/g dw. ΣHCHs had the widest range of concentration in surface sediments (0.01-0.69 ng/g dw). Historical profiles of POPs in several of these lakes are discussed in Section 5.3.

Geographic trends in deposition of PCBs and DDT in lake sediments

Recent (1990s) fluxes (ng/m²/yr) of ΣPCBs and ΣDDTs in sediment, corrected for particle focusing, for selected lakes in the Canadian Arctic, Alaska, and Svalbard are shown in Figure 4·19. Lakes for which past local inputs were thought to be significant, such as Watson and Little Atlin Lakes in the Yukon (Rawn *et al.*, 2001), and the lake Tenndammen near mining towns in Svalbard, were omitted, as were Lakes 6 and 7 due to direct inputs of sediments from Mackenzie River flooding (Graf Pannatier, 1997). ΣDDT fluxes in all of the high latitude lakes, were two-fold or more lower than reported for Yukon or NWT lakes, but similar to fluxes found in northern Alaska (Gubala *et al.*, 1995), and to previous reports for cores from four High Arctic lakes collected in the late 1980s and early 1990s (Muir *et al.*, 1995a; 1996a). ΣDDT fluxes ranged widely; Fox, Lindeman, and Hanson Lakes in the Yukon had similar fluxes to Great

Slave and Yaya Lakes, while Lake Laberge had a much higher flux reflecting some continued input from old sources within the watershed. ΣPCB fluxes in all of the high latitude lakes in Canada and in Svalbard (Rose *et al.*, 2003) were also lower than lakes in the Yukon and Northwest Territories, but higher than in most Alaskan lakes (Cleverly *et al.*, 1996; Gubala *et al.,* 1995). A statistically significant decline in fluxes of ΣPCBs and ΣDDTs with latitude was observed, reflecting the higher fluxes in the western Canadian Arctic lakes (Figure 4·19). This decline with increased northern latitude was also observed for higher chlorinated PCBs by Muir *et al.* (1996a) and for ΣDDTs by Muir *et al.* (1995a) when remote lakes from northwestern Ontario were included in the regression.

4.3.2.5. PCDD/F fluxes to lake sediments

Cleverly *et al.* (1996) reported planar PCBs and PCDD/Fs in a sediment core from Chandler Lake in northern Alaska. The flux of total TCDD TEQs, based on PCBs and PCDD/Fs were 8.7 pg TEQ/m^2/yr in the surface slice from this core. The TEQs were mainly due to CB126, 2,3,7,8-TCDD, and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin. PCDD/Fs have also been determined in sediments from a laminated core from Lake DV09 on Devon Island (Stern and Evans, 2003). The surface and maximum deposition flux values for PCDDs to Lake DV09 were calculated to be 0.01 and 0.36 pg TEQ/m^2/ yr, respectively. The historical trends in PCDD/F deposition in this core, which had much higher temporal resolution than the one from Chandler Lake, are discussed in Section 5.3.

Using the PCDD/F emission inventory for Canada and the U.S., Commoner *et al.* (2000) predicted 'dioxin' toxic equivalents (TEQ) deposition of about 4-53 pg TEQ/m^2/yr to terrestrial surfaces near eight communities in the eastern Canadian Arctic which is in reasonable agreement with observations of Cleverly *et al.* (1996) but an order of magnitude higher than reported for the Devon Island core.

Evans *et al.* (1996) determined PCDDs and PCDFs in surface sediments and sediment cores from Great Slave Lake (Figure 4·20). PCDD concentrations were highest in sediments offshore of the Slave River mouth and decreased with increasing distance. This, combined with the higher sedimentation rates in this region, indicates that contaminant fluxes of these compounds to the sediments were substantially greater offshore of the river than with increasing distance away. The converse pattern was observed for PCDFs, which tended to occur in high concentrations in the East Arm of the lake.

No reports were found on PCDD/Fs or coplanar PCB deposition to sediments in the European Arctic.

4.3.2.6. 'New' chemicals in Arctic sediments

Tomy *et al.* (1999) determined SCCPs in three Arctic lake sediment cores previously analyzed by Muir *et al.* (1996a) and Lockhart (1997). Surface concentrations (0-1 cm) ranged from 257 ng/g dw in Fox Lake (Yukon) to 1.6 ng/g dw in Yaya Lake (Mackenzie Delta). Lake Hazen had intermediate concentrations of SCCPs. Stern and Evans (2003) reported maximum concentrations of SCCPs (17.6 ng/g dw) in the surface slice of a core from Lake DV09 on Devon Island. The possibility of contamination from SCCPs, which are widely used as flame retardant plasticizers and in cutting oils for metal machining cannot be ruled out, especially where there is a significant amount of small-boat traffic such as in Fox Lake. However, the results also indicate that long-range atmospheric transport and deposition were probably the major pathways for SCCPs to the very remote lakes (Yaya, DV09, and Hazen).

No reports were found on SCCPs or other 'new' POPs in lake sediments from the European Arctic.

4.3.2.7. PAHs in Arctic lake sediments

PAHs in freshwater sediments were not assessed in the previous AMAP assessment. Here we confine the discussion primarily to pyrogenic PAHs in dated lake sediment cores. Fernández *et al.* (1999; 2000) calculated fluxes of 23 PAHs for the lake Arresjøen on northwestern Svalbard (79°40'N) and Øvre Neådalsvatn (62°46'N) in the Caledonian mountain range of central Norway. Major PAHs in Arresjøen were primarily pyrolytic in origin (i.e. resulting from combustion of coal and hydrocarbon fuel burning) such as phenanthrene, fluoranthene, pyrene, chrysene/triphenylene, indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene. Fernández *et al.* (1999) concluded that the PAH deposition pattern in high altitude mountain lakes, including Arresjøen, paralleled sulfate deposition, pointing to combustion particles as the main input pathway. Rose *et al.* (2003) determined 15 PAHs in surface and prehistorical slices of sediment cores from four lakes in Svalbard. Highest fluxes were found in the lake Tenndammen (360 μg/m^2/yr) a lake within 20 km of the coal mining towns of Barentsburg and Longyearbyen. PAH fluxes in the four Svalbard lakes appeared to decline with distance from the Barentsburg/Longyearbyen area.

Fluxes of ΣPAH (the same 23 PAHs as analyzed by Fernández *et al.* (1999) minus perylene and retene) have also been reported in a series of studies of dated sediment cores from the Canadian Arctic (Lockhart, 1994; 1996; 1997; Muir and Lockhart, 1994; Lockhart *et al.*, 1995; 1997). Total PAH fluxes in Yukon lakes ranged from 9.1 μg/m^2/yr in remote Kusawa Lake to 174 μg/ m^2/yr in Little Atlin Lake (Lockhart *et al.*, 1997). Two remote lakes in the Mackenzie River Basin, Lac Sainte Therese and Yaya Lake, had high ΣPAH fluxes (68 and 140 μg/m^2/yr, respectively) (Lockhart, 1997).

Graf Pannatier (1997) determined PAHs (unsubstituted as well as methyl naphthalenes and phenanthrenes) in sediment cores from four 'closure' lakes in the Mackenzie River Delta. Concentrations of ΣPAHs in surface sediments (0-1 cm) ranged from 650 to 900 ng/g dw. Due to high sedimentation rates in these lakes resulting from annual deposition in the spring freshet, fluxes of ΣPAHs in these lakes were in the range of 4-11 mg/m^2/ yr, well above fluxes for nearby Yaya Lake which is flooded less frequently. High ΣPAH values have also been found in Mackenzie River suspended particulates and they are thought to be mainly of petrogenic origin (Yunker and Macdonald, 1995).

Concentrations and fluxes of PAHs were also determined in sediment samples from Great Slave Lake
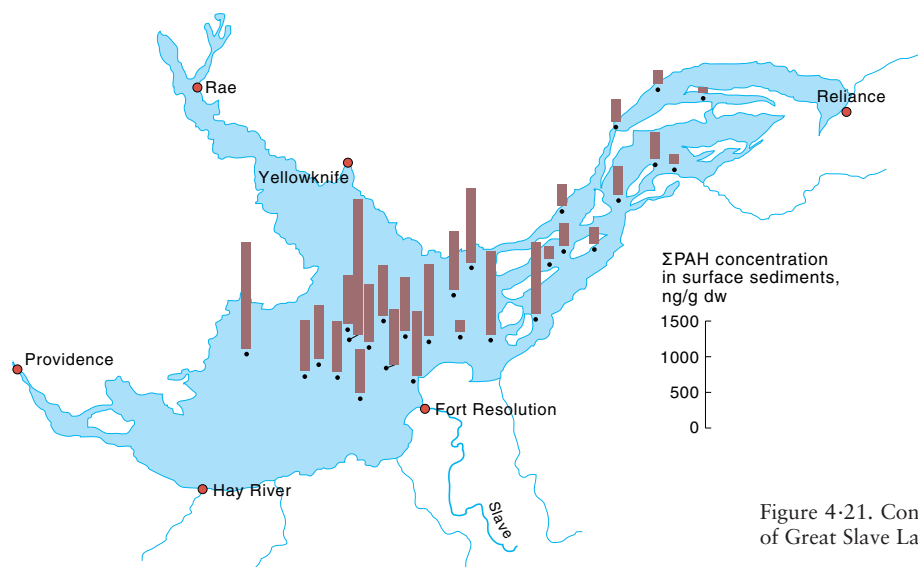
Figure 4·21. Concentrations of PAHs in surface sediments of Great Slave Lake (NWT, Canada) (Evans *et al.*, 1996).

(Evans *et al.*, 1996). PAH concentrations, like those for PCDD/Fs, were highest in sediments offshore of the mouth of the Slave River and decreased with increasing distance (Figure 4·21).

The recent (late 1980-1990s) PAH fluxes for the European and Canadian Arctic are compared in Figure 4·22. In general, excluding the lake Tenndammen, higher fluxes of substituted PAHs have been found in the Mackenzie valley and Yukon lakes compared with the European Arctic lakes. The large range of PAH fluxes in Canadian Arctic lake sediment cores demonstrates that sources of PAHs are complex and could be due to natural petrogenic sources within the basin while at the same time showing some characteristics of pyrolytic inputs.

4.3.3. Freshwater fish and invertebrates

Freshwater fish are an important component in the diet of many northern communities, and a variety of tissues may be consumed. OC concentrations observed in freshwater invertebrates and fish appear to be predominantly controlled by exposure (i.e. regional differences) and trophic level, with levels in various tissues determined by lipid content. OCs have been shown to biomagnify in Arctic freshwater food webs, which results in the greatest concentrations in the highest trophic-level fish (Kidd *et al.*, 1998). To accurately assess spatial and temporal trends of OCs in fish, the length, age and growth rates need to be considered because all can have an impact on observed OC concentrations (Johnston *et al.*, 2002). In light of this, observed relationships in this section need to be viewed with caution because these parameters were not considered in most studies, making comparisons of different studies difficult.

A fairly large dataset on OCs in freshwater fish and invertebrates was assessed for the first AMAP POPs assessment (de March *et al.*, 1998); since 1996, a smaller amount of additional data has been produced. This is likely due, in part, to the low concentrations of OCs generally found in Arctic freshwater systems when compared to temperate freshwater and Arctic marine systems. In general, concentrations (lipid corrected) of OCs in freshwater fish of the same species are similar throughout the Arctic (within an order of magnitude), with a few important exceptions that can be attributed to increased exposure or unique biological variations. For example, elevated levels of OCs in the lake Ellasjøen on Bjørnøya, north of Norway, have resulted in high OC
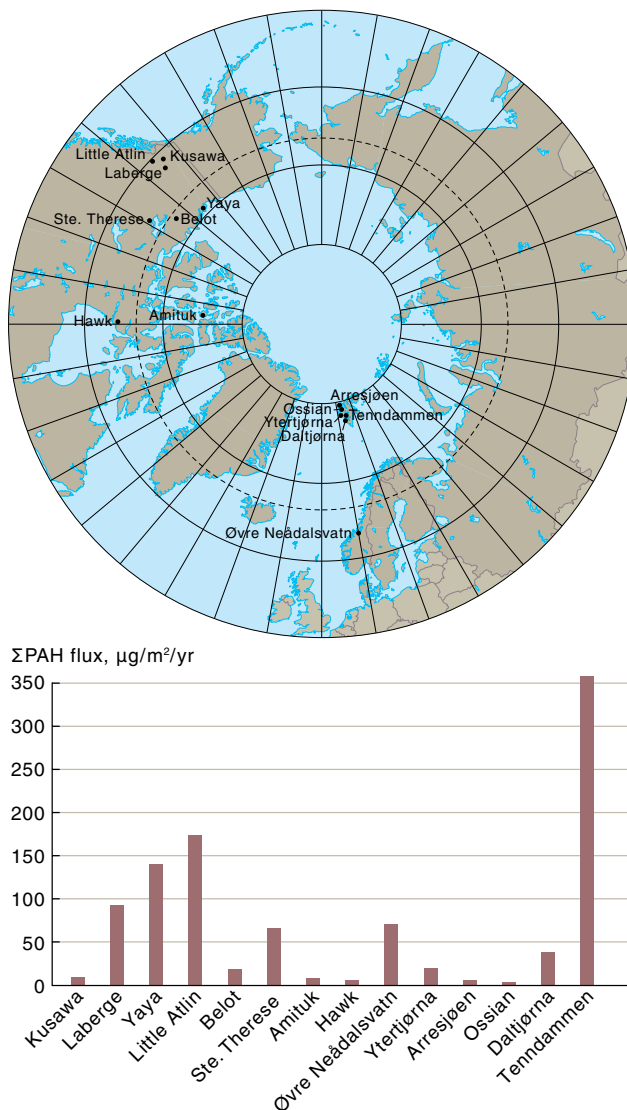

Figure 4·22. Recent fluxes of total PAH (23 PAHs minus perylene and retene) in dated lake sediment cores from the Canadian and Norwegian Arctic. Lakes are organized longitudinally from west to east.

concentrations in landlocked Arctic char from this lake (Section 4.3.5). PCBs and toxaphene continue to be the predominant OCs in freshwater invertebrates and fish, although data on toxaphene in the European Arctic are limited, and some exceptions do exist.

4.3.3.1. Invertebrates

A fairly comprehensive dataset on OCs in zooplankton from the Canadian Arctic was reviewed in the first AMAP assessment report. Observed spatial trends were attributed to a combination of differences in water concentrations and lake plankton biomass. Since this first AMAP assessment, there have been few studies on OCs in freshwater zooplankton (Annex Table 7). This is likely due to the low concern about OCs in freshwater zooplankton because of low concentrations and the fact that they are not a human diet item.

Data on OC concentrations in freshwater invertebrates were generated as part of a large study of OCs in the lakes of Bjørnøya (see Section 4.3.5). Zooplankton and benthic invertebrate samples were collected from three lakes (Skutilen, Ellasjøen, and Øyangen) on Bjørnøya in 1996 and in 1999. Chironomid larvae and pupae were also collected from fish stomachs in 1996 and in 1999. The levels of ΣPCBs, HCB and ΣDDTs in pooled samples of zooplankton and benthic organisms (*Chironomidae* sp. and *Lepidurus arcticus*) were greatest in Ellasjøen, consistent with results in sediment and fish (Figures 4·27 and 4·28, page 76). Sampled zooplankton from Ellasjøen had higher concentrations of all the measured contaminants than zooplankton from Skutilen, followed by Øyangen with the lowest concentrations. Chironomids from Ellasjøen had higher contaminant levels than the *Lepidurus* samples from the two other lakes. *L. arcticus* from Øyangen had higher levels of contaminants than *L. arcticus* from Skutilen. The lipid content was very low in *Lepidurus* from Skutilen. Calculated on a lipid weight basis, the contamination levels were higher in *Lepidurus* from Skutilen than from Øyangen.

4.3.3.2. Freshwater fish

Russian Arctic fish
POP analyses including PCDD/Fs were conducted on samples of various tissues (liver and muscle) from a number of fish species collected in 2000-2001 from four regions of the Russian Arctic: Kola Peninsula; Pechora Basin; Taymir Peninsula (Dudinka and Khatanga); and, Chukotka (Kanchalan and Lavrentiya) (RAIPON/ AMAP/GEF Project, 2001) (Annex Table 16). Species analyzed for each location are found in Annex Tables 7 and 16. This project addresses a major data gap for OCs in Russian freshwater biota identified in the first AMAP assessment report (de March *et al*., 1998). However, the somewhat limited sample numbers, current lack of biological data (e.g., body size), and lack of lipid data confounds efforts to statistically compare the sites within Russia with other locations, and such comparisons should be viewed with caution.

PCBs and DDTs were the predominant OCs found across all species in Russian freshwater fish, followed by chlordane and HCH (Annex Table 7). The highest con-
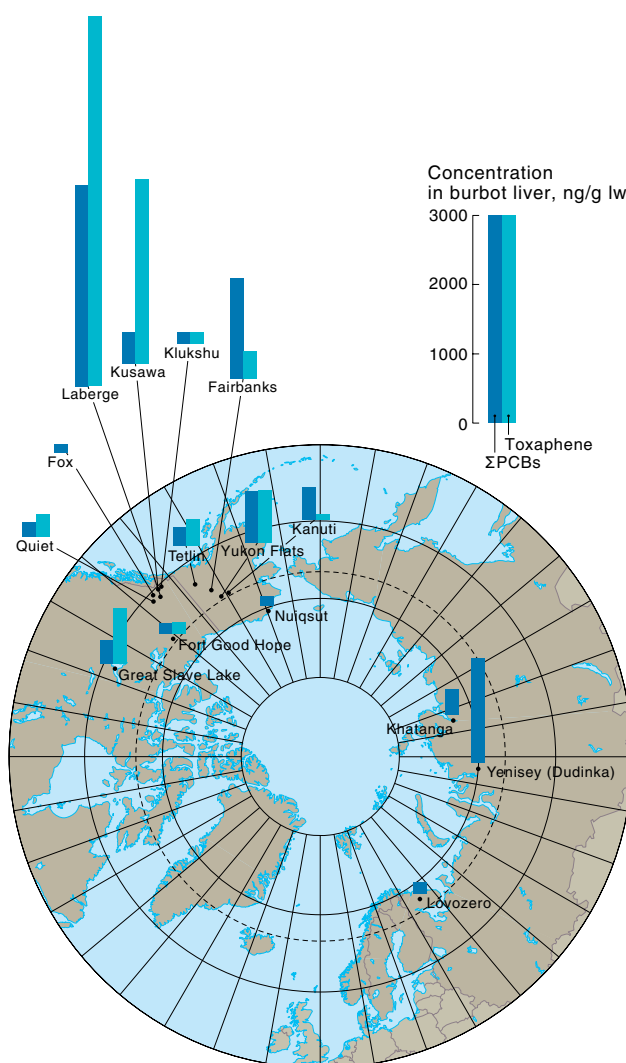

Figure 4·23. Spatial trends of ΣPCBs and toxaphene in burbot collected in Arctic Canada, Alaska, and Russia. Data for Lake Lovozero, Dudinka and Khatanga (Russian samples) were the sum of ten PCB congeners (no lipid content data was available for these samples, and this was therefore assumed to be 30%); for Fairbanks, Kanuti, Tetlin, and Yukon Flats, data were generated by the Aroclor method; all other data by the summation of >50 PCB congeners. Russian data from RAIPON/AMAP/GEF Project (2001); Fairbanks, Kanuti, Tetlin, and Yukon Flats data are from Mueller and Matz (2000); Nuiqsut data from Hoekstra (2002a), Great Slave Lake data from Evans and Muir (2001), and Fort Good Hope and Fox Lake data from Stern *et al*. (2001a); all other data are from Roach (2002).

centrations were observed in burbot (*Lota lota*) livers. This was attributable to their predatory nature as well as the high lipid content of their liver. The lowest concentrations were found in the whitefish species (*Coregonus clupeaformis*), a non-predatory fish. The relative differences in concentrations between species in Russia are similar to those observed in the Canadian Arctic.

Regional comparison of POP levels in Russian Arctic fish is difficult because no one species was collected in all regions. In burbot, the highest concentrations of ΣPCBs and ΣDDTs were observed in samples collected from Dudinka on the Taymir Peninsula, which were 5-10 times higher than concentrations observed on the Kola Peninsula and Khatanga on the Taymir Peninsula (Annex Table 7). In general, concentrations of PCBs in burbot from Dudinka are among the highest found in

Arctic burbot, but levels on the Kola Peninsula and at Khatanga are among the lowest (Figure 4·23). Again, without information on lipid levels, it is difficult to draw conclusions about spatial trends. Since these data were only recently generated, in-depth evaluation will be a future priority.

Comparison of PCDD/F levels between fish species in different regions of Russia is also difficult due to limited sample size and a lack of biological data (e.g., lipid contents) (Annex Table 16). In general, PCDD/F concentrations were similar between species with the exception of Arctic char from Lavrentiya, where concentrations of PCDD were ten times higher. These fish are likely sea-

Figure 4·24 Spatial trends of PCDD/Fs in muscle of whitefish collected from Russian lakes and rivers in 2000-2001 (RAIPON/AMAP/GEF Project, 2001), and Great Slave Lake, NWT, Canada in 1994 (Evans and Muir, 2001).

run, which may explain the higher level observed. In whitefish, PCDD/F concentrations were slightly higher in samples from the Kola Peninsula and Pechora Basin compared to eastern sites in Russia (Figure 4·24). Levels of PCDDs are higher and PCDFs are lower in the Russian Arctic whitefish compared to levels observed in Great Slave Lake whitefish in 1995 (Figure 4·24). PCDDs in the Russian fish were dominated by octachlorodi-benzo-*p*-dioxin, and 2,3,7,8-tetrachlorinated dibenzo-furan (TCDF) had the highest concentrations among PCDFs.

Great Slave Lake study

A variety of studies have been conducted investigating contaminants in biota in Great Slave Lake, Canada. Most of these studies were conducted in the mid-1990s, but monitoring has continued for a number of fish spe-

cies (Evans and Muir, 2000; 2001). In addition to water, the Peace and Athabasca rivers, which flow into the Slave River, transport tremendous amounts of sediments from the south into the Great Slave Lake ecosystem. This raises the possibility that increased development to the south may be resulting in increased contaminant transport to the lake through the Slave River, in addition to input via the atmosphere.

OC concentrations were similar between four species of predatory fish (northern pike (*Esox lucius*), walleye (*Stizostedion vitreum*), burbot, and inconnu (*Stenodus leucichthys*)) collected in the same region of Great Slave Lake (Annex Table 7), which is likely due to the fact that all of these species predate predominantly on fish. OC concentrations (on both a wet and lipid weight basis) tended, however, to be slightly higher in fish collected in the East Arm of Great Slave Lake compared with the West Basin in 1993 and 1999, although this varied somewhat with the contaminant and/or fish species. The variation in concentrations between basins could be due to differences in the characteristics of the fish (e.g., length and/or age) collected for the two regions and/or the characteristics of the two basins. OC concentrations and sedimentation rates tended to be higher in lake sediments from the West Basin than in the East Arm. Lake water in the East Arm is clear with low particulate concentrations, and invertebrates such as mysids and amphipods are strongly benthic. In contrast, in the West Basin, waters are turbid with high concentrations of suspended silts and clays, and invertebrates spend less time in close contact with the sediments than in the East Arm. Biota inhabiting the East Arm of Great Slave Lake may be accumulating higher body burdens of persistent OCs than in the West Basin because these contaminants are more bioavailable to them.
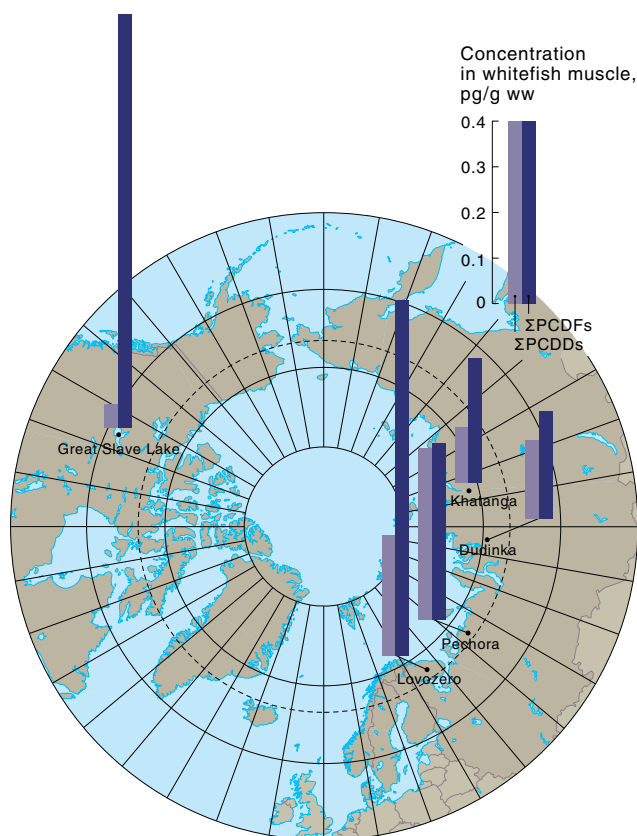
Lake trout

Concentrations of OCs were determined in lake trout muscle from a number of lakes in the Yukon and Northwest Territories in the late 1990s (Stern *et al*., 2000; Evans and Muir, 2001; Roach, 2002). Previous work on the Yukon lakes in 1993 found that OC concentrations were particularly high in Lake Laberge, which was attributed to local point sources and a long food web (Kidd *et al*., 1995). Since that time, concentrations in Lake Laberge lake trout have decreased up to four-fold, over the five-year period from 1993 to 1998 (see Section 5.3.3). When the lipid-adjusted OC levels in lake trout from Lake Laberge are compared to the other Yukon lakes (1998 and 1999 collections only), levels in the Lake Laberge trout do not stand out as they did in the early 1990s. However, caution is warranted in interpreting these results as no effort was made to account for differences in biological characteristics (e.g., size or age) between the lake trout sampled in each lake. In some lakes, much smaller trout were sampled.

Concentrations of the more lipophilic contaminants, such as toxaphene and PCBs, were much higher in lake trout from Kusawa Lake (1998-1999), while lake trout from Atlin Lake had the highest concentrations of the less lipophilic OCs (ΣHCH and ΣCBz) (Figure 4·25). The lakes Kusawa and Atlin receive water from glacial melt, which may, in part, explain high OC levels in fish from these lakes. Glacial melt has been implicated as a
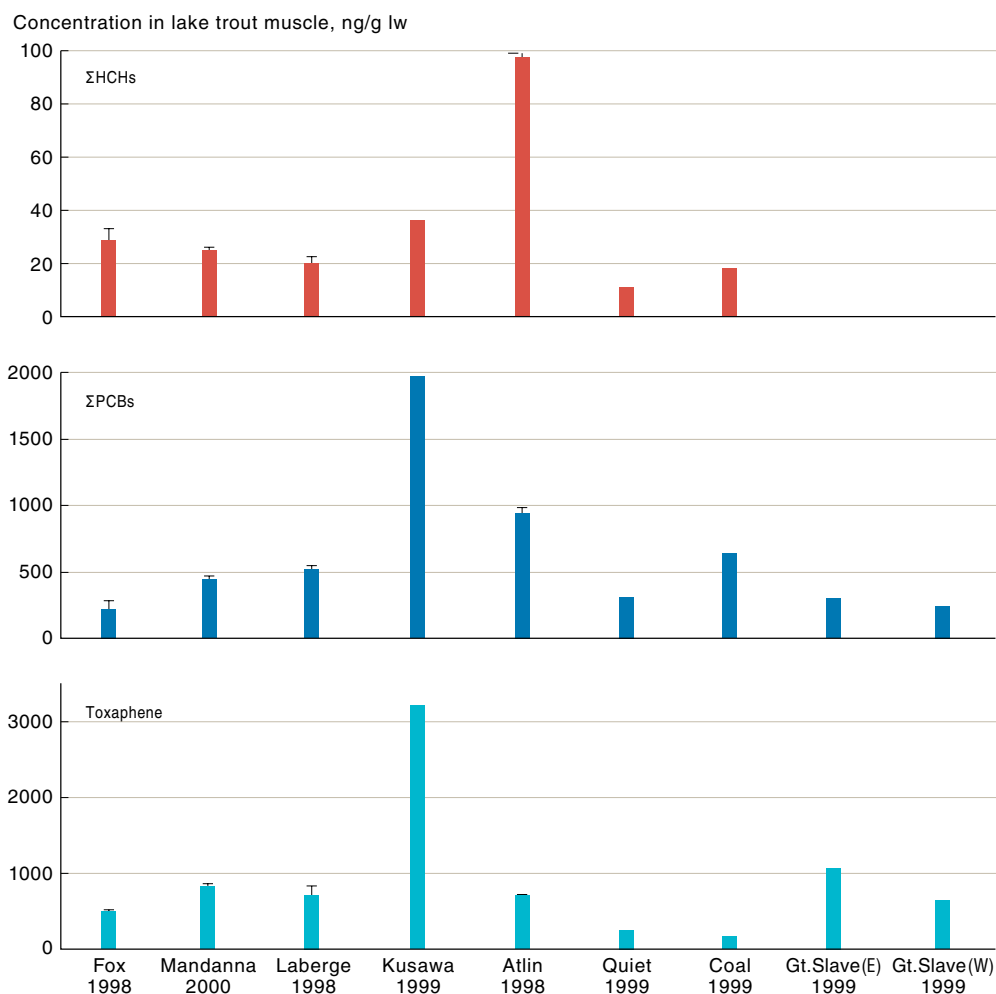
Concentration in lake trout muscle, ng/g lw

Figure 4·25. ΣHCH, ΣPCB, and toxaphene concentrations in lake trout from the Canadian Arctic. Great Slave Lake data from Evans and Muir (2001), all other data from Roach (2002).

source of higher levels in fish from some lakes in Alberta (Blais *et al.*, 2001). The levels of the different OC groups are not consistent between Kusawa Lake and Atlin Lake, however, and OC levels in burbot liver from these two lakes are not higher than those observed in other Yukon and NWT lakes. These data need to be assessed in light of variable biological characteristics of the fish collected from each lake. For example, lipid was found to be a significant co-variate of OC concentrations in lake trout from the Yukon lakes (Stern *et al.*, 2000). Concentrations (lipid corrected) of most OCs were higher in the Yukon lakes compared to Great Slave Lake (Figure 4·25).

Lake trout from several sites in northern Norway had ΣPCB levels of 0.23-3.2 ng/g ww in muscle (Annex Table 7) (Schlabach *et al.*, 2001). PCDD/F and non-*ortho* PCB levels expressed as TEQs were 0.17-0.84 pg/g ww (13-34 pg/g lw) (Annex Table 16).

Burbot

There is a fairly large dataset on OCs in burbot that was reported in the previous AMAP assessment (de March *et al.*, 1998). Levels of OCs in burbot have received attention because indigenous people consume their high-lipid liver, and the species has a wide distribution. In addition to Russian studies discussed above, a small number of studies have been carried out on POPs in burbot in North America since the previous AMAP assessment, and all were focused on Alaska and the western Canada Arctic.

Levels of POPs were assessed in burbot livers from Alaska (Fairbanks and Yukon Flats, Tetlin, and Kanuti National Wildlife Refuges on the Yukon, Koyukuk, and Tanana rivers) in 1998, in part, to assess the influence of long-range transport of POPs on the freshwaters of the Alaskan interior (Mueller and Matz, 2000) (Figure 4·23). This study highlighted the influence of biological variability on OC concentrations. Lipid concentrations were significantly positively correlated with dieldrin and heptachlor epoxide concentrations. Weight was significantly positively correlated with α-chlordane, dieldrin, HCB, heptachlor epoxide, mirex, toxaphene, and *trans*-nonachlor concentrations. This study also showed that OC concentrations could vary between fish populations that are fairly close geographically. General patterns of greater OC contamination in burbot livers from Yukon Flats and Fairbanks compared to Tetlin and Kanuti were consistent, with significant differences in concentrations for some analytes. Analysis of the data was complicated by differing lipid concentrations in samples, differing fish weights among sites, and by a small sample size at Yukon Flats. The greater concentrations of DDT and its metabolites and ΣPCBs found at Fairbanks compared with other sites likely reflect historical use of these compounds within the city of Fairbanks and at nearby military bases. Toxaphene concentrations were generally low.

There were variations in OC concentrations in the liver of burbot collected in the Alaskan, Russian, and Canadian Arctic (Figure 4·23). The highest OC concentrations, including ΣPCBs and ΣDDTs, were found in

Lake Laberge burbot, but these OC levels are similar to previous measurements in burbot from this lake (Kidd *et al.*, 1995; 1998). Burbot from Fairbanks and Yukon Flats had somewhat lower mean ΣPCB concentrations than at Lake Laberge. The ΣPCB concentrations observed in burbot of Fairbanks and Yukon Flats are likely due to local sources. Mean ΣPCB concentrations in Russian burbot from Dudinka were similar to levels found in burbot from Fairbanks and Yukon Flats, but ΣDDT levels were higher. Information is lacking to completely evaluate the Russian data.

For the remaining lakes, with the possible exception of Lake Laberge, atmospheric deposition is the dominant route of OC delivery (Kidd *et al.*, 1995). For these lakes, OC levels varied much less and were generally within a factor of two of each other. The OC concentrations in burbot from these lakes are lower than those previously reported for burbot collected from the Mackenzie River in the Canadian Arctic in the 1980s (Muir *et al.*, 1990a). For Canada, all of these sites are fairly close to the Mackenzie, so the lower concentrations in the recently collected burbot most likely reflect temporal changes as opposed to spatial differences between the sites (see Section 5.3.3).

Burbot liver from northern Norway had TEQ levels based on PCDD/Fs and non-*ortho* PCBs (see Annex Table 16) of 12.8 pg/g ww (110 pg/g lw) (Schlabach *et al.*, 2001).

Landlocked Arctic char

Landlocked char have been collected over a number of years from lakes near the community of Qausuittuq (Resolute) in the Canadian High Arctic (Muir *et al.*, 2001a). The effect of diet and trophic level on OC levels was investigated using stable isotopes of carbon and nitrogen. A few fish have $\delta^{15}N$ values that were up to 3.8 parts per thousand (‰) higher than others. This reflects differences in trophic level because concentrations of the heavier isotope of nitrogen, ^{15}N, are progressively enriched from prey to predator at an average of 3 to 5 ‰ (Peterson and Fry, 1987). Landlocked char populations are known to develop a behavioral dichotomy wherein some individuals at a certain 'escape size' adapt to a cannibalistic feeding habit, while other individuals may not. In Char Lake, a system containing only char, Hobson and Welch (1995) associated $\delta^{15}N$ values of 13.7 ‰ with piscivory in char. They also found a significant increase in the $\delta^{15}N$ of these fish with size that they attributed to cannibalism within the population. There were no significant correlations of $\delta^{15}N$ with length or weight in Resolute Lake char. ΣPCB, ΣDDT, and ΣCHL concentrations (lipid-normalized) were significantly correlated with $\delta^{15}N$ in char from Resolute Lake collected in 1997 and 1999, suggesting that biomagnification of OCs is occurring within the char population due to the presence of piscivorous char. These results support the hypothesis (Muir *et al.*, 2001a) that the reason for higher levels seen in char sampled in 1993 in Char Lake was that piscivorous char were analyzed.

In 1998, dorsal axial muscle from landlocked (non-anadromous) Arctic char from the lakes Ellasjøen and Øyangen (all caught in 1996) located on Bjørnøya, were analyzed for stable isotopes of nitrogen, PCBs, and a number of pesticides. An overview of the Bjørnøya lake studies is provided in Section 4.3.5. The $\delta^{15}N$ values in muscle tissue of Arctic char were generally higher in Ellasjøen (mean 18.1‰) than in Øyangen (mean 8.8 ‰), suggesting a different food web structure between the lakes or an input of N that was enriched in ^{15}N. Consistent with the higher $\delta^{15}N$ values, the mean concentrations of OCs were greater in the Ellasjøen char compared with the Øyangen char. The largest concentration differences were found for the heavier PCB congeners, ΣDDTs, and oxychlordane (Figures 4·27 and 4·28). There was no significant difference for HCHs. ΣPCB concentrations (seven congeners) in Arctic char were 694 ng/g ww for fish from Ellasjøen and 49 ng/g ww for fish from Øyangen. The congener pattern was generally similar for both lakes, with CB138 and CB153 having the highest levels, followed by CBs 180, 118, 156, 105, and 101. However, CB138 co-eluted with CB160 and 163, leading to an overestimation of this value. The mean concentration of *p,p*'-DDE in char muscle tissue was 57.7 ng/g ww in Ellasjøen and 3.4 ng/g ww in Øyangen. Over 97% of the ΣDDT in Arctic char from Ellasjøen was *p,p*'-DDE. In Øyangen, the corresponding number was 79%. The concentrations of chlordane, heptachlor, heptachlor epoxide, aldrin, and trifluralin were below detection limits in almost all fish samples.

In 1999, small Arctic char (from 7-64 g, presumed to be prey fish) from the two lakes (Ellasjøen and Øyangen, n = 3 for both lakes) were analyzed in order to supplement the already analyzed material (consisting mostly of larger fish). In these smaller Arctic char, $\delta^{15}N$ values in Ellasjøen char were higher than in the char from Øyangen (average 17.42 and 8.65‰, respectively) but were very similar to the larger Arctic char sampled previously for these two lakes. Not surprisingly, OC concentrations were very different between the two lakes for the small char but very similar to results in the larger char. The average ΣPCB_7 concentration in small Arctic char from Ellasjøen was 642.7 ng/g ww (range 373.6-906.6 ng/g ww) and the corresponding value for small Arctic char from Øyangen was 37.1 ng/g ww (range 18.2-55.9 ng/g ww). For ΣPCB, concentrations were 1139.1 ng/g ww (range 596.0-1629.6 ng/g ww) for small Arctic char from Ellasjøen and 64.8 ng/g ww (range 32.2-97.5 ng/g ww) for small Arctic char from Øyangen.

In another study in Ellasjøen, Arctic char were found to have PCDD/F and non-*ortho* PCB concentrations (see Annex Table 16) expressed as TEQs of 7.4 pg/g ww (566 pg/g lw) (Schlabach *et al.*, 2001). The PCBs contributed most to the TEQs.

Arctic char were sampled from a mountain lake in the Faroe Islands in 2000 and 2001 (n = 25 and 40, respectively) and muscle tissue was analyzed for OCs (Hoydal *et al.*, 2001). The single OC occurring with the overall highest concentration was *p,p*'-DDE, with a mean of approximately 1 ng/g ww in a char size group of 36-38 cm fork length. The next highest concentrations were for HCB and CB153 at 0.9 ng/g ww for both. Concentrations of CB153 and DDE increased with fish length but HCB did not.

Arctic char from a freshwater lake on the island of Jan Mayen were analyzed for OCs (Gabrielsen *et al.*, 1997). The lake is near cliffs with nesting seabirds. The char have relatively high liver concentrations of ΣPCB (155 ng/g ww) and ΣDDT (71 ng/g ww), which may be

indicative of seabird guano inputs, similar to the situation at Ellasjøen on Bjørnøya.

Faroe Islands brown trout

In 1997, liver from landlocked brown trout (*Salmo trutta*) were collected for OC analyses from two lakes (Fjallavatn and Leitisvatn) in the Faroe Islands (Larsen and Dam, 1999). Fish from Fjallavatn were combined into two pools, one containing the larger specimens (n = 9, mean length 28.6 cm) and one containing the small individuals (n = 19, mean length 23.4 cm). The fish from Leitisvatn were of similar length but were combined into two, mixed-size pools. HCB, *p,p'*-DDE and *trans*-nonachlor were detected in the four liver pools at 0.5 ng/g ww, 3-4 ng/g ww and at 1-2 ng/g ww, respectively. For PCBs, only CBs 153, 138 (+163), and 180 were detected in all samples at approximately 2 ng/g ww, 1 ng/g ww and 1 ng/g ww, respectively. These concentrations are similar to those observed in Arctic char from the Faroe Islands (Hoydal *et al.*, 2001).

Yukon River study

A number of fish species have been sampled and analyzed for OCs from headwater lakes in the Yukon River system since 1996 in response to detection of high concentrations of toxaphene (Palmer and Roach, 2001). Results for lake trout and burbot are covered previously in this section. OC concentrations in whitefish collected in 1998 from Lake Laberge are lower than those observed in lake trout on a wet weight basis but similar when concentrations are normalized to lipid content (Annex Table 7). OC concentrations in Lake Laberge are lower than those observed in Watson Lake (collected in 1997 and 1998), although the Watson Lake whitefish are larger. OC concentrations in inconnu collected from Peel River in 1999 are low compared to most other species of fish from the Yukon region, but are similar to inconnu collected in Great Slave Lake in 1996 (Annex Table 7). Concentrations of OCs in fish from the Yukon region are consistently below levels that result in any health advisories (Palmer and Roach, 2001).

Finnish Arctic fish

Recently a study was conducted on levels of OCs in the muscle tissue of four species of freshwater fish (Arctic char, northern pike, European perch (*Perca fluviatilis*), and whitefish) in Finland (Mannio, 2002) (Annex Table 7). A majority of OC concentrations were less than 1 ng/g ww, one to two orders of magnitude below concentrations observed in similar species in the Canadian Arctic. The lipid content of the muscle tissue of these fish was very low (<1%), which explains some of the differences with the Canadian samples. One group of whitefish collected in the river Tornionjoki had much higher OC concentrations than all other fish collected from Finland (see Annex Table 7) but this was because these fish were anadromous.

Alaskan slimy scuplin

Slimy sculpin (*Cottus cognathus*) from twelve locations within the Cook Inlet Basin were collected to assess levels of OCs in this region (Frenzel, 2000). These twelve locations included sites along roadways and in remote areas. This region has a population of approximately 350 000 people but with minimal industrial activity. The slimy scuplin is a non-migratory, bottom-feeding fish, which makes it suitable for assessing levels of OCs in sediment. OCs, including PCBs, were detected in just three samples from the 12 analyzed. DDE and DDT concentrations (whole body) of 9.0 and 6.1 ng/g were found at one site; HCB concentrations of 5.7 ng/g at another; and, ΣPCB concentrations of 79 ng/g at a third. These concentrations are low and in the range found for other similar benthic fish from this region (see Annex Table 7 for other benthic species).

4.3.4. 'New' chemicals in freshwater fish

There has been limited work on 'new' chemicals in Arctic freshwater fish and most of it has focused on PBDEs (Annex Table 17).

In the European Arctic, data are only available for burbot and trout from northern Norway, and for Arctic char from Ellasjøen on Bjørnøya (Schlabach *et al.*, 2001). Trout muscle ΣPBDE levels (BDEs 47 and 99) are low at 0.10-0.36 ng/g ww (8-14 ng/g lw). Burbot liver had ΣPBDE levels (BDEs 47 and 99) of 20 ng/g ww (175 ng/g lw). For both species, the PBDE levels are a factor of 2-10 times lower than ΣPCB$_7$ levels. The Arctic char at Bjørnøya have elevated levels of ΣPBDE of 16.3 ng/g ww (1250 ng/g lw), but these are a factor of 30-40 times lower than ΣPCB concentrations. The congener pattern in all three species is evenly distributed between BDE47 and BDE99, and resembles the PeBDE technical product. Measurable amounts of PCNs and SCCPs were also found in these fish. PCN concentrations were 8.6-16 ng/g ww in trout muscle, 13 ng/g ww in Arctic char muscle and 643 ng/g ww in burbot liver. SCCP concentrations were 3.3 ng/g ww in trout, 6.9 ng/g ww in Arctic char, and 38 ng/g ww in burbot.

PBDEs were measured in the livers of burbot collected in the Mackenzie River (Canada) in 1988, 1999, and 2000 as part of a project on temporal trends (Stern *et al.*, 2001a) (see Section 5.3.3). BDEs 47 and 99 were the predominant congeners in the burbot, but levels (<2 ng/g lw per congener) were below those observed in the Norwegian fish (Annex Table 17). BDE congeners 100, 153, and 154 were also detected in the burbot but at levels lower than congeners 47 and 99.

4.3.5. Bjørnøya lake study

In 1994, an investigation of contaminants in sediments and fish from Ellasjøen on the island of Bjørnøya was initiated (Evenset *et al.*, 2002). This pilot study was based on a very limited number of samples, but found some of the highest PCB and DDT concentrations in freshwater sediments and fish ever seen in the Arctic. Other studies from the same area have shown high PCB levels in glaucous gulls (Gabrielsen *et al.,* 1995; Bustnes, 1998). In a follow-up study, the contamination level in Ellasjøen was compared to Øyangen, another lake on Bjørnøya. Plankton, benthic animals and landlocked Arctic char from both lakes were analyzed for contaminants and stable isotopes to provide information on contaminant levels and bioaccumulation in the food chain.
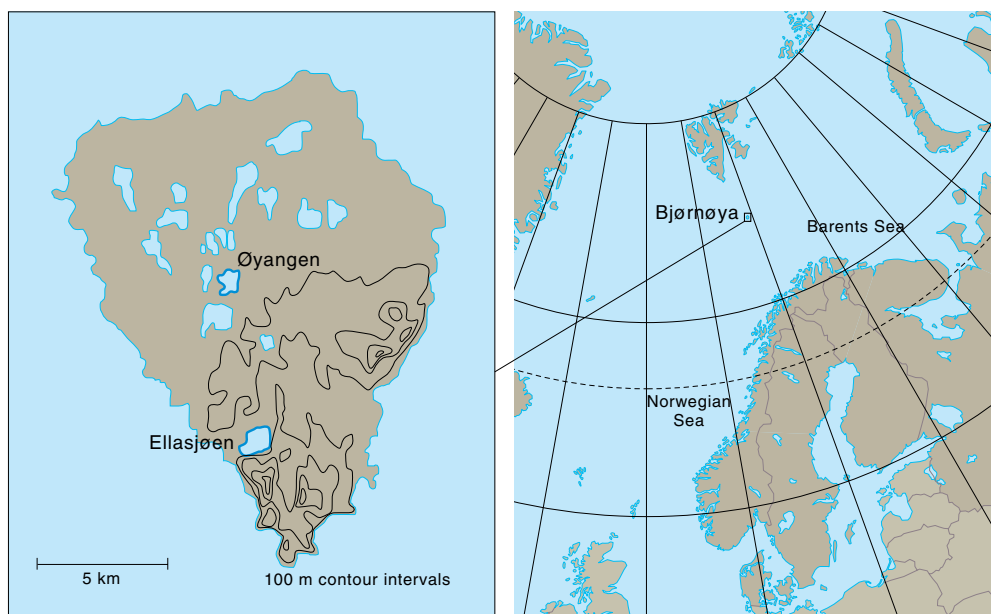
Figure 4·26. The locations of Bjørnøya, and the lakes Ellasjøen and Øyangen (from Evenset *et al.*, 2002).

Bjørnøya (74°30'N, 19°E) is situated halfway between the mainland of Norway and Svalbard (Figure 4·26). Bjørnøya has a surface area of 178 km² and measures 20 km from north to south. The annual average temperature is –3.8°C. Precipitation is low, with an annual rate of 367 mm (information from Det Norske Meteorologisk Institutt). The southern part of the island is mountainous with altitudes up to 536 m asl. Seabirds breed on the steep cliffs along the south coast. The main species are common guillemot (*Uria aalge*), Brünnich's guillemot (*Uria lomvia*), kittiwake (*Rissa tridactyla*), little auk/dovekie (*Alle alle*), and glaucous gull. The terrain in most of the middle and north parts of Bjørnøya is flat (30-40 m asl). The island has about 740 lakes which cover 11% of the surface area. More than 600 of these lakes are found on the central and northern plains, and their depths seldom exceed 2 m. Fewer than ten lakes reach depths between 5 and 10 m and these are found in the southern parts of the island. Ellasjøen is the deepest lake on the island (maximum depth of 34 m). Water temperatures are low, typically below 7°C in summer. There is no summer stratification, but the lakes are cold monomictic (i.e. sub-polar). The upper littoral zone generally comprises a rocky margin, 0.5-1 m deep.

Ellasjøen, with an area of 0.72 km² (21 m asl), is situated in the southern, mountainous part of Bjørnøya. The catchment area is 6.1 km², and the lake has an estimated retention time of 6.5 years. In the southern part of the catchment area (Alfredfjellet), there is a large colony of little auks. Large flocks of kittiwakes (hundreds to thousands) can be observed on the lake during the summer period. At the outlet of the lake, there is a colony of glaucous gulls (approximately 100 pairs). The birds present in the catchment area seem to have a large impact on the lake, as indicated by the growth of green algae on the shores directly below the colony. Mosses and lichens occur around the northern and western shore close to the lake, although in general, the catchment area is devoid of vegetation. The lake has a very well developed profundal and pelagic zone, and is inhabited by landlocked Arctic char (Klemetsen, 1985).

The littoral zone in the northern part of the lake is also well developed but in the southern part it is very steep, and near the shore the depth is 15 to 20 meters.

The lake Skutilen is situated in the same catchment area as Ellasjøen. The lake has an area of 0.08 km² and a maximum depth of 2 m. The primary outlet flows to Ellasjøen. Birds are seldom seen on Skutilen, but Arctic char have been observed in this lake. There is almost no vegetation in the catchment area, except for some mosses. The lake has no pelagic or profundal zone.

Øyangen (33 m asl) is situated on the central plains of Bjørnøya. The lake has an area of 0.35 km² and a maximum depth of 5 m. Most of the lake, however, is less than 1 m deep. The total catchment area is approximately 2.2 km², and the estimated retention time is 0.9 years. The area around Øyangen is very flat and consists mainly of boulders. On Øyangen, flocks of kittiwakes can be observed, but the flocks are smaller and not seen as frequently as on Ellasjøen. There is almost no vegetation in the catchment area except for some mosses. The lake has no pelagic or profundal zone, but Øyangen has a population of landlocked Arctic char.

The studies carried out in the limnic ecosystems on Bjørnøya have shown that Ellasjøen is significantly more contaminated by OCs than Øyangen (Figures 4·27 and 4·28), and that Ellasjøen has a higher 'basic trophic level' (Skotvold *et al.,* 1999). Possibly, the higher 'basic level' of isotopes is caused by guano-input to the lake. Seabirds feed in the marine environment and may bring in nutrients (through guano) with different isotopic composition than other nutrients that are transported to the lake (i.e. runoff from land, decomposed material). Guano can also function as a transport medium for contaminants from the marine environment to the limnic environment in Ellasjøen. This theory was also supported by the fact that there was a similarity between the CB99:CB101 ratios in guano samples of seabirds and char from Ellasjøen, but none in char from Øyangen.

Analysis of toxaphene congeners provided further evidence of the influence of seabird guano. From the nine chorobornane congeners analyzed, only three, Parlars 26, 40, and 50, were found in considerable amounts in
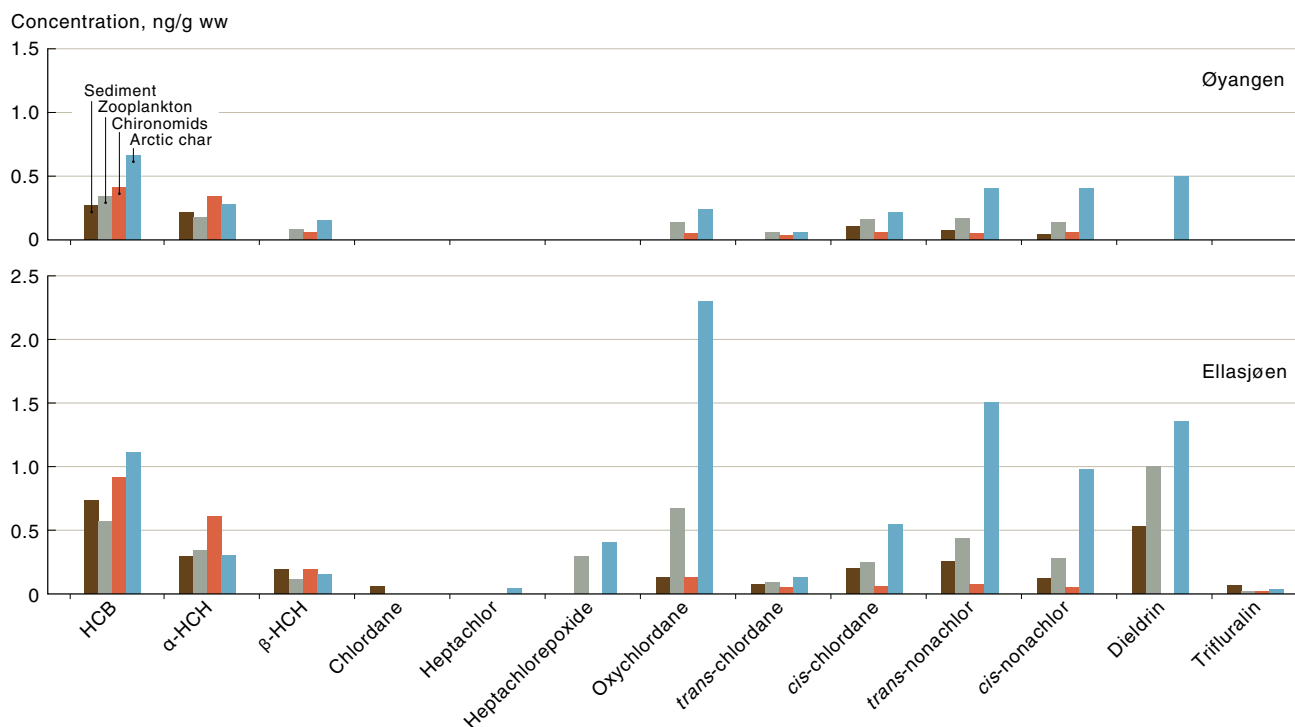
Concentration, ng/g ww

Figure 4·27. Concentrations of pesticides in sediment and biota from the lakes Ellasjøen and Øyangen on Bjørnøya (from Evenset *et al.*, 2002).
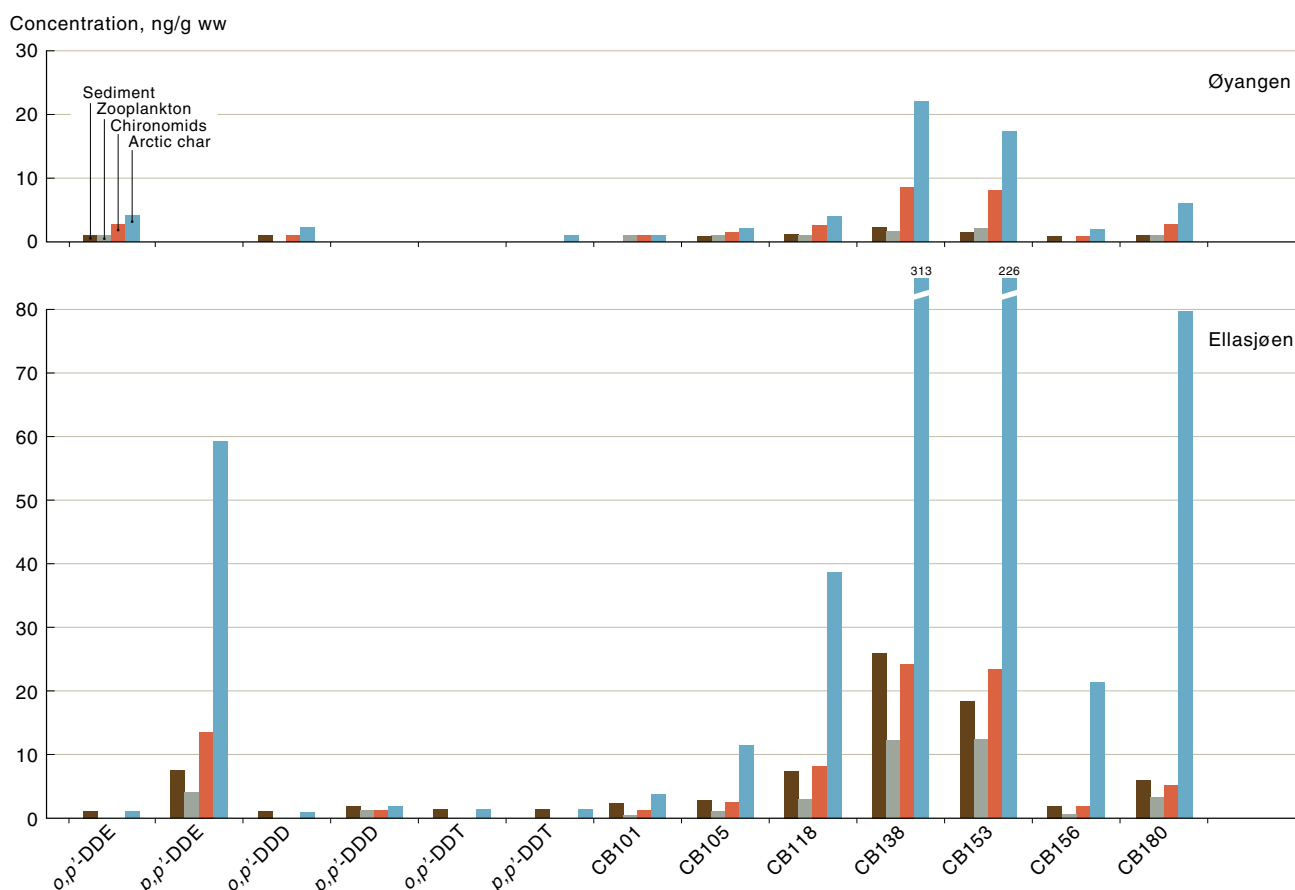
Concentration, ng/g ww

Figure 4·28. Concentrations of DDT (including metabolites) and seven PCB congeners in sediment and biota collected from the lakes Ellasjøen and Øyangen on Bjørnøya in 1996 (from Evenset *et al.*, 2002). Note that CB138 may have co-eluted with CB160 and 163, inflating its value.

the analyzed biota samples from Bjørnøya. Levels found for all samples from Øyangen were very low, often not exceeding the detection limits. The generally low levels found at Øyangen were consistent with low levels of PCBs found in this lake. As with the PCB results, con-

siderably higher chlorobornane levels were found in biota samples from the Ellasjøen catchment area. Almost no chlorobornanes were observed in zooplankton from Øyangen. In Ellasjøen, Parlar 50 concentrations of 1.2 ng/g ww were found in zooplankton, and a signifi-

cant increase from zooplankton (sum of Parlars 26, 40 and 50: 1.2 ng/g ww) to Arctic char (average sum of Parlars 26, 40 and 50: 8.1 ng/g ww) was found. Glaucous gull gut from Ellasjøen had the highest toxaphene concentrations (sum of Parlars 26, 40, and 50: 84.2 ng/g ww). Although significant differences were found between Øyangen and Ellasjøen samples, the highest chlorobornane concentrations, found in the pooled Ellasjøen glaucous gull gut sample, cannot be considered unusually high compared to published literature data reported for Arctic marine top predators. A comprehensive review article presents levels up to 4000 ng/g ww (Σchlorobornanes) for marine mammals (de Geus *et al.*, 1999). However, based on the results of the present study, glaucous gull guano was identified as one of the major chlorobornane sources for the Ellasjøen freshwater system.

The Bjørnøya lake study has highlighted the important influence of locally defined and restricted ecological, geographical, and meteorological environmental factors on overall contaminant levels (e.g., precipitation, presence of local seabird nesting colonies, and resting areas). Based on these results, seabirds at Bjørnøya seem to function effectively as a transport link for POPs from the marine ecosystem to the freshwater ecosystem. It can also be assumed that in other locations seabird guano may be a potential contamination source for persistent pollutants, for example on Jan Mayen. Not only in Arctic regions can such a seabird linkage between freshwater and marine ecosystems result in elevated OC concentrations.

4.3.6. Summary and conclusions – freshwater environment

The years 1996-2001 saw few new studies of POPs in river water in the Canadian Arctic, northern Norway or in northern Russia, although a major project was initiated in Russia in 2001-2002 to study contaminants in the rivers Yenisey and Pechora (RAIPON/AMAP/GEF Project, 2001). However, results reported in the previous AMAP POPs assessment were independently verified by several researchers, confirming the original results and deriving flux estimates for ΣDDTs and ΣHCHs. The flux estimates suggest that, at least until 1996, rivers such as the Ob and Yenisey contributed significant amounts of ΣDDTs and lindane to the Arctic Ocean, assuming that what was measured at downstream sampling stations was eventually carried to the northern Russian seas.

New measurements of OC pesticides and PCBs in freshwater sediments were available for lakes in Canada, on Svalbard and Bjørnøya, and on the Kola Peninsula. The limited number of studies provided evidence for contamination from both local sources and long-range transport. In the case of Ellasjøen, levels of ΣPCBs and ΣDDTs were up to ten times higher in its surface sediments compared to Øyangen surface sediments due to inputs of seabird guano. This unusual input pathway was not important in Canadian Arctic lake sediments; however, local sources from past uses of DDT, toxaphene, SCCPs, and PCBs were clearly important in explaining some differences in fluxes of these compounds in Yukon lakes. The significant declining trend of PCBs and DDT fluxes with latitude in lake sediments within the Cana-

dian Arctic may be partly attributable to the influence of local sources in the Yukon and the complete absence of these sources in most of the High Arctic lakes.

The recent data for POPs in freshwater are too limited to draw any additional conclusions about spatial trends or the presence of new contaminants. Results from studies of Canadian Arctic lakes did provide new information on degradation pathways of α-HCH, indicating relatively rapid degradation compared to ocean waters and an inverse relationship between enantioselective degradation and lake trophic status. These findings may be useful for interpreting the fate of other POPs in Arctic lake waters.

There has been a considerable amount of research focused on OCs in Arctic freshwater biota since the first AMAP POPs assessment, although less than that carried out in the marine environment. Similar to the terrestrial environment, levels of OCs in most freshwater biota of the Arctic are low compared with the marine environment but are similar to terrestrial predators. The exceptions are freshwater systems that receive additional POP contamination via non-atmospheric routes. An excellent example is the high levels of POPs found in the sediment and biota of Ellasjøen on Bjørnøya. This lake receives a large amount of seabird guano, which is likely acting as a vector to transport and concentrate POPs from the marine environment and deposit them in a freshwater environment.

Toxaphene and PCBs continue to be the predominant OCs measured in freshwater biota, as was observed for Canada and Greenland in the first AMAP POPs assessment. New data from Bjørnøya suggest that toxaphene is a major OC contaminant in freshwater invertebrates and fish of the European Arctic. Toxaphene and PBDE were not found in Russian water or sediments, but the detection limits were above levels normally found in the Arctic. PBDEs were found to be higher in freshwater fish from Bjørnøya lakes and northern Norway compared with fish from the Mackenzie River in Canada. Levels were well below legacy OCs and lower than levels of PBDEs in marine biota. Lack of data on 'new' chemicals, particularly perfluorinated compounds, is a significant gap for the freshwater environment.

The Bjørnøya study and results from Alaskan and Russian burbot studies all highlight the potential for OC levels to vary significantly between geographically close locations. Elevated levels of OCs can occur due to local point sources, although these are rare in the Arctic, or through unique ecological or biological scenarios. The results of the Alaskan burbot study also highlight the importance of biological characteristics on fish OC levels. Proper statistical analysis of spatial and temporal trends of OCs in freshwater fish requires biological data, in particular size and age. Other factors, such as meltwater from glaciers, may also influence OC levels in fish.

ΣPCB concentrations in many of the predatory freshwater fish of the Canadian, Russian, and Alaskan Arctic, as well as fish from Ellasjøen on Bjørnøya exceeded the most conservative guidelines for the protection of aquatic wildlife of 15-48 (Canada) to 160 (USEPA) ng/g ww (de March *et al.*, 1998) (Table 6.1). Few fish exceeded the U.S. guidelines. Information on the health of these fish populations is limited but there is no evidence to suggest that the populations are currently compro-

mised. No fish muscle samples were found to exceed the PCB guideline limit for human consumption and export of fish of 2 µg/g ww, which is widely used in Europe and North America.

Circumpolar trends of OCs in freshwater fish were evaluated using the Arctic char in the first AMAP assessment report (de March *et al.*, 1998). Circumpolar OC data for freshwater fish have not become available since that report, are not available even for Arctic char and, in particular, are lacking for invertebrates. However, evaluation of OC levels in different species of predatory fish suggest that concentrations of OCs in freshwater biota of the circumpolar Arctic are similar with a few notable exceptions (e.g., Ellasjøen on Bjørnøya), and lakes in the Yukon Territory in the western Canadian Arctic. New data for OC concentrations in Russian freshwater fish are difficult to assess as little biological information is available, but they suggest that some freshwater systems of the Russian Arctic are among the most contaminated in the circumpolar Arctic (see Section 4.3.3.2). Slight differences in OC levels of predatory fish within Great Slave Lake, one of the largest lakes within the Arctic, provide evidence that abiotic environment and/or food web characteristics can influence OC levels.

4.4. Marine environment

The marine environment has historically received the most attention with regard to OC and PAH contaminants in the Arctic environment. It was also the first Arctic system to be examined for the presence of OC contaminants (Holden, 1970). The level of research on OC contamination of the marine environment has continued to outdistance efforts in the freshwater and terrestrial Arctic. This is clearly due to the higher levels observed in this system and the role of marine organisms in the diet of northern populations. Since the first AMAP POPs assessment (i.e. post 1996), there has been a large amount of data produced for the marine environment, in particular for seals and whales, and a number of comprehensive studies on dynamics and mechanisms of OCs in this environment. There have also been new initiatives to produce data for regions that were under-represented in the previous AMAP assessment, in particular the Alaskan and Russian Arctic.

This review and assessment of the post-1996 data will focus on persistent organohalogen compounds (mainly OCs, as well as recent measurements of brominated and fluorinated organics and TBT). However, PAHs are not included because sources in the aquatic marine environment are considered to be predominately of petrogenic origin (either from natural sources or anthropogenic uses) rather than from combustion and atmospheric deposition sources (Robertson, 1998). A future review of petrogenic PAHs will be conducted under the updated AMAP assessment of 'petroleum hydrocarbons' that is due to be published in 2006.

4.4.1. Seawater
4.4.1.1. Overview

A large number of measurements of OC pesticides and PCBs have been made in Arctic Ocean waters in the period of 1996 to 2001 (Annex Table 8) mainly as a result of scientific cruises organized by circumpolar countries. During this period, there were also several peer-reviewed publications on results of measurements of OCs in seawater pre-1996 (Rice and Shigaev, 1997; Hargrave *et al.*, 1997; Jantunen and Bidleman, 1998; Strachan *et al.*, 2001); however, those results were included in the previous assessment (de March *et al.* 1998) and reviews (Macdonald *et al.*, 2000), and are included only for comparison here.

The new measurements have, for the most part, been conducted from oceanographic research vessels in a series of cruises (Figure 4·29). The Swedish *Oden* cruise in 1996 conducted sampling from the ice edge to the North Pole in the northern Barents Sea (Harner *et al.*, 1999). In 1997, a Canadian supply trip (JOIS) for the Surface Heat Budget of the Arctic (SHEBA) study (Perovich *et al.*, 1999) was used to obtain seawater from the western Canadian Arctic Archipelago in September. In May-June 1998, the Northwater Polyna study in Northern Baffin Bay (NOW '98) provided another platform for sampling. In 1997-1998, the SHEBA study permitted continuous sampling of seawater over the Beaufort/Chukchi Seas. The Swedish Tundra Northwest study (TNW '99) traversed the Canadian Arctic Archipelago during July/August, 1999. An Arctic to Antarctic cruise by the RV *Polarstern* provided seawater samples from the East Greenland Sea in 2000 (Lakaschus *et al.*, 2002). Schultz-Bull *et al.* (1998) reported PCBs in large-volume samples collected in the North Atlantic Ocean around Iceland which are also relevant to this discussion and Sobek and Gustafsson (2002) presented preliminary results from the *Oden* cruise to the North Pole in 2001. Studies have also been conducted in the Marginal Ice Zone of the Barents Sea north of Svalbard (Olsson, 2002) and in the Laptev Sea (Utschakowski, 1998).

The new measurements have filled in some of the information gaps on spatial trends of OCs in the Arctic Ocean. Sampling and extraction techniques were more uniform than in the 1980s and early 1990s, with large-volume (20 to >100 L) samples collected and extracted using resin columns to minimize airborne contamination. Some investigators used filtration (Harner *et al.*, 1999) or continuous centrifugation (Strachan *et al.*, 2001) to remove particles; however, samples for HCH analyses were often unfiltered (Lakaschus *et al.*, 2002). HCH isomers were the most commonly measured chemicals in the Arctic Ocean and adjacent seas. These compounds are present at ng/L concentrations and there are few problems with contamination on ships or in the laboratory. PCBs were the next most prominent contaminants (Annex Table 8); however, there were far fewer measurements. PCB measurements in seawater are challenging because of low levels and potential for shipboard as well as laboratory contamination. Comparison among different studies and with previous work on PCBs in Arctic and northern temperate seawaters (Iwata *et al.*, 1993; Schultz-Bull *et al.*, 1998; Sobek and Gustafsson, 2002) raises questions about contamination and the effects of different sampling techniques. These include possible differences between whole (unfiltered) water versus filtered samples, and the use of *in situ* collection using remotely deployed samplers versus submersible pumping onto the ship.
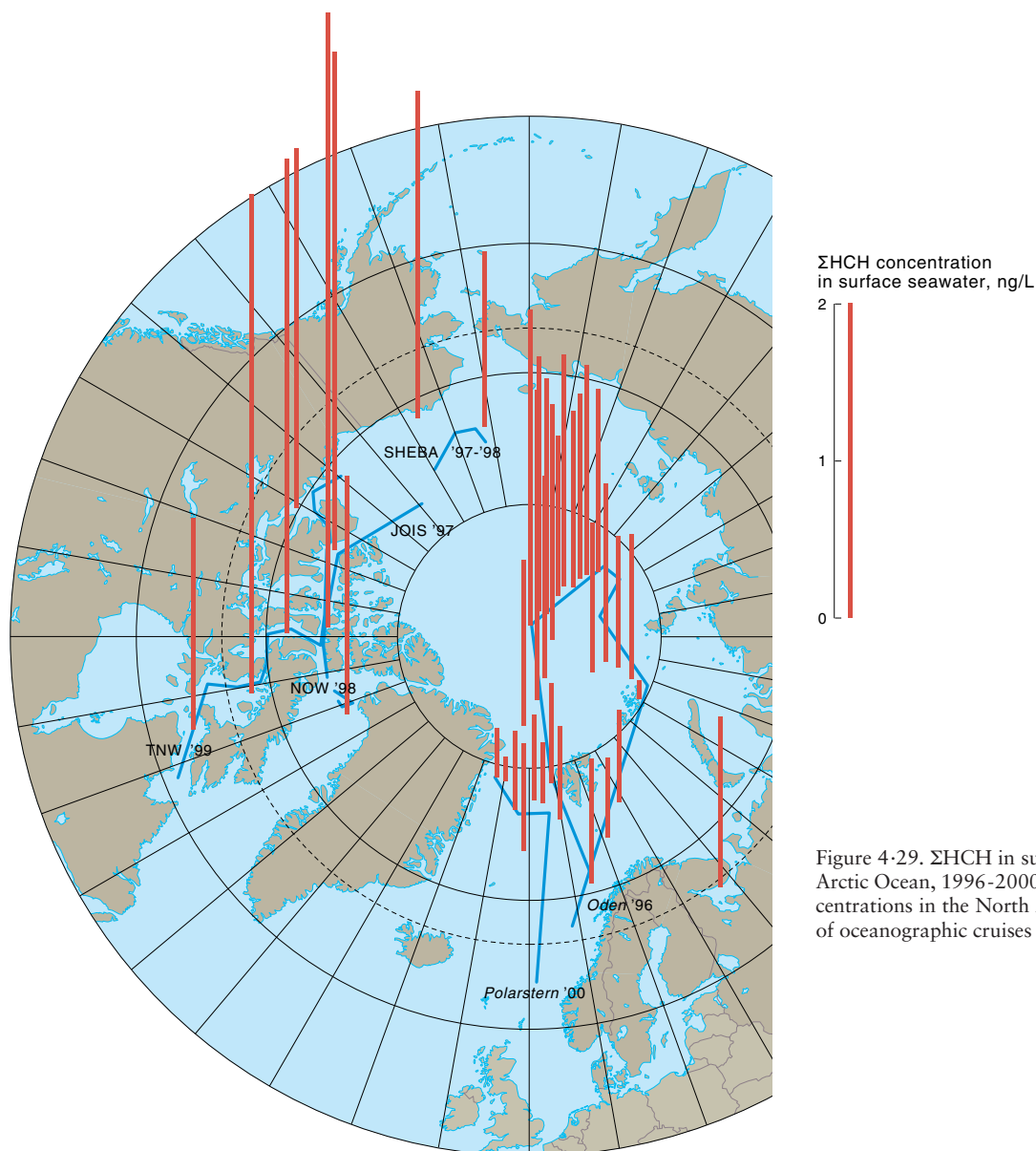
Figure 4·29. ΣHCH in surface seawater from the Arctic Ocean, 1996-2000, illustrating higher concentrations in the North American Arctic. Tracks of oceanographic cruises are shown in blue.

4.4.1.2. **HCHs**

Harner *et al.* (1999) determined HCH isomers and ERs of α-HCH in a large series of surface and deepwater samples from the northern Barents Sea and central Arctic Ocean (80-88°N, 11-143°E) (Annex Table 8). The mean concentrations for surface water were 1.18 ± 0.408 ng/L for ΣHCHs. These agreed well with measurements by Strachan *et al.* (2000) on the same cruise and also with values reported by Gaul (1992) for a 1985 survey of the northeast Atlantic (ΣHCHs = 1.25 ng/L). Both α- and γ-HCHs increased with latitude between 74-88°N (r² = 0.58 and 0.69 for α- and γ-HCH, respectively). Values similar to those on the *Oden* cruise were found during 1994 in the eastern Arctic Ocean north of Spitsbergen (ΣHCHs = 1.17 ng/L) and in the Greenland Sea (ΣHCHs = 0.83 ng/L) (Jantunen and Bidleman, 1996; 1998).

Vertical profiles at 11 *Oden* cruise stations indicated that concentrations at depths of 250-1000 m were approximately 40% of surface values for α-HCH and approximately 60% for γ-HCH (summarized as ΣHCHs in Annex Table 8). Tracer studies in this region (Nansen Basin) indicate that the water masses at 250-1000 m have ages on the order of 12-20 years, which coincides with the time of heaviest usage of HCH (Li *et al.*, 1998a).

Lakaschus *et al.* (2002) determined α- and γ-HCH in surface (11 m depth) seawater along an east-west transect in the Greenland Sea. Concentrations in this region (ΣHCHs = 0.57 ± 0.20 ng/L east; 0.13-0.698 ng/L west) were similar to those in surface water and deeper water in the Barents Sea (Harner *et al.*, 1999), but two to four times lower than in the Beaufort Sea (Annex Table 8). However, ΣHCH concentrations in the Greenland Sea (68-75°N) were three to five times higher than in the eastern Atlantic near the Bay of Biscay because of much higher levels of α-HCH in Arctic waters (Lakaschus *et al.*, 2002).

ΣHCH concentrations in the White Sea (Kandalasksha Bay and central basin) in northwestern Russia were similar to those in the Beaufort Sea (1.1 ± 0.11) and two-fold higher than in the Barents Sea near Svalbard (Harner *et al.*, 1999; Muir *et al.*, 2002a). In general, surface concentrations of HCHs are highest in the central Canadian Arctic Archipelago, intermediate in the Beaufort/Chukchi Seas and at the North Pole, and lowest in the Greenland Sea and northern Barents Sea (Figure 4·29).

The large number of measurements of HCH during the 1980s and 1990s in the Bering/Chukchi/Beaufort Seas, as well as in the Greenland Sea, also permits an examination of mass balances over time and temporal trends. These are discussed in Section 5.1. Other measurements in the nearshore waters of the southern Beaufort Sea also show higher ΣHCH levels (Hoekstra *et al.*, 2002b) than in the eastern Canadian Arctic (northern Baffin Bay).

The lowest ΣHCH concentrations (mean 18 pg/L) were found by Utschakowski (1998) in seawater collected annually in the summers of 1993 to 1996 in the southern Laptev Sea near the Lena River Delta. These concentrations were lower than previously reported levels for the same region (20-150 pg/L; de March *et al.*, 1998).

β-HCH, which is not as abundant in the Arctic abiotic environment, has not been as well studied. This is partly due to its low concentrations, which have posed analytical challenges. However, there is growing concern over its potential risks as it is the most bioaccumulating of the HCH isomers and may be an environmental estrogen (Willett *et al.*, 1998). Due to its greater water solubility (low Henry's law constant), β-HCH is more efficiently scavenged by rain and snow than α-HCH and is preferentially deposited closer to the source regions in high-precipitation areas in the northern North Pacific. Ocean currents then transport β-HCH farther north into the Bering Sea through the Bering Strait (Li *et al.*, 2002). Direct atmospheric transport of β-HCH is a minor pathway. This means that, unlike α-HCH, β-HCH concentrations in seawater peak in the Bering-Chukchi region and then decrease northward into the Arctic Ocean interior. This indicates that β-HCH that was maximally deposited in the North Pacific during 1970-1985 is now entering the Arctic Ocean as a pulse to the Bering Sea, delayed by some unspecified time, perhaps a decade or more (Li and Bidleman, 2003).

4.4.1.3. PCBs

After the HCHs, PCBs are the next most prominent group of persistent OCs in Arctic seawater. As noted above, comparison among different studies and with previous work on PCBs in the Arctic Ocean and nearby northern seas (Iwata *et al.*, 1993; Schultz-Bull *et al.*, 1998; Sobek and Gustafsson, 2002) raises important questions about contamination and effects of different sampling techniques. Schultz-Bull *et al.* (1998) and Sobek and Gustafsson (2002) have reported concentrations of PCBs which are about ten times lower than other measurements summarized in Annex Table 8. These latter groups have used ultra-clean techniques. Schultz-Bull *et al.* (1998) employed the 'Kiel' *in situ* sampler, a remotely deployed filtration/extraction system (Petrick *et al.*, 1996) to sample large volumes of seawater (230-1070 L) through glass fiber filters (GFF) and XAD-2 resin. Sobek and Gustafsson (2002) employed a stainless steel seawater intake system directly into the *Oden* followed by on-line collection using GFF and polyurethane foam (PUF) in a 'clean' room on board. Seawater sampling on the earlier *Oden*, TNW, and JOIST cruises for PCB analysis involved use of a stainless steel lined 'Go-Flo' bottle followed by GFF and XAD-2 resin but did not employ clean room techniques

during the sampling phase. Sampling on the SHEBA study and nearshore samples at Barrow, Holman, and in the White Sea used *in situ* samplers (Axys Instruments, Sidney BC) and GFF/XAD-2 resin deployed from ships or through sea ice.

The results in Annex Table 8 summarize the current state of the art of PCB measurements in the Arctic Ocean. Up to 100 PCB congeners were determined by some investigators; however, for this assessment results for the sum of ten major PCB congeners were also included, where possible, to make comparisons more equitable. Although all studies employed solid phase extraction (mainly XAD-2 resin) for collection of PCBs, and followed strict protocols to avoid contamination, there is nevertheless major disagreement between measurements, especially between those made using samples collected with 'Go-Flo' bottles or other large-volume containers and those with *in situ* or direct online sampling of water. There are also major differences between results for PCBs determined by *in situ* sampling with 'Axys' systems and the 'Kiel' sampler.

There are similar irreconcilable differences between results from Strachan *et al.* (2001) for the PCBs in the Bering Sea and results from Iwata *et al.* (1993) from the Bering Sea (previously reported in the 1998 AMAP assessment). The latter study used GFF/PUF sampling from an online water system while the former used a submersible pump, a continuous centrifuge to separate particles and solvent extraction with dichloromethane. Iwata *et al.* (1993) reported mean concentrations of 0.0084 ng/L at three locations in the Chukchi Sea and 0.012 ng/L for four locations in the Bering Sea from their 1990 cruise. Strachan *et al.* (2001) reported dissolved phase concentrations averaging 1.0 ng/L in the Bering Sea (seven sites) and means of 0.6-0.9 ng/L in the Chukchi Sea. Given that both cruises covered the same area and sampled approximately the same depth, it is difficult to attribute the differences except to contamination introduced from the ship. The results of Iwata *et al.* (1993) for the Chukchi Sea are consistent with those of Sobek and Gustafsson (2002), Schultz-Bull *et al.* (1998), and Utschakowski (1998) in terms of the range of concentrations but cannot be compared directly because of different numbers of congeners analyzed.

With these caveats in mind we have limited the discussion of results to data from Schultz-Bull *et al.* (1998), Utschakowski (1998), Olsson (2002), and Sobek and Gustafsson (2002); and to the 'Axys' *in situ* sampler work conducted on the SHEBA study and in nearshore waters (Annex Table 8) recognizing that even the latter results may be confounded by contamination introduced on handling and storage or in the laboratory.

There are too few PCB measurements to assess spatial trends of PCBs, nevertheless some general conclusions can be drawn from the data of Schultz-Bull *et al.* (1998) and Sobek and Gustafsson (2002). ΣPCB concentrations in the upper 50 m water column under the permanent ice cap are much lower (mean ΣPCB_{10} = 0.00055 ± 0.00043 ng/L) than in the northern North Atlantic (range 0.0014-0.0021 ng/L). Similar ΣPCB concentrations (0.0016-0.0021 ng/L; dissolved + particulate) were found in an ice-covered and a pelagic sampling site in the marginal ice zone north of Svalbard (Olsson, 2002). Somewhat higher ΣPCB concentrations

(mean in the dissolved phase of 0.0034 ng/L (range 0.0001-0.011 ng/L)) were found by Utschakowski (1998) in the southern Laptev Sea near the Lena River Delta. Utschakowski (1998) found that PCBs were present at similar concentrations in the particulate phase at this location.

In situ sampling during the SHEBA study (Macdonald *et al.*, 2001) and in nearshore waters (Hoekstra *et al.*, 2002b) also found higher ΣPCB concentrations in nearshore waters of the Canadian Arctic Archipelago and southern Beaufort Sea (ΣPCB$_{10}$ means of 0.040-0.060 ng/L). ΣPCB$_{10}$ levels in the central basin of the White Sea (0.028±0.014 ng/L) were lower than in the Canadian Arctic Archipelago, using the same sampling equipment and analytical techniques, despite the proximity of urban areas of Dvina Bay (eastern White Sea) and Kandalaksha Bay (western arm).

Although the PCB measurements in the northern Chukchi Sea (Figure 4·30) may be confounded by con-

tamination they are internally consistent in that they show a remarkable transition from the Canada Basin to the Chukchi Plateau. East of the plateau (about 77°N, 160°W), the PCB profile consisted mainly of mono-, di- and trichlorinated CB congeners (Figure 4·30 a). Over the southern edge of the Chukchi Plateau (April), the profile appears far more strongly influenced by the technical mixture component (Figure 4·30 b). As SHEBA drifted back toward the interior ocean, the profiles in July (Figure 4·30 c) and September (Figure 4·30 d) revealed a strengthened lower chlorinated PCB congener profile. The PCB profile in waters west of the Chukchi Plateau bore a greater resemblance to technical PCB mixtures such as the Russian 'Sovol' (Schulz *et al.*, 1989; Ivanov and Sandell, 1992) (Figure 4·30 e) and Aroclor 1254. Given the stratification of the water column and ice cover, these changes were not due to ice melt or biological processes. It seems much more plausible that the PCB compositions along the track reflect the various
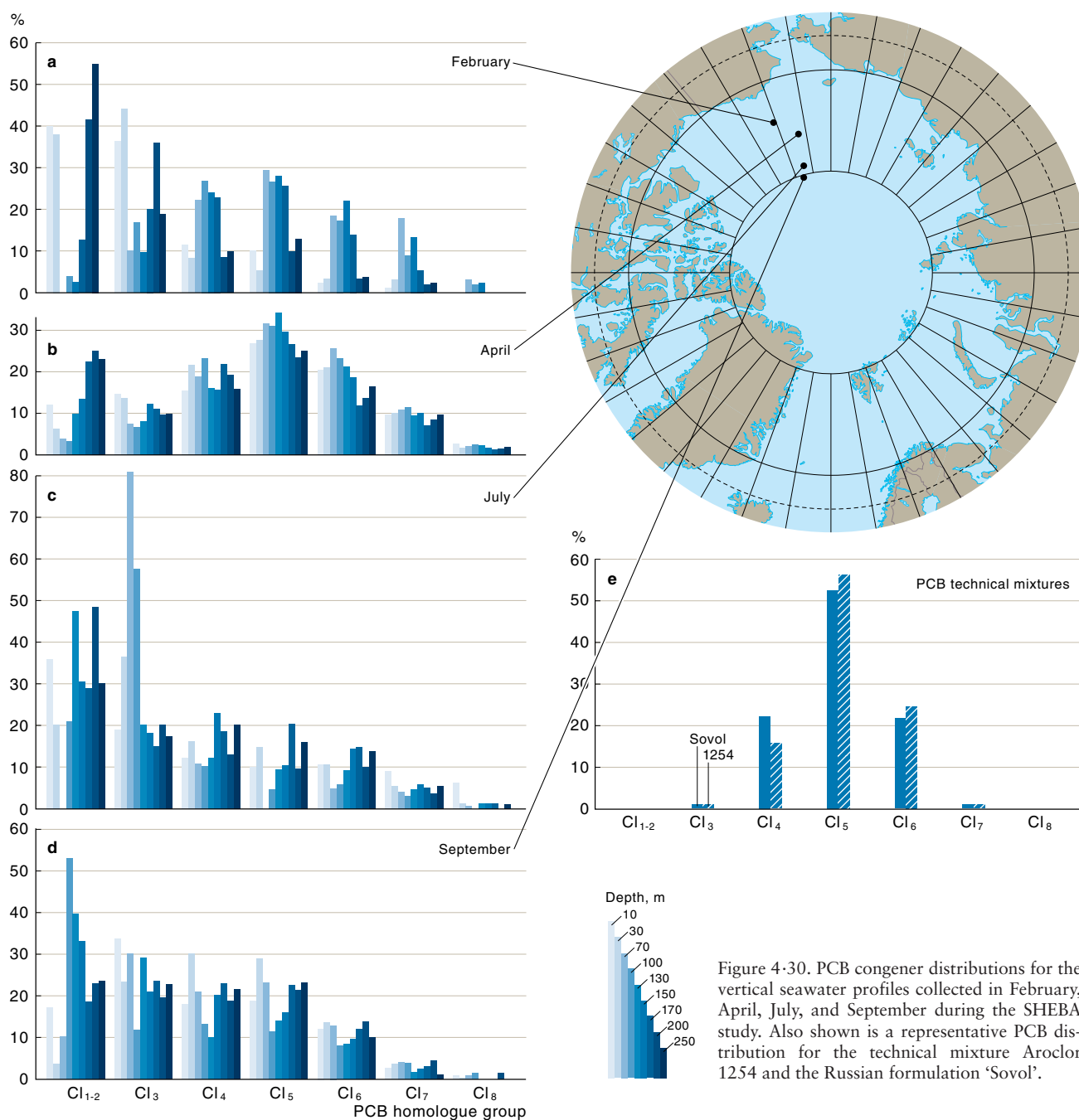

Figure 4·30. PCB congener distributions for the vertical seawater profiles collected in February, April, July, and September during the SHEBA study. Also shown is a representative PCB distribution for the technical mixture Aroclor 1254 and the Russian formulation 'Sovol'.

water masses through which SHEBA passed. The dominant contribution from technical mixtures seen in April (Figure 4·30 b), strongly suggests that this profile has been imported from the Pacific Ocean/Bering Sea. The profiles collected in February, July, and September, on the other hand, probably reflect a stronger influence of Canada Basin interior water that has accumulated an important component of its PCB inventory from the atmosphere. The inference to be drawn here is that PCBs have been delivered via the Bering Sea in water directly contaminated through, for example, runoff or spills, whereas the interior Arctic Ocean owes a significant portion of its PCB content to condensation and/or air–sea exchange which favors the lighter components as one progresses northward (Wania and Mackay, 1993; Muir *et al.*, 1996a).

4.4.1.4. Toxaphene

Only a limited number of new measurements of toxaphene in seawater have been reported since the previous AMAP POPs assessment, and they are too few to fully assess spatial trends. Total toxaphene levels in sea-

Figure 4·31. Comparison of mean (± SE) concentrations (ng/L) of individual toxaphene congeners in surface waters from the White Sea (n = 5) and the southern Beaufort Sea (Hoekstra *et al.*, 2002b).

water in the North American Arctic were higher in northern Baffin Bay than in the southern Beaufort Sea (Hoekstra *et al.*, 2002b). Lower toxaphene levels were found in seawater in the White Sea and in the northern Chukchi Sea than in the southern Beaufort Sea or northern Baffin Bay (Annex Table 8). The recent measurements have included chlorobornane congeners, thus allowing some insights into the degradation of toxaphene. Levels of individual chlorobornanes are in the low pg/L range (Figure 4·31). The congener profile of toxaphene in the Beaufort Sea was dominated by hexa- and heptachlorobornanes, especially B6-923 and B7-1001 (these have no Parlar numbers). These are terminal residues from dechlorination of many toxaphene congeners (Fingerling *et al.,* 1996) and are prominent in lake water in the Great Lakes (Muir *et al.*, 1999a; Muir *et al.*, 2001b). The White Sea had a different congener pattern with undetectable levels of B6-923 and more prominent octa- and nonachlorinated congeners. This pattern suggests a fresher, less degraded source of the technical product. Polychlorocamphene or toxaphene was widely used in Russian agriculture at least until the late 1980s (McConnell *et al.*, 1996). Toxaphene was also present in sediments of a harbor area in Kola Bay (near Murmansk) (Section 4.4.2) indicating other possible uses such as insect control on ships (Savinova *et al.*, 2000a).

4.4.1.5. Other 'legacy' OC pesticides

ΣDDT and chlordane-related compounds, as well as HCB were determined in several studies (Annex Table 8) and were present at much lower concentrations than toxaphene, PCBs or HCH isomers. Similar to the pattern for PCBs, DDT residues were higher (by 5 to 20 times) in seawater from the Canadian Arctic Archipelago and nearshore waters of the Beaufort Sea than over the Chukchi Plateau or in the central Arctic Ocean. ΣCHL had a similar pattern although differences were not as pronounced. This suggests that gas exchange and melting are important sources for ΣDDTs and ΣCHLs. Hargrave *et al.* (1997) found generally higher levels of *cis*- and *trans*-chlordane and toxaphene under ice-covered conditions in the central Canadian Arctic Archipelago compared to the open-water season. These authors concluded that net deposition by seawater–air exchange of toxaphene and chlordanes during the open-water period was equivalent to 50 to more than 100% of the surface layer inventory. Thus, lower concentrations of the more hydrophobic OCs, such as PCBs and DDT under the ice pack, are probably due to slow removal by sedimentation and lack of resupply from the atmosphere.

ΣDDT levels in White Sea seawater were lower than in the southern Beaufort Sea or in the northern Barents Sea (Annex Table 8). Despite possible ongoing use in urban areas in the White Sea and Kola regions (Savinov *et al.*, 2003; AMAP, 2003), there was relatively little spatial variation of ΣDDT among ten sampling sites (0.002-0.005 ng/L) ranging from Dvina Bay (eastern White Sea) to the western end of Kandalaksha Bay (western arm).

Utschakowski (1998) found ΣDDT concentrations ranging from 0.0001 to 0.00178 ng/L in the dissolved phase and from 0.00036 to 0.00087 ng/L on particles in seawater from the southern Laptev Sea collected in 1993
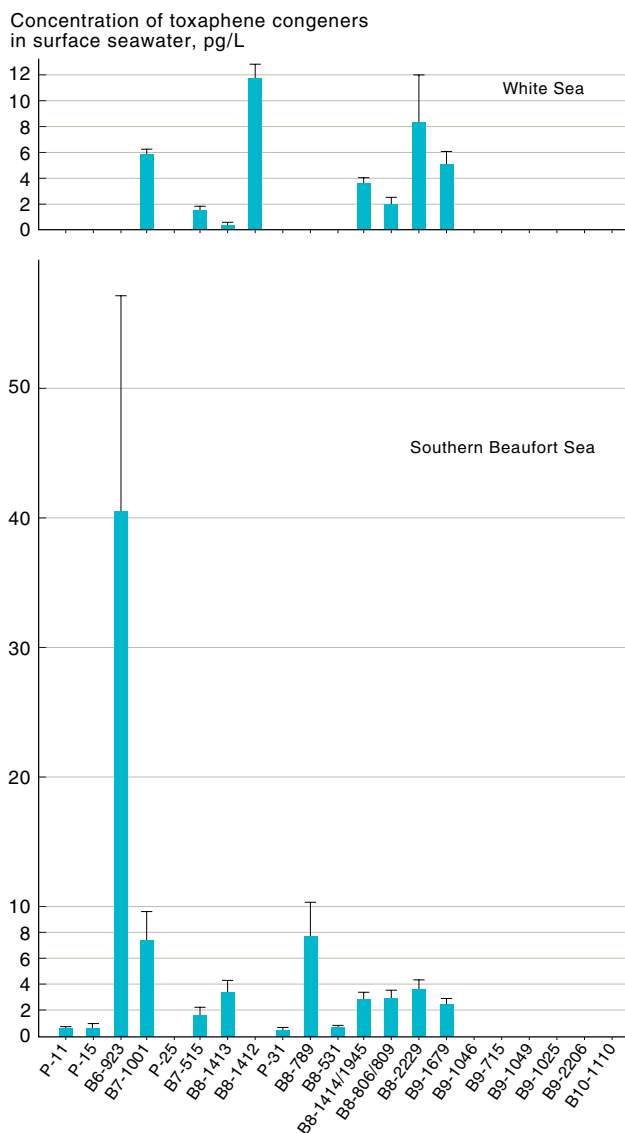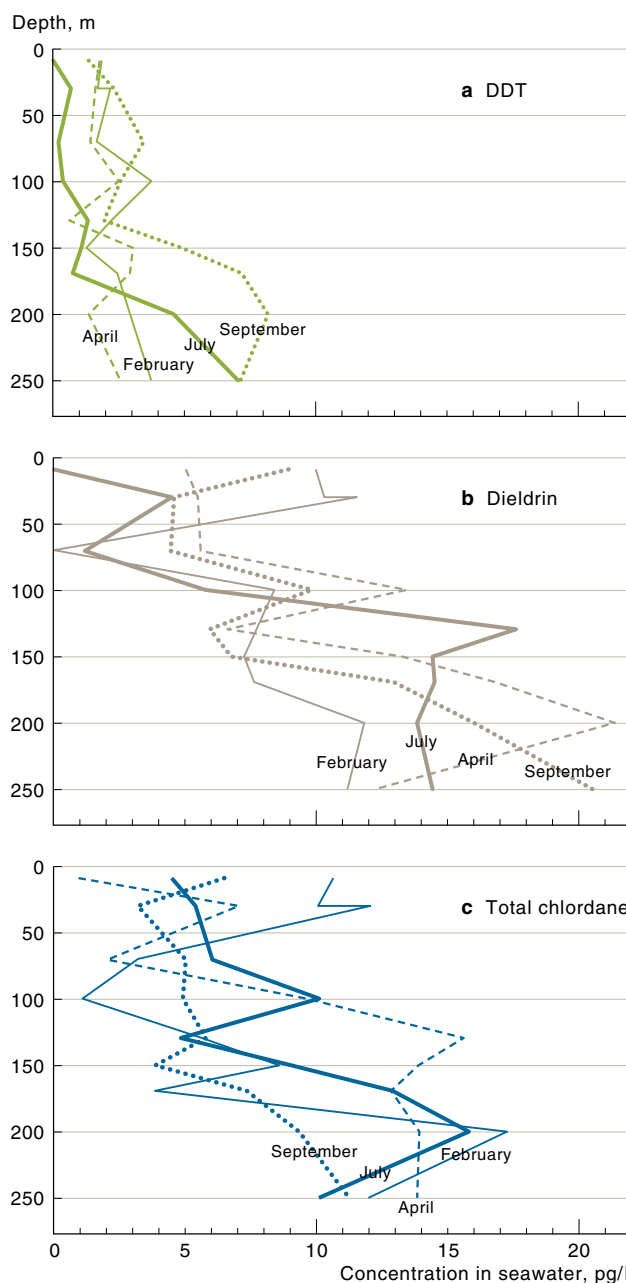
to 1994. The DDT residues in this region were predominately in the form of *p,p'*-DDE.

Macdonald *et al.* (2001) reported on the vertical distribution of DDT, dieldrin and chlordane over the Canada Basin and Chukchi Plateau (Figure 4·32 a-c) as part of the SHEBA study. The vertical distributions of these OC pesticides were very different from those observed for the HCHs where concentrations are found to decrease from their highest values near the surface to very low values below depths of 200-300 m. This may have been due to changes in water mass. Taking DDT as perhaps the best example, however, it seems likely that there is also a seasonal signal related to the biological cycle. In April and February of 1998, the DDT profiles were somewhat noisy, but reasonably uniform at about 2 pg/L through the water column down to 250 m (Figure 4·32 a). By July, however, this uniformity was disrupted, with much lower ΣDDT concentrations evident in the top 100-150 m of the water column and higher concentrations at about 200-250 m. In September, the surface concentrations of DDT were again uniform at about 2 pg/L, but higher concentrations are evident at or below approximately 150 m. Although water mass changes may contribute partly to the observed behavior, there appears also to be a transfer of DDT from surface to deeper waters in spring when biological production produces a vertical flux of organically rich particles.

4.4.1.6. Current-use chemicals

Endosulfan and lindane (γ-HCH) are the only pesticides in current use in circumpolar countries that are reported to date in Arctic Ocean water. Levels of lindane are generally highest in the Canadian Arctic Archipelago and southern Beaufort Sea, and lowest in the central Arctic Ocean (Strachan *et al.*, 2000), over the Chukchi Plateau and in the White Sea. Lakaschus *et al.* (2002) found lindane concentrations in the North Sea (0.33 ng/L) within the range of concentrations observed in the Greenland Sea (0.072-0.50 ng/L). White Sea waters were characterized by higher γ-HCH than in the Barents Sea, reflecting use in urban areas within the watershed. Within the White Sea, higher lindane concentrations were found in Kandalaksha Bay (0.19-0.41 ng/L) compared with the Central Basin (0.16-0.37 ng/L) (Muir *et al.*, 2002a). However, in general, γ-HCH levels in the White Sea were lower than those in the southern Beaufort Sea. α/γ-HCH ratios averaged 1.8±0.05 in the White Sea, compared with 2.2 ±0.52 in the Greenland Sea, 3.4±0.77 in the northern Barents Sea/central Arctic Ocean, and 2.3±0.77 in the Beaufort Sea (Hoekstra *et al.*, 2002b; Macdonald *et al.*, 2001).

Endosulfan is a widespread contaminant in Arctic seawater although present at much lower levels than lindane. Endosulfan (sum of α- and β-isomers) concentrations ranged from <0.0005 to 0.003 ng/L with no clear spatial trends. Hargrave *et al.* (1997) found endosulfan concentrations were higher during open water periods in the central Canadian Arctic Archipelago reflecting inputs from gas exchange and freshwater. During a twelve month study in 1993, endosulfan concentrations increased three-fold during the late summer and autumn months, paralleling increasing air concentrations. This was possibly related to summer use of endosulfan in mid-latitude North America.

Figures 4·32. Vertical profiles of 'legacy' OC pesticides (DDT, dieldrin, and chlordane) in seawater sampled during four intervals (February, April, July, and September) over the Canada Basin and Chukchi Plateau (see Figure 4·30) in 1998 (Macdonald *et al.*, 2001).

Chlorobenzenes are prominent contaminants in Arctic seawaters; however, the number of measurements of chlorobenzenes is limited. Di- to hexachlorobenzenes have been reported (Strachan, 2002). HCB concentrations appear to be relatively uniform compared to other compounds. Concentrations ranged from 0.006 ng/L in the southern Beaufort Sea to means of 0.005 ng/L in the White Sea. There are no data for chlorobenzenes in seawater from the European Arctic except for the White Sea (Annex Table 8).

4.4.1.7. Modeling latitudinal trends of α-HCH in ocean waters

It is of particular interest, from an Arctic perspective, to examine the global fate of α-HCH. By the 1990s, the concentration levels in the Canadian Arctic Ocean were
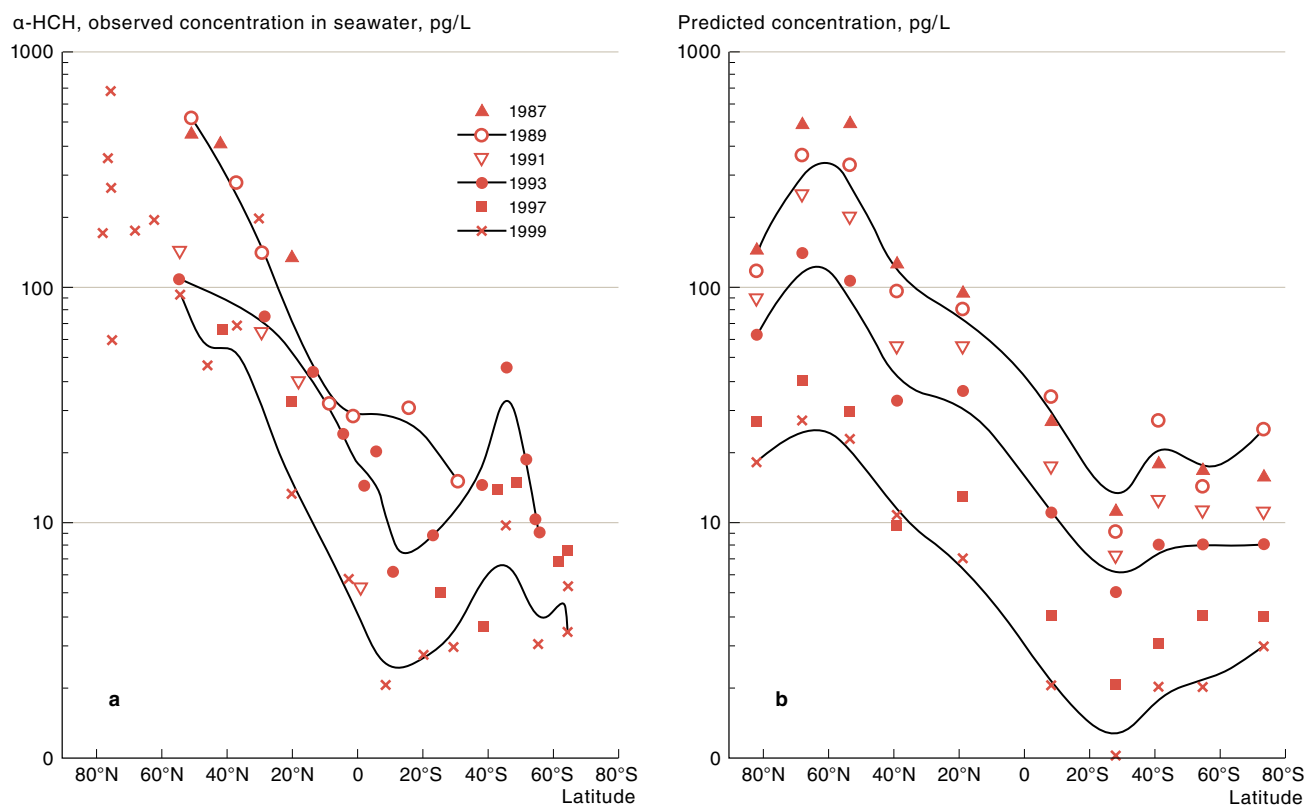
Figure 4·33. Latitudinal trends in a) observed and b) predicted seawater concentrations of α-HCH in the Atlantic Ocean (Lakaschus *et al.*, 2002). Concentrations were predicted with the 'Globo-POP' model of Wania and Mackay (2000).

higher than anywhere else in the global marine environment, notably an order of magnitude higher than in the Indian Ocean and the western Pacific, which are much closer to the major source regions (Iwata *et al.*, 1993; Wania and Mackay, 1996; de March *et al.*, 1998). α-HCH, the major component of technical HCH, was used in massive quantities in Asia during the 1970s. There has been a steady decline in use since then, and it is now virtually out of use worldwide (Li *et al.*, 1996; 1998a; Li 1999a; 1999b). Compared to most other OC pesticides, it is relatively water-soluble, relatively volatile, and less persistent. Calculations using the 'Globo-POP' global distribution model (Wania and Mackay, 2000) suggested that this inverted latitudinal concentration gradient developed during the two decades of declining emissions and was the result of α-HCH being trapped and preserved in the cold Arctic Ocean, whereas the levels in source regions declined as a result of degradation and volatilization. This is illustrated in Figure 4·33. Thus, the Arctic Ocean constitutes the last global refuge of α-HCH (Macdonald *et al.*, 2000). Interestingly, this highlights the fact that inverted concentration gradients can be established even if only a small percentage of the globally emitted amount is transferred to Arctic latitudes. In fact, the model predicted that the bulk of the α-HCH never left the agricultural systems in which it had been applied. Relatively small amounts can result in high concentrations in the Arctic because of the relatively small size of the Arctic as a whole and of the environmental phases with high capacity for adsorbing hydrophobic organic chemicals (organic soils, vegetation, organic sediments) within the Arctic. By binding substances such as HCH, these phases reduce the amount present in the atmosphere and in aquatic systems. The

model also suggested that ocean currents are as important in the northbound transport of α-HCH as the atmosphere. Most of the α-HCH in the Arctic originated in the northern temperate zone, which also was a net exporter of α-HCH to low latitudes. While α-HCH accumulated in the north, it was rapidly degraded under tropical conditions. Comparisons showed that calculated and measured α-HCH concentrations in the atmosphere and seawater generally agree within an order of magnitude (Wania *et al.*, 1999a; Lakaschus *et al.*, 2002) (Figure 4·33). Deviations are due to the zonal averaging characteristics of the model and uncertainties associated with the environmental degradation rates of α-HCH.

4.4.2. Marine sediments

The previous AMAP assessment report presented a large dataset on ΣPCBs, ΣDDTs, HCB, and ΣHCHs in marine sediments based on results from the early 1990s (de March *et al.*, 1998). Those results showed relatively uniform low levels of OCs in marine surface grab samples (all concentrations <10 ng/g dw). Thus, a general understanding of the distribution of the different contaminants in the Arctic was established during AMAP Phase I. No widescale regional geographic trends were apparent. However, there were distinct differences between nearshore and offshore sampling sites especially in Norway, which pointed to the need for further understanding of 'hot spots' and their importance as a source for contamination of adjacent areas. Previous studies in the Canadian Arctic have identified harbors in communities with military radar bases as having higher ΣPCB concentrations in sediment (Bright *et al.*, 1995b).

Svalbard

POPs were determined in surficial sediments collected in the Svalbard area of the Barents Sea in 1997 (Akvaplan-niva, 1998). Sampling sites included Kongsfjorden (western Svalbard), Questrenna (north of Svalbard), Lomfjorden and Hinlopen Strait (northern Svalbard), Erik Eriksen Strait (eastern Svalbard), and Strofjorden (southern Svalbard) (Figure 4·34). The samples were from relatively deep stations offshore (56-363 m depth, and 2224 m at Questrenna) and did not include harbor areas. ΣPCB levels were very low, ranging from 0.025 to 0.61 ng/g dw (sum of seven congeners multiplied by two to estimate total PCBs). Levels were similar to those reported around Franz Josef Land (Killie *et al.*, 1997; de March *et al.*, 1998). The deep sediment sample (Questrenna) had higher concentrations than other sites and a distinctly different PCB pattern, with higher proportions of hepta- and octachlorinated biphenyls. No influence on samples was evident from possible local PCB sources in harbors of towns on Svalbard.

ΣDDTs were present at similar levels as ΣPCBs with highest levels at the deep site (0.62 ng/g dw). DDE predominated at the deep site, while higher proportions of DDT and DDD isomers were found in most nearshore samples, suggesting some past use of DDT on Svalbard.

Northern Norway/Kola Peninsula and the White Sea

A study was conducted of OCs in sediments from six harbors in northern Norway and northwest Russia, an area that has been determined to be a key monitoring area by AMAP. The results allowed comparison of concentrations and the composition of congeners of the different OCs in the two countries (Dahle *et al.*, 2000).

When comparing the results for the six different harbors, some differences in study set-up should be noted. The most polluted areas in the Norwegian harbors were generally known, and the stations were positioned in order to confirm the local 'hot spots' and to check the degree to which contaminants had been spread to other parts of the harbor areas. The study in the Russian harbors was a screening study based on a limited number of stations.
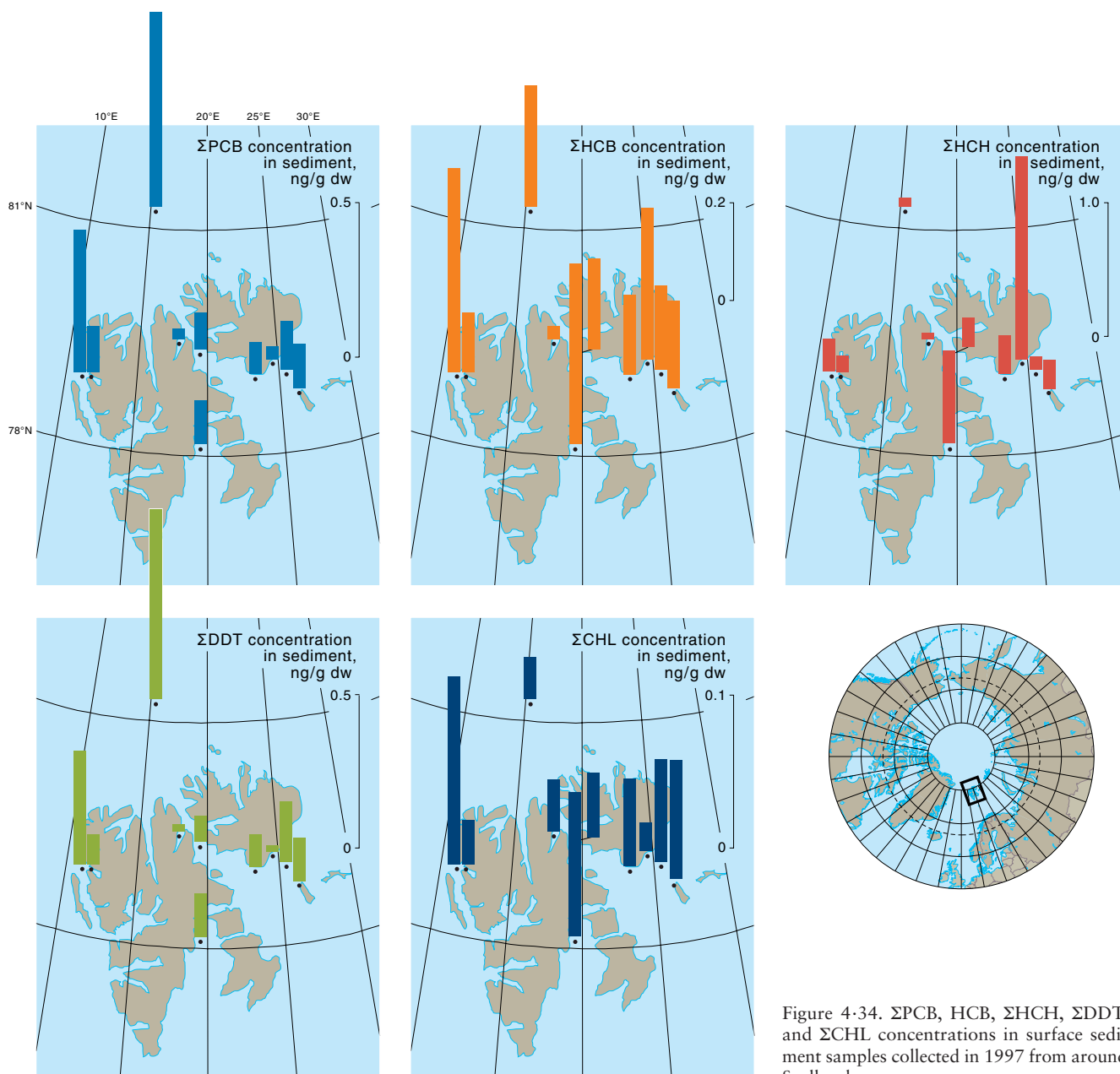

Figure 4·34. ΣPCB, HCB, ΣHCH, ΣDDT, and ΣCHL concentrations in surface sediment samples collected in 1997 from around Svalbard.