

Temporal Variations in POP Levels

A critical component of the assessment of POPs in the Arctic is knowledge of the temporal trends of these chemicals in the abiotic and biotic environment. The relationship between contaminant input into the Arctic and the levels and effects seen in wildlife and humans is ultimately tied to the use and restriction of these chemicals and any remedial action that is taken. It is, therefore, important to know if POPs are decreasing or increasing in the Arctic, and whether this varies throughout the Arctic and between various media. Temporal-trend datasets provide a tool to assess remedial actions, and also serve as an early warning system for potential changes in contaminant levels. Most of the Arctic nations have applied restrictions and bans on many of the major OCs for decades, resulting in significant declines of these chemicals in temperate and Arctic regions in the 1970s and 1980s. Continued use of chemicals such as PCBs, and emissions from areas where chemicals are still in use, however, provides a continuing source of contamination. The signing of the Stockholm Convention on Persistent Organic Pollutants in May 2001 (UNEP 2001), which calls for bans on a number of chlorinated pesticides, and reductions of use and emissions of POPs that are by-products, is likely to result in further declines. New concerns have arisen for current-use chemicals such as brominated flame retardants. The use of these chemicals is increasing and, consequently, levels in the environment have been increasing as well.

The first AMAP POPs assessment included a very limited number of good temporal-trend datasets with which to assess long-term trends of OCs in the Arctic. Many of the datasets were confounded by changes in analytical methodologies. For example, much of the older data were generated using packed column gas chromatography rather than current capillary column technology. The best temporal-trend datasets available include the monitoring of OCs in Arctic marine biota dating back to the early 1970s, and the database available on OCs in fish from northern Scandinavia dating back to the late 1960s. These datasets showed a decreasing trend in OCs in the 1980s but a reduction in the rate of decline during the early 1990s.

The assessment of temporal trends, however, is not a simple process and requires datasets from numerous locations and matrices. Regional differences in sources, changes in atmospheric and oceanic currents, and variability associated with biota all can influence OC levels and temporal trends. During the 1990s, weather patterns changed in the northern hemisphere, with an increase in the number of deep storms, and these storms penetrated deeper into the Arctic. The result has been a stronger connection between industrial areas of Europe and North America and the Arctic (Macdonald *et al.*, 2003). This may mean that there has been increased transport of contaminants to the Arctic during the past decade, which would affect temporal-trend monitoring.

The high degree of variability normally observed in OC data in both air and biotic matrices therefore, requires that temporal-trend datasets cover a large number of sampling years and have sufficient sample numbers for robust statistical analysis.

5.1. Air and precipitation

5.1.1. Temporal trends in air

Data on sub-decadal (3-6 years) temporal trends of POPs in Arctic air are available from air monitoring stations at Alert (Nunavut, Canada), Stórhöfði (Iceland), Ny-Ålesund (Svalbard, Norway) and Pallas (Finland). Shorter-term (1-3 years) results are also available from Dunai (eastern Russian Arctic) and Amderma (western Russia). Comparisons of levels of major OCs and PAHs among these stations were made in Section 4.1. In this section, temporal trends in air concentrations of PCBs, PAH, and OC pesticides are evaluated and compared. Hung *et al.* (2001; 2002b) examined the temporal trends of PCBs and OC pesticides at Alert using both a temperature-normalization method (where concentrations are expressed as partial pressures and adjusted to a standard temperature (288°K)), and a digital filter method (where concentrations are expressed as partial pressures and short- and long-term variations are extracted using cut-off filters). The estimated half-lives from their work are included in the discussion of each chemical group. Similar time trend analyses are not available for the European Arctic stations with long-term data.

5.1.1.1. OC pesticides

DDT

Time series for DDT-related compounds in Arctic air are available for Alert (1993-1998), Stórhöfði (1995-1999), Ny-Ålesund (1993-2000), and Pallas (1996-1999). DDT results are also available from Tagish (1993-94) and Dunai (1993) and these full datasets have been discussed previously (Halsall *et al.*, 1998). Since these stations did not operate beyond 1994, no data were generated in Phase II of AMAP. With the exception of Stórhöfði, where there was indication of local sources (Section 4.1.1), the DDT transformation products *p,p'*- and *o,p'*-DDE were mainly found. Figure 5-1 presents the concentration distribution of *p,p'*-DDE over the period 1993-2000. Concentrations at Ny-Ålesund and Stórhöfði were generally higher than at Alert and tended to be lower in 1999 than in earlier years. Indications of seasonal variation can be seen for all sites. The highest concentrations were always found during winter (January/February) and the lowest values were found in summer (August). The most extreme case is at Ny-Ålesund where *p,p'*-DDE concentrations increased 8 to 10 fold above prevailing concentrations in winter and early spring months, especially in 1996, 1997, and 1999. This reflects the association of DDE with parti-

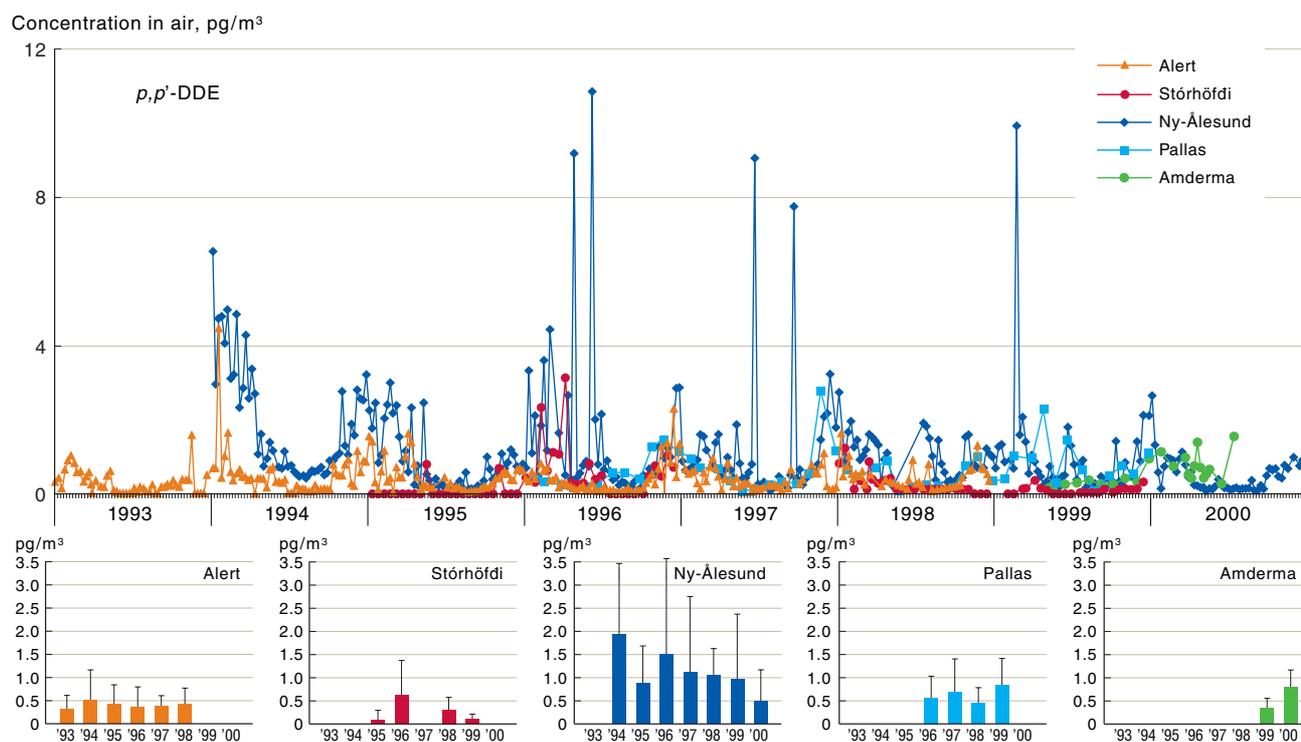


Figure 5-1. Temporal trends of p,p' -DDE in Arctic ambient air at five monitoring stations from 1993 to 2000.

cles under prevailing winter temperatures and higher particle concentrations during the winter associated with Arctic haze (Halsall *et al.*, 1998). p,p' -DDE is strongly associated with soils and may be transported with aeolian dusts that are advected into the Arctic (Welch *et al.*, 1991; Hung *et al.*, 2002b). Using temperature-adjusted data, Hung *et al.* (2002b) concluded that

p,p' -DDE is decreasing slowly at Alert (estimated half-life of 19 years). Hung *et al.*, (2002b) also found that o,p' -DDT actually increased, though not significantly, in concentration at Alert over the period of 1993 to 1998 (Table 5-1). The presence of o,p' -DDT implies a continued source of technical DDT entering the Arctic atmosphere.

Table 5-1. Half-lives ($t_{1/2}$) of selected OC pesticides and PCBs at Alert (developed using the digital filtration method; Hung *et al.*, 2001) and comparison with the Great Lakes region and western Europe.

OC	Alert, Nunavut		Great Lakes (Eagle Harbor, Lake Superior)		Great Lakes (Sleeping Bear Dunes, Lake Michigan)		Northern U.K. ^b
	$t_{1/2}$ ^a (yr)	r^2	$t_{1/2}$ ^a (yr)	\pm SE	$t_{1/2}$ ^a (yr)	\pm SE	
α -HCH	17	0.79	3.0	0.2	3.2	0.4	
γ -HCH	4.9	0.88	4.4	0.6	3.4	0.6	
<i>trans</i> -chlordane	8.3	0.48	6.9	2.9	5.2	1.7	
<i>cis</i> -chlordane	4.1	0.71	23	25	9.7	4.9	
<i>trans</i> -nonachlor	6.2	0.71	33	53	6.0	2.1	
Dieldrin	incr.	<0.10	3.7	0.7	2.4	0.4	
p,p' -DDE	19	<0.10	–	–	–	–	
o,p' -DDT	incr.	0.29	–	–	–	–	
PeCA	3.9	0.71	–	–	–	–	
α -endosulfan	incr.	0.25	–	–	–	–	
Tetrachloroveratrole	incr.	<0.10	–	–	–	–	
CB28 (Cl ₃)	12	0.58	–	–	2.7	0.6	1.7-4.2
CB52 (Cl ₄)	3	0.86	–	–	4.3	1.3	1.6-2.3
CB101 (Cl ₅)	11	0.73	–	–	2.9	0.7	2.1-4.3
CB153 (Cl ₆)	17	0.18	–	–	1.8	0.4	2.3-6.6
CB180 (Cl ₇)	4	0.78	–	–	–	–	–

^a $t_{1/2}$ = half-life, calculated as $\ln 2/s$ where s = slope of the linear regression. For Alert s = slope of the time trend developed using the digital filtration method. For other sites s = slope between $\ln P_{288}$ and t (where t = time (years) and P_{288} = partial pressure of the chemical at 288 Kelvin). Data with increasing time trends are indicated as 'incr.'. r^2 values give an indication of the statistical significance of the relationship of $\ln P$ vs. time.

^b Results from Sweetman and Jones (2000).

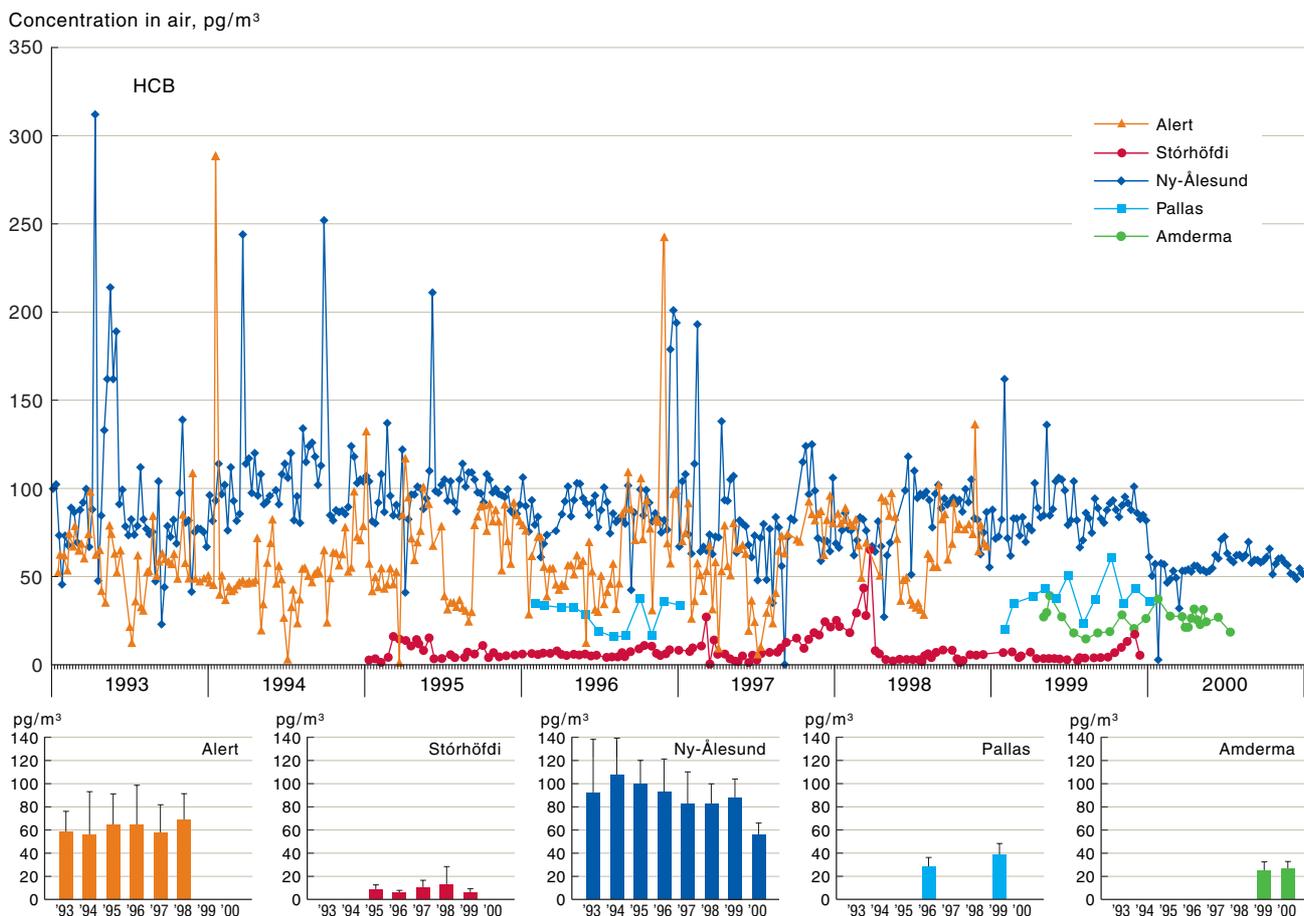


Figure 5-2. Temporal trends of HCB in Arctic ambient air at five monitoring stations from 1993 to 2000.

HCB

No indication of major trends in concentrations of HCB in the period of 1993 to 1999 were found in the data reported from the three stations with the longest time series (Figure 5-2). HCB was relatively constant with occasionally elevated levels, especially at Ny-Ålesund and Alert. The sources of these elevated HCB concentrations have not been investigated. HCB concentrations show significant 'break-through' of the polyurethane foam collection material even at low temperatures (averaging 25.9%; P. Blanchard, pers. comm.), and thus, the concentrations might be underestimated. In 1997-1999, there were fewer short episodic increases in HCB concentrations at Ny-Ålesund and Alert than in earlier years.

HCH

The time series for concentrations of α - and γ -HCH are presented in Figure 5-3. A discernible decrease in concentration of α -HCH from 1993 to 2000 at Ny-Ålesund and from 1995 to 1999 at Stórhöfði, is apparent from the raw data in Figure 5-3. γ -HCH concentrations show no general tendencies. In all Arctic air samples except those from Stórhöfði, γ -HCH represents about 15-20% of the total α - and γ -HCH burden. Unlike several other semivolatile OCs (dieldrin, endosulfan, *cis*-chlordane), α - and γ -HCH concentrations at Alert were not correlated with air temperature (Halsall *et al.*, 1998; Hung *et al.*, 2002b). This lack of correlation reflects the importance of long-range transport events that bring higher concentrations to each site. This is most

evident for γ -HCH in spring-time samples (weeks 14-27) at Ny-Ålesund between 1993 and 1997 and Stórhöfði in 1995-96 (Figure 5-3). A spring increase in γ -HCH was also observed at Alert; however, sharp increases, like those found in springtime at Ny-Ålesund and Stórhöfði were mainly observed in October-December samples at Alert. The reason for this is not clear, although it could be due to agricultural practices in Canada (a major lindane user during the 1990s) where autumn plowing may release residual lindane that was used for seed treatment in oilseed crops. Decreases in γ -HCH at Ny-Ålesund and Stórhöfði in 1999-2000 may reflect reductions and changing use patterns of lindane in Europe. In mid-1998, lindane use ceased in France, the main user in western Europe.

Linear regression analysis of the 'temperature-normalized' or 'digitally filtered' data revealed that α -HCH and γ -HCH concentrations are declining at Alert (Table 5-1). The decline of γ -HCH was more rapid than that of α -HCH over the five-year period (1993-1998) (Hung *et al.*, 2002b). Jantunen and Bidleman (1995) have shown α -HCH to be outgassing from the Arctic Ocean, which will buffer the concentrations in the overlying atmosphere, and may help to explain the long half-life found in this study. On the other hand, γ -HCH in Arctic air has a half-life comparable to that found at temperate sites (Table 5-1). Haugen *et al.* (1998) reported no trend for γ -HCH in air from southern Norway (Lista air station) between 1991 and 1995. This probably reflects the effect of a strong European signal at that site.

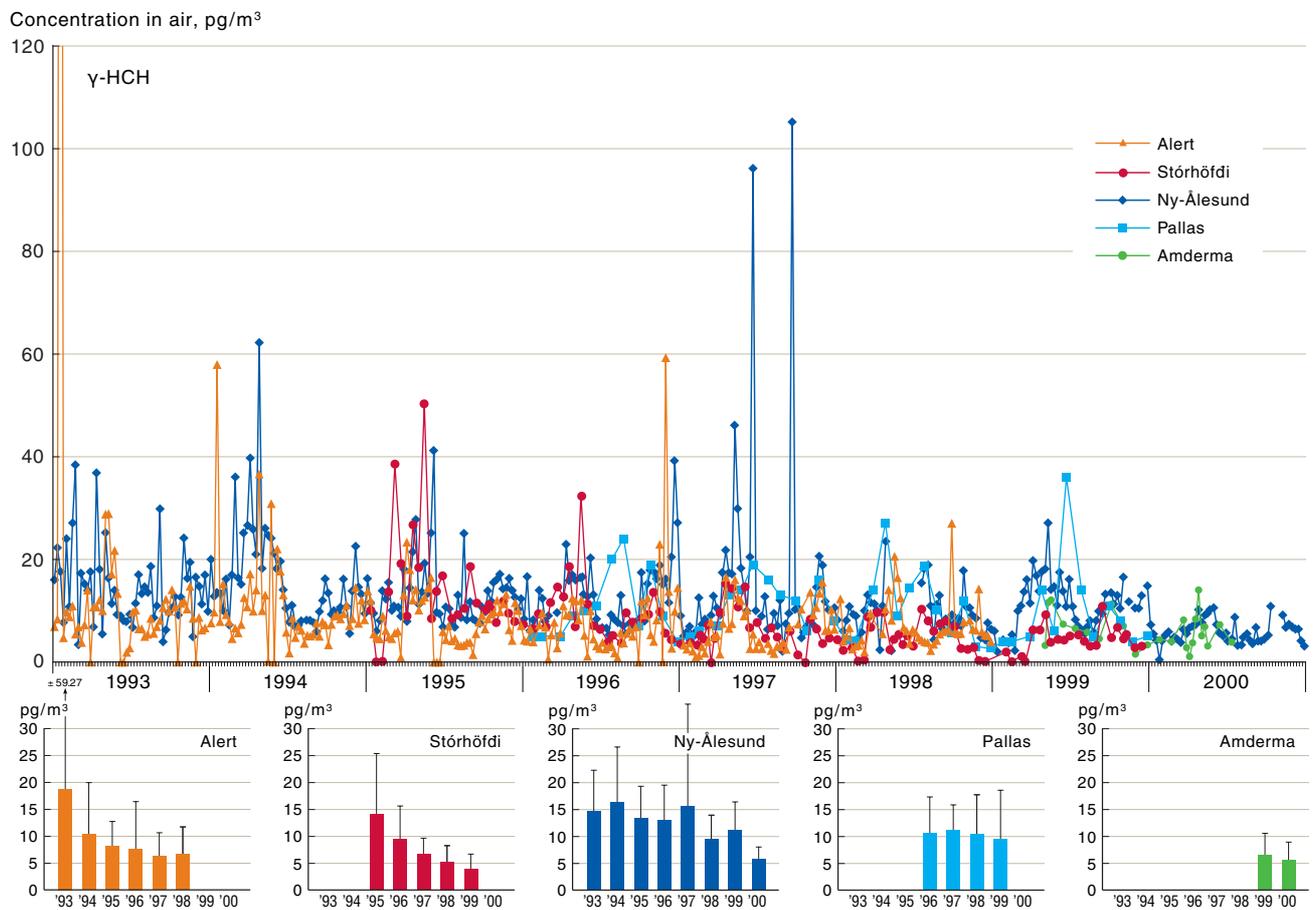
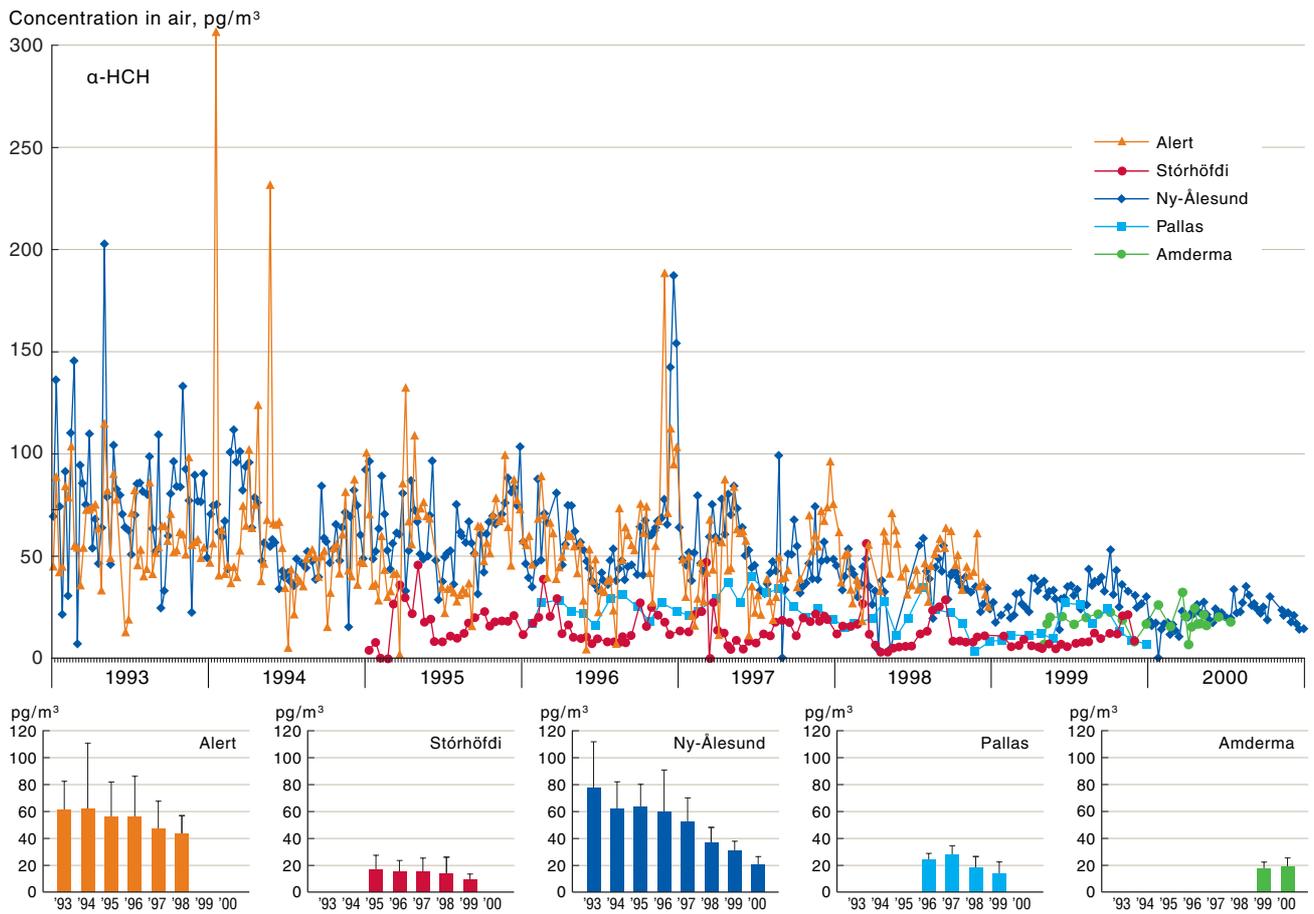


Figure 5-3. Temporal trends of α - and γ -HCH in Arctic ambient air at five monitoring stations from 1993 to 2000.

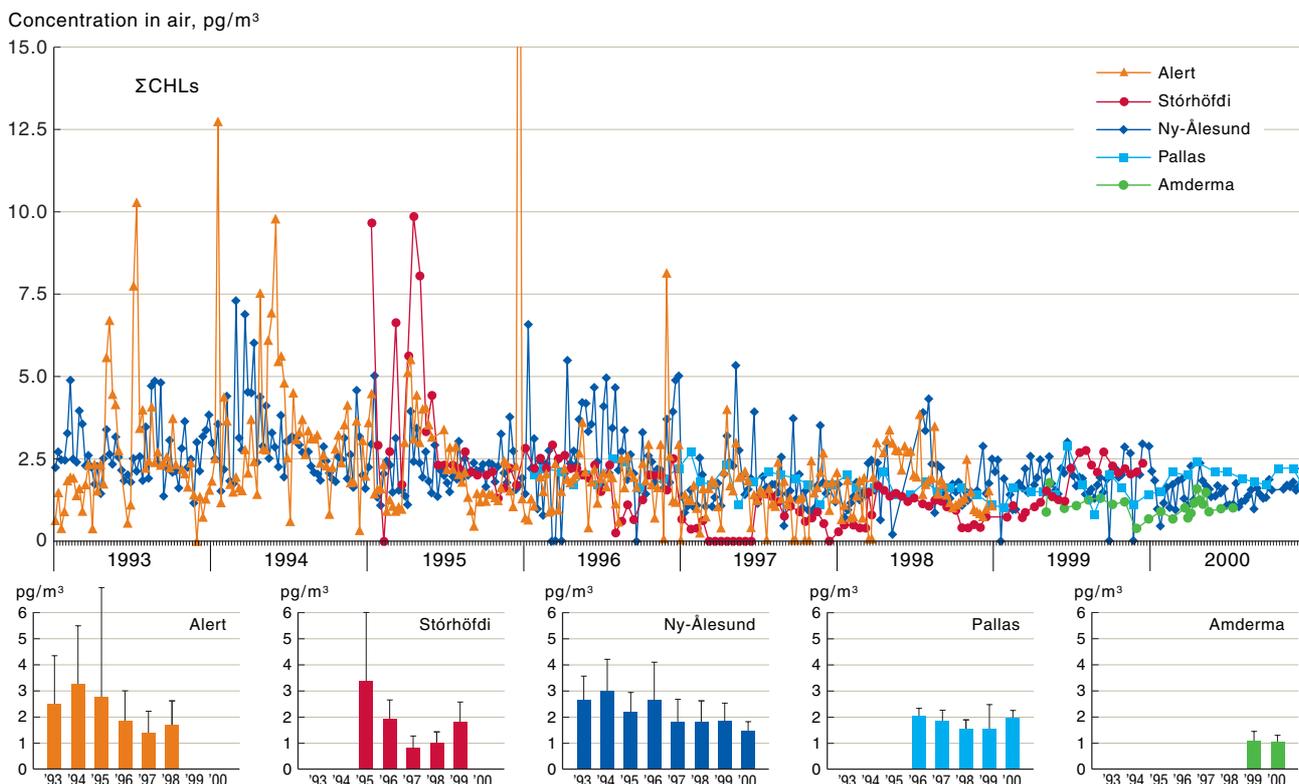


Figure 5-4. Temporal trends of total chlordanes (sum of *cis/trans*-chlordanes, *cis/trans*-nonachlor) in Arctic ambient air from 1993 to 2000.

Cyclodiene pesticides including chlordanes

Time trends for ΣCHLs and dieldrin are presented in Figures 5-4 and 5-5. For purposes of comparison, ΣCHLs was restricted to *cis/trans*-chlordanes and *cis/trans*-nonachlor. Alert shows relatively high average values of ΣCHLs from 1993-1994 and a subsequent continuous decrease in average concentrations until 1998. The time series of ΣCHLs at Alert, Ny-Ålesund, and Stórhöfði are characterized by sharp weekly episodes during the win-

ter months as well as a general rise in concentrations during summer. This trend was not apparent in northern Finland. These weekly episodes might be due to fresh use of chlordanes-based pesticides (Hung *et al.*, 2002b). Previous episodes of elevated *trans*-chlordanes at Ny-Ålesund were traced to North American sources (Oehme *et al.*, 1995b), which might explain why the seasonal trend is not as apparent at Pallas or Amderma. *Cis/trans*-nonachlor and *cis*-chlordanes were significantly correlated

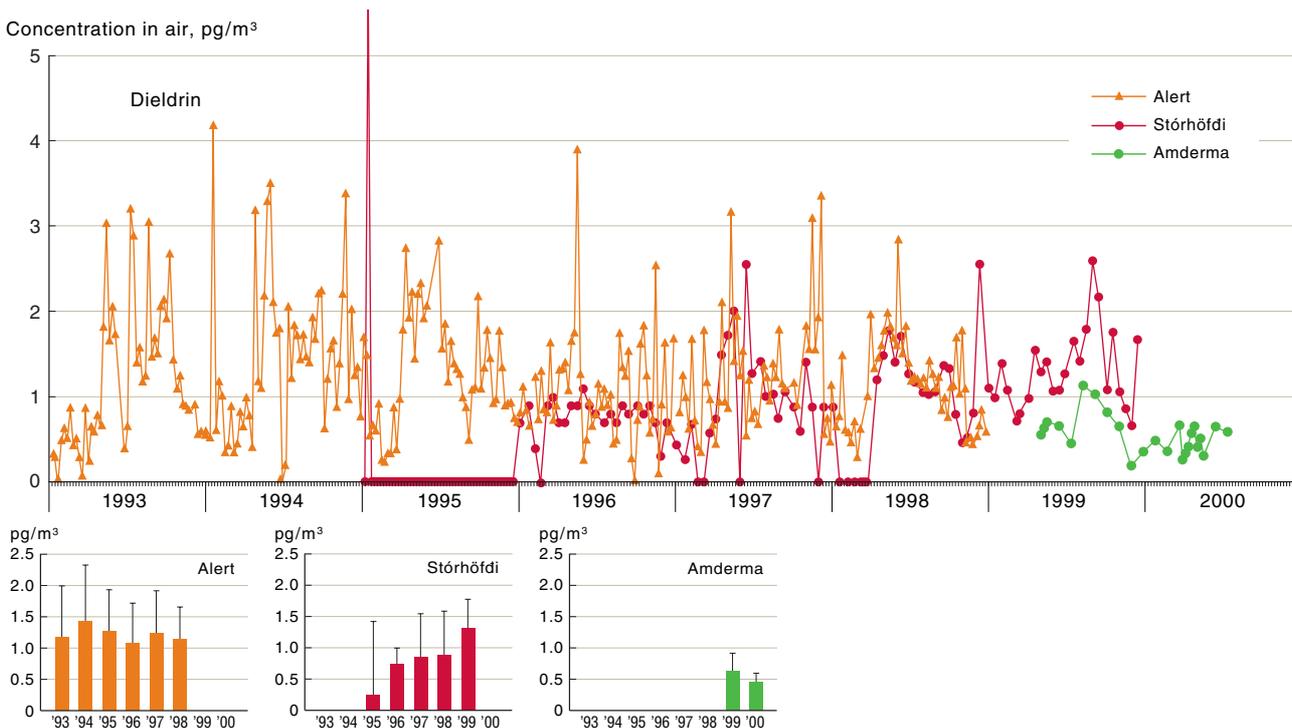


Figure 5-5. Temporal trends of dieldrin in Arctic ambient air from 1993 to 2000.

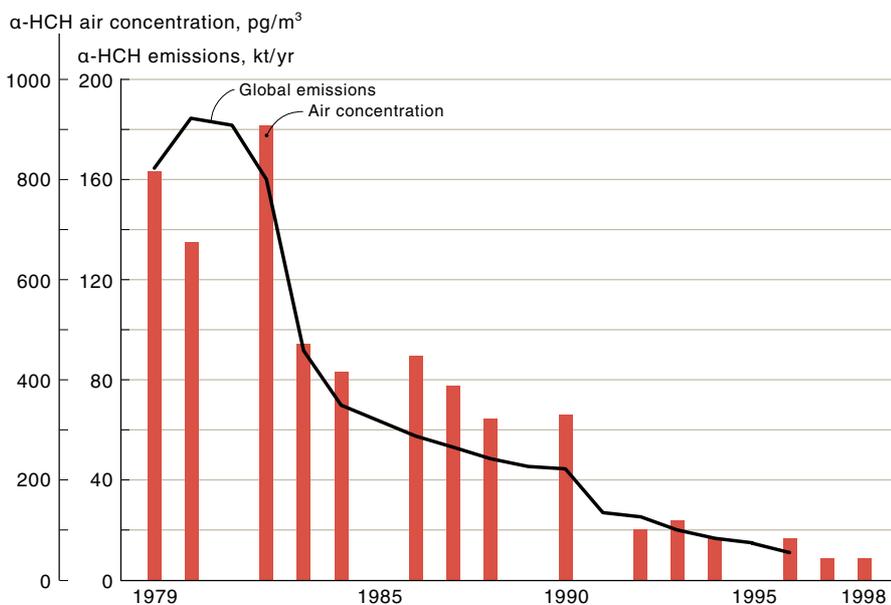


Figure 5-6. Global emissions of α -HCH and mean concentrations of α -HCH in Arctic air from 1979 to 1996. Air concentration data for α -HCH in the Arctic have been measured at different stations by several research groups (i.e. Tanabe and Tatsukawa, 1980; Oehme and Ottar, 1984; Hargrave *et al.*, 1988; Patton *et al.*, 1989; 1991; Hinckley *et al.*, 1991; Oehme, 1991; Iwata *et al.*, 1993; Bidleman *et al.*, 1995; Falconer *et al.*, 1995; Jantunen and Bidleman, 1995; 1996; Oehme *et al.*, 1995c; Pacyna and Oehme, 1998).

with air temperature at Alert (Hung *et al.*, 2002b). Concentrations of Σ CHLs also declined at Stórhöfði until 1997 and then increased in 1999. Using digitally filtered data, Hung *et al.* (2002b) concluded that *cis-trans*-chlordane and *trans*-nonachlor concentrations declined significantly at Alert with half-lives of 4.1, 8.3 and 6.2 years, respectively (Table 5-1). These half-lives were comparable (within a factor of 2) to half-lives calculated for these pesticides at rural sites in the Great Lakes (Table 5-1) (Simcik *et al.*, 1999).

Hung *et al.* (2002b) concluded that dieldrin concentrations did not change significantly from 1993 to 1998 at Alert. Dieldrin concentrations appeared to increase at Stórhöfði from 1995 to 1999 (Figure 5-5). Dieldrin was not reported at the Ny-Ålesund or Pallas stations. Dieldrin concentrations were significantly correlated with air temperature at Alert and typically showed higher concentrations during summer at both Alert and Stórhöfði.

Concentrations of α -endosulfan at Alert increased over the period of 1993 to 1998 (Hung *et al.*, 2002b). Unlike the more persistent, now banned, OC pesticides discussed above, this is explained by continued use of endosulfan in southern Canada and throughout the U.S. (NCFAP, 2001).

Other OC compounds

Tetrachloroveratrole, a by-product of wastewater and wood pulp chlorination also increased in concentration at Alert (Hung *et al.*, 2002b). PeCA declined in concentrations at Alert over the same time period. Time trends of other by-products and current-use pesticides measured at Alert (Section 4.1.1) have not been reported, mainly due to their low atmospheric concentrations, nor have they been studied at other monitoring stations.

Other time series for HCH, toxaphene, and chlordane

Li *et al.* (1998a) studied the relationship between the global trends in use of technical-HCH and air concentrations in the Arctic atmosphere by combining data mainly from short-term measurement campaigns in the Bering Sea, western Canadian Arctic and Svalbard from the 1980s and 1990s. Two significant drops in global technical HCH usage were identified, one in 1983 and

another one in 1990. Figure 5-6 shows the long-term trends in global emissions of α -HCH and its mean air concentrations in the Arctic regions from 1979 to 1998. The trends shown here are similar to those shown by Li *et al.* (1998a), who reported technical HCH emissions. By comparing these two figures, it was found that concentrations of α -HCH in the Arctic air are more highly correlated with global α -HCH emissions than with global technical HCH usage (Li *et al.*, 2000; Li and Bidleman, 2003).

Li *et al.* (2001b) also examined the emissions of toxaphene in the U.S. and their influence on levels in Arctic air. Figure 5-7 shows the temporal trends in concentrations of toxaphene in Canadian Arctic air and the estimated emissions of toxaphene from the U.S. from 1985 to 1995. The estimated emissions of toxaphene are, in general, consistent with the concentrations of toxaphene in Canadian Arctic air in the summer. The consistency between toxaphene emissions from agricultural soils in

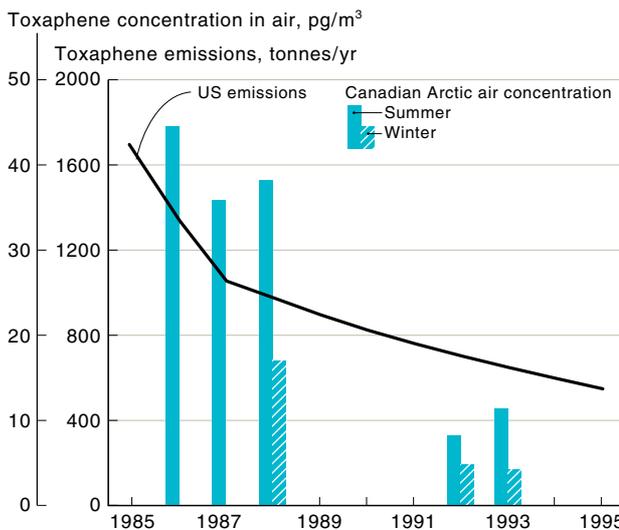


Figure 5-7. Temporal trends in concentrations of toxaphene in Canadian Arctic air and the calculated emissions of toxaphene from the United States from 1985 to 1995. (Sources of air concentration data: data for 1986 and 1987, Patton *et al.* (1989); data for 1988, Patton *et al.* (1991); Hinckley *et al.* (1991); data for 1992, Bidleman *et al.* (1995); Fellin *et al.* (1996); data for 1993, de March *et al.* (1998); Macdonald *et al.* (2000)).

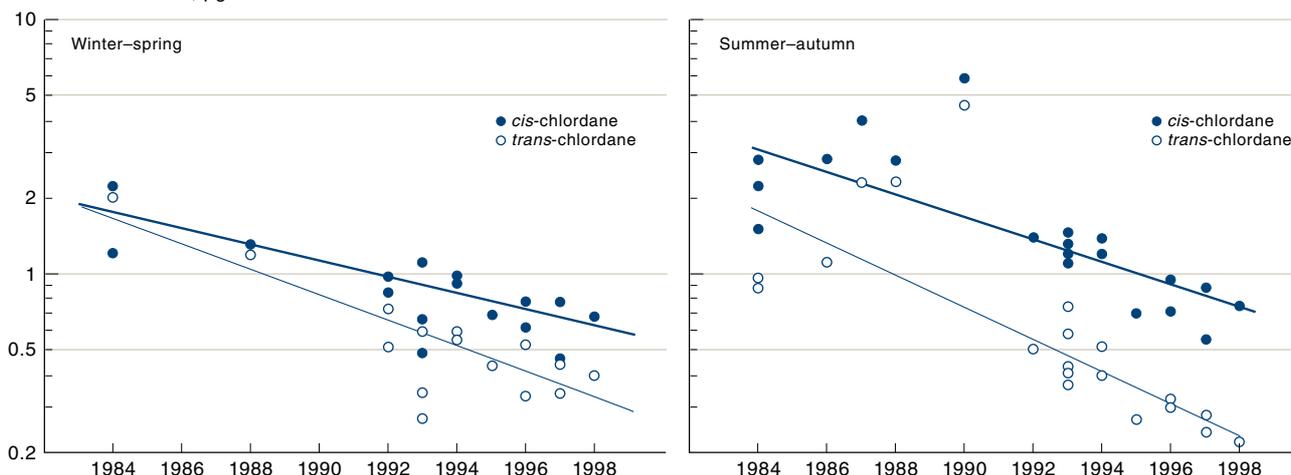
Concentration in air, pg/m³

Figure 5-8. Long-term time trends of *trans*- and *cis*-chlordane concentrations in Arctic air during winter-spring and summer-autumn (from Bidleman *et al.*, 2002a).

the U.S. and air concentrations of toxaphene in Canadian Arctic regions illustrates that toxaphene residues in the United States, the southeastern part in particular, could be the major sources of toxaphene in the Canadian Arctic atmosphere. Other sources of toxaphene could include countries in other regions, since toxaphene was still in use in Russia and eastern Europe during the 1980s (HELCOM, 2001). For example, Bidleman *et al.* (1987) found that toxaphene reached southern Sweden during 1984/1985 from eastern Europe and western Russia.

Bidleman *et al.*, (2002a) examined temporal trends of chlordane compounds in Arctic air over a 14-year period 1984-1998. Results for *cis*-/*trans*-chlordane and

trans-nonachlor were combined from literature reports from numerous monitoring programs beginning with measurements in Canada (Alert and Mould Bay) and Norway (Ny-Ålesund and Jergul) in 1984. Winter-spring and summer-autumn results were grouped and separated since previous reports had shown changing ratios of *trans*- to *cis*- compounds between these seasons. Significant declines for *cis*- and *trans*-chlordane were found (Figure 5-8) as well as for *trans*-nonachlor (not shown). Half-lives in Arctic air for *cis*- and *trans*-chlordane, and *trans*-nonachlor, were estimated to be 6.4, 9.7 and 6.3 years, respectively, in agreement with estimates of Hung *et al.* (2002b).

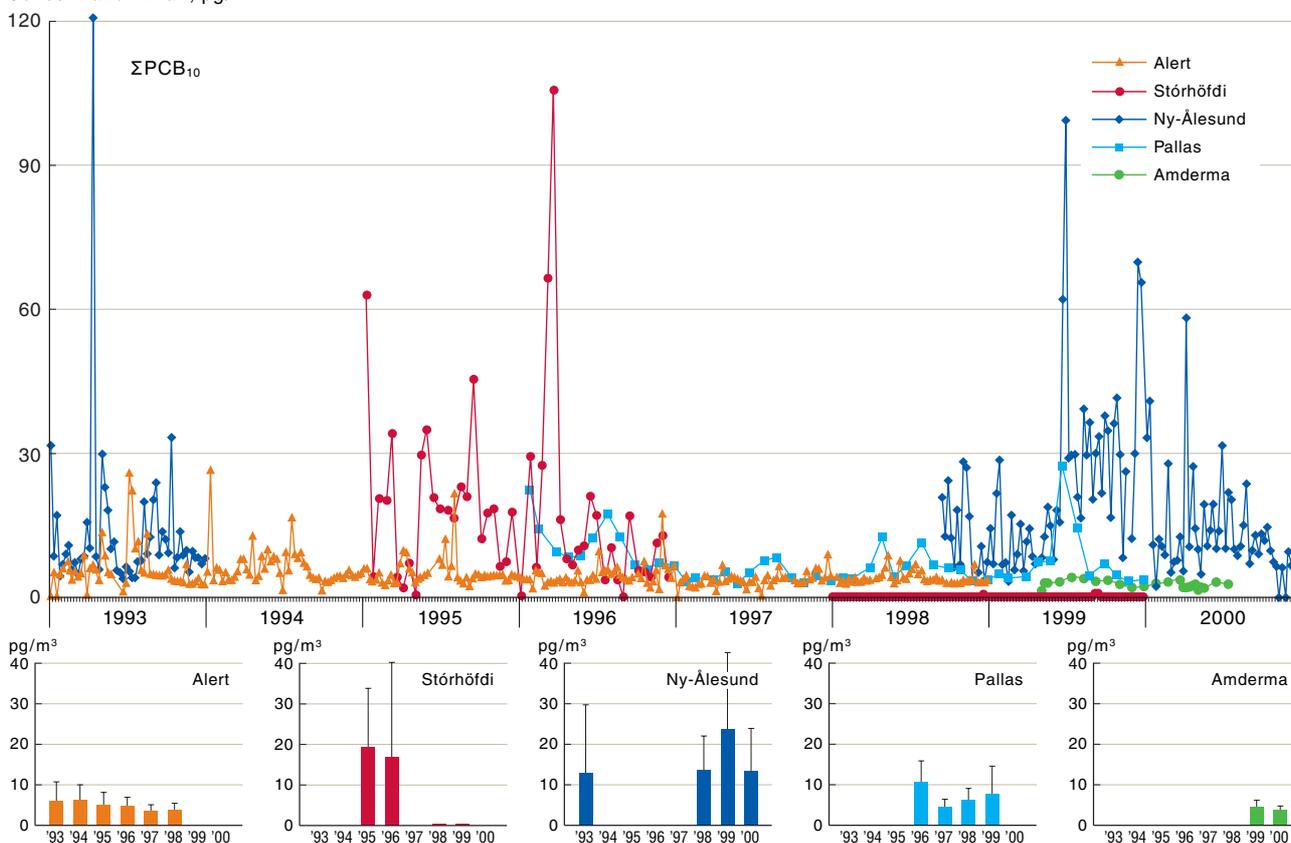
Concentration in air, pg/m³

Figure 5-9. Temporal trends of PCB (sum of ten congeners) in Arctic ambient air at five monitoring stations (1993-2000).

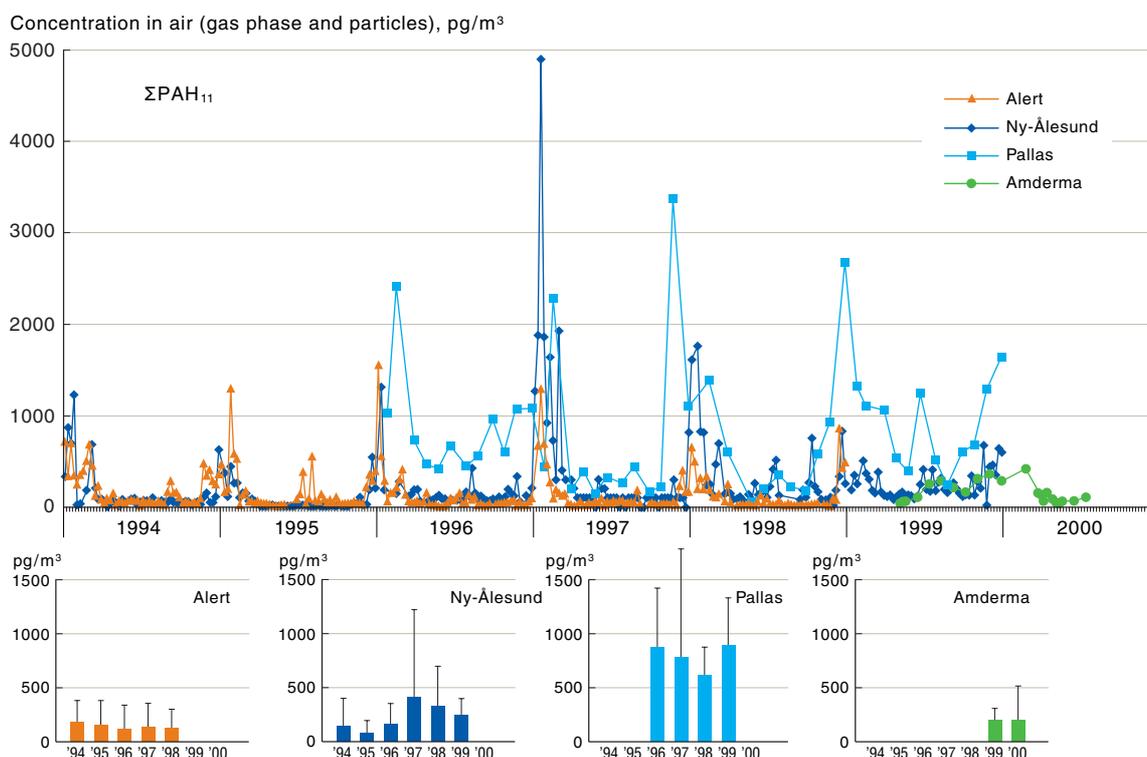


Figure 5-10. Temporal trends of Σ PAHs (11 compounds) in air (gas phase and particles) at Alert, Amderma, Ny-Ålesund, and Pallas.

5.1.1.2. PCBs

The time series for PCBs at five air-monitoring stations is shown in Figure 5-9. A sum of ten PCB congeners was used to represent the time series because the total number of congeners measured at each station varied (see Section 4.1.1). The 1992 data from Alert, as well as data from Ny-Ålesund (1994-97), may reflect some on-site contamination and were therefore not used here or in previous studies of the datasets (Stern *et al.*, 1997; Hung *et al.*, 2001). PCB concentrations tend to be elevated in summer at all stations and, like OC pesticides, show sharp concentration ‘episodes’ in both winter and summer months. No clear downward trend is evident, except for Alert, where a distinct reduction in PCB levels from 1993 to 1998 is apparent. At Alert, penta- and hexachlorobiphenyls were significantly correlated with air temperature, while di- and trichlorobiphenyls were not. The lack of temperature dependence of the less chlorinated congeners suggests that regional/local revolatilization does not have a marked effect on atmospheric levels of the predominant PCBs in the Arctic atmosphere, and emphasizes the importance of long-range transport to the Arctic (Hung *et al.*, 2001).

Hung *et al.* (2001) found declining trends for several of the lower chlorinated congeners in the High Arctic atmosphere at Alert (Table 5-1). The half-lives observed for most of the PCBs at Alert were longer than those observed at a rural site in northern England (Sweetman and Jones, 2000) and at background/rural sites in the Great Lakes (Table 5-1) (Simcik *et al.*, 1999). Haugen *et al.* (1999) did not find an obvious decrease in atmospheric levels of PCBs (1992-1995) from Lista in southern Norway. However, longer time series combined with temperature adjustment would probably be needed to see any such trend. At Alert, CB180 (heptachlorinated)

showed a clear downward trend, with a calculated half-life of only four years (compared to 15 years for CB153). It is therefore possible that heavier congeners might be subjected to different removal processes than the lighter ones, including scavenging by precipitation.

5.1.1.3. PAHs

Data for two or more years were available only for the Alert (1994-1998), Ny-Ålesund (1994-1999), and Pallas (1996-1999) stations and, with missing sampling times, from Amderma (1999-2000). The three longer-term stations determined from 11 to 25 PAH compounds of which anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b,j,k]fluoranthenes, benzo[g,h,i]perylene, chrysene, dibenz[a,h]anthracene, fluoranthene, indeno[1,2,3-cd]pyrene, phenanthrene, and pyrene were common to all measurement programs. Trends for Σ PAH₁₁ at the four stations are shown in Figure 5-10. All sites show an annual cycle of higher concentrations in the winter months, especially during November to February, coinciding with the dark period at these latitudes and with the Arctic haze season. The air sampled at the Ny-Ålesund and Pallas stations is distinguished from Alert by significantly higher PAH concentrations in all seasons, particularly in winter months, over the period of 1996/7 to 1999. Unlike some OCs, no consistent trends can be derived from the PAH data at Ny-Ålesund or Alert. Maximum concentrations generally increased from 1994 to 1997, but were lower in 1998-1999 than in previous years. Ny-Ålesund also had consistently higher ratios of B[a]P:B[e]P, an indicator of reactive versus stable atmospheric PAH, indicating fresher sources than at Alert. B[a]P:B[e]P averaged 2.9 (range <0.1-10) compared with an average of 0.4 (range <0.1-1.7) at Alert. B[a]P concentrations at Ny-Ålesund were highest in 1994 and

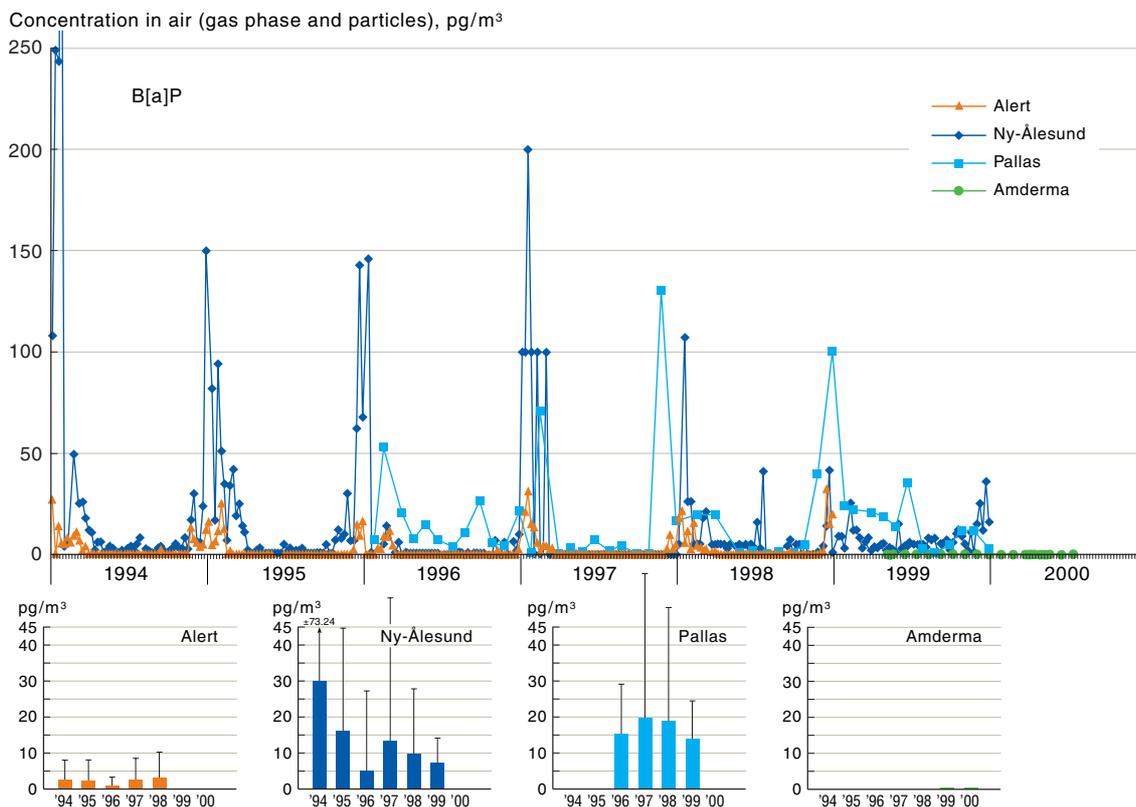


Figure 5-11. Temporal trends of B[a]P in air (gas phase and particles) at Alert (Nunavut), Ny-Ålesund (Svalbard) and Pallas (Northern Finland), and Amderma from 1994 to 2000. B[a]P is predominantly found on particles.

declined during the 1990s. During the summer months, B[a]P concentrations at Ny-Ålesund and Pallas were similar to those seen at Alert. However, much higher winter maxima were observed (Figure 5-11). No investigations of PAH trends similar to those carried out for PCB and OC pesticide data have been made to date.

5.1.2. Temporal trends in wet deposition

The time series of bulk deposition of PAHs, PCBs, and HCHs at Oulanka and Pallas in northern Finland during the summers (June to September/October each year) from 1993 to 2001 (Korhonen *et al.*, 1998; 2002) is shown in Figure 4-9. Highest deposition values for ΣPAHs were observed in 1993. Elevated PCB concentrations were found in mid-summer 1994, autumn 1995, and mid-summer 1998. Highest ΣHCH concentrations were observed in mid-summer 1998. Total PCBs in precipitation at Pallas appear to have declined significantly over the period of 1993 to 2001, while no trend was evident for PAHs or ΣHCHs.

5.1.3. Temporal trends in snow cores

5.1.3.1. OC pesticides

Snow and ice samples were collected from the Lomonosovfonna Ice Cap, Svalbard, to identify the historic inputs of organic industrial contaminants and pesticides in the European Arctic (Matthews, 2001). The upper 38 m of an ice core, representing approximately the past 70-80 years, were analyzed for OC pesticides, while shorter cores and pit samples were also analyzed for PCBs. Dating results are not complete, so only depth is available for trend evaluation so far. The ice core results show that

the maximum concentrations of all measured contaminants occur below the snow surface, indicating that inputs have declined in recent years (Figure 5-12). The contaminant with the highest concentration at any depth is α-HCH (12 600 pg/L) followed by γ-HCH (2780 pg/L), and *p,p'*-DDT (2710 pg/L) (Matthews, 2001). These results provide the first detailed picture of deposition of persistent chlorinated organics in the European Arctic. In the only other comparable study, from the Canadian Arctic, Franz *et al.* (1997) reported OC pesticides in snow layers dating from the late 1980s and early 1990s from the snow core on the Agassiz Ice Cap. The same layers were also analyzed for PCBs (Gregor *et al.*, 1995). Concentrations of all major OC pesticides in subsurface layers were about 10 fold lower than in the Lomonosovfonna core. Comparison of samples collected on the surface of the Agassiz Ice Cap with subsurface layers collected one to two years later and dating to the time of original collection at the surface, however, showed a 40% to more than 100% decrease following deposition. The greatest decrease was seen for the more volatile OCs, such as α-HCH and α-endosulfan. The loss is thought to be due to changes in surface area as the deposited snow undergoes metamorphosis, which revolatilizes the POPs (Wania, 1997).

The DDT results in the Svalbard study are unusual, both qualitatively and quantitatively. DDT, when manufactured, is 65%-85% *p,p'*-DDT, and the remainder is mainly *o,p'*-DDT with small amounts of other compounds, including *p,p'*-DDE and *p,p'*-DDD. In the environment, DDT normally degrades to either DDE (most common) or DDD. The amount of *p,p'*-DDT present relative to total DDT ranges from 62 to 90%, with an average of 76%. These numbers are very similar to those

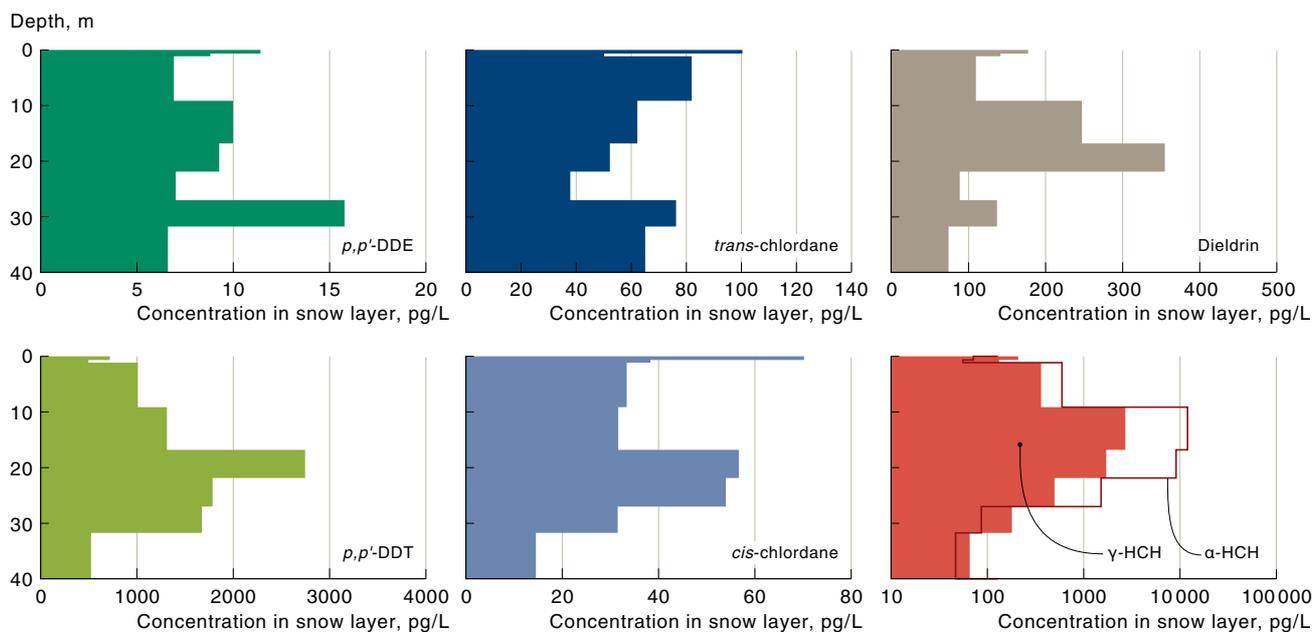


Figure 5-12. OC concentrations in snow cores collected on the Lomonosovfonna glacier in Svalbard (1999). Note: logarithmic scale on HCH graph.

found in the undecomposed technical product (Matthews, 2001). The high concentration and proportion of *p,p'*-DDT in the Lomonosovfonna ice core relative to both degradation products indicate that DDT was transported from its source to Svalbard without degrading, or that the much more volatile DDE and DDD evaporated from the snow surface following deposition. DDT use peaked before or during the 1970s in areas that are the closest source regions to Svalbard such as northwest Russia and Scandinavia (HELCOM, 2001). The proximity of Lomonosovfonna to population centers on Svalbard makes it more susceptible to accumulation of local contaminants. Evidence that sediments from an isolated lake near the coal-mining towns of Barentsburg and Longyearbyen had high PCBs and PAHs (Rose *et al.*, 2003; Section 4.3.2) lends support to this hypothesis.

Subsurface maxima of α - and γ -HCH were found at Lomonosovfonna, although the maxima were in more recent deposits than maxima for DDT isomers, *cis*-chlordane, and dieldrin. α - : γ -HCH ratios in deeper samples from Lomonosovfonna suggest some losses of α -HCH, but in more recent samples, the pattern is characteristic of observations in other parts of the world. Samples covering the last 20 years show that the ratio has been decreasing, which corresponds to the phasing-out of α -HCH-containing technical products and increasing use of lindane. Technical HCH, consisting of about 80% α -HCH and about 15% γ -HCH was the major form of HCH released into the environment prior to 1980 (Li *et al.*, 1998a). The HCH isomers were the predominant OCs measured in snow at Svalbard, which is somewhat unusual because they are also the most volatile. Their high volatility has led other snow investigators to suspect high amounts of evaporation of HCH isomers following deposition to the snow surface (Wania *et al.*, 1999d). If true, the original concentrations of these compounds at Svalbard would have been even greater. Lomonosovfonna concentrations near the surface are similar to lake and river water concentrations throughout much of the Arctic. The highest concentrations are similar to the Yenisey River in Russia in 1993, one of the

most contaminated Arctic rivers (de March *et al.*, 1998). Overall, these HCH trends are consistent with what has been observed elsewhere in the Arctic in air, where higher concentrations of α -HCH were seen in the 1980s (Li *et al.*, 1998a).

Dieldrin concentrations are much lower than α - and γ -HCH or DDT (Figure 5-12), the subsurface maxima coinciding with that of *p,p'*-DDT. The results suggest a steady decline in deposition of dieldrin at Svalbard, probably since the mid-1970s.

Total chlordane was present at similar concentrations to dieldrin, but did not show clear subsurface maxima. Chlordane has two major isomers, *cis*-chlordane and *trans*-chlordane. The latter is less stable, being subject to photolysis in the atmosphere and decomposition in sunlight. The depth profile of the *cis*- : *trans*-chlordane ratio was consistently less than 1, and thus did not indicate large-scale degradation of *trans*-chlordane.

5.1.3.2. PAHs

Masclat *et al.* (2000) reported a high-resolution historical profile of PAHs on particulate filtered from snow/ice cores collected in 1993 at Summit, Greenland. A strong seasonal variation was observed, with the highest PAH concentrations in winter, except for retene (Figure 5-13, next page). Retene deposits in snow dated to spring/summer 1991, corresponded to intense fires in the boreal forests of Canada and Siberia. PAH deposition correlated strongly with black carbon showing the same seasonal variation. Black carbon has the same source as PAHs, from anthropogenic and natural combustion, and its high correlation with PAH suggests a common source region. Total PAHs in the snow particulate were not strongly correlated with sulfate, another indicator of combustion (e.g., coal burning). However, maxima of fluoranthene and pyrene concentrations coincided with elevated sulfate in four strata indicating common sources. Since only the insoluble phase of the snow was analyzed for PAH, the lack of complete correspondence with sulfate is not surprising. Jaffrezo *et al.* (1994) found good

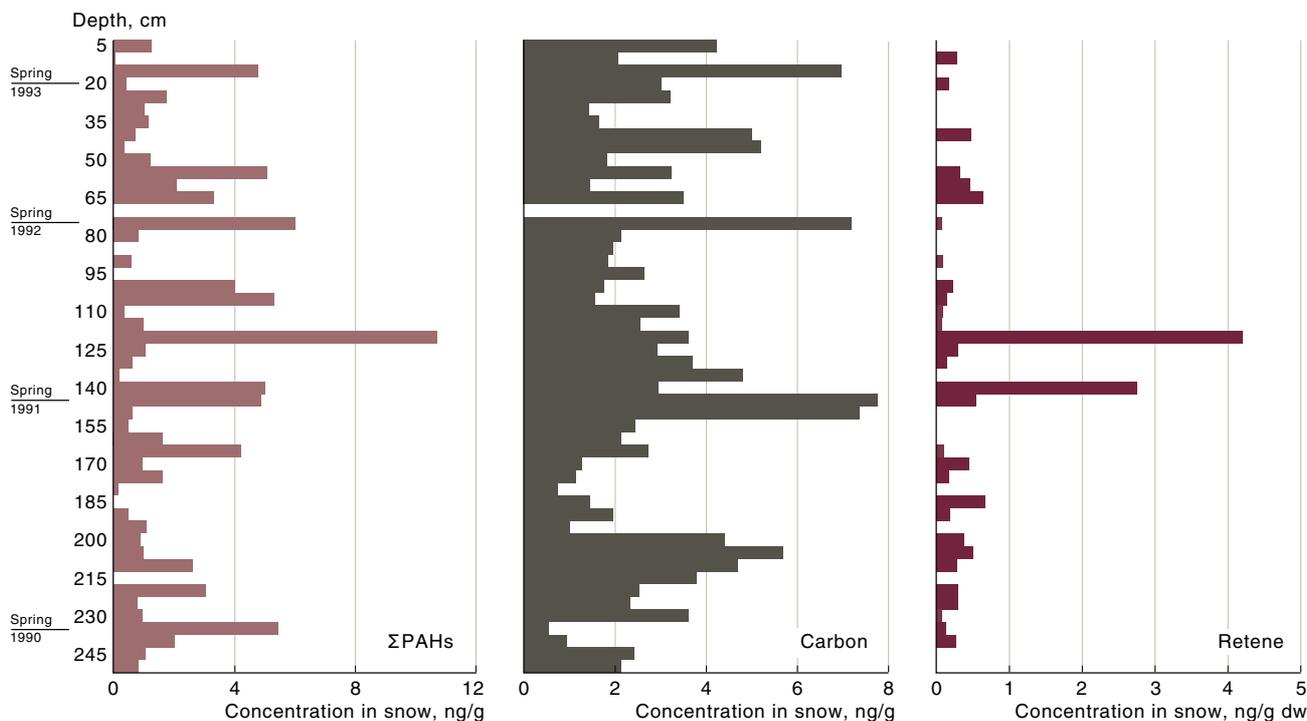


Figure 5-13. PAH concentrations in a snow core from Summit, Greenland, showing the relationship to black carbon and retene (an alkylated PAH generated in forest fires). Spring time each year is inferred from maximum deposits of calcium. Results adapted from Masclet *et al.* (2000).

correspondence between sulfate and Σ PAHs in a snow core from Summit that included the analysis of dissolved and particulate phases. These authors also noted post-depositional declines in concentrations of phenanthrene, fluoranthene, and B[a]P in the snow pack over a four-year period. In the case of B[a]P, possible degradation by OH radicals produced on the ice and snow surfaces was suggested as the main loss pathway. In the case of phenanthrene and fluoranthene, volatilization from snow as it undergoes metamorphosis may also occur (Jaffrezo *et al.*, 1994).

5.1.4. Conclusions on temporal trends in air and precipitation

A sufficiently large dataset now exists to examine temporal trends for a number of POPs in Arctic air. Unfortunately, the detailed analysis of the data, which requires adjustment for temperature for comparison among sites and with temperate latitude, has been conducted only for data from Alert. The trends appear to be similar at Ny-Ålesund, but further study is required.

Comparisons of trends in the Arctic with temporal trends at rural sites in the Great Lakes show that, after temperature adjustment, half-lives of most OC pesticides and PCBs are similar overall, considering the associated margin of error, although interesting differences have been observed. For example, the half-life of α -HCH at Alert is five times longer than at two sites in the Great Lakes. Outgassing of α -HCH from the Arctic Ocean will buffer the concentrations in the overlying atmosphere at Alert. This process could also explain the apparent lack of decline of other OCs with similar air-water fugacity ratios (e.g., HCB, lower chlorinated PCBs, endosulfan).

The estimated half-lives of tri- to heptachlorobiphenyl congeners at Alert were typically longer than those

from rural Great Lakes locations. This might be due to lower temperatures encountered in the Arctic, coupled with winter darkness, which will slow both biotic and abiotic degradation relative to temperate regions. In theory, global fractionation (Wania and Mackay, 1995), a process whereby chemicals may be latitudinally fractionated according to ambient temperature and physical-chemical properties, will have the effect of maintaining Arctic air concentrations, while levels in temperate regions are showing apparent reductions. In support of this, in northwest England at a site much closer to major urban sources in the U.K., a suite of tri- to heptachlorobiphenyl congeners have half-lives of 2-6 years, which is shorter than those at Alert. The high week-to-week variation of air concentrations at Alert, Ny-Ålesund, and other sites, and the lack of a strong relationship with temperature indicates that, for the Arctic in general, long-range transport is having a marked influence on atmospheric levels, accounting for the large degree of scatter in the temporal database. This uncertainty will probably be reduced with longer-term datasets.

The unique, long-term datasets for α -HCH, toxaphene, and chlordane demonstrate that the atmosphere plays a significant role in the global distribution of both compounds and responds rapidly to changes in emissions. Atmospheric long-range transport provides rapid dispersion of these OC pesticides from their areas of emission (primarily China in the case of HCH, and southern U.S. in the case of toxaphene and chlordane) into the Arctic. The results further imply that a reasonable estimate of historical air concentrations of HCH isomers and toxaphene in the western Canadian Arctic, and possibly in the Arctic as a whole, can be inferred from the global emission data, or emission data for the major-use area.

The historical trends of OC pesticides in a snow core from Svalbard provide the first insights into the histori-

cal inputs to the European Arctic. Unfortunately, direct comparisons with previous snow core work on the Agassiz Ice Cap on Ellesmere Island (de March *et al.*, 1998; Macdonald *et al.*, 2000) are not possible because that core was analyzed only for PCBs (Gregor *et al.*, 1995) and PAHs (Peters *et al.*, 1995). The results for DDT at Svalbard suggest a local source, possibly the mining towns within 50 km of the glacier. The dates of deposition are also unknown at present. However, maximum deposition of DDT around 1970 suggests that maximum deposition of HCH isomers and dieldrin was reached post-1970 (Matthews, 2001). For HCH, this is consistent with use in the northern hemisphere which peaked in the 1980s based on concentrations in Arctic air (Macdonald *et al.*, 2000) and global use patterns (Li *et al.*, 1998a; Li, 1999b). In the case of PAHs in snow cores at Summit, Greenland, and the Agassiz Ice Cap, there is a clear linkage to combustion sources in the mid-latitudes of North America and Eurasia.

Overall, the results for the depositional profiles of the OC pesticides and PAHs in glacial cores appear to have better temporal resolution than Arctic sediment cores, reflecting high annual deposition rates compared to most Arctic lakes or marine sediments. The post-depositional volatilization of semi-volatile organics such as HCH, HCB, and phenanthrene from snow as its density increases and its surface area decreases, may, however, confound the interpretation of temporal trends. Further study is needed to understand the basic processes governing the fate of semi-volatile organics in snow.

5.2. Terrestrial environment

A number of temporal-trend datasets for the terrestrial Arctic were reported in the previous AMAP POPs assessment (de March *et al.*, 1998), but none of these programs have been continued. This is likely due to the low levels found in this environment. Consistent with studies in the freshwater and marine systems, levels of OCs were found to be decreasing in the terrestrial environment prior to 1996.

One temporal-trend dataset that was not reported in the previous AMAP assessment examined OCs in Alaskan peregrine falcons from 1979 to 1995 (Ambrose *et al.*, 2000). Dieldrin, *p,p'*-DDE, heptachlor epoxide, oxychlorane, and total Aroclor PCBs were consistently detected and measured, and were tested statistically for relationships with time and productivity. Mirex was only measured from 1988 to 1995, but was detected in all samples. HCB, *p,p'*-DDD, *p,p'*-DDT, β -HCH, and *trans*-nonachlor were detected in >50% of samples, but were not tested for relationships with time or productivity because they were not consistently analyzed. α -HCH, γ -HCH, *cis*-chlordane, *trans*-chlordane, *o,p'*-DDD, *o,p'*-DDE, *o,p'*-DDT, endosulfan II, and endrin were detected in <50% of samples, and because of the large proportion of data below detection limits, none were tested for time or productivity relationships. The five persistent OC contaminants that were consistently measured (dieldrin, *p,p'*-DDE, heptachlor epoxide, oxychlorane, total PCBs) declined significantly from 1979 to 1995, but the trend was weaker for total Aroclor PCBs than other contaminants.

5.3. Freshwater environment

5.3.1. Water and sediments

Russian river water and sediment

Monitoring data on OC pesticides in river water from the 1980s and early to mid-1990s have recently been published (Gordeev and Tsirkunov, 1998; Petrosyan *et al.*, 1998; Alexeeva *et al.*, 2001; Zhulidov *et al.*, 2002). This permits a historical perspective of pesticide loadings to Russian northern seas. Gordeev and Tsirkunov (1998) summarized the estimated fluxes of Σ HCHs and Σ DDTs for 32 rivers in Russia including 11 flowing to the Arctic Ocean. To obtain fluxes, they used annual arithmetic mean concentrations, summarized by Petrosyan *et al.* (1998), and river discharges taking into account seasonal variability in flows. Alexeeva *et al.* (2001) used a similar approach to estimate fluxes for the same pesticides for the period of 1990 to 1996. They used monitoring data from the regional laboratories of ROSHYDROMET and thus, used data from the same pesticides monitoring program that Gordeev and Tsirkunov's (1998) study used. The combined results (Figure 5-14) show a general decline in loadings of HCH and DDT isomers over the period of 1981 to 1996, coinciding with the reduction in use of HCH in Russia following conversion to use of lindane, and the complete cessation of agricultural use of DDT in the 1970s.

Zhulidov *et al.* (2002) reported temporal trends of Σ DDTs (*p,p'*-DDT, DDE, and DDD) and Σ HCHs (γ - and α -isomers) in water and sediments from eight Russian Arctic rivers for the period of 1988 to 1994. OC levels in burbot liver were also determined from the same rivers (Section 5.3.4). DDT was not detected in any sediment, and DDE and DDD were only detected in sediments of three rivers. DDD was not detected in river water, and DDT and DDE were only present in North Dvina and Pechora River water. However, the detection limits for the methods used were relatively high in both

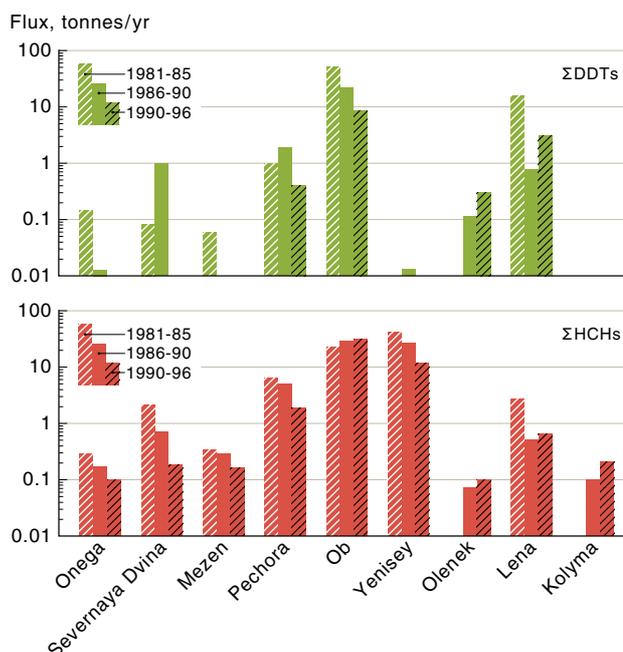


Figure 5-14. Temporal trends in fluxes of Σ DDTs and Σ HCHs in major rivers flowing in the Russian northern seas for the periods 1981-1985, 1986-1990, and 1990-1996 (from Gordeev and Tsirkunov (1998) and Alexeeva *et al.* (2001)).

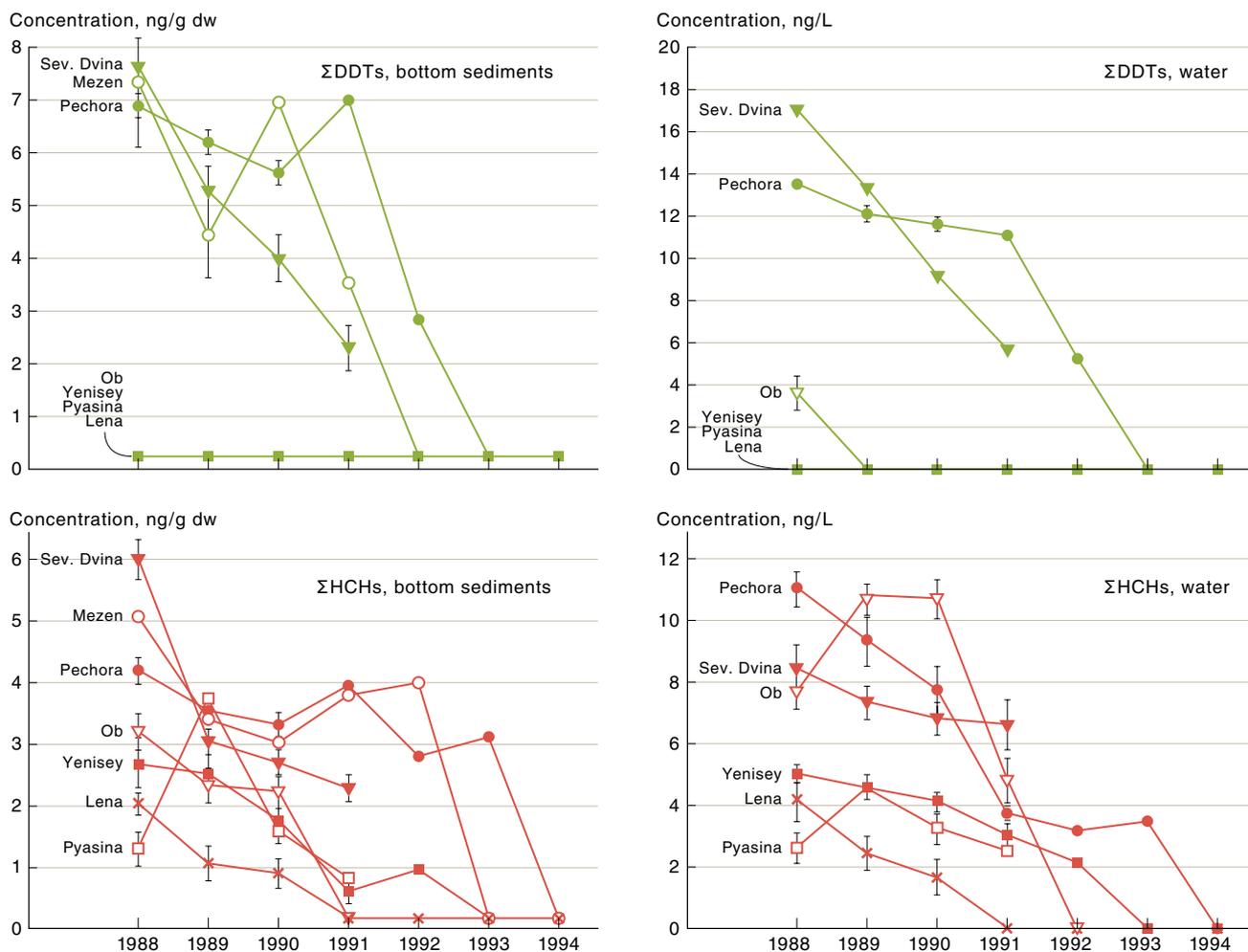


Figure 5-15. Temporal trends in concentrations of DDT and HCH isomers in water and sediments from major rivers flowing into the Russian northern seas for the periods 1988 to 1994 (Zhulidov *et al.*, 2002).

sediment and water. Both HCH isomers (α - and γ -) were detected in all river sediments except Kolyma River and in water from all rivers. Concentrations of both DDT and HCH declined significantly over the period of 1988 to 1992 and were near detection limits for all chemicals in most rivers by 1992 (Figure 5-15).

Dated sediment cores from Canadian Arctic lakes

Outside of the Arctic, analysis of dated sediment cores has been used to infer the depositional history of POPs in the Great Lakes region (Jeremiason *et al.*, 1994; Wong *et al.*, 1995; Pearson *et al.*, 1998) and in European alpine lakes (Fernandez *et al.*, 1999; 2000; Grimalt *et al.*, 2001). The previous AMAP POPs assessment included results for PCBs and PCDD/Fs in Arctic sediment cores from Alaska, Canada, and Finland. These cores all showed a later onset of PCB deposition than that observed in most lakes closer to sources, as well as maximum inputs near or at the surface, indicating continuing inputs from atmospheric deposition. Further analysis of the data from Canadian lakes showed that lower chlorinated PCBs predominated in High Arctic cores, while sediments from temperate lakes had higher proportions of Hx-, Hp- and OcCBs (Muir *et al.*, 1996a). The sediment records from Arctic lakes, therefore, can provide information on temporal trends of deposition of these hydrophobic contaminants in the Arctic. However, interpretation of sediment records can be complicated by

'direct' input from non-atmospheric sources, and dynamic lake processes including bioturbation, sediment focusing, and re-suspension. Factors unique to Arctic lakes, such as long periods of ice cover and low sedimentation rates, may limit inputs to bottom sediments and make them a less significant reservoir for hydrophobic organics than temperate lakes (Macdonald *et al.*, 2000).

Additional sediment cores collected in the Canadian Arctic in the mid- to late 1990s have been analyzed for POPs since the previous AMAP assessment (Lockhart, 1997; Lockhart *et al.*, 1997; Macdonald *et al.*, 2000; Stern and Evans 2003; Muir *et al.*, 2002b; Rose *et al.*, 2000). Undated cores were also analyzed from Bjørnøya (Kallenborn, 2002b). However, there were no cores reported from other circumpolar countries.

A series of cores in the Yukon (western Canadian Arctic) were analyzed for PCBs and OC pesticides (Rawn *et al.*, 2001). DDT was found to be the most prominent OC in the sediment profiles of most of the lakes. Maximum Σ DDT levels (0.86 ng/g dw to 21.4 ng/g dw) were observed in sediment slices dated to the 1950s from lakes (Lake Laberge and Fox Lake) near populated areas, (Figure 5-16), as well as in Watson Lake (not shown). In contrast, in more remote lakes (Hanson and Lindeman Lakes), maximum Σ DDT concentrations were observed in sediments dated to the 1980s and 1990s, similar to other Arctic lakes (Muir *et al.*, 1995a). The sediment profiles from lakes situated near populated areas and

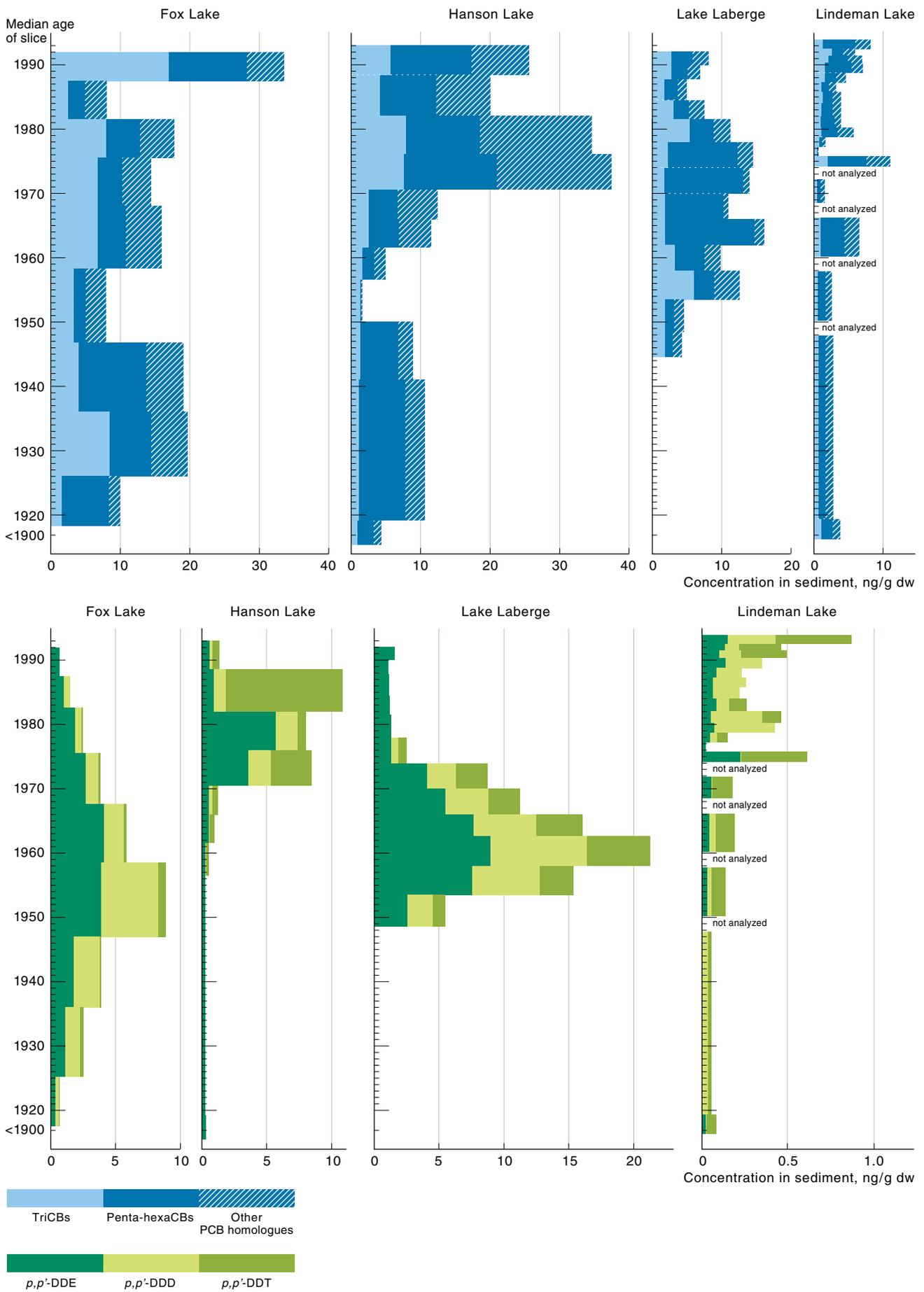


Figure 5-16. Historical profiles of PCBs and DDT-related compounds in four lakes within the Yukon River watershed (Rawn *et al.*, 2001), two remote lakes (Hanson, Lindeman) and two lakes nearer to populated areas (Fox, Laberge).

along the Alaska Highway in the Yukon indicate PCB and DDT contamination has occurred mainly from local usage and waste disposal, rather than long-range transport and deposition. The onset of appearance and maximum concentrations and fluxes of Σ PCBs and Σ DDTs are similar to cores from southern Canada, and coincide well with the use profile of these chemicals in North America in general, and with the known history of use in the Yukon as well. The historical profile of Σ PCBs and Σ DDTs in most of these Yukon sediments is quite different from sediments in the High Arctic, where delayed onset has been found (Muir *et al.*, 1996a). Even in the remote, glacier-fed Lindeman Lake, the lower chlorinated PCB congeners made relatively small contributions to Σ PCBs. This may be due to volatilization losses of the lower chlorinated congeners from melting snow and flowing glacial streams (Macdonald *et al.*, 1999; Blais *et al.*, 2001). The results suggest that glacial runoff is a significant source of OCs to small high-elevation lakes (Lindeman Lake) but not to larger lakes within the Yukon River drainage basin which are also affected by glacial sources (Lake Laberge, Kusawa Lake).

Historical deposition of toxaphene in five Yukon lakes is shown in Figure 5-17. Elevated toxaphene levels had been found in fish tissues from several of the large lakes in the Yukon River Basin system (Kidd *et al.*, 1993; 1995), and thus, the source of toxaphene was of interest. Sediment core results confirm that the source is mainly atmospheric rather than local. The exception is Hanson Lake which was treated with toxaphene in 1963 (Walker *et al.*, 1973). The toxaphene congeners in this lake consist almost entirely of a hexa- (B6-923) and heptachlorobornane (B7-1001) (these have no Parlar numbers). These same two congeners were also predominant in the sediment of two toxaphene-treated

lakes located in Alberta, Canada (Miskimmin *et al.*, 1995; Stern *et al.*, 1996), but not in remote lakes exposed only to atmospheric sources (Muir *et al.*, 1999a; Rose *et al.*, 2001). B6-923 and B7-1001 are formed via anaerobic reductive dechlorination of other, less stable, chlorobornanes present in the technical mixture but not generally in air (Vetter *et al.*, 1999). The toxaphene profile in Watson Lake (Figure 5-17) is not entirely consistent with what would be expected based solely on atmospheric deposition (i.e. peak levels occurring in the early to mid-1970s). The higher subsurface levels of toxaphene congeners B6-923 and B7-1001 (Stern and Evans, 2003) and the overlap of the toxaphene and Σ DDT historical concentration profiles, suggest that toxaphene usage in the Watson Lake area occurred prior to the banning of DDT, possibly for use as a fish toxin or as an additional active ingredient in the insecticidal DDT mixtures.

A laminated core from a lake on Devon Island (Nunavut) has been analyzed for a wide array of OC compounds (Figure 5-18). The laminations are due to annual layers of sediment, with differing color or texture. These form detectable laminations that can be counted. This is the first laminated core analyzed for POPs in the Arctic and provides an unusual degree of temporal resolution compared to most other cores from the High Arctic. Σ DDT concentrations peaked between the mid-1950s and early 1970s. An increase in toxaphene was first observed in the early 1970s, reaching a maximum in the 1980s. These results are consistent with the known historical usage of DDT and toxaphene in North America (Voldner and Li, 1995; Li *et al.*, 2001b).

Concentration profiles for total PCDD/Fs in a second sediment core from Lake DV09 on Devon Island, normalized to organic carbon, are also shown in Figure 5-18 (Stern and Evans, 2003). PCDF levels start to in-

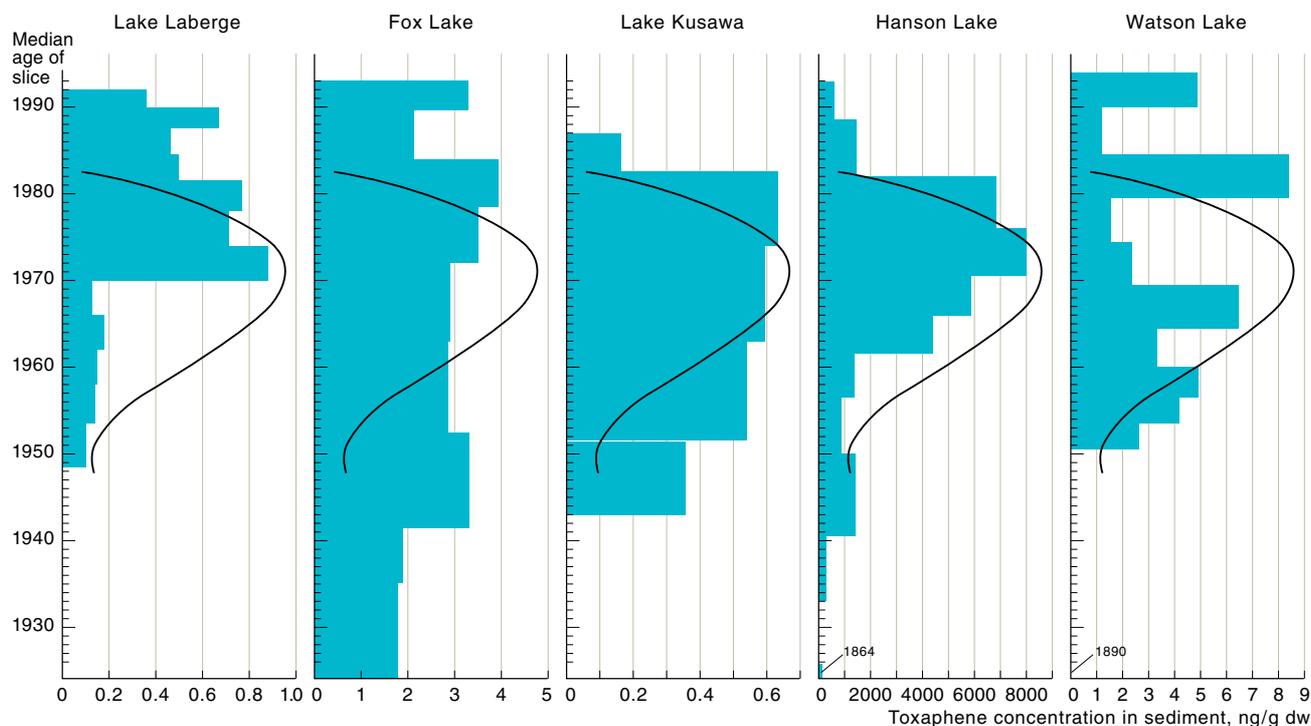


Figure 5-17. Concentration profiles of toxaphene in sediment cores from five Yukon lakes. Elevated concentrations in Hanson Lake are the result of application of toxaphene to this lake in 1963. The curves correspond to the atmospheric input functions for toxaphene derived by Rapaport and Eisenreich (1988) from peat cores.

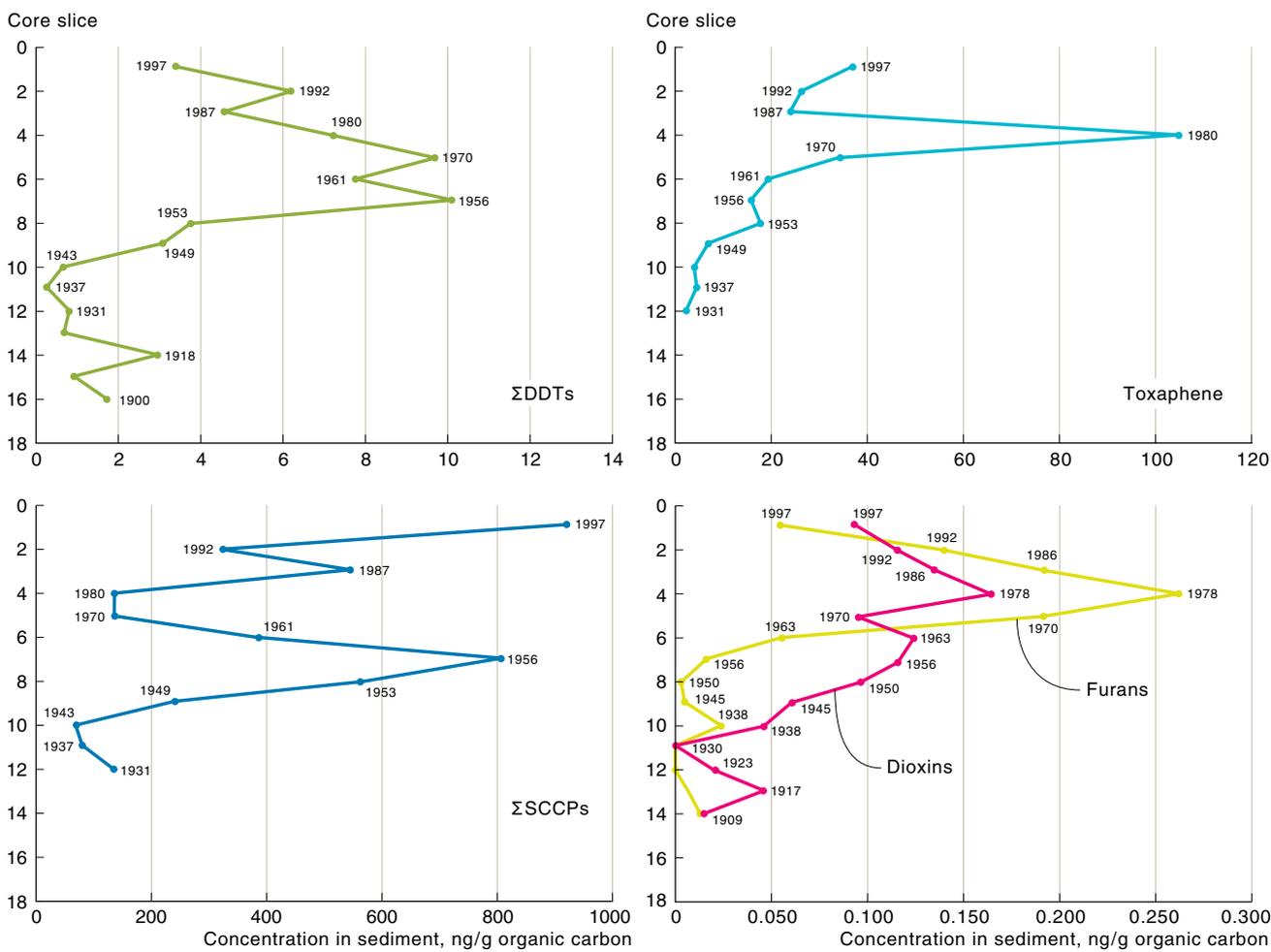


Figure 5-18. Concentration profiles of DDT, toxaphene, SCCPs, and PCDD/Fs in dated, laminated cores from Lake DV09 on Devon Island, Nunavut, Canada. Concentrations are in ng/g organic carbon.

crease in the early 1950s, peak at 0.27 ng/g organic carbon in 1978, and are dominated by the TCDF homologue group, in particular the 1,2,4,8-TCDF congener. PCDD levels start to increase about ten years earlier but also peak in 1978. Between 1938 and 1963, sediment core slices were dominated by octachlorinated dibenzo-p-dioxin (OCDD) ($64 \pm 9\%$). This homologue profile is consistent with a signature resulting from usage of pentachlorophenol as a wood preservative. OCDD is the major impurity in the PCP technical mixtures and can also be formed by photolytic degradation of PCP (Crosby *et al.*, 1981). From 1970 to 1992, the PCDD/F profiles are indicative of signatures arising from combustion of coal and wood (Kjeller *et al.*, 1996).

The DV09 core was also analyzed for SCCPs (Figure 5-18). Maximum concentrations occur in the surface sediment and in the core slice dated to 1956. Maximum usage of SCCPs occurred much later, probably between 1978 and 1985 (Muir *et al.*, 2000a), and thus, the historical profile in this core is not consistent with historical usage or historical profiles in other lakes (Tomy *et al.*, 1999). Shorter carbon chain length and lower chlorinated C_{10} and C_{11} formula groups become more predominant downward in the core, suggesting microbial degradation of the longer chain, more highly chlorinated compounds, over time, and/or that the earlier emissions had higher proportions of more volatile SCCPs.

Sediment cores from lakes on Bjørnøya

Sediment cores were taken from two small lakes (Ellasjøen and Øyangen) on Bjørnøya, approximately half way between Norway and Svalbard, in 1996 for OC analysis as part of a larger study (see Section 4.3.5). ΣPCB_7 concentrations decreased downward in the sediment to 0.5 and 0.4 ng/g dw at 13-15 cm in Ellasjøen and Øyangen, respectively (Figure 5-19). In Ellasjøen, $\Sigma DDTs$ was 6.9 ng/g dw in surface sediment, of which *p,p'*-DDE comprised about 90%. In Øyangen, the corre-

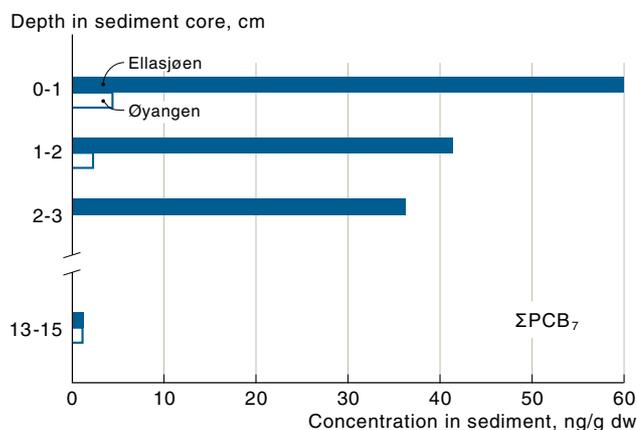


Figure 5-19. ΣPCB_7 concentrations in sediment cores sampled from the lakes Ellasjøen and Øyangen on Bjørnøya in July, 1996 (Evenset *et al.*, 2002).

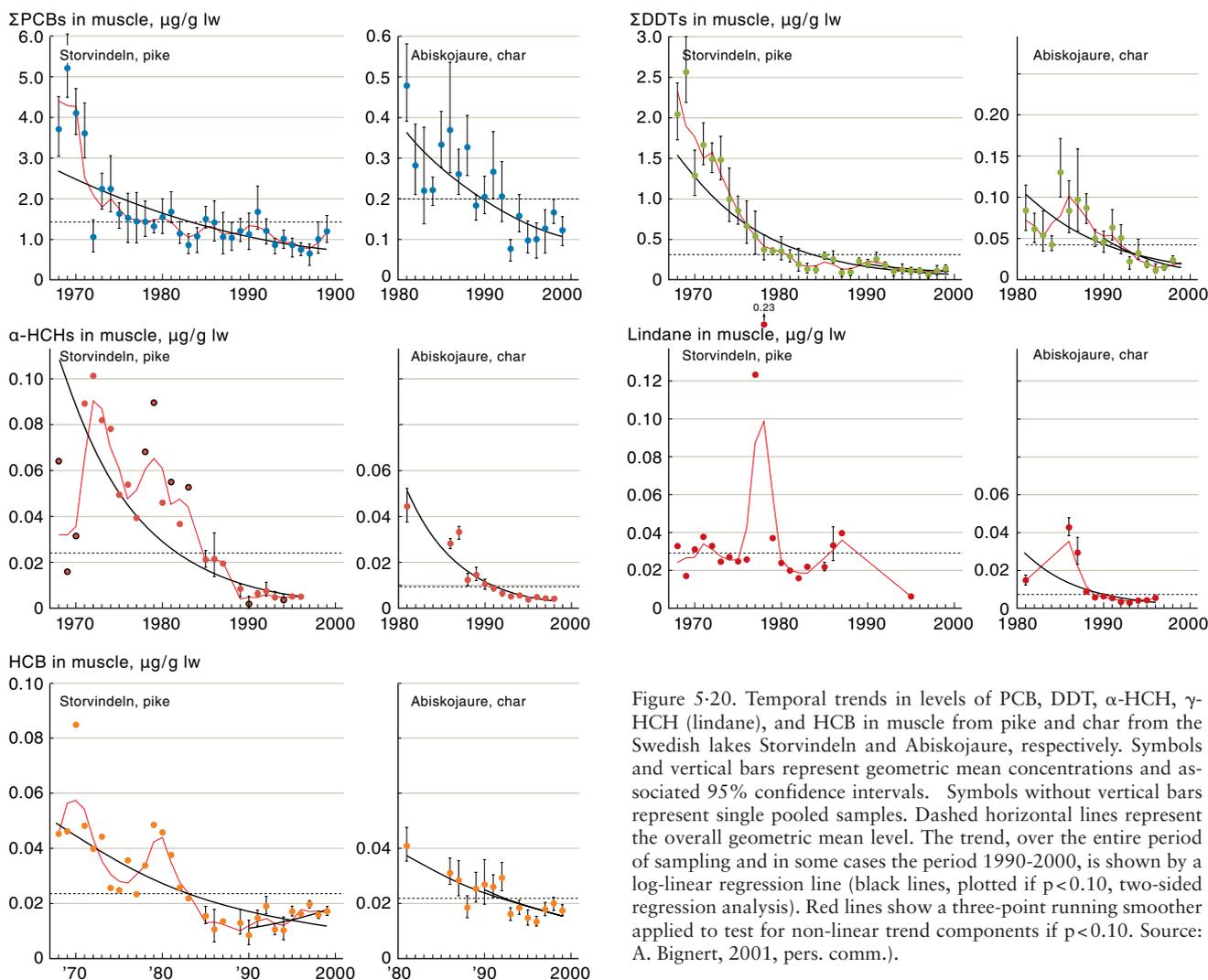


Figure 5-20. Temporal trends in levels of PCB, DDT, α -HCH, γ -HCH (lindane), and HCB in muscle from pike and char from the Swedish lakes Storvindeln and Abiskojaure, respectively. Symbols and vertical bars represent geometric mean concentrations and associated 95% confidence intervals. Symbols without vertical bars represent single pooled samples. Dashed horizontal lines represent the overall geometric mean level. The trend, over the entire period of sampling and in some cases the period 1990-2000, is shown by a log-linear regression line (black lines, plotted if $p < 0.10$, two-sided regression analysis). Red lines show a three-point running smoother applied to test for non-linear trend components if $p < 0.10$. Source: A. Bignert, 2001, pers. comm.).

sponding numbers were 0.8 ng/g dw and 63%, respectively. The concentrations at 13-15 cm were 0.05 ng/g dw in Ellasjøen and 0.2 ng/g dw in Øyangen. These results imply that loadings of PCBs and DDT have been increasing in these systems, which is not consistent with other temporal trends in the Arctic. The sediment slices were not dated, however, and therefore, caution is needed regarding these trends.

5.3.2. Temporal trends in fish in northern Scandinavia

In 1967, a Swedish program was initiated to monitor PCB, DDT, HCB, and HCH levels in fish from areas that had little or no known point sources of pollution (Olsson and Reutergerdth, 1986; Olsson and Bignert, 1997). Muscle samples from 20 northern pike have been collected every year since 1967 from Lake Storvindeln, a forest lake near the Swedish Alps occupying an area of 55 km². Beginning in 1980, muscle samples from 20 Arctic char have been collected from the lake Abiskojaure (Åbeskojåvre), 200 km north of the Arctic Circle. Efforts have been made to collect specimens that are of similar sex, age, size, and in the same sampling season. This program has yielded an unparalleled temporal-trend dataset for OCs in the Arctic and subarctic.

As was reported in the previous AMAP POPs assessment (de March *et al.*, 1998), levels of OCs in Swedish

freshwater fish have declined significantly since the late 1960s into the 1990s (Figure 5-20 and Table 5-2). However, the rates of decline have slowed in the 1990s, and no significant decline has been observed for the past ten years. The concentrations of Σ PCBs and Σ DDTs have been decreasing at a rate of approximately 3-7% and 10% per year, respectively, in all investigated time series (i.e. both southern and northern Sweden and in both species of fish). Since the monitoring began in 1967/68 for pike and 1981 for Arctic char, the temporal trend is long enough to be able to detect a change of this magnitude. For the last ten years, the decreasing trends in PCBs seem to have slowed in the northern parts of Sweden, as no significant decreasing trends are found for these years (Table 5-2). For DDT, over the past ten years, the decreasing trends have leveled off in the southern parts of Sweden, but continued at approximately the same annual rate (8-14%, significant decrease) in the northern parts.

HCH levels have decreased rapidly during the studied time period, more than 10% annually, following the bans and restricted use of technical HCH and lindane in countries neighboring Sweden. The concentrations in Swedish freshwater biota are now below or close to the detection limit (during recent years all samples have been below). A significant decreasing trend is also found for the last ten years in the northern part of Sweden. The high peak for lindane in pike from Lake Storvindeln dur-

ing 1977-1978 is, as yet, unexplained. HCB concentrations have decreased at a rate of approximately 5% per year, but northern pike have shown a nearly significant ($p < 0.1$) increasing trend over the past ten years.

The comprehensive nature of this dataset, comprised of many samples and time points covering a long time period, provides an invaluable tool in assessing the time trends of OCs in the European Arctic. Olsson and Bignert (1997) found that the annual rate and the onset of the decline (1971-1972) in concentrations of DDT compounds did not differ between the Arctic and other remote areas of northern Sweden, or between the southern parts of the Baltic Sea and lakes in the southern part of the Swedish mainland. The results of this program have demonstrated that the banning and reduction of use of

Table 5-2. Mean annual rate of change (%) in concentrations in pike and Arctic char in two lakes in northern Sweden.

OC	Pike Location: Storvindeln		Arctic char Abiskojaure	
	Annual change (%) 1967-1999	Annual change (%) 1990-1999	Annual change (%) 1980-1999	Annual change (%) 1990-1999
ΣDDT	-10	-8.3	-9.9	-14
ΣPCB	-4.1	-4.1	-6.7	-6.0
α-HCH	-11	-10	-17	
γ-HCH	-3.4		-15	
HCB	-4.8	5.4	-5.0	-5.5

OCs in much of the world has resulted in significant declines in Arctic biota. However, in recent years this reduction has slowed, suggesting that residual sources of OCs are likely to continue to contaminate Arctic biota for some time to come.

5.3.3. Temporal trends in freshwater fish in the North American Arctic

A number of temporal-trend datasets for OC pesticides and PCBs are now available for North American Arctic freshwater fish. These datasets are of much shorter length, and comprise fewer sample collections compared to the monitoring studies currently being carried out in Sweden (Section 5.3.2). Therefore, they lack the statistical power to make conclusive statements about temporal trends of OCs, but they do provide some insights. Most of these studies do not include data prior to 1990. A number of studies can be combined to provide better insight into temporal trends. No definitive pattern emerges, but in general, OC concentrations appear to be decreasing in freshwater fish.

Concentration in burbot liver, ng/g ww

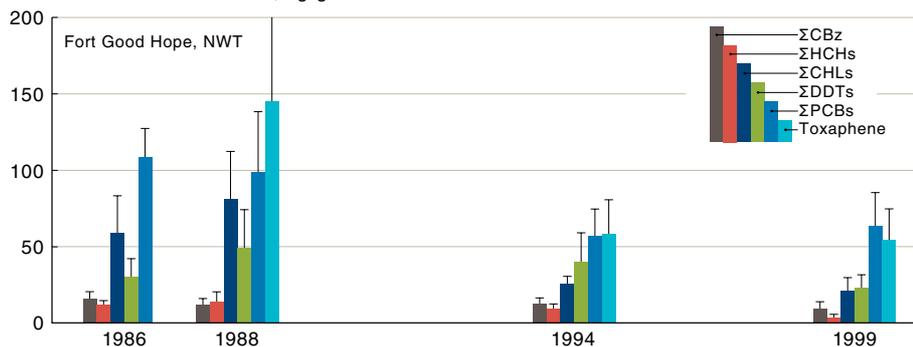


Figure 5-21. Trends in concentrations of major OC groups in liver of burbot at Fort Good Hope, NWT, Canada (1986-1999).

Fort Good Hope burbot

POPs were measured in the livers of burbot collected at Fort Good Hope, NWT, in 1988 and 1999 to examine temporal trends of OCs (Stern *et al.*, 2001a). Significant declines, 2.0- and 3.1-fold, were observed for both α- and γ-HCH over this 11-year time period. β-HCH concentrations were below the detection limit in all samples. Interestingly, the α-:γ-HCH ratio has increased from 4.5 to 6.9, which is opposite to what one might have expected based on the decreased usage of the technical mixture (α-HCH (60-70%), β-HCH (5-12%), and γ-HCH (10-15%)) and the corresponding increase in the usage of lindane in western Canada since the early 1990s (Waite *et al.*, 2001; Li and Bidleman, 2003). This is likely due to the ability of the burbot to more efficiently degrade the γ- compared with the α-isomer. The γ-isomer is generally found to be the most easily degraded in biota (Moisey *et al.*, 2001). ΣDDT concentrations did not change over this 11-year time interval; however, a 1.8-fold decline and a 2.2-fold increase in the concentration of *p,p'*-DDT and its metabolite, *p,p'*-DDE (not age adjusted), respectively, was observed. These changes translated into a significant increase in the *p,p'*-DDE:ΣDDT ratio from 0.39 to 0.60 and suggests 'old' rather than recent DDT inputs. Overall, a 1.7-fold decline in the lipid-adjusted mean concentrations of ΣCHLs was observed. Oxychlordane, the principal metabolite of *cis*- and *trans*-chlordane, and second only to *trans*-nonachlor as the most abundant chlordane-related residue in the Fort Good Hope burbot liver, did not change significantly over this 11-year period. The decreasing *trans*-:*cis*-CHL ratio suggests 'old' rather than recent chlordane inputs. ΣTrCB concentrations have increased 2.9 fold, while all other PCB homologue groups have either declined in concentration or did not change significantly. ΣPCB levels declined 1.3 fold. No significant differences were observed in levels of nPCBs 77, 81 or 169. CB126 levels decreased 1.8 fold. Toxaphene and dieldrin concentrations decreased by 1.7 and 1.5 fold, respectively.

Combining the OC data generated for burbot by Stern *et al.* (2001a) with previously published data for burbot at Fort Good Hope (Muir *et al.*, 1990a; Muir and Lockhart, 1996), which includes the years 1986, 1988, and 1994, provides a longer-term dataset (Figure 5-21). The results from 1988 reported by Stern *et al.* (2001a) are much lower than those reported previously (Muir *et al.*, 1990a) and are excluded. Slow declines in all of the major OC groups and toxaphene are observed in the Fort Good Hope burbot, although the rate of change varies with the chemical and the period concerned.

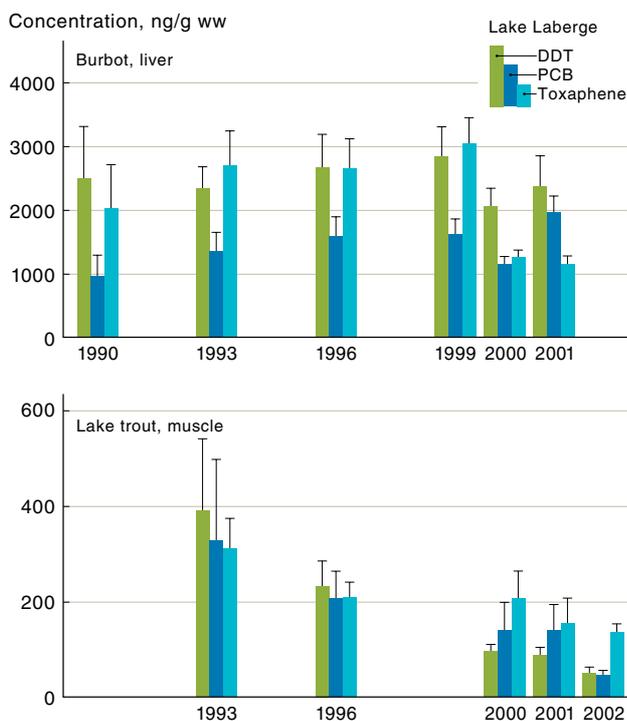


Figure 5-22. Concentrations (mean \pm 1 SD) of DDT, PCBs, and toxaphene in liver of burbot and muscle of lake trout from Lake Laberge, Yukon, Canada (1990-1999).

Lake Laberge lake trout and burbot

Combining data from a number of studies on OCs for burbot and lake trout from Lake Laberge also allows an examination of temporal trends spanning almost twelve years (Muir and Lockhart, 1992; Kidd *et al.*, 1998; Stern *et al.*, 2000; Palmer and Roach, 2001; Ryan *et al.*, 2003). Levels of DDT and toxaphene in lake trout from Lake Laberge declined between 1993 and 2002 by approximately 86% and 55%, respectively (Figure 5-22). Although PCB levels also appear to have declined considerably (approx. 85%) since 1993, the high variability in the samples over this period has resulted in a marginally insignificant statistical result ($p = 0.06$). Lipid levels in lake trout also show a significant decrease since 1993, which may account for some of the decrease in contaminants. This decline is in contrast to that observed in burbot collected in Lake Laberge, which showed no decline in DDT and PCB concentrations in liver between 1990 and 1999 (Figure 5-22). However, a significant decline in toxaphene concentrations in burbot (approx. 57%) was observed between 1993 and 2001 (Figure 5-22). Lake Laberge burbot liver displayed only a marginal decrease in fat content, which may be attributed to sampling variation (spring and summer fish). Studies on the Lake Laberge system continue (Stern *et al.*, 2001b).

Great Slave Lake burbot and lake trout

OC data spanning six years (1993-1999) in burbot and lake trout are also available for Great Slave Lake (Evans and Muir, 2000; 2001). No clear trend emerges for Σ PCBs in either species using lipid-normalized data, but Σ CHLs, Σ DDTs, and toxaphene do appear to be declining slowly (see Annex Table 7). These conclusions should be used with caution, because no effort has been made to correct for biological variables such as size or growth rate.

5.3.4. Temporal trends in fish in the Russian Arctic

Zhulidov *et al.* (2002) studied temporal trends of Σ DDTs and Σ HCHs in burbot livers collected from eight Russian north-flowing rivers from 1988 to 1994. Three DDT isomers (*p,p'*-DDT, DDE, and DDD) and two HCH isomers (γ and α) were measured. Levels in sediment and water were also assessed from the same rivers (Section 5.3.1). Σ DDTs (up to 70 ng/g ww) and Σ HCHs (up to 18 ng/g ww) both declined significantly in burbot liver between 1988 and 1994 (Figure 5-23) in parallel with declines in river water. The magnitude of the declines for Σ DDTs in burbot was up to 10 fold depending on the river system, and much more rapid than observed in burbot from the Mackenzie River (Canada) over the same period. This may reflect the response to the relatively recent cessation of DDT use within some of the watersheds, and in Russia in general (see Section 2.3.1). A 3- to 4-fold decline was seen for Σ HCHs in burbot from the eight Russian rivers, which is similar to the decline in HCHs in burbot in the Canadian Arctic.

5.4. Marine environment

5.4.1. Temporal trends of TBT effects in invertebrates

There is only a limited amount of information concerning temporal trends in TBT and its effects on subarctic and Arctic biota. The only available information on effects within the AMAP area is for imposex (i.e. the development of a penis and vas deferens in female marine snails). This occurs only within neogastropods (Mollusca) and has been examined in dogwhelks.

Svavarsson (2000) studied imposex in dogwhelks in southwestern, western, and northwestern Iceland in 1998, and compared the imposex levels to those reported from Iceland in 1992-1993 by Svavarsson and Skarphéðinsdóttir (1995). There has been a substantial decline in the level of imposex in dogwhelks in Icelandic waters since 1992/1993. At 24 of the 31 studied localities in Iceland, the Vas Deferens Sequence Index (VDSI) was lower in 1998 than in 1992-1993 (Svavarsson, 2000). At one site, the species was extinct, at five sites the index was higher in 1998 than previously, and at one site, no change had occurred. The most pronounced changes occurred near large harbors, such as Reykjavik and Hafnarfjörður harbors, where effects had been previously most pronounced. Changes were also evident in the Relative Penis Size Index (RPSI) at both small and large harbors.

Similar imposex declines have been seen in dogwhelks in Norway just south of the AMAP area (Følsvik *et al.*, 1999). No evident improvements have, however, occurred in northern Norway (Green *et al.*, 2002) and in the Faroe Islands (FEA, 2002). Among eight studied sites in northern Norway, the VDSI levels were high (greater than 3) at six of these stations. Some improvement may have occurred at two stations, but the situation was worse at one station (Green *et al.*, 2002). In the Faroe Islands, no improvements were seen at the studied sites, apart from possibly one site (Kirkjutangi) (FEA, 2002). The study sites were few, and most had been observed previously to have both high VDSI and RPSI in dogwhelk. The latter is high only where tissue levels of TBT are very high.

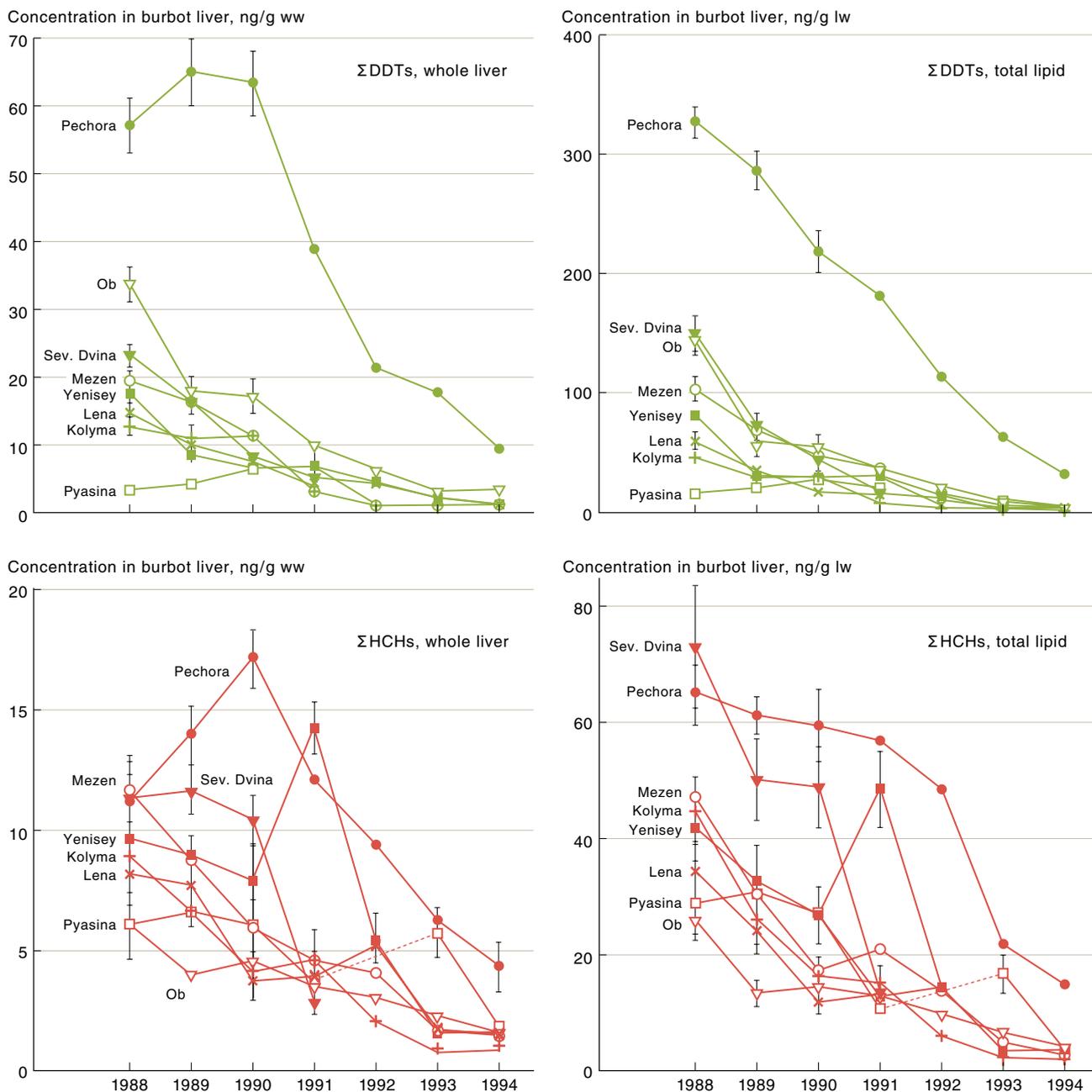


Figure 5-23. Temporal trends in concentrations of Σ DDTs and Σ HCHs in liver of burbot from major rivers flowing into the Russian northern seas for the periods 1988 to 1994 (Zhulidov *et al.*, 2002). Results are reported on a wet weight and lipid weight basis.

The declines in imposex seen in Iceland and southern Norway have been related to restrictions implemented in Iceland and Norway on the use of TBT on vessels smaller than 25 m (Følsvik *et al.*, 1999; Svavarsson, 2000). Svavarsson (2000) also related these changes to a change in marketing of paint in 1993 in Iceland. At that time, large Icelandic producers of anti-fouling paints started encouraging their customers to use non-TBT-based paints. Additionally, these improvements may partly be explained by developments in paint technology (see Bennett, 1996). The earlier paints were 'free association' paints, while later paints were copolymer paints with uniformly chemically bonded TBT with a constant, but minimal, release of TBT (Bennett, 1996; Svavarsson, 2000).

Studies of the occurrence of imposex in dogwhelks in the Faroe Islands were conducted in 1996 and in 2001

(FEA, 2002). Although the results do not indicate any major changes over the five years from the first to the second sampling period, and the occurrence of imposex in the Faroe Islands is still widespread, there are sites where the phenomenon is hardly seen.

5.4.2. Temporal trends in marine fish

Temporal-trend data for marine fish were not available for the previous AMAP POPs assessment (de March *et al.*, 1998). Two studies have however been reported for the current AMAP assessment.

The first of these is a temporal-trend study on the OC levels in liver of Atlantic cod and dab in the coastal waters of Iceland (Yngvadóttir and Halldórsdóttir, 2002). This study covers the period 1991 through 2000, with data missing only from 1993, and includes the major

Concentration in Atlantic cod liver, ng/g ww

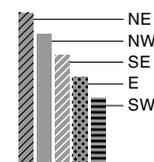
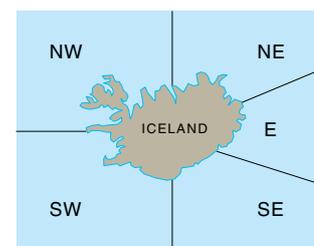
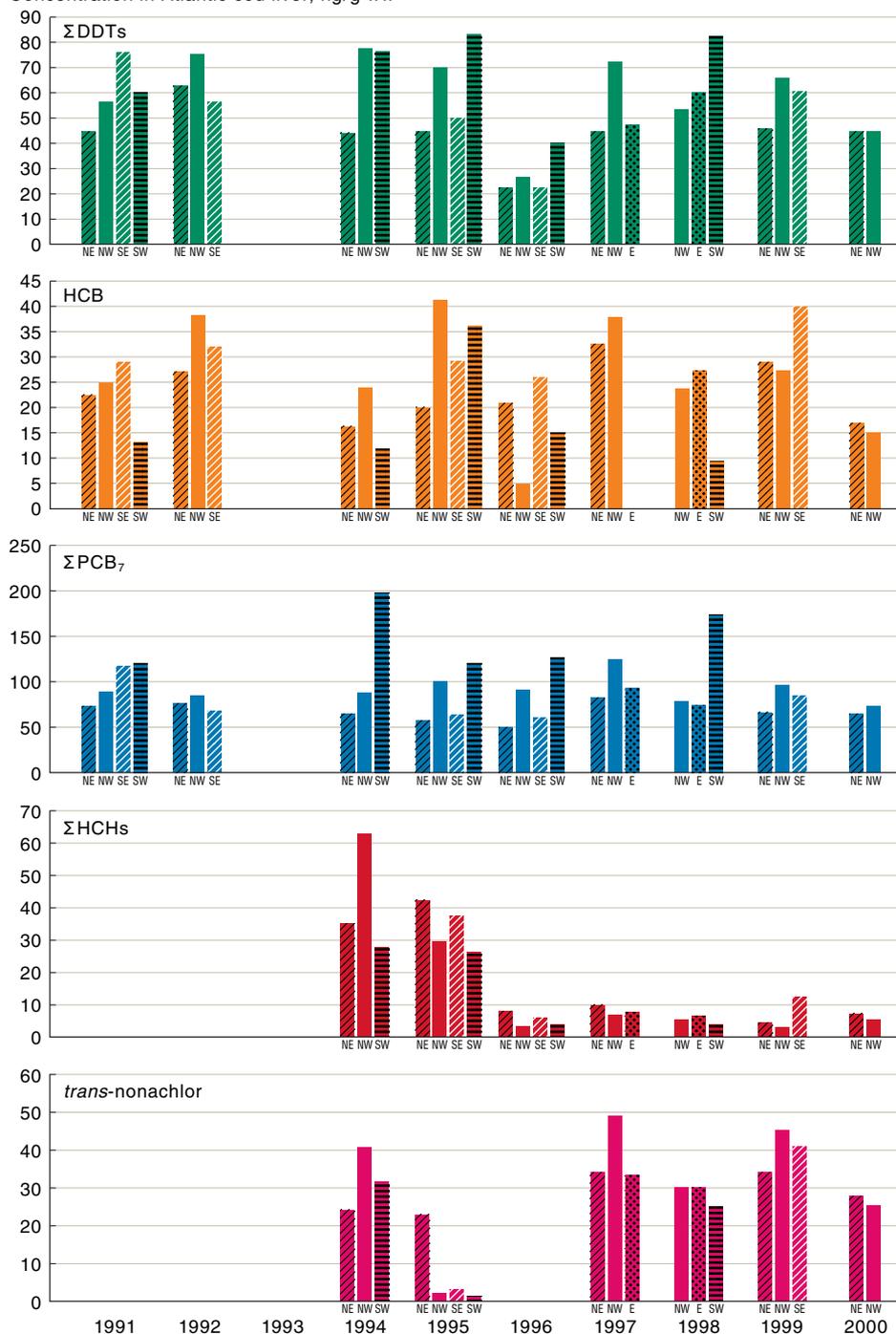


Figure 5-24. Average concentrations of OCs in the livers of Atlantic cod (length = 30-45 cm) in Icelandic waters, 1991-2000.

OC groups and toxaphene. The study involves collection of similar sized fish at a number of locations around the coast of Iceland. No significant temporal trends were found for any of the OC groups in either Atlantic cod or dab (Figures 5-24 and 5-25).

OCs have also been measured in cod (*Gadus morhua callarias*) liver from the Vestertana Fjord (N. Norway) from 1987 to 1998 (Sinkkonen and Paasivirta, 2000). Significant decreases in DDD, α -HCH, and γ -HCH were observed, but no trends were found for DDE, TCDF, PCBs, chlordanes, PCNs, HCB or polychlorinated diphenyl ethers (PCDEs). Hepta- and octaCDFs were found to increase from 1987 to 1994, and to increase steeply from 1994 to 1998, probably due to the use of a chlorophenol product as a wood preservative.

5.4.3. Temporal trends in seabirds

The previous AMAP POPs assessment detailed a number of studies on temporal trends of OCs in Arctic seabirds. These studies showed a downward trend in all 'legacy' OCs in seabirds around the circumpolar Arctic (de March *et al.*, 1998). There have been a number of new studies on OCs in Arctic seabirds, but few were designed to address temporal trends, and insufficient new data have been added to warrant reexamination of these time series in this report. Further, studies that were designed specifically to evaluate temporal trends however do provide results that yield firmer and more convincing conclusions about temporal trends.

One such study has monitored temporal trends of OCs in Arctic seabird eggs in the eastern Canadian Arc-

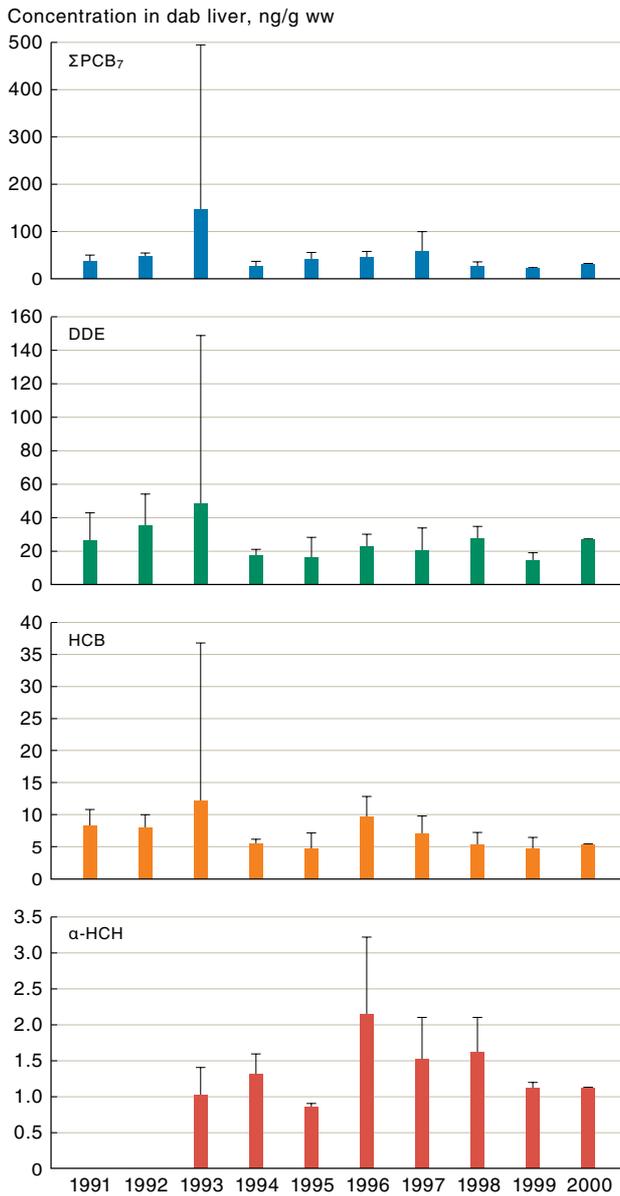


Figure 5-25. Average concentrations of OCs in the livers of dab in Icelandic waters, 1991-2000.

tic at Prince Leopold Island (Braune *et al.*, 2001a; 2001b). This study encompasses three species of seabirds and covers a long time period, 1975-1998 (Braune *et al.*, 2001a; 2001b). At the time of egg formation, OC compounds are transferred along with lipids to the eggs (Mineau *et al.*, 1984). Contaminant burden in the egg reflects residues assimilated over a long time period by the female and, particularly in migratory species, may integrate exposure from a number of different locations (Hebert, 1998; Monteiro *et al.*, 1999).

With the exception of ΣHCHs, OC compounds showed declines or, in some cases, no significant change in levels between 1975 and 1998. Levels of ΣPCBs and ΣDDTs (Figure 5-26) as well as ΣCBz decreased significantly in eggs of all three species, while ΣCHLs, dieldrin and mirex levels decreased in kittiwake eggs only. Kittiwakes, whose migration pattern would have historically brought them into closer contact with industrial sources of contaminants, such as PCBs, in the more temperate latitudes, showed the most dramatic declines through to 1998. The significant declines in

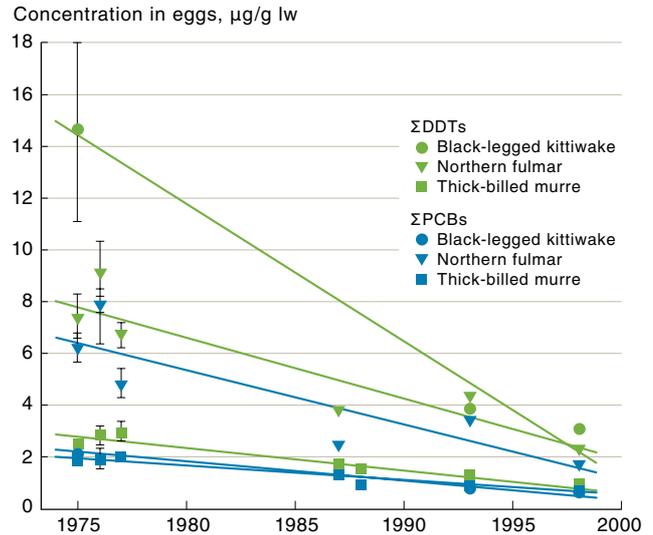


Figure 5-26. Concentrations of ΣDDTs and ΣPCBs in seabird eggs collected between 1975 and 1998 on Prince Leopold Island (Braune *et al.*, 2001a; 2001b).

concentrations of ΣPCBs and ΣDDTs in this study have also been observed in seabirds from other areas including the Baltic Sea (Olsson and Reutergårdh, 1986; Andersson *et al.*, 1988; Bignert *et al.*, 1995), the Barents Sea (Barrett *et al.*, 1996), and the Great Lakes (Hebert *et al.*, 1997). The only OC compound in this study for which a significant increase in concentrations was seen, was for ΣHCHs, particularly for β-HCH in murre (Figure 5-27) and fulmars. Stable-nitrogen isotope analyses ($\delta^{15}\text{N}$) indicated that the temporal trends

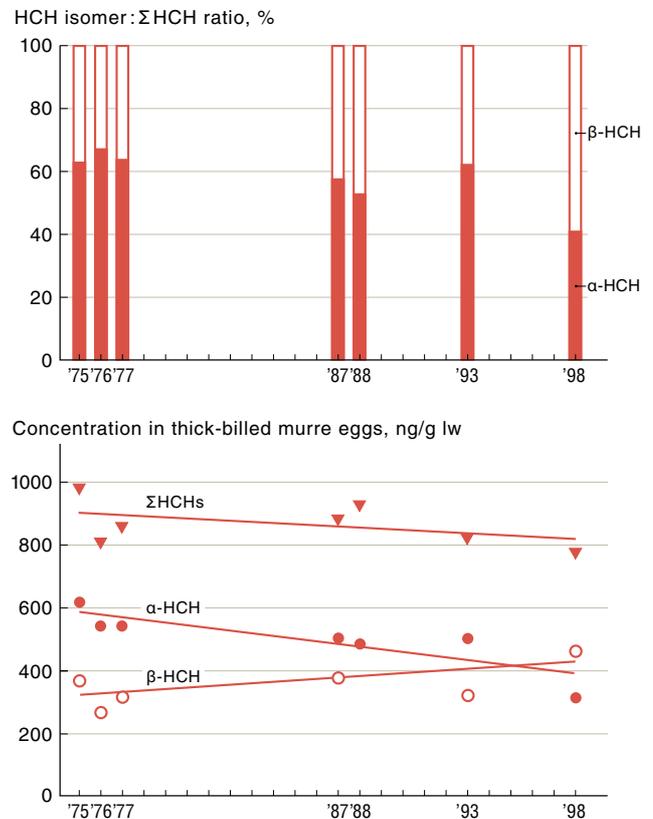


Figure 5-27. Temporal trends in relative proportions and concentrations of HCH isomers in thick-billed murre eggs. β-HCH shows a significant increase vs α- and γ-HCH (Braune *et al.*, 2001c). γ-HCH is <5% of ΣHCH.

observed in OC and trace metal concentrations in seabird eggs were not the result of shifts in trophic level over time (Braune *et al.*, 2001b). More likely, the trends reflect changes in contaminant deposition into the various marine environments that these birds occupy throughout the year, as well as the toxicokinetics of each contaminant as it is transported through the food chain.

Data from the late 1970s for two seabird colonies in the Bering Sea (common guillemot at St. George Island and thick-billed murres from Bogoslof Island) are available (Ohlendorf *et al.*, 1982) for comparison with data generated for 1999 and 2000 (Vander Pol *et al.*, 2002). There were significant ($p < 0.05$) declines in mean concentrations of *p,p'*-DDE, oxychlorane and heptachlor epoxide in the common guillemot eggs, and *p,p'*-DDE and *cis*-nonachlor in the thick-billed murre eggs. HCB and dieldrin did not appear to have declined over the 20-year period. PCB concentrations were not compared due to analytical differences between the two studies. These temporal trends are consistent with what has been seen in guillemot eggs in the Baltic Sea (Bignert *et al.*, 1995) and in murres from Prince Leopold Island (Braune *et al.*, 2001b).

PCDD/Fs and toxaphene have also been measured in Canadian Arctic seabirds over a period of almost 20 years (Braune *et al.*, 2000), providing a time-series dataset. Liver samples of thick-billed murres, northern fulmars and black-legged kittiwakes collected in 1975 and 1993 from Prince Leopold Island, as well as egg samples from 1993, were analyzed for PCDDs, PCDFs and non-*ortho* PCBs (nPCBs) (Annex Table 16). In the kittiwake liver samples, concentrations of total PCDDs, PCDFs and nPCBs decreased from 1975 to 1993. In fulmar liver samples, concentrations of total PCDDs and PCDFs decreased, and nPCBs increased from 1975 to 1993. In murre liver samples, concentrations of total PCDDs and PCDFs increased and nPCBs decreased from 1975 to 1993. CB126 was the predominant nPCB congener in all years and in all Arctic seabird samples analyzed. The nPCB fraction of the TEQ decreased, and the PCDF fraction increased from 1975 to 1993 in kittiwake and murre livers. In fulmars, the PCDFs constituted the dominant fraction in both 1975 and 1993 livers. Calculated TEQ values were highest in northern fulmars both in 1975 and 1993 (Annex Table 16). The highest estimated level of toxaphene was found in the pool of kittiwake eggs from 1993 (64 ng/g ww), and the second highest level was found in the 1993 pool of fulmar eggs (53 ng/g ww), suggesting increasing concentrations.

PBDEs were also analyzed in kittiwake, northern fulmar, and thick-billed murre liver samples from 1975 and 1993 from Prince Leopold Island (Braune *et al.*, 2001a). PBDEs were below detection limits in samples from 1975 while low ng/g concentrations were found in those from 1993. These preliminary data indicate that PBDEs are increasing in concentration in seabirds as they are in other marine biota in the Canadian Arctic.

PCDDs and PCDFs, including the nPCBs (CBs 77, 126, and 169), were analyzed in guillemot eggs sampled in 1989 in Greenland, Iceland, and in the Faroe Islands (Cederberg *et al.*, 1991). Guillemot eggs were collected from the Faroe Islands in 2000 ($n=10$) and

analyzed for PCDD/F (Mikkelsen, 2002). The results indicate a decrease in concentrations of PCDD/Fs, as TEQ decreased from 160 pg/g lw in 1989 to 66 pg/g lw in 2000.

5.4.4. Temporal trends in pinnipeds and cetaceans

The previous AMAP POPs assessment noted that there were relatively few long-term (multi-decade) studies of POPs in Arctic marine mammals (de March *et al.* 1998). This is still the case. However, additional studies conducted using archived samples or analysis of new samples from previously studied sampling locations have significantly increased the information available.

5.4.4.1. Pinnipeds

Ringed seals

Temporal trends of PCBs, Σ DDTs, β -HCH, and γ -HCH have been studied in ringed seals from the Canadian Arctic, sampled at the communities of Ausuittuq (Grise Fiord), Ikpiarjuk (Arctic Bay), and Holman (Addison and Smith, 1998; Muir *et al.*, 2001c). In the case of Holman, the results are part of a long-term study (Addison and Smith, 1998). Elsewhere, sampling locations were selected based on whether previous results were available (Muir *et al.*, 1988; Weis and Muir, 1997). At all three locations, results were available from the early 1970s to the late 1990s and 2000.

At all locations, only samples from female seals were selected for analysis in order to minimize age-related effects on OC levels (Addison and Smith, 1974). Mean concentrations ($\pm 95\%$ confidence limits; ng/g lw) in ringed seals for Σ DDTs, PCBs, Σ HCHs and Σ CHLs, along with ratios of recalcitrant members of each class for each location, are shown in Figure 5-28 a-c. Σ PCB₁₀ (sum of CBs 28, 31, 52, 101, 105, 118, 138, 153, 156, and 180) in seals from Ikpiarjuk declined significantly (2.4 fold) from 1975 to 2000 (Figure 5-28 a) and 1.5 fold at Ausuittuq, based on the comparison of arithmetic means. Σ PCB₁₀ was used for comparison with earlier data rather than all congeners. All previous results, including the samples from 1972-1975, were based on capillary gas chromatography with quantitation using authentic standards (Muir *et al.*, 1988; 1999b; Muir, 1996; Weis and Muir, 1997; Muir *et al.*, 1999b).

At Holman, Σ PCBs (based on conversion of Aroclor 1254 to a Σ PCB value consisting of 20 major congeners) was significantly higher in 1972 than in 1981 and declined significantly over the ten-year period from 1991 (510 ± 133 ng/g lw) to 2001 (335 ± 18 ng/g lw). The overall decline for PCBs is 5.5 fold. Ratios of CB153: Σ PCBs increased over the 25-year period at Ikpiarjuk and Ausuittuq and between 1991 and 2001 at Holman, reflecting the slower elimination of CB153 over time by the seals, compared to other PCBs.

Σ DDTs declined significantly in female ringed seals from all three sites, between the early/mid-1970s and late 1990s/2000. Σ DDTs exhibited the largest decline of any 'legacy' OC: 2.5 fold at Ausuittuq, 3.3 fold at Ikpiarjuk and 3.3 fold at Holman over the 25-30-year period. Significant increases in *p,p'*-DDE: Σ DDT ratios were also found at all three locations, reflecting the shift from fresh DDT to 'weathered' or degraded older sources.

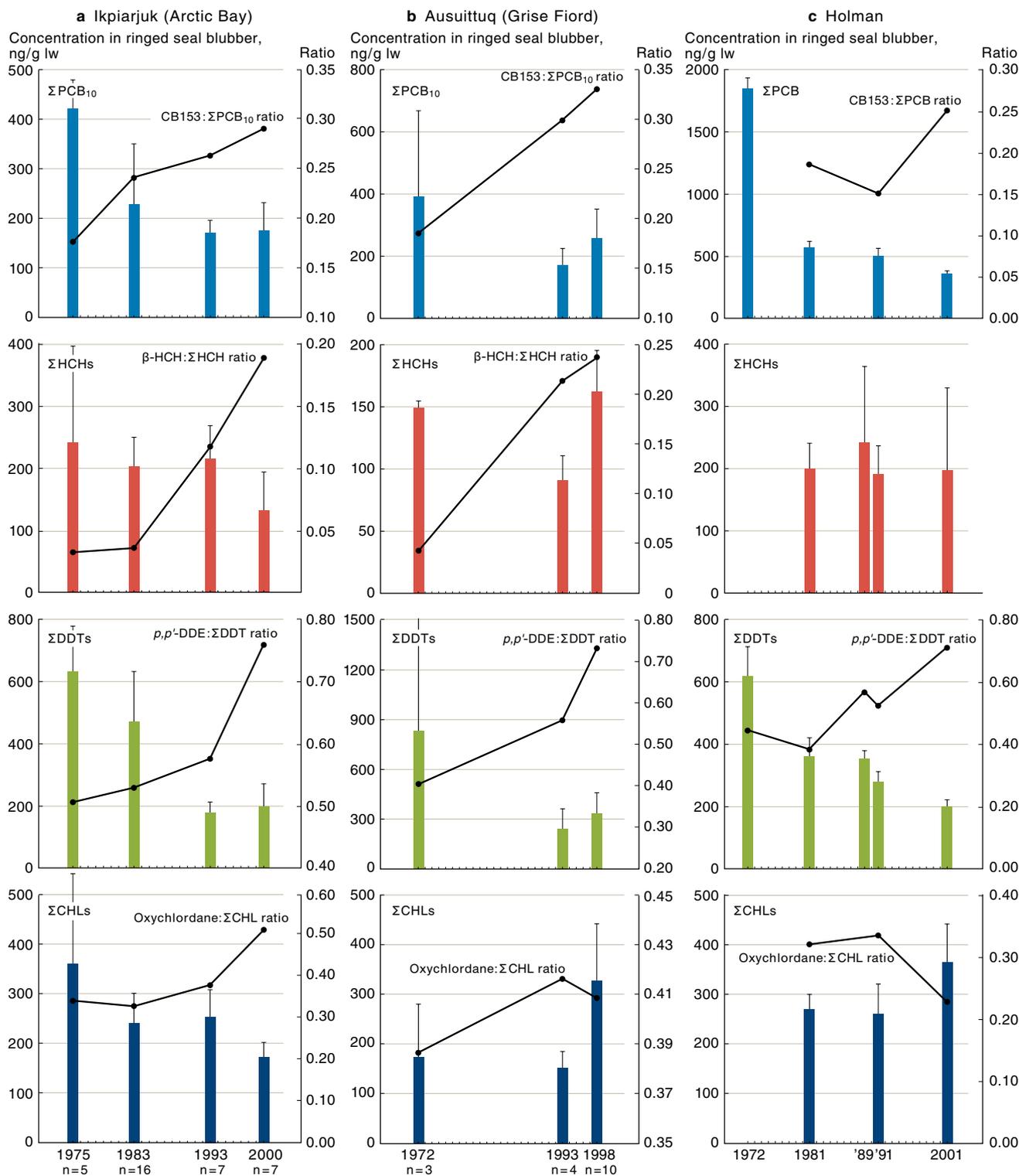


Figure 5-28. Temporal trends in concentrations and proportions of major OC components in blubber of female ringed seals from three sites in the Canadian Arctic Archipelago. Bars are arithmetic means and vertical lines are 95% confidence intervals. a) Ikpiarjuk (Arctic Bay); significant differences between 1975 and 1993 were found in the case of ΣPCB_{10} and ΣDDTs . b) Ausuittuq (Grise Fiord); no significant differences over time were found because of small sample sizes from 1972 and 1993. Nevertheless, the results suggest similar trends to those observed at Ikpiarjuk for concentrations and proportions of major components. c) Holman, NWT, in the western Canadian Arctic Archipelago. At Holman, ΣPCB includes all congeners analyzed.

ΣHCH concentrations showed no significant changes in concentrations from the 1970s (1981 in the case of Holman) to 2001. However, $\beta\text{-HCH}:\Sigma\text{HCH}$ ratios increased (3 fold at Ikpiarjuk). This shift in the composition of HCH, with higher proportions of $\beta\text{-HCH}$, has also been reported in seawater in the western Canadian Arctic during the 1980s and 1990s (Li *et al.*, 2002) (see Section 4.4.1.2).

ΣCHLs showed quite a different trend from ΣDDTs , with increasing concentrations at Holman and Ausuittuq, and a slow decline (2.1 fold over 25 years) at Ikpiarjuk. Proportions of oxychlordane, a recalcitrant metabolite of chlordane in mammals, increased at all three locations.

Ikonomou *et al.* (2002) examined temporal trends of non- and mono-*ortho* PCB and PCDD/F concentrations

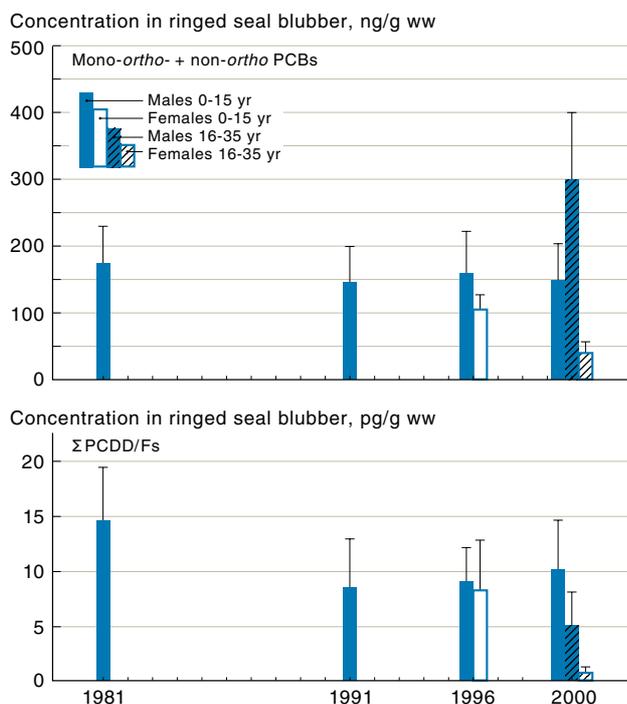


Figure 5-29. Concentrations of mono-ortho- and non-ortho-PCBs and PCDD/Fs in ringed seals from Holman, NWT, in the Canadian Arctic Archipelago (Ikonomidou *et al.*, 2002).

in male ringed seals from Holman. Concentrations of non- and mono-ortho PCBs (149-174 ng/g ww) and PCDD/Fs (8.6-14.6 pg/g ww) in ringed seals aged 0-15 years remained approximately constant from 1981 to 2000 (Ikonomidou *et al.*, 2002) (Figure 5-29). Total PCB concentrations did not decline significantly in males or females over the period of 1981 to 1991 (Addison and Smith, 1998). Older male seals (16-35 yr) from the 2000 sampling group have higher levels of non- and mono-ortho PCBs than their younger counterparts (0-15 yr; 302 vs. 150 ng/g ww). In female seals from 1996 and 2000, non- and mono-ortho PCB levels are much lower in the 16-35-year age group from 2000 (43 ng/g ww) than the 0-15-year age group from 1996 (105 ng/g ww).

No other temporal-trend studies of OCs in Arctic ringed seals have been reported. At Svalbard and northern Norway, where results are available since the mid-1990s, it is likely that this will be accomplished in the near future. In the White Sea, mean levels of PCBs, DDTs, chlordanes, HCHs, and HCB declined between 2 and 3 fold in blubber samples taken from harp seal pups between 1992 and 1998 (Muir *et al.*, 2002c). Mirex levels in 1998 samples were about one quarter of their 1992 levels, in the same study. These declines should be viewed with caution since there could be regional differences in exposure of adult harp seals to PCBs and DDT within the White Sea area depending on their proximity to urban areas.

No significant temporal trend in butyltin concentrations was observed in Steller sea lions sampled from Alaska between 1976 and 1985 (Kim *et al.*, 1996a). This was despite the fact that the annual consumption of organotin compounds doubled in the U.S. during the same period. The authors suggest that the butyltin compounds are degraded faster than the intake from diet in Steller sea lions.

Muir *et al.* (2000e) examined temporal trends in levels of a wide range of OC compounds in archived (1978) samples of northwestern Greenland walrus as well as more recently collected samples (1988) (Annex Table 12). They did not detect any significant differences in mean concentrations of any OCs in male walrus from the two time periods, but for females, they found significantly higher levels of di- and trichlorobiphenyls, dieldrin, toxaphene, α -HCH, and Σ HCHs in the 1988 material, but no differences for PCBs or DDT compounds.

5.4.4.2. Cetaceans

Belugas

Stern (1999) and Stern and Addison (1999) examined temporal trends of 'legacy' OCs in blubber of beluga from Cumberland Sound (southeast Baffin Island) between 1982 and 1997 (Annex Table 13). They reported a significant decline in α -HCH concentrations over the 15-year interval from 1982 to 1997, while no significant differences were observed for the β - and γ -HCH isomers (Figure 5-30). In this regard, belugas differ from seabirds, ringed seals and polar bear, which all show increasing proportions of β -HCH. Σ DDT concentrations did not change over this 15-year interval. However, a 2.2-fold decline and a 1.3-fold increase in the (age-adjusted) concentration of p,p' -DDT and its metabolite p,p' -DDE, respectively, was observed (Figure 5-31). These changes translated into a significant increase in the p,p' -DDE: Σ DDT ratio from 0.37 to 0.48 and suggests 'old' rather than recent DDT sources. Two of the most abundant congeners in technical chlordane, *cis*- and *trans*-nonachlor, increased in concentration by 1.4 and 1.7 fold, respectively, from 1982 to 1997, while only *cis*-chlordane showed any significant decline. Overall, a 1.2-fold increase in the concentrations of Σ CHLs

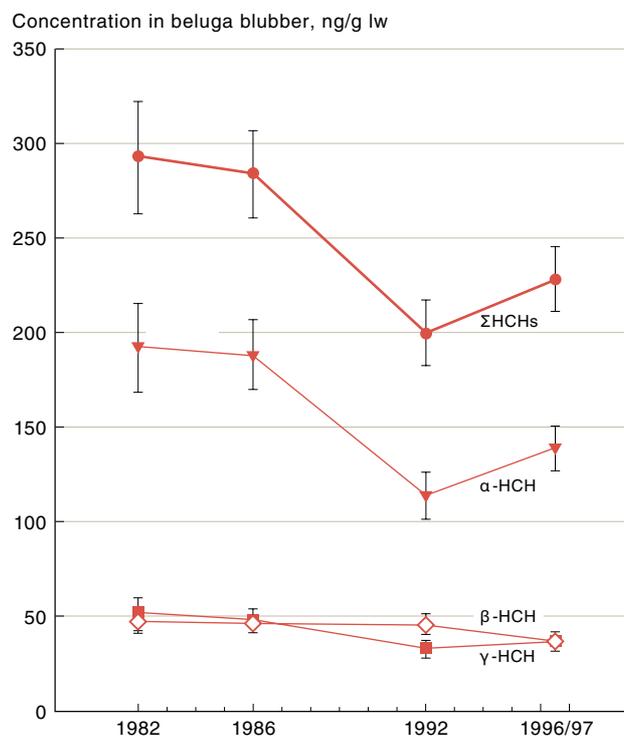


Figure 5-30. Temporal trends of age-adjusted concentrations of Σ HCHs, α -HCH, β -HCH, and γ -HCH in male beluga blubber samples from Pangnirtung, Nunavut.

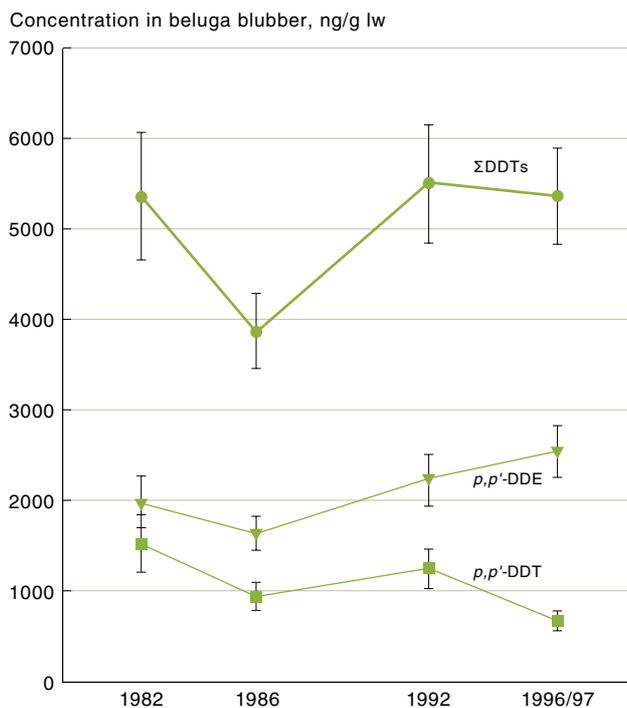


Figure 5-31. Temporal trends of age-adjusted concentrations of ΣDDTs, p,p'-DDE and p,p'-DDT in male beluga blubber samples from Pangnirtung, Nunavut.

was observed. Levels of oxychlordan, the principal metabolite of *cis*- and *trans*-chlordan, second only to *trans*-nonachlor as the most abundant chlordan-related residue in the southeast Baffin beluga blubber, did not change significantly over this 15-year period. For total toxaphene and Parlars 26 and 50, no clear trends were evident (Figure 5-32). For PCB congeners, significant

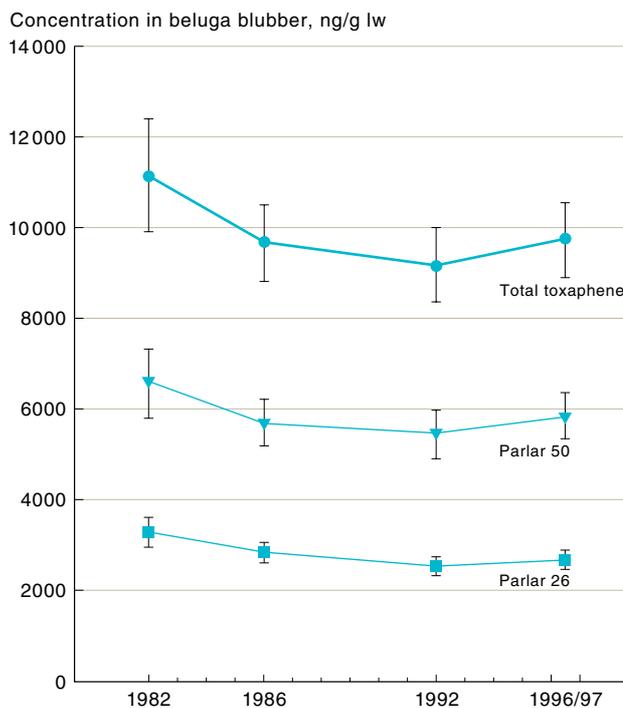


Figure 5-32. Temporal trends of age-adjusted concentrations of total toxaphene and Parlars 50 and 26 in male beluga blubber samples from Pangnirtung, Nunavut.

declines, ranging from 1.7 fold for CB81 to 2.8 fold for CB126, were observed (Figure 5-33). Non-ortho PCB TEQs (CBs 77, 126, and 169) declined from 16 to 6.1 pg/g lw (2.6 fold) from 1982 to 1997. Age-adjusted concentrations of major PCB homologue groups (hexa-, heptachlorobiphenyls) did not show a consistent decline over the 15-year period (Stern and Addison, 1999).

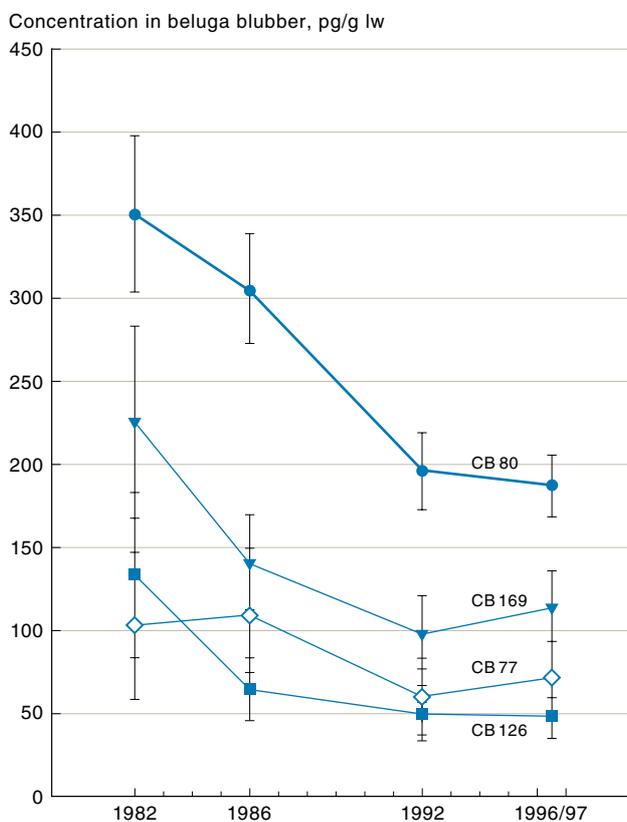
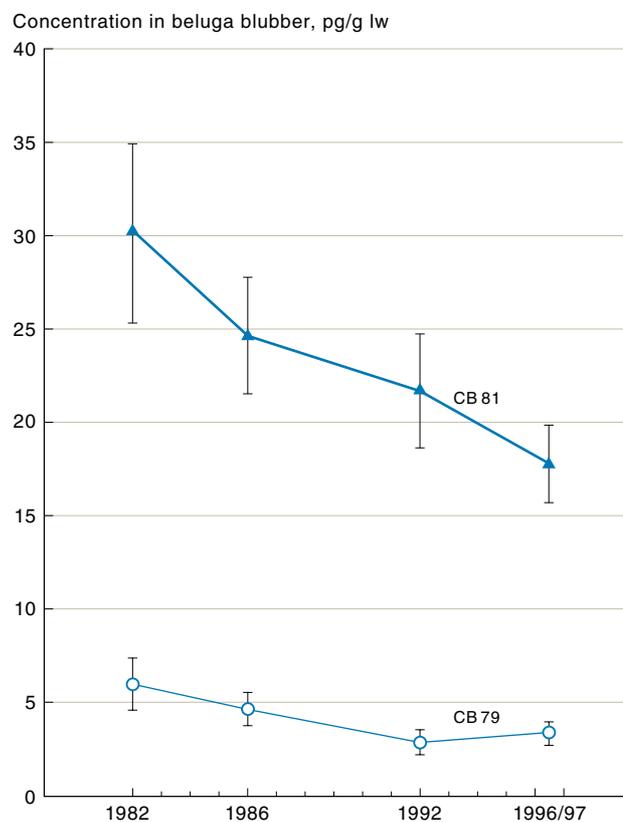


Figure 5-33. Temporal trends of age-adjusted concentrations of PCB congeners 77, 79, 80, 81, 126, and 169 in male beluga blubber samples from Pangnirtung, Nunavut.



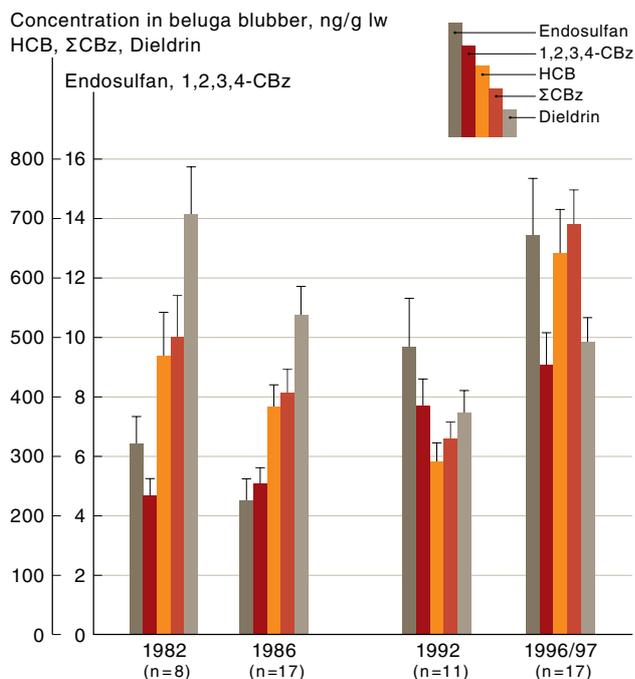


Figure 5-34. Temporal trends of age-adjusted concentrations of endosulfan, 1,2,3,4-chlorobenzenes, HCB, sum of tetra-, penta- and hexachlorobenzene (Σ CBz), and dieldrin in blubber of male belugas from Cumberland Sound, Nunavut, in the eastern Canadian Arctic (Stern and Addison, 1999).

A 2.1-fold increase in age-adjusted mean concentrations of endosulfan sulfate and a 1.4-fold decline in dieldrin were also observed over the 15-year period (Stern and Addison, 1999) (Figure 5-34).

Pilot whales

In 1997, a large number of pilot whale blubber samples were taken in the Faroe Islands to study levels of OCs (Dam and Bloch, 2000). Samples were analyzed in pools sorted according to sexual maturity and sex. Temporal trends were examined by comparing results from a subset of individual 1997 pilot whale samples (Dam, 2001) with a previous study of pilot whales collected in the Faroes in 1987 (Borrell, 1993). Statistical analysis of the data for the adult females and adult males from 1987 and 1997 showed a significant decrease during the ten-year interval for both PCB and DDT concentrations (Mikkelsen, 2002). There are some weaknesses in the statistical analysis since the total PCB concentration in the subset of adult females analyzed individually was slightly lower than in the entire 1997 bulk of adult females. The level was quite similar in the adult males, however, and this indicates that the observed decrease is real.

Narwhal

Results for OCs in blubber of narwhal from the Baffin Bay-Lancaster Sound region (Pond Inlet) of the Canadian Arctic were available from previous work (Muir *et al.*, 1992a), and more recent data for the same region are available (Stern, 2001). Using this information, it was possible to make a qualitative assessment of temporal changes in 'legacy' OCs in narwhal from this region over a 12-16-year period (1982-83 to 1999). Male narwhal were selected for temporal-trend comparisons because, unlike seals, they show little relationship between PCB concentrations and age (Muir *et al.*, 1992a,b). In agree-

ment with findings outlined in the previous AMAP assessment report (de March *et al.*, 1998), male narwhal from Pond Inlet showed no discernible changes in concentrations of Σ PCBs, Σ DDTs, Σ CHLs or toxaphene. Σ HCHs and Σ CBz also showed no statistically significant trends over this time period. This lack of change in Σ DDTs, Σ CHLs, Σ PCBs, and toxaphene concentrations in narwhal is consistent with results for beluga in south-eastern Baffin Island. One difference however between these two odontocetes was the decline in Σ HCHs in beluga, while no such decline was found in narwhal.

5.4.5. Temporal trends in polar bear

5.4.5.1. Canadian Arctic polar bears

Temporal trends of the major OC groups in polar bears from the Churchill area of western Hudson Bay (Canada) are presented in Figure 5-33. Biopsy samples from adult female polar bears were chosen to study temporal trends because there is no significant effect of age on OC levels, whereas there is a significant effect (increase with age) of highly chlorinated PCBs in male polar bears (Bernhoft *et al.*, 1997; Norstrom *et al.*, 1998). Bears less than five years old were also excluded because levels of some OCs are higher due to high exposure in milk the first two years of life. The trends observed in adult female polar bears are therefore more likely to represent the actual changes in OC levels in the polar bear food chain. Biopsy samples were collected opportunistically nearly every year throughout the 1990s (Norstrom, 2001). Archived adipose tissue samples from 1968, 1984, and 1989 were included to extend the time period for comparison. There were no consistent upward or downward trends over the period 1968 to 1989 for most OCs; therefore, only trends in the 1990s were analyzed statistically. There were no statistically significant ($p < 0.05$) increasing trends in female bears over the entire nine-year period. There were however statistically significant ($p < 0.05$) downward trends for total chlorobenzenes, α -HCH, and Σ PCBs between 1991 and 1999. There were no significant ($p < 0.05$) changes in chlordanes, Σ DDTs (mostly p,p' -DDE), dieldrin, β -HCH, and Σ HCHs.

There was a consistent (and significant) decrease in Σ DDTs throughout the entire 1968 to 1990s time period. Such strong trends are unusual in Arctic biota, suggesting that the phenomenon may be related to local conditions around Hudson Bay. Spraying of DDT for biting-insect control in communities and military bases in the Hudson Bay area in the 1950s and 1960s may have contributed a significant load to Hudson Bay during this period. This likely declined after the DDT ban and closing of the large military base at Churchill, and may not have contaminated other nearby areas. In support of this hypothesis, it can be seen in Annex Table 14 that Σ DDT levels were 2-3 times higher in polar bear fat from western Hudson Bay than in other areas of the Canadian Arctic in 1984.

The overall trend for Σ CBz appears to be an increase between 1968 and 1984, followed by a consistent downward trend since that time. Most of the decline in Σ CBz was due to HCB, which decreased with a half-life of approximately nine years during the 1990s. HCB and 1,2,4,5-TeCBz were each roughly half of the total, with a minor contribution from PeCBz. The pro-

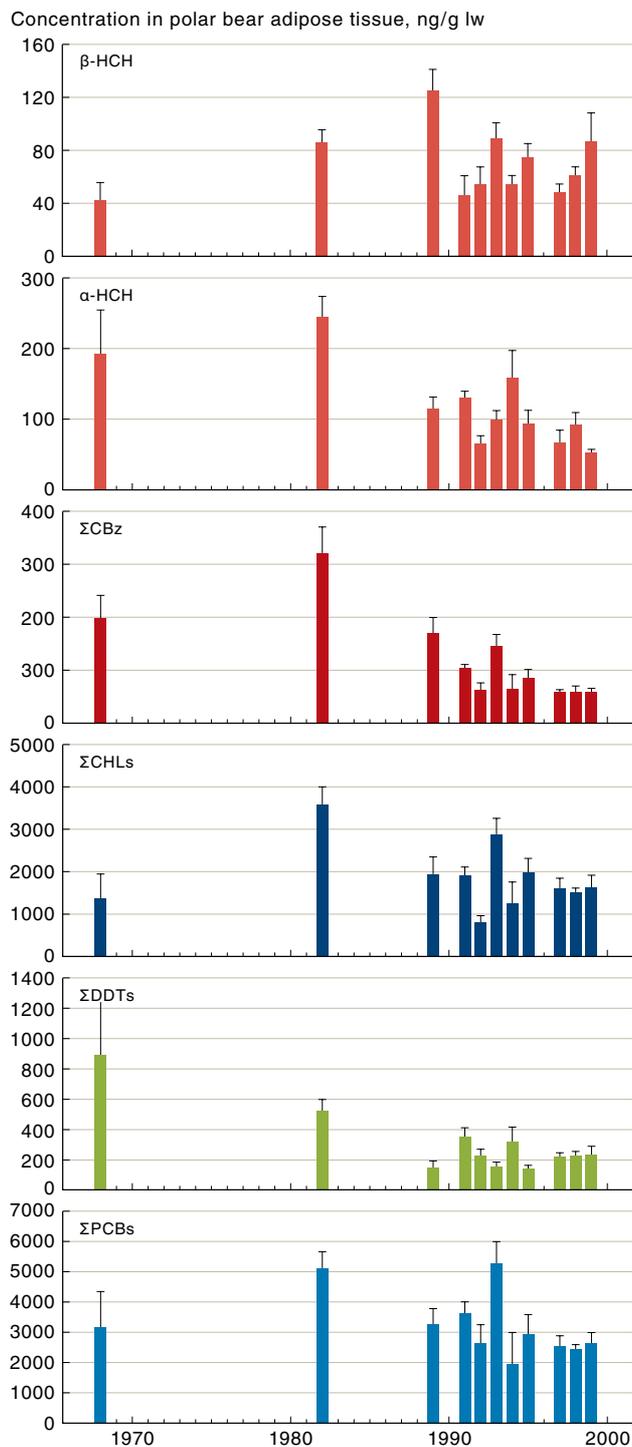


Figure 5-35. Trends of major OC compounds in female polar bear adipose tissue from the Churchill area of western Hudson Bay (Canada) from 1968 to 1999. Samples from 1991 to 1999 are fat biopsies, but earlier samples are adipose tissue.

portion of 1,2,4,5-TeCBz peaked at 53% between 1995 and 1997, and then decreased to values similar to the pre-1995 period of 40-45%.

The downward trend of Σ HCHs in Hudson Bay polar bears in the 1990s was not significant (Norstrom, 2001), but it was significant if 1984 and 1989 were considered (Figure 5-35). However, comparing Σ HCH trends is complicated by differences in temporal trends of α -HCH and β -HCH (α -HCH declines and β -HCH increases). γ -HCH was less than 2% of Σ HCHs and could not be reliably quantified in the majority of samples.

The apparent half-life of α -HCH in the 1990s was approximately ten years, very similar to that of HCB. The decrease in the 1990s appears to be part of a general trend. Levels of α -HCH were approximately two to three times higher in 1968 and 1984 than the average in the 1990s. By contrast, β -HCH concentrations were lower in 1968 than in any subsequent year, and the overall trend in the 1980s and 1990s is rather flat. As a consequence, a significantly higher proportion (approximately 50%) of present day Σ HCHs in polar bears from Hudson Bay is β -HCH compared to 1984 (25%) and 1968 (17%). A parallel trend is observed in ringed seals, the major prey of the polar bears (Section 5.4.4.1).

Σ PCBs decreased fairly steadily throughout the 1990s, but with a long half-life of approximately 18 years. The shift in composition of the PCBs was subtle over the decade, but there was a clear tendency for the proportion of less chlorinated congeners to increase, and the highly chlorinated congeners to decrease. Thus, CB99 increased from approximately 10% to 12% of Σ PCBs, CB153 was relatively stable at approximately 35%, and CB180 decreased from 17% to 14%. The trends in these three congeners indicate that the half-life of CB153 (19 years) was similar to that of Σ PCBs. The half-life of CB180 (13 years) was shorter, and the half-life of CB99 (>50 years, not significant) was longer than Σ PCBs. Thus, the decreasing trend in Σ PCBs is driven by loss of the highly chlorinated congeners. There is less than a factor-2 difference in Σ PCB levels through the 1968-1999 period, and no long-term trend is apparent. Concentrations in the early 1990s in Hudson Bay were similar to those in the late 1960s, in sharp contrast to areas such as the Great Lakes or the North Atlantic, where PCB concentrations in herring gull eggs were on the order of ten times higher in the late 1960s and early 1970s than at present (Hebert *et al.*, 2000).

Shorter-term temporal trends in polar bears from Queen Maud Gulf (I) in the western Canadian Arctic Archipelago, Barrow Strait (II) in the central archipelago, and northern Baffin Bay (III) and Davis Strait (IV) in the eastern archipelago, and also one area in western Hudson Bay (V) were reported by Muir and Norstrom (2000) (Annex Table 14). In that comparison, samples were taken from eight to ten individual adult male polar bears per area in each of 1984 and 1989/1990. PCDD/PCDF concentration changes were also determined in pooled samples. There were significantly lower concentrations of Σ HCHs, Σ DDTs, and dieldrin in (I), a significant decrease in dieldrin in (II), no changes in (III), a significant increase in Σ CHLs in (IV), and a significant decrease in Σ CBz, Σ DDTs, and Σ PCBs in (V), between 1984 and 1989.

Results for Σ PCDD concentrations in pooled samples of polar bear adipose tissue from polar bear areas (I), (II), (III), and (IV) in the Canadian Arctic Archipelago in 1984 and 1990 (Norstrom, 1997) are given in Annex Table 16. PCDDs consisted almost entirely of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD. Other PCDDs and all PCDFs were at sub-pg/g lw concentrations. Concentrations of TCDD were low and tended to be more evenly distributed in 1990 (0.8-3.1 pg/g lw) than in 1984 (2.0-15 g/g lw), as was the case for the other OCs. Because pooled samples were analyzed, the significance of the differences cannot be established. Nevertheless, con-

centrations of TCDD in (I) and (II) were a factor of 4-5 lower in 1990 than 1984. The results are consistent with the findings of Norstrom *et al.* (1990) in which ringed seal, beluga, and polar bears were analyzed. It is apparent that PCDD/Fs are at very low concentrations in the polar bear food chain and are unlikely to be of toxicological significance.

5.4.5.2. East Greenland polar bears

Dietz *et al.* (2004) compared concentrations of PCBs and OC pesticides in polar bear from central East Greenland collected in 1999-2001 with results for 1990 reported by Norstrom *et al.* (1998). Overall a significant decrease was observed in OC contaminants in all age and sex groups studied over the period from 1990 to 1999-2001. Using the same congeners to calculate Σ PCB for both groups, Σ PCB showed a reduction of 78%. PCB congener proportion also changed over the ten-year period. A less chlorinated PCB congener like CB99 comprised 7.3% of the 1999-2001 bears from East Greenland, a slight decrease compared to the 8.3% that Norstrom *et al.* (1998) reported from the trans-Arctic survey of polar bears from 1989 to 1992. The decreases in Σ DDT and *p,p'*-DDE in East Greenland since 1990 (34% and 29%, respectively) were also significant, although less pronounced than for other OCs, and the estimated half-life for *p,p'*-DDE was the longest of all OCs measured (17.5 years). Total chlordane-related compounds and dieldrin were both found to decrease (between about 31% to 75% dependent of the sex and age group studied). Σ HCH concentrations declined about 60% over the ten-year period. β -HCH increased in western Hudson Bay polar bears during the 1990s (Norstrom, 2001) and a similar pattern was expected in East Greenland. However, this was not the case, as α -HCH showed an increase from 18% to 25% and β -HCH showed a decrease from 82% to 75%. The high percentage of β -HCH is consistent with findings from the Svalbard region where Bernhoft *et al.* (1997) reported β -HCH to constitute 81% of Σ HCH. In general, the decrease in PCB and OC concentrations in East Greenland polar bear is faster than that observed over the same period in Canada, but similar to the decrease found in polar bears from Svalbard.

Relative change in concentration in polar bear plasma from 1967-1993/94

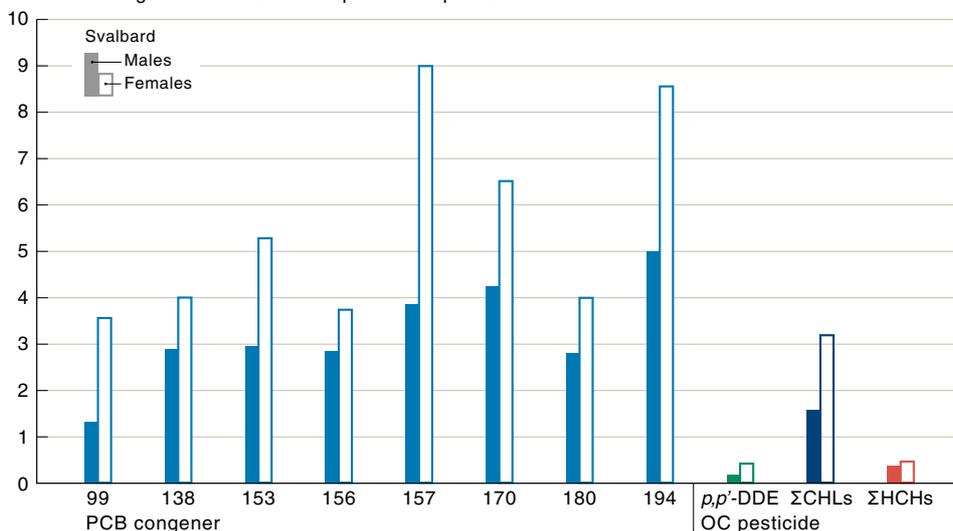


Figure 5-37. Relative change in major PCB congeners and OC pesticides from 1967 to 1993-94 for adult female and male polar bear samples at Svalbard, Norway (from Derocher *et al.*, 2003). Results for 1993-94 are from Skaare *et al.* (2001d) and Bernhoft *et al.* (1997). Values <1 imply a decrease in concentration.

Concentration in polar bear plasma, ng/g ww

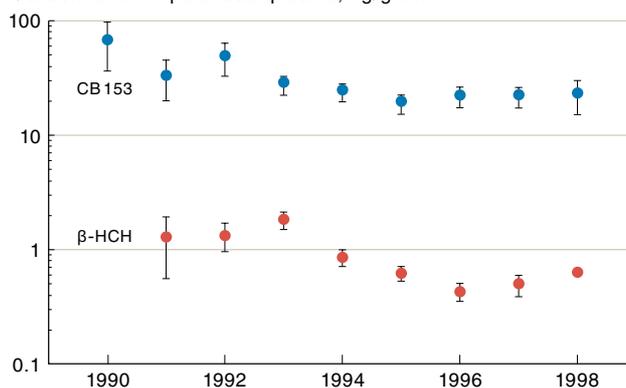


Figure 5-36. Temporal trends of two major OCs (β -HCH and CB153) in polar bear plasma from Svalbard (means \pm 95% C.I.) for the period 1990-1998. CB153 concentrations are adjusted for covariates (extractable lipids, condition index and sampling site longitude).

5.4.5.3. Svalbard polar bears

Henriksen *et al.* (2001) studied the trend in CB153 concentrations in blood from polar bears at Svalbard that was collected annually between 1990 and 1998. Decreases of approximately 40% occurred in the early 1990s, and stabilized thereafter (Figure 5-36). This is a somewhat steeper trend than was found in Hudson Bay during the same time period. However, Svalbard bears had significantly higher levels of PCBs in 1990 than those in Hudson Bay, probably due to the proximity of Svalbard to European sources. Svalbard PCB levels may have approached steady state with global distribution of PCBs later than in Hudson Bay because of this proximity. It is well established that trends of POPs in environments close to sources tend to follow production and use of the chemical rather closely, whereas those in environments remote from sources are significantly dampened. That is, peak concentrations are lower, took longer to be reached, and take longer to decrease than those near sources. Present results indicate that further decreases in PCB contamination of the Arctic may be slight.

β -HCH also declined in plasma of polar bears from Svalbard between 1991 and 1999 (Lie and Skaare, 2002). Concentrations were similar from 1991 to 1993 and declined about 3 fold between 1993 and 1996 (Figure 5-36).

The trend for β -HCH in Svalbard polar bears differs from that in the Hudson Bay bears, where concentrations appeared to increase during the same time period.

Derocher *et al.*, (2003) compared PCBs and OC pesticides in blood plasma collected in 1967 from 32 polar bears in eastern Svalbard with results from 1993 and 1994. Most major, persistent, PCB congeners in polar bears (CBs 99, 138, 153, 180, 194) showed significant increases from 1967 to 1993-94 in both males and females (Figure 5-37). Chlordane compounds also increased while *p,p'*-DDE and HCH isomers declined. These increases for chlordanes, PCBs and decline in *p,p'*-DDE over the 26-27-year period were similar to trends in the eastern Canadian Arctic polar bears over the period 1969 to 1984 (Muir and Norstrom, 2000) (Figure 5-35).

5.4.6. Temporal trends of 'new' POPs in marine mammals

5.4.6.1. PBDEs

Ikonomou *et al.* (2002) reported exponential increases in Σ PBDEs (di- to heptabromodiphenyl ethers) in male ringed seals aged 0-15 years from Holman in the western Canadian Arctic over the period of 1981 to 2000 (Figure 5-38). Σ PBDEs increased 9 fold over this period. Pe- and HxBDEs were found to be increasing at approximately the same rate ($t_2 = 4.7$ yr and 4.3 yr, respectively) and more rapidly than TeBDEs ($t_2 = 8.6$ yr), while TrBDEs showed no increase in this age/sex group. The

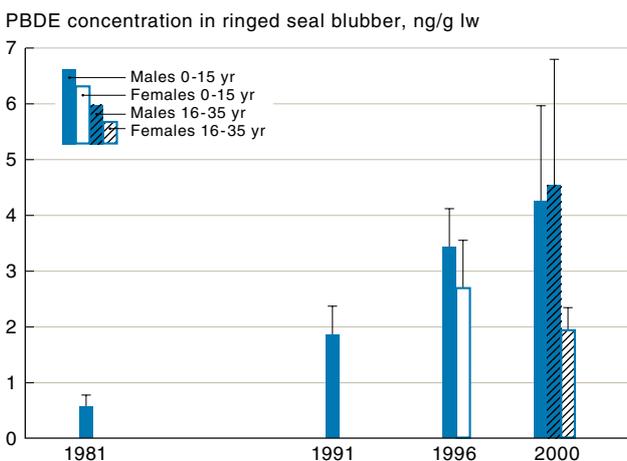


Figure 5-38. Temporal trends of PBDEs in blubber of ringed seals from Holman, NWT, in the western Canadian Arctic, 1981-2000 (Ikonomou *et al.*, 2002).

three most prevalent PBDE congeners: BDEs 47, 99, and 100, all increased over the 19-year period. However, only BDEs 47 and 100 increased in parallel with Σ PBDEs. BDE99 increased exponentially in a similar manner to Σ PBDEs and BDEs 47 and 100 from 1981 to 1996. However, the 2000 samples show that the levels of BDE99 are stabilizing. This suggests a shift in sources or change in composition of PBDE products. No difference in PBDE levels (both total and of individual congeners), were observed between younger (0-15 yr) and older (16-35 yr) male seals in 2000 ($p = 0.98$ for Σ PBDEs), suggesting that, for the older seals, recent PBDE accumulation dominates potential historic accumulation.

Stern and Ikonomou (2000; 2001) studied temporal trends of PBDEs and polychlorinated diphenyl ethers

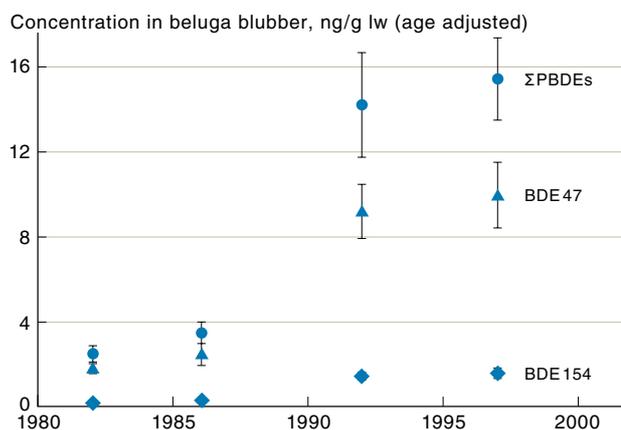


Figure 5-39. Temporal trends of PBDEs in blubber of beluga whales from southeast Baffin Island in the eastern Canadian Arctic, 1982-1997 (Stern and Ikonomou, 2000; 2001).

(PCDEs) in beluga blubber samples from southeast Baffin Island in the eastern Canadian Arctic. Levels of the total PBDEs (Di- to HpBDEs) and major congeners increased significantly in the southeast Baffin Bay beluga over the period of 1982 to 1997. Age-adjusted concentrations of BDE47, the most predominant PBDE congener, increased 6.5 fold over this 15-year period, while BDE154 increased 30 fold (Figure 5-39). Over the 15-year time span, contributions of the TrBDE homologue group and BDE47 to total PBDEs declined by 7% and 3%, respectively. Conversely, PeBDE and HxBDE contributions have increased by 20% and 80%, respectively. This change in the beluga could be related to the shift in composition of commercial PBDEs to more highly brominated mixtures (de Boer *et al.*, 2000).

5.4.6.2. PCDEs

PCDE concentrations declined in the same beluga samples that were analyzed for PBDEs (Stern and Ikonomou, 2000). Maximum concentrations were found in samples from 1982 (Figure 5-40). The two most abundant congeners were CDE99 (2,2',4,4',5-CDE) and CDE154 (2,2',4,4',5,6'-CDE), which declined 2.5 fold and 1.8 fold, respectively, over the 15-year period. These congeners are prominent contaminants in pentachlorophenol-based wood preservatives, and the decline most likely reflects the ban on PCP use in Canada and use restrictions in the U.S.

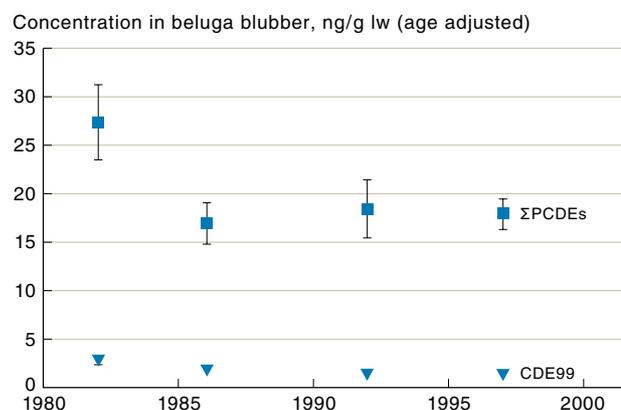


Figure 5-40. Temporal trends of PCDEs in blubber of beluga from southeast Baffin Island in the eastern Canadian Arctic, 1982-1997 (Stern and Ikonomou, 2000; 2001).

5.4.7. Modeling temporal trends of PCBs and DDT in pinnipeds

Evaluating temporal trends of OCs in marine mammal populations, and linking them to trends in other biota or environmental media can be confounded by factors that affect tissue concentrations such as age, life span, sex, reproductive activity, and blubber thickness. OC concentrations in marine mammals also reflect their exposure history over many years, which could result in a significant lag in response to changes in their exposure levels. These factors can be accounted for quantitatively using species-specific dynamic bioaccumulation models as has been shown in an examination of the history of PCB contamination in the St. Lawrence beluga whale population (Hickie *et al.*, 2000). Similar individual- and population-based models developed for ringed seals (Kingsley and Hickie, 1993) are used here to reconstruct the history of accumulation of selected POPs (Σ PCBs, Σ DDTs, Σ CHLs, α -HCH, and β -HCH), and to predict their potential future trends in Arctic populations. In Figure 5-41, some results for males are compared to temporal-trend data for ringed seals from Holman Island, NWT from 1972 to 1991 (Addison and Smith, 1998) and from 2001 (Hoekstra *et al.*, 2003a).

For these simulations, the entire diet of ringed seals was assumed to consist of Arctic cod. Average POP concentrations reported for Arctic cod from several locations in the Canadian Arctic in the 1990s (Hargrave *et al.*, 1992; Muir *et al.*, 1999b) were used to calculate baseline average concentrations (ca. 1996) for use in simulations that extended over the period 1970 to 2010. Resulting baseline concentrations were 4.7 ng/g ww for Σ PCBs, 3.8 ng/g ww for Σ DDTs, 4.5 ng/g ww for Σ CHLs, 2.1 ng/g ww for α -HCH, and 0.32 ng/g ww for β -HCH. Since temporal-trend data are lacking for Arctic cod in the Canadian Arctic, trends back to the early 1970s were estimated using temporal trends derived from the Lancaster Sound seabird egg monitoring program (Braune *et al.*, 2001a) using log_e-linear regressions. Where discrepancies in temporal trends were noted between the three bird species examined, trends from thick-billed murres were used owing to their year-round Arctic residence. Significant declines were noted for Σ PCBs ($-5.4\%/yr$) and Σ DDTs ($-5.6\%/yr$) over the period of 1975 to 1998, while β -HCH levels increased over time ($4.2\%/yr$). Although trends for Σ CHLs and α -HCH were not statistically significant, resulting slopes ($-1.1\%/yr$ and $-0.4\%/yr$, respectively) were used in model simulations. These trends were assumed to remain in effect in simulations to predict possible future concentrations up to the year 2010. Chemical elimination half-lives for seals used in these simulations were 4.1 years for Σ PCBs, 6.9 years for Σ DDTs, 3.3 years for Σ CHLs, 2.4 years for α -HCH and 1.8 years for β -HCH. These were derived from model calibration exercises using independent datasets (Hickie, 2002). The half-life estimate of Σ PCBs was based on the weighted sum of half-life estimates for the 20 most abundant PCB congeners.

Overall, the simulations showed good agreement with observed temporal trends in the Holman ringed seal population for all five chemicals examined, and demonstrated that the temporal trends evident in ringed seals are consistent with those in seabirds, and likely reflect changes throughout lower trophic levels in the marine

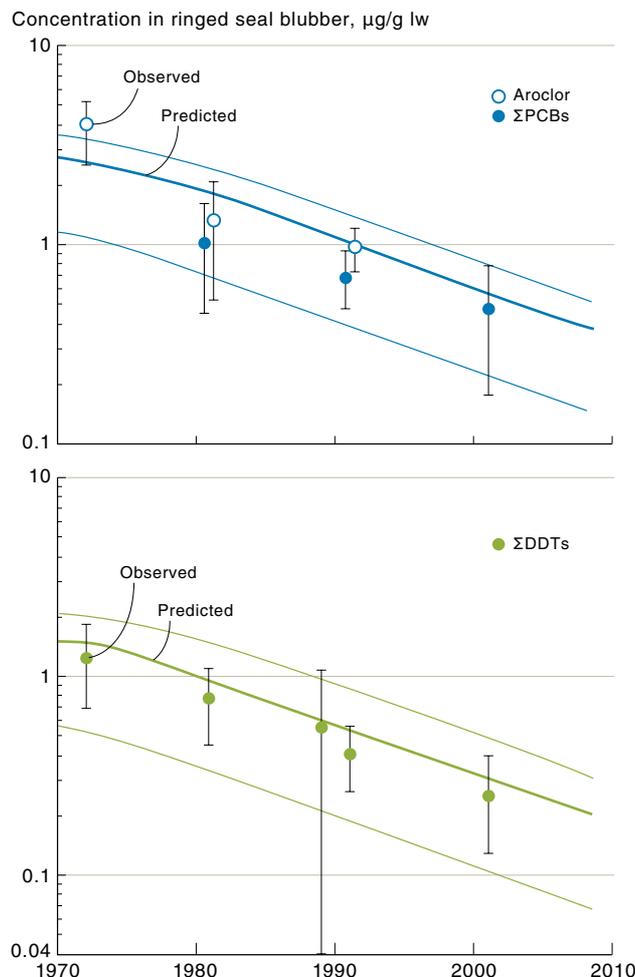


Figure 5-41. Modeled temporal trends of Σ PCBs and Σ DDTs in blubber of male ringed seals from 1972-2001 with projection into the near future.

ecosystem. The results also suggest that contaminant levels in ringed seal populations do not show any appreciable lag in response when contaminant exposure concentrations change gradually over time, as appears to be the case in the Arctic. The lack of a lag in response can be attributed to the relatively rapid elimination rates for the chemicals examined, combined with the effect of population turnover. The good agreement between the simulations and monitoring data serves to validate the model, and indicates that it can be used with some confidence in forecasting responses to potential future loading scenarios. Concentrations of Σ PCBs and Σ DDTs in blubber are predicted to decline by about 40% between 2000 and 2010, to ranges of 150-500 ng/g ww Σ PCBs and 60-300 ng/g ww Σ DDTs for the scenarios presented here.

5.5. Summary and conclusions – temporal trends

A critical question in the assessment of POPs in the Arctic is whether concentrations are increasing or decreasing. The previous POPs assessment found a general lack of information on temporal trends of POPs in biota within the circumpolar Arctic, particularly for the High Arctic. While results for fish in northern Sweden demonstrated declines over the period of 1968 to 1996, there were only a few long-term datasets from other circumpolar countries. In the abiotic environment, temporal-

trend information was limited to sediment cores, which had relatively poor temporal resolution in most locations and measurements of HCH in seawater from the Bering Sea and the western Canadian Arctic. For the current assessment, considerably more data on temporal trends was available. Previous studies have been extended so that a 25 to 30-year perspective is now available for polar bears, seabirds, and ringed seals in the Canadian Arctic, as well as for fish in the Swedish Arctic. Studies covering a 10 to 15-year period are available for polar bear at Svalbard, peregrine falcons in Alaska, Atlantic cod in Iceland, glaucous gulls in Svalbard, burbot, lake trout and beluga whales in Canada and walrus in northwestern Greenland. Continuous air monitoring of POPs extends from 1992-93 to 2001 at Alert, Ny-Ålesund, and Pallas, although results were only available to 1998 for Alert and 1999 for Pallas. 'New' chemicals such as PBDEs have been added to the list of chemicals for which temporal trends are available in marine biota.

PCBs, the major OC contaminants in the Arctic, appear to be declining in most media. In air, half-lives of tri- to heptachlorobiphenyl congeners, based on digitally filtered results at Alert, ranged from 3 to 17 years. These are much longer than in temperate locations (Great Lakes and the U.K.), but they do indicate a slow, downward trend. Downward trends in air were also found for HCH and chlordane isomers; however, their half-lives were also generally longer at Alert than in the Great Lakes.

In the case of *p,p'*-DDE, *o,p'*-DDT, dieldrin, and endosulfan, slight increases in air at Alert were found during the 1990s. This is unexpected in the case of DDE and dieldrin because the use of their precursors (DDT and aldrin/dieldrin) has been restricted for more than ten years, and in some cases, up to 30 years in circumpolar and most northern-hemisphere countries. It does not parallel observations for marine or freshwater biota. The increases may be unique to the particular five-year dataset examined by Hung *et al.* (2002b) for Alert. At Ny-Ålesund, in the Norwegian Arctic, a pronounced decline in Σ DDTs in air was observed at least from 1997 to 2000. The great variation in concentrations of most OCs in air, particularly DDT at Ny-Ålesund, makes evaluation of temporal trends in air difficult. Long-range transport events appear to be very important for delivering DDT, PCBs and other OCs to these sampling sites and this may have been affected by changes in weather patterns during the 1990s (Macdonald *et al.*, 2003). Digital filtering and temperature normalization (Hung *et al.*, 2001; 2002b) have proved useful in interpretation of air data. Unfortunately, this detailed analysis has only been applied to data from Alert. The trends appear to be generally similar at Alert and Ny-Ålesund, but further study is required.

Temporal trends of POP concentrations in air and biota in the Arctic are not expected to parallel each other given the strong influence of the inventories of chemicals in the Arctic Ocean. This is illustrated in the case of Σ HCHs in ringed seals and polar bears. Air concentration data for α -HCH, collected since 1979 by various groups at different Arctic locations, have been collated into a time series up to 1996 (Li and Bidleman, 2003; Li *et al.*, 2002). HCH levels decreased more than 20 fold in air from 1979 to 1996. However, there has been only a modest change in concentrations in ringed seals and polar bears in the eastern Canadian Arctic over

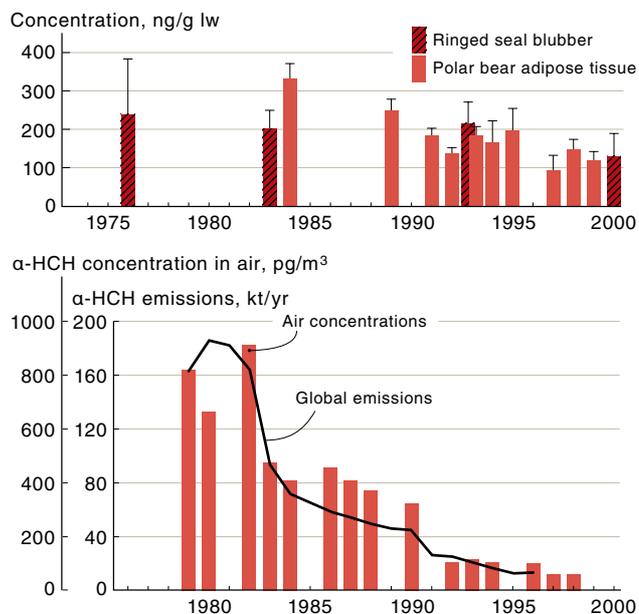


Figure 5-42. Comparison of temporal trends of Σ HCHs in ringed seals and polar bears and trends of α -HCH in Arctic air (mainly from sites in the Bering/Chukchi/Beaufort Seas), as well as estimated emissions of α -HCH (Li *et al.*, 2002) over the same time period.

the same time period (Figure 5-42). The observed trends in biota agree better with the much smaller estimated reduction (3%/yr) of Σ HCHs in surface seawater (Bidleman *et al.*, 1995; Jantunen and Bidleman, 1995). Unfortunately, no time-trend data are available for any other persistent OC compound concentrations for air (or seawater) over this long period. The comparison of air and biota indicates the long times needed to affect a change in concentration in long-lived marine biota following reductions in emissions of a chemical with multiple sources (e.g., a re-emitted chemical that is recycled globally) and long half-lives for some components (e.g., β -HCH), which assume increasing importance in seals and polar bears over time.

While declines of major OC concentrations in biota are slow because of global cycling and long half-lives, the increasing concentrations of PBDEs in ringed seals and beluga (Figure 5-43) demonstrate that newly emit-

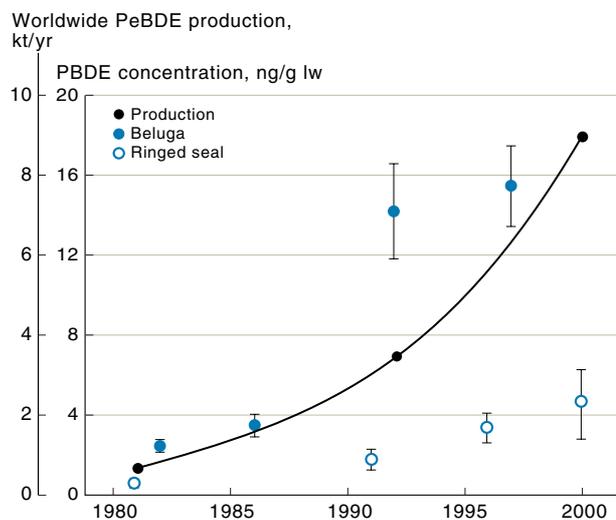


Figure 5-43. Comparison of temporal trends of Σ PBDE (Br_2 - Br_7) in ringed seals and beluga in the Canadian Arctic to the estimated annual global production of PeBDE for the same time period.

ted persistent semi-volatile chemicals can increase in circumpolar countries in parallel with emissions. The doubling time for Σ PBDE concentrations in beluga during the early 1990s ($t_2 = 3.0$ yr) was faster than in Holman ringed seals ($t_2 = 4.5$ yr). By comparison, in the Great Lakes region, PBDE concentrations in herring gull eggs and lake trout are increasing at approximately the same rate as in beluga (t_2 approximately 3 yr) (Norstrom *et al.*, 2002; Luross *et al.*, 2003). If the same rate of increase of PBDEs and declines in PCBs were to continue, PBDEs will reach parity with PCBs in Canadian Arctic ringed seals sometime between 2015 and 2025.

No temporal trends of PBDEs are available from the European Arctic to compare to the somewhat different temporal trends being seen in the Baltic Sea and northern Europe (exponential increases in the 1980s, with declines or no change occurring in some time series from the mid- or late 1990s) (Kierkegaard *et al.*, 1999; 2004; Sellström, 1999; Sellström *et al.*, 2003; Norén and Meironyté, 2000). The changing (and in some cases, declining) temporal trends of lower brominated congeners in Europe after voluntary withdrawal of the PeBDE product show the close relationship between discontinued use/production, reduced emissions, and decreased concentrations in the environment. The European Union (EU) will ban the PeBDE technical product in 2004, which should continue the reduction in emissions in Europe in the long term. However, it is not clear what effect this will have on PBDE concentrations in the Arctic, since no reductions in PeBDE use are presently in force in North America, and no temporal trends for PBDEs have been performed in the European Arctic.

A major unanswered question is the extent to which the temporal trends observed for various POPs to date apply throughout the circumpolar Arctic. This is partly addressed in Table 5-3 using the annual percent declines

of major OCs from the 1960s/early 1970s to late 1990s/early 2000s or from late 1980s/early 1990s to late 1990s/early 2000s, reported for selected species from remote locations. In general, declines are more rapid if calculated for the 25-30-year period than the more recent period, as seen in the pike and char from northern Sweden. The annual declines are best examined within species. A statistical comparison of temporal trends of HCB, Σ HCHs, and Σ PCBs among seabirds, ringed seal, and polar bear in the Canadian Arctic showed significant differences in rates of decline among species (Braune *et al.*, 2001c). This reflects different biological half-lives of the contaminants in each species as well as migratory behavior in the case of Arctic seabirds, and illustrates the need to have multi-species data when evaluating temporal trends.

One of the most rapid declines of POPs was observed by Zhulidov *et al.* (2002) who found that Σ DDTs and Σ HCHs declined 15 and 13% respectively in burbot over a six-year period in the Pechora River and at a similar rate in the Yenisey River. These rates are comparable to those for DDT and HCH isomers in char and pike in northern Sweden but much higher than in burbot in the Mackenzie River in Canada over the same period. This rapid decline may be related to reductions in the use of DDT and technical HCH during the 1980s in Russia, whereas this decline occurred earlier in Canada and Sweden due to usage bans in the early 1970s. Annual declines of PCB and β -HCH in polar bear from Svalbard and Hudson Bay during the 1990s differ. PCBs declined more rapidly, while β -HCH actually increased in Hudson Bay bears and declined in Svalbard. These temporal-trend results illustrate the need for information from multiple sites within the Arctic in assessing temporal trends of 'legacy' OCs, taking into account the history of POPs use within a given region.

Table 5-3. Annual percent declines for major OCs calculated from long-term temporal-trend data.

Species	Location	Time period	Σ DDTs	Σ PCBs	α -HCH ^a	γ -HCH	HCB ^b
<i>Freshwater fish</i>							
Pike	Northern Sweden	1967-1999	-10	-4.1	-11	-3.4	-4.8
Pike	Northern Sweden	1990-1999	-8.3	-4.1	-10		5.4
Char	Northern Sweden	1980-1999	-9.9	-6.7	-17	-15	-5.0
Char	Northern Sweden	1990-1999	-14	-6.0			-5.5
Burbot	Mackenzie River	1986-1999	-1.8	-3.2	-5.2		-2.5
Burbot	Pechora River	1988-1994	-15		-13		
Burbot	Yenisey River	1988-1994	-16		-15		
<i>Marine mammals</i>							
Ringed seals	Eastern Canadian Arctic	1975-2000	-2.8	-1.8	-2.2	-0.8	-2.1
Ringed seals	Eastern Canadian Arctic	1983-2000	-2.6	0.5	-2.2	-0.2	-1.5
Ringed seals	Western Canadian Arctic	1972-2001	-2.4	-2.8	-3.3		
Ringed seals	Western Canadian Arctic	1991-2001	-3.7	-4.4			
Beluga	Eastern Canadian Arctic	1982-1997	0.3	0.5	-1.2		3.5
Polar bear	Eastern Canadian Arctic	1968-1999	-4.1	-0.3	-1.1		-1.4
Polar bear	Eastern Canadian Arctic	1989-1999	2.7	-2.7	-11.7		-18.3
Polar bear	Svalbard	1990-1998		-6.1	-7.2 ^a		
<i>Seabirds</i>							
Black-legged kittiwake	Central Canadian Arctic Archipelago	1975-1998	-3.6	-3.9	0.5		-3.0
Black-legged kittiwake	Central Canadian Arctic Archipelago	1975-1998	-7.3	-7.5	1.8		-2.2
Northern fulmar	Central Canadian Arctic Archipelago	1975-1998	-3.2	-3.1	0.9		-2.1
Northern fulmar	Central Canadian Arctic Archipelago	1975-1998	-0.4	-2.4	3.0		0.5
Thick-billed murre	Central Canadian Arctic Archipelago	1975-1998	-2.4	-2.5	2.8		-2.6
Thick-billed murre	Central Canadian Arctic Archipelago	1975-1998	-5.1	-5.6	-1.1		-5.5

^a Σ HCH except for pike, char and ringed seals; β -HCH for polar bears at Svalbard.

^b Total Te-HxCBz except for pike, char, and ringed seals.