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Trends in Organochlorine Residue Concentrations in Ringed Seal (*Phoca hispida*) from Holman, Northwest Territories, 1972–91

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ABSTRACT. Samples of blubber for organochlorine (OC) analysis were collected from ringed seals (*Phoca hispida*) taken during subsistence hunts at Holman, Northwest Territories, in 1972, 1981, 1989, and 1991. DDT-group residue burdens did not change appreciably between 1972 and 1981, but after 1981 concentrations of *p,p'*-DDE and *p,p'*-DDT began to fall. By 1991, *p,p'*-DDE concentrations were less than half, and *p,p'*-DDT concentrations about 20%, of their 1972 values. Concentrations of polychlorinated biphenyls (PCB) fell to about one-third of their 1972 values by 1981, and then stayed constant until 1991; small but significant changes in the relative proportions of individual congeners, probably resulting from metabolism, occurred between 1981 and 1991. Concentrations of hexachlorobenzene (HCB) fell by 40 to 50% between 1981 and 1991, but those of α- and γ-hexachlorocyclohexanes (HCH) did not change. Only minor changes were seen in the distribution of other OC pesticides (oxychlordane, *cis*- and *trans*-chlordane, *cis*- and *trans*- nonachlor, mirex, heptachlor epoxide and dieldrin). Female ringed seals consistently had lower blubber DDT-group and PCB concentrations than males. These temporal trends are consistent with changes in the production and use pattern of some OCs, and with their expected environmental behaviour as inferred from their physico-chemical properties.

Key words: DDT, PCB, congeners, organochlorine, trends, ringed seal, *Phoca hispida*, western Arctic, Holman

RÉSUMÉ. En 1972, 1981, 1989 et 1991, on a prélevé des échantillons de lard de phoques annelés (*Phoca hispida*) pris durant des chasses de subsistance à Holman (Territoires du Nord-Ouest), en vue d'en analyser les organochlorés. Les charges des résidus du groupe DDT n'ont pas changé de façon appréciable entre 1972 et 1981, mais après 1981 les concentrations de *p,p'*-DDE et de *p,p'*-DDT ont commencé à chuter. En 1991, les concentrations de *p,p'*-DDE étaient de plus de 50 p. cent inférieures à leurs valeurs de 1972, et celles de *p,p'*-DDT, d'environ 20 p. cent. En 1981, les concentrations de diphényles polychlorés (PCB) avaient baissé pour atteindre environ un tiers de leurs valeurs de 1972, puis elles se sont stabilisées jusqu'en 1991; des changements faibles mais significatifs dans les proportions relatives des congénères analysés individuellement, résultant probablement du métabolisme, se sont produits entre 1981 et 1991. Les concentrations d'hexachlorobenzène (HCB) ont diminué de 40 à 50 p. cent entre 1981 et 1991, mais celles des α- et γ-hexachlorocyclohexanes (HCH) n'ont pas varié. Seuls des changements mineurs ont été observés dans la distribution d'autres pesticides organochlorés (oxychlordane, *cis*- et *trans*-chlordane, *cis*- et *trans*-nonachlore, mirex, époxyde d'heptachlore et dieldrine). Les concentrations de substances du groupe DDT et celles de PCB dans le lard des phoques annelés femelles étaient systématiquement moindres que dans celui des mâles. Ces tendances temporelles sont en harmonie avec les changements survenus dans la production et le schéma d'utilisation de certains organochlorés, ainsi qu'avec le comportement environnemental que leurs propriétés physico-chimiques laissent prévoir.

Mots clés: DDT, PCB, congénères, organochloré, tendances, phoque annelé, *Phoca hispida*, Arctique septentrional, Holman

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INTRODUCTION

Organochlorine (OC) compounds like the DDT-group of insecticides and the polychlorinated biphenyls (PCBs) are widespread environmental contaminants. They have entered Arctic marine food webs by atmospheric transport from distant sources (Barrie et al., 1992) and, probably to a lesser extent, from local use (e.g., Addison and Brodie, 1973; Bright et al., 1995). Arctic marine mammals accumulate appreciable amounts of OCs, and some of these, particularly PCBs, may present a threat to the health of the Inuit who eat their tissues (Dewailly et al., 1989, 1993). We therefore wish to know the extent of, and trends in, OC contamination of Arctic marine mammal populations, especially as these may indicate more generally the status of Arctic contamination. In a previous paper (Addison et al., 1986), we compared OC concentrations in ringed seals (*Phoca hispida*) sampled from Holman, Northwest Territories, in 1972 and in 1981. PCB

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concentrations fell during that period, apparently in response to restrictions on the manufacture and use of PCBs during the 1970s. DDT-group residue burdens seemed not to fall, however, and this suggested that there was some continuing supply of DDT to the western Arctic, probably by atmospheric transport from distant sources. In this paper, we extend our analyses of the time series of Holman seal samples to 1989 and 1991 to show long-term trends in the extent of OC contamination of this population.

A problem in analysing long time series of samples for OCs is that methods evolve with improved instrumentation. The information available from modern analyses therefore may not be directly comparable with that obtained earlier. This point is illustrated by the case of the PCBs, which were analysed in the early 1970s by packed column gas chromatography (GC) with electron capture detection (ECD) and estimated by comparing a few major peaks in an environmental sample with those in a commercial PCB mixture such as Aroclor 1254. Now, individual PCB congeners are measured, usually by high-resolution capillary column GC, and are identified and quantified by mass spectrometry (MS). Analysis of the same sample by these two approaches does not necessarily yield the same estimate of total PCBs present. In the work described here, we have avoided this difficulty in two ways: (a) by analysing some of the older samples by both procedures and establishing a "correction factor" to allow analyses to be compared, and (b) by analysing with one procedure the standard mixtures used to calibrate the other, to allow direct comparisons between the results obtained by different methods. The calculations required for these comparisons are published in detail elsewhere (Addison, 1997).

MATERIALS AND METHODS

Samples of blubber were taken from the mid-dorsal region of ringed seals killed during subsistence hunts at Holman, Northwest Territories (70°44′ N, 117°43′ W) between mid-March and early June of 1972, 1981, 1989, and 1991. Between seven and sixteen individuals of each sex were sampled, reproductive status and condition were recorded, and a sample of canine teeth was taken for ageing. Blubber samples were wrapped in solvent-washed aluminum foil, labelled and frozen (in a domestic freezer), and shipped to the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia, for analysis.

Table 1 shows the analyses that were performed on each group of samples. Samples from 1972 and 1981 were analysed by packed column GC with ECD as described previously (Addison and Smith, 1974). PCB concentrations were estimated by comparison with a standard of Aroclor 1254. Seventeen of the 1981 samples were re-analysed, and all the 1991 samples were analysed, by Axys Laboratories in Sidney, British Columbia. After extraction with dichloromethane and clean-up on Biobeads SX-3 and Florisil, samples were subjected to high-resolution GC on a 60 m × 0.25 mm i.d. column of DB-5, and components were identified and estimated by

TABLE 1. Year in which ringed seals (*Phoca hispida*) were sampled at Holman, Northwest Territories, residues analysed, and laboratories at which the analyses were undertaken.

Year sampled:	1972	1981	1989	1991
Residue:				
p,p'-DDE	BIO[a]	BIO, Axys[b]	BIO	Axys
p,p'-DDT	BIO	BIO, Axys	BIO	Axys
PCB (Aroclor 1254)	BIO	BIO, Axys		
PCB (congeners)		Axys		Axys
HCB		Axys	BIO	Axys
α-HCH		Axys	BIO	Axys
γ-HCH		Axys	BIO	Axys
Miscellaneous OCs[c]		Axys		Axys

[a] Bedford Institute of Oceanography, Dartmouth, Nova Scotia
[b] Axys Analytical Laboratories, Sidney, British Columbia
[c] Oxychlordane, *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, mirex, heptachlor epoxide, and dieldrin

low-resolution MS (LRMS) in a Finnigan INCOS 50 MS operated at unit mass resolution in the multiple ion detection mode. Samples from 1989 were analysed at BIO by capillary column GC with ECD and with occasional structure confirmation by LRMS (Addison et al., 1986). Standard mixtures of 13 OC pesticides used at BIO for the 1989 analyses were analysed by capillary column GC-MS by Axys. Details of the comparisons between analyses performed by different laboratories and at different times are given by Addison (1997).

Results of the re-analysis by Axys of 17 samples from 1981 previously analysed at BIO are shown in Table 2. Comparison by paired *t*-test showed that lipid content differed slightly but significantly between the two analyses, probably because of differences in the extraction methods used. There were no significant differences between the two laboratories' analyses for *p,p*'-DDE and *p,p*'-DDT. Analysis by Axys of the standard solutions used at BIO supported this conclusion: for 12 OCs reported by both laboratories, nominal BIO concentrations were within 11% of concentrations measured by Axys, which is well within the range expected for independent analyses of an OC sample (e.g., Topping and Holden, 1978). The only exception was α-hexachlorocyclohexane (α-HCH), for which the difference between nominal and measured concentrations was 25%, and the BIO analyses of α-HCH (in 1989 only) were corrected for comparison with Axys's analyses of 1981 and 1991 samples. Data are presented in detail in Addison (1997).

We conclude from these data that analyses of *p,p*'-DDE and *p,p*'-DDT concentrations from 1972 to 1991 are directly comparable, as are analyses of HCB, γ-HCH and α-HCH (after correction of 1989 data) from 1981 to 1991.

PCBs in the 1981 samples were measured first as Aroclor 1254 by BIO and later as individual congeners in 17 samples by Axys. Summing the PCB congeners led to an estimate of Aroclor 1254 which differed from that derived from the "external standard" approach used by BIO. Regression of the Axys estimates of Aroclor 1254 on the data of BIO for the

TABLE 2. Comparison by paired *t*-test of analyses by Axys and BIO laboratories of lipid content and *p,p'*-DDE and *p,p'*-DDT concentrations in 17 samples of blubber from 1981 Holman ringed seals (*Phoca hispida*). Data are given as mean ± SD.

	Axys	BIO	*t*	*p*
Lipid (% wet wt.)	89.6 ± 3.23	97.6 ± 3.47	– 7.24	< 0.01
p,p'-DDE (ng/g lipid)	344 ± 265	273 ± 188	1.22	0.24
p,p'-DDT (ng/g lipid)	272 ± 157	308 ± 249	– 1.27	0.22

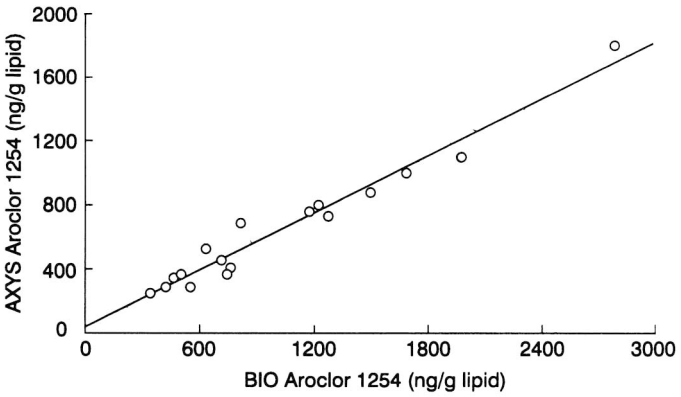

FIG. 1. Regression of Aroclor 1254 concentrations estimated by summing PCB congeners (Axys) on concentrations calculated from external standards of Aroclor 1254 (BIO) as described in text, in 17 blubber samples of ringed seals (*Phoca hispida*) from Holman, NWT, 1981. Regression has the form: $y = 0.594\ x + 39.7$; $r = 0.98$

same samples showed that the Axys procedure underestimated Aroclor 1254 by about 40% (Fig. 1). To compare the 1991 Axys analyses with the earlier BIO analyses, the 1991 data were adjusted according to the regression equation (Addison, 1997). We emphasize that this adjustment was made simply to allow comparisons over the time series: it does not imply the true PCB concentrations in the samples.

Data were analysed statistically using "Statistica" software from Statsoft, Tulsa, Oklahoma. Concentrations were analysed by *t*-test, ANOVA, and simple linear regression, as appropriate. Percentage compositions (of *p,p'*-DDE as a percentage of DDT-group residues and of PCB congener distribution as a percentage of total PCB) were analysed after arcsine transformation.

RESULTS AND DISCUSSION

DDT-group Concentrations, 1972–91

Table 3 shows biological variables and DDT-group concentrations in female and male seals (respectively) from 1972 to 1991. In both sexes, *p,p'*-DDE concentrations were highest in 1972 but had declined by 1981 to about half their 1972 value. However, as we noted previously (Addison et al., 1986), the decline in residue *concentrations* does not necessarily imply a decline in residue *burdens,* as the 1981 samples were in better condition (i.e., had thicker blubber) than those taken in 1972; the increased blubber thickness would in effect "dilute" the 1981 concentrations. If residue concentrations were increased by 30% (to reflect the difference in blubber thickness, and assuming the blubber mass to approximate a right cylinder: Addison et al., 1986), there would be no significant differences in *p,p'*-DDT concentrations between the 1972 and 1981 samples of either sex; *p,p'*-DDE and (*p,p'*-DDE + *p,p'*-DDT) concentrations would differ significantly between 1972 and 1981 in females ($p < 0.05$), but not in males. Blubber thickness did not differ between the 1972 samples and the 1989 and 1991 samples; nonetheless, *p,p'*-DDE concentrations in the two later samples were also lower than those taken in 1972, though not significantly so in the case of the 1989 females. Concentrations of *p,p'*-DDT thus continued to decline after 1981, though in some comparisons the small sample size (e.g., 1991 females) or the wide variance caused by the dependence of residue concentrations on age in males (Addison, 1989) led to nonsignificant differences between years. There were no differences in *p,p'*-DDE or *p,p'*-DDT concentration in either sex between 1989 and 1991.

A consequence of the declining concentrations of *p,p'*-DDT after 1981 is that the proportion of the DDT-group represented by *p,p'*-DDE increased in 1989 and 1991. This is sometimes considered to indicate the "age" of the residues, as *p,p'*-DDT is slowly and irreversibly converted to *p,p'*-DDE (Addison et al., 1973; Aguilar, 1984). The increase in the relative proportion of *p,p'*-DDE is consistent with a slower rate of supply of *p,p'*-DDT to the western Arctic ecosystem after 1981.

As we have noted previously (Addison and Smith, 1974), *p,p'*-DDE and *p,p'*-DDT concentrations were consistently and usually significantly lower in females than in males (details in Addison, 1997). Furthermore, their concentrations were usually independent of age in females, but increased with age in males, as has been observed elsewhere (reviewed by Addison, 1989).

We conclude that DDT-group burdens in Holman ringed seals did not fall consistently between 1972 and 1981, but began to decline slowly between 1981 and 1989, probably because of reductions in the supply of *p,p'*-DDT. By 1991, *p,p'*-DDE concentrations had fallen to about 50% of their 1972 value, and *p,p'*-DDT concentrations to about 20%.

DDT-group concentrations did not change appreciably between the mid-1970s and early 1980s in other marine mammals from the Canadian Arctic. Ringed seals from Admiralty Inlet sampled in 1983 contained DDT concentrations apparently similar to those in samples taken there in 1975–76 (Muir et al., 1988), though the authors stated that sample sizes were too small to allow statistical comparisons. In polar bears from the eastern Arctic and western Hudson Bay, which prey on ringed seals among other food, DDT-group concentrations did not decline between

TABLE 3. Age (y), blubber thickness (cm) and DDT-group residue concentrations (ng/g wet wt.) in ringed seal (*Phoca hispida*) from Holman, Northwest Territories, 1972–91. Data are given as mean ± SD. Within each sex, data followed by the same letter do not differ significantly between years ($p > 0.05$) using one-way ANOVA.

	1972	1981	1989	1991
Females:	(n = 13)	(n = 15)	(n = 14)	(n = 7)
Age	10.9 ± 8.9 a	9.6 ± 7.2 a	8.1 ± 4.5 a	14.3 ± 7.3 a
Blubber thickness	3.59 ± 0.52 a*	4.55 ± 0.73 b	3.56 ± 1.42 a	4.24 ± 0.94 a,b
p,p'-DDE	278 ± 97.6 a	135 ± 97.8 b	192 ± 55.9 a,b	141 ± 52.5 b
p,p'-DDT	297 ± 137 a	183 ± 122 b	81.2 ± 28.3 c	61.2 ± 19.6 b,c
p,p'-DDE as % (*p,p'*-DDE + *p,p'*-DDT	49.5 ± 14.4 a	41.0 ± 15.6a	70.5 ± 9.3 b	69.0 ± 7.93 a,b
Males:	(n = 15)	(n = 16)	(n = 16)	(n = 11)
Age	14.5 ± 9.0 a	8.9 ± 5.4 b	8.6 ± 6.8 b	12.3 ± 3.6 a,b
Blubber thickness	3.20 ± 0.72 a	4.48 ± 0.68 b	2.90 ± 1.25 a	3.45 ± 0.90 a
p,p'-DDE	729 ± 358 a	393 ± 320 b	386 ± 325 b	307 ± 119 b
p,p'-DDT	526 ± 235 a	382 ± 99 a,b	183 ± 212 b,c	110 ± 43.7 c
p,p'-DDE as % (*p,p'*-DDE + *p,p'*-DDT)	57.0 ± 9.58 a	51.5 ± 11.8 a	70.8 ± 9.61 b	73.4 ± 5.29 b

* n = 8

1969 and 1983–84 (Norstrom et al., 1988). However, as the decline in DDT-group concentrations in ringed seals occurred after 1981, there would presumably have been some time lag before that decline was reflected in polar bear residue concentrations.

This temporal trend differs from that in northwest Atlantic seals, where DDT-group concentrations in Sable Island grey seals fell by about 60% between 1976 and 1982 (Addison et al., 1984). In Gulf of St. Lawrence harp seals, DDT-group concentrations fell by about 80% between 1971 and 1982 (Addison et al., 1984). (Somewhat slower declines in DDT-group concentrations were also observed in male beluga whales from the Gulf of St. Lawrence: Muir et al., 1996.) These declines probably reflect effects of the restrictions on DDT use in North America imposed during the 1970s (Dunlap, 1981; Barrie et al., 1992). The absence of a similar decline in Holman ringed seals between 1972 and 1981 may indicate continued use of DDT in the Far East during this period (Addison et al., 1986). The more recent data (1989 and 1991 samples) suggest that this usage may have declined during the 1980s, as *p,p'*-DDT concentrations and the ratio of *p,p'*-DDT to *p,p'*-DDE declined after 1981 (Table 3). Unfortunately, it is very difficult to obtain reliable information about worldwide DDT use during this period to support this conclusion.

In juvenile ringed seals from the Baltic, total DDT-group concentrations declined by about 90% between the early 1970s and the 1980s (Blomkvist et al., 1992), probably in response to restrictions on DDT use in western Europe. Although only age was controlled among the biological variables known to affect OC residue concentrations in seals (Addison, 1989), unless blubber thickness differed widely between the samples, this difference is probably large enough to reflect real changes in environmental contamination. DDT-group concentrations in California sea lions in the late 1980s had fallen to about 1% of their 1970 value; this decline was attributed to control of local DDT emissions (Lieberg-Clark et al., 1995). Again, there was apparently little attempt to control biological variables known to affect residue concentrations. However, in striped dolphin from the western North Pacific, DDT-group concentrations in adult males of similar age and size (but whose blubber thickness was not reported) did not decline between 1978–79 and 1986 (Loganathan et al., 1990).

PCB Concentrations, 1972–91

PCB concentrations estimated as Aroclor 1254 fell significantly between 1972 and 1981, as noted previously (Addison et al., 1986); even after correcting for the difference in blubber thickness between the sets of samples, as described above for the DDT-group, this difference was statistically significant. Between 1981 and 1991, there was no further significant decline in PCB concentrations as Aroclor 1254 (Table 4). If the 1981 concentrations were increased by 30% (to allow for these samples being about 30% fatter, thereby "diluting" OC burdens), there was still no significant decline by 1991 in females, but concentrations in males declined significantly ($p < 0.05$).

PCB concentrations in females were significantly lower than those in males in all three sets of samples (1972, 1981, and 1989: Addison, 1997).

This decline in total PCB residues (as Aroclor 1254) is consistent with the changes in patterns of PCB manufacture and use during the 1970s and with changes in PCB concentrations seen in other seal populations. PCB manufacture effectively stopped during the mid-1970s (de Voogt and Brinkman, 1989). Although PCBs would have been released for some time after that, it is reasonable to expect that environmental burdens should have begun to decline some time during the 1970s. Figure 2 shows a comparison of total PCB production in OECD countries (data from de Voogt and Brinkman, 1989) and PCB concentrations in Holman female ringed seals, which suggests that PCB concentrations in the Holman seals

TABLE 4. PCB concentrations (as Aroclor 1254, ng/g wet wt.) in blubber of ringed seal (*Phoca hispida*) from Holman, Northwest Territories, 1972–91. Data are given as mean ± SD (no. of samples). Within each sex, data followed by the same letter do not differ significantly between years ($p > 0.05$) by one-way ANOVA.

Year:	1972	1981	1991
Females	1846 ± 827 a (9)	557 ± 256 b (15)	510 ± 180 b (7)
Males	3830 ± 1283 a (15)	1279 ± 751 b (16)	962 ± 255 b (11)

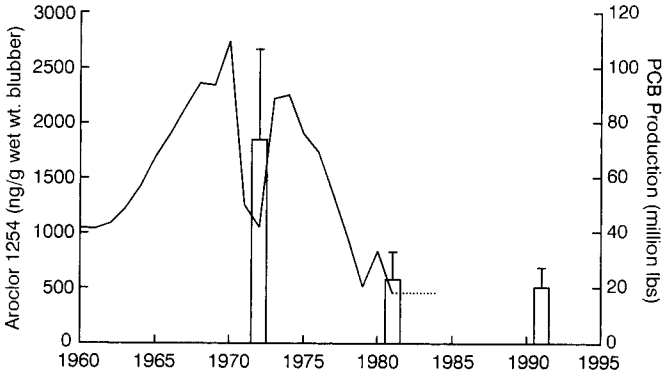

FIG. 2. Comparison of PCB concentrations (ng/g wet wt. blubber of Aroclor 1254) in ringed seal *(Phoca hispida)* from Holman NWT (bars) with annual PCB manufacture (10^6 lb/y) in OECD countries, 1960–84 (continuous line). Data for 1981–84 are annual means calculated from cumulative production over this interval.

generally follow the pattern of PCB production. The rate of decline of PCB concentrations in these seals (about a 65% reduction between 1972 and 1981) is similar to that in Gulf of St. Lawrence harp seals (about a 55% reduction between 1971 and 1982; Addison et al., 1984). The simplest interpretation of these data is that PCB concentrations in both seal populations reflect the same source function, a global reduction of PCB emissions starting in the early 1970s.

In female ringed seals of Admiralty Inlet, total PCB concentrations declined by about 50% between 1975–76 and 1983 (Muir et al., 1988). (No statistical analyses were performed on these data.) However, in polar bears from the central Arctic, PCB concentrations actually increased between 1969 and 1983–84 (Norstrom et al., 1988). In juvenile Baltic ringed seals (Blomkvist et al., 1992), PCB concentrations declined between the early 1970s and the 1980s, though not as rapidly as did DDT-group concentrations in this population. In high trophic level biota from other Northern Hemisphere sites, such as lake trout from the upper Great Lakes (DeVault et al., 1986) and beluga whales from the Gulf of St. Lawrence (Muir et al., 1996), PCB concentrations have also declined since the 1970s. However, Pacific striped dolphin showed no declines in PCB concentrations between 1978–79 and 1986 (Loganathan et al., 1990).

The relative proportions of PCB congeners changed between 1981 and 1991 (Fig. 3). Among the major congeners present (arbitrarily defined as compounds each of which

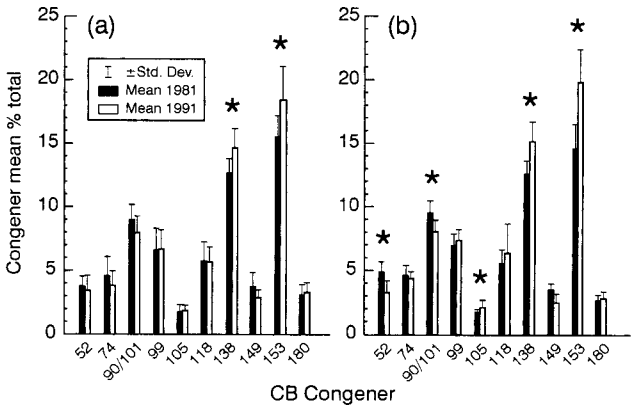

FIG. 3. Comparison of the distribution of major chlorobiphenyl congeners (compounds each of which accounts for > 3% total) in female (a) and male (b) Holman ringed seals (*Phoca hispida*) in 1981 (solid bars) and 1991 (clear bars). Data as congener % total PCBs; asterisks indicate differences between 1981 and 1991 significant at $p < 0.05$.

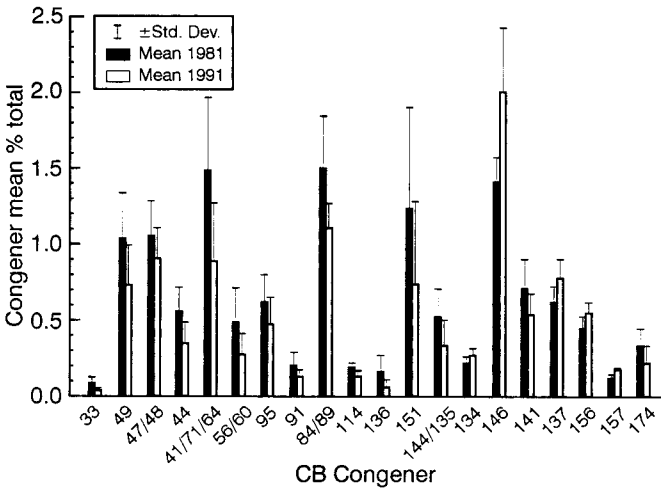

FIG. 4. Comparison of the distribution of minor chlorobiphenyl congeners (compounds each of which accounts for < 3% total) which changed significantly ($p < 0.05$) in either male or female Holman ringed seals (*Phoca hispida*) between 1981 (solid bars) and 1991 (clear bars). Data as congener % total PCBs.

represented more than 3% of the total) the proportions of PCB 138 and PCB 153 (numbered as by Ballschmiter and Zell, 1980) increased slightly, though significantly ($p < 0.05$), in both sexes. In males, the relative proportions of PCB 52 and PCB 90 declined and that of PCB 105 increased. Among the minor congeners (each representing less than 3% of the total) the proportions of tetra- and pentachloro substituted compounds usually declined significantly between 1981 and 1991; some hexachloro substituted compounds declined and some increased, and one heptachloro substituted compound increased (Fig. 4). The relative proportions of compounds which had one or more pairs of vicinal unsubstituted positions (PCBs 33, 52, 49, 47 and/or 48, 44, 41, 56 and/or 60, 95, 91, 84 and/or 89, 90 and/or 101, 114, 136, 151, 144 and/or 135, 149 and 141) declined between 1981 and 1991. However, not all compounds with vicinally unsubstituted positions declined; the relative proportions of PCBs 105, 134, 137, 138,

156, and 157 (all of which have this structure) increased between 1981 and 1991. Other compounds whose proportions increased between 1981 and 1991 included PCB 146 and PCB 153, which have no vicinally unsubstituted positions.

The data shown in Table 4 suggest that the decline in total PCB concentrations in Holman ringed seal blubber during the 1970s was due to changes in PCB inputs to the environment. However, some of the changes in congener distribution after 1981 (Figs. 3 and 4) can be attributed to metabolic degradation. Metabolism of PCBs is believed to proceed at least partly by hydroxylation, which depends on the availability of vicinal unsubstituted positions for epoxidation (e.g., Safe, 1989). The preponderance of vicinally unsubstituted compounds among the congeners whose relative proportions declined between 1981 and 1991 suggests that these changes may result from metabolic degradation (via hydroxylation) rather than from changing inputs of PCBs.

HCB and HCH, 1981–91

Between 1981 and 1991, concentrations of α-HCH and γ-HCH usually did not differ significantly. However, concentrations of hexachlorobenzene (HCB) declined significantly by 1989 to about 50% of their 1981 values in both male and female seals. Data are shown in Table 5. Unlike the DDT-group and the PCBs, the HCBs showed no significant differences in concentration between the sexes in any of the sample sets analysed (1981, 1989, and 1991; Addison, 1997).

Some information is available about the production and use of these materials. Rapaport and Eisenreich (1988) showed that total United States chlorobenzene production reached a peak around 1965–70 and then declined until the early 1980s. The decline in HCB concentrations in Holman ringed seals during the 1980s would be consistent with a similar trend in the HCB source (from the United States or elsewhere) to the western Arctic. However, HCB may also be formed as a by-product of other industrial processes that involve electrolysis using carbon electrodes and chlorine (Mumma and Lawless, 1975), and these may not necessarily follow trends in chlorobenzene manufacture.

Total chlorobenzenes (including HCB) concentrations did not change in Admiralty Inlet ringed seals between 1975–76 and 1983 (Muir et al., 1988).

The behaviour of HCHs in the Arctic is probably better understood than that of the other OCs found in Arctic ecosystems. HCH concentrations in air over the Bering and Chukchi Seas and over the Canadian Basin declined by more than 50% between 1979 and 1993 (Jantunen and Bidleman, 1995), probably in response to reductions in global HCH use over this period (Li et al., 1998). However, water concentrations, which were oversaturated, have declined much more slowly. Between 1988 and 1993, air concentration over the Bering and Chukchi Seas fell enough for the water to begin to "outgas" α-HCH, although γ-HCH continued to partition (slowly) into the water (Jantunen and Bidleman, 1995). The main route for OC accumulation in marine mammals is via food, so HCH concentrations in the Holman ringed seals are expected to reflect trends in water concentrations after an appropriate lag for accumulation in the food web. Since the "signal" of a sharp decline in HCH use in the early 1980s had not been detected in seal HCH concentrations in 1991 (Fig. 5), we conclude that this lag must be at least a decade, for reasons we discuss further below.

TABLE 5. Concentrations (ng/g lipid) of HCB, α-HCH and γ-HCH in blubber of ringed seal (*Phoca hispida*) from Holman, Northwest Territories, 1981–91. Data are given as mean ± SD (no. of samples in which residues were detected). Data followed by the same letter do not differ significantly between years ($p > 0.05$) using one-way ANOVA.

Year:	1981	1989	1991
Females:			
HCB	38.9 ± 9.9 a (7)	18.9 ± 9.7 b (14)	19.3 ± 6.1 b (7)
α-HCH	146 ± 65 a (7)	222 ± 226 a (14)	183 ± 58 a (7)
γ-HCH	6.63 ± 2.50 a (4)	23.3 a (1)	7.10 ± 5.60 a (7)
Males:			
HCB	37.1 ± 14.4 a (11)	22.4 ± 16.1 b (16)	25.8 ± 9.8 a,b (11)
α-HCH	187 ± 55.1 a (11)	215 ± 155 a (16)	199 ± 108 a (11)
γ-HCH	13.0 ± 5.90 a (8)	18.9 ± 5.80 a (4)	7.8 ± 6.80 a (11)

Ratios of α-HCH to γ-HCH concentrations were usually around 25:1 in both 1981 and 1991 samples, except in 1981 males, where it was approximately 15:1 (Table 5). This ratio is well above the ratio of 4–7:1 observed in surface waters of the Bering and Chukchi Seas (Jantunen and Bidleman, 1995) and presumably indicates some selective degradation of γ-HCH in the Arctic food web.

In ringed seals from Admiralty Inlet, HCH concentrations did not change between 1975–76 and 1983 (Muir et al., 1988), which is consistent with the discussion above. (No information about α-HCH:γ-HCH ratios was presented.) However, in striped dolphin from the western North Pacific, both total HCH and HCB concentrations fell significantly between 1978–79 and 1986 (Loganathan et al., 1990).

Other OC Residues, 1981–91

High-resolution GC-MS of 1981 and 1991 samples yielded information about a range of other OC compounds, most of which were present at the low ng/g range (Table 6). Concentrations in male samples from 1981 were usually higher than in 1991, though the difference was significant only in the cases of *cis*- and *trans*-nonachlor; no difference between 1981 and 1991 concentrations of these residues was seen in females. Concentrations of oxychlordane, heptachlor epoxide, and dieldrin were

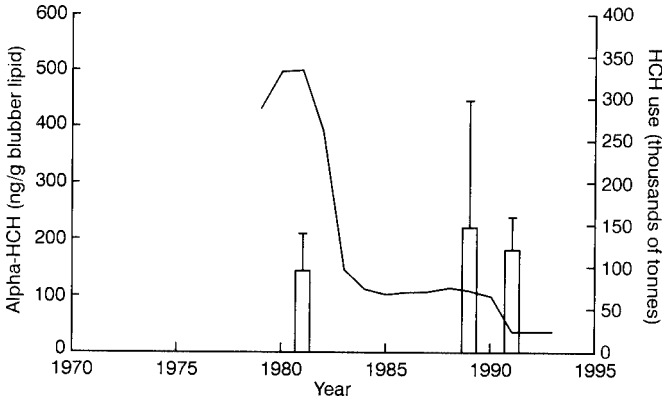

FIG. 5. Comparison of α-HCH concentrations (ng/g blubber lipid) in female ringed seal *(Phoca hispida)* from Holman, NWT, (bars) with annual world HCH usage (10^3 tonnes/y) as described in text (continuous line).

TABLE 6. Concentrations (ng/g lipid) of other OC pesticides in blubber of ringed seal (*Phoca hispida*) from Holman, Northwest Territories, 1981 and 1991. Data are given as mean ± SD (no. of samples in which residues were detected).

	Females		Males	
	1981	1991	1981	1991
Oxychlordane	86.8 ± 41.3 (6)	87.9 ± 16.2 (7)	188 ± 92.5 (10)	169 ± 74.5 (11)
trans-Chlordane	3.19 ± 1.80 (5)	2.58 ± 1.28 (5)	7.24 ± 5.14 (8)	3.62 ± 2.13 (6)
cis-Chlordane	27.2 ± 25.9 (6)	37.3 ± 22.0 (7)	69.0 ± 67.1 (10)	61.0 ± 24.9 (11)
trans-Nonachlor	109 ± 36.0 (6)	93.0 ± 75.9 (7)	314 ± 293 (10)	100 ± 40.9* (10)
cis-Nonachlor	18.0 ± 11.8 (6)	12.1 ± 6.94 (7)	46.5 ± 37.3 (10)	18.1 ± 8.29 * (11)
Mirex	5.20 (1)	5.18 ± 2.92 (5)	12.4 ± 13.4 (4)	5.20 ± 1.55 (8)
Heptachlor epoxide	23.3 ± 9.76 (6)	29.0 ± 5.35 (7)	47.1 ± 21.2 (10)	43.7 ± 13.0 (11)
Dieldrin	46.6 ± 14.8 (6)	37.0 ± 9.00 (7)	87.6 ± 39.9 (10)	64.0 ± 29.5 (11)

* Significantly different from 1981 concentration in males ($p < 0.05$)

significantly lower ($p < 0.01$) in females than in males (both years); concentrations of other OCs did not differ between sexes. The only data comparable to these are for the ringed seals of Admiralty Inlet (Muir et al., 1988); total chlordanes in those samples were at concentrations generally similar to the sum of chlordane components listed in Table 6, and dieldrin concentrations in the two sample suites were also similar.

OVERVIEW AND CONCLUSIONS

Analyses of OC residues in the Holman ringed seal population over approximately 20 years show that concentrations of some residues are falling, though slowly. The absence of any decline in DDT-group concentrations between 1972 and 1981 differs from the trend seen in northwest Atlantic seal populations and suggests a different source for DDT entering the western Arctic from that in the northwest Atlantic ecosystem. Without reliable information about the production or use of DDT, it is difficult to identify this source; however, our data from 1989 and 1991 suggest that the supply of DDT to the western Arctic may have begun to decline during the 1980s. PCB concentrations in Holman ringed seals declined between 1972 and 1981 at about the same rate as that seen in East Coast seals (presumably reflecting the global restrictions on PCB manufacture and use imposed in the early 1970s) but total concentrations fell no further during the 1980s. Any future decline in PCB concentrations in these animals will probably depend on slow metabolic degradation in arctic biota, rather than on changing PCB inputs to the Arctic. HCH concentrations did not fall between 1981 and 1991, in spite of a dramatic reduction in HCH use, which was reflected in falling atmospheric HCH concentrations during the 1980s. In contrast, HCB concentrations fell appreciably over this interval.

Why did PCB concentrations in Holman ringed seals apparently respond rapidly (in well under ten years) to changes in PCB emissions, while HCH concentrations seem to have responded much more slowly? The answer may lie in the physico-chemical properties of these compounds which control their environmental behaviour, and in the relative concentrations of these chemicals in the Arctic. First, HCH concentrations in Arctic water were oversaturated until 1988–93 (Jantunen and Bidleman, 1995). The entry of HCH into the Arctic food web probably depends initially on adsorption to particulate material, which in turn depends on an equilibrium between water and particulate material concentrations, indicated by some derivative of the octanol/water partition coefficient, $K_{o/w}$. Thus, the partitioning of HCH into the food web would not fall until water concentrations were reduced, i.e., between 1988 and 1993. PCBs have a much lower water solubility than HCH, but a much higher Henry's Law constant (the equilibrium ratio of air-to-water concentrations) and a much higher $K_{o/w}$ (Mackay, 1982; Hawker and Connell, 1988; Barrie et al., 1992). Consequently, PCBs will be adsorbed much more readily to particulate material than HCHs, and so the marine food web may respond more rapidly to changes in PCB emissions to the atmosphere. To put it another way, since HCH is relatively soluble in water, the water "compartment" may delay changes in atmospheric HCH from reaching marine food webs.

Both the DDT-group and HCB would probably behave more like PCBs than the HCHs because of their low water solubilities (e.g., Chiou et al., 1982) and high $K_{o/w}$, and so the slow decline in DDT-group (and especially *p,p'*-DDT) concentrations in the Holman seals probably indicates a slow reduction in the DDT supply to the western Arctic beginning during the early 1980s. The more rapid decline in HCB concentrations in seals during the 1980s probably indicates a reduction in HCB inputs to the Arctic during the late 1970s and early 1980s.

If these interpretations of the trends in OC concentrations are correct, then we can predict the following:

a) The "outgassing" of α-HCH from Arctic waters, which began between 1988 and 1993, should be reflected in a decline in α-HCH concentrations in seals, beginning probably in the mid-1990s. As γ-HCH continued to partition into seawater from the atmosphere until 1993, its concentration in seals should not decline as soon as that of α-HCH, though this projected trend may be balanced by a more rapid selective metabolism of γ-HCH.
b) Since recent trends in PCB concentrations in seals seem to reflect slow metabolism rather than changes in the supply of PCBs to the Arctic, we should expect only small changes in total PCB burdens in seals, and only small qualitative changes in the relative proportions of individual congeners.
c) If reliable production-and-use data for *p,p'*-DDT and HCB become available, they should show a reduction in global emissions beginning around the early 1980s.

These data and conclusions have implications for monitoring programmes in the Arctic. As seals are relatively long-lived and occupy high trophic levels, we should expect that trends in tissue OC concentrations will be detectable over periods of years to decades, rather than from year to year. Since a long time-series of Holman ringed seal samples already exists (including archived samples), it is attractive to continue sampling at intervals of five years or so for OC analysis. Such a sampling protocol should allow us to detect expected responses to signals, such as the decline in HCH usage during the early 1980s and would provide continued information about changes in human exposure to these chemicals.

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