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PCBs and organochlorine pesticides in krill, birds and water from Antarctica

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Abstract—The concentration levels of various congeners of PCBs and organochlorine pesticides were determined in krill, bird (emperor penguin) feathers and polynya water from different places around Dakshin Gangotri, Antarctica. t-HCH (α + γ isomers) was found to be present in considerable amounts in krill (141.3–164.3 pg g^{-1}) but much less in penguin feathers (103.6–112.8 pg g^{-1}) and polynya water (85.6–90.7 pg l^{-1}). t-DDT (pp′-DDT + op′-DDT + pp′-DDE + op′-DDE) was detected in the range 31.1–44.4 pg g^{-1} in krill, 30.8–35.7 pg g^{-1} in the feathers and 24.8–26.5 pg l^{-1} in polynya water. A few congeners of PCBs were identified and quantified in all the samples, e.g. CB-101, CB-136, CB-151, CB-118, CB-153, CB-138. The concentration levels of PCBs in different samples are in the range 146.9–166.2 pg g^{-1} in krill, 105.8–113.6 pg g^{-1} in penguin feathers, and 96.8–103.8 pg l^{-1} in polynya water.

INTRODUCTION

Several attempts have been made by different scientists to identify and quantify the residues of highly persistent organochlorine compounds in the antarctic atmosphere and hydrosphere. Sladen *et al.* (1966) and George and Frear (1966) were the first to report the presence of chlorinated hydrocarbons in wildlife of the Antarctic. Subsequently, Peterle (1969), Risebrough and Carmignani (1972), Risebrough (1977), Lukowski (1978), Hidaka and Tatsukawa (1981) and Norheim *et al.* (1982) detected these substances in varying quantities in birds and seals from antarctica. Moreover, Tanabe *et al.* (1982, 1983) carried out extensive studies on the presence of these organochlorines in the antarctic atmosphere and biosphere, eventually bringing a clear understanding of the transport phenomenon of these compounds into the antarctic. The concentration levels of various organochlorine pesticides in sediments from different lakes in the Schirmachen Oasis, Antarctica, near Dakshin Gangotri (Fig. 1), an Indian research station, have been reported (Sarkar and Fondekar, 1990; Sarkar *et al.*, 1994). The present study deals with the identification and quantification of various chlorinated hydrocarbons in krill, penguin feathers, and water from antarctica.

MATERIALS AND METHODS

Samples were collected from various places on Antarctica, near Dakshin Gangotri (S 70°05′; E 12°00′) (Fig. 1), during the 7th Indian scientific expedition to Antarctica

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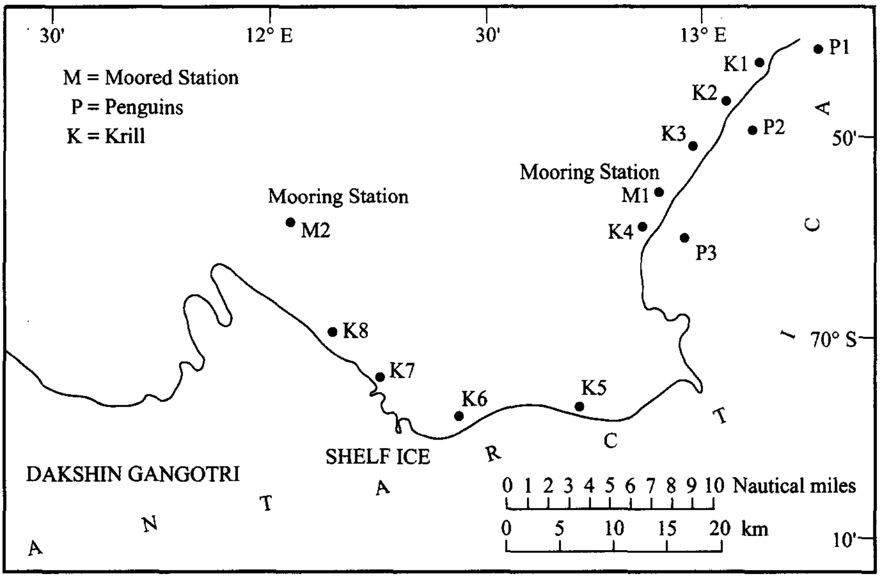

Fig. 1. Location of sample collection sites in Antarctica. M: Moored station; P: penguins; K: krill.

(December 1987–January 1988). A large number of samples of krill were collected by towing nets from polynya water to evaluate the abundance of various organochlorine compounds in the biota as well as the water. The krill were about 2–8 cm in size. Emperor penguin feathers were collected in large numbers (100–150) from different places around Dakshin Gangotri when they were moulting. The reason for collection of bird feathers was to observe the levels of contamination of various organochlorine compounds in Antarctic animals without destroying the ecosystem. Penguins are known to moult every 2 years, and the feathers can be expected to provide a measure of accumulation of pesticide. The bird feathers were dried in the sun and cut into small pieces for further processing. All samples were deep-frozen immediately.

EXTRACTION FROM BIOTA

Organochlorine compounds were extracted from krill and bird feathers by soxhlet extraction using double distilled hexane for about 10 h. Five to ten grams of each of the samples were thoroughly mixed with purified anhydrous sodium sulfate in order to remove water from the wet samples. The percentage of recovery was determined using an internal standard (CB-88). The recovery was found to be quite satisfactory, within the range 95 ± 5%. Each sample was extracted in triplicate in order to determine the standard deviation of the analysis. The volume of the extract was reduced by evaporation over a hot water bath using a Kuderna Danish concentrator. The concentrated extracts were treated with activated copper powder to remove sulfur and then subjected to alumina clean up followed by silica column chromatography using the micro-column technique (Sarkar *et al.*, 1994). The lipid contents of all the samples were determined prior to the purification step. Organochlorine pesticides were separated from the non-polar organochlorine compounds like PCBs by fractionation through silica column chromatography.

EXTRACTION FROM WATER

Organochlorine pollutants were extracted from the Antarctic water by deploying a mooring instrument, Seastar® *in situ* sampler fitted with a XAD-2 resin column in the polynya. The XAD-2 macroreticular resin column acts as an extractor for organochlorine compounds from the water (Sarkar and Sen Gupta, 1989). The Seastar® *in situ* sampler is designed to pump large volumes of water through an extraction column to concentrate chlorinated hydrocarbons. It provides accurate measurement of the volume of water extracted. It is a self-contained instrument comprised of a small pump, a flow meter, a micro-processor controller and a pack of 20 D cell batteries (Sarkar and Sen Gupta, 1989). A window provides a liquid crystal display for the total volume of water which has passed through the column. The instrument was moored about 20 m below the surface and kept on for about 5 days to allow an adequate volume of water (1000 l) to pass through the column. Prior to the deployment of the instrument, the efficiency of the macroreticular XAD-2 resin column was determined (Table 1).

Immediately after sampling, the column was removed and kept in deep freeze and subsequently eluted with distilled methanol followed by dichloromethane and hexane. The extracts were then transferred to hexane. The solvent extracts were evaporated to 1 ml using a Kuderna Danish concentrator over a hot water bath. The concentrated extracts were purified, as described earlier, for analysis (Sarkar *et al.*, 1994). The purified samples were then analysed by gas chromatography (Perkin Elmer 8700) coupled with an electron capture detector (^{63}Ni) and capillary column (SE-54, 60 m × 0.25 mm). The temperature of the oven was programmed as follows: initial temperature = 110°C for 2 min, raised to 180°C at the rate of 10°C per min and held for 8 min, raised to 220°C at the rate of 4°C per min and held for 5 min, and finally raised to 270°C at the rate of 4°C per min and held for 15 min. The temperatures of the column, injector and detector were fixed at 200°C, 250°C and 340°C, respectively. Argon with 5% methane was used both as the carrier and make-up gas. The gas pressure was maintained at 25 psi. Chlorinated hydrocarbons were identified and quantified with respect to standards obtained from Supelco, Switzerland. The percentage of recovery was determined using reference samples of tissues of copepod homogenate and mussel homogenate obtained from IAEA, Monaco; the results were quite satisfactory, within the range 95.5 ± 4.5%.

The detection limits of pesticides in 1 μl injections under normal operational conditions of the GC-ECD system were 0.25 to 0.50 pg for α- and γ-HCH, 1.5–3.0 pg for pp′-DDT, op′-

Table 1. Documentation of the extraction of chlorinated hydrocarbons from seawater by XAD-2 resin column in the laboratory using Seastar in situ *sampler*

Compound	Retention(%) ($x \pm$s.d., $n = 3$)	Recovery(%) ($x \pm$s.d., $n = 3$)	Column efficiency(%) ($x \pm$s.d., $n = 3$)
pp′-DDT	95.4±0.5	85.2±10.5	81.28±10.4
op′-DDT	96.6±0.4	80.3±8.5	86.14±8.5
pp′-DDE	92.9±0.5	88.9±1.5	82.59±1.8
op′-DDE	96.5±0.3	89.5±1.9	86.37±2.1
γ-HCH	100±2.1	100±2.5	100±4.6
α-HCH	100±2.4	100±2.3	100±4.7
PCB-88	98.5±2.1	98.4±2.4	98.00±4.5

DDT, pp′-DDE and op′-DDE. The detection limits for PCBs determined with respect to each individual congener of PCBs were in the range 1.2–1.5 pg.

RESULTS AND DISCUSSION

The concentration levels of various congeners of polychlorinated biphenyls and organochlorine pesticides such as HCHs and DDTs (Table 2 and Table 3) clearly indicate the level of contamination of various chlorinated hydrocarbons in krill, penguin feathers and polynya water. The concentrations of total-HCH are much more pronounced than that of total-DDT in almost all the samples, particularly in the krill. Of the organochlorine pesticides detected, t-HCH was found to be the highest in krill (mean conc. 153.95 pg g^{-1} dry wt) followed by penguin feathers (mean conc. 108.26 pg g^{-1} dry wt) and polynya water (mean conc. 90.15 pg l^{-1}). In the case of t-DDT, the mean concentration levels are 37.08 pg g^{-1} in krill; 33.1 pg g^{-1} in penguin feathers and 25.65 pg l^{-1} in water. PCBs are present in considerable amounts in all the samples, krill (mean conc. 152.55 pg g^{-1}), penguin feathers (mean conc. 109.06 pg g^{-1}) and water (mean conc. 100.3 pg l^{-1}). The occurrence of such organochlorine compounds in different types of samples clearly substantiate the fact that the highly persistent organochlorine compounds with hydrophobic and lipophilic characteristics are being carried into the antarctic environment by atmospheric transport.

Among the isomers of HCHs, γ-HCH was found to be the most dominant constituent and contributed substantially with an average value of 56.87% in krill, 59.06% in penguin feathers and 63.65% in water (Fig. 2). Such variations in composition can be envisaged from the fact that HCH is used in large quantities in tropical and temperate regions during

Table 2. Concentration of organochlorine pesticide residues in antarctic samples

Sample	Nos	t-HCH ($x \pm d, n = 3$)	t-DDT ($x \pm d, n = 3$)	PCBs ($x \pm d, n = 3$)
Krill (pg g^{-1}, dry wt)				
	1	164.3 ± 16.6	40.5 ± 9.6	166.2 ± 18.4
	2	160.7 ± 15.7	36.7 ± 8.6	147.9 ± 16.7
	3	156.4 ± 14.6	34.3 ± 7.5	146.9 ± 19.7
	4	151.9 ± 12.7	38.3 ± 7.6	151.6 ± 12.8
	5	163.3 ± 10.5	32.7 ± 8.3	153.7 ± 11.6
	6	141.3 ± 9.8	31.1 ± 6.5	156.1 ± 10.6
	7	145.5 ± 8.6	44.4 ± 7.5	152.9 ± 12.6
	8	148.2 ± 6.8	38.6 ± 6.5	147.5 ± 14.6
Penguin feather (pg g^{-1}, dry wt)				
	1	103.6 ± 7.8	30.8 ± 4.1	105.8 ± 17.3
	2	112.5 ± 8.6	35.7 ± 3.8	113.6 ± 16.9
	3	108.7 ± 7.6	32.8 ± 4.3	107.8 ± 13.8
Polynya water (pg l^{-1})				
	1	94.7 ± 9.6	26.5 ± 8.5	103.8 ± 12.8
	2	85.6 ± 7.8	24.8 ± 6.7	96.8 ± 15.6

Standard deviations for t-HCH: 8.58 (krill); 4.47 (P.F); 6.43 (water); t-DDT: 4.06 (krill); 2.46 (P.F.); 1.20 (water); PCBs: 6.32 (krill); 4.05 (P.F); 4.95 (water).

Table 3. Concentration of various congeners of PCBs in antarctica

No.	CB-101 ($x\pm$s.d., n = 3)	CB-136 ($x\pm$s.d., n = 3)	CB-151 ($x\pm$s.d., n = 3)	CB-118 ($x\pm$s.d., n = 3)	CB-153 ($x\pm$s.d., n = 3)	CB-138 ($x\pm$s.d., n = 3)
Krill (pg g^{-1}, dry wt)						
1	28.5±3.2	30.6±4.1	24.5±2.8	22.8±2.4	27.6±2.5	32.2±3.4
2	25.3±2.3	29.5±3.2	20.4±2.4	19.7±2.9	22.5±2.8	30.5±3.1
3	24.8±3.6	28.4±3.1	21.6±3.3	18.9±2.6	23.6±3.4	29.6±3.7
4	27.7±3.4	27.5±3.2	23.5±3.1	19.7±2.9	24.5±3.2	28.7±3.0
5	26.6±2.9	28.6±3.1	22.6±3.4	21.5±2.8	26.5±3.3	27.9±4.1
6	27.8±3.1	29.3±3.2	20.8±3.4	21.7±3.2	27.8±2.9	28.7±3.8
7	28.3±3.4	28.4±3.5	21.4±2.8	21.5±3.1	23.8±3.2	29.5±2.6
8	24.5±2.8	26.5±3.1	22.5±2.6	20.6±3.2	24.7±2.7	28.7±2.2
Penguin feather (pg g^{-1}, dry wt)						
1	18.5±2.6	16.5±2.4	17.8±3.6	15.5±2.4	16.6±3.4	20.9±2.9
2	17.8±2.7	18.9±2.6	17.5±3.2	18.8±2.2	16.3±3.2	24.3±3.0
3	16.3±2.3	17.5±2.2	18.7±2.4	16.2±2.3	17.5±2.4	21.6±2.2
Polynya water (pg l^{-1})						
1	17.6±2.1	15.7±2.2	16.8±2.3	14.9±1.9	18.5±2.3	20.3±2.0
2	16.8±3.0	14.8±2.8	17.5±2.2	13.8±2.4	17.6±2.6	16.3±2.8

summer; the resulting high levels in the atmosphere were reflected by elevated atmospheric levels in antarctica during summer and autumn (Larsson *et al.*, 1992). t-HCH detected in the atmosphere over antarctic seas has been reported to be 95.75 pg m^{-3}, whereas in snow it is 4900 pg g^{-1}, in ice 310 pg g^{-1}, and in lake water 330 pg l^{-1} (Tanabe *et al.*, 1983) (Table 4). This clearly indicates the mode of transport of HCHs into the antarctic environment.

Figure 3 shows the percentage composition of various isomers and metabolites of DDT. Both pp′-DDT and pp′-DDE are the most dominant isomer and metabolite of DDT, being present in almost equal percentages in krill, whereas in penguin feathers and polynya water

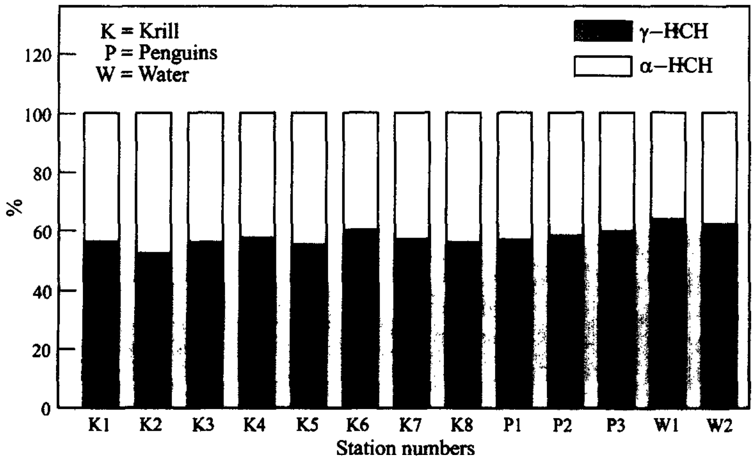

Fig. 2. Percentage composition of HCH compounds. K: krill; P: penguins; W: water.

Table 4. *Concentration of various organochlorine pesticides in antarctica*, 1975–1994

Sample specification	t-DDT(pg g^{-1})	t-HCH(pg g^{-1})	Year	Reference
Snow				
(0–5 m)	0.63	—	1975	Risebrough *et al.* (1976)
(5.5–6 m)	2.31	—	1975	Risebrough *et al.* (1976)
(3.5–4 m)	4.27	—	1975	Risebrough *et al.* (1976)
Chinstrap penguin liver	600	—	1977–1979	Norheim *et al.* (1982)
Macaroni penguin liver	500	—	1977–1979	Norheim *et al.* (1982)
Snow petrel	600	—	1977–1979	Norheim *et al.* (1982)
Air (average value)	150	—	1980–1981	Tanabe *et al.* (1982)
Water (average value)	30.7	1665	1980–1981	Tanabe *et al.* (1982)
Atmosphere over Antarctic seas	118	95.75	1981–1982	Tanabe *et al.* (1982)
Snow	16	4900	1981–1982	Tanabe *et al.* (1983)
Ice	9.8	310	1981–1982	Tanabe *et al.* (1983)
Lake water	1.3	330	1981–1982	Tanabe *et al.* (1983)
Lake sediment	605.03	123.2	1990	Sarkar and Fondekar (1990)
Zooplankton and phytoplankton	11,000	19,000	1991	Joiris and Overloop (1991)
Antarctic atmosphere	0.2–145	0.5–118	1988–1990	Larsson *et al.* (1992)
Winter Quarters Bay, sediment	0.5–4000	—	1988	Risebrough *et al.* (1990)
Lake sediments	844.9	92.9	1986–1987	Sarkar *et al.* (1994)
Krill	37.1	153.9	1987–1988	Present study
Penguin feather	33.1	108.2	1987–1988	Present study
Polynya water	25.6	90.2	1987–1988	Present study

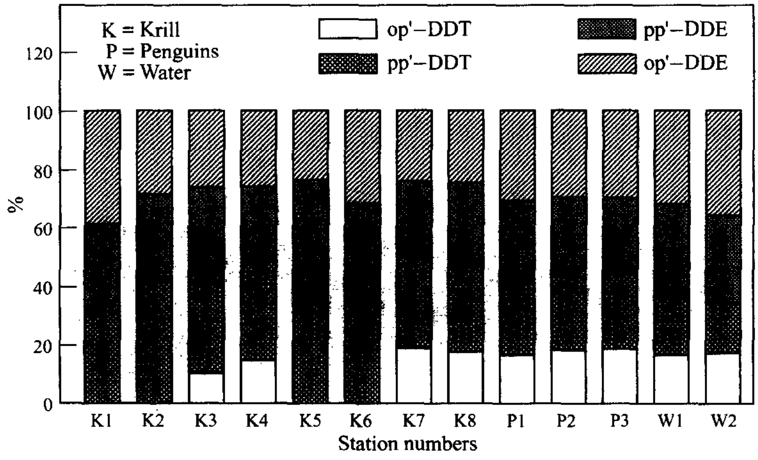

Fig. 3. Percentage composition of DDTs compounds. K: krill; P: penguins; W: water.

pp′-DDE and op′-DDE dominate over DDT. Such a variation in the composition of various isomers and metabolites of DDT may presumably be due to seasonal changes in partitioning of pollutants between the volatilized stage, airborne particles and water as evident from seasonal variation in the distribution of atmospheric pollutants over Sweden (Larsson and Okla, 1989). The most striking observation is that the concentration levels of various chlorinated hydrocarbons detected were lowest in the polynya water (Table 2), suggesting their removal from water because of their higher affinity towards particles (Sarkar *et al.*, 1994), which explains the high concentration of t-DDT (844.9 pg g^{-1}) in the glacial lake sediments (Table 4).

The congeners of PCBs detected in different types of samples are PCB-101 (2,2′,4,5,5′-pentachlorobiphenyl); PCB-118 (2,3′,4,4,5′-pentachlorobiphenyl); PCB-138 (2,2′,3,4,4′,5′-hexachlorobiphenyl); PCB-151 (2,2′,3,5,5′-hexachlorobiphenyl); PCB-153 (2,2′,4,4′,5,5′-hexachlorobiphenyl), and PCB-138 (2,2′,3,4,4′,5′-hexachlorobiphenyl). PCB-138 and PCB-136 are the most dominant congeners (Table 3). The low PCB concentration in water can be attributed to their close association with sedimentary particles, causing them to be removed from the water. The varying concentration levels of the chlorinated hydrocarbons in different phases is probably due to seasonal changes in atmospheric pollutant transport. Seasonal variation of pollutant distribution in the atmosphere was indicated in North America (Hermanson and Hites, 1989; Manchester-Neeswig and Andren, 1989).

The distribution of pollutants between water and biota is largely dependent on the bioconcentration factor, which is closely related to the partition coefficient of each chlorinated hydrocarbon. Moreover, the fat content of the antarctic animals changes seasonally, and pollutants are highest during the antarctic spring and autumn (Larsson *et al.*, 1992). Various metabolic changes take place in the physiological system of birds and krill due to seasonal changes as indicated by the high concentration levels of t-DDT in the liver of the Chinstrap and Macaroni Penguins (Table 4). Moreover, various physico-chemical properties of the antarctic polynya water also may play an important role in the degradation of these compounds to their isomers and other metabolites (Sarkar, 1991; Sarkar and Banerjee, 1987). However, the presence of these highly persistent chlorinated compounds in the antarctic samples can be attributed to atmospheric transport, observed by Tanabe *et al.* (1982, 1983), Risebrough (1977) and Risebrough *et al.* (1976).

The concentration levels of various organochlorine compounds during 1975–1994 (Table 4) clearly indicate the wide variation in the occurrence and distribution of organochlorine contaminants in various compartments of the antarctic environment. Further studies in the region on the level of contamination of these compounds with respect to seasonal changes will be of utmost importance from the point of view of environmental pollution in this pristine environment.

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