

# Pesticide residues in the sediments from the lakes of Schirmacher Oasis, Antarctica

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**ABSTRACT.** Concentration levels of various organochlorine pesticides and their derivatives — namely, hexachlorocyclohexanes (HCH) and the DDT compounds pp'-DDT, op'-DDT, pp'-DDE, op'-DDE, pp'-DDD, and op'-DDD — were determined in the sediments from eight different lakes of the Schirmacher Oasis, near Dakshin Gangotri, the Indian station (70° 45'S, 11° 44'E) during the Sixth Indian scientific expedition to Antarctica (December 1986 to February 1987). Concentration levels of HCHs ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) and t-DDT (pp'-DDT + op'-DDT + pp'-DDE + op'-DDE + pp'-DDD + op'-DDD) in sediments of these lakes were found to be in the ranges of 37.7–155 pg/g and 512.9–1131 pg/g, respectively. Among the isomers of HCH, gamma-HCH was most prominent, followed by alpha-HCH, whereas in the case of metabolites of DDT and its isomers, pp'-DDT was found to be dominant over others. However, all the other compounds of the DDT family were present in considerable amounts in all the lakes. There was no significant change in the monthly variation of the concentration levels of HCHs and DDTs in the lakes.

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## Introduction

Studies on pollution of the Antarctic by organochlorine compounds started with their identification and quantification in wildlife and snow in the mid and late 1960s (Sladen and others 1966; George and Frear 1966; Tatton and Ruzicka 1967; Peterle 1969). These substances have since been found in different quantities in birds and seals (Risebrough 1977; Lukowski 1978; Hidaka and Tatsukawa 1981; Norheim and others 1982). Moreover, Tanabe and others (1982, 1983) confirmed the presence of DDT, HCH, PCBs, and their metabolites in the snow, ice, and lake water of the Antarctic, as well as in the atmosphere over Antarctica and the adjoining oceans.

All these findings clearly indicated the dispersion of these pollutants in the Antarctic environment, and thus new ideas were generated concerning their transport and behaviour. However, most of the studies hitherto have dealt with wildlife, snow, lake water, sea water, and, to some extent, the atmosphere of Antarctica. Despite the fact that persistent organochlorine pesticides can be expected to accumulate in the sediments of the Antarctic lakes, few data on the residue levels of different organochlorine pesticides in lake sediments have been available (Sarkar and Fondekar 1990). This study is an attempt to identify and quantify the residues of organochlorine compounds in sediments from different lakes of Schirmacher Oasis, Antarctica.

Schirmacher Oasis is situated near Dakshin Gangotri, the Indian Antarctic station (70° 45'S, 11° 44'E). Lying between shelf ice and land ice, it consists of 35 km<sup>2</sup> of ice-free area with lakes, lagoons, ponds, water streams, dome-shaped hills, and gentle slopes (Sarkar and Fondekar 1990). Most of Schirmacher Oasis is moraine-covered,

bare ground. The weathering products and glacial deposits from these exposed rocks form the soil. Small ponds and lakes are formed because of glacial melt water.

## Materials and methods

Sediment samples were collected from eight different lakes of Schirmacher Oasis (between 70° 44'S, 11° 47'E and 70° 46'S, 11° 41'E) (Fig. 1). The surface sediment samples (0–5 cm) were collected by a teflon core (30 cm) from the lakes for three successive months (December 1986, January 1987, and February 1987) in order to assess the variation in the residue levels of various organochlorine compounds. The period of this study allowed for climatic changes resulting in the accumulation of various contaminants into the lakes of Schirmacher Oasis by means of snowfall and the inflow of glacial melt water.

Immediately after collection, sediment samples were wrapped in aluminium foil (cleaned with bidistilled hexane) and kept in a deep freezer at –25°C to avoid biodegradation of the pesticides. After thawing, 100–125 g of each of the sediment samples was transferred to different precleaned conical flasks (250 ml), thoroughly mixed with 5 ml of 1 N ammonium chloride, and kept overnight for equilibration in order to facilitate the desorption of the pesticides from sedimentary particles (Sarkar and Sen Gupta 1987, 1988a, 1988b). In order to estimate the water content of each of the samples, 4–5 g were dried in different petri dishes in an oven at 120°C until constant weight was attained.

Organochlorine pesticides were analyzed following a modified method (Sarkar and Sen Gupta 1987; Tanabe and others 1982; Duinker and others 1983). Organochlorine pesticides were extracted by shaking the sediment samples, first with 150–200 ml acetone for about 10 hours on a flat-bottomed rotary shaker, followed by a post extraction with 150 ml of a mixture of acetone and hexane (1:1). The combined extract of each of the samples was then shaken with 100 ml bidistilled water to remove the acetone layer, and all the extracted materials were transferred into hexane. The hexane extract was concentrated to 1 ml by

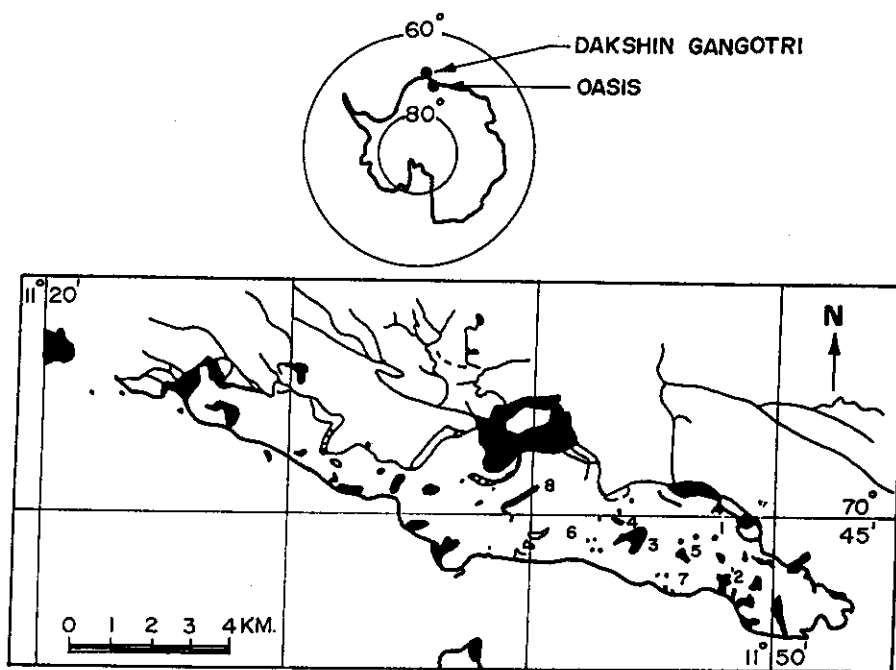


Fig. 1. Study area, showing the eight lakes that served as observation and data points in the Schirmacher Oasis, Antarctica.

evaporation in a Kuderna Danish (KD) evaporator. 0.5 ml of distilled nanograde iso-octane was added to each of the solvent extracts in order to prevent them from becoming completely dry. Sulphur was removed from the solvent extract by treatment with activated copper powder. The sulphur-free extracts were purified by alumina clean up following the micro-column technique (Duinker and oth-

ers 1983). Organochlorine pesticides were separated from PCBs by fractionating the extract through pre-cleaned silica column chromatography using the micro-column technique. Pesticides were collected in the second fraction, as the separation point was determined at the elution volume of 8.5 ml. The percentage of recovery was determined by spiking 100  $\mu$ l of 0.1 ppm IUPAC-88 as an internal standard into each of the samples before the extraction. The recovery of the extracts was found to be within the range of 98.5–99.5%. Five replicates of each of the samples were extracted in order to determine the standard deviation of analysis.

The aliquots were then analyzed by a gas chromatograph (Perkin Elmer 8700)

equipped with an Ni<sup>63</sup> electron capture detector and a capillary column (SE-54, 60 m in length and 0.25 mm in diameter). The temperature of the oven was programmed as follows: initial temperature was 110°C for 2 min; it increased to 180°C at the rate of 10°C per min and was held for 8 min; it was then raised to 220°C at the rate of 4°C per min and was held for 5 min; it finally reached 270°C at the

Table 1. Organochlorine pesticide residue concentrations (pg/g) in sediments from the lakes in Schirmacher Oasis, Antarctica. D = December 1986; J = January 1987; F = February 1987.  $\bar{x}$  = mean concentration; sd = standard deviation; n = replicates. The standard deviations for each of the pesticides were: HCH, 35.12; pp'-DDT, 106.75; op'-DDT, 86.08; pp'-DDE, 38.0; op'-DDE, 60.18; pp'-DDD, 25.7; op'-DDD, 22.87; t-DDT, 179.46.

Lake No.	HCH (A+B+Y)	DDT compounds						
		pp'-DDT	op'-DDT	pp'-DDE	op'-DDE	pp'-DDD	op'-DDD	t-DDT
	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ ) n = 5	( $\bar{x} \pm \text{sd}$ )
D1	84.8 $\pm$ 5.8	315 $\pm$ 17.8	56.8 $\pm$ 3.6	77.3 $\pm$ 4.5	92.8 $\pm$ 7.2	85.6 $\pm$ 6.5	70.2 $\pm$ 3.8	697.1 $\pm$ 25.6
J1	37.7 $\pm$ 2.5	327 $\pm$ 15.4	76.1 $\pm$ 4.5	109 $\pm$ 8.7	104 $\pm$ 6.4	95.5 $\pm$ 7.5	91.3 $\pm$ 6.5	802.9 $\pm$ 49.0
F1	59.8 $\pm$ 3.6	335 $\pm$ 12.4	127 $\pm$ 8.5	86.4 $\pm$ 4.7	66.4 $\pm$ 1.5	98.6 $\pm$ 8.5	95.3 $\pm$ 3.8	808.7 $\pm$ 39.4
D2	110 $\pm$ 6.5	350 $\pm$ 15.5	150 $\pm$ 7.8	79.7 $\pm$ 3.8	75.6 $\pm$ 6.8	75.6 $\pm$ 7.2	93.6 $\pm$ 6.4	824.5 $\pm$ 47.5
J2	54.1 $\pm$ 2.6	400 $\pm$ 12.6	165 $\pm$ 8.7	74.6 $\pm$ 4.2	51.2 $\pm$ 3.4	90.3 $\pm$ 9.7	83.3 $\pm$ 4.5	864.4 $\pm$ 43.1
F2	89.4 $\pm$ 5.2	452 $\pm$ 15.5	105 $\pm$ 9.6	85.4 $\pm$ 5.1	248 $\pm$ 9.8	130 $\pm$ 10.5	120 $\pm$ 8.5	1040 $\pm$ 59.0
D3	123 $\pm$ 9.2	65.5 $\pm$ 2.5	70.4 $\pm$ 4.6	117 $\pm$ 8.6	175 $\pm$ 8.9	65.5 $\pm$ 7.5	50.9 $\pm$ 2.5	544.3 $\pm$ 34.6
J3	70.6 $\pm$ 4.8	70.5 $\pm$ 5.2	78.5 $\pm$ 3.5	92.4 $\pm$ 6.7	93.1 $\pm$ 7.5	89.5 $\pm$ 8.5	88.9 $\pm$ 5.6	512.9 $\pm$ 37.0
F3	67.5 $\pm$ 3.5	115 $\pm$ 6.5	119 $\pm$ 9.5	48.8 $\pm$ 2.8	23.4 $\pm$ 2.6	130 $\pm$ 15.6	122 $\pm$ 8.7	558.8 $\pm$ 45.7
D4	150 $\pm$ 9.6	149 $\pm$ 10.8	195 $\pm$ 9.8	28.5 $\pm$ 2.6	135 $\pm$ 9.6	86.5 $\pm$ 10	76.4 $\pm$ 5.6	670.4 $\pm$ 48.4
J4	155 $\pm$ 8.8	282 $\pm$ 15.9	206 $\pm$ 8.6	56.5 $\pm$ 3.6	94.3 $\pm$ 8.5	150 $\pm$ 18	105 $\pm$ 8.6	893.8 $\pm$ 72.0
F4	146 $\pm$ 9.8	175 $\pm$ 12.8	375 $\pm$ 9.5	172 $\pm$ 8.4	146 $\pm$ 9.3	135 $\pm$ 12	128 $\pm$ 9.7	1131 $\pm$ 60.9
D5	74.8 $\pm$ 5.6	196 $\pm$ 10.6	280 $\pm$ 8.6	113 $\pm$ 7.5	36.3 $\pm$ 3.2	158 $\pm$ 15	142 $\pm$ 9.6	925.3 $\pm$ 60.1
J5	132 $\pm$ 8.6	190 $\pm$ 12.5	250 $\pm$ 7.8	126 $\pm$ 9.6	212 $\pm$ 8.7	135 $\pm$ 16	132 $\pm$ 8.5	1045 $\pm$ 63.1
D6	103 $\pm$ 6.5	183 $\pm$ 12.8	180 $\pm$ 8.5	91.6 $\pm$ 5.6	70.3 $\pm$ 5.8	98.5 $\pm$ 9	86.8 $\pm$ 6.4	710.2 $\pm$ 48.1
J6	105 $\pm$ 9.8	295 $\pm$ 15.6	285 $\pm$ 9.6	59.2 $\pm$ 3.6	132 $\pm$ 8.6	110 $\pm$ 12	105 $\pm$ 7.9	987 $\pm$ 57.3
D7	57.8 $\pm$ 6.5	227 $\pm$ 14.8	230 $\pm$ 7.5	76.5 $\pm$ 6.5	72.8 $\pm$ 5.6	92.5 $\pm$ 7.7	95.3 $\pm$ 6.9	794.1 $\pm$ 48.3
J7	66.8 $\pm$ 5.8	230 $\pm$ 12.5	210 $\pm$ 10.5	162 $\pm$ 9.8	178 $\pm$ 8.6	105 $\pm$ 1.5	115 $\pm$ 9.4	1000 $\pm$ 65.8
D8	79.2 $\pm$ 6.9	260 $\pm$ 11.6	240 $\pm$ 15.2	148 $\pm$ 8.5	75.2 $\pm$ 4.5	120 $\pm$ 18	110 $\pm$ 8.2	953.2 $\pm$ 66.0

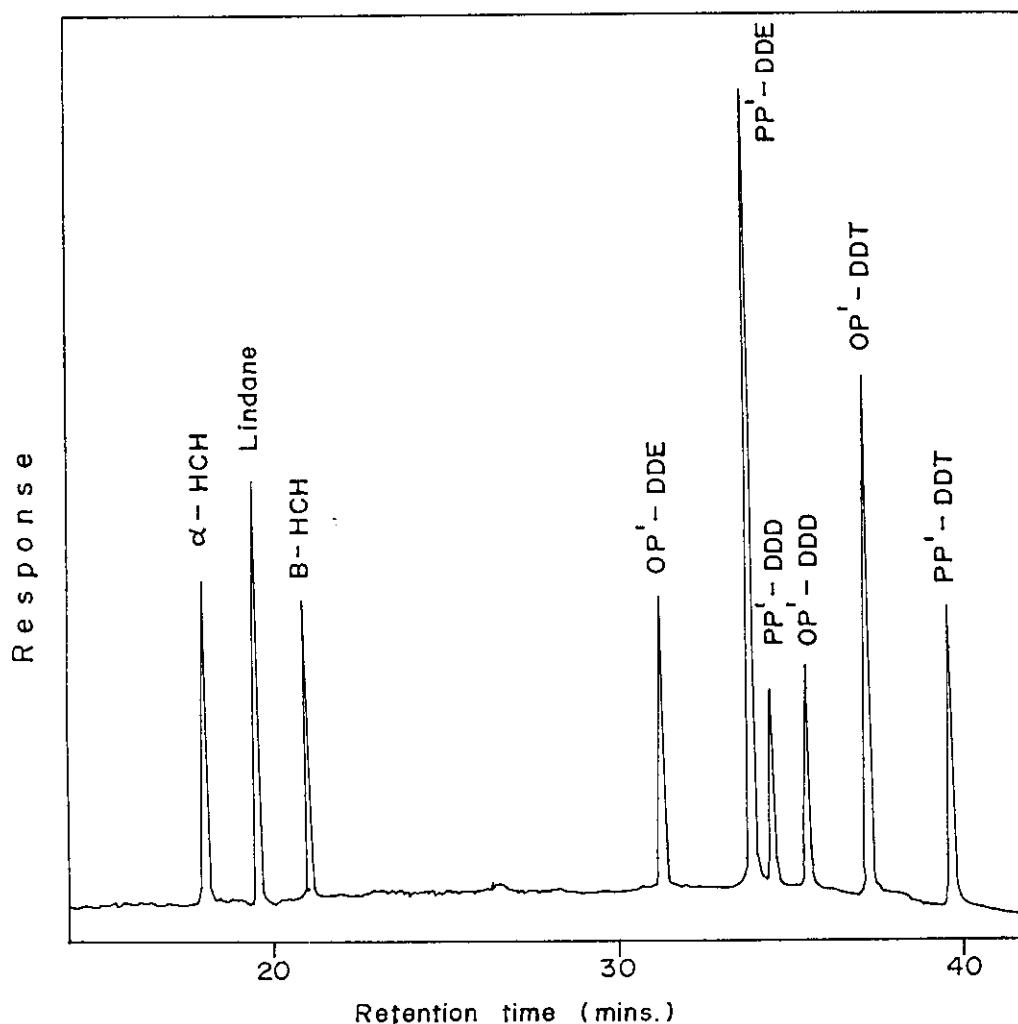


Fig. 2. A typical chromatogram of different pesticides.

rate of 4°C and remained isothermal for 15 min. The equilibration time was 2 min. The temperature for the detector and the injector was fixed at 340°C and 200°C, respectively. The sample aliquots were injected at splitless mode and, after 2 min, were shifted to split mode.

Highly pure argon mixed with 5% methane gas was used both as carrier and make-up gas. The gas pressure throughout the analysis was kept at 90 kPa. In order to check the reproducibility of each of the chromatograms 100 µl of 0.1 ppm IUPAC-88 was spiked into 0.9 ml of a standard solution containing HCH (α, β, γ), aldrin, dieldrin, endrin, pp'-DDT, op'-DDT, pp'-DDE, op'-DDE, pp'-DDD, op'-DDD, etc.

The organochlorine pesticides were identified and quantified by calibrating with respect to the peaks of the standard pesticide obtained from Supelco Switzerland. The method of analysis was standardized with respect to certified materials obtained from IAEA Monaco. The results of recovery of different organochlorine compounds are in close proximity with those of the original concentration — for example, alpha-HCH, 0.928 (0.93 ng/g); gamma-HCH, 0.478 (0.48 ng/g); pp'-DDD, 5.585 (5.6 ng/g); pp'-DDE, 5.675 (5.7 ng/g); pp'-DDT, 10.195 (10.2 ng/g). The detection limits for different pesticides and their metabolites were as follows: 1 µl injection under normal

operating conditions, 0.010 pg HCB, and 0.025–0.050 pg, alpha, beta, γ-HCH, op'-DDD, pp'-DDD, op'-DDE, pp'-DDE, op'-DDT, and pp'-DDT. A copy of a typical chromatogram of different pesticides is shown in Figure 2.

### Results and discussion

Concentration levels of various organochlorine pesticides and their metabolites in sediments of different lakes of Schirmacher Oasis indicated that total HCH was present in considerable amounts in all the lakes (Table 1). It was found to be highest (155.5 pg/g) in lake 4 and lowest (37.7 pg/g) in lake 1 during January 1987. The average concentration of various pesticide residues and their standard deviations clearly show an overview of the extent of contamination of each of the lakes of Schirmacher Oasis (HCH, 92.97 pg/g (35.12); pp'-DDT, 243 pg/g (106.75); op'-DDT, 178.88 pg/g (86.08); pp'-DDE, 94.94 pg/g (38.00); op'-DDE, 109.54 pg/g (60.18); pp'-DDD, 107.95 pg/g (25.71); op'-DDD, 100.57 pg/g (22.87); t-DDT, 829.66 pg/g (179.46)).

Among the compounds of the DDT family, pp'-DDT and op'-DDT were found to be dominant in almost all the lakes. Almost all the metabolites of DDT were detected in all the lakes. The highest concentrations of pp'-DDT (452.8 pg/g) and op'-DDT (374.5 pg/g) were recorded in

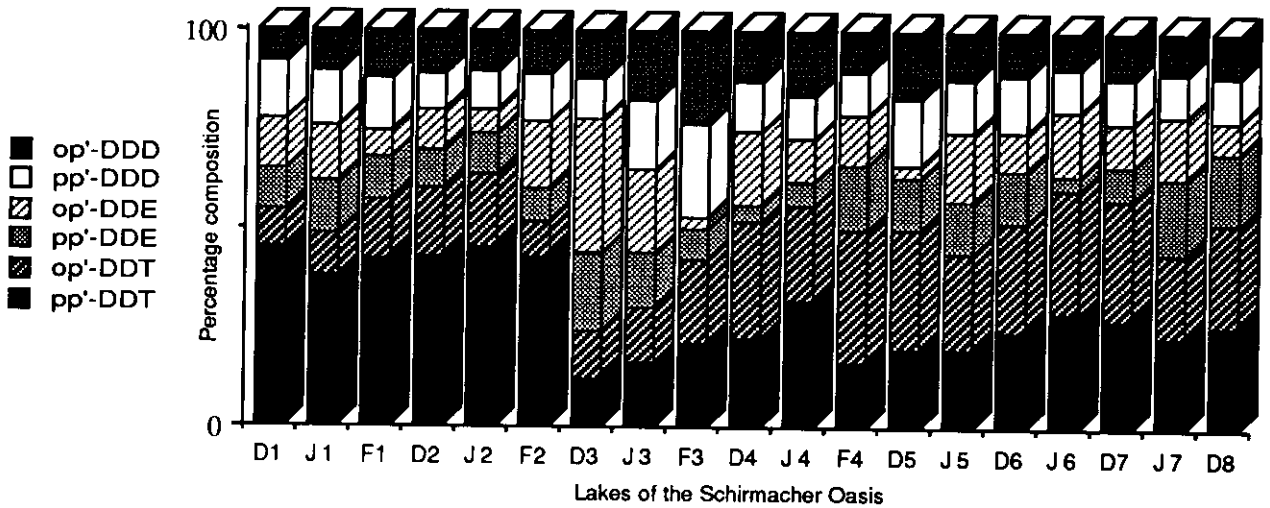


Fig. 3. Percentage composition of DDT isomers in sediments of the lakes.

lakes 2 and 4, respectively.

An increasing trend in the residue levels of HCH, *op'*-DDE, and *pp'*-DDE was observed in lakes 1 through 4 during December 1986. But there was no specific trend of variation in the concentration levels of pesticide in the sediments during January and February 1987. Such a trend of variation in the residue levels of various chlorinated compounds in Antarctic lakes may be attributed to the atmospheric transport of the pollutants and the glacial flow of melted ice (Tanabe and others 1982, 1983) into the lakes. In fact, in Antarctic regions, there are large snowfalls during the summer (December through February). Thus aerial chlorinated hydrocarbons are removed by snowfall in this period. Moreover, the prevailing wind in this section of the Antarctic is northwest throughout the year. It has been reported that the use of organochlorine pesticides in northern lands and the direction of the winds to Antarctica seem to have led to variations in the transportation of various pollutants in the Antarctic (Tanabe and others 1983). The observed variation in the concentration

of different pesticides in different lakes of the Antarctic can be expected to be due to the variation in physico-chemical properties of the lake water, such as pH, salinity, temperature, organic matter, and clay mineral concentrations. Moreover, various benthic organisms present in the bottom sediments of the lakes might also play an important role in the degradation of DDT to its metabolites (Sarkar and Banerjee 1987).

Figures 3 and 4 depict the variation of the percentage composition of DDT compounds with respect to total DDT, and the isomers of HCH with respect to total HCH in the sediments from different lakes. They clearly indicate that the variation of the percentage composition of *pp'*-DDT with respect to the lakes and time is much more pronounced than its metabolites. Both *pp'*-DDE and *op'*-DDE were almost equally distributed in all the lakes. The most striking point is that although both the isomers of DDT — *pp'*-DDT, and *op'*-DDT — were identified in almost all the lakes, their percentage composition with respect to total DDT was found to be in an almost inverse

Fig. 4. Percentage composition of HCH isomers in sediments of the lakes.

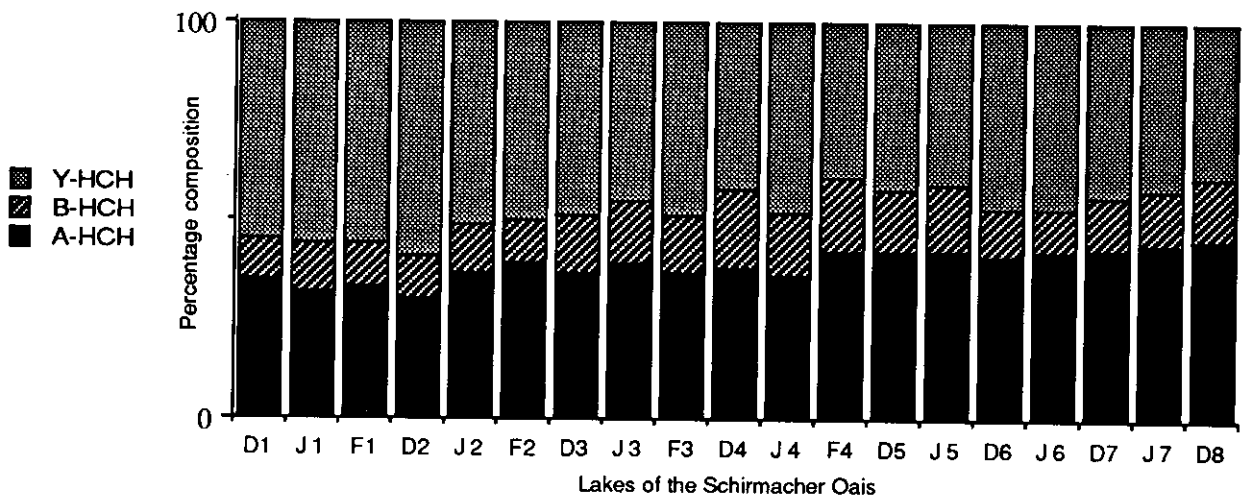


Table 2. Concentrations of various organochlorine pesticides in Antarctica during the period 1975–1993.

Sample specification	t-DDT (pg/g)	t-HCH (pg/g)	Year	Reference
Snow (0-5m)	0.63	—	1975	Risebrough and others (1976)
(5.5–6m)	2.31	—	1975	Risebrough and others (1976)
(3.5–4m)	4.27	—	1975	Risebrough and others (1976)
Chinstrap Penguin liver	600	—	1977–79	Norheim and others (1982)
Macaroni Penguin liver	500	—	1977–79	Norheim and others (1982)
Snow Petrel	600	—	1977–79	Norheim and others (1982)
Air (average value)	150	—	1980–81	Tanabe and others (1982)
Water (average value)	30.7	1665	1980–81	Tanabe and others (1982)
Atmosphere over Antarctic seas	118	95.75	1981–82	Tanabe and others (1983)
Snow	16	4900	1981–82	Tanabe and others (1983)
Ice	9.8	310	1981–82	Tanabe and others (1983)
Lake water	1.3	330	1981–82	Tanabe and others (1983)
Lake sediment	605.03	123.2	1990	Sarkar and Fondekar (1990)
Zooplankton and phytoplankton	11000	19000	1991	Joiris and Overloop (1991)
Antarctic atmosphere	0.2–145	0.5–118	1988–90	Larson and others (1992)
Winter Quarters Bay, sediment	0.5–4000	—	1988	Risebrough and others (1990)
Lake sediments	844.9	92.9	1986–87	Sarkar and others (present)

relationship.

A comparison of the concentrations of various organochlorine pesticides in Antarctic snow, lake water, sea water, and lake sediments (Table 2) shows that the concentration of pesticides in the sediments from the Antarctic lakes of Scirmacher Oasis is relatively high. Such a high concentration of pesticides in the lake sediments might be due to accumulation of the residues of pesticides from the surrounding regions, atmospheric transport of pollutants, or human activities. Adsorption of the pesticide residues on the sedimentary particles may also be enhanced due to the presence of organic matter in the sediment (Sarkar and Sen Gupta 1987).

A large number of congeners of PCBs were also detected in different samples. However, a detailed study on their identification and quantification with respect to different individual congeners of PCBs will be published in an upcoming paper.

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