

PCB congeners, DDTs and hexachlorobenzene in Antarctic fish from Terra Nova Bay (Ross Sea)

SILVANO FOCARDI, L. LARI and L. MARSILI

Dipartimento di Biologia Ambientale, Università di Siena, Via delle Cerchia 3, 53100 Siena, Italy

Abstract: Chlorinated hydrocarbons were measured in seven species of Antarctic fish (*Pagothenia bernacchii*, *P. hansonii*, *Trematomus centronotus*, *T. newnesi*, *Chionodraco hamatus*, *Cygnodraco mawsoni*, and *Gymnodraco acuticeps*) from in the Ross Sea near Terra Nova Bay (74°40'S 164°10'E). Hexachlorobenzene (HCB), *pp'* DDT and its derivatives DDE and DDD, and about 20 congeners of polychlorinated biphenyls (PCBs) were found in muscle and liver. Levels of *pp'* DDE were positively correlated with body length in *P. bernacchii* and the plot of concentrations showed higher values in males than females of the same body weight class. The results confirm the presence of these chlorinated hydrocarbons in the Antarctic marine food chain and an increase of PCBs with respect to DDTs. The "fingerprint" of *C. hamatus* is different from that of other Antarctic organisms and of fish from other parts of the world, suggesting possible metabolic differences.

Received 23 April 1991, accepted 30 August 1991

Key words: Antarctic fish, organochlorines, PCB congeners, Ross Sea

Introduction

Chlorinated hydrocarbons are a class of persistent contaminants present in many ecosystems (Risebrough *et al.* 1968). They are found even in remote areas such as the Arctic and Antarctic (Risebrough *et al.* 1976, Ballschmiter *et al.* 1981, Norheim *et al.* 1982, Subramanian *et al.* 1983, Tanabe *et al.* 1983, Oehme & Mano 1984, Subramanian *et al.* 1986, Tanabe *et al.* 1986, Norström *et al.* 1988, Wolff 1990).

In Antarctica, the presence of these contaminants has been associated with the activities of the scientific stations, but the main source of pollutants for this remote area is atmospheric transport. It is very important to identify any input of pollutants into this continent and we report here the results of the analyses for organochlorines in seven species of Antarctic fish collected during the third and fourth Italian expeditions (December 1987–February 1988, December 1989–February 1990) to the Italian scientific station at Terra Nova Bay (74°40'S, 164°10'E).

The fish studied belong to species which live their whole lives in Antarctic waters (Gon & Heemstra, 1990). Unlike migratory species, they can therefore give specific indications of the levels of pollution in the areas in which they are fished.

Materials and methods

Fish samples were caught by line or net in Terra Nova Bay. The species were *Pagothenia bernacchii*, *P. hansonii*, *Trematomus centronotus*, *T. newnesi*, *Chionodraco hamatus*, *Cygnodraco mawsoni*, *Gymnodraco acuticeps*. Nomenclature follows Gon & Heemstra (1990). After the weight, length and sex had been determined, samples of the muscle and liver were frozen or freeze dried. Extractions were performed using Soxhlet apparatus with pesticides-free, vacuum distilled

n-hexane. Sulphuric acid clean up was followed by Florisil chromatography. Analyses were performed with Perkin-Elmer model 8700 gas chromatograph equipped with Ni63 electron capture detector. A Supelco SBP-5 bonded phase (0.25 Em film thickness) fused silica capillary column (30 m long, internal diameter 0.2 mm) was used. The carrier gas was helium at 110 kPa, with a split ratio of 100 1⁻¹. The detector scavenger was argon/methane (95/5) at a flow of 30 ml min⁻¹. Oven temperature was 100°C for 10 min and was then increased by 3°C min⁻¹ to 280°C. The injector (PTV) was kept at 50°C until the time of injection, after which the temperature was quickly raised to 250°C. Detector temperature was 300°C. A mixture of specific isomers was used for instrumental calibration, recovery, evaluation and confirmation.

Results and discussion

Capillary gas chromatography revealed hexachlorobenzene (HCB), *pp'* isomers of DDT and its derivatives DDE and DDD, *op'* DDT and about 20 congeners of polychlorobiphenyls (PCBs) in the liver and muscle of the Antarctic fish (Tables I–IV). The data from the two sampling periods were pooled because there were no statistically significant differences between them. The percentage of extracted lipids (EOM%) is given in Table III.

HCB was found in all the species studied with mean values in muscle ranging from 0.17 ng g⁻¹ in *T. centronotus* to 0.61 ng g⁻¹ in *C. hamatus*. In the liver the levels were about an order of magnitude higher (6.4 ng g⁻¹ in *P. bernacchii* and 8.4 ng g⁻¹ in *C. hamatus*). The higher levels in the liver are due to the higher percentage of fat in liver tissue (see EOM values).

Comparison with the literature is difficult with only one report of HCB in Antarctic fish — 30 ng g⁻¹ in *Dissostichus*, a large predator caught in the subantarctic (Ballschmiter *et al.*

Table I. Concentrations (ng g⁻¹ dry weight) of HCB and DDT components in fish muscle (\bar{x} = mean; sd = standard deviation; number of specimens in brackets; nd = not detected).

species	HCB		pp'DDE		pp'DDT		pp'DDD	
	\bar{x}	sd	\bar{x}	sd	\bar{x}	sd	\bar{x}	sd
BATHYDRACONIDAE								
<i>C. mawsoni</i> (2)	0.22	0.36	0.83	0.89	0.48	0.61	nd	
<i>G. acuticeps</i> (10)	0.44	0.27	3.59	1.94	1.00	0.58	0.88	0.51
CHANNICHTHYIDAE								
<i>C. hamatus</i> (20)	0.61	0.27	1.89	0.90	0.59	0.32	0.22	0.10
NOTOTHENIIDAE								
<i>T. newnesi</i> (12)	0.33	0.23	1.56	0.81	0.46	0.40	0.43	0.27
<i>T. centronotus</i> (6)	0.17	0.18	1.23	0.67	0.34	0.25	0.36	0.19
<i>P. hansonii</i> (10)	0.34	0.29	2.70	1.41	0.85	0.75	0.70	0.46
<i>P. bernacchii</i> (58)	0.27	0.20	2.24	1.15	0.68	0.33	0.78	0.30

Table II. Average, standard deviation and range of HCB and DDT components (ng g⁻¹ d.w.) in fish liver.

	<i>C. hamatus</i> (n=12)	<i>P. bernacchii</i> (n=16)
HCB	8.4±2.6 (5.0–12.2)	3.4±1.3 (1.2–6.5)
pp'DDE	25.0±5.0 (17.2–31.9)	52.7±9.5 (23.5–75.6)
pp'DDT	14.6±5.1 (8.5–21.0)	8.1±4.0 (5.3–15.3)
pp'DDD	4.4±2.1 (1.6–9.7)	7.0±4.6 (3.3–12.4)
op'DDT	6.7±2.5 (3.1–10.8)	1.4±0.9 (0.3–4.4)

Table III. DDTs and PCBs (ng g⁻¹ d.w.), Extracted Organic Matter (EOM% d.w.) in different fish (M=muscle; L=liver).

species	EOM%	DDTs	DDE/DDTs	PCBs	DDTs/PCBs
<i>C. mawsoni</i> (M)	3.4	1.4	0.59	2.8	0.50
<i>G. acuticeps</i> (M)	3.6	5.9	0.61	12.4	0.47
<i>C. hamatus</i> (M)	6.1	3.3	0.57	9.5	0.34
<i>C. hamatus</i> (L)	38.3	49.2	0.50	201.8	0.22
<i>T. newnesi</i> (M)	2.8	2.7	0.58	7.3	0.36
<i>T. centronotus</i> (M)	3.2	1.9	0.64	4.7	0.40
<i>P. hansonii</i> (M)	3.7	4.6	0.58	6.1	0.75
<i>P. bernacchii</i> (M)	2.5	4.0	0.56	12.8	0.31
<i>P. bernacchii</i> (L)	9.8	67.3	0.78	186.5	0.36

1981). At higher trophic levels, 10–30 ng g⁻¹ have been reported in penguins (gentoo and rock-hopper) and in the black-browed albatross (Balschmiter *et al.* 1981). In other areas, Ober *et al.* (1987) reported 200 ng g⁻¹ d.w. in *Trachurus murphyi* from the Pacific coast of Chile, Vuorinen *et al.* (1985) 100–400 ng g⁻¹ in Baltic salmonids and Skare *et al.* (1985) 5–100 ng g⁻¹ in fish of the Norwegian fiords.

Table IV. Concentrations (ng g⁻¹ d.w.) of PCB congeners in the liver of *C. hamatus* and *P. bernacchii* (\bar{x} = mean; sd = standard deviation; % = percentage of total residue).

IUPAC number	<i>C. hamatus</i> (n=12)			<i>P. bernacchii</i> (n=16)			
	\bar{x}	sd	%	\bar{x}	sd	%	
Pentachlorobiphenyls							
22'44'5	99	30.5	18.2	15.6	8.6	3.5	4.6
22'455'	101	3.1	1.7	1.5	3.0	2.5	1.6
23'44'5	118	3.5	2.2	1.7	5.5	3.2	3.0
Hexachlorobiphenyls							
22'33'44'	128	21.5	14.3	11.0	4.5	2.9	2.4
22'344'5'	138	15.0	9.9	7.7	32.7	20.8	17.7
22'3455'	141	10.1	7.6	5.2	--	--	---
22'34'55'	146	7.5	4.8	3.8	6.7	4.2	3.6
22'34'5'6	149	2.1	1.0	1.0	3.8	1.8	2.0
22'355'6	151	24.3	15.4	12.4	6.0	3.9	3.2
22'44'55'	153	20.9	12.7	10.7	39.6	17.9	21.4
Heptachlorobiphenyls							
22'33'44'5	170	4.1	2.3	2.1	12.2	5.6	6.6
22'33'455'	172	5.5	4.6	2.8	0.9	0.4	0.5
22'33'456'	174	3.3	1.8	1.7	7.4	2.8	4.0
22'33'4'56	177	1.8	0.9	0.9	4.3	2.0	2.3
22'344'55'	180	7.1	3.5	3.6	19.7	12.4	10.6
22'344'5'6	183	2.0	0.7	1.0	5.3	2.2	2.8
22'34'55'6	187	6.2	2.7	3.2	14.0	6.8	7.5
233'44'5'6	191	6.2	4.6	3.2	0.3	0.1	0.2
Octachlorobiphenyls							
22'33'44'55'	194	0.4	0.3	0.2	2.6	1.1	1.4
22'33'44'56	195	16.4	15.6	8.4	1.8	1.0	1.0
22'33'44'5'6	196	2.3	3.7	0.1	2.2	1.1	1.2
22'33'4'55'6	201	1.1	0.5	0.6	3.4	2.3	1.8

In the DDT group, the derivative pp'DDE showed the highest levels, which ranged from a mean of 0.85 ng g⁻¹ in the muscle of *C. mawsoni* to 3.79 ng g⁻¹ in *G. acuticeps*. In the liver the highest levels (52.7 ng g⁻¹) were found in *P. bernacchii*. Though varying from species to species, the ratio DDE/DDTs (Table III) confirmed that pp'DDE accounted for more than 50% of the DDTs. The isomer pp'DDT ranged from 0.34 ng g⁻¹ in the muscle of *T. centronotus* to 1 ng g⁻¹ in *G. acuticeps*. In the liver, the highest levels were found in *C. hamatus* (14.6 ng g⁻¹). In many species, pp'DDD was also found, and in muscle was highest in *G. acuticeps* (0.88 ng g⁻¹). In the liver of *C. hamatus* and *P. bernacchii*, op'DDT was also detected with mean levels of 6.7 ng g⁻¹ and 1.4 ng g⁻¹ respectively. Levels of DDTs (Table III) ranged from 1.4 ng g⁻¹ in the muscle of *C. mawsoni* to 5.9 ng g⁻¹ in *G. acuticeps*; in the liver, mean levels of 59.2 and 77.3 ng g⁻¹ were found in *C. hamatus* and *P. bernacchii* respectively.

Previous studies on Antarctic fish (Subramanian *et al.* 1983, Hidaka *et al.* 1984) measured DDTs in four species collected around Syowa station, but out of the range of influence of the station. Slightly higher concentrations were found there than the present study area. Syowa, (69°00'S, 39°00'E) is exposed to winds from the Indian Ocean which is amongst the most

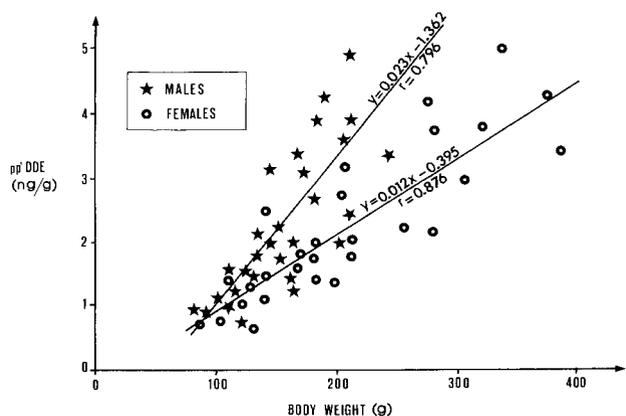


Fig. 1. *pp'*DDE vs. body weight in muscle of *Pagothenia bernacchii*.

polluted of all seas (Bidleman & Leonard 1982). This may explain the higher levels in fish from near Syowa, but it may also be a sign of a slight world-wide decrease in the levels of this contaminant. As far as Antarctic organisms of other trophic levels are concerned, *pp'*DDE and *pp'*DDT values between 0.1 and 0.5 ng g⁻¹ d.w. have been reported in mosses and lichens of the Ross Sea (Focardi *et al.* 1991), 45–1450 ng g⁻¹ in the eggs and fat of different species of seabirds (Ballschmiter *et al.* 1981, Schneider *et al.* 1985, Tanabe *et al.* 1986, Luke *et al.* 1989) and 10–500 ng g⁻¹ in the muscle and fat of the Weddell and crabeater Seals (Hidaka *et al.* 1984, Schneider *et al.* 1985). These values in Antarctic organisms are much lower than those in other region supporting human activities.

Correlations were sought between levels of DDT and its derivatives and the age of *P. bernacchii*, the species with the largest number of specimens. The concentrations of the different contaminants plotted against body weight showed a positive correlation with body weight levels of *pp'*DDE (Fig. 1). This is consistent with the results of Subramanian *et al.* (1983) in *P. borchgrevinki* collected near Syowa and with those of Hidaka *et al.* (1984) in *Trematomus bernacchii* collected in the same area. An increase in the concentrations of organochlorines with age has also been observed by Connel (1987) in the striped bass and by Larsson *et al.* (1991) in Norwegian eels. These findings show that the curves for males and females have different slopes. The plot of concentrations in the present study shows higher values in males than females for the same body-weight class (Fig. 1). Two hypotheses are possible to explain this difference: (1) it depends on the different growth rate of the two sexes; in the same body-weight class a female is younger than a male and therefore has had shorter exposure, (2) females eliminate these compounds during reproduction, as happens in marine mammals during pregnancy and lactation (Tanabe *et al.* 1982, Aguilar & Borrel 1988).

Table III shows PCBs levels as the sum of about 20 congeners

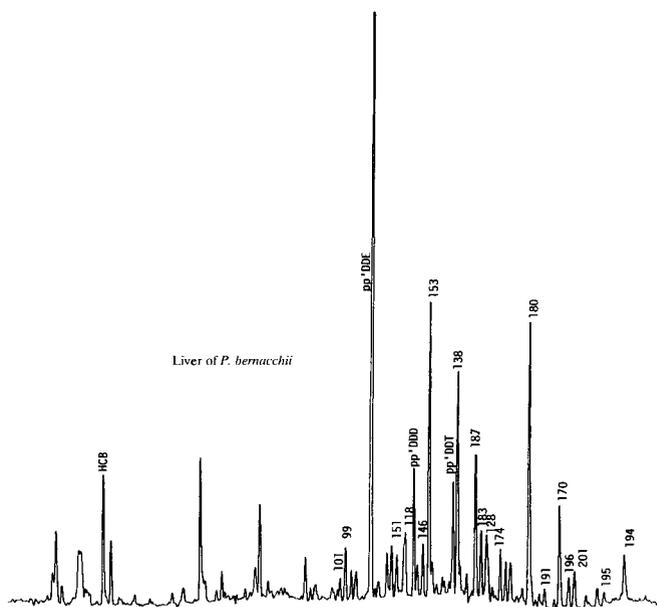


Fig. 2. High resolution capillary column gas chromatogram of a sample of liver of *P. bernacchii*. IUPAC numbers are reported for PCBs.

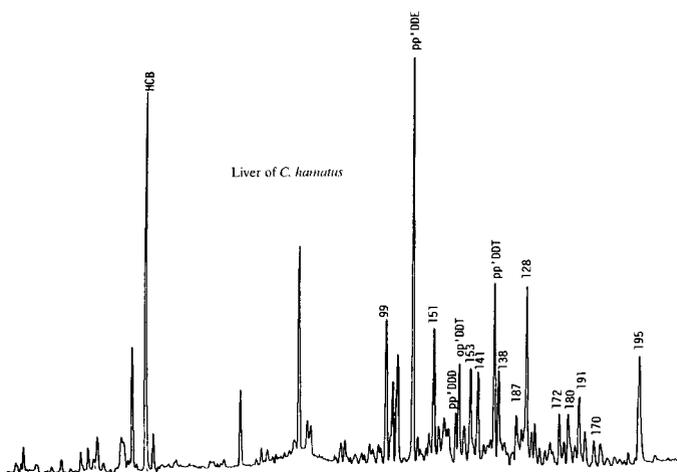


Fig. 3. High resolution capillary column gas chromatogram of a sample of liver of *C. hamatus*. IUPAC numbers are reported for PCBs.

and isomers. The levels found in the muscle of the various species ranged from 2.8 ng g⁻¹ in *C. mawsoni* to 12.8 ng g⁻¹ in *P. bernacchii*. Comparison with EOM shows that these differences cannot be explained simply on the basis of the different fat content of the tissue. They could be due to metabolic capacities and characteristics which vary between species. The PCBs content of these samples is higher than in the samples of Subramanian *et al.* (1983) in some of the same species collected at Syowa station, and much lower than in samples from other seas and oceans which have higher industrial and human activities (Vuorinen *et al.* 1985, Larsson

et al. 1991). The ratio DDTs/PCBs was always less than one (Table III) confirming the general observation of the world-wide increase of PCBs with respect to DDTs over the last few years.

PCB composition was investigated in the liver of *C. hamatus* and *P. bernacchii* (Table IV) and showed the presence of at least 22 isomers and congeners, mainly with 5–8 chlorines (Figs 2 & 3). Pentachlorobiphenyls account for 19% of the total residue in *C. hamatus* and only 9.2% in *P. bernacchii*; in the former there is a high proportion of 22'44'5, characterized by IUPAC number 99 (Ballschmitter & Zell 1980). Hexachlorobiphenyls constituted most of the residue in both cases (52% and 50.5%); in *C. hamatus* the isomers 22'355'6 (no. 151), 22'33'44' (no. 128) and 22'44'55' (no. 153) each account for more than 10% of the total residue whereas in *P. bernacchii*, 22'44'55' (no. 153) and 22'344'5' (no. 138) predominate. Of heptachlorobiphenyls, only the isomers 22'344'55' (no. 180) in *P. bernacchii* exceeded 10% of the total residue. Among octachlorobiphenyls, 22'33'44'56 (no. 195) is to be noted in *C. hamatus*.

Comparison with the literature shows that the fingerprint of *P. bernacchii* is quite similar to that of fish from temperate regions (Larsson *et al.* 1991) and other organisms from Antarctica (Tanabe *et al.* 1986) or from other geographical areas (Focardi *et al.* 1988). The "fingerprint" of *C. hamatus* showed significant differences in that its predominating congeners (nos. 128, 141, 151) are only a minor component of the total residue in other organisms. It is interesting to observe that differences in the multi-enzymatic systems involved in the metabolism of xenobiotic compounds were found between *C. hamatus* and *P. bernacchii* by Focardi *et al.* (1989).

Acknowledgements

This work is in the framework of the Italian National Programme for Antarctic Research.

References

- AGUILAR, A. & BORREL, A. 1988. Age- and sex- related changes in organochlorine compound levels in Fin Whales (*Balaenoptera physalus*) from the Eastern North Atlantic. *Marine Environmental Research*, **25**, 195-211.
- BALLSCHMITER, K. & ZELL, M. 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Zeitschrift für Analytische Chemie*, **302**, 20-31.
- BALLSCHMITER, K., SCHOLZ, C., BUCHERT, H., ZELL, M., FIGGE, K., POLZHOFFER, K. & HOERSCHELMANN, H. 1981. Studies of the global baseline pollution. V. Monitoring the baseline pollution of sub-Antarctic by penguins as bioindicators. *Fresenius Zeitschrift für Analytische Chemie*, **309**, 1-7.
- BIDLEMAN, T.F. & LEONARD, R. 1982. Aerial transport of pesticides over the Northern Indian Ocean and adjacent seas. *Atmospheric Environment*, **16**, 1099-1107.
- CONNELL, D.W. 1987. Age to PCB concentration relationship with the striped bass (*Morone saxatilis*) in the Hudson River and Long Island Sound. *Chemosphere*, **16**, 1469-1474.
- FOCARDI, S., LEONZIO, C. & FOSSI, C. 1988. Variations in polychlorinated biphenyl congener composition in water birds in relation to position in the food chain. *Environmental Pollution*, **52**, 243-255.
- FOCARDI, S., FOSSI, C., LEONZIO, C. & DI SIMPLICIO, P. 1989. Mixed-function oxidase activity and conjugating enzymes in two species of Antarctic fish. *Marine Environmental Research*, **28**, 31-33.
- FOCARDI, S., GAGGI, C., CHEMELLO, G. & BACCI, E. In press. Organochlorines residues in moss and lichen samples from two Antarctic areas. *Polar Record*.
- GON, O. & HEEMSTRA, P.C. (eds) 1990. *Fishes of the Southern Ocean*. Grahamstown: J.L.B. Smith Institute of Ichthyology, 462 pp.
- HIDAKA, H., TANABE, S., KAWANO, M. & TATSUKAWA, R. 1984. Fate of DDTs, PCBs and chlordane compounds in the Antarctic marine ecosystem. *Memoirs of National Institute of Polar Research, Tokyo*, **32**, 151-161.
- LARSSON, P., HAMRIN, S. & OKLA, L. 1991. Factors determining the uptake of persistent pollutants in an eel population (*Anguilla anguilla* L.). *Environmental Pollution*, **69**, 39-50.
- LUKE, G., JOHNSTONE, G.W. & WOEHLE, E.J. 1989. Organochlorine pesticides PCBs and mercury in antarctic and subantarctic seabirds. *Chemosphere*, **19**, 2007-2021.
- NORHEIM, G., SOMME, L. & HOLT, G. 1982. Mercury and persistent chlorinated hydrocarbons in antarctic birds from Bouvetoya and Dronning Maud Land. *Environmental Pollution*, **28**, 233-240.
- NORSTRÖM, R.J., SIMON, M., MUIR, D.C.G. & SCHWEINSBURG, R.E. 1988. Organochlorine contaminants in Arctic marine food chains: identification, geographical distribution, and temporal trends in polar bears. *Environmental Science and Technology*, **22**, 1063-1071.
- OBER, A., VALDIVIA, M. & SANTA MARIA, I. 1987. Organochlorine pesticide residues in Chilean fish and shellfish species. *Bulletin of Environmental Contamination and Toxicology*, **38**, 528-533.
- OEHME, M. & MANO, S. 1984. The long-range transport of organic pollutants to the Arctic. *Fresenius Zeitschrift für Analytische Chemie*, **319**, 141-149.
- RISEBROUGH, R.W., REICHE, P., PEAKALL, D.B., HERMAN, S.G. & KIRVEN, M.N. 1968. Polychlorinated biphenyls in the global ecosystem. *Nature*, **220**, 1098-1102.
- RISEBROUGH, R.W., WALKER, W., SCHMIDT, T.T., DELAPPE, B.W. & CONNORS, C.W. 1976. Transfer of chlorinated biphenyls to Antarctica. *Nature*, **264**, 738-739.
- SCHNEIDER, R., STEINHAGEN-SCHNEIDER, G. & DESHER, H.E. 1985. Organochlorine and heavy metals in seals and birds from the Weddell Sea. In SIEGFRIED, W.R., CONDY, P.R. & LAWS, R.M., eds. *Antarctic Nutrient Cycles and Food Webs*. Berlin: Springer-Verlag, 652-655.
- SKARE, J.U., STENERSEN, J., KVESETH, N. & POLDER, A. 1985. Time trends of organochlorine chemical residues in seven sedimentary marine fish species from a Norwegian fjord during the period 1972-1982. *Archives of Environmental Contamination and Toxicology*, **14**, 33-41.
- SUBRAMANIAN, B.R., TANABE, S., HIDAKA, H. & TATSUKAWA, R. 1983. DDT and PCB isomers and congeners in Antarctic fish. *Archives of Environmental Contamination and Toxicology*, **12**, 621-626.
- SUBRAMANIAN, AN., TANABE, S., HIDAKA, H. & TATSUKAWA, R. 1986. Bioaccumulation of organochlorines (PCBs and pp'DDE) in Antarctic Adélie penguins (*Pygoscelis adeliae*) collected during a breeding season. *Environmental Pollution*, **40**, 173-189.
- TANABE, S., HIDAKA, H. & TATSUKAWA, R. 1983. PCBs and chlorinated hydrocarbon pesticides in antarctic atmosphere and hydrosphere. *Chemosphere*, **12**, 277-288.
- TANABE, S., SUBRAMANIAN, AN., HIDAKA, H. & TATSUKAWA, R. 1986. Transfer rates and pattern of PCB isomers and congeners and pp'DDE from mother to egg in Adélie penguins (*Pygoscelis adeliae*). *Chemosphere*, **15**, 343-351.
- TANABE, S., TATSUKAWA, R., MARUYAMA, K. & MIYAZAKI, N. 1982. Transplacental transfer of PCBs and chlorinated hydrocarbon pesticides from the pregnant Striped Dolphin (*Stenella coeruleoalba*) to her foetus. *Agricultural and Biological Chemistry*, **46**, 1249-1254.
- WOLFF, E.W. 1990. Signals of atmospheric pollution in polar snow and ice. *Antarctic Science*, **2**, 189-205.
- VUORINEN, P.J., PAASIVIRTA, J., PIILOLA, T., SURMA-AHO, K. & TARHANEN, J. 1985. Organochlorine compounds in Baltic salmon and trout. I. Chlorinated hydrocarbons and chlorophenols. *Chemosphere*, **14**, 1729-1740.