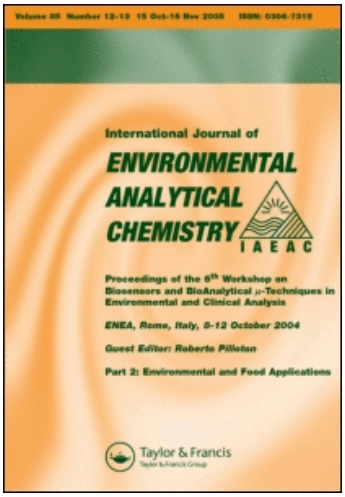

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POLYCHLOROBIPHENYLS IN SEDIMENT, SOIL AND SEA WATER SAMPLES FROM ANTARCTICA

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The presence of PCBs was evaluated in environmental samples collected in Antarctica during the 1990–91 and 1991–92 Italian Expeditions by using an optimized procedure for GC-ECD peak assignment. In particular, marine sediment samples from Terra Nova Bay and Ross Sea, and lake sediment and soil samples from Victoria Land, near to the Italian Base (BTN) (1990–1991 expedition) were collected and analyzed. The relevant PCB concentrations ranged between 30–160, 60–120 and 40–70 pg/g respectively, and were strongly dependent on the particle size distribution of each sample as found in previous expeditions. The depth profiles of PCB content in marine sediment samples collected in a few stations clearly show that PCBs are confined in a surface layer of about 10 cm. A coastal sea water depth profile of PCBs before and after pack ice melting was also obtained by collecting samples in Terra Nova Bay—Gerlache Inlet (1990–91 expedition). The total PCB concentration was about 140 pg/l and was practically constant up to 25 m deep. At 250 m which is near the sea bed, an increase of PCB content up to about 200 pg/l was observed. Finally, PCBs were measured in sea water samples collected in the same area (1991–92 expeditions), showing an increase of about 70% in the surface water layer after pack ice melting.

KEY WORDS: Antarctica, PCBs, sea water, marine and lake sediments, soils.

INTRODUCTION

The importance of PCBs in environmental studies is mainly due to the fact that they have been used in many industrial applications for about forty years, without any precaution to prevent environmental contamination. In addition, their high chemical stability and ability to accumulate in organisms are responsible for long residence times in the environment and for toxic effects on biota, respectively[1–4].

For these reasons a monitoring program of PCBs was begun in 1988 within the Environmental Impact—Chemical Methodologies framework of the Italian Research Programme in Antarctica (PNRA). The main aim was to evaluate the presence of PCBs in Antarctica and to gain a better understanding of the diffusion mechanisms of these contaminants in Antarctica over time by sampling those matrices, such as sediments, which have recorded information on past events in their depth-dependent chemical composition.

The results relevant to the analysis of samples collected during previous italian expeditions in Antarctica (1988–89, 1989–90 and, some of the samples from 1990–91) have already been discussed[5,6].

The present paper deals with the 1990–91 and 1 991–92 expeditions, whose aims were the following:

1990–91 Expedition

- to complete a map on the presence of PCBs in marine sediments in a large area of the Ross Sea (Figures 1 and 2);
- to evaluate the PCB depth profile in marine sediments;
- to confirm the presence of PCBs in Antarctica by sampling soils and lake sediments in the area of Victoria Land around the Italian Base (Figure 2), already studied during previous expeditions;
- to investigate the effect of pack ice melting on the PCB depth profile in coastal sea water at Gerlache Inlet (Figure 3).

1991–92 Expedition

- to verify the effect of pack ice melting on the PCB content in the surface sea water layer at Gerlache Inlet (Figure 3).

The results on the PCB content in marine sediment, lake sediment, soil and sea water samples are presented, including depth profiles in sediments and coastal sea water. An optimized procedure for chromatographic peak assignment is also discussed.

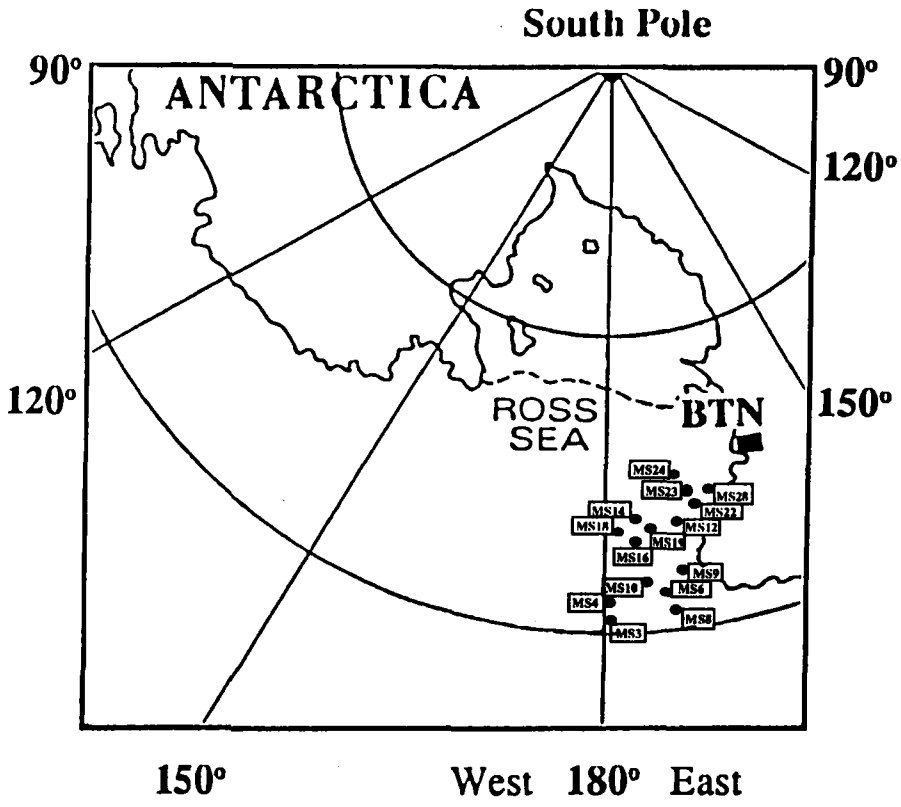

Figure 1 Location of sampling stations of marine sediment (MS) samples gathered during the 1990–91 Italian expeditions in Antarctica. At stations MS10, MS18 and MS22 samples were collected at different depths. (The dotted line represents the pack ice edge).

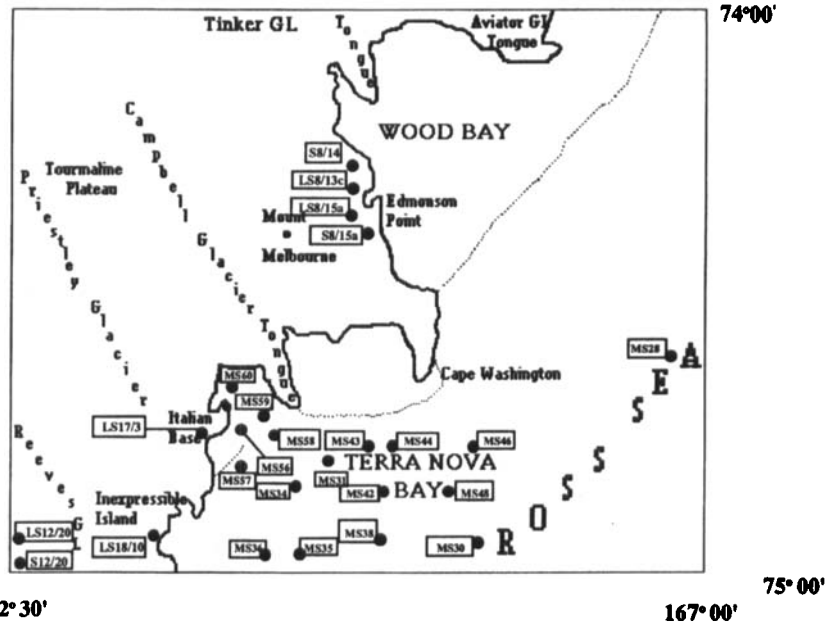

Figure 2 Location of sampling stations of marine sediment (MS), lake sediment (LS) and soil (S) samples gathered during the 1990–91 Italian expeditions in Antarctica. At station MS38 samples were collected at different depths. (The dotted line represents the pack ice edge).

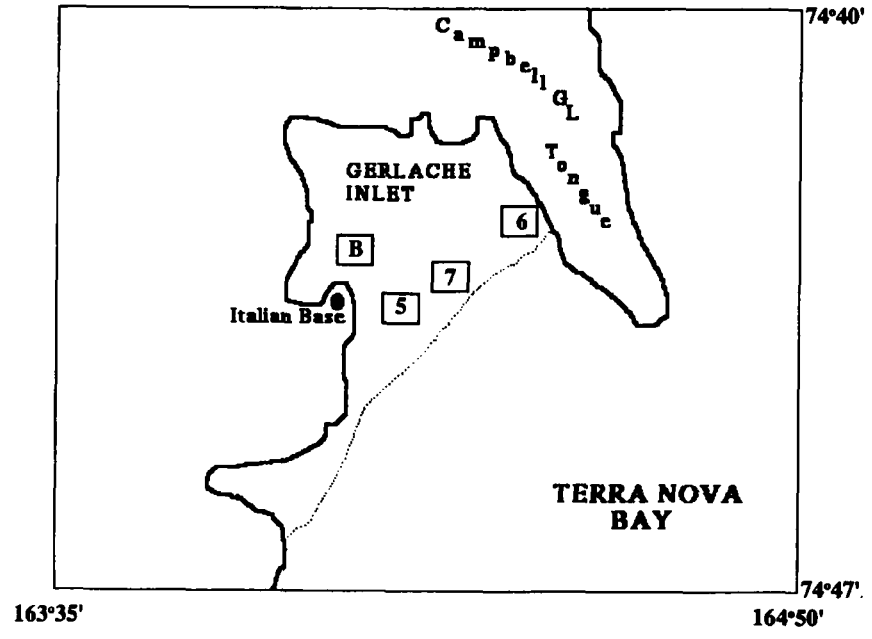

Figure 3 Location of sampling stations of sea water samples gathered before and after pack ice melting during the 1990–91 (Station B) and the 1991–92 (stations B, 5, 6 and 7) Italian expeditions in Antarctica. (The dotted line represents the pack ice edge).

EXPERIMENTAL

Reagents

n-Hexane, acetone and dichloromethane Pesticide Grade; Na_2SO_4 and Hg RPE-ACS; Cu powder RLE and Florisil RS (60–100 mesh) were supplied by Carlo-Erba (Italy). Aroclor 1221, 1232, 1248, 1260 (35 μg/ml) and individual PCB congeners (35 μg/ml) standard solutions were supplied by AccuStandards (USA). Reference marine sediment samples CS-1 and HS-2, containing 1.2 ng/g and 112 ng/g of total PCBs respectively, expressed as Aroclor 1254, were supplied by the National Research Council of Canada. Reference soil samples, containing 91 ng/g of Aroclor 1260, were supplied by Environmental Resources Associated (USA). Reagent pre-treatments are described elsewhere[5].

Apparatus

A supercritical fluid chromatograph (SFC) mod. 3000 (Carlo Erba Strum., Italy), used in the GC mode, and a gas chromatograph (GC) 5160 Mega series (Carlo Erba Strum., Italy), both equipped with automatic cold on-column injection port mod. OC516 and electron capture detector (ECD) were used. Chromatographic separation was always performed on a chemically bonded fused silica capillary column CP-Sil 8CB (Chrompack Italy S.r.l.) 0.25 mm I.D., 0.25 μm film thickness, 50 m length, connected to 2 m long deactivated fused silica capillary pre-column 0.32 mm I.D.. The chromatographic conditions were:column heated at 60°C isothermal for 2 min, then 15°C/min up to 180°C and isothermal for 6 min, 4°C/min up to 220°C and isothermal for 2 min, 5°C/min up to 280°C and isothermal for 25 min; detector temperature 320°C, carrier gas helium, make-up gas nitrogen. A mass spectrometric detector mod. 5971 (Hewlett Packard Italiana, Italy) coupled to a GC was used for the identification and assignment of chromatographic peaks. A Microtrac particle analyzer (Leeds & Northrup Int., USA) equipped with two optical benches, which permits analysis in the 0.12–42 μm and 1.2–300 μm particle size ranges, was used to evaluate the particle size distribution of sediment and soil samples.

Sampling

Sediment and soil samples: Figures 1 and 2 show the sampling stations of marine sediment, lake sediment and soil samples collected during the 1990–91 expedition. Marine sediments were generally collected with a stainless steel grab. In four stations, namely MS10, MS18, MS22 and MS38, samples were collected with a box-corer system and aliquots between 0–15 cm and 15–30 cm were collected, with the exception of station MS22 where aliquots were collected at 0–10, 10–20 and 20–30 cm. Lake sediment and soil samples were collected in the same area already studied in previous expeditions. In particular, lake sediments were collected manually in four small lakes which were generally 30–150 m wide and 60–150 cm deep. Three of the lakes were located along the coast line and one was located 20 Km from the coast (Figure 2); soil samples were also collected manually in three sites near the lakes when possible (Figure 2). All the samples were stored at –20°C in polyethylene containers suitably cleaned and conditioned before use.

Sea water samples: Figure 3 shows the sampling stations of sea water samples collected at different depths (station B: 0.5, 10, 25, and 250 meters) and at the surface (stations B, 5, 6, 7: 0.5 meters deep) during the 1990–91 and 1991–92 expeditions, respectively. Sampling was performed with a "go-flo" system with teflonated bottles or a teflon pumping system. Samples were stored in 20-liter stainless steel containers (Sartorius, mod. SM 17S32) at –20°C.

Analytical methods

The analytical procedures used, including the evaluation of accuracy and precision for PCB determination in the matrices considered, have been discussed elsewhere[5,6]. In particular, sea water samples were extracted with n-hexane, and the stainless steel container also rinsed with the same solvent. These aliquots were mixed together, dried, and reduced to a volume of about 1.5 ml. As far as sediments and soils is concerned, 20 g of sample were weighed, made homogeneous and divided into two aliquots of 15 g and 5 g each. The 5 g aliquot was used to evaluate the percentage of water in the sample and to perform particle size analysis. The 15 g aliquot was extracted with 1:1 n-hexane/acetone mixture in an ultrasonic bath. The extract was treated with Cu powder and Hg for sulphur removal, and reduced to about 1.5 ml.

For all the samples, the final extract was loaded on a Florisil column, from which PCBs were selectively eluted with 10 ml of n-hexane. The eluate was concentrated at 100 µl right before the analysis performed by GC-ECD or GC-MS.

RESULTS AND DISCUSSION

Identification of PCBs

The content of individual PCB congeners in Antarctic sediment, soil and sea water samples is very low, and is generally below the detection limit of GC-MS. This occurs even if large quantities of samples are extracted (20 g for sediment and soil samples, and 20 l for sea water samples) and the final extracts are concentrated at a final volume as low as 100 µl which can still be weighed with an acceptable accuracy. This makes GC-ECD the only useful technique for quantitative analysis. In this case peak assignement is made on the basis of the expected retention times within a fixed time window. A time window of 0.1 min was used in previous works as generally reported in literature[1]. If we consider the chromatogram B shown in Figure 4 it becomes evident that at this PCB concentration level there could be a lot of interfering signals which may affect peak assignment.

In order to minimize incorrect peak assignment it is therefore extremely important to calculate a statistically significant time window. This was done by calculating the mean retention times (RT_{mean}) referred to two internal standards, namely PCB36 and PCB209, and the sample standard deviations (s_{RT}) of nine selected PCB congeners on the basis of the results relating to 5 injections of standard solutions (Table 1). The corresponding 95% confidence limits (±0.012 min) were then obtained and used as a time window for peak assignement.

The correctness of this assumption was confirmed by analyzing standard solutions and certified sediment samples: the relevant chromatograms were evaluated by using both the time windows 0.1 and 0.012 min, and two values of concentrations were calculated.

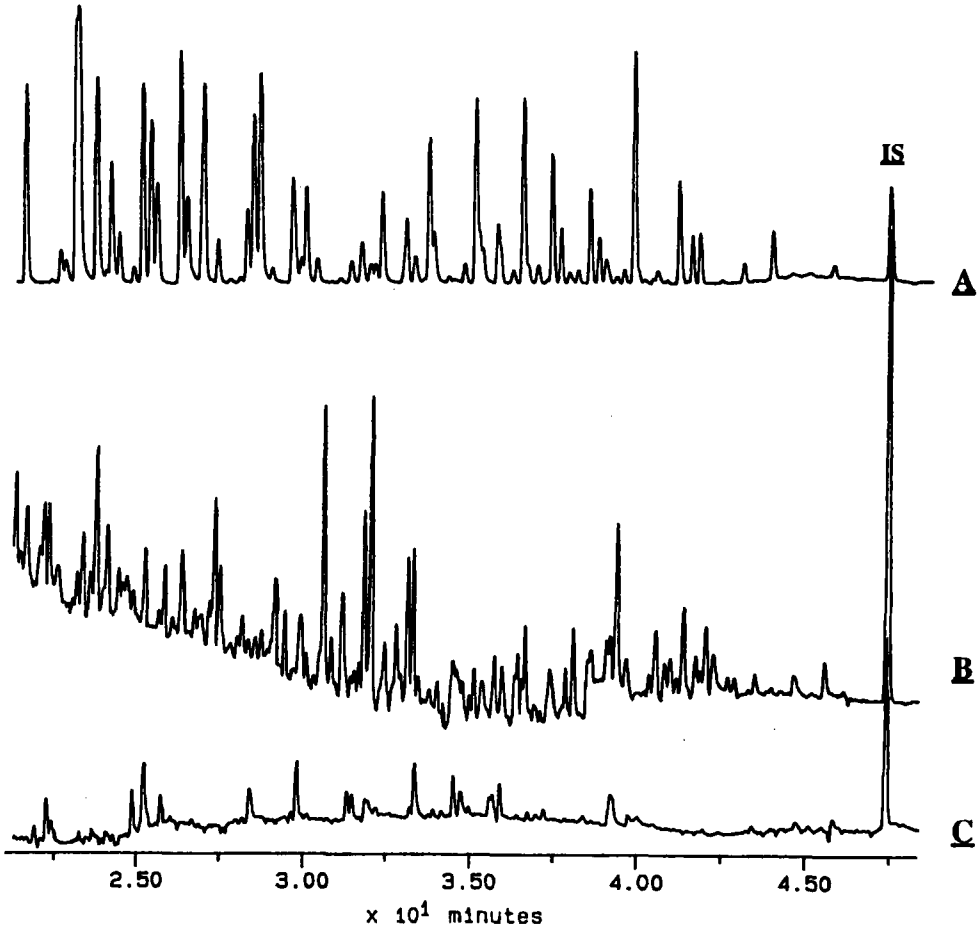

Figure 4 ECD-gas chromatograms of *A*) Aroclor mixture standard solution (Aroclor) 1221, 1232, 1248 and 1260: about 300 pg of total PCBs injected); *B*) extract of an Antarctic sea water sample (30 pg estimated total PCBs injected); *C*) blank. (*IS* = internal standard; for experimental conditions see text).

These two values were both in agreement with the expected ones and their differences were about 5% and 10% for standard solutions and certified sediment samples, respectively. The same procedure was used to evaluate the chromatograms of all the samples collected, which showed much higher differences. In particular, the PCB concentration of sediment and sea water samples decreased typically by a factor of 1.3 and 3 respectively, when the time window was decreased from 0.1 to 0.012 min.

At present, a supercritical fluid extractor (SFE) coupled with a cold trap-GC-MS system is being developed in our laboratory which will permit us to inject higher volumes (50–100 µl) into the chromatographic column, thus allowing the determination of organic micropollutants in environmental samples by a mass spectrometric detector even at low pg/l levels.

Table 1 Reproducibility of the retention times of nine PCB congeners. The mean values (RT_{mean}) and the sample standard deviations (S_{RT}) were obtained on 5 repeated measurements.

PCB (IUPAC number)	RT_{mean} *(min)*	S_{RT} *(min)*
28	27.053	0.011
52	29.047	0.010
101	34.957	0.012
118	39.794	0.011
153	41.643	0.009
105	41.934	0.008
138	43.935	0.009
156	48.154	0.009
180	49.270	0.011

Analysis of sediment and soil samples

Tables 2 and 3 show the results relevant to marine sediments, and Table 4 those relevant to lake sediments and soils. Actually, the amount of PCBs present in samples such as sediments or soils, is much more likely to be related to the particle surface area per volume unit, where they are adsorbed, than to the mass unit[6]. For this reason, the concentration of each sample, expressed in pg/g dry weight, was normalized by dividing it for the relevant calculated specific surface area (CS) as obtained by particle size analysis[5,6]. The following concentration ranges—expressed in (pg/g)(m^2/cm^3) dry weight—were found: marine sediments 90–230 (mean value: 145), lake sediments 170–240 (mean value: 218) and soils 120–160 (mean value: 137). In the four stations where marine sediments were collected at different depths, a concentration of about 100–200 (pg/)(m^2/cm^3) was observed in a surface layer of about 10–15 cm, while in deeper layers PCBs were below the detection limit. Only for sample MS38 a very low quantity of PCBs—about 20 (pg/g)(m^2/cm^3)—was measured in the second layer.

From all these results the following conclusion can be drawn:

- no significant differences of normalized PCB content in marine sediments among stations located in open sea [stations from MS3 to MS28, mean value: 142 (pg/g) (m^2/cm^3)] and those located closer to the coastal line [stations from MS30 to MS60, mean value: 148 (pg/g)(m^2/cm^3)] were observed. This slight and constant contamination may exclude any direct source of PCB pollution in Antarctica. The same situation was also observed for lake sediments and soils;
- the results relevant to depth profiles in marine sediments showed that PCBs were confined in a surface layer of about 10 cm. This result is supported by the fact that PCBs began to be used at an industrial level in 1930 and a sediment layer 10-cm deep corresponds to about 100 years according to the sedimentation rate of the area under study which was 0.05–0.1 cm/year as estimated by using the ^{210}Pb method[7]. The very low content found in the second layer of station MS38 may be explained by considering bioturbation processes; although a slight contamination of this sample cannot be excluded "a priori";
- lake sediments show the highest normalized PCB content. These results, as already stated[6], might be explained by considering the nature of Antarctic lakes, which are

formed during the deglacial season, and taking into account the PCBs trapped in the ice matrix during its formation which come from the atmospheric particulate[8–10].

Analysis of sea water samples

The results relevant to the samples collected during the 1990–91 expedition before and after pack ice melting at different depths, namely 0.5, 10, 25 and 250 m, have already been described in a previous paper[6]. However all the chromatograms were reprocessed according to the procedure for peak assignment described above, which showed much lower PCB content (Table 5). These results highlighted the low PCB contamination of the area under observation (typically 150 pg/l). In particular, the PCB content along the water column before pack ice melting ranged in a narrow interval around 140 pg/l, with a consistent increase near the sea bed at 250 m, which is probably due to remobilization

Table 2 Total PCB content of marine sediment samples gathered at Terra Nova Bay and Ross Sea during the 1990–91 Italian expedition in Antarctica (the relative standard deviation of mean values is reported in brackets).

Sampling station	*PCBs (pg/g dry weight)*	*CS (m^2/cm^3)*	*PCBs/CS ($(pg/g)/(m^2/cm^3)$)*
MS3	100	0.80	120
MS4	140	0.71	200
MS6	110	0.78	140
MS8	80	0.76	110
MS9	90	0.68	130
MS10	60	0.61	100
MS12	150	0.66	230
MS14	50	0.50	100
MS16	90	0.45	200
MS18	50	0.35	140
MS19	60	0.51	120
MS22	50	0.50	100
MS23	70	0.48	150
MS24	100	0.56	180
MS28	60	0.53	110
MS30	160	0.44	170
MS31	60	0.37	160
MS34	30	0.23	130
MS35	40	0.42	100
MS36	30	0.27	110
MS38	110	0.56	200
MS42	70	0.37	190
MS43	40	0.39	100
MS44	50	0.54	90
MS46	80	0.52	150
MS48	70	0.49	140
MS56	70	0.33	210
MS57	60	0.35	170
MS58	30	0.28	110
MS59	60	0.50	120
MS60	100	0.45	220
mean value	75 (45%)		145 (28%)

Table 3 Depth profile of total PCB content in marine sediment samples gathered at Terra Nova Bay and Ross Sea during the 1990–91 Italian expedition in Antarctica.

Sampling station	*Depth (cm)*	*PCBs (pg/g dry weight)*	*CS (m^2/cm^3)*	*PCBs/CS ($(pg/g)/(m^2/cm^3)$)*
MS10	0–12	60	0.61	100
	13–25	n.d.	0.89	n.d.
MS18	0–14	50	0.35	140
	15–28	n.d.	0.61	n.d.
MS22	0–10	50	0.50	100
	11–20	n.d.	0.58	n.d.
	21–30	n.d.	0.53	n.d.
MS38	0–15	110	0.56	200
	16–34	15*	0.75	20*

n.d. = not detectable; (*) approximate value

Table 4 Total PCB content of lake sediment and soil samples gathered at Terra Nova Bay and Victoria Land during the 1990–91 Italian expedition in Antarctica (the relative standard deviation of mean values is reported in brackets).

Sampling station	*PCBs (pg/g dry weight)*	*CS (m^2/cm^3)*	*PCBs/CS ($(pg/g)(m^2/cm^3)$)*
lake sediment			
LS8/13c	60	0.35	170
LS8/15a	90	0.39	230
LS17/3	120	0.43	280
LS18/10	70	0.40	170
LS12/20	90	0.38	240
mean value	86(27%)		218 (22%)
soil			
S8/14	50	0.32	160
S8/15a	40	0.33	120
S12/20	70	0.52	130
S17/3	60	0.45	130
mean value	55 (23%)		135 (13%)

Table 5 Total concentration of PCBs in sea water samples gathered at Terra Nova Bay – Gerlache Inlet before and after pack ice melting during the 1990–91 Italian expedition in Antarctica.

Sampling station	*Depth (m)*	*PCBs (pg/l)*	
		Before pack ice melting	*After pack ice melting*
B	0.5	130	170
B	10	150	120
B	25	140	160
B	250	210	220

Table 6 Total concentration of PCBs in surface sea water samples gathered at Terra Nova Bay – Gerlache Inlet before and after pack ice melting during the 1991–92 Italian expedition in Antarctica.

Sampling station	*PCBs (pg/l)*	
	Before pack ice melting	*After pack ice melting*
5	150	290
6	220	250
7	170	230
B	140	370
mean value	170 (21%)	285 (22%)

processes involving sediments. In this case, no significant change in PCB content was observed after pack ice melting, while during the 1991–92 expedition an increase of about 70% in the PCB content in the surface layer of sea water after pack ice melting was found (Table 6). The pack ice and sea water samples collected during the 1993–94 expedition are currently being analyzed and this will confirm whether this increase can be explained once again by considering the transfer to sea water of PCBs associated with the atmospheric particulate trapped in the pack ice.

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