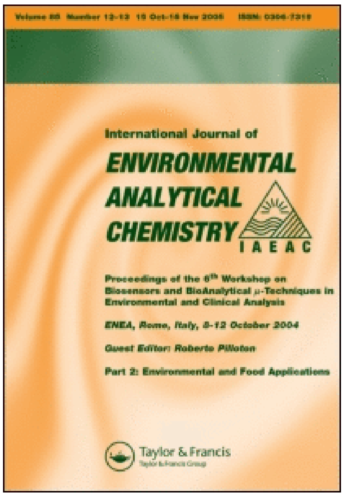

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DETERMINATION OF POLYCHLOROBIPHENYLS IN ENVIRONMENTAL SAMPLES FROM ANTARCTICA

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The analysis of PCBs in sea water samples gathered during the 1990–91 Italian expedition in Terra Nova Bay—Gerlache Inlet showed a typical total concentration of 550 pg/l. A slight increase in PCB content was observed in the surface layer of the water column before pack ice melting, while an increase by a factor of about two was found in the same water layer after pack ice melting. PCBs were also measured in marine sediment, lake sediment and soil samples collected at Terra Nova Bay, Wood Bay and Victoria Land during the 1989–1990 Italian expedition. The relevant concentrations ranged between 45–361, 102–560 and 61–120 pg/g respectively and were strongly dependent on the total particle surface of each sample. PCB congener distributions were centered on 3- to 6-substituted and on 4- to 7-substituted congener classes for sea water and sediment/soil samples respectively, and were typical for each matrix considered.

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

INTRODUCTION

The widespread environmental occurrence of polychlorobiphenyls (PCBs) has already been proved by many studies carried out in the last few years which have made the data on PCB content available for a variety of environmental matrices[1]. The interest in these compounds is mainly due to their high chemical stability and to their toxic effects on biota, comparable to those of dioxins[2–4]. For these reasons a monitoring program was begun within the Environmental Impact—Chemical Methodologies framework of the Italian Research Programme in Antarctica (PNRA). Its main aim was to evaluate the presence and the distribution of PCBs in different environmental compartments of the area studied, and also to investigate the effect of pack ice melting on PCB content in sea water[5]. Several sea water, sediment and soil samples were collected at different sampling stations during five Italian scientific expeditions in Antarctica, and were analyzed for PCB determination.

This paper presents the results of the PCB content of sea water, marine sediment, lake sediment and soil samples gathered during the 1989–90 and 1990–91 Italian expeditions in Antarctica. The marine depth profile of PCBs, the effect of pack ice melting on PCB content of sea water near the Italian Base, the correlation between PCB content and particle size distribution, for sediment and soil samples, along with the individual determination of PCB congeners and distribution among congener classes, are discussed.

EXPERIMENTAL

Reagents

n-Hexane, acetone, 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 (35μg/ml), 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 sample, containing 91 ng/g of Aroclor 1260, was 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 8 CB (Chrompack Italy S.r.l.) 0.25 mm I.D., 0.25 μm film thickness, 50 m length, connected to 2 m long disactivated fused silica capillary pre-column 0.32 mm I.D.. The chromatographic conditions were Ti=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 with 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 for evaluating the particle size distribution of sediment and soil samples.

Sampling stations and sampling techniques

Sea water samples were gathered during the 1990–91 expedition in one sampling station which was located in the Gerlache Inlet near the Italian Base at 74° 40′07″ latitude South and 164°07′17″ longitude East (Figure 1). Four samples were collected before pack ice melting, and four after pack ice melting, at four different depths (0.5, 10, 25 and 250 m) by means of a "go-flow" system and were subsequently stored at –20°C in 20–1 stainless steel containers (Sartorius, mod. SM 17S32). Marine sediment, lake sediment and soil samples were gathered during the 1989–90 Italian expedition in Antarctica. Marine sediments were collected at seventeen sampling stations located in Terra Nova Bay and Wood Bay, along the coast between 74° 15′00″ and 75° 00′00″ latitude South (Figure 2). The samples were collected with a stainless steel grab and subsequently stored at –20°C in polyethylene containers. Lake sediments were collected in six small lakes which were generally 30–150 m wide and 60–150 cm deep. Five of the lakes were located along the coast line in the same area where marine sediments were collected, and one was located 20 Km from the coast (Figure 2). The samples were collected manually and subsequently stored at – 20°C in polyethylene containers. Finally, five soil samples were collected near the lakes, when possible (Figure 2), and subsequently stored at –20°C in polyethylene containers. All of the containers were suitably cleaned and conditioned before use.

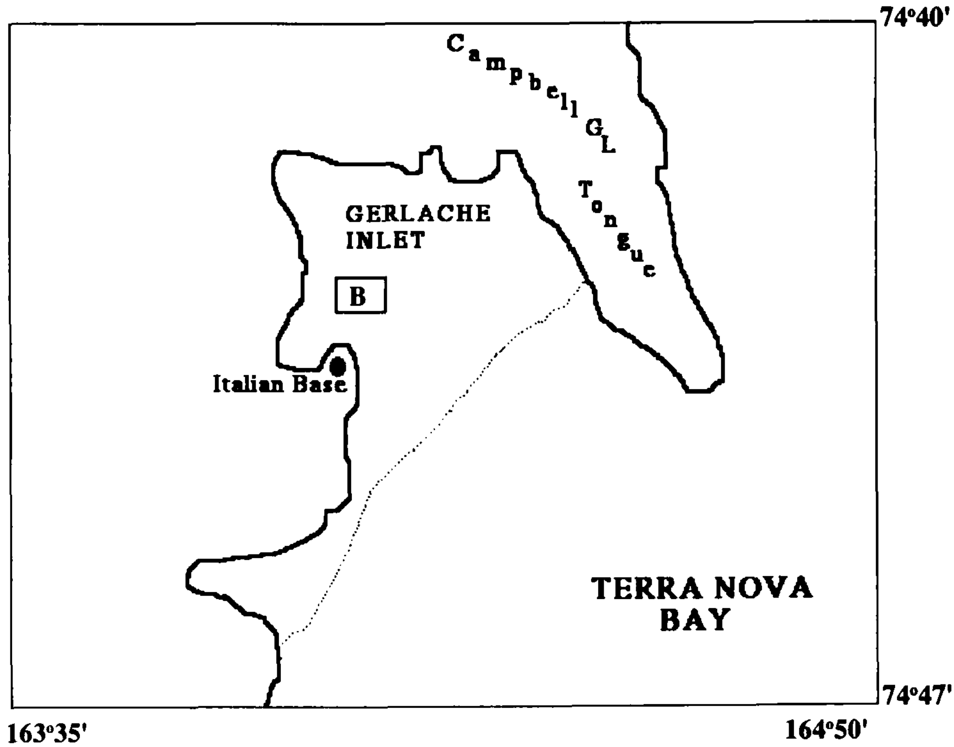

Figure 1 Location of the sea water sampling station (B) during the 1990–91 Italian expedition in Antarctica.

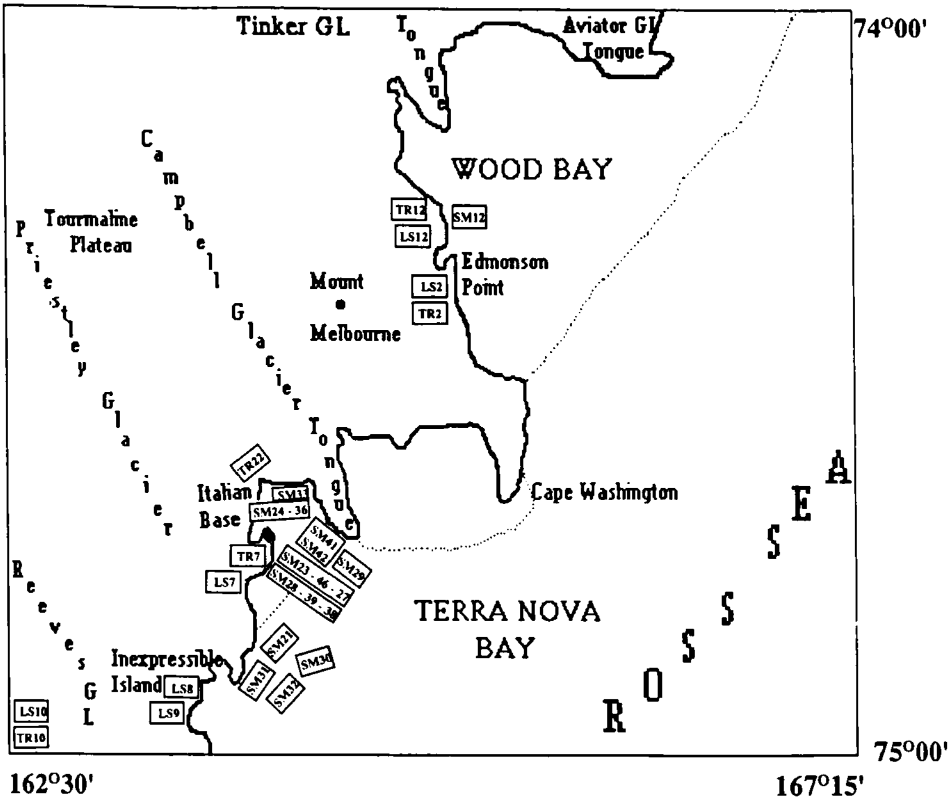

Figure 2 Location of the marine sediment, lake sediment and soil sampling station during the 1989–90 Italian expedition in Antarctica.

Procedure

The procedure used for sea water sample and particulate matter analysis is described elsewhere[5]. In particular, for sea water samples liquid-liquid extraction was preferred to solid-liquid extraction since the latter may suffer from low recoveries, undesirable and irreproducible losses and the release of interfering compounds during the elution step[6,7], especially when volumes of water as large as 1,000 liters are processed[7], as in the case of reference 8, where very low PCB level in Antarctic sea water samples are reported. Sediment and soil samples were analyzed by following a slightly different procedure. Frozen samples were allowed to melt in a clean laboratory. Immediately after sample melting, 20 g of wet sediment or soil were weighed, made homogeneous and then divided into two aliquots of 15g and 5g each. The 15g aliquot was analyzed for total PCB content and the 5g aliquot was used to evaluate the percentage of water in the sample and to perform particle size analysis. In some cases, one more 15g aliquot was taken and spiked with a standard solution containing Aroclor 1221, 1232, 1248 and 1260 in order to measure the recovery and accuracy of the procedure used. The 15g aliquot was put into a 25 ml pyrex bottle and extracted twice with 12 ml of 1 : 1 n-hexane/acetone mixture in an ultrasonic bath for 20 min. After separation from the solid sample, which was rinsed with 5 ml of solvent mixture, the extracts were mixed together, reduced to 15 ml under a mild nitrogen flow at room temperature and then treated for two hours with Cu powder and Hg under magnetic stirring for sulphur removal. After separation, the extract was reduced to about 0.3 ml and loaded on a pre-conditioned Florisil column with about 1g of Na_2SO_4 on top. PCBs were selectively eluted with 16 ml of n-hexane, of which 5 ml five were subsequently reduced to 50–100 µl and analyzed by GC. In these conditions the interferences by other tested chlorinated pesticides which may have been present in the sample were negligible[5]. All of the extraction and clean-up operations were performed in a class 100 laminar flow hood.

RESULTS AND DISCUSSION

Identification and quantification

PCB congeners were identified by gas chromatography—mass spectrometry on a standard solution containing 0.1 ng/µl each of Aroclor 1232, 1248 and 1260, and 0.2 ng/µl of Aroclor 1221. The relative retention time (RRT) for each congener was then calculated by using octachloronaphtalene (OCN) as an internal standard (IS) and applied for chromatographic peak assignment of real samples. Response factors (RFs) were also experimentally obtained for some selected PCB congeners and for OCN in the concentration range of 1–20 pg/µl. Relative response factors (RRFs) to OCN were then calculated and used in turn to calculate the RRFs for all congeners by extrapolating the values reported by Mullin[9]. Final extracts of real samples were analyzed by GC after the addition of a known amount of OCN, and quantification of chromatographic peaks was performed by using a commercial computer program (Maxima, Carlo Erba) which automatically assigns peaks on the basis of RRTs and calculates the concentration of each congener on the basis of RRFs and OCN concentration/peak area ratio.

Accuracy and precision

The evaluation of accuracy and precision for PCB determination in sea water samples was done by means of spiked samples and is discussed elsewhere[5]. A typical recovery of 77% was found and used to calculate PCB concentration of the samples also in the present case. As far as sediments and soil samples are concerned, the accuracy and precision of the described procedure were evaluated by means of spiked and reference marine sediment and soil samples. The total PCB content of the reference sediment and soil samples was obtained as a mean value of three replicate measurements of the total peak area expressed as ng/g of Aroclor 1254 and 1260, respectively. The total PCB content of the spiked samples was calculated by summing the individual concentrations of the identified congeners. Table 1 shows the results obtained. At the 0.5ng/g PCB level, the recovery was always better than 70%, with an rsd of 32%, and was used for calculating the PCB concentration in real samples.

Table 1 Recovery and precision for total PCB determination in certified and spiked sediment and soil samples (PCB concentrations were calculated as the sum of the concentration of identified congeners, unless otherwise specified).

Sample	*total PCBs (ng/g dry)*			
	certified	*found*	*% Recovery*	*rsd*[a]
marine sediment				
SM12	1.20[b]	0.94[b]	78	30
HS-2	112.0[b]	105.1[b]	94	7
Spiked 1	0.5	0.35	70	32
soil				
Reference	91.0[c]	86.0[c]	95	5
Spiked 1	0.5	0.38	76	30
Spiked 2	5.0	4.20	84	22

[a] on three replicate measurements
[b] expressed as Aroclor 1254
[c] expressed as Aroclor 1260

Analysis of sea water samples

Evidence of slight PCB contamination in Terra Nova Bay was found by the analysis of sea water samples gathered in the same area during the 1988–89 expedition[5]. These results also showed an increase in the PCB content in sea water after pack ice melting. The aim of the 1990–91 campaign was to first confirm the conclusion of the former expedition, and then to study the effect of the mixing process, along the water column, between sea and pack ice melting waters on the PCB content by collecting samples at four different depths, namely 0.5, 10, 25 and 250 m, before and after pack ice melting. Table 2 shows the total PCB content in sea water samples. These findings show that the PCB content along the water column before pack ice melting ranged in a narrow interval (500–600 pg/l), with an increase of about 50% in the surface sea water layer. After pack ice melting a more significant increase in PCB content confined to the same sea water layer was found, while the concentration below 25 m did not change at all. This increase may be explained by considering the following effects:

—the increase in anthropogenic activities. This had already been shown during the 1988–89 expedition by comparing the PCB content in sampling stations located at different distances from the Italian Base[5];

—the transfer of PCBs contained in the pack ice to sea water. These PCBs come from the air where they are present either in vapor phase or adsorbed on atmospheric particulate matter[10]. They are trapped into pack ice during ice formation and released during its melting. In this respect it must be pointed out that PCB content in Antarctic air samples (0.02–0.16 ng/m^3)[8] is only slightly different from values reported for the Mediterranean area (0.05–0.3 ng/m^3)[11] and, consequently, since atmospheric transport is the most important process in the spread of PCBs in the environment[10–12], and taking into account Antarctic climate conditions (low temperatures, dry precipitations, etc.), the differences in PCB content of sea waters between these two areas might not be so large as expected. However, we must also be aware of possible systematic errors in the analytical procedure used, possibly due to interference

Table 2 Total PCB content of sea water samples gathered during the 1990–91 Italian expedition in Antarctica (Terra Nova Bay—Gerlache Inlet).

Before pack ice melting			*After pack ice melting*		
Sampling station	*depth (m)*	*PCBs[a] (pg/l)*	*Sampling station*	*depth (m)*	*PCBs[a] (pg/l)*
B6A	0.5	910	B8A	0.5	1600
B6B	10	650	B8B	10	920
B6C	25	620	B8C	25	540
B6F	250	500	B8F	250	590

[a] mean value on three repeated measurements, r.s.d. was always better than 10%

and sample contamination effects which should be carefully considered. In particular, polychloroterpenes have been shown to interfere in the determination of PCBs in environmental samples[13–14].

The PCB content associated with particulate matter was always lower than 30%. The distribution of PCBs among congener classes (Figure 3) is centered on 3- to 6-substituted regardless of the depth, and this confirms the previous results obtained in the same area[5].

Analysis of sediment and soil samples

In order to get a better understanding of PCB contamination in the area under study, marine sediment, lake sediment and soil samples were gathered at Terra Nova Bay, Wood Bay and

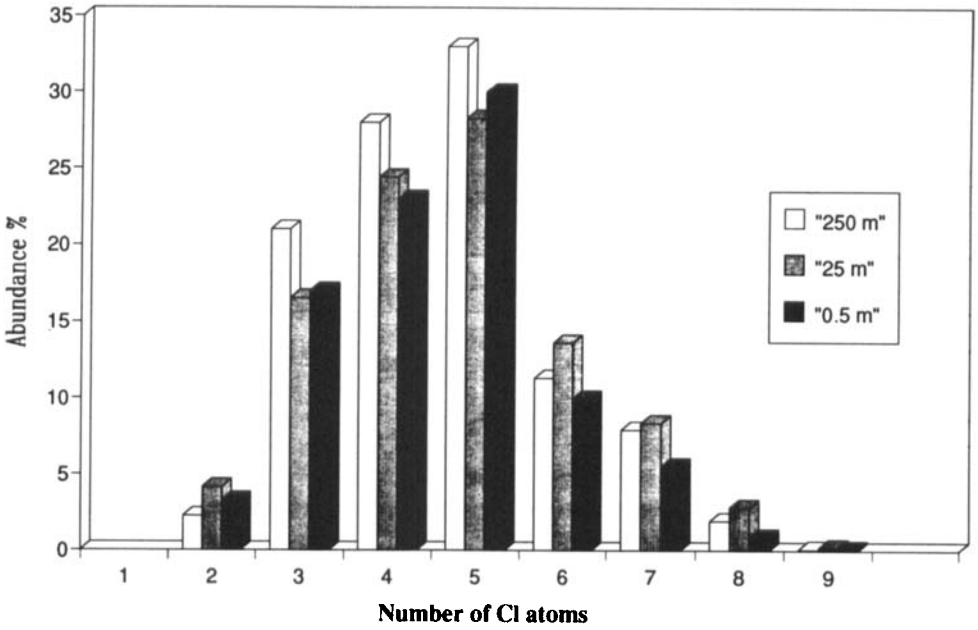

Figure 3 Histograms of the relative abundance of PCB congener classes in sea water samples gathered in the Gerlache Inlet (Antarctica) during the 1990–91 Italian expedition.

Table 3 Total PCB content of marine sediment, lake sediment and soil samples gathered at Terra Nova Bay, Wood Bay and Victoria Land during the 1989–90 Italian expedition in Antarctica.

Sample	*PCBs* *pg/g dry*	*CS* m^2/cm^3	*PCBs/CS*	n^0 *of congeners identified*
marine sediment				
SM12	80	0.25	320	58
SM21	84	0.34	247	59
SM23	91	0.34	268	54
SM24	102	0.43	237	64
SM27	45	0.20	225	63
SM28	61	0.34	179	57
SM29	92	0.37	249	57
SM30	172	0.82	210	69
SM31	361	1.30	278	68
SM32	171	0.80	214	60
SM33	53	0.25	212	68
SM36	141	0.53	266	70
SM38	192	0.79	243	72
SM39	101	0.39	259	71
SM41	54	0.40	135	55
SM42	82	0.32	256	76
SM46	44	0.23	191	61
mean value	113±78		235±42	
lake sediment				
LS2	140	0.55	255	57
LS7	297	0.85	349	73
LS8	560	1.33	420	69
LS9	102	0.49	208	53
LS10	174	0.51	341	70
LS12	115	0.33	348	72
mean value	231±175		320±76	
soil				
TR2	61	0.26	234	57
TR7	101	0.65	155	58
TR10	120	0.60	200	55
TR12	80	0.48	167	54
TR22	59	0.35	169	61
mean value	84±26		185±32	

Victoria Land during the 1989–90 Italian expedition. Table 3 shows the total PCB concentrations found in all the samples analyzed, along with the calculated specific surface area (CS, expressed in square meters per cubic centimeter: m^2/cm^3) and the number of congeners identified on the basis of RRTs. For some samples, namely SM31, SM38, SM30, LS8 and TR10, GC-MS analysis was performed in order to confirm congener identification. Since PCBs are adsorbed on the surface of particles, it may be assumed that their concentration is directly related to the total available surface. On this basis, CS values, obtained by particle

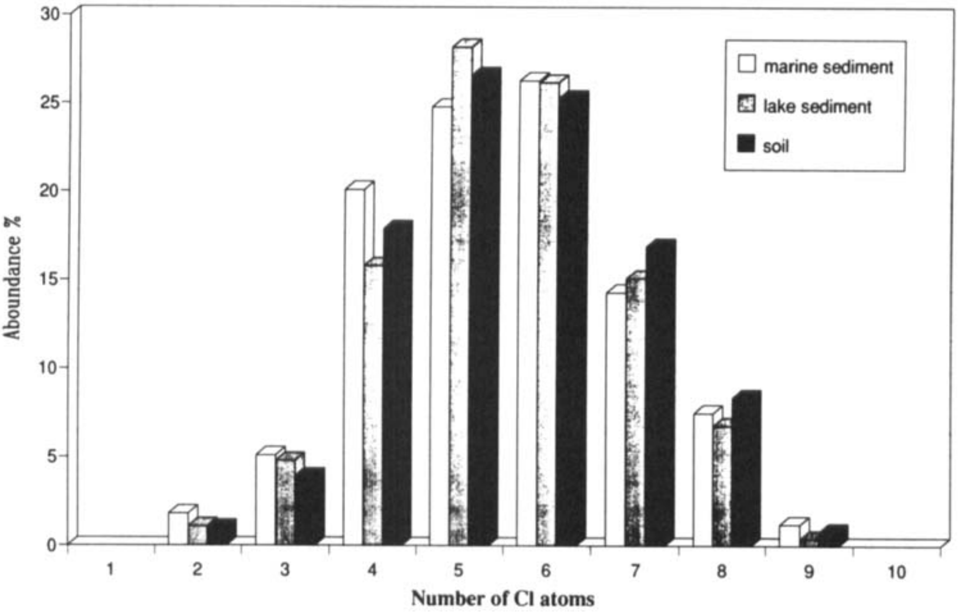

Figure 4 Histograms of average relative abundance of PCB congener classes in marine sediment, lake sediment and soil samples gathered in Terra Nova Bay, Wood Bay and Victoria Land (Antarctica) during the 1989–90 Italian expedition.

size analysis, were used for normalizing PCB concentrations. The values of total PCB concentration divided by CS (PCBs/CS) are also reported in Table 3. Figure 4 shows the PCB distribution among congener classes obtained by averaging, for each matrix, those relevant to all the samples analyzed.

These results clearly support the following considerations:

—the comparison of total PCB concentrations among stations, may highlight significant spatial effects. F.i., stations SM31 and SM38 for marine sediments, and station LS8 for lake sediments present concentrations which are two or three times higher than the relevant mean value. Actually, the amount of PCBs present in samples such as sediments or soils, is much more related to the particle surface area per volume unity than to the mass unity. In fact, when the concentration of each sample, expressed in pg/g, is normalized by dividing it for the relevant calculated specific surface area (CS), the relative standard deviation values (r.s.d.) become 18 (70), 24(76) and 17(31)% for marine sediment, lake sediment and soil samples respectively (in brackets are reported the r.s.d. values of total PCB concentrations in pg/g), and the spatial distribution effects disappear. Furthermore, the fact that r.s.d. values of normalized data are similar to those of replicate measurements, is a proof that the spread of concentration is not statistically significant. This indicates a very low and quite homogeneous PCB contamination of the area considered and is not in agreement with the previous results obtained on sea water samples collected during the

1988–89 Italian expedition, which showed a significant decrease in PCB concentrations at increasing distances from the Italian Base[5]. This may be explained in terms of the increase in PCBs in sea water due to a local effect of limited duration which did not significantly affect the PCB content in sediments;

—lake sediment samples have the highest value of PCBs/CS ratio (320 ng m^2/g cm^3), followed by marine sediment (235 ng m^2/g cm^3) and soil samples (185 ng m^2/g cm^3). This might be explained, once again, in terms of different contributions of atmospheric particulate matter, the primary vehicle of transport and diffusion of PCBs in the environment, as mentioned before. This contribution seems to be considerably higher for lake sediment samples and is probably due to the nature of Antarctic lakes, which are formed during the deglacial season from ice melting water that is quite rich in particulate matter from the atmosphere;

—there is no significant difference between PCB distribution among congener classes (Figure 4) for sediment and soil samples, as was expected. In particular, they are centered on 4- to 7-substituted, which are typical of these matrices.

The analyses of the samples gathered during the 1991–92 Italian expedition in Antarctica are in progress. In particular, PCB depth profile in sediments will be obtained and will allow us to get a more complete picture of the contamination process in Antarctica on the time scale.

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References

1. M. D. Erickson, *Analytical Chemistry of PCBs*, Butterworth Publishers Stonehouse, MA (USA), pp. 24 (1986).
2. V. Lang, *J. Chrom.* **595,** 1–43 (1992).
3. J. T. Borlakoglu and R. R. Dils, *Chem. Brit.*, 815–818 (Sept. 1991).
4. D. E. Tillitt, J. P. Giesy and G. T. Ankley, *Environ. Sci. Technol.* **25,** 87–92 (1991).
5. R. Fuoco, M. P. Colombini and C. Abete, *Ann. Chim(Rome)* **81,** 383–394 (1991).
6. P. Desideri, L. Lepri and L. Checchini, *Ann. Chim(Rome)*, **79,** 589–605 (1989).
7. J. I. Gomez-Belinchon, J. O. Grimalt and J. Albaiges, *Environ. Sci. Technol.*, **22,** 677–685 (1988).
8. S. Tanabe, H. Hidaka and R. Tatsukava, *Chemosphere*, **12,** 277–288 (1983).
9. M. D. Mullin, C. M. Pochini, S. McCrindle, M. Romkes, S. H. Safe and L. M. Safe, *Environ. Sci. Technol.*, **18,** 468–476 (1984).
10. J. C. Dulnker and F. Bouchertall, *Environ. Sci. Technol.* **23,** 57–62 (1989).

11. S. W. Fowler, *PCBs and the Environment: the Mediterranean marine Ecosystem*, in *PCBs and the Environment (J. S. Waid, ed.)*, CRC Press, Boca Baton, Fl., Vol III, Chap 8, pp. 209–239 (1986).
12. P. Larsson and A. Sodergren, *Water, Air and Soil Pollution*, **36**, 33–37 (1987).
13. K. Ballschmiter and M. Zell, *Inter. J. Environ. Anal. Chem.*, **8**, 15–35 (1980).
14. J. O. Stromberg, L. G. Anderson, G. Bjorg, W. N. Bonner, A. C. Clark, A. L. Dick, W. Ernst, D. W. S. Limbert, D. A. Peel, J. Preddle, R. I. L. Smith and D. W. H. Walton, *State of marine Environment in Antarctica*, UNEP Regional Seas Reports and Studies No. 129, UNEP 1990.