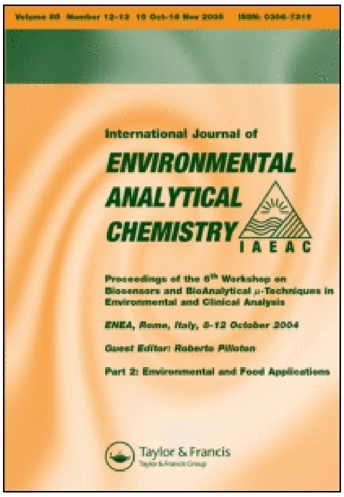

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THE EFFECT OF SEASONAL PACK ICE MELTING ON THE SEA WATER POLYCHLOROBIPHENYL CONTENTS AT GERLACHE INLET AND WOOD BAY (ROSS SEA – ANTARCTICA)*

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The effect of seasonal formation/melting process of pack ice on the PCB level of sea water at Gerlache Inlet and Wood Bay (Ross Sea, Antarctica) was investigated during four Italian expeditions, i.e. 1988–89, 1990–91, 1991–92, and 1993–94. Surface sea water samples from Gerlache Inlet and Wood Bay before pack ice melting showed a typical total PCB concentration of 133 pg/l and 120 pg/l, respectively, which increased by a factor of about 1.3 in both sampling sites during pack ice melting. This effect was attributed to the transfer of PCBs contained in the pack ice to sea water, and salinity was used as a tracer to verify this hypothesis. In this respect, pack ice and sea water samples were collected during the 1993–94 Italian expedition, and both salinity (S) and total PCB content were measured. A fairly good agreement was observed between the experimental PCB concentration and the value calculated by the dilution model which was applied to the mixing process between sea and pack ice melting waters. Although this effect seems to be limited in time and space it is nevertheless significant because it happens during summer when biological species have their highest activity.

Keywords: Antarctica (Ross Sea); polychlorobiphenyls; sea water; pack ice

INTRODUCTION

Antarctica plays a very significant role in the global processes of our planet, and observing selected chemical parameters in the Antarctic ecosystem is very important for a better understanding of these processes. The Environmental Pol-

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lution Monitoring Project of the Italian Research Programme in Antarctica (PNRA) is aimed at studying these processes by monitoring organic and inorganic pollutants in different environmental components, elucidating the relevant diffusion and distribution processes, and evaluating their change in the short and long terms by sampling those matrices that retain this information, i.e. sediments and ice. Within this framework, our specific interest was concerned with the presence of polychlorobiphenyls (PCBs) in Antarctica. The importance of PCBs is mainly due to the fact that these compounds were used in many industrial applications from around 1930 to 1970, and dumped without any precautions to prevent environmental pollution. Moreover, they are chemically very stable and are able to accumulate in organisms[1,2]. These characteristics are responsible for long residence times in the environment and for toxic effects on biota, thus making the monitoring of PCBs in the environment of prime importance.

This paper shows the most significant findings relevant to four surveys performed at Gerlache Inlet and Wood Bay (Ross Sea – Antarctica) during the 1988–89, 1990–91, 1991–92 and 1993–94 Italian expeditions. In particular, sea water and pack ice samples were collected during the pack ice melting in order to evaluate the role of the seasonal formation/melting process of pack ice on the transfer process of PCBs from the atmosphere to sea water.

EXPERIMENTAL

Reagents

Acetone, n-hexane, dichloromethane Pesticide Grade; Na_2SO_4 RPE-ACS; and Florisil RS (60–100 mesh) were supplied by Carlo Erba (Italy). Na_2SO_4 and Florisil were activated for twelve hours at 450°C, and for four hours at 650°C, respectively, and kept at 130°C for two hours before use. Aroclor 1221, 1232, 1248, 1260 (35 mg/ml) and individual PCB congeners in iso-octane or methanol standard solutions (35 mg/ml) were supplied by AccuStandards (USA). Certified reference material of ten PCBs in iso-octane (CRM 365) were supplied by the European Community-Standards, EC-SM&T Programme (Belgium) (Table I).

Apparatus

A GC mod. 5880A (Hewlett Packard Italiana, Italy), coupled with a mass spectrometric detector (MSD) mod. 5971A (Hewlett Packard Italiana, Italy) and equipped with a cold on-column injection port, was used for the identification of chromatographic peaks and the quantitative determination of PCBs. Chromatographic separation was always performed on a chemically bonded fused silica capillary column MS-5 (Hewlett Packard Italiana, Italy) 0.25 mm I.D., 0.25 μm film thickness, 30 m length, connected to 2 m long deactivated fused silica capillary pre-column 0.32 mm I.D. The chromatographic conditions were Ti = 50°C or 80°C for n-hexane or iso-octane solution, respectively, and 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; the carrier gas was helium at 190 KPa.

TABLE I PCBs in iso-octane CRM 365

IUPAN No.	*Content, μg/g*
PCB8	11.4 ± 0.3
PCB 20	15.2 ± 0.9
PCB 28	24.8 ± 1.1
PCB 35	14.3 ± 0.8
PCB 52	14.8 ± 0.6
PCB 101	14.4 ± 0.6
PCB 118	14.9 ± 0.8
PCB 138	8.6 ± 0.6
PCB 153	14.2 ± 0.6
PCB 180	15.2 ± 0.6

Sampling area and sampling techniques

Sea water samples were collected at about 0.5 m from the surface by a teflon pumping system at Gerlache Inlet (sampling stations Nos. 1, 2, 3 and 4) and Wood Bay (sampling station No. 5) (Figure 1). Before pack-ice melting a hole in the ice was made by a manual drilling system. Pack ice was collected during this operation, and sea water was collected underneath the inner surface of the pack-ice, at a depth of about 0.5 m. The samples were either immediately extracted with n-hexane in the clean-room facility at the Italian Base or stored at −20°C and sent to Italy and analysed in our laboratory. All samples were stored in pre-cleaned 20 1 stainless steel containers.

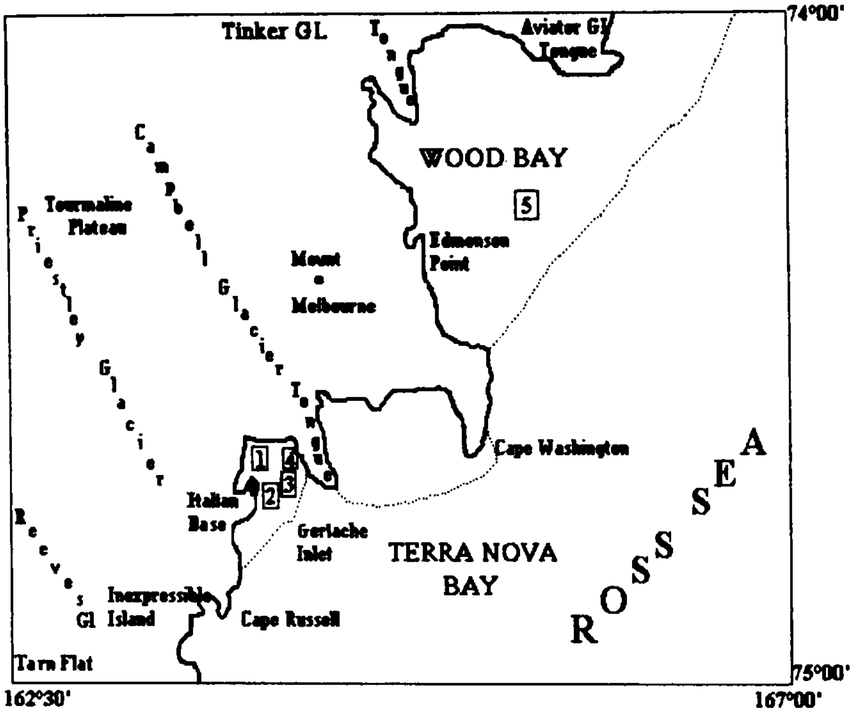

FIGURE 1 Location of the sea water sampling stations before and during pack ice melting at Gerlache Inlet, (1988–89, 1990–91, and 1991–92 Italian expeditions) and Wood Bay (1993–94 Italian expedition)

Analytical procedures

The analytical procedure for total PCB determination in sea water has been described elsewhere[3,4]. The same procedure was also applied to pack ice samples. In short, the samples were liquid-liquid extracted either by mechanical shaking in a separator funnel or by a custom-made high efficiency extraction system[5] which allows the use of about 10 ml of n-hexane to extract 10 litres of water. In both cases the extract was cleaned up on a Florisil column (50×10 mm), from which PCBs were selectively eluted with a suitable volume of n-hexane, typically 10 ml. Right before the analysis, the eluate was concentrated at a suitable volume, and analysed by gas chromatography-mass spectrometry.

Total PCB concentration was always obtained by measuring the individual concentration of 60–70 congeners. In particular, PCB congeners were firstly identified by GC/MSD on a standard solution of several Aroclors (i.e., 1221, 1232, 1248 and 1260). The relative retention time (RRT) for each identified congener was then calculated by using one or more internal standards (ISs). RRTs were finally applied for chromatographic peak assignment of real samples analysed by either GC/MSD or GC/ECD. Experimental response factors (RFs) were generally obtained for a limited number of selected PCB congeners (i.e., IUPAC Nos. 8, 20, 28, 35, 52, 101, 118, 138, 153, 180) and for the IS, in a selected concentration range. Relative response factors (RRFs) to the IS were then calculated and used in turn to calculate the RRFs for all congeners by extrapolating the values reported by Mullin[6]. If an MS detector in the Selected Ion Monitoring mode is used, at least three ions should be selected: one as target and two as qualifiers.

Analytical quality control and quality assurance

Analytical quality control and quality assurance programs were run in the laboratory during sample analysis in order to get reliable data. These programs were based on the use of standard solutions suitably prepared and stored, and spiked samples, since reference sea water samples with a certified PCB content are unfortunately not available. Table I shows the concentration of ten PCB congeners which are present in the certified reference material CRM 365, while Figure 2 shows a typical control chart for the determination of PCB153 in CRM 365, as obtained during the analysis of sea water and pack ice samples.

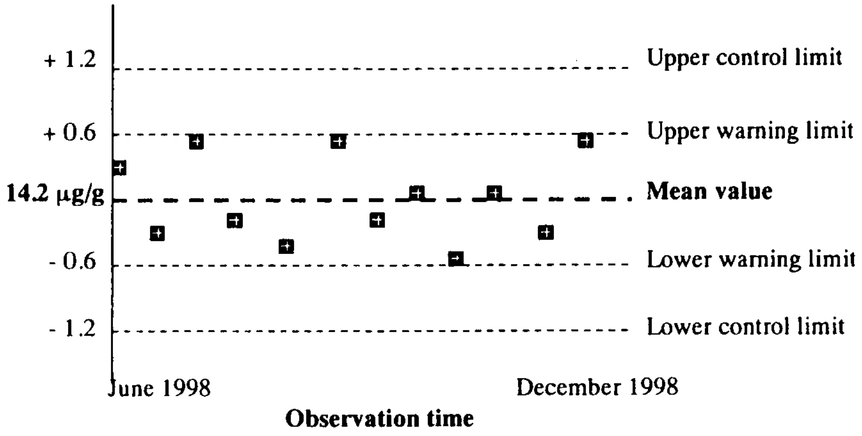

FIGURE 2 Working analytical quality control chart for PCB153 determination in iso-octane certified standard solution CRM 365

RESULTS AND DISCUSSION

Table II shows the total PCB content of surface sea water samples collected during four Italian expeditions in Antarctica before and during pack ice melting. The concentration ranges refer to samples collected in all the sampling stations for each expedition. In particular, before pack ice melting a mean value of 133 and 120 pg/l was observed at Gerlache Inlet and Wood Bay, respectively. These concentrations increased during pack ice melting by a factor of about 1.3 in both sampling sites (180 pg/l at Gerlache Inlet, 160 pg/l at Wood Bay). In order to evaluate whether this effect might be attributed to the transfer of PCBs contained in the pack ice to sea water, salinity was used as a tracer. In fact, by measuring salinity (S) and total PCB content in both pack ice and sea water samples it should be possible to evaluate the mixing process between sea and pack ice melting waters which affects the superficial layer of sea water for a limited period of time.

TABLE II Effect of pack ice melting on the total PCB content in surface sea water samples collected at Gerlache Inlet and Wood Bay, Ross Sea-Antarctica (The mean value is reported in brackets.)

Expedition	*Location*	*Sampling stations*	*Tolal PCBs, pg/l*	
			Before pack ice melting	*During pack ice melting*
1988–89	Gerlache Inlet	4	100 – 160 (120)	150–180 (160)
1990–91	Gerlache Inlet	1	140	180
1991–92	Gerlache Inlet	4	90 –180 (140)	160 – 2<30 (205)
1993–94	Wood Bay	2	120	160

The dilution factor of each sample can be described by the following equation:

$$\alpha = \frac{V_{sw}}{V_{sw} + V_{pk}} = \frac{(S_i - S_{pk}^0)}{(S_{sw}^0 - S_{pk}^0)} \tag{1}$$

where:

V_{sw} = volume of sea water; V_{pk} = volume of water from pack ice melting; S_i = sample salinity; S^0_{pk}= pack ice salinity; S^0_{sw} = sea water salinity before pack ice melting.

Before pack ice melting the variables have the following values:

$$V_{pk} = 0 \qquad S_i = S_{sw}^0 \qquad \alpha = 1$$

and during pack ice melting:

$$V_{pk} > 0 \qquad S_i < S^0_{sw} \qquad \alpha < 1$$

If this model holds, and in the absence of other sources of PCBs in the studied area, the total PCB concentration of each sample can be calculated by the following equation:

$$C_i = C^0_{pk} - (C^0_{pk} - C^0_{sw})\alpha_i \tag{2}$$

where:

C_i = total PCB concentration of the sample; $C^0{}_{pk}$ = total PCB concentration of pack ice sample; $C^0{}_{sw}$ = total PCB concentration of sea water sample before pack ice melting.

Figure 3 shows four depth profiles of salinity obtained at Wood Bay from 27 November 1993 to 28 January 1994. These results show that:

- on 27 Nov 1993 the pack ice melting process had not yet begun;
- on 15 Dec 1993 the decrease in the salinity in the surface layer of sea water due to pack ice melting was clearly evident;
- on 9 Jan 1994 the largest variation of salinity was observed and was confined in a layer of sea water about 80 m thick.

Since the scientific activities at the Italian Base had to be concluded on 31 Jan 1994, it was not possible to observe the evolution of the salinity profile for longer. Nevertheless, it was known that the formation of new ice patches on the sea surface in the studied area began in the middle of February, thus pack ice melting was over at that time. Consequently, the time lag during which pack ice melting affected the PCB content of sea water was about two months, from 15 December to 15 February. In order to verify this hypothesis, the total PCB content was determined in sea water and pack ice samples, before and during pack ice melting, and compared with the calculated value according to equation (2). Table III shows the results for the samples collected at Wood Bay during the 1993–94 expedition. In particular, the pack ice showed a salinity of 6 ‰, whereas the salinity of sea water samples collected at the surface before (profile of 27 Nov 1993, Figure 3) and during (profile of 9 Jan 1994, Figure 3) pack ice melting was 34.7 ‰ and 33.6 ‰, respectively. The corresponding value of the dilution factor (α) calculated by equation (1) was 0.96. On the other hand, the total PCB content in both sea water and pack ice samples collected on 27 November 1993 was 120 and 750 pg/l, respectively. This shows a quite high total PCB content in pack ice samples. Finally, the total PCB content in sea water sample collected on 9 January 1994 was 160 pg/l. A fairly good agreement between the total PCB content calculated by equation (2) (145 pg/l), and the experimental one (160 pg/l) was observed. According to the value of the standard deviation, as obtained in five replicate measurements, the increase in PCB con-

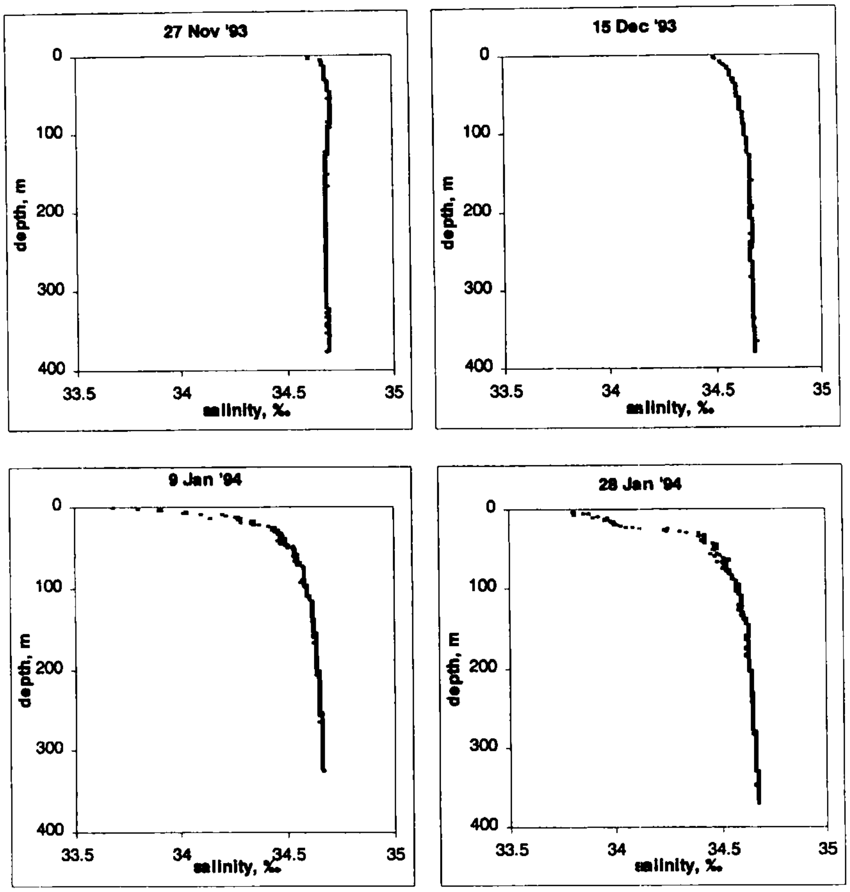

FIGURE 3 Depth profile of salinity at Wood Bay, Ross Sea, as obtained during the 1993–94 Italian expedition

centration was statistically significant at a 90% confidence level, and should be attributed to pack ice melting if we assume that there was no local source of PCB contamination.

TABLE III Total PCB content and salinity of sea water and pack ice samples collected at Wood Bay during the 1993–94 Italian expedition

Sample	*Salinity, g % o*	α	*Total PCBs, pg/l*
Sea water, before pack ice melting	34.7	1.00	120
Pack ice	6.0		750
Sea water, during pack ice melting	33.6	0.96	Experimental 160 Calculated (*) 145

(*) The calculated value was obtained by equation (2), see text.

This increase might be explained considering that ice acts, during its formation, as an accumulator which traps atmospheric particulate material that is realeased, along with the pollutants adsorbed on it, to the sea water during melting. Although this effect seems to be limited in time and space, and the PCB content only increases by about 30%, it is nevertheless significant because it happens during summer time when biological species have their highest activity.

Acknowledgements

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