Persistent organic pollutants (POPs) at Ross Sea (Antarctica)

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ABSTRACT

The most significant findings on the presence of persistent organic pollutants (POPs) in the marine ecosystem at Ross Sea are presented. Seawater samples were collected in many sampling sites located in a large area of the Ross Sea during various Italian expeditions in Antarctica. Two classes of POPs were considered, namely polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). The results highlighted the presence of these compounds in seawater samples at a total concentration level of about 50 pg/l for PCBs, and 220 pg/l for PAHs. Moreover, seawater samples showed low to high molecular weight PAHs (LMW/HMW) and phenanthrene to anthracene (PHE/ANT) ratios higher than 1 and 5, respectively, which may suggest the predominance of a petrogenic source (i.e. petroleum product contamination). Results were also obtained on the POP depth profile in the water column at Cape Adere, where two water masses converge and mix, i.e. the Modified Circumpolar Deep Water (MCDW) and the High Salinity Shelf Water (HSSW). According to both the PAH and temperature profiles a two-fold higher PAH and PCB concentration was observed for MCDW samples with respect to HSSW. This result represents the first experimental evidence of the external input of pollutants in this area of the Ross Sea coming from the outer oceanic circulation.

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1. Introduction

The Antarctic region is an ideal place for environmental studies of the marine ecosystem both near the coastal line and off-shore, due to the almost total absence of local pollution sources. In fact, pollutants reach Antarctica almost exclusively by long range transport processes involving both the atmosphere and the hydrosphere. Snow depositions are responsible for the transfer of pollutants from the atmosphere, since aerosols and vapours are trapped in the snowflakes that fall on both continental and marine surfaces. The Circumpolar Deep Water (CDW), which is the largest circulation feature of the Southern Ocean, is mainly responsible for the rather limited exchange processes between the Antarctic seas, i.e. the Ross Sea, and the outer oceans [1,2], thus it might be a possible source of POPs. The Environmental Pollution Monitoring Project of the Italian Research Programme in Antarctica (PNRA) which started in 1987 monitored both organic and inorganic pollutants in various environmental components of the area studied (Victoria Land and Ross Sea). It has helped to explain the diffusion and distribution processes of various environmentally important chemical compounds.

Polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are two of the most important classes of persistent organic pollutants (POPs). Their carcinogenic and endocrine disrupting effects

on biota have been proved [3–7]. Before presenting some data on the presence of these pollutants in the environment, it should be highlighted that data comparison is rather critical owing to the lack of an internationally accepted agreement on the meaning of “total PCBs” and “total PAHs”, in terms of the compounds whose individual concentrations are included in the calculation of the total content. The seven most abundant PCB congeners, namely PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180, and various selections of the following PAHs: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Benzo[a]fluoranthene, Pyrene, Benz[a]anthracene, Crysene, Benzo[a]pyrene, Dibenzo[a,h]anthracene, Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene are generally considered. Seawater samples from the Baltic Sea showed low PCB concentrations (60–400 pg/l), with a reasonably homogeneous distribution and a substantial difference between winter and summer [8,9]. PAH concentration in sub-surface seawater samples from Alexandria's Mediterranean coast ranged between 13 and 120 ng/l [10]. Similar values (30–50 ng/l) were found in coastal water samples of the Gulf of Gdansk (Southern Baltic) [11], which are higher than the data (2–7 ng/l) obtained between 1992 and 1998, in 313 surface and deep seawater samples collected in the Baltic Sea [12]. There is very little data on the presence of POPs in the Antarctic seas. Total PCB concentrations ranging between 50 and 120 pg/l were observed at Gerlache Inlet (Terra Nova Bay, Ross Sea, Antarctica), which increased right after pack ice melting [13]. The enrichment of PCBs and PAHs in the sea surface micro-layer and the depth profile of these pollutants in the water column were also investigated at Gerlache Inlet. PCBs and

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PAHs showed a concentration range in the water column of 30–120 pg/l and 150–400 pg/l, respectively, and these values were very much dependent on the suspended matter content [14].

Source identification of POPs and input sources in the Antarctic area is another very important task. PAHs are generally divided into two classes: low molecular weight (LMW) with two or three condensed aromatic rings, and high molecular weight (HMW) with four to six condensed aromatic rings. LMWs (i.e. LMW/HMW > 1) generally dominate in the petrogenic source [15–17]. Moreover, the Phenanthrene/Anthracene (PHE/ANT) concentration ratio can also be used to distinguish between pyrolytic and petrogenic origins. The PHE/ANT ratio is temperature-dependent with high temperature pyrolytic processes being characterized by low PHE/ANT values and petrogenic contamination leading to much higher PHE/ANT values [15]. Therefore, two different categories have been defined: PHE/ANT higher than about 5 for the dominance of petrogenic sources, and PHE/ANT lower than about 5 for the dominance of pyrolytic sources [16,18,19], although selective photo-degradation of different PAH isomers may play a role in long-range atmospheric transport.

This paper describes the most significant findings on the presence of PCBs and PAHs in seawater samples collected in a large area of the Ross Sea during various Italian expeditions in Antarctica. A hypothesis is also made about a possible PAH source. Finally, some results are discussed on the mixing between the Modified Circumpolar Deep Water (MCDW) and the High Salinity Shelf Water (HSSW), with respect to their POP content.

2. Materials and methods

2.1. Reagents

N-hexane was Pesticides Grade and was supplied by Labscand (Ireland); and anhydrous Na₂SO₄ by J. T. Baker (the Netherlands). Standard solutions of polycyclic aromatic hydrocarbons (PAHs) were supplied by AccuStandard (USA), and standard solutions of polychlorobiphenyls (PCBs) by Supelco (USA). Deuterated PAH solutions were supplied by NRC-CN (National Research Council-Canada,

Canada), while ¹³C-PCB solutions by CIL (Cambridge Isotope Laboratories, UK). Standard working solutions were obtained by diluting the certified ones with Pesticide Grade n-hexane.

2.2. Apparatus

A gas chromatograph mod. Star 3400 CX (Varian, USA), equipped with a split/splitless injection system mod. sp 1078 (Varian, USA) and coupled with a mass spectrometric detector mod. Saturn 2000 “ion trap” (Varian, USA) operating in the MS-MS mode, were used for the determination of PCBs. The injection system was kept at 60 °C during sample injection and then heated at 200 °C/min up to 300 °C.

A gas chromatograph mod. 5890A (Agilent, USA), equipped with a PTV injection system mod. 6890, and coupled with a mass spectrometric detector mod. 5973A (Agilent, USA) operating both in SIM (Selected Ion Monitoring) and TIC (Total Ion Current) modes, was used for the determination of PAHs.

In both cases, chromatographic separation was performed on a fused silica capillary column MS-5 (Hewlett Packard Italiana) 95% dimethyl-5% phenyl polysiloxane chemically bonded stationary phase, 0.25 mm internal diameter, 0.25 µm film thickness, 30 m length; the column was connected to a 2 m long 0.32 mm internal diameter deactivated fused silica capillary pre-column. The temperature profile of the chromatographic oven was the following: initial temperature, 50 °C isothermal for 2 min; 10 °C/min up to 120 °C and isothermal for 5 min, 4 °C/min up to 295 °C and isothermal for 30 min. Helium 99.995% purity (Rivoira, Italy) was used as a carrier gas at constant flow (1 ml/min) and 90 kPa at initial temperature. The sample volume injected was 40 µl, unless otherwise specified.

2.3. Sampling area and sampling techniques

Seawater samples were collected during the 1997–1998, 2000–2001 and 2002–2003 Italian expeditions in Antarctica in a large area of the Ross Sea and Terra Nova Bay (Fig. 1), either by a teflon pumping system at 0.5 m depth near the cost or by a “go-flo” stainless steel sampling system for off-shore sampling. The “go-flo” system was also

Fig. 1. Location of seawater sampling stations at Ross Sea, Antarctica.

Table 1PAHs and PCBs included in the total content Σ PAH and Σ PCB.

PAHs			
ACY	Acenaphthylene	FLU	Fluorene
PHE	Phenanthrene	ANT	Anthracene
FLA	Fluoranthene	PYR	Pyrene
BaA	Benz[a]Anthracene	CRY	Crysene
BbF	Benzo[b]Fluoranthene	BkF	Benzo[k]Fluoranthene
BaP	Benzo[a]Pyrene	DBA	Dibenz[a,h]Anthracene
IPY	Indeno[1,2,3-cd]Pyrene	BPE	Benzo[ghi]Perylene

PCBs	
PCB28 2,4,4'-trichlorobiphenyl	PCB52 2,2',5,5'-tetrachlorobiphenyl
PCB101 2,2',4,5,5'-pentachlorobiphenyl	PCB118 2,3',4,4',5-pentachlorobiphenyl

PCB153 2,2',4,4',5,5'-hexachlorobiphenyl	PCB138 2,2',3,4,4',5'-hexachlorobiphenyl
PCB180 2,2',3,4,4',5,5'-heptachlorobiphenyl	

used for collecting samples at various depths in G station (2002–2003 expedition), which was located in front of Cape Adere. Seawater samples collected near the coast were transferred to the analytical laboratory at the Italian Base for further treatment, whereas all the others were treated on board the ice-breaker following the procedure described below.

2.4. Analytical procedure

The analytical procedures for PCB and PAH determination in seawater samples have been described elsewhere [10,20,21]. The PCB and PAH total content was calculated as the sum of the concentration of the compounds listed in Table 1, which were individually quantified. Very briefly, seawater samples were extracted with n-hexane as soon as possible after sampling, either in the clean laboratory at the “Mario Zucchelli” (former Terra Nova Station) Italian Base in Antarctica or in the analytical laboratory onboard the ice-breaker by a high efficiency liquid–liquid extraction system [22]. The organic extracts were sent to the laboratory in Italy for the instrumental analysis. Immediately before the analysis the organic extract was dried with Na_2SO_4 , concentrated at a suitable volume under a mild nitrogen flow, and finally, analysed by gas chromatography/mass spectrometry. Two different standard solutions of labelled analytes were added to the sample: the standard “method”,

Table 2Concentrations of D-PAH and ^{13}C -PCB in “method” and “injection” standard solutions.

Standard solution “method”			
PCBs	$\mu\text{g/ml}$	PAHs	$\mu\text{g/ml}$
^{13}C -PCB28	0.51	D-PYR	1.75
^{13}C -PCB52	0.51	D-BaA	1.10
^{13}C -PCB101	0.51	D-CRY	1.10
^{13}C -PCB153	0.51	D-BbF	0.65
^{13}C -PCB138	0.51	D-BaP	0.65
^{13}C -PCB180	0.51	D-DBA	0.22
^{13}C -PCB209	0.51	D-BPE	0.44
Standard solution “injection”			
PCBs	$\mu\text{g/ml}$		
^{13}C -PCB77	0.50		
^{13}C -PCB126	0.50		
^{13}C -PCB169	0.50		

Table 3

LMW/HMW and PHE/ANT values for a 0.5 M NaCl water solution containing known concentration of PAHs.

Sample	LMW/HMW			PHE/ANT		
	A	B	err. %	A	B	err. %
1	2.0	1.8 (0.2)	– 10	5.0	5.3 (0.4)	+ 6
2	2.0	1.7 (0.1)	– 15	5.0	4.6 (0.5)	– 8
3	2.0	1.9 (0.2)	– 5	5.0	4.9 (0.3)	– 2

(In brackets the standard deviation).

A = expected value; B = measured value.

and the standard “injection”. The first one was added to the organic extract immediately after being extracted in Antarctica: this allows analyte concentration changes to be evaluated. Such changes are likely in seawater extracts owing to their very long storage time. Standard “injection” was added to the final extract immediately before being injected into the GC-MS system: this allows both the injected quantity and the instrumental response to be controlled. Table 2 shows the composition of such standard solutions.

3. Results and discussion

Suitable analytical quality control and quality assurance programs were run in the laboratory during sample analysis in order to guarantee data reliability. These programs are generally based on the use of standard reference materials (SRMs), and on the use of standard solutions suitably prepared and stored [23]. Since seawater SRMs certified for the POP content are not available, replicate analyses of blank samples spiked with a standard solution at almost the concentration level expected in real samples were performed. The use of a mass spectrometric detector means that both deuterated PAH and ^{13}C -labelled PCBs can be added as standards, which makes the control very effective. The results showed a typical CV of 20%, and a bias of about 10%. These solutions were periodically analysed, at least once per day, in the period during which Antarctic seawater samples were analysed.

Since the ratio of selected PAH isomers can be very useful for evaluating pollutant sources, as already mentioned, a recovery study was done in order to verify to what extent, if any, the procedure for reducing the organic extract volume alters the PAH isomer ratios with respect to the original samples. A 0.5 M NaCl water solution was added with a methanol PAH standard solution. Concentration levels similar to those measured in Antarctic sea water samples were obtained, namely ACY 10 $\mu\text{g/l}$, FLU 30 $\mu\text{g/l}$, PHE 50 $\mu\text{g/l}$, FLA 40 $\mu\text{g/l}$, ANT 10 $\mu\text{g/l}$, PYR 20 $\mu\text{g/l}$, CRY 10 $\mu\text{g/l}$, BaA 10 $\mu\text{g/l}$, BbF + BkF 10 $\mu\text{g/l}$, BaP 5 $\mu\text{g/l}$, DBA 5 $\mu\text{g/l}$, IPY 5 $\mu\text{g/l}$, and BPE 5 $\mu\text{g/l}$. The water solution was analyzed in triplicate following the same analytical procedures as those applied to Antarctic samples, including volume reduction under a mild nitrogen flow. The results (Table 3) show that the error percentage on the ratio values ranges between – 15% and 6%, with a systematic negative bias

Table 4Total content of PAHs (Σ PAH) and PCBs (Σ PCB) in surface seawater samples collected at Ross Sea, Antarctica.

Italian expedition	Sampling station	Σ PCB ($\mu\text{g/l}$)	Σ PAH ($\mu\text{g/l}$)
1997–1998	Y1	55	122
	Y2	55	222
	Y4	83	200
	Y5	84	151
	Y6	58	330
	B1	74	292
2000–2001	B2	65	208
	D	23	360
	CA2	23	328
2002–2003	D	36	139
	F	41	167
	B	53	96
	G	45	281
Mean value (CV)		50 (36%)	220 (38%)

Table 5

Concentration (pg/l) of selected PAHs in surface seawater (SSW) samples collected at Ross Sea, Antarctica.

	1997–98 expedition							2000–01 expedition		2002–03 expedition			
	Y1	Y2	Y4	Y5	Y6	B1	B2	D	CA2	D	F	B	G
ACY	4	5	6	9	7	13	8	11	12	6	15	4	9
FLU	17	11	20	23	44	60	15	20	79	13	20	22	21
PHE	31	65	58	41	97	88	67	104	94	24	47	24	72
ANT	5	13	7	4	14	8	7	16	8	4	7	2	8
FLA	18	60	49	36	80	45	75	80	54	55	20	16	28
PYR	19	31	23	8	33	28	20	38	32	16	18	9	31
BaA	4	6	8	5	12	11	13	7	11	5	8	10	6
CRY	6	7	10	6	16	13	10	7	15	4	8	3	10
BbF + BkF	3	8	6	6	8	9	7	4	4	5	11	5	6
BaP	3	3	4	2	4	4	6	2	5	2	3	1	4
DBA	4	5	3	4	6	5	4	4	3	4	2	5	3
IPY	5	4	3	2	5	2	4	3	2	3	6	5	2
BPE	3	4	3	5	4	6	6	4	7	6	7	3	5
ΣPAH	122	222	200	151	330	292	208	295	326	147	162	109	205

CV on three repeated measurements was always lower than 15%.

on the LMW/HMW ratio lower than 15%. This implies that LMW/MW and PHE/ANT concentration ratios are not significantly affected by the analytical procedure, thus supporting the correctness of the application of such ratios to the evaluation of PAH sources. The negative bias on LMW/HMW ratio might be due to a slightly greater loss of more volatile PAHs with low molecular weights.

The presence of PAHs and PCBs has been investigated in a large area of the Ross Sea by collecting surface seawater samples during various Italian expeditions. Fig. 1 shows the sampling stations, and Table 4 the PCB and PAH total content in all surface seawater samples. The results highlighted a low and quite homogeneous contamination of the area under investigation: the mean value of total PCBs and total PAHs was 50 pg/l and 220 pg/l, respectively. A typical coefficient of variation of about 35% was obtained, which is quite satisfactory considering the very low concentration levels and the observation time period (1998 to 2003) during which all samplings were performed. Table 5 shows the individual PAH concentration of all the surface seawater samples, whereas Table 6 shows the LMW/HMW and PHE/ANT values for all surface seawater samples collected in various areas of the Ross Sea, both near the coast and off-shore. LMW includes ACY, FLU, PHE, FLA, ANT, and HMW includes PYR, CRY, BaA, BbF, BkF, BaP, DBA, IPY, BPE. The low to high molecular weight PAH ratio was always higher than 1, ranging from 1.6 to 3.2. Moreover, all but three samples had PHE/ANT values higher than 5, ranging from 6.3 to 12.0. This would seem to indicate a predominant petrogenic

source of PAH contamination, although the use of PAH ratios for source identification could be questionable in remote areas such as Antarctica, since the PAH distribution pattern of the primary source may have been affected by the difference in the kinetic parameters of the photo-degradation reaction of different isomers.

Some data was also obtained on the mixing process between two important water masses present in the area of the Ross Sea under investigation: the Modified Circumpolar Deep Water (MCDW) and the High Salinity Shelf Water (HSSW) (Fig. 1). The MCDW, which is relatively warmer, comes from the external oceanic circulation since it is generated in the Pacific sector of the Southern Ocean, whereas the HSSW, which is relatively colder, is generated inside the Ross Sea basin. Both move toward Cape Adere (Fig. 1) where they mix. Thus, a depth profile was performed in the area of Cape Adere (sampling station G) in

Table 6

LMW/HMW and PHE/ANT values for surface seawater samples collected at Ross Sea during the 1997–1998, 2000–2001 and 2002–2003 Italian expeditions in Antarctica.

Sample	LMW/HMW	PHE/ANT
<i>1997–1998 expedition</i>		
Y1	1.6	6.2
Y2	2.3	3.3
Y4	2.3	8.2
Y5	3.0	10.2
Y6	2.8	6.9
B1	2.7	11.0
B2	2.0	9.6
<i>2000–2001 expedition</i>		
D	3.2	6.5
CA2	3.1	11.8
<i>2002–2003 expedition</i>		
D	2.2	3.7
F	1.6	6.7
B	1.7	12.0
G	2.0	9.0

Fig. 2. Depth profile of total PCB content and temperature in seawater at sampling station G in the area of Cape Adere, Ross Sea (Antarctica).

order to learn about the mixing process and the external input of pollutants in this area of the Ross Sea basin. Six seawater samples were collected at various depths in station G (30, 60, 170, 190, 350 and 470 m). Fig. 2 shows both depth profiles of total PCB content normalized with respect to the highest value measured at a depth of 200 m, and the temperature that was measured on-site by a multi-parametric probe system during sample collection. The intrusion of the relatively warmer MCDW in the colder HSSW is clearly evident: the very sharp change in the temperature at about 170 m depth from -1.5°C (typical of the HSSW) to $+0.2^{\circ}\text{C}$ (typical of MCDW) is in very good agreement with a sudden change in the PCB concentration by a factor of two. The same behaviour was also observed for the total content of PAHs. This is the first experimental evidence of the pollutant input in the Ross Sea basin from the external oceanic circulation, which happens in a period of the season when the ecosystem is particularly sensitive since the biological activity is at its peak. More detailed surveys in the area of Cape Adere have been planned and will be performed in the near future in order to better characterize this process.

4. Conclusions

A low and quite homogeneous contamination was observed in the studied area of the Ross Sea. There was no significant difference between seawater samples collected near the coast and off-shore, which should rule out any local source of pollution. The PAH isomer ratio may indicate a predominance of petrogenic source. However, the use of PAH ratios for source identification might be doubtful in areas such as Antarctica owing to selective photo-degradation of various PAH isomers which may occur during the long-range atmospheric transport. Finally, the experimental evidence of PCB and PAH input in the Ross Sea, which is carried out by the Modified Circumpolar Deep Water, is discussed.

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