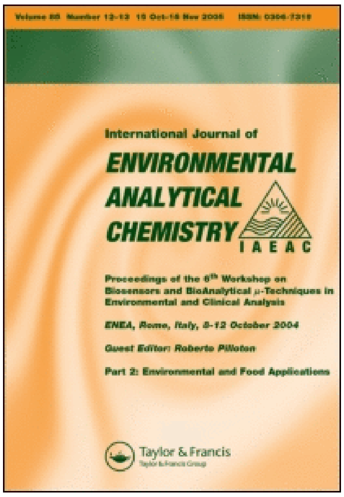

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Evolution of Cadmium and Lead Contents in Antarctic Coastal Sea Water During The Austral Summer

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EVOLUTION OF CADMIUM AND LEAD CONTENTS IN ANTARCTIC COASTAL SEAWATER DURING THE AUSTRAL SUMMER

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The seasonal evolution of the cadmium and lead distribution in the water column of the Gerlache Inlet (Ross Sea) was studied during the 1990–91 austral summer. Measurements were carried out by Anodic Stripping Voltammetry in Antarctica immediately after the collection and filtration of samples. The concentrations of both metals were homogeneous before the phytoplankton bloom with mean values of 0.71 (SD 0.10) and 0.116 (SD 0.014) nmol/l for cadmium and lead respectively. A subsequent depletion in metal concentration was observed in the shallow waters. The surface concentration of cadmium decreased to about 0.1 nmol/l at the end of the season. The vertical distribution of lead was less affected by the seasonal evolution and the mean surface concentration decreased to 0.044 nmol/l in the same period. The results are evaluated with respect to physical and biological processes in the area examined and compared with those obtained on previous expeditions in the same area.

Keywords: Cadmium; lead; DPASV; seawater; Terra Nova Bay; Antarctica; seasonal evolution

INTRODUCTION

The coastal seas of the Antarctic Continent are subjected to meteorological, climatic and environmental conditions which differentiate them markedly from all other marine ecosystems. As well as the extreme climatic conditions and

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the remoteness from all direct pollution sources, seasonal change is reduced to two long periods. The winter is characterised by darkness and the presence of sea ice; in this period photosynthesis is precluded and only the respiration and decomposition of organic compounds are possible. The summer is characterised by a continually light period, the dissolution of pack ice, a sudden phytoplankton bloom and, at the end of the summer, the formation of new marine ice.

In the framework of the Italian Research Programme in Antarctica, investigations were carried out into the distribution and speciation of some trace metals (Pb, Cd, Cu) in the surface seawaters of Terra Nova Bay (Ross Sea) and the base levels of metal concentrations during the austral summer were established in three successive expeditions (1987–88, 1988–89 and 1989–90)[1–6]. The metal concentrations were in good agreement with values obtained by other researchers in the Southern Ocean[7–13], although data variability was higher than that observed in the Weddell Sea and the Indian sector of the Southern Ocean[7–10]. In particular our previous studies on cadmium concentration showed high variability both spatially and temporally[2,5] and a depletion during the summer[2].

However, our previous investigations were carried out on sub-surface samples; no information was available for the vertical distribution and nor was the complete temporal evolution investigated.

During the 1990–91 expedition a more systematic study of the summer seasonal evolution of metal concentration in the water column of the Gerlache Inlet (in Terra Nova Bay) was carried out in order to explain the variability of the previously observed data and to highlight possible anthropogenic contamination. The investigation began well before the dissolution of pack ice and carried on until the end of the austral summer. Samples were analysed on site by one of the authors (G.S.) immediately after sampling in the clean chemistry laboratory of the Italian Station at Terra Nova Bay.

In this paper we present the results obtained on samples collected during the 1990–91 expedition for cadmium and lead, two elements characterised by different geochemical properties. Cadmium, although it is not known to be essential biologically, exhibits a nutrient-type distribution (recycled element) and is involved in shallow regeneration cycles similar to those of phosphate and nitrate[14]. The influence of processes of production and remineralization of biogenic particles on the distribution of dissolved cadmium has already been reported in the literature for different geographical areas[15,16]. Lead is a typical scavenged element substantially influenced by local inputs[17]. Results of the present study will be compared with those obtained in the same area from previous expeditions.

EXPERIMENTAL

Sampling

During the 1990–91 austral summer seawater samples were collected along a water column of the Gerlache Inlet (called station B; 74°40′07″ S, 164°07′15″ E; distance from the Italian Station of Terra Nova Bay about 5 km; sea floor about 270 m) on Nov. 29, Dec. 7 and 26, Jan. 6 and 30, and Feb. 11 (see Figure 1). During this period the site was covered by pack until about mid-January. In general samples were collected at the following depths (in m): 0.5, 10, 25, 50, 100, 250. On Nov. 29 and Dec. 7 seawater was gathered only from 0.5, 25 and 100 m depths. On February 11th the site selected for the study was occupied by an iceberg and samples were collected a few hundred metres away from it (74°40′02″ S, 164°07′45″ E); in this case the bottom sample was drawn at a depth of 290 m instead of the usual 250 m due to the deeper sea floor (315 m).

In the presence of pack, samples were collected through a hole drilled by an ice corer (Duncan, UK, Model BTC). Subsurface water (about 0.5 m below the seawater level) was collected by an air-driven diaphragm pump in Teflon (Disco, Italy, Mod. DL15) and temporarily stored in a 50 l polyethylene tank until filtration (see below). Deeper samples were collected by 20 or 30 l Go-Flo samplers (General Oceanics, USA), coated with Teflon internally and with pressurization capability. A non-metallic (Kevlar) hydrowire and a Teflon covered ballast attached to the wire at least 10 m below the sampler, were used.

Samples were filtered through membrane filters of 0.45 μm pore size immediately after sampling (within 2–3 hours), by pressurizing (pressure lower than 0.5 bar) the polyethylene tank or the Go-Flo bottle with pure nitrogen (chromatographic grade) and pushing the sample through a Teflon filtration apparatus (Sartorius, holder for in-line pressure filtration, SM 16540; cellulose nitrate membrane filter, SM 11306, 142 mm diameter). After discarding a first aliquot of about 3–5 litres of water, filtered samples were collected directly in 2 l FEP bottles and stored at +4°C until analysis (carried out on site within 1–2 weeks). Aliquots of samples were also stored frozen (−20°C) for speciation analysis to be performed later in Italy (not considered here).

Polyethylene tanks, Go-Flo bottles, filtration apparatus, filters and storage bottles were acid cleaned and conditioned to minimise sample contamination from the material used; the detailed cleaning procedures have been reported previously[18]. Handling and treatment of the samples were carried out in the clean chemistry laboratory (Class 100) available at the Terra Nova Bay Station in Antarctica.

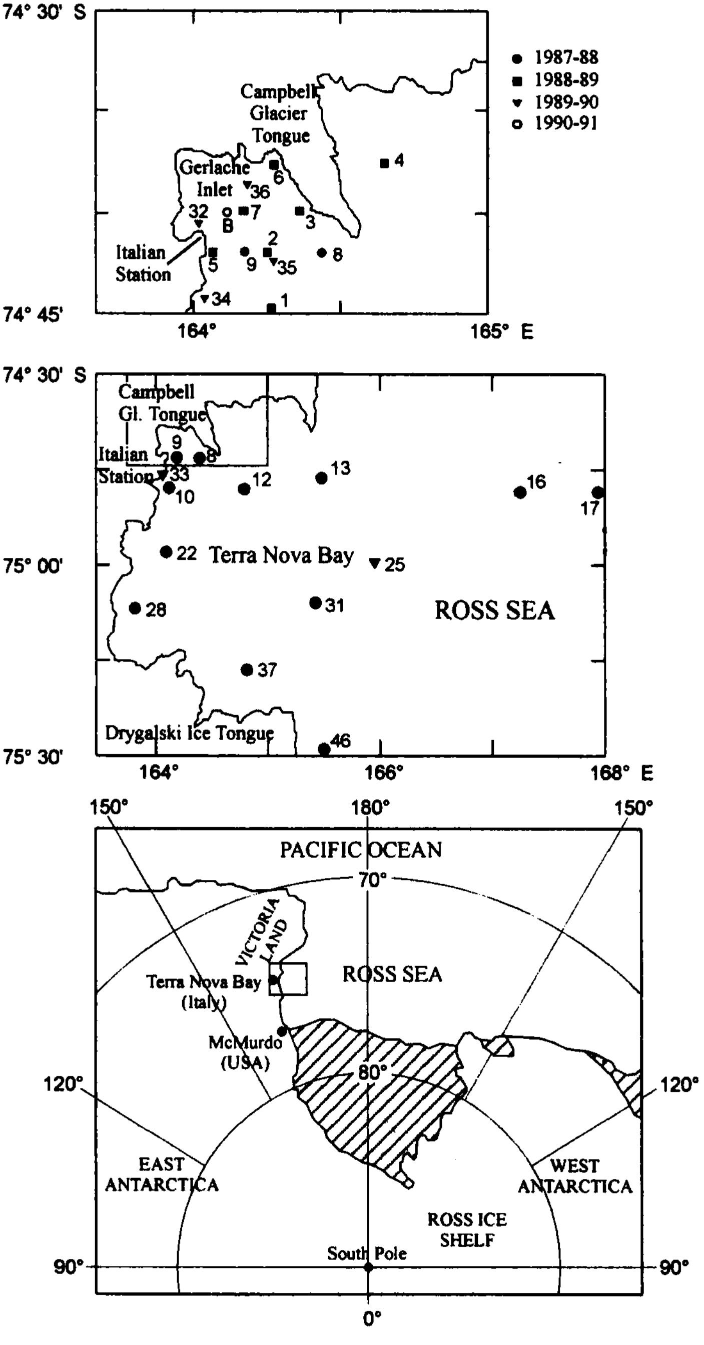

FIGURE 1 Sampling stations in Terra Nova Bay during expeditions from 1987–88 to 1990–91.

Subsurface samples collected during previous expeditions (1987–88: sample ref. 8, 9, 10, 12, 13, 16, 17, 22, 28, 31, 37 and 46; 1988–89: ref. 1, 2, 3, 4, 5, 6 and 7, in positions 5, 6, 7 samples were collected before (ref. 5P, 6P, 7P) and after pack melting; 1989–90: ref. 25, 32, 33, 34, 35 and 36) were collected and treated in similar way. Details on procedures and locations (see also Figure 1) have already been reported[1,2,4].

The sampling/filtration procedure was previously tested to be contamination-free through an international intercalibration exercise on seawater sampling for trace metal determination[19,20].

Temperature (T), salinity (S) and chlorophyll concentration (Chl) were measured along the water column by a multiparametric probe (ME, Meerestechnik), equipped with a back scattering fluorometer (Dr. Haardt, Backscat). Unfortunately the probe was available on-site for the present study only for a limited period, between December 15 and January 15. Thus T, S and Chl profiles are available only for observations carried out on December 26 and January 6.

Voltammetric Analysis

Metal concentrations were determined by Differential Pulse Anodic Stripping Voltammetry (DPASV) carried out on a Thin Mercury Film Electrode (TMFE). An EG&G 384B Polarographic Analyzer was used. The electrochemical cell (EG&G, mod Rotel 2), specifically designed to detect ultra-low metal concentrations present in sea water, has been described previously[18,21]. The cell is equipped with a Rotating Glassy Carbon Disc Electrode (RGCDE), on which the TMFE is electrochemically plated, an Ag/AgCl,KCl(sat.) reference electrode and a platinum auxiliary electrode.

The mercury film was prepared daily immediately prior to each analysis using the procedure summarized below[1,2,4,18]. The graphite surface was polished using wetted alumina (0.05 μm grain size, 1000 rpm rotation rate), then washed with diluted (1:200) ultrapure HCl (Merck, Suprapur) and plentifully rinsed with ultrapure water (Millipore, Milli-Q). The mercury deposition was obtained by electrolysis from a solution containing KCl about 2.5×10^{-2} mol/l and $Hg(NO_3)_2$ 10^{-4} mol/l at -1.000 V for 20 min using a rotation rate of 4000 rpm. After the film formation the cell cleanup was tested by a differential pulse voltammetric scan in the positive direction; if the blank voltammogram did not show peaks and the base line was satisfactory analysis of the sample (previously outgassed for 20 min with nitrogen flow) was started. Before transferring the sample to the measurement position the electrochemical cell was rinsed with ultrapure water previously outgassed with ultrapure nitrogen (chromatographic grade).

Total dissolved metal determinations were carried out on samples digested in ultrapure HCl for at least 24 hours. Digestion was carried out directly into the Teflon vessel used as the cup of the electrochemical cell adding 100 μl of HCl (32%, NIST, Gaithersburg MD, U.S.A.) to approximately 50 ml of the sample (pH about 2). A more precise measurement of the volume was carried out subsequently, at the end of the determination (see below). Tests carried out to verify the efficiency of digestion procedure confirmed the complete release of the metals from organic ligands[1,2].

Voltammetric measurements were performed applying the following experimental conditions: deposition potential −0.950 V, deposition time 20 min, electrode rotation rate 4000 rpm, equilibration period 30 s, mode DPASV, scan rate 10 mV/s, pulse amplitude 50 mV, pulse frequency 5 s^{-1}, final potential −0.180 V. After the voltammetric scan the electrode was allowed to remain at a potential of −0.200 V for 5 min to ensure complete removal of the amalgamated metals. Quantification was obtained by the multiple standard additions method; three spikes of metal standard solutions were always made. At the end of the measurement cycle the sample volume was detected with more precision (±0.5 ml) using a cylinder.

The blank for the digestion procedure was obtained by adding the ultrapure HCl to a KCl solution (about 3×10^{-2} mol/l prepared with ultrapure water and KCl of Suprapur grade, Merck) and analysing it before and after the acid treatment. The concentration difference was always lower than the detection limit for Cd and Pb (about 0.2 ng/l) so the blank contribution was considered to exert no influence on the determination.

Statistical Analysis

A multivariate statistical approach was applied to analyse data of the 1987–88 and 1989–90 seasons. Samples were characterized through measurement of the concentration of metals[1,2,4–6], nutrients[22,23], chlorophyll[24–26], temperature[24,27,28] and salinity[23,25,28]. Details of the variables used are given below. Unfortunately the 1990–91 season cannot be included in the present comparison because of the lack of data concerning other than trace metals.

Principal component analysis (PCA)[29] was applied to identify variable associations, to obtain a dimension reduction and to observe the group structure of the data. PCA was carried out on standardized data due to the different measurement units, magnitude and variability of the variables.

The UNISTAT[30] statistical package for computer was used for all the required computations.

HYDROGRAPHY

The Weddell and Ross seas are the areas where the larger part of the Antarctic Bottom Water is formed. Because of its high density the Bottom Water flows down the continental slope into the South Atlantic and eastward through the Indian and Pacific Ocean sectors of the Southern Ocean[31].

The hydrological characteristics of the Ross Sea and Terra Nova Bay (a small bay west of the Ross Sea, between Cape Washington and the Drygalski Ice Tongue) were studied during earlier oceanographic cruises and a general circulation pattern of water masses has been proposed[22–24,27,28,32–36]. The Ross Sea is affected by a branch of the Antarctic Coastal Current which, with a cyclonic movement, follows the coast from east to west and successively from south to north through the McMurdo Sound and Victoria Land[31,33,35]. However, the coastal irregularities, bottom topography and localized phenomena, such as polynyas, give rise to several deviations from this general circulation, principally on a small scale. During the summer the surface layer features a low salinity ($<34.5‰$) typical of Antarctic Surface Water (AASW), whose properties are affected by processes such as seasonal warming or surface freezing and interaction with meltwater from continental or sea ice; in particular, higher temperatures are observed in the southern part of the Sea where pack opens up earlier in the season[32,33]. Circulation below the AASW is controlled by Circumpolar Deep Water (CDW), characterized by relatively high temperature and salinity. This water type represents the only water of external origin near the continental shelf, so it gives rise to the other water types by mixing and cooling and by input of precipitation, meltwater or brine. On the basis of salinity and $\delta^{18}O$ measurements it has been proposed that the combination of brine deriving from the freezing of sea surface, glacial meltwater and precipitation could generate the High Salinity Shelf Water (HSSW), principally in the Western Ross Sea although the formation mechanism has not been completely clarified[33]. Flow of CDW along the continental slope helps to confine the HSSW in the depression of the Shelf, particularly, along the shore of Victoria Land[32,33].

In Terra Nova Bay the structure of the water column in summer is quite simple. It is generally characterised by a relatively warm and low salinity surface layer of 10–50 m ascribed to AASW over a homogeneous saltier and colder water extending down to the floor and tending to HSSW[24,27,28,35,36]. The physical and chemical characteristics of surface water, which presents variable currents principally driven by the wind, are affected by local processes and seasonal evolution. Significant interannual variability was observed for the salinity and temperature of the surface layer during the 1987–88 and 1989–90 seasons (average values were 1.0 °C and 34.19 ‰ in 1987–88[27] and 0.5 °C and 33.58 ‰ in

1989-90[14,28]). Deep waters, as normally observed, are much more homogeneous and reproducible, with temperature and salinity of about −1.9 °C and 34.8 ‰, respectively[24,27,28], i.e. characteristic values of Ross Sea HSSW[33]. The hydrodynamics of deep layers show more stable currents and a low vertical component[35], especially in coastal areas. The latter circumstance could be explained, as supposed by Stocchino and Lusetti[36] by the presence of a relative temperature minimum delimiting the surface layer.

In the Gerlache Inlet the summer current shows a clockwise direction both in the surface and in the deeper layers[35]. Temperature and salinity profiles measured during the pack melting in each case show a warm surface layer and a deep water with characteristics tending to HSSW (see Figures 2a and 3a). The T versus S plot (see Figures 2b and 3b) enables the water masses observed in the Gerlache Inlet to be characterized on the basis of domains identified in the Ross Sea[33,37]. The surface presents a very thin, well stratified layer (a few meters) having low temperature (−1 °C) and low salinity (<34 ‰), probably

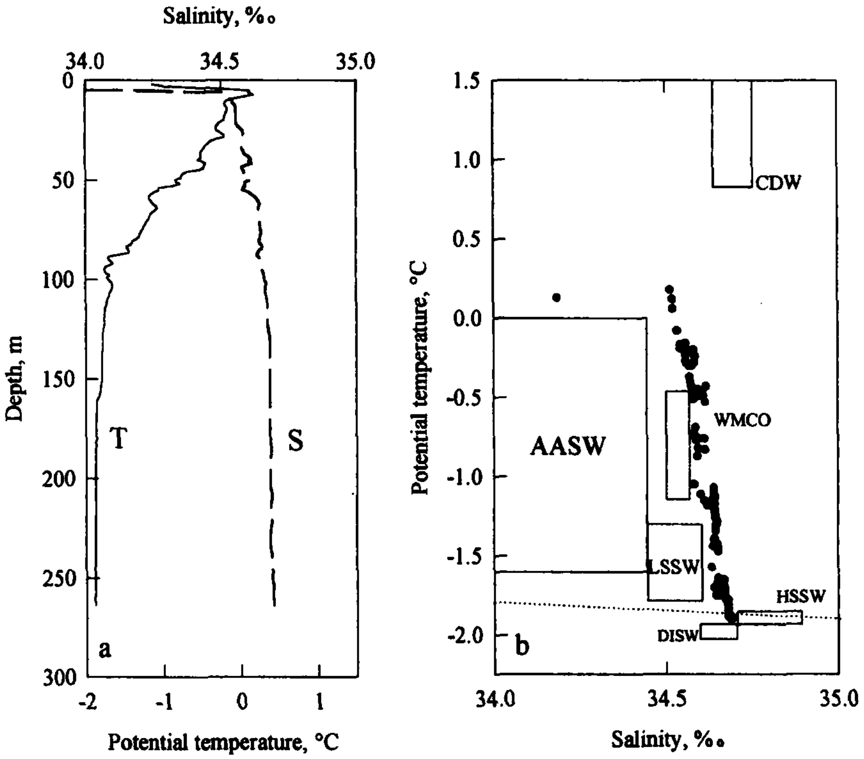

FIGURE 2 Vertical profiles for salinity and potential temperature (a), and potential temperature/salinity plot (b) for December 26, 1990. Abbreviations and domains defined in Jacobs et al.[33].

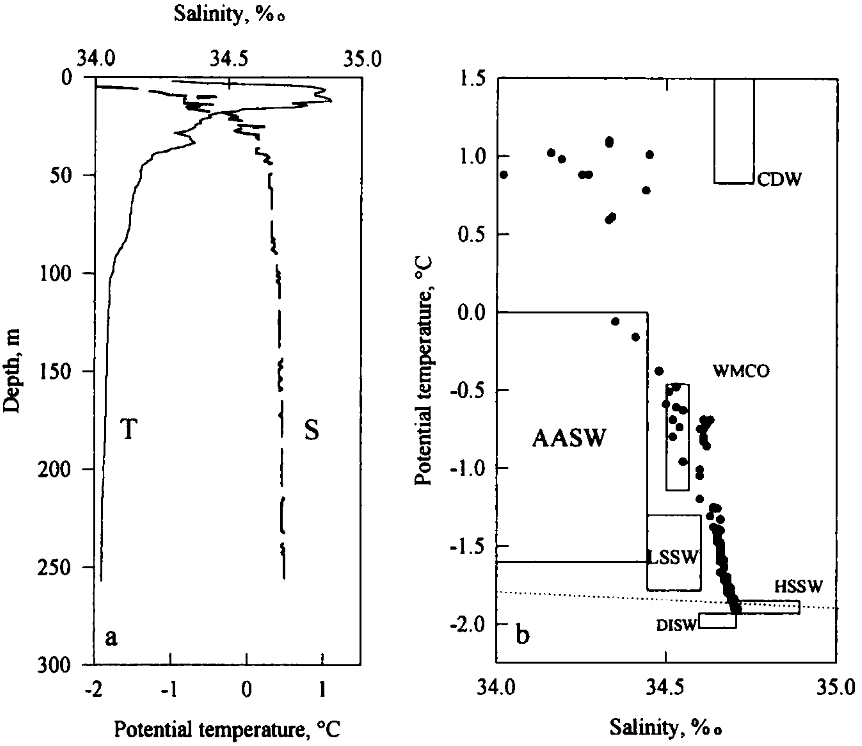

FIGURE 3 Vertical profiles for salinity and potential temperature (a), and potential temperature/salinity plot (b) for January 6, 1991. Abbreviations and domains defined in Jacobs et al.[33].

resulting from recent pack melting. Beneath it are two major water masses. An upper layer of 20–100 m can be distinguished from the deep waters; this layer shows quite different characteristics for the two profiles. On December 26 the first 20 m layer assumes a temperature of about 0 °C and lies on a layer (comprised between 20 and 100 m) which shows a gradual transition to HSSW (temperature between 0 and −1.9 °C, salinity between 34.5 and 34.7 ‰). This latter water mass, presenting characteristics similar to a warm core (WMCO) (see Figure 2b) could represent the result of intrusion of water masses related to the winter polynya in the Terra Nova Bay[33,35]. On January 6, immediately before pack melting, the upper layer presents a temperature of about 1 °C and a salinity of about 34.3 ‰, showing characteristics similar to AASW (see Figure 3b), although the temperature assumes higher values than those reported by Jacobs et al.[33]. Below this upper layer, a water mass can be recognized with characteristics similar to WMCO (which presents a relative temperature minimum at a depth of 30 m) and an intermediate homogeneous layer of between

50 and 80 m with a mean temperature of −1.5 °C and a salinity of 34.66 ‰; deeper, the water mass shows a gradual transition to HSSW. Measurements are not available for the complete seasonal evolution, so it is impossible to evaluate if the hydrodynamic regime was different before December 26 and after January 6, but the available profiles seem to show the intrusion in the top layers of Gerlache Inlet of surface water from the Terra Nova Bay during the pack melting.

Distribution of nutrients in Terra Nova Bay during the seasons 1987–88 and 1989–90 were reported by Catalano et al.[22,23]. Vertical profiles showed a surface depletion, affecting the first 20–50 m layer, where the concentrations were about halved with respect to deeper layers. The concentrations reported for deep water are in excellent agreement with values observed in the Weddell Sea where, contrary to Terra Nova Bay, only slight surfacial depletion was observed[7,9].

Considering for example the 1989–90 data set, and particularly the coastal subset (more relevant for the present study) a few interesting observations can be made. Nitrate, phosphate and silicate concentrations were well correlated and, as usual, correlation coefficients increased in passing from data referred to the upper 25 m surface layer ($0.89 \leq \text{corr} \leq 0.96$) to data of complete vertical profiles (all correlations equal to 0.98). Moreover the nitrate/phosphate molar concentration ratio, for the complete profiles, was 14, a value in excellent agreement with typical values reported for the Antarctic ocean[7], and slightly lower than that estimated for global oceanic waters, i.e. 16, by Redfield et al.[38].

As regards the relationships between nutrients and salinity contrasting results can be observed if one considers shallow and deep samples separately. In particular the correlation of nitrate, phosphate and silicate with salinity is significantly lower in shallow (corr 0.64, 0.67 and 0.69, respectively) than in deep waters (corr 0.97, 0.95 and 0.87). Moreover, the slope of the regression line obtained by plotting nitrate as a function of salinity was 6.6 μM/psu for shallow samples and 21.6 μM/psu for deep samples.

In conclusion, the presence of a marked depletion of nutrients in the shallow layer of the coastal area of Terra Nova Bay, together with nutrients/salinity relationships which show correlation and regression coefficients which are significantly lower than those obtained in deep waters, emphasize an inefficient regeneration of nutrients in the upper part of the water column, which seems in agreement with the low vertical flux measured by Stocchino and Manzella[35]. As a consequence, it can be concluded that the nutrient distribution is mainly influenced by physical processes in deep waters and by biological activity in the shallow waters.

RESULTS

Results of cadmium and lead concentration measurements as a function of the depth for the samples collected during the 1990–91 expedition are reported in Tables I and II. Two or more replicates were carried out for all the samples except for those referring to the last sampling because very little time was available before the closure of the field laboratory.

Table III reports data related to surface samples collected during the 1987–88 and 1989–90 expeditions, to be considered for the statistical analysis. Cadmium and lead concentration, salinity, temperature, chlorophyll and nutrients content are given. References are cited therein.

Cadmium

The distribution of cadmium in the water column (see Figure 4) presents different features according to the period of observation.

At the beginning of the summer season, until about mid-December (and presumably during the winter), the vertical profile of Cd concentration is homogeneous with a mean value of 0.71 (SD 0.10) nmol/l. The relatively high concen-

TABLE I Cadmium concentration in samples collected in Gerlache Inlet during the 1990–91 Italian expedition. In parentheses mean values.

Depth m	*Cadmium concentration, nmol/l*					
	Nov 29	*Dec 7*	*Dec 26*	*Jan 6*	*Jan 30*	*Feb 11*
0.5	0.76, 0.68, 0.79, 0.72, 0.72 (0.73)	0.86, 0.85, 0.97, 0.93 (0.90)	0.72, 0.71, 0.66, 0.83 (0.73)	0.19, 0.19 (0.19)	0.17, 0.15, 0.15 (0.16)	0.10 (0.10)
10			0.10, 0.10, 0.11, 0.13 (0.11)	0.14, 0.15, 0.18 (0.16)	0.18, 0.22 (0.20)	0.10 (0.10)
25	0.61 (0.61)	0.70, 0.69 (0.70)	0.14, 0.10, 0.10 (0.11)	0.17, 0.14 (0.16)	0.26, 0.25, 0.26 (0.26)	0.11 (0.11)
50			0.26, 0.32, 0.26 (0.28)	0.61, 0.55, 0.57 (0.58)	0.30, 0.32, 0.31 (0.31)	0.12 (0.12)
100	0.67, 0.67 (0.67)	0.67, 0.64, 0.67, 0.66 (0.66)	0.64, 0.70, 0.68 (0.67)	0.61, 0.69 (0.65)	0.63, 0.74 (0.68)	0.54 (0.54)
250			0.76, 0.66, 0.55 (0.66)	0.64, 0.75, 0.75, 0.80, 0.68 (0.72)	0.34, 0.31, 0.37 (0.34)	
290						0.25, 0.28 (0.26)

TABLE II Lead concentration in samples collected in Gerlache Inlet during the 1990–91 Italian expedition. In parentheses mean values

Depth, m	*Lead concentration, nmol/l*					
	Nov 29	*Dec 7*	*Dec 26*	*Jan 6*	*Jan 30*	*Feb 11*
0.5	0.102, 0.100, 0.087, 0.085, 0.108 (0.096)	0.106, 0.110 (0.108)	0.102, 0.100, 0.119, 0.094, 0.114 (0.106)	0.056, 0.074 (0.065)	0.068, 0.042, 0.060 (0.057)	0.044 (0.044)
10			0.088, 0.070 (0.079)	0.030, 0.034, 0.044 (0.036)	0.027, 0.025 (0.026)	0.037 (0.037)
25	0.114 (0.114)	0.117, 0.142 (0.130)	0.030, 0.040, 0.044 (0.038)	0.261, 0.218 (0.240)[a]	0.027, 0.023 (0.025)	0.028 (0.028)
50			0.109, 0.138, 0.124 (0.124)	0.052, 0.040, 0.044 (0.045)	0.043, 0.049 (0.046)	0.034 (0.034)
100	0.134, 0.130 (0.132)	0.109, 0.119, 0.127 (0.118)	0.080, 0.118, 0.116 (0.105)	0.133, 0.123 (0.128)	0.024, 0.025 (0.024)	0.053 (0.053)
250			0.130, 0.093, 0.113 (0.112)	0.123, 0.119, 0.096, 0.133, 0.102 (0.115)	0.139, 0.144, 0.131 (0.138)	
290						0.116 (0.116)

[a] Contaminated sample.

TABLE III Metal concentrations[1,2,4–6] and other hydrological data[22–28] obtained in the surface water of Terra Nova Bay in the 1987–88 and 1989–90 seasons

Station	*Cd* *nmol/l*	*Pb* *nmol/l*	*Cu* *nmol/l*	*Salinity* *‰*	*Chlorphyll* *mg/l*	*Temperature* *°C*	SiO_4^{4-} *µmol/l*	PO_4^{3-} *µmol/l*	NO_3^- *µmol/l*	NO_2^- *µmol/l*
					1987–88 Campaign					
8	0.24	0.063	4.3	34.85	0.83	1.99	56.9	0.68	15.6	0.06
9	0.19	0.114	2.8	34.61	0.44	2.10	64.9	0.79	16.9	0.04
10	0.26	0.061	2.4	34.82	1.20	2.00	61.3	0.64	15.2	0.04
12	0.15	0.035	1.6	34.81	0.76	0.80	61.3	0.93	22.3	0.05
13	0.19	0.032	1.4	34.84	1.04	0.74	54.6	0.84	20.3	0.05
16	0.08	0.026	1.8	34.10	1.10	1.02	52.4	0.79	18.4	0.08
17	0.10	0.038	0.9	32.80	1.44	0.03	54.2	0.81	20.1	0.25
22	0.09	0.038	1.4	34.75	0.85	0.60	65.6	1.14	20.3	0.04
28	0.13	0.034	0.9	34.69	0.36	1.65	63.6	1.05	17.5	0.04
31	0.14	0.025	2.0	34.52	2.44	0.86	53.4	0.79	18.4	0.07
37	0.15	0.027	1.6	34.33	1.83	0.73	57.5	0.79	18.0	0.10
46	0.40	0.029	2.7	33.78	2.35	−0.23	55.3	1.01	19.2	0.14
					1989–90 Campaign					
25[a]	0.071	0.034	1.9	34.50	4.10	−0.75	68.0	1.46	24.6	0.15
32	0.094	0.032	1.7	33.72	2.82	0.77	18.5	0.62	8.8	0.28
33	0.053	0.015	2.1	33.70	1.44	1.28	15.3	0.31	9.6	0.25
34	0.036	0.031	2.5	33.81	2.48	0.19	24.6	0.83	11.5	0.22
35	0.046	0.032	1.6	33.25	0.18	0.85	7.6	0.32	6.2	0.32
36	0.027	0.018	—[b]	33.62	3.68	0.84	16.0	0.47	8.5	0.24

[a] Depth 20 m. [b] In PCA the missing value was replaced by the mean value of the variable for the 1989–90 data set.

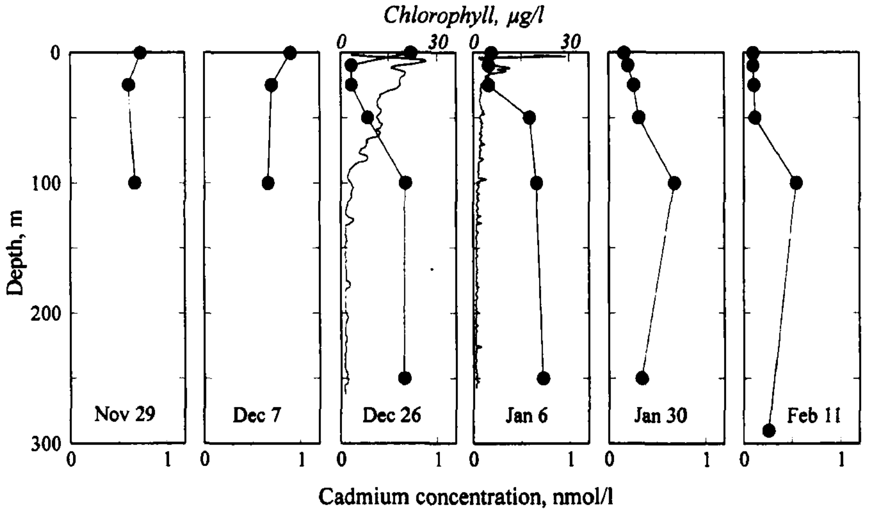

FIGURE 4 Seasonal evolution of depth profile for cadmium concentration (•) and chlorophyll (—). 1990–91 campaign.

tration level and the homogeneity are accounted for by the upwelling of enriched deep water to the surface and by the absence of an efficient scavenging process or uptake by organisms. Values are in agreement with typical concentrations observed in deep waters of Antarctic regions[7,9] (Weddell Sea, 0.5–0.9 nmol/l) and Subantarctic regions[16] (Pacific sector, 0.58–0.65 nmol/l), and similar homogeneous profiles are observed in upwelling areas of the Weddell Sea[7,9]. Lower values are reported for Antarctic seawater in samples collected later in the summer season by us[2,5], 0.026–0.69 nmol/l Ross Sea, and by others[11], 0.15–0.48 nmol kg^{-1} Weddell Sea, but higher results are also reported for the Atlantic-Indian sector of the Southern Ocean[12], 0.91–1.28 nmol kg^{-1}

Later in the season (see Table I), contemporarily with ice melting and with the development of the phytoplankton bloom (see profiles of December 26 and January 6), a marked depletion of the cadmium concentration is observed. The depletion, not present on December 7 and already underway on December 26 (when a minimum of 0.11 nmol/l was observed at a depth of 10–25 m), extends gradually to a depth of 50 m after the pack ice is completely melted (see profile of January 30). Finally (February 11) the entire 50-m upper layer presents an almost homogeneous concentration with a mean value of 0.11 (SD 0.01) nmol/l.

The last two profiles present maxima at a depth of about 100 m and unexpected lower values in the bottom. At present no explanation is given for this apparently anomalous behaviour which is nevertheless observed in two profiles;

a more complete interpretation of these data would require a more detailed knowledge of local marine currents.

The observed depletion is much more pronounced than that shown in profiles obtained in regions characterized by an efficient upwelling of the Weddell Sea[7,9] for which, however, the temporal variation (behaviour) is not available. Conversely an analogous remarkable depletion is reported for the surface layers of the Scotia Sea[7] and of the Subantarctic region southwest of New Zealand[16].

Two hypotheses can be formulated to explain the quite rapid depletion of Cd concentration in shallow waters of the Gerlache Inlet as observed in the temporal investigation carried out during the summer 1990–91.

The first explains the phenomenon in terms of merely the physical effect of marine currents. It considers that a surfacial intrusion of low salinity, low Cd content water mass (AASW) enters the Gerlache Inlet from the Bay, interrupts the (slowly flowing) upwelling and extends rapidly to the first 50-m layer. In this event, because the depletion would derive from a dilution of surface waters, the normal correlation of Cd concentration with salinity should still be retained in the surface layer.

According to the second hypothesis, Cd depletion has a biological origin, due to interaction of metal with particles produced by processes taking place during the phytoplankton bloom; the Cd distribution would then follow that of major nutrients. In this event cadmium/salinity and major nutrients/salinity plots would show, for shallow waters, a different behaviour with respect to the lower water column and, consequently, lower correlation should be obtained for the entire data set.

To gain more insight into the cause of surface cadmium depletion it is useful to consider the relationships of the metal concentration with temperature, chlorophyll and salinity for the two profiles for which corresponding data are available (i.e. December 26 and January 6). Here clear negative correlations are observed for cadmium concentration with temperature (corr −0.82) and chlorophyll (corr −0.71) (see also Figure 4). Conversely, no correlation is observed between Cd concentration and salinity (corr 0.07), although high correlation emerges when one considers only samples from deeper than 25 m (corr 0.75). The latter evidence together with: (i) the available chlorophyll profiles (Figure 4), which show the highest concentrations in the 50–100 m surface layer, (ii) the above observations on nutrient distribution and on the low vertical fluxes in coastal area of Terra Nova Bay, and (iii) the general knowledge about the behaviour of cadmium as a nutrient-type element[17], suggest that an important explanatory factor for the cadmium depletion is the quick summer increase in biological activity in the whole area. Of course the contribution of the transport of depleted water mass from the centre of the bay (where the biological processes may have begun) through the existing current to the Inlet, particularly below the pack ice in the early summer cannot be excluded; indeed this could partly explain the rapidity of the phenomenon.

In conclusion, the joint effect of biological and physical processes can very probably explain the rapid cadmium depletion observed in the Gerlache Inlet within 2–3 weeks since it may derive from processes started in the open bay even before December. Further elements supporting this interpretation are obtained from the multivariate statistical analysis of data of the 1987–88 and 1989–90 seasons and reported below.

Differently from other oceans, the polar seas offer a unique opportunity to observe vertical metal distribution when the photosynthetic activity is negligible due to the absence of light (or low illumination) and the presence of marine ice. The present results in Antarctica show that at the beginning of the summer, and presumably in the winter, the cadmium vertical profile is completely homogeneous. This observation gives further evidence in favour of the general interpretation of Cd surface depletion in the Oceans in terms of its involvement in the biological cycles[17].

It is interesting to note that during the period of observation, the Cd concentration in the surface water is decreased by about one order of magnitude; in particular it passed from about 0.8 nmol/l in the first period of observation (November–December) to 0.19, 0.16 and 0.10 nmol/l on January 6, January 30 and February 11, respectively (see Figure 5, 1990–91 campaign). This high seasonal variability can explain the different values obtained in different years,

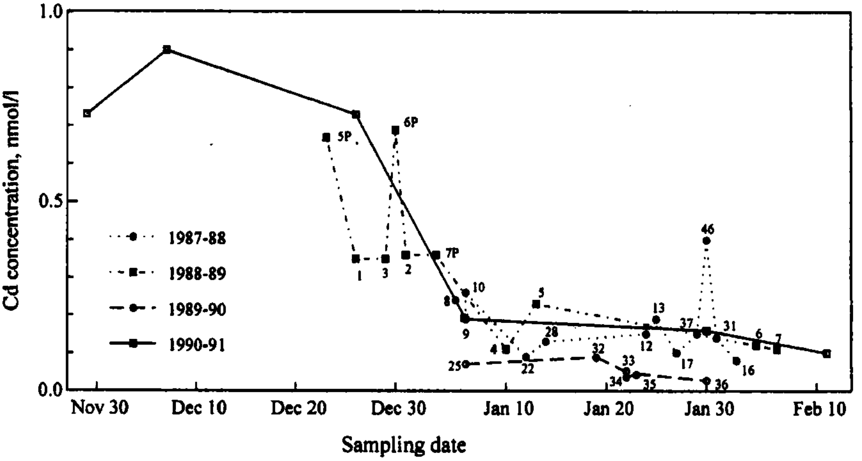

FIGURE 5 Summer variation of cadmium surface concentration in Terra Nova Bay during four successive campaigns.

when samples were collected in different periods of the seasons or when the seasonal evolution of biological activity was brought forward or delayed due to different meteorological and climatic conditions which may occur from year to year.

To clarify this aspect further the results obtained in previous expeditions are added in Figure 5. From this plot it can be observed that the surface cadmium concentration in Terra Nova Bay follows approximately the same decreasing temporal trend in each season irrespective of the spatial location of samples in the bay and of the year of observation. The only deviation seems to be represented by the data obtained in the summer of 1989–90, when the observed concentrations were about half the mean values obtained on the same date during the two previous seasons. Actually the 1989–90 season was exceptional from a climatic point of view, with an early temperature increase[39] (by about 15 days) and a very intensive phytoplankton bloom[40] (see also the subsequent discussion on the 1987–88 and 1989–90 seasons). As a consequence the points in Figure 5 referring to the 1989–90 season should probably be considered as needing to be shifted to the right with respect to the actual sampling date. It can therefore be concluded that, as a general rule, the temporal factor appears dominant for determining the Cd concentration level and for explaining its variation observed either in the same season or from year to year.

Lead

Data reported in Table II show that the lead concentrations in the water column vary from 0.024 to 0.132 nmol/l. These values are comparable with literature data reported for the Weddell Sea[11] (0.015–0.062 nmol/l) and for the Weddell and Scotia Seas[8] (0.010–0.103 nmol/l); moreover they are consistent with upwelling antarctic areas subject to the influence of volcanic and hydrothermal activities (Mt. Melbourne and Mt. Erebus volcanoes are located in the area) and with the presence of polynhyas[8].

The variations recorded during the campaign (Figure 6) are generally lower than those observed for cadmium. The effect of both the high analytical variability, due to the extremely low concentration involved, and the very occasional contamination of the samples also superimposes on the actual lead variation. Consequently the seasonal behaviour of lead is registered in a less marked manner. Nevertheless a few interesting considerations can be made on the basis of the data.

The surface concentration, practically constant to about 0.1 nmol/l from November 29 to December 26, then decreases rapidly to 0.065 nmol/l on January 6;

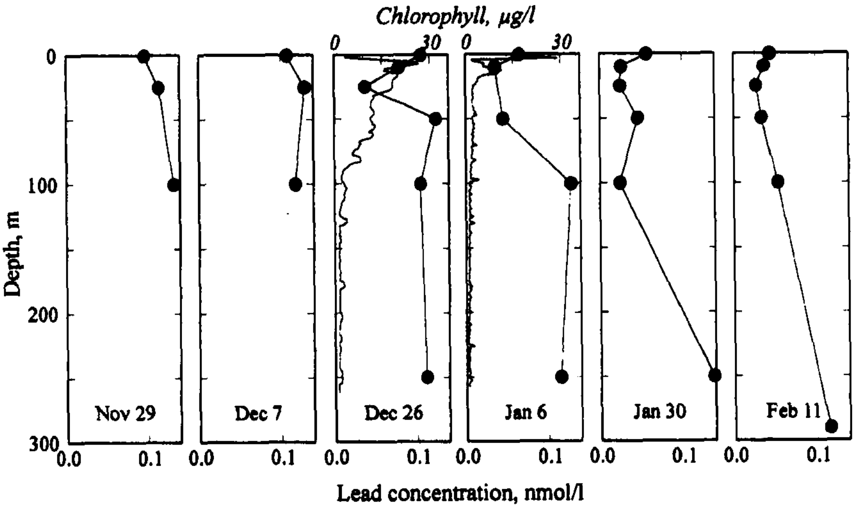

FIGURE 6 Seasonal evolution of depth profile for lead concentration (•) and chlorophyll (—). 1990–91 campaign.

subsequently a more gradual decline is observed to reach the value of 0.044 nmol/l on February 11 (see Figure 7). This interval includes practically all the values obtained in the same area (Gerlache Inlet) during previous expeditions, when samples were collected at different moments of the climatic and biological evolution of the summer season (in nmol/l 1987–88: 0.025–0.114[1]; 1988–89:

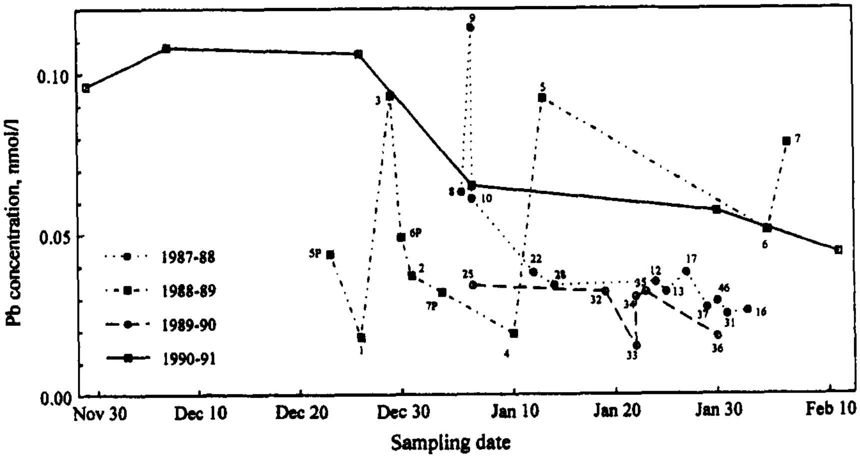

FIGURE 7 Summer variation of lead surface concentration in Terra Nova Bay during four successive campaigns.

0.018–0.093[6]; 1989–90: 0.015–0.044[6]). In the case of lead it is to be remembered that different concentration levels have already been recognised (1987–88 season) between the inner area of Gerlache Inlet (0.061–0.114 nmol/l) and the open sea of Terra Nova Bay (0.025–0.038 nmol/l)[1]. Thus the spatial effect cannot be neglected in comparing data obtained in different years from different locations. In particular this effect is responsible for the discrepancies in the lowest values observed between the results of the present work (1990–91 season) and those previously reported (see above). Nevertheless the plot of all the data against the date of collection (Figure 7) also confirms a general decreasing trend during the summer for lead, although to much smaller degree than cadmium.

A rapid depletion of lead in Antarctic surface seawater has also been emphasized for the Weddell and Scotia Seas and interpreted in terms of particulate scavenging processes during periods of intense primary production in the austral summer[8].

As regards the deep water (Figure 6) it can be observed that the vertical profile of lead concentration appears practically uniform at the beginning of the season, with values at the same level as those of the surface water, while a significant depletion of the concentration begins to occur in the subsurfacial layers when the biological activity is increasing rapidly (see chlorophyll profile in Figure 6). At the end of the process the Pb concentration in these layers is reduced to about one third of the initial value and, differently from what happen for Cd, the depletion extends deeper and deeper during the season, down to at least 100 m.

It has been observed that a surface enrichment is typical of the oceans subject to atmospheric input originating from remote anthropogenic sources or of coastal areas subject to local immission[17]. From the present study the absence of a marked surface increase of metal concentration with respect to the deep baseline values indicates the absence in Terra Nova Bay of significant Pb pollution coming from remote or local areas.

Comparison of the 1987–88 and 1989–90 Seasons

The combined effects of physical and biological processes in determining metal distributions in the surface waters of Terra Nova Bay together with evidence of year to year variations with respect to the summer evolution of biological activity can be exploited better by comparing data collected during the 1987–88 and 1989–90 expeditions. A multivariate statistical approach is used for this comparison. Unfortunately a general comparison with the other seasons investigated, including 1990–91, and the analysis for deep waters are not possible due to the incompleteness of data.

The variables used for the statistical analysis are the concentrations of cadmium and lead[1,2,5,6], copper[4], silicates, phosphates, nitrates and nitrites[22,23], chlorophyll[24–26], temperature[24,27,28] and salinity[23,25,28]. Principal Component Analysis (PCA)[29] is used mainly to elucidate the variable association and the group structure in the data set. The first three, varimax rotated, principal components (cumulative explained variance 82.0%) are considered relevant for the study and interpretation of the data.

PCA results, presented in terms of biplots[29,41] in Figure 8, show clear associations between nutrients (except nitrites), salinity and cadmium on the first PC, and metals (including Cd) on the third PC, while the second contrasts temperature and chlorophyll.

Considering that nutrients in surface waters (as described above) are consumed by productive activity, and that variation of salinity is due to physical processes, it follows that the first PC accounts for both processes, which cannot be separated and which together contribute to the variability of cadmium concentration (at least in part). These results are in agreement with the interpretation of cadmium data given above.

The scatter plot of data on principal components (Figure 8) shows a net separation of the 1989–90 samples from those of 1987–88 confirming the overall different behaviour of the two seasons as pointed out by biological studies (see above)[40]. The differentiation is observed mainly along the first PC then determined for the most part by nutrient content, salinity and cadmium. The only exception is sample 25, which was collected at a depth of 20 m (all the others are surface water). A subgroup consisting of samples 8, 9, 10 and 46 can be observed in the 1987–88 data set. This differentiation, which emerges when the third PC is considered (explained variance 12.2%) and is mainly determined by the Pb, Cu and Cd content, has already been recognised previously in terms of spatial location of samples[1,4].

DISCUSSION

Metal concentration in oceanic waters is governed by the balance between their rate of addition and their rate of removal. The major sources of trace metals in sea water derive from (i) atmospheric or riverine input and (ii) the interaction of waters with newly formed oceanic crustal material and hydrothermal activity[42]. Trace elements mobilised from human activities and transported via atmosphere

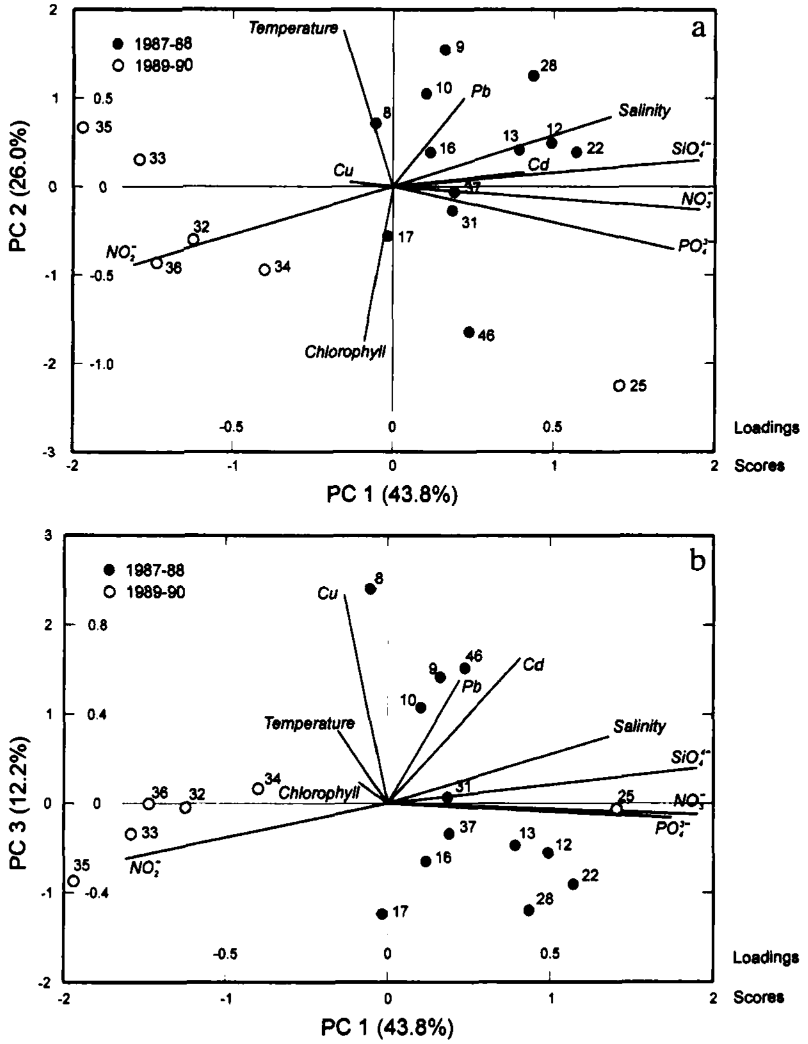

FIGURE 8 Principal component biplot (after varimax rotation) with respect to (a) the first two PCs and (b) the 1st and 3rd PCs. Data from 1987–88 and 1989–90 expeditions.

can contribute significantly to their distribution in the oceanic regions[17]. For most elements the main removal process is via sedimentary deposition and burial; however, before being ultimately removed from the sea water reservoir to the sediments, they can undergo varying degrees of internal recycling as a result of biogeochemical processes[43]. The recycling can involve the uptake of trace elements by particulate phases produced principally by phytoplankton in the photic layer and regeneration into the deep ocean where the particles are largely redissolved as a consequence of respiration and oxidation processes. Biological cycles appear to be responsible for the transport of a wide range of elements from the surface to the deeper layers[17,42,43].

The processes of particle production and dissolution are well-separated in space and time, and much can be understood about particle-water interactions from the observation of vertical profiles of the dissolved and particulate constituents in coastal and oceanic waters[42]. In particular studies of the seasonal evolution of vertical profiles of the elements and their relationship with other oceanographic parameters (e.g., temperature, salinity, nutrients) carried out in areas with uncomplicated hydrodynamic processes (for example in oligotrophic subtropical gyres characterised by minimal vertical mixing and low productivity), have enabled processes to be elucidated which control the element distribution[13,17,42,44,45].

A rough measurement of the intensity of the particle-water interactions for different elements can be the mean oceanic residence times[42]. On the basis of these and the consequent patterns of the vertical profiles, the elements can be subdivided into accumulated, recycled and scavenged elements[17]. Accumulated elements (residence time $>10^5$ years) exhibit a higher concentration in sea water relative to their crustal abundance and a uniform vertical profile (when normalised to sea water salinity). Recycled elements (intermediate residence time, between 10^3 and 10^5 y) tend to be involved in the biological particle cycle; their vertical profile presents a significant surface depletion and deep regeneration (typical nutrient profile). Scavenged elements (residence time $<10^3$ y) interact strongly with particulate matter and are removed on time scales shorter than a single stirring cycle of the ocean reservoir. These elements, present in sea water at very low concentrations relative to their crustal abundance (especially in deep water), exhibit different profiles according to their primary input; normally a surface maximum is displayed because they enter the sea via aeolian dust (possibly enriched due to anthropic influence) or from the ocean margin.

Interpretation of data obtained in the present work should account for the different geochemical characteristics of cadmium and lead, the different interaction processes of metals with phytoplankton and particles and the seasonal evolution of biological processes during the investigation.

Cadmium and lead are typical recycled and scavenged metals, respectively[17]. At the very beginning of the summer season, when both biological activity and new formation particle density are at a minimum, both metals exhibit homogeneous vertical distributions at the higher concentration levels; these are consistent with a coastal region with an upwelling hydrodynamic regime, reduced processes of biological uptake and scavenging and without high local sources. The presence of a polynya in the area of Terra Nova Bay[33,35] highlights vertical flows in the winter and the consequent homogeneization of the water column. Concentration values are comparable with those observed in the coastal Pacific Ocean[17]. Subsequently a general decrease in metal content is observed both in the surface and in the shallow waters. The amount of this depletion, the temporal trend and the layer which is the most affected by the phenomenon (as shown by the shape of the deep profile and its change during the season) are remarkably dependent on the metal considered.

Cadmium, as a nutrient-type element, interacts with particulate matter, being subject to uptake from biological systems and subsequently discarded with detritus and fecal pellets. A quick depletion of the metal is observed in the euphotic layer when the phytoplankton bloom starts. This depletion increases during the summer season but it remains confined to approximately the same layer and does not affect deeper strata. Note that the highest chlorophyll concentrations in the Terra Nova Bay are located in the 20–30 m upper layer (see results in Figure 4 and in Innamorat et al.[46]).

Lead, a scavenged metal, interacts with particulate by adsorption and reaches the sediment in association with the host particles of the highest dimensions. These particles are generated from chemical reactions, biologically mediated, tending to destroy their organic components and compacting the smaller particles into a larger one. Consequently the sedimentation process for this metal is maximum when the number of particles of higher dimensions is maximum[41].

The suspended matter in the Ross Sea originates mainly from biological activity[46,47] and the maximum density of the largest particles is located deeper with respect to the zone of maximum production. In the coastal area the largest particles present a more homogeneous vertical distribution than the smaller ones and they reach the maximum concentration during a late or senescent phase of a bloom[47]. This explains the slow decreasing trend of Pb concentration in the vertical profile starting in December which became more consistent and extended to almost all the vertical profile in February, when particles of higher dimension became prevalent.

Finally it is to be noted that the temporal trend of the Pb profile observed here is in agreement with observations carried out in the Pacific, where the residence time of lead was evaluated as about two years in surface waters and several hundred years in the deep ocean[45].

CONCLUSIONS

Measurements carried out in Antarctica in different periods of the summer and at different depths have confirmed that DPASV is sufficiently sensitive to be used for direct determination of Cd and Pb in Antarctic seawater, thus avoiding lengthy enrichment procedures which are susceptible to sample contamination. This feature, together with the easy transport-capability of the instrumentation (low cost, small size, low weight, minimal facilities required) allows determinations to be carried out in the remotest areas of the world, like research stations in Antarctica or ice-breaking ships in polar regions, provided that a clean chemistry laboratory is available. The ability to obtain reliable measurements on site immediately after seawater collection is of particular relevance to checking samples and sampling procedures (modified or adjusted in case of contamination) and to providing reference values to be compared with later results obtained in the laboratory after a long storage period.

The seasonal evolution obtained for the metal content along the water column of Terra Nova Bay during the 1990–91 austral summer emphasizes the substantial difference in the mechanisms which control the distribution of Cd and Pb in seawater. The prevalent interactions of cadmium with biological systems and of lead with particulate matter are also hypothesized in the polar coastal area studied. A definitive clarification of this aspect requires an ad hoc campaign planned to obtain more frequent observations and contextual, detailed information from both the hydrological and hydrodynamical points of view. The seasonal variation observed at the surface explains the variability of metal concentration observed in the previous three expeditions in the same area.

The vertical distributions of cadmium concentration are homogeneous before both the pack defrosting and the phytoplankton bloom start in the whole area; afterwards, in a few weeks, biological activity generates the typical nutrient profile characteristic of cadmium, with a surface variation which confirms the trend observed in a previous study[2]. An apparently similar behaviour is observed for lead; in this case, however, a lower and delayed effect is noted in the concentration depletion which nevertheless extends to deeper layers during the season than that for cadmium.

Again with respect to lead it is important to observe that the vertical profile does not show the high surface increase typical of anthropized areas[44], so serious problems of pollution deriving from local or remote sources can be excluded. This conclusion is in agreement with lead data obtained for snow in Victoria Land which showed a drastic reduction of the lead content during the last decade to a value typical of the beginning of the century[48].

At present other aliquots of the same samples considered here (transported frozen to Italy) are being subjected to laboratory analysis for metal determination and speciation according to the methodology already used in the same area[1,2,4]. As well as the obvious aim of confirmation of the general findings from stored samples, the new data will enable discussion of the aspects of metal distribution during the summer in terms of metal speciation. Finally a further contribution to the same subject is expected from the results of a similar investigation now in progress in Wood Bay, an area more distant from the Italian Station than Terra Nova Bay.

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