Cadmium, Lead and Copper Complexation in Antarctic Coastal Seawater. Evolution during the Austral Summer

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PLEASE SCROLL DOWN FOR ARTICLE

CADMIUM, LEAD AND COPPER COMPLEXATION IN ANTARCTIC COASTAL SEAWATER. EVOLUTION DURING THE AUSTRAL SUMMER

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The evolution of cadmium, lead and copper complexation by organic ligands was studied along the water column during the 1990/91 summer in the Gerlache Inlet (Antarctica). The complexation was estimated by determination of the total dissolved concentration of metals, the labile concentration, the ligand concentrations and the relative conditional stability constants. The mean value of the total dissolved cadmium concentration was 0.83 nM until mid-December; the concentration was gradually depleted initially in the subsurface layer then down to the bottom. The mean concentration along the water column in February was 0.15 nM. The labile fraction represented 90% of the total until December, and it was reduced to about 20% in the upper 50 m by February. The cadmium was complexed by one class of ligands detectable after mid-December. Initially it was present only in the surface layers and later was extended to the bottom. The ligand concentration reached a maximum (2.2 nM) during the phytoplankton bloom in December. The mean total dissolved concentration for lead ranged from 0.083 nM until December to 0,030 nM in the upper 100m at the end of the summer. The labile fraction did not change during the season and meanly represented 39% of the total dissolved concentration. The lead was complexed by one class of ligands, its mean concentration ranges between 0.60 nM at the beginning of the summer to 1.2 nM at the end of the season. The total dissolved copper concentration ranged between 1.6 to 3.8 nM. The labile fraction was strongly dependent on depth and time, ranging from values lower than 1% in surface water to a maximum value of 40% in deep water. The copper was complexed by two classes of ligand, the first present only in surface layers and the second homogeneously distributed along the water column. The results for the three metals are compared to those obtained for surface samples collected in the whole of Terra Nova Bay between summer 1987/88 and summer 1989/90.

Keywords: Heavy metals; complexation; sea water; DPASV; Terra Nova Bay; Antarctica

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INTRODUCTION

The Ross Sea and the Weddell Sea represent the most important sources of Antarctic bottom waters that affect the characteristics of all oceanic bottom waters. However only recent papers have paid attention to the distribution of trace metals in the Southern Ocean (Antarctica)[1-3]; most investigations were carried out in the Weddell Sea and at the Weddell/Scotia Confluence. Very few data are available on trace metal distribution in the Ross Sea area; early measurements on copper distribution in surface waters between New Zealand and the Ross Sea were reported by Boyle and Edmond[4] and more recently some investigations were carried out during the oceanographic campaigns included in the Italian National Program in Antarctica (PNRA)[5-9].

Very few studies have dealt with metal speciation, though it is well known that the different chemical forms in which metals are present in natural water interact differently with biota and suspended matter (the biogeochemical cycle that determines their distribution and fate). Some papers emphasised the fundamental role played by organic compounds in binding metals to define their distribution and transport[10-12] and their bio-availability[13-15]

Macromolecular organic compounds originated by biological processes (deriving from degradation, stress or as exudates of biological systems), as emphasized in recent papers, may have a complexing capacity for some micro elements (Cd, Cu, Pb, Zn)[15-18] and the chemical forms in which elements are present can affect their capacity to interact with particles[10-12, 19]. Bruland et al.[16] emphasized that the biology strongly influences the distribution and chemical speciation of bioactive metals and on the other hand the level of the bioavailable fraction of these elements may influence levels of primary production, the taxonomy of phytoplankton population and the trophic structure. Therefore the occurrence of any event that changes the metal distribution or their speciation in natural waters will affect the bio-geochemical cycle in which they are involved.

In our previous paper[20] we discussed the temporal evolution of cadmium and lead distribution along the water column during the 1990–91 austral summer on the basis of in-field measurement. Particular emphasis was placed on the considerable decrease in concentration of both the metals during the season, and the difference in the behaviour of the two elements was discussed. However, no speciation results for the two metals nor any data of copper distribution were reported and discussed.

In this paper we will examine the distribution for cadmium, lead and copper by means of measurements carried out in the Venice laboratory about six months after the sampling date. The copper distribution was examined because it repre-

sents a bioactive element that features a distribution characterized by a deep water scavenging process superimposed on a nutrient type profile. Analysis and discussion of the results will consider the speciation changes observed during the summer season considering also the distribution and speciation obtained in the same area during two previous expeditions.

HYDROLOGY

The hydrology of the studied area has previously been discussed on the basis of physical and chemical parameters[20]. Temperature and salinity profiles measured during the pack melting in each case show a warm surface layer and deep water with characteristics tending to high salinity shelf water (HSSW). The surface is characterised by a thin well-stratified layer presenting a temperature of about −1°C and low salinity, probably resulting from recent pack melting. Beneath this is a relatively high temperature (about 0°C) layer that changes its characteristics as the season progresses.

Terra Nova Bay and the coastal area of the Victoria land in general is characterised by high productivity conditions[21]. The nitrate concentration in the bottom water is about 30 μM, while in January the concentration in the upper 20 m is generally lower than 15 μM and in the Gerlache Inlet reaches values lower than 10 μM [22]. Martin et al.[23] quantify the nitrate uptake rate in the coastal water of the Victoria Land near the area examined here and determine one value of 2.54 μmol NO_3 kg^{-1} d^{-1}, which means that the nitrate depletion from the value they measured in deep waters (25 μmol NO_3 kg^{-1}) to that measured in surface waters (5 μmol NO_3 kg^{-1}) would take about 3 weeks when there are no limiting factors to primary production.

The depletion of nutrients in the shallow layer observed in the coastal area of Terra Nova Bay[24-25], together with nutrient/salinity relationships previously discussed[20], emphasise 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[26]. Analogous results were obtained by Martin et al.[23]; they concluded that in the coastal area of Victoria Land the nitrate provided by upwelling in surface water is not enough to compensate for the depletion by phytoplankton bloom. As a consequence, we could assert that the nutrient distribution is mainly influenced by physical processes in deep water and by biological activity in the shallow waters. In conclusion, the shallow distribution of those species involved with biological processes is strongly affected by biological activity in the examined area.

SPECIATION PROCEDURE

The use of ASV to study the speciation of metals in seawater has been developed by several researchers[27–29] and details of the procedure adopted have been reported[5, 30]. The approach is based on the ability of DPASV to differentiate two fractions of the metal: the first, ASV-labile, is composed of metal ions and metal complexes which are electroactive at the selected deposition potential (inorganic complexes and electrochemically labile organic complexes); the second consists of inert forms of metals, i.e strong organic complexes which are thermodynamically and kinetically stable.

The procedure involves the titration of organic ligands present in the sample by the metal to be studied, and the voltammetric measurement, initially and after each addition, of the oxidation peak current due to the labile fraction.

Considerations about the reaction of complexation and the relative conditional stability constants, including the competing reaction with inorganic ligands, have beenn previously reported[5, 30]. The electroactive metal concentration measured after each addition consists essentially of ionic forms and inorganic complexes, $[M']$, and experimentally is evaluated as:

$$[M'] = i_P/S \tag{1}$$

where i_p is the peak current measured after each metal addition and S is the sensitivity (evaluated as the slope of the titration curve measured when inert organic ligands have been saturated). The concentration of complexed metal, $[ML]$, after each addition is calculated by the mass balance as the complement of $[M']$ to the total concentration, M_t.

If one ligand, or one class of ligands, is present and the stoichiometry of the reaction of complexation is 1:1, and if equilibrium is reached after each addition, the $[M']/(M_t-[M'])$ versus $[M']$ follow the equation[29, 31, 32]:

$$[M'] /(M_t - [M']) = [M'] /C_L + 1/(C_L K') \tag{2}$$

where C_L is the total ligand concentration.

If more ligands are present, the transformed plot of titration data, $[M']/(M_t-[M'])$ versus $[M']$, will assume a curved shape, and in particular will follow the equation[5, 30]:

$$\frac{[M']}{M_t - [M']} = 1/ \sum_{i=1}^{n} \left(\frac{C_{L_i}}{[M'] + 1/K_i'} \right) \tag{3}$$

Studies of metal speciation in seawater and the present work show that cadmium and lead fit well the model which considers one ligand[6, 7, 33, 34] and cop-

per fits the model which considers two classes of ligands[5, 19, 31, 35]; thus equation 3 becomes :

$$\frac{[M']}{M_t - [M']} = 1 \Big/ \left[\frac{C_{L1}}{([M'] + 1/K'_1)} + \frac{C_{L2}}{([M'] + 1/K'_2)} \right] \quad . \qquad (4)$$

The models described can be applied to estimating the extent of cadmium, lead and copper complexation. In a solution presumably consisting of a complex mixture of organic ligands complexing the metals of interest, the complexation parameters deriving from these simplified models applied to the titration data may not be completely correct, from a thermodynamic point of view, with respect to the actual organic ligands present in the sample; however, if the experimental data fit such simple models well, determination of these parameters allows us to describe the metal complexing properties of natural ligands and their apparent influence on metal speciations.

Some authors have hypothesised that application of the ASV technique to study of trace metal complexation give rise to an overestimation of the labile fraction[36–38] due to direct reduction of metal-organic complexes in the preconcentration step (thermodynamic lability) or to the dissociation of complexes at the electrodic interface (kinetic lability). These problems were widely discussed when the methodology was applied to study the complexation of copper, cadmium, zinc and lead[30, 33–35, 39, 40]. The results showed that only the cadmium complexes were kinetic labile when the residence time in the diffusion layer at the electrode interface was sufficiently long[39]. To minimize the risk with respect to this problem and to maximize sensitivity a Rotating Disk Electrode at its highest rotation rate was used in this work.

In sea water, some organic ligands forming strong complexes can be electrochemically labile; one example is thiol molecules as cysteine[41, 42] that form complexes with trace metals with high values of stability constant (normally higher than 10^9)[43]. Sea water is a multi-component system in which all the metals are present at concentrations normally lower than 10 nM and simple organic molecules such monocarboxilic acids and amino acids are minor constituents of dissolved oceanic organic matter[44, 45] (concentrations are usually lower than 10 nM). By considering the side reactions with all the other competing metals, the complexes formed by these ligands will not have high conditional stability constants in sea water. In these conditions, their complexes represent minor metal species[36, 46] and affect the metal speciation only slightly. However, when metal complexation studies are carried out in environmental systems where these organic components represent an important part of dissolved organic matter, results of ASV measurements could lead to an overestimation of inorganic metal species.

In this study, to minimise the direct electrochemical reduction of metal-organic complexes use was made of deposition potentials negative enough to reduce only the more labile forms of the examined metals[7, 35, 40], which were selected on the base of pseudo-polarographic experiments.

Tests to evaluate the accuracy of the DPASV approach to metal speciation were previously reported using model ligands in studying the complexation of zinc, cadmium, lead and copper in seawater[33–35, 40]. Results of ligand concentration and conditional stability constants obtained were in agreement with the theoretical data.

EXPERIMENTAL

Sampling

Seawater samples were collected in the Gerlache Inlet during the 1990–91 austral summer along the water column at station B; 74°40′07″ S, 164°07′15″ E (see Figure 1)(sea depth about 270 m). The site B was covered by pack until about mid-January. On Dec 26, Jan. 6 and 30 and Feb 11 the samples were collected at the following depths (in m): 0.5, 10, 25, 50, 100 and 250. On Dec. 7 the samples were collected at 0.5 and 100 m depths while on Nov. 24 and 29 seawater was gathered only from 0.5 m depth. The deeper sample collected on Feb 11 (74°40′02″ S, 164°07′45″ E; depth 315 m) was gathered at 290 m due to the greater bottom depth.

The samples under the pack 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 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), internally coated with Teflon and with pressurization capability. The sampling bottles were deployed on Kevlar hydrowire, tripped by a Teflon messenger and weighted by a Teflon-covered ballast attached to the wire at least 10 m below the sampler.

Samples were filtered within 2–3 hours through acid-clean cellulose nitrate membrane filters (0.45 µm pore, Sartorius, SM 11306, 142 mm diameter). The water was forced through a Teflon filtration apparatus (Sartorius, SM 16540) pressurising the polyethylene tank or the Go-Flo bottle (pressure lower than 0.5 bar) with filtered nitrogen (chromatographic grade). The first water aliquot of about 3–5 litres was discarded and then the filtered samples were collected directly in 2 l FEP bottles and stored at −20 °C until analysis.
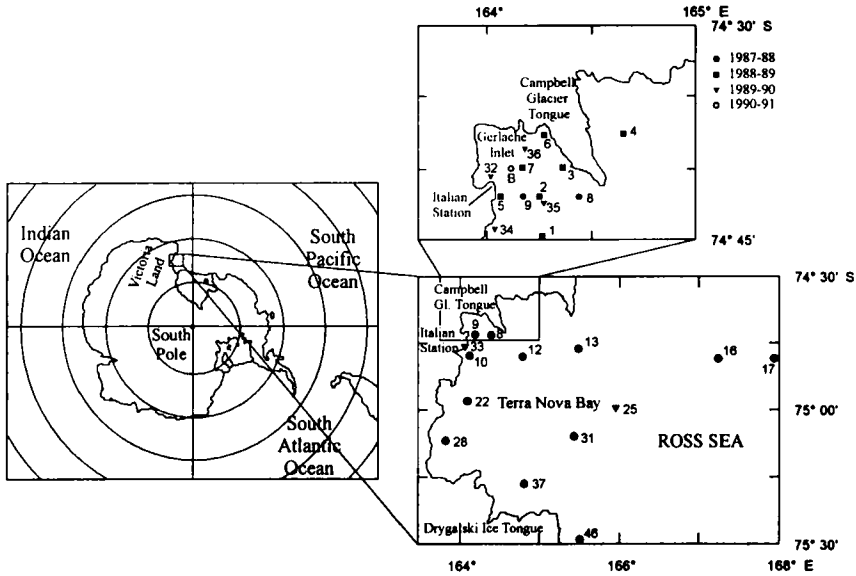
FIGURE 1 Sampling sites in Terra Nova Bay during the 1987/88, 1988/89, 1989–90 and 1990/91 expeditions

All the containers and materials were acid-cleaned and conditioned to mini-mise sample contamination following the cleaning procedures previously reported[30]. Handling and treatment of the samples were carried out in the clean chemistry laboratory (Class 100) at the Terra Nova Bay Station in Antarctica; analyses were carried out in the clean laboratory (Class 100) in Venice about 6 months later.

Subsurface samples (see Figure 1) 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 and 35) were also analysed[5–7].

The sampling, filtration and storage procedures were tested to guarantee the sample integrity by analysing aliquots of the same samples on board immediately after collection and in the Venice laboratory after about 5–10 months of storage at −20 °C. The results for cadmium and lead concentrations were previously reported and the values showed an excellent agreement[39].

Temperature (T), salinity (S) and chlorophyll concentration (Chl) were meas-ured along the water column by a multiparametric probe (ME, Meerestechnik),

equipped with a back scattering fluorometer (Dr. Haardt, Backscat) on December 26 and January 6 (see Figure 2).
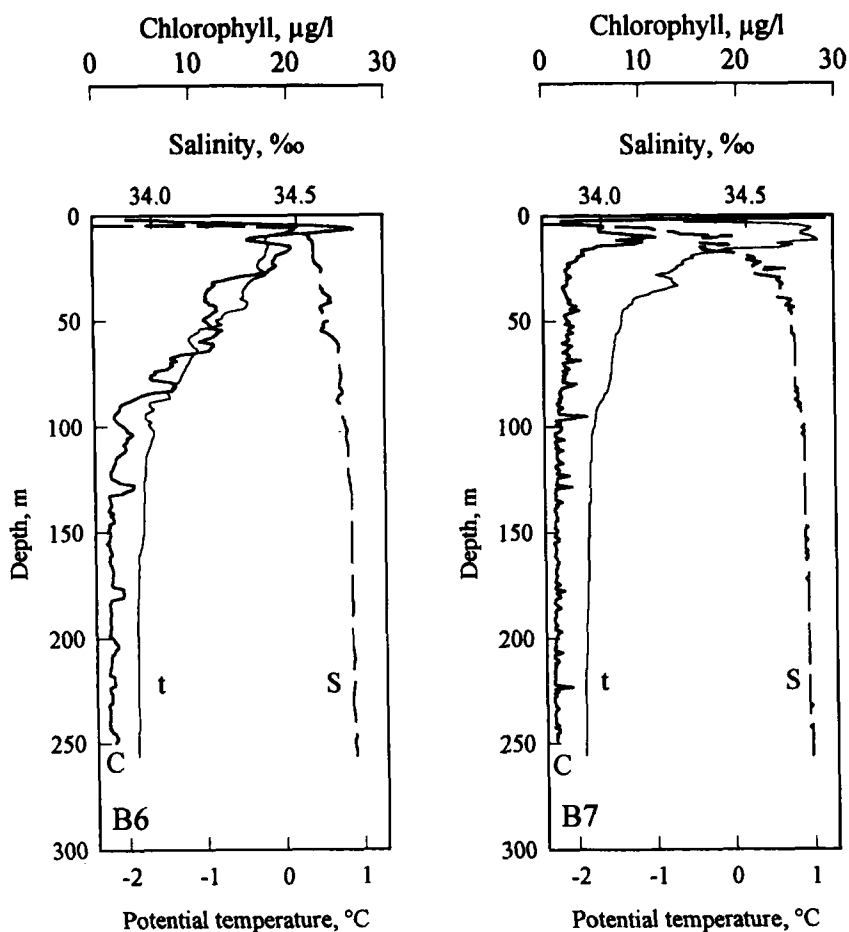
FIGURE 2 Profiles of salinity (S), temperature (t) and chlorophyll (C) at sampling site B during the 1990/91 campaign. B6, profile December 26; B7, profile January 6

Instrumentation

Previous description of the instrumentation[30] should be referred to for further details. Anodic Stripping Voltammetry measurements were carried out by a Multipolarograph Analyzer EG&G mod. 384 B in Differential Pulse mode; the polarograph was equipped with an electrochemical cell EG&G Rotel 2, designed for ultra-trace metal determination. The working electrode was a thin mercury

film deposited on a rotating glassy carbon disk. A platinum electrode and an Ag/AgCl, KCl saturated electrode were used as auxiliary and reference respectively. The mercury film was prepared daily immediately prior to each analysis, according to the previously reported procedure[7].

To check the film cleanness, a voltammetric scan was carried out when the film was ready at a scan rate of 10 mV s^{-1}, pulse amplitude of 50 mV and pulse frequency 5 s^{-1}. If the voltammogram did not show peaks and the base line was satisfactory, the electrochemical cell was rinsed with one aliquot of sample previously purged with nitrogen, after which the deaerated sample was placed in the analytical position and the measurement was started.

Total concentration

Total concentration of dissolved cadmium (C_{Cd}), lead (C_{Pb}) and copper (C_{Cu}) was determined in filtered samples. Aliquots were transferred into the Teflon cup of the electrochemical cell and acidified at pH 2 with HCl (Suprapur, Merck; Ultrapure, NIST) at least 48 hours prior to analysis in order to release metals complexed by organic ligands. The determinations were performed by DPASV, using the multiple standard additions method. The deposition potential used for the determination of Cd and Pb was –0.95 V and –0.85 for Cu (vs. Ag/AgCl, KCl sat), the deposition time was 20–40 minutes depending on the metal concentration (rotation speed 4000 rpm). The deposition was allowed with a quiescent period of 30 seconds keeping the electrode at the same potential, then a differential pulse voltammetric scan was started (scan rate 10 mV s^{-1}, pulse amplitude 50 mV, pulse frequency 5 s^{-1}) in a positive direction until a final potential of –0.18 V was reached for the determination of Cd and Pb and at –0.15V for Cu. The rotating electrode was conditioned applying a potential of -0.18 V for 5 minutes to remove the residual amalgamated metals completely before subsequent measurement was started.

The completeness of mineralization obtained by acid digestion was verified by comparing results with those obtained after UV irradiation of acidified samples for 6–24 hours (1.2 kW lamp Hanovia, Ace Glass Inc.) the results were previously reported[5–7] and did not show significant differences in the metal concentrations.

The blank for the digestion procedure was tested by the addition of HCl to a solution of KCl 0.03 M (100 μl of HCl 30% Suprapur Merck or 32% Ultrapure NIST to 50 ml of KCl solution), which was analyzed to detect the metal contents before and after the addition of HCl. When the Merck Suprapur HCl was used, the Cd, Pb and Cu blanks were found to be 17pM, 19 pM and below the detection limit respectively. When the NIST Ultrapure acid was used, all the blanks were below the detection limit.

TABLE I Concentration of cadmium (total dissolved concentration, C_{Cd}, and labile concentration, $[Cd']$), ligand concentration complexing cadmium (C_{L-Cd}) and the logarithm of the conditional stability constant ($logK'_{Cd}$) in samples collected in the Gerlache Inlet during the 1990–91 Italian expedition. Concentration in nM

Depth m	B1, Nov 24				B2, Nov 29				B4, Dec 7				B6, Dec 26			
	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$
0.5	0.99	0.99	udl	---	0.76	0.63	0.13	---	1.0	0.94	udl	---	0.74	0.056	2.2	9.54
10													0.12	0.036	1.5	9.64
25													0.060	0.021	0.96	9.61
50													0.27	0.16	1.0	9.05
100									0.57	0.48	0.53	9.49	0.62	0.55	udl	---
250													0.52	0.45	udl	---

Depth m	B7, Jan 6				B8, Jan 30				B9, Feb 11			
	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$	C_{Cd}	$[Cd']$	C_{L-Cd}	$logK'_{Cd}$
0.5	0.16	0.081	0.76	9.86	0.12	0.010	1.2	9.62	0.12	0.011	1.4	9.46
10	0.12	0.024	1.3	9.40	0.22	0.073	1.5	9.07	0.14	0.033	1.3	9.80
25	0.16	0.093	0.59	9.40	0.14	0.029	1.5	9.40	0.11	0.024	1.3	9.80
50	0.60	0.53	0.535	9.20	0.31	0.17	0.70	9.24	0.11	0.027	1.6	9.47
100	0.71	0.71	udl	---	0.78	0.69	0.35	9.10	0.22	0.12	0.57	9.39
250	0.79	0.79	udl	---	0.27	0.19	0.51	9.17	0.20^a	0.069	0.74	9.61

[a] Sample collected at a depth of 290 m.
udl=under detection limit.

TABLE II Concentration of cadmium (total dissolved concentration, C_{Pb}, and labile concentration, $[Pb']$), ligand concentration complexing cadmium (C_{L-Pb}) and the logarithm of the conditional stability constant ($logK'_{Pb}$) in samples collected in the Gerlache Inlet during the 1990–91 Italian expedition. Concentration in nM

Depth m	B1, Nov 24				B2, Nov 29				B4, Dec 7				B6, Dec 26			
	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$
0.5	0.060	0.020	0.67	9.66	0.080	0.030	0.49	9.51	0.29[a]	0.10	0.47	10.0	0.106	0.030	1.2	9.54
10													0.077	0.036	0.37	9.84
25													0.033	(0.006)	0.76	9.77
50													0.10	0.014	0.55	9.68
100									0.22[a]	0.030	0.78	9.89	0.11	0.012	0.56	9.86
250													0.10	0.022	0.64	9.89

Depth m	B7, Jan 6				B8, Jan 30				B9, Feb 11			
	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$	C_{Pb}	$[Pb']$	C_{L-Pb}	$logK'_{Pb}$
0.5	0.059	0.040	0.33	9.73	0.064	0.023	1.2	9.61	0.042	0.013	1.4	9.43
10	0.026	0.008	0.35	9.68	0.033	0.017	0.63	9.58	0.033	(0.006)	0.77	9.77
25	0.21[a]	0.074	0.32	9.91	0.031	(0.009)	1.1	9.37	0.029	0.018	1.0	9.76
50	0.046	0.020	0.49	9.91	0.031	(0.010)	1.6	9.12	0.026	0.013	1.3	9.43
100			0.15		0.026	0.010	1.1	9.44	0.025	0.013	1.2	9.63
250	0.083	0.031	0.46	9.89	0.15	0.045	1.2	9.70	0.12[b]	0.076	1.3	9.53

[a] Probably contaminated samples.
[b] Sample collected at a depth of 290 m.

TABLE III Concentration of copper (total dissolved concentration, C_{Cu}, and labile concentration, [Cu']), ligand concentrations complexing copper (C_{L1} and C_{L2}) and logarithm of the conditional stability constants ($logK_1'$ and $logK_2'$) in samples collected in the Gerlache Inlet during the 1990–91 Italian expedition. Concentration in nM

Depth m	B1, Nov 24						B2, Nov 29						B4, Dec 7						B6, Dec 26					
	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$
0.5	2.0	0.11	udl	---	28.	8.63	3.7	0.05	udl	---	28.	8.77	3.0	0.12	udl	---	22	9.00	3.0	$(4\ 10^{-4})$	19.3	13.	55.	8.42
10																			2.9	$(3\ 10^{-4})$	3.8	14.	57.	8.52
25																			1.9	0.14	udl	---	63	8.37
50																			3.7	0.23	udl	---	45	8.35
100							2.2	0.07	udl	---	24.	8.71							3.6	0.69	udl	---	52	7.92
250																			2.2	0.89	udl	---	32	8.20

Depth m	B7, Jan 6						B8, Jan 30						B9, Feb 11					
	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$	C_{Cu}	[Cu']	C_{L1}	$logK_1'$	C_{L2}	$logK_2'$
0.5	1.9	(0.15)	0.55	14.	47.	8.04	2.4	$(9\ 10^{-3})$	3.6	11.3	61.	8.04	3.6	$(5\ 10^{-3})$	10.	11.	70.	7.88
10	1.6	0.35	0.40	16.,	31.	8.25	2.5	$(5\ 10^{-4})$	2.8	15.	60.	8.85	2.2	$(1\ 10^{-4})$	4.9	13.	56.	7.62
25	2.4	0.37	udl	---	16.	8.85	1.8	$(4\ 10^{-3})$	1.6	15.	55.	7.76	2.5	(0.12)	1.5	14.	58.	8.11
50	3.7	0.35	udl	---	28.	8.79	3.8	(0.04)	3.4	13.	62.	8.18	2.2	0.10	udl	---	62.	8.71
100							3.6	0.25	udl	---	71.	8.65	2.3	0.31	udl	---	70.	8.65
250	2.6	0.25	udl	---	62.	8.71	3.7	0.49	udl	---	24.	8.52	2.6[a]	0.09	udl	---	42.	8.73

a Sample collected at a depth of 290 m. udl=under detection limit.

Speciation procedure

The study of complexation of each metal was carried out individually on separate aliquots of the sample, freshly unfrozen and untreated.

The titration was carried out using 15–20 metal standard additions in order to follow the curve with sufficient precision and to reach the linear part of the titration curve with certainty. At the end of the titration the concentrations reached were meanly 15 nM for Cd, 8 nM for Pb, 150 nM for Cu. After each standard addition an equilibration time of 20 min for cadmium and 30 min for lead and copper were used.

The voltammetric sequence was the same as that described above in the context of total concentration measurement and only differences are outlined here. The deposition potential was selected on the basis of pseudopolarograms and values of −0.95, −0.85 and −0.75 V were applied for cadmium, lead and copper, respectively. The deposition time was 20 min and in the case of very low metal concentration (especially lead), measurement on the unspiked sample was carried out with a higher deposition time (normally 30–40 min), to enhance sensitivity, and was repeated two or three times to ensure conditioning of the working electrode and repeatability. The currents were then normalized[34, 47] to the deposition time of the rest of the titration, given the linear relationship observed between the two quantities[48].

For cadmium and lead the plot of $[M']/(C_M-[M'])$ versus $[M']$ assumed a linear shape indicating the presence of one single class of ligands. Therefore the concentration of ligands complexing these elements was obtained by fitting the experimental titration data to the linear equation (2).

Studies of copper speciation in seawater showed that this element is frequently complexed by two classes of ligands, one class of stronger ligands (ligand concentration and conditional stability constant will be indicated as C_{L1} and K_1' respectively) and one class of weaker ligands (ligand concentration and conditional stability constant will be indicated as C_{L2} and K_2' respectively). The results of measurements carried out in this study show that the copper was complexed by more than one ligand only in the samples collected after 15th December 1990 at depths less than 50 m. In these cases, the model of two classes of ligands given by equation (4) showed the best fit with the experimental titration data and the parameters relative to the complexation were obtained by a nonlinear fitting procedure using the Marquart-Levenberg algorithm. Details of the evaluation of the initial values for the parameters used in the fitting procedure have been reported previously[5, 30]. The initial approximated values of C_{L1} and K_1' were calculated from the slope and the intercept obtained by application of equation (2) to the first few measurements of the titration. The initial values of

C_{L2} and K'_2 were obtained by the data obtained in the final part of the titration measurements, where the $[Cu']/(C_{Cu}-[Cu'])$ versus $[Cu']$ approximately follows a straight line of which slope and intercept are $1/(C_{L1}+C_{L2})$ and $(C_{L1}/K'_1+C_{L2}/K'_2)/(C_{L1}+C_{L2})$, respectively[29].

For the remaining samples, the plot of $[Cu']/(C_{Cu}-[Cu'])$ versus $[Cu']$ assumed a linear shape indicating the presence of one single class of ligands, so the complexing parameters were obtained by the same procedure adopted for the lead and cadmium.

The ASV labile concentrations of lead and copper for samples which presented values below the detection limit were evaluated through equilibrium calculations using the ligand concentrations and the conditional stability constants obtained through titration. Calculations were performed by the TITRATOR program[49], these values are reported in brackets in Tables II and III.

The ionic metal concentrations were calculated for the three metals from the labile concentration and by the inorganic side-reaction coefficients ($\alpha_M=[M']/[M]$) as defined by Ringbom and Still[50]. The values of α_M were calculated for seawater at pH=8.2, at temperatures ranging from 0 to $-2.0°C$ along the water column using the thermodynamic data presented by Byrne and co-workers[51]. The α_{Cd} values range between 30.8 (for t= 0°C) and 30.5 (for t= -2 °C); the α_{Pb} values range between 18.6 and 17.7; the α_{Cu} values range between 6.9 and 6.4.

Accuracy and precision

The accuracy of total dissolved metal concentration was periodically verified by analysing a standard seawater sample with a certified content of heavy metals (NASS-3 or NASS-4, National Research Council of Canada[52, 53]). Measurements on samples were carried out only after results on reference samples came within the tolerance interval of the certified value for lead, cadmium and copper.

The repeatability of measurements of total metal concentration was computed from 5 repetitions on an *ad hoc* sample; the values were 12, 9 and 9% (as RSD) for cadmium, lead and copper respectively at the levels of 0.12 nM of Cd, 0.077 nM of Pb and 2.9 nM Cu. Measurements of repeatability for the speciation parameters for the three metals have been reported in previous papers[5, 7, 39] and were verified for some samples collected for this study. The relative standard deviation obtained for the ASV labile fraction (from 3 measurements) ranged between 15 and 30% for Cd, between 20 and 40% for lead and when detectable was around 50% for copper; the repeatability for the ligand concentration ranged between 10 and 30% for cadmium and lead ; for copper the repeatability for the two classes of ligands was around 20 and 10%, respectively. The repeatability for the conditional stability constants expressed as RSD was generally higher than

20%, the K_1' value for the first class of ligands of copper presented a very high standard deviation, so only the order *of* magnitude is reported; when the RSD was lower than 100% only one significant figure is reported.

The results of total metal concentrations of each of the data reported here, represent the average of at least three measurements; other results are obtained from two measurements, or more in case of uncertainty.

RESULTS AND DISCUSSION

Cadmium

Results of cadmium concentration and speciation on samples collected along the water column between 24 November 1990 and 11 February 1989 are reported in Table I. To emphasise the profile evolution, the results of samples collected after the beginning of December are reported in Figure 3. The differences of total dissolved concentration obtained by measurements in the field[20] and the results reported here obtained in the Venice Laboratory are smaller than the experimental error.

The concentration until the first half of December is relatively high (0.83 nM) consistent with the value found in deep waters of Antarctic regions[1, 3, 54], subantarctic regions[55] and with the global distribution of dissolved cadmium[56]. The labile fraction was meanly higher than 90% of total dissolved concentration; only in the samples collected in Nov. 29 (surface) and Dec. 7 (depth 100 m) was this fraction significantly lower than the total dissolved concentration.

The total dissolved concentration in the samples collected after the second half of December was gradually depleted, initially in the subsurface layer (10–50 m), then down to the bottom (290 m) and at the same time the inorganic cadmium fraction was reduced to a minimum of 8% of the total. The mean value for the labile fraction in the first 50 m was 20% of the total.

Cd-complexing ligands were detectable after the middle of December when the pack ice break-up and the phytoplankton bloom had started, initially in the first surface layers and gradually along the whole water column. Samples collected before December only occasionally showed complexation by organic ligands. The free ionic metal concentration (see Figure 3B) ranges from 16 pM to 32 pM for samples collected before 26 December, while for samples collected after that date the concentration ranges from 0.3 pM (subsurface sample collected on 30 January) to 26 pM (sample collected at a depth of 250 m on 6 January).
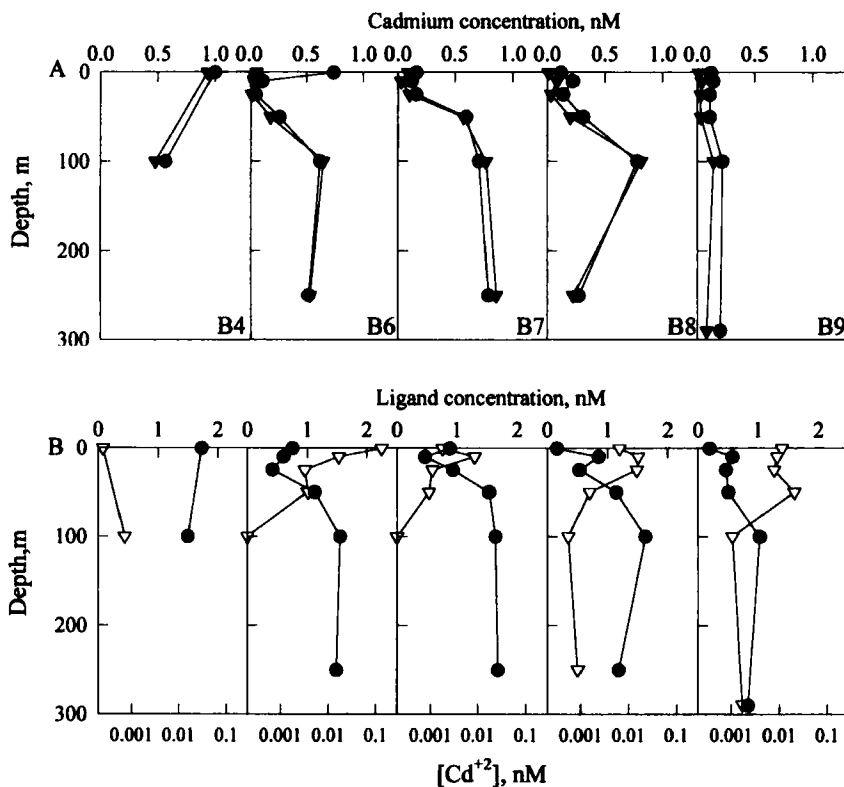
FIGURE 3 Summer variation of cadmium speciation in the Gerlache Inlet during the 1990–91 campaign. (A) Vertical distribution of total dissolved copper concentration (●), ionic cadmium concentration (▼). (B) Vertical distribution of ionic cadmium concentration (●), ligand concentration $C_{L\text{-}Cd}$ (∇)

The results show that the summer depletion of dissolved cadmium concentration is associated with a different speciation for this element. The total dissolved concentration presents a very good correlation with the labile concentration (r=0.92) and a negative correlation with ligand concentration (r= −0.61). Figure 4a shows the total surface concentration and the labile fraction as a function of sampling date, for samples collected during the 1988/89 and 1990/91 campaigns in the Gerlache Inlet. The dotted lines in Figures 4a and b emphasize the correspondence between the rapid increase of ligand concentration and the depletion of total dissolved cadmium concentration. The complexed cadmium concentration (Figure 4b) shows the maximum values between 15 December and 15 January correspondent to the quick decrease of total dissolved concentration.
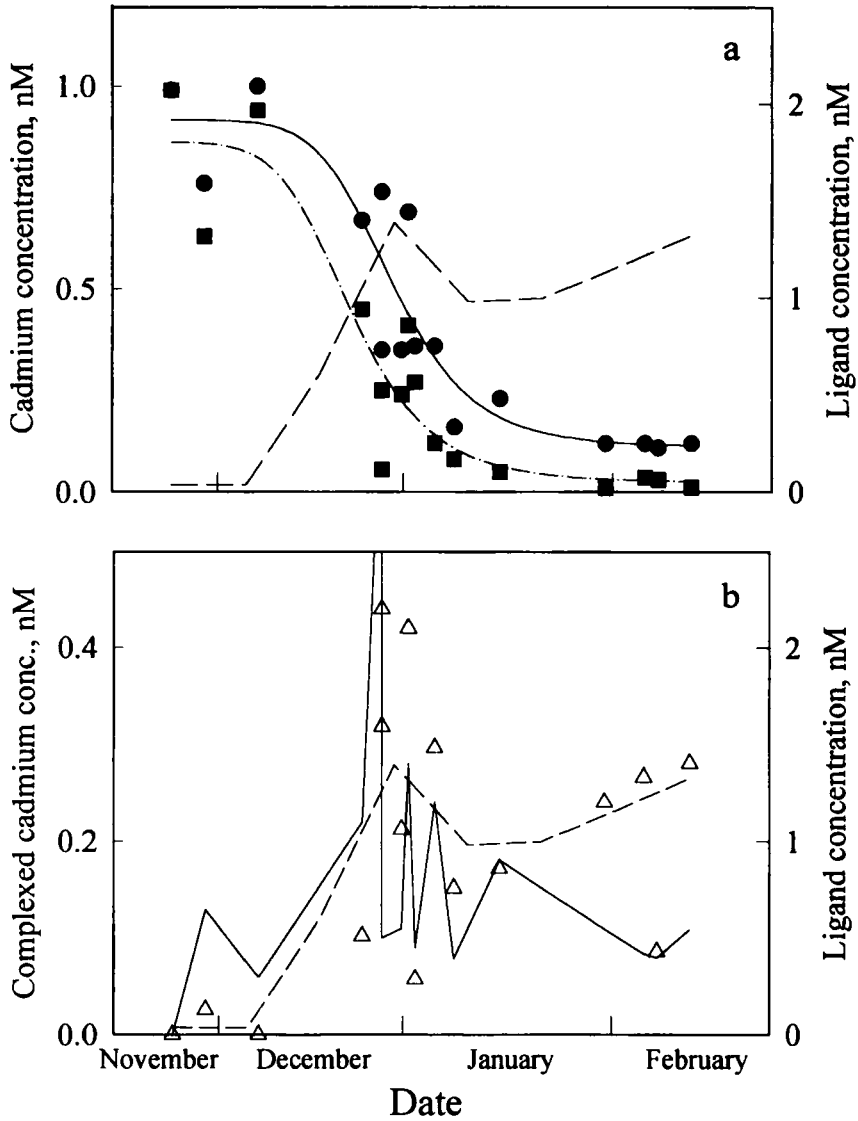
FIGURE 4 Summer variation of cadmium concentration and speciation in the Gerlache Inlet during the 1988–89 and 1990–91 expeditions. (a) ● total dissolved concentration, ■ labile fraction concentration, – curve fitting experimental data of the total dissolved concentration, – • – curve fitting experimental data of the labile fraction concentration and – – curve obtained by filtering ligand concentration data. (b) –complexed metal concentration, (△) ligand concentration

TABLE IV Concentrations of total dissolved metals, labile fractions, ligands[5–7] and other hydrological data[24, 25, 57–61] obtained in the surface water of Terra Nova Bay in the 1987–88, 1988–89 and 1989–90 campaigns. For symbols see Table I-III

Station	C_{Cu} nM	$[Cu']$ nM	C_{L1} nM	C_{L2} nM	C_{Pb} nM	$[Pb']$ nM	C_{L-Pb} nM	C_{Cd} nM	$[Cd']$ nM	C_{L-Cd} nM	Temper. °C	Chlor. µg/l	Salinity ‰
							1987–88 Campaign						
8	4.3	0.59	0.15	14.	0.063	0.014	0.50	0.24	0.07	0.66	1.99	0.83	34.85
9	2.8	0.06	1.8	31.	0.114	0.027	0.60	0.19	0.09	0.55	2.10	0.44	34.61
10	2.4	0.03	1.7	39.	0.061	0.017	0.90	0.26	0.09	0.51	2.00	1.20	34.82
12	1.6	0.08	0.70	37.	0.035	0.017	0.30	0.15	0.09	0.25	0.80	0.76	34.81
13	1.4	0.16	0.15	41.	0.032	0.010	0.30	0.19	0.04	0.57	0.74	1.04	34.84
16	1.8	0.07	1.4	42.	0.026	0.013	0.40	0.08	0.04	0.51	1.02	1.10	34.10
17	0.9	0.08	0.4	25.	0.038	0.019	0.30	0.10	0.05	0.43	0.03	1.44	32.80
22	1.4	0.03	1.0	36.	0.038	0.019	0.50	0.09	0.05	0.36	0.60	0.85	34.75
28	0.9	0.04	0.4	31.	0.034	0.015	0.70	0.13	0.07	0.21	1.65	0.36	34.69
31	2.0	0.10	1.7	21.	0.025	0.010	0.40	0.14	0.05	0.27	0.86	2.44	34.52
37	1.6	0.06	1.8	31.	0.028	0.010	0.30	0.15	0.10	0.13	0.73	1.83	34.33
46	2.7	0.05	1.0	32.	0.029	0.016	0.40	0.40	0.28	0.12	-0.23	2.35	33.78
							1988–89 Campaign						
1	4.8	0.20	--	35.	0.018	0.013	0.44	0.35	0.25	1.6			
2	2.9	0.15	1.8	31.	0.037	0.013	0.35	0.36	0.27	0.29			

Station	C_{cu} nM	$[Cu']$ nM	C_{L1} nM	C_{L2} nM	C_{Pb} nM	$[Pb']$ nM	$C_{L,Pb}$ nM	C_{Cd} nM	$[Cd']$ nM	$C_{L,Cd}$ nM	Temper. °C	Chlor. µg/l	Salinity ‰
1987–88 Campaign													
3	2.3	0.02	1.0	24.	0.093	0.027	0.42	0.35	0.24	1.1			
4	1.7	0.10	1.1	32.	0.019	0.010	0.28	0.11	0.06	1.4			
5	2.5	0.04	1.1	34.	0.092	0.014	0.29	0.23	0.05	0.86			
6	1.1	0.02	0.50	25.	0.051	0.011	1.06	0.12	0.04	1.3			
7	1.8	0.06	1.7	23.	0.078	0.040	0.37	0.11	0.03	0.43			
5P	2.8	0.04	--	30.	0.044	0.022	0.51	0.67	0.45	0.51			
6P	2.0	0.10	0.60	32.	0.049	0.015	1.06	0.69	0.41	1.1			
7P	1.5	0.07	--	36.	0.032	0.014	1.48	0.36	0.12	1.5			
1989–90 Campaign													
25[a]	1.9	0.16	0.15	34.0	0.034	0.005	0.38	0.071	0.021	1.7	-0.75	4.10	34.50
32	1.8	0.01	3.8	33.0	0.032	0.024	1.40	0.097	0.022	1.2	0.77	2.82	33.72
33	2.0	0.10	2.0	16.0	0.015	0.005	0.48	0.053	0.011	0.68	1.28	1.44	33.70
34	2.3	0.01	3.5	31.0	0.026	0.016	1.73	0.026	0.026	1.2	0.19	2.48	33.81
35	1.4	0.01	2.2	29.0	0.044	0.016	0.69	0.042	0.005	1.8	0.85	0.18	33.25

[a]Depth 20 m.

To improve knowledge of the cause of surface depletion and change of speciation we consider the relationships between total dissolved metal, the labile metal and the ligand concentrations with temperature, chlorophyll and salinity for the samples collected along the profiles B6 and B7 for which corresponding data are available (see Figures 2 and 3). The analysis of results shows that total dissolved cadmium concentration is negatively correlated to the temperature (r=-0.62) and positively correlated with the labile cadmium concentration (r = 0.77). The ligand concentration is negatively correlated with the labile metal (r = −0.76) and positively correlated with the chlorophyll amount (r = 0.87).

Analogous results were by obtained extending the analysis of correlation to all the samples collected in Terranova Bay for which data of temperature, chlorophyll and salinity are available (1987/88 and 1989/90 expeditions, Table IV). The coefficient of correlation between the total dissolved cadmium concentration versus the labile concentration and the temperature are 0.83 and −0.60 respectively. The correlation coefficient between the ligand concentration versus the labile cadmium and chlorophyll are −0.51 and 0.58 respectively.

Studies of cadmium complexation carried out in different oceanic areas showed that a large amount of cadmium in surface and subsurface layers is organically complexed[6, 33, 62]. The relation between ligand concentration and the biological activity emphasised by the correlation between ligand concentration and chlorophyll content is in agreement with the results obtained by other authors. Sakamoto-Anold et al.[62] reported that the ASV-labile fraction of cadmium within the upper 250 m of a Gulf Stream warm-core ring, ranged from 8% to 67%, while the inorganic forms were 99% of the total dissolved cadmium at depths greater than 300m; however they did not perform sample titrations, so any estimation of ligands complexing cadmium are impossible and further comparisons of results are limited. Bruland[33] detected one class of ligands in the photic layer of the nothern Pacific gyre. Although he found that the concentration was about ten times lower than the values reported here, probably as a consequence of the different hydrological characteristics, the ligand distribution along the water column showed the same trend observed in the Gerlache Inlet in December and at the beginning of January. On the basis of ligand distribution we can hypothesise that the organic matter complexing cadmium is constituted by labile matter quickly decomposed along the water column and related to primary production.

Westerlund and Ohman, studying cadmium distribution in the Weddell sea[3], showed a relatively high concentration and little surface depletion for samples collected in the centre of the Weddell Sea. They compared the total dissolved cadmium concentration and the recoverable metal by an imminodiacetic resin on samples at natural pH. The results showed that, for samples collected in the

Filchner shelf, the cadmium recovered by Chelex resin in the upper 500 m of the water column was considerably lower than the total concentration and concluded that this layer probably contains organic matter complexing this element. At the same time, they stressed that cadmium concentration in suspended matter is considerably higher in surface and subsurface samples. On the basis of these observations they concluded that cadmium circulation at the surface is related to easily decomposed carbon particles of biological origin. An analogous observation was made by Frache et al.[8] studying the metal distribution along the water column in Wood Bay (Ross Sea).

Lead

Results of lead concentration and speciation for samples collected during the 1990–91 expedition are reported in Table II. The mean total dissolved concentration ranges from 0.083 nM, at the beginning of the summer when the larger part of Terra Nova Bay was still covered by pack, to 0.03 nM in the superficial 100 m at the end of the summer. The surface level (depth 0.5 m) presents a concentration which is systematically at least 30% higher than the 10–25 m layer both when the pack was still present and when it had melted. The inorganic lead fraction (ASV-labile) does not change during the season and meanly represents 39% of the total dissolved amount ; its concentration is well correlated to the total dissolved concentration (r=0.81)

The lead is complexed by a single class of ligands, the mean concentration of which ranges from 0.66±0.28 nM at the beginning of the summer to 1.2±0.3 nM at the end of season. The increase of ligand concentration during the summer suggests a relation between that of organic matter and biological activity. Because the increase was evident after the second half of January (see Table II) when phytoplankton ageing occurred in Terra Nova Bay[63], we can stress that this organic matter originated from degradation of biological tissues. The presence of organic ligands complexing lead throughout the study and their homogeneous distribution along the water column suggests that an important part of this organic matter features a refractory nature with a life time longer than the annual cycle. The conditional stability constant measured during the entire season, considering the repeatability of measurements, is constant and the mean value is $5 \times 10^9 \pm 2 \times 10^9$ l·mol^{-1}.

The free ionic metal concentration reported in Figure 5 ranges from 0.3 pM to 4.1 pM; the minimum values (0.3–0.7 pM) were calculated for subsurface samples (10–50 m) collected after 26 December, while the higher values (1.1–4.1 pM) were calculated for samples collected before that date or at greater depths. Considering the uncertainty attached to evaluation of the ionic concentra-

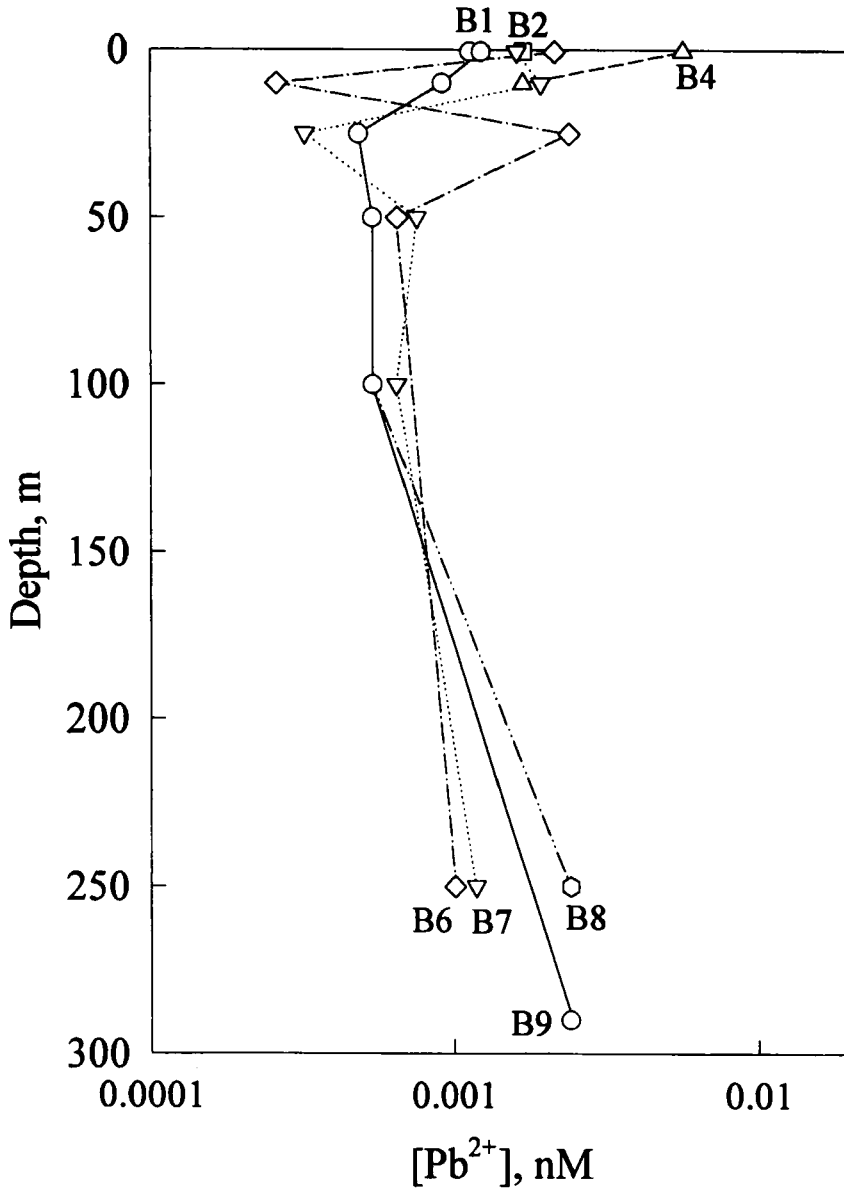tion, we can conclude that during the summer variations are detectable only for surface layers.

FIGURE 5 Vertical distribution of ionic lead concentration in the Gerlache Inlet during the 1990–91 campaign

Results obtained for surface samples collected during the 1987/88, 1988/89 and 1989/90 campaigns (see Table IV) in the Coastal area (1987/88 campaign, samples 8, 9, 10, 22 28; 1988/89 campaign, all the samples ; 1989/90 campaign, samples 32, 33, 34 and 35) show a high variability as a function of time without a clear trend either for the total dissolved concentration or for the labile concentration. The concentration is dependent on hydrodynamic or local processes (mean value 49±27 pM). The surface distribution in the off-shore area in Terra Nova Bay shows a much more constant concentration (mean value 31±4 pmol/l).

An analysis of correlations was carried out between total dissolved metal, the labile metal and the ligand concentrations with temperature, chlorophyll and salinity for the samples which corresponding data are available (1987/88 campaign ; 1989/90 campaign ; 1990/91 campaign, profiles B6 and B7). The results show a correlation of total dissolved lead with the labile lead concentrations, with the dissolved cadmium concentrations (r=0.64) These results suggests that the distribution of dissolved lead, although not perfectly overlapped, presents some similarities to the vertical distribution of dissolved cadmium. From these observations we can hypothesise that concomitant phenomena are controlling the presence of these elements. This hypothesis seems to conflict with knowledge of the geochemical characteristics of lead and cadmium. By considering the large variability of lead concentration in coastal areas emphasised above, we can hypothesise that more phenomena are responsible for lead distribution. However, the eutrophic processes producing the quick depletion of cadmium could generate particles affecting the distribution of scavenged elements like lead.

Very few studies of lead complexation have been carried out in oceanic areas; the investigation carried out by Capodaglio et al.[34] in the Eastern North Pacific Ocean reported levels of total dissolved lead, inorganic fraction and ligand concentrations comparable to those measured in the open sea in the Terra Nova Bay area. De Gregori et al. reported results of lead complexation in a coastal area of the South Pacific Ocean[64]; they observed that the labile fraction ranges between 30 and 50% as a function of distance from the coast, but they did not report any data of concentration of ligands complexing lead and the level of metal concentration was decidedly higher than in our samples. The results were therefore difficult to compare.

Copper

Table III reports the results of copper concentration and speciation for samples collected during the 1990–91 expedition. The total dissolved concentration of copper ranges from 1.6 to 3.8 nM (see Figure 6). Although the decrease of copper concentration during the season is not so large as those observed for cad-

mium, the distribution shows a subsurface depletion in January which extends along the water column in February. Values are in agreement with those measured in surface water samples collected in the whole of Terra Nova Bay during the 1987/88, 1988/89 and 1989/90 campaigns (see Table IV). The surface concentration for water collected between 1987 and 1991 (Figure 7), independently of the position in the Bay, was meanly lower when sampled between January and the beginning of February (1.8±0.5 nM) compared with the mean concentration measured in November, December and later in February (3.0±0.9 nM).
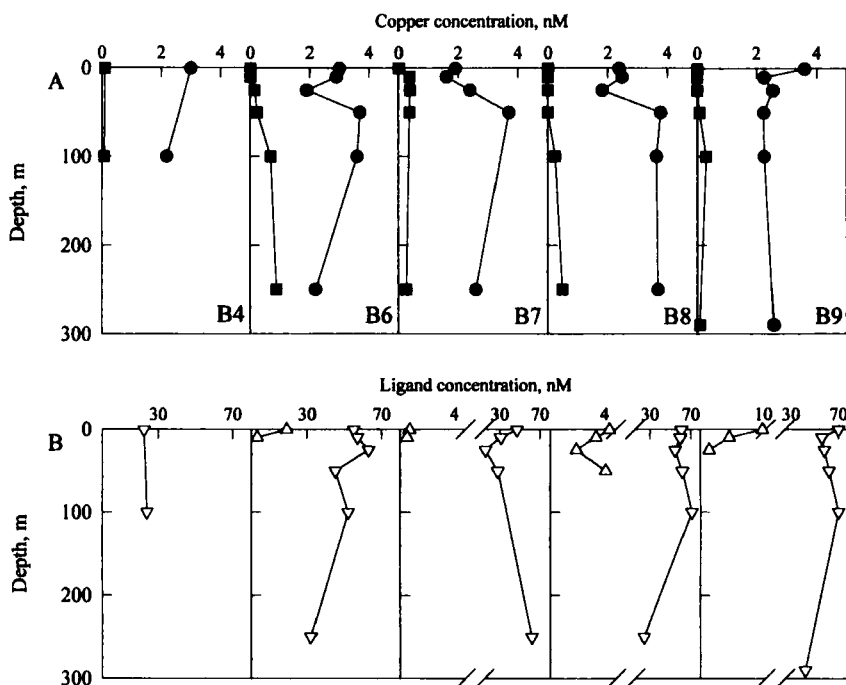

FIGURE 6 Summer variation of copper speciation in the Gerlache Inlet during the 1990–91 campaign. (A) Vertical distribution of total dissolved copper concentration (●) and labile copper concentration (■). (B) Vertical distribution of ligand concentration C_{L1} (△), ligand concentration C_{L2} (▽)

The total dissolved concentration did not present significant correlation with the other metals and is consistent with its general distribution in the ocean[65]. We always observed a minimum at a depth of 10–25 m (1.6–2.2 nM) compared with a higher surface concentration (2.0–3.6 nM); the concentration further increased to values between 2.2 to 3.7 near the bottom. In general both the surface and the deeper water concentrations are intermediate between Atlantic and Pacific values[65].
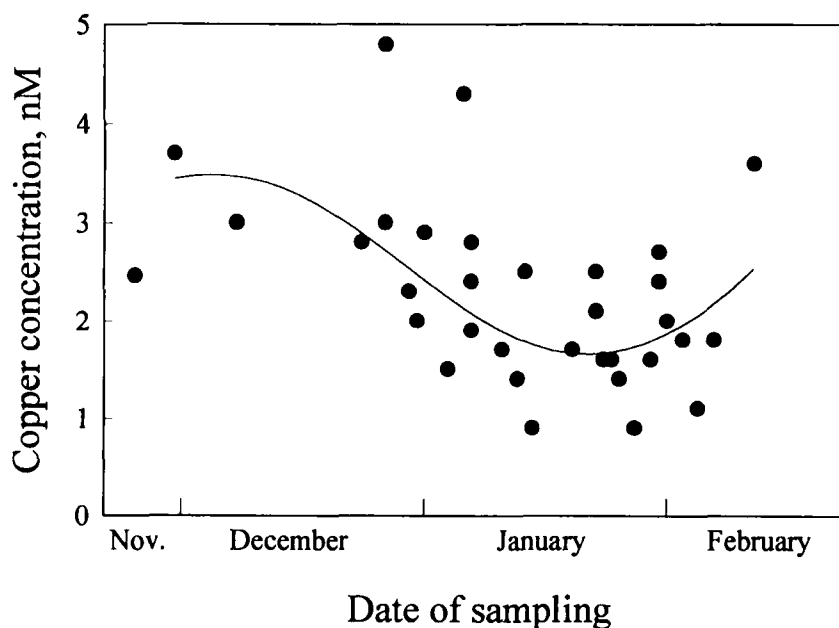
FIGURE 7 Summer variation of copper concentration in Terra Nova Bay during expeditons from 1987–88 to 1990–91

A minimum of concentration at an intermediate depth was frequently observed in coastal oceanic areas[9, 66–68]. Saager et al., studying the distribution of copper along profiles of the Indian Ocean in near-shore areas[66] emphasised the presence of a minimum of concentration at a depth of about 500 m. They explained this as the effect of an important local surface source, a subsurface decrease as a result of particle scavenging and a further linear increase to values between 2 and 3 nM in deep waters. This surface maximum was also observed by Boyle and Edmond in the surface water of the Pacific[67]. The same authors provided evidence that such maxima may be transient features resulting from the advection of Cu-rich near-shore surface water into the off-shore regions of the ocean[68]. It must be stressed that although the trend observed by us was not so marked and regular as the results of Saager et al., some similar general considerations can be made. In fact glacier transport and the ice pack formation/dissolution cycle can play a fundamental role in the composition of surface coastal sea water. However, without information about the local sources (eolian durst composition and deposition rate, glacier composition and dissolution rate, effect of pack ice dissolution and formation) it is not possible to establish the origin of the surface water enrichment.

Only few studies have been carried out in the Antarctic region, the more extensive studies of interest being carried out in the Scotia-Weddel seas[1-3]. The results showed a complex vertical copper distribution strongly dependent on the position as a consequence of the hydrography of the area; in general for shelf profiles a weak surface/subsurface depletion was observed (1.6–2 nM) compared with the deep water concentration (about 3 nM); the depletion was extended to the bottom for shore water. Very few data of interest concerning copper concentration in the Ross Sea were reported; normally only surface waters were examined[4, 5]. Only one vertical profile off shore at C. Adere, an area affected by the coastal Antarctic current[9], was reported ; however, the low values reported seem in contrast with the cumulative copper increase in deep water from the Atlantic to the North Pacific normally observed[65]. The studies carried out in the Ross Sea show that copper is enriched in the surface waters of the Antarctic upwelling areas; the concentration ranges between 1 nM in the convergence area to 3.25 nM in the Antarctic coastal current.,

The copper is complexed by two classes of ligands, the stronger (L1) presented a concentration (C_{L1}) of just a few nM, reaching a maximum value of 19 nM at the end of December, in coincidence with the phytoplankton bloom (see Figure 6) and it seemed to follow a vernal stratification. The vertical distribution of the weaker ligand (L2), present at a concentration of C_{L2}, does not show an evident trend, but in the surface/subsurface waters there was an evident increment in average concentration during the summer. The mean concentration ranged from 26 ± 3 nM until the beginning of December to 60 ± 10 nM in February (Figure 6). The temporal trend throughout Terra Nova Bay seems to have been affected by seasonal evolution; in fact, the mean concentration for samples collected in the Bay during 1987/88, 1988/89 and 1989/90 was 30 ± 5 nM and did not show a particular trend (see Table IV). The vertical distribution and its presence also at the beginning of the summer suggests the refractory nature of this compound with a lifetime longer than the mixing time of the water column.

The concentration of the first class of ligands determined in 1990/91 samples presents a correlation with ligands complexing cadmium (C_{L-Cd})(r=0.64); however, a more extended data set would be necessary for statistically significant results to be obtained. The two classes of ligands (L1 and L2) for the all samples for which temperature, chlorophyll and salinity data are also available, show a correlation with chlorophyll content (r=0.51 and 0.60 for C_{L1} and C_{L2} respectively).

The labile metal fraction in the 1990/91 samples was strongly dependent on depth and time; in shallow waters, with the stronger ligand(s) present, it was lower than 1%, while a value always higher than 5% was observed at depths greater than 100 m early in November and December. A maximum value of 40%

was reached at a depth of 250 m on 26 December. For the same samples the free ionic copper concentration reported in Figure 8 ranges from 0.01 pM to 0.14 nM. Minimum values (0.01–1 pM) were calculated for subsurface samples (0.5–10 m) collected after 26 December, while the higher values (0.04–0.14 nM) were calculated for samples collected at greater depths (100–290 m). The ionic copper concentration in the first 25m decreased by about four orders of magnitude as a function of the time and about the same difference was observed at the end of January between the surface and the deeper water.

This high variation of the ionic metal concentration can influence plankton species succession in the local community. Brand et al.[69] showed that in water where the $[Cu^{2+}]$ reached values as high as 10^{-10} M only eucaryotic algae maintained their maximum reproduction rate; procaryotic cyanobacteria reduced their reproductive rate when the ionic copper was higher than 10^{-11} M. Di Tullio and Laws[70] speculated that in upwelling waters the high concentration of free copper can cause a decline in cyanobacteria abundance. Knox studying the seasonal production cycle in the McMurdo Sound[71], showed that the phytoplankton population was dominated by diatoms in the early summer until mid-December followed by the Pheocystis bloom in December and by a diatom bloom in January-February. Measurements of picoplankton carried out in Terra Nova Bay, very close to the Gerlache Inlet, showed an increase in abundance of microbial population from January to February[72].

Studies of copper complexation by organic ligands have been carried out in oceanic areas[19, 73, 74] and the results always showed that organic complexation strongly affects its speciation. Studies carried out both in the Pacific Ocean and Atlantic Ocean emphasised frequently that copper is complexed by two classes of organic ligands, one of them is located at a depth corresponding to the chlorophyll maximum. The presence of these strong ligands at levels of few nM in the euphotic zone seems to dominate copper speciation along the water column. Coale and Bruland showed that in the northern Pacific Ocean the inorganic copper fraction varies between 0.1% in the euphotic zone and 30–40 % in the deeper water where the stronger ligands were absent.

Very few studies of copper complexation by organic ligands have been carried out in the southern Ocean. In the Weddell Sea Westerlund and Ohman[3] estimated the inorganic copper by recovery of the metal using an imminodiacetic resin at natural pH. The results showed that it represents meanly 30% of the total dissolved concentration without a clear trend, although some differences were observed when comparing shelf waters and open sea waters.

On the basis of copper concentration in suspended matter and the high concentration of silica in settling particles, the same authors concluded that the sedimentation of copper is due to inert particles rich in silica. This idea was also
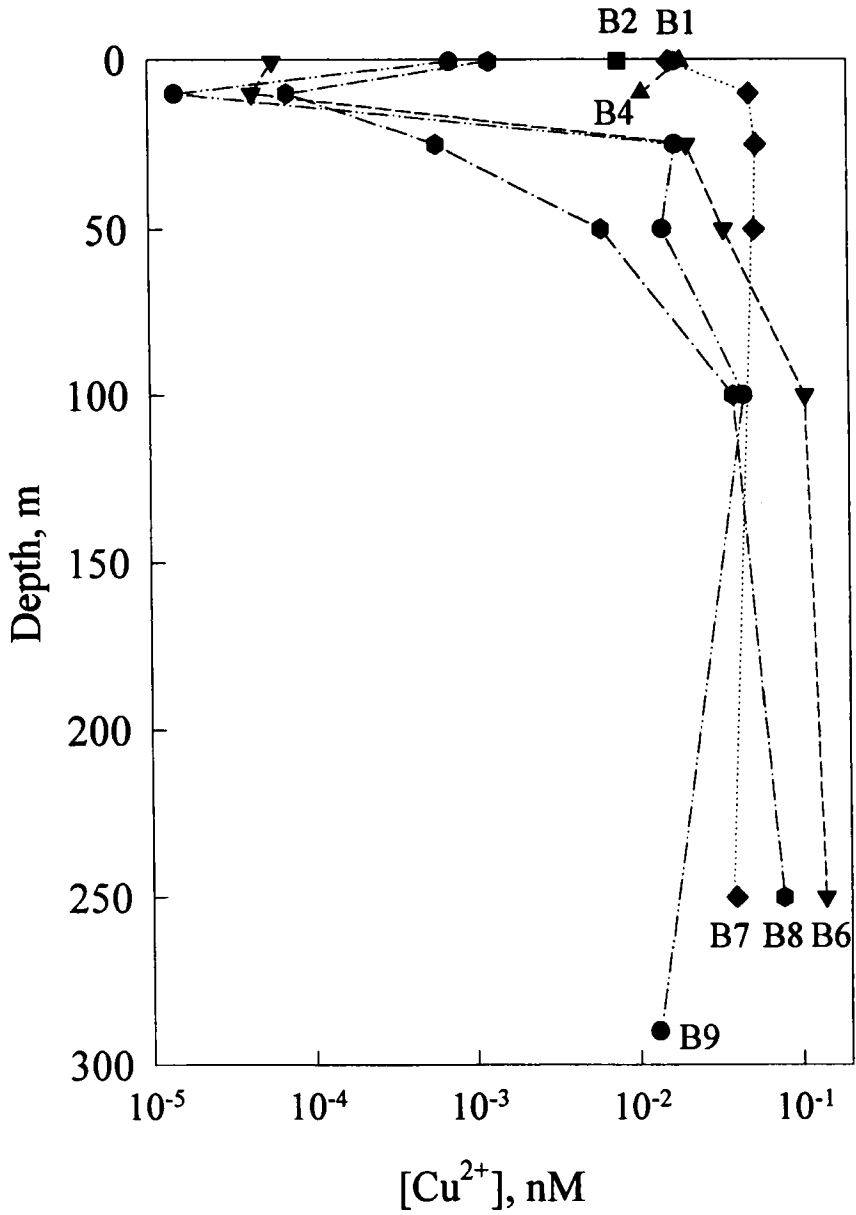
FIGURE 8 Vertical distribution of ionic copper concentration in the Gerlache Inlet during the 1990–91 campaign

supported by covariance between copper and silica. The conclusion seems in agreement with our observation that, differently from cadmium, the distribution of dissolved copper concentration do not seem affected by organic ligands.

CONCLUSION

The differences in the geochemical characteristics of cadmium, lead and copper, emphasized by their vertical profiles and by the seasonal evolution of profile, are also highlighted by changes in their speciation along the water column and during the summer.

The cadmium is complexed by one class of labile (easily decomposed along the water column) ligands originated by biological activities in the area. The negative relation between cadmium and its ligands for the samples collected during the 1990/91 expedition, emphasised by the correlation analysis, shows that the cadmium distribution can be related to its chemical form. The results reported here and those reported by other authors[33] lead to assume that this organic ligand could be able to deplete it quickly in the surface layers and release it at deeper a layer when the organic ligand is oxidized. As hypothesized by Capodaglio and al.[12] the organic complexation of cadmium could be responsible for adsorption of cadmium on suspended matter, however the experimental data cannot show if there is a direct relation between these parameters.

The lead is complexed by one class of organic ligands. It is observed for surface samples collected in all the expeditions that the ligand concentration increases with the season, which constitutes an indication that the presence of ligands is related to biological activity in the studied area. However, the presence of these organic ligands at the beginning of the summer and their homogeneous distribution along the water column indicates that these compounds are products of the degradation of biological matter with refractory nature and a large portion of these features a life time which is longer than the annual cycle.

The copper distribution seems to be controlled by a more complex process involving both classes of ligands complexing this element; the stronger and easly decomposed ligand present in the surface layer controls its speciation reducing the free ionic copper concentration at levels lower than 10^{-14} M, which could contribute to the seasonal species succession in the local phytoplankton community. The second ligand, presenting a more refractory nature, could affect the interaction of copper with settling particles.

The results presented here emphasize that trace metal complexation by organic ligands plays a central role in their speciation also in polar regions and that it

could be part of the mechanism controlling its interaction with suspended matter. Although similar conclusions were previously[12] reached studying the trace metal speciation in a temperate area presenting characteristics very different from the polar region examined here, doubts could exist that the results are the fruit of local phenomena. A more extended study must therefore be carried out in different geographical areas, both polar and non-polar before definitive conclusions can be reached.

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