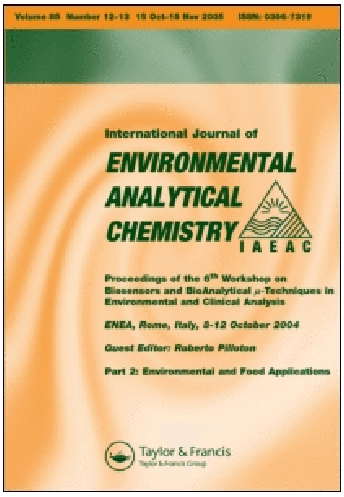

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EFFECTS OF ICE MELTING ON Cu, Cd AND Pb PROFILES IN ROSS SEA WATERS (ANTARCTICA)

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In the framework of the Italian Research Programme in Antarctica, evolution of dissolved and particulate Cu, Cd and Pb profiles in the coastal waters of Gerlache Inlet (Terra Nova Bay, Western Ross Sea) was studied during the Austral Summer 1997/98. In order to relate the distributions of trace metals with the physical and biological processes, a series of temperature and salinity measures were made, and water samples were collected to determine nutrients and chlorophyll. Samples of pack ice and marine microlayer (50–150 μm) were also collected and analysed.

Concerning the surface layer, it was found that metal concentrations are mainly affected by the dynamic of the pack ice melting and phytoplankton activity. The first process influences both the input of metals from meltwaters and the covering of the seawater surface, allowing atmospheric dust input only when all ice has been melt or removed. Direct release of particulate Cu from ice was clearly shown by surface maxima and by the high concentrations of suspended particulate matter and particulate metals found in the ice core section interfaced with the seawater. Differently, the high amount of Cd in the particulate included in the pack ice seems not to affect the concentration in surface particulate; on the contrary, the corresponding increase of dissolved Cd indicates that it is released in dissolved form when the pack ice melts. Surface distribution is further complicated by the effect of phytoplankton activity, which removes Cu and Cd from water, incorporating them into organic particulate. Finally, in absence of pack ice, there is evidence of inputs of Pb and Cu due to atmospheric dust brought into the column water through marine microlayer.

In intermediate and deep waters, the vertical distribution of Pb and Cd was characterised by substantially constant profiles, while Cu shown, during the end of the summer and in absence of a well-defined water column stratification, a "scavenging-type" distribution which overlaps its "nutrient-type" behaviour.

Keywords: Copper; cadmium; lead; seawater; Terra Nova Bay; Antarctica; seasonal evolution

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INTRODUCTION

The present work is part of the research project "Evolution and biogeochemical cycles of contaminants" of the National Antarctic Research Programme (P.N.R.A.), which final aim is to study transport and distribution of organic and inorganic micropollutants in Antarctic ecosystem. The results obtained during ten years of scientific expeditions and activity are reported in a recent review [1].

In particular, the influence of the presence of pack ice and of its thawing on Cu, Cd and Pb concentration in particulate matter and dissolved phase along the water column has been extensively studied.

In our first studies we had already an indication that a major contribution of particulate metals could derive from particulate matter entrapped in the pack ice and released during ice melting [2]. In order to confirm this hypothesis, during the successive expeditions (1990/91, 1991/92), some suspended matter sampling, in presence and absence of pack ice, where carried out [3]. Although some detailed descriptions of dissolved metals distribution along the water column were obtained [4,5], unfortunately, the number of samples was not sufficient in order to obtain significant results for particulate distribution.

In the next expedition (1993/94) it was possible to collect a bigger amount of data which outlined that Cd, Cu and Fe concentration in particulate matter increases significantly after pack ice melting [6].

Nevertheless, in order to complete these studies and to get to a thourogh knowledge of the entire biogeochemical cycle of such elements, it was necessary to: (i) study the dynamic of the pack ice thawing process and of the relative metal distribution along the underlying water column; (ii) evaluate the distribution of the same elements along the pack ice core, in particular at the ice-water interface; (iii) correlate the elements concentration with the biological processes taking place in the water column.

To this aim, during the XIII expedition (1997/98), in two sites near the Italian Base (Gerlache Inlet, Ross Sea), we have effected the sampling of sea water, pack ice and microlayer along a suitable period of time, in order to evaluate the variation of the particulate and dissolved metals concentration together with the chemical, physical and biological parameters, as temperature and salinity of sea water and the amount of chlorophyll and nutrient salts.

EXPERIMENTAL

Sampling

The two sampling sites were located in Gerlache Inlet – Terra Nova Bay (see Figure 1). The main one was called B2 (74° 42.632′ S; 164° 11.178′ E; 430 m deep) and the reference one was called B4 (74° 42.137′ S; 164° 09.149 E; 220 m deep).

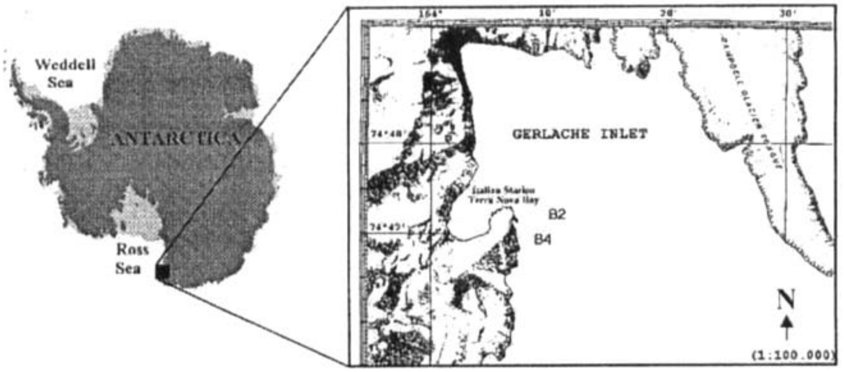

FIGURE 1 Sampling stations

During the period November 1997 – February 1998 the sea water was sampled, along the column at different depths, 4 times in station B2 (3 times in presence of pack ice and once after ice melting) and 3 times in station B4 (twice in presence of pack ice and once after ice melting). In order to evaluate the physical and biological variations along the water column, every week a series of temperature and salinity measures and of water samplings for nutrients and chlorofill determination were carried out.

Moreover, during the first period (November), a sample of pack ice was collected near station B2. Finally, samples of microlayer (50–150 μm) were collected, after pack ice melting, together with the underlying water (0.5 m deep), in order to evaluate the concentration factor.

The sampling and treatment procedures for the various sample typologies were of course differentiated, so they will be described separately.

Sea water and suspended marine particulate

Sampling of sea water was effected using 301 Go-Flo bottles fixed on a Kevlar wire. When pack ice was present a 1 m diameter hole was realized in the ice in order to make the bottles reach the water. When pack ice was absent the sampling was effected from a boat. Immediately after the sampling, sea water was carried to a Class 100 laboratory and filtered on 0.4 μm PC filters, using a home made PTFE apparatus, under nitrogen pressure. Filters (for the analysis of metals and chlorophyll) and water (for the analysis of metals and nutrients) were stored at −30° until analysis.

Physical parameters along the water column were measured during the sampling by a Seabird 9/11+ CTD probe.

Pack ice

The sample of pack ice was collected by means of manually-driven titanium corer, having an inner diameter of 10 cm. The pack ice was about 1.5 meters thick. The obtained sample was divided in four parts under a laminar flow hood: the superficial and the two central parts were about 45 cm long, while the part at the sea water interface was about 10 cm long. Each part was left at room temperature under the hood in a poliethylene box until melted and then filtered under vacuum on 0.4 μm PC filters, using a PC apparatus.

Microlayer

During the middle summer, when pack ice was absent, a suitable wire-controlled sampler (M.U.M.S.) [7] was used to collect three samples of superficial microlayer. For each sample the corresponding underlying water (0.5 m deep) was also collected. Samples were filtered using the same procedure reported for the pack ice, and stored at − 30°C until analysis.

Analytical measurements

A Varian Zeeman SpectrAA 300 was used for the determination of Cu, Cd and Pb in particulate matter, after the solubilization with HNO_3 8 M by a CEM DS 2000 microwave digestor. The dissolved concentration of cadmium, lead and copper was determined in acidified samples at pH 2 with HCl (Romil, Upa grade), irradiated by an UV high power lamp (Hanovia, 1200 W). The determinations were performed by DPASV following the procedure previously reported [8] using a Polarographic analyser EG&G PARC mod. 384B and a EG&G Rotel 2 electrochemical cell. The blank for the digestion procedure was tested by addition of 100μl of Romil HCl Upa grade to 50 ml of a KCl solution 0.03 M, the acid contribution to the metal concentration was always below the detection limit.

Accuracy for the particulate metal determination was verified by the certified material CRM-414 (Community Bureau of Reference – BCR – marine plankton), while the accuracy for dissolved metal determination was checked by analysing certified standard seawater samples (NASS-5, National Research Council of Canada); results are shown in Table I.

TABLE I Cu, Pb and Cd determination in certified reference materials

	CRM-414 Plancton (conc. μg/g)	
	Certified	*Found*
Cu	29.5 ± 1.3	30.8 ± 2.0
Pb	3.97 ± 0.19	3.94 ± 0.30
Cd	0.383 ± 0.014	0.412 ± 0.030
	NASS-5 Seawater (conc. μg/l)	
Cu	0.297 ± 0.046	0.274 ± 0.055
Pb	0.008 ± 0.005	0.007 ± 0.001
Cd	0.023 ± 0.003	0.025 ± 0.002

The results of total metal concentrations of each of the data reported here, represent the average of at least three measurements.

Measurements of nutrients were performed by an Autoanalyzer Techicon II, according to the Hansen and Grasshoff methods [9].

The chlorophyll a content was determined by spectrofluorimetry [10,11].

RESULTS AND DISCUSSION

The temporal variations of temperature, salinity and chlorophyll a concerning station B2 are shown in Figure 2. Contour plots were obtained reporting the time in days (t=0 corresponds to November 13th), against the depth, and interpolating with iso-value curves a sufficiently high number of measures. Figure 2 shows clearly a substantial constant temperature and salinity from the beginning of November until the 60th day, followed during the period 65–85 by an increase of the surface temperature corresponding with a progressive pack ice melting. This melting is highlighted by the consequent decrease of surface salinity which begins around the 60th day and becomes very wide and evident after the 90th day.

Concerning biological activity, the data show a first phytoplanctonic bloom between the 30th and the 50th day, extended until the depth of 50 m, and a second bloom, wider and marked, beginning from the 70th day. Nutrient concentration data (nitrates, ammonium, silicates and phosphates) confirm these results.

In Figure 3, Cd, Cu and Pb concentration profiles in particulate matter concerning stations B2 and B4 are reported. For better comparison it must be noted that station B2 profiles are relative to the days: 0, 10, 37 and 86, while the B4 profiles are relative to the days: 3, 43, 82. Moreover, it has to be considered that

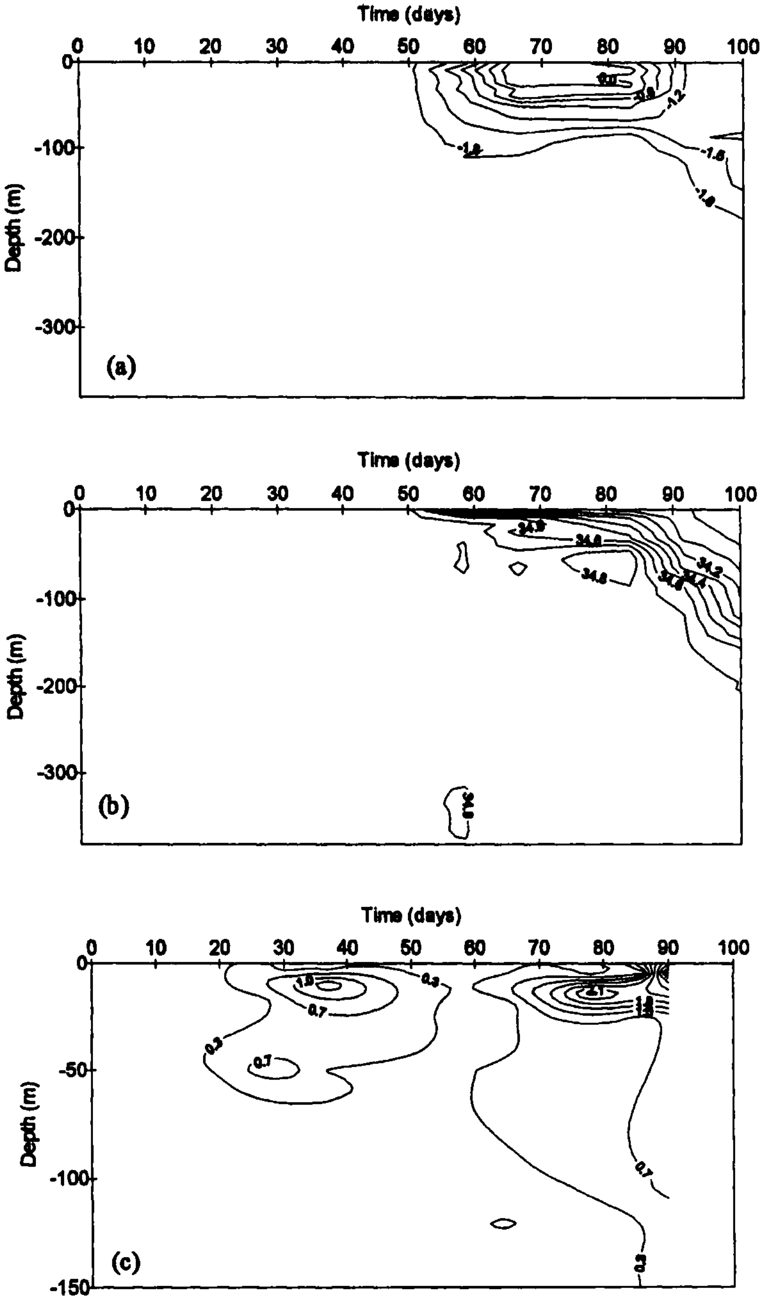

FIGURE 2 Temperature (a), salinity (b) and chlorophyll (c) variations in station B2

profiles B2–1,2,3 and B4–1,2 correspond to the situation in presence of pack ice, while the others correspond to the situation in absence of pack ice.

The following discussion will focus on each matrix separately.

Dissolved and particulate metals in the water column

Dissolved Cu concentration vary from 0.9 nM to 3.75 nM (average value of 30 measurements 2.66 nM), while particulate Cu amount ranges from 0.01 nM to 1.64 nM (average value of 32 measurements 0.32 nM). These results, showed in figure 3a, are similar to those reported in the literature, both in coastal areas and in open sea [2,6,12–19]. It is interesting to note that Cu is mainly present in dissolved phase.

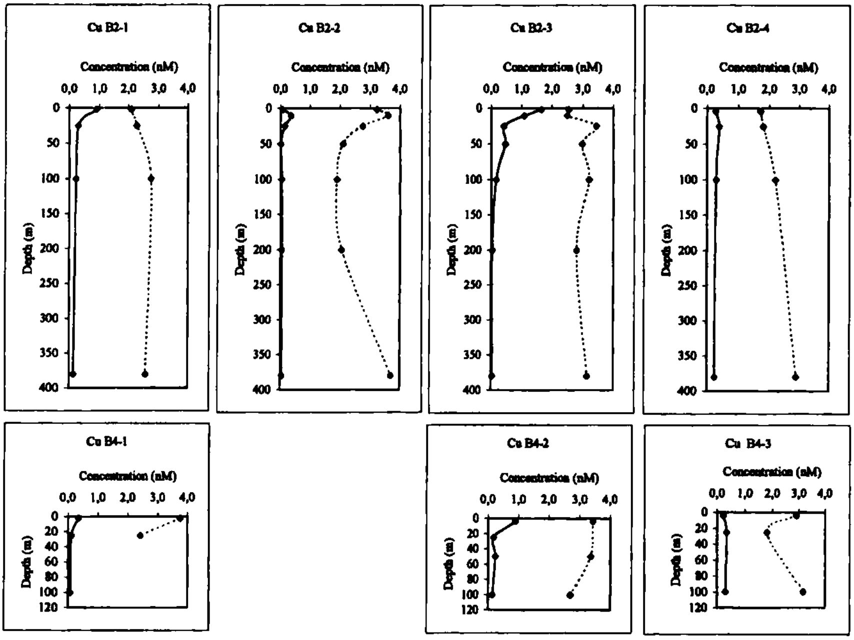

FIGURE 3A Concentration profiles of Cu in station B2 and B4 (dotted line: dissolved metal; solid line: particulate metal)

In all profiles regarding the presence of pack ice (B2–1,2,3 and B4–1,2), particulate Cu shows a trend with surface or subsurface maxima and a concentration decrease with depth (Figure 3a).

As regards profiles B2–1,2 and B4–1, no phytoplanktonic activity was observed during the sampling period (Figure 2c); so it can be supposed either

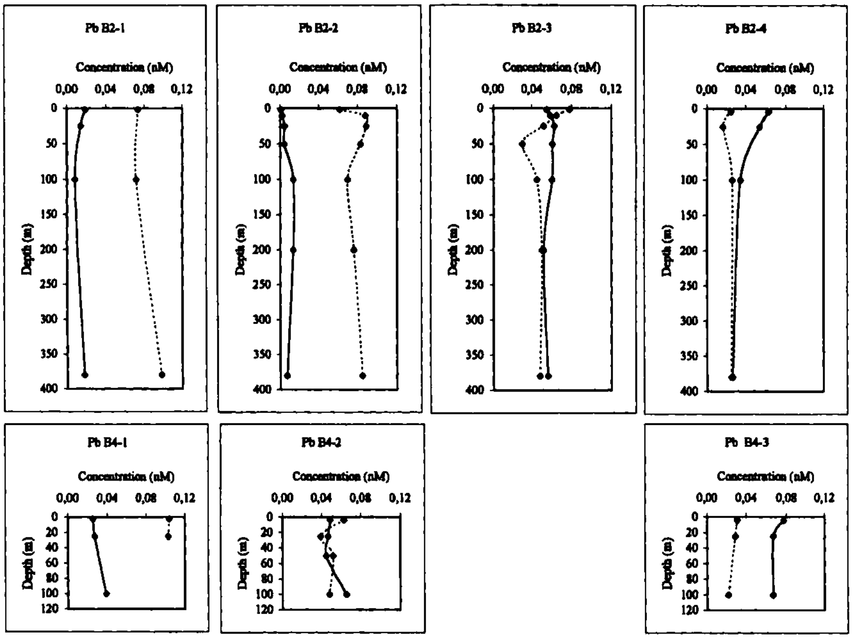

FIGURE 3B Concentration profiles of Pb in station B2 and B4. (dotted line: dissolved metal; solid line: particulate metal)

that particulate copper in surface waters is released by pack ice during melting, or that the biological material entrapped in the pack ice, as soon as this melts, begins the uptake of Cu, that is an important micronutrient. This hypothesis seems to be confirmed both from previous data on particulate Cu in presence of pack ice [6] and from recent data regarding the same samples of this work, where particulate Fe and Mn (micronutrients themselves) present the same trend of Cu [20].

The high Cu amount present in surface particulate in profiles B2–3 and B4–2 is explained with uptake of dissolved Cu from the phytoplankton [21]. In fact, during this period, the chlorophyll (Figure 2c) and nutrients values highlight a phytoplanktonic bloom even if pack ice is still present. This is confirmed by the presence of a surface minimum in the dissolved Cu profile in correspondence with a particulate Cu maximum.

The two remaining profiles (B2–4, B4–3) show a subsurface maximum, though not so sharp, and a constant and high concentration under 100 m. It is still evident some uptake from phytoplankton, also highlighted by dissolved Cu pro-

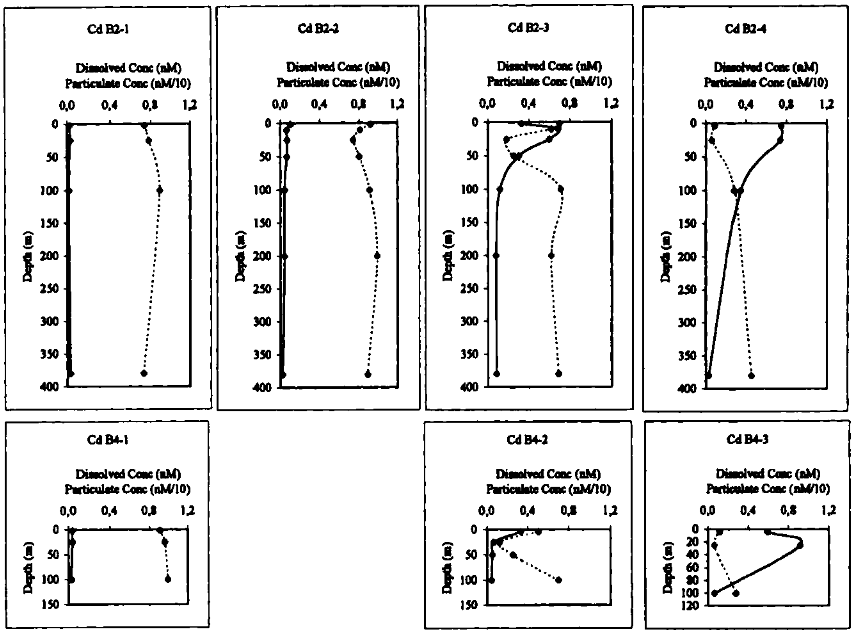

FIGURE 3C Concentration profiles of Cd in station B2 and B4 (dotted line: dissolved metal; solid line: particulate metal)

file, but there is, as noted in previous work [6], a sort of "overlapping" of this phenomenon with a very rapid scavenging in intermediate and deep waters. This particular behaviour of Cu is rather common: infact this metal is the only one with both the characteristics of a "nutrient type" and a "scavenging type" element [22].

Dissolved Pb concentration ranges from 0.02 nM to 0.10 nM (average value of 30 measurements 0.06 nM), while particulate Pb amount ranges from 0.01 nM to 0.08 nM (average value of 32 measurements 0.04 nM). These results, showed in figure 3b, are comparable to those found in previous expedition [4,5,23], and are similar to Ross Sea offshore data [20]. Both dissolved and particulate lead present an homogeneous distribution along the water column before the beginning of the pack ice melting and the first phytoplankton bloom (Figure 3, profile B2–1, B2–2 and B4–1).

As regards particulate Pb, the profiles B2–1,2 and B4–1 observed before the phytoplankton bloom, present low amounts of Pb, while the profiles B2–3 and B4–2 are characterized by higher concentrations (compare Figures 3c and 2c).

This lead distribution is not common; it is known the lead is a "scavenging type" element, therefore we expect its concentration increases in particulate matter with depth. However, because the coincident maximum of particulate lead during the first phytoplankton bloom we can hypothesize the scavenging of lead by particulate matter generate from biological activity before the pack ice thawing. Further study are necessary in the same conditions or to rely on more data to give an interpretation of this phenomenon.

In absence of pack ice (profiles B2–4 and B4–3) the concentration of particulate lead presents surface maxima, which overlaps the rather high amount in intermediate and deep waters, that is caused by the scavenging of Pb from particulate. The surface situation is probably due to the contribution of atmospheric particulate. To confirm this hypothesis it will be useful a comparison with microlayer data that will be illustrated later on.

The atmospheric particulate does not seem to affect the amount of dissolved Pb. The mean dissolved Pb decreases during the austral summer from a mean value of 0.08 nM in november to a value of 0.02 nM in February; therefore, in agreement with the observation made about the particulate lead distribution, we can hypothesize the lead distribution during the austral summer is controlled by an efficient scavenging process.

Dissolved Cd concentration vary from 0.08 nM to 0.99 nM (average value of 32 measurements 0.58 nM). Particulate Cd amount is lower, ranging from 0.002 nM to 0.09 nM (average value of 32 measurements 0.021 nM). Again these data are in good agreement with the results obtained in previous cruises, both from coastal and offshore areas [4,5,19].

Cd presents a homogeneous trend at low concentration in the profiles B2–1,2 and B4–1, as shown in Figure 3b. In the other profiles, it is evident a concentration maximum in surface and subsurface particulate. This is in good agreement with chlorophyll trend, indicating an uptake from phytoplankton confirmed also by the dissolved Cd profiles (Figures 3c, B2–3 and B2–4). Although the Cd is not generally believed to have a biological function, for years the hypothesis to explain its nutrient type distribution was that it is assimilated because of a lack of discrimination in the uptake mechanism [24,25]. Recent studies showed that it can play a role in biological systems when low Zn and CO_2 are present [26].

Metals in particulate included in pack ice

It is evident from the high amount of TPM and particulate Cu, Cd and Pb trapped in the pack ice ice (Table II) that this region is affected by high crustal inputs.

TABLE II Particulate Cu, Pb and Cd concentration in pack-ice (station B2)

	Core section	*TPM*	*Cu*	*Pb*	*Cd*
	(cm)	*(mg/l)*	*(nM)*	*(nM)*	*(nM)*
Surface	45	1.04	27..9 ± 0.8	14.7 ± 1.7	4.8 ± 1.3
Intermediate 1	46	0.87	5.3 ± 0.3	2.6 ± 0.5	3.4 ± 0.4
Intermediate 2	43	5.20	16.7 ± 0.5	5.1 ± 0.1	6.1 ± 0.8
Bottom (interface with SW)	10	137	35.3 ± 0.5	1.7 ± 0.2	45.4 ± 0.6

Other authors [12] found lower levels of particulate metals, but in ice cores sampled in remote areas; therefore a direct comparison is not feasible.

Particularly, the core section at the sea water interface, is enriched in Cu and Cd. As regards Cu, this can justify the contribution to the higher level of this element in surface particulate of the first profiles. On the other hand, the high amount of Cd seems not to affect the concentration in surface particulate. Moreover, the same core section is particularly rich of particulate matter (Table II), which consists principally of biological material. We can assume that Cd is mainly associated with this material and that it is released in dissolved form when the pack ice melts. This hypothesis is supported by data regarding dissolved Cd concentration in the water column (Figure 3c) where dissolved Cd amount in surface water was higher in presence of pack ice.

Finally, we can note that Pb concentration is higher in the surface section, according to the hypothesis of an atmospheric contribution, as already pointed out for the water column in absence of pack ice. Even Cu presents a higher amount in surface section, while Cd has a constant concentration in the first three core sections.

Metals in surface microlayer particulate

It is well known the important role of microlayer for exchange and accumulation processes between sea and atmosphere. To this aim, metals concentration were determined in particulate matter sampled in microlayer (50–150 μm). Results are shown in table III and compared with the concentration of the same elements in particulate collected at 0.5 m of depth. TPM amount is also reported.

We can observe that for Pb and Cu the concentration in the microlayer is higher respect to the underlying water, confirming the atmospheric input of these elements previously supposed. Atmospheric contribution seems to be negligible for

Cd, which concentration is lower in the microlayer than in the underlying water. This result is in good agreement with the distribution of Cd in the pack ice.

TABLE III Particulate Cu, Pb and Cd average concentration in microlayer (50–150 micron) and in the underlying water (0.5 m)

Station	*Depth*	*Cu*	*Pb*	*Cd*	*TPM*
	(m)	*(nM)*	*(nM)*	*(nM)*	*(nM)*
Gerlache Inlet	microlayer	0.94±0.15	0.25±0.03	0.04±0.01	1.6±0.3
	0.5	0.59±0.08	0.14±0.02	0.14±0.01	2.8±0.1

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