

Trace metals distributions in coastal sea ice of Terra Nova Bay, Ross Sea, Antarctica

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Abstract: In an attempt to clarify the release of trace elements from the seasonal coastal sea ice, samples were periodically collected in a nearshore station inside the Gerlache Inlet (Terra Nova Bay, Western Ross Sea), during the summer 2000/01 and analysed for dissolved and particulate cadmium, copper, iron, manganese and lead, as well as salinity, suspended particulate matter, nutrients and phytoplankton pigments. In order to provide insight on the metal association with the particles included in the sea ice, the metal solid speciation was also investigated. Both vertical distributions within the ice cores and temporal variations at the seawater interface were studied, in an effort to fully characterize the system and correlation among the considered parameters. Concentrations and speciation patterns clearly indicate metal incorporation within the annual sea ice due to resuspension of sediments, followed by release of particulate metals during melting as a primary process affecting trace metal availability in the Antarctic coastal waters.

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Introduction

Sea ice is an important component of the Antarctic marine ecosystem, which has a determining influence on fundamental planetary processes, such as the formation of oceanic water masses and atmospheric CO₂ levels. The circumpolar ring of sea ice surrounding the Antarctic continent, varying from 4 to 20 10⁶ km² seasonally, is an extensive and highly variable system and plays an important role in global climate (Gordon & Comiso 1988, Smith *et al.* 1990). Antarctic coastal polynyas have been regarded as "sea ice factories", and it is believed that a significant fraction of the annual sea ice surrounding Antarctica is produced within such polynyas (Cavaliere & Martin 1985, Gordon & Comiso 1988). The latent heat released from ice production over the continental shelf is likely to be a primary factor in the production of saline shelf water and ultimately in bottom water formation (Zwally *et al.* 1985).

Sea ice also plays a key role in regulating primary productivity in the Southern Ocean and, consequently atmospheric CO₂. Sea ice presence drastically influences the amount of irradiance within the surface mixed layer (Marra & Boardman 1984, Smith & Sakshaug 1990), while its melting results in a well-stratified water column, allowing different regimes of primary productivity. During the early spring, productivity is limited by irradiance, due to wind mixing, unfavourable solar angle and substantial amount of ice cover (Smith *et al.* 2000). Later in spring, the phytoplankton bloom appears to be initiated when vertical stability is imparted by sea ice melting coincident with greater daily insolation (Smith *et al.* 2000). Moreover, sea ice itself is an heterogeneous habitat for organisms (Ackley & Sullivan 1994), and associated biological communities

may influence the development of ice edge blooms in the water column by providing an inoculum or "seed population".

The release of micronutrients (e.g. iron) during the sea ice melting is another process which may influence the seasonal cycle of phytoplankton productivity and growth (Sedwick & DiTullio 1997, Fitzwater *et al.* 2000, Sedwick *et al.* 2000). The importance of trace-metal availability in limiting phytoplankton productivity has been widely discussed (Martin *et al.* 1990, de Baar *et al.* 1990, 1995, 1997, 1999, Lancelot *et al.* 1993, Sedwick & DiTullio 1997, Timmermans *et al.* 1998, Fitzwater *et al.* 2000, Sedwick *et al.* 2000, Coale *et al.* 2004). Elevated concentrations of iron coincide with increased productivity, phytoplankton biomass and nutrient drawdown, indicating that iron availability may influence the uptake of N, P and Si by phytoplankton and, hence, control location and period of blooms. However, the source of iron and other bioactive trace elements (Zn, Mn, Ni, Cu, Cd) is not well constrained. Direct atmospheric dust deposition as major iron source was ruled out by Martin *et al.* (1990), because of their findings of low surface-water dissolved Fe concentrations in offshore Drake Passage waters. The atmospheric dust load in the Southern Ocean is known to be amongst the lowest in the world (Prospero 1981, Duce & Tindale 1991, Delmonte *et al.* 2002, EPICA community members 2004); the contribution of over-winter particulate Fe deposition in snow found on seasonal sea ice is probably quite low (Fitzwater *et al.* 2000) but may be important for localized blooms (Sedwick & DiTullio 1997, Sedwick *et al.* 2000).

Resuspension of continental shelf sediments appears to be a major source of particulate iron for coastal phytoplankton

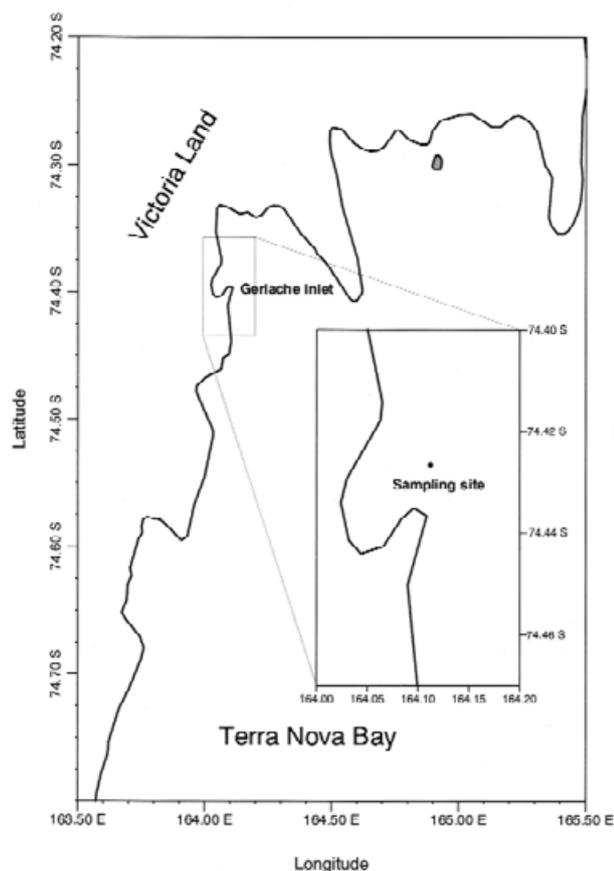


Fig. 1. Sampling site.

(Schoemann *et al.* 1998, Johnson *et al.* 1999, Fitzwater *et al.* 2000, Sedwick *et al.* 2000). Fitzwater *et al.* (2000) and Sedwick *et al.* (2000) postulated that annual sea ice may incorporate resuspended shelf sediments during formation over winter and release particulate metals as the ice melts.

In the framework of the Italian Research Programme in Antarctica (PNRA), the distribution of trace elements in the coastal area of Terra Nova Bay (Ross Sea) was recently investigated (Grotti *et al.* 2001, Frache *et al.* 2001a, Dalla Riva *et al.* 2003). The direct release of particulate Fe and Cu from sea ice were clearly indicated by surface water concentration maxima and by the high concentrations of suspended particulate matter (SPM) and particulate metals detected in sea ice near the seawater interface. Moreover, results suggest complex dissolved/particulate partitioning dynamics, which may account for the temporal uncoupling between maximum values of particulate and dissolved metals. However, these studies highlighted the need for a more complete and specific investigation of the distribution and speciation in these trace metals in coastal sea ice.

Therefore, a field study was undertaken to measure trace metal, nutrient and chlorophyll concentrations in sea ice cores collected in Terra Nova Bay during the summer 2000/01 (from 5 November–11 January), in an attempt to improve the understanding of the release of trace elements

from seasonal coastal sea ice.

Analytical methodology

Study site and sampling

Sea ice cores were collected at a nearshore station positioned inside the Gerlache Inlet, Terra Nova Bay (74°42.632'S, 164°11.178'E, 430 m deep, 2 km from the coast, see Fig. 1), during summer 2000/01, approximately every 15 days, from 5 November 2000–11 January 2001.

Snow was cleared from the surface of the sea ice, and cores were collected by means of a manually driven 8 cm diameter titanium corer (Duncan, UK, Model BTC). Samples were handled using polyethylene gloves and stored at -30°C in clean polyethylene bags until processing. Five replicates cores were sampled within an approximately 5 m² area. Eventual contamination due to sample collection was eliminated by sub-coring treatment (see below).

Seawater and SPM under the pack ice were collected through a hole drilled by an ice corer, using the *in situ* filtration system FIS500 (Grotti *et al.* 2003a). This system has been developed specifically for trace element determination and successfully tested in Antarctic waters. Minimisation of metal contamination sources was realised by careful choice of materials and designing a “closed-open-closed” electronic procedure for the soaking of the system. Materials coming into contact with the samples are zirconia (pump piston), teflon and polypropylene (fittings). In order to check the contamination due to these materials, ultrapure water (18.2 MΩ•cm, Milli-Q) was pumped through the system and the concentration of Fe, Mn, Cu, Cd and Pb in out-flowing and in-flowing water determined. Since no significant differences between the values were found (*t*-test, $\alpha = 0.05$), it was concluded that the metal release due to the system components can be neglected.

Finally, the storage procedure of filtered non-acidified seawater samples had been previously tested in the framework of PNRA by Capodaglio *et al.* (1995), by analyzing a number of samples directly after collection as well as after storage. The values showed a good agreement, proving the absence of systematic errors due to freeze storage.

Sample preparation

Sea ice core processing. Each core was divided into seven fractions: the upper six sections were about 40 cm long, while the part at the sea water interface was about 10 cm long. After, each ice core portion was decontaminated by sub-sampling the 2.5 cm diameter inner core, using a custom-built teflon-covered titanium corer. Cutting and sub-coring were carried out at -30°C under a laminar flow hood. Contamination levels introduced during the sea ice processing were checked by performing the same procedure on an artificial ice core made of ultrapure water

(18.2 M Ω •cm, Milli-Q). No significant difference (*t*-test, 95% confidence level) was found between the metal concentration in the "blank" ice before and after the sample processing.

After melting at room temperature, the samples were filtered under vacuum, using a custom-built filtration apparatus specifically designed for trace element determinations. It consists of two or four independent units, each made of a Plexiglas vacuum chamber containing the LPDE collecting bottle (Nalgene Polylow 102080). The chamber is connected, by a silicone tube (Nalgene 8040-0120), directly to the sampling bottle, through the filtration cartridge (Sartorius, SM 16508B, 50 mm diameter) containing the polycarbonate membrane filter (0.4 μ m isopore, Millipore HTTP04700, 47 mm diameter). Filtration was performed in a laminar flow work area. All the containers and materials coming into contact with the samples were cleaned with hot 1M nitric acid (Carlo Erba, Milan, Italy) before assembly; the sampling bottles were washed with 0.1N hydrochloric acid of suprapure grade quality (Merck, Whitehouse Station, NJ, USA) and Milli-Q water before use. Membrane filters were systematically washed with 0.1N hydrochloric acid (suprapure grade quality, Merck) and Milli-Q water. Five serial cleaning treatments were performed, since previous experiments highlighted that the metal concentrations in the washing solutions reach constant values after the fourth treatment.

Filters were dried under a laminar flux hood and weighed with an accuracy of ± 0.00001 g (Sartorius BP 210 D).

Preconcentration of dissolved metals. Determination of heavy metals in filtered seawater and sea ice samples was carried out according to a procedure previously reported (Grotti *et al.* 2003b). Briefly, the preconcentration system consisted of a multi-channel peristaltic pump (Technicon, Dublin, Ireland), with a set of Tygon pump tubes which connected the samples with the micro-columns. Ready-to-use micro-columns filled with iminodiacetic resin (IC-Chelate plus, bed volume 1.5 ml; amount of resin 200 mg; size range 150–300 μ m; exchange capacity 2.9 meq g⁻¹) were purchased from Alltech (Deerfield, IL, USA). The resin and the connecting tubes were cleaned by passing 1 M nitric acid (500 ml, 2 ml min⁻¹). The resin was then treated with 1 M ammonium acetate buffer (pH 5.5, 2 ml min⁻¹, 5 min), in order to replace the H⁺ ions with the NH₄⁺ ions. The samples were then passed through the micro-columns at 2 ml min⁻¹ flow rate. Sample volumes ranges from 300 to 500 ml, depending on the analytical concentration. The sea ice samples were buffered with 0.11 mg l⁻¹ Na₂CO₃, while seawater samples did not require any buffer. At the end of the preconcentration step, a pre-elution with 1 M ammonium acetate (pH 5.5, 2 ml min⁻¹, 15 min) was performed in order to remove the major elements before analyte elution for spectrometric determination. Finally, the preconcentrated analytes were eluted with 1 M nitric acid,

Table I. Procedural blanks and detection limits (DL) for dissolved and particulate metal determination (pM)*

	Dissolved metal determination		Particulate metal determination	
	Blank	DL (3 α , n = 12)	Blank	DL (3 α , n = 10)
Cd	8 \pm 3	9	3 \pm 1	3
Cu	176 \pm 14	42	47 \pm 13	39
Fe	1701 \pm 82	246	751 \pm 190	570
Mn	134 \pm 16	48	55 \pm 7	21
Pb	47 \pm 4	12	6 \pm 2	6

Note: *Computed considering preconcentration factor of 100 and SPM concentration of 2 mg l⁻¹.

collecting 3 ml of solution in pre-cleaned sampling cups. The preconcentration procedure was performed in a laminar flow work area. All reagents were of suprapure grade quality (Merck). Procedural blanks and detection limits are reported in Table I. The accuracy of the procedure was verified by analysing various certified reference materials: river waters (SLRS-1, SLRS-3), estuarine water (SLEW-3), coastal and off-shore sea-waters (CASS-3, NASS-5), supplied by the National Research Council Canada.

SPM dissolution. The SPM incorporated into sea ice and that collected in underlying seawater were solubilized with 8 M nitric acid (suprapure grade quality, Merck), using a microwave digestion system (CEM DS 2000). Digestion was conducted for 40 min with a maximum (control) pressure of 150 psi, using 100% power. Finally, samples were transferred into graduated flasks and diluted to 10 ml. For each run, two blanks and one certified reference sample were also prepared to check contamination and analytical accuracy.

In order to avoid significant sample contamination during this step, before each run, the vessels were filled with 8 M nitric acid (suprapure grade quality, Merck) and the microwave-assisted digestion program performed. After, the vessel were washed with Milli-Q water and dried under laminar flow hood. Procedural blanks and detection limits are reported in Table I. The accuracy of the procedure was verified by analysing the certified reference material CRM-414 (marine plankton, Community Bureau of Reference).

Solid speciation procedure. The trace metal solid speciation was studied by applying the sequential extraction scheme by Rauret *et al.* (2001). Three selective chemical digestions were carried out sequentially. In the first step, the sample is treated with acetic acid (0.11 M; pH 2.8), which should remove the exchangeable ions and the metals bound to the carbonate phases, labile oxides and organic matter. In the second step, hydroxylamine hydrochloride (0.5 M; pH 2) is added to the residue of the previous step to extract metals associated with Fe and Mn oxides. In the third step, a microwave-assisted treatment with hydrogen peroxide (30%, pH 2) is carried out to solubilise sulphides and organic matter. At the end of this last step, ammonium

Table II. Procedural blanks and detection limits (DL) for metal solid speciation ($\mu\text{g g}^{-1}$)

	Step 1*		Step 2*		Step 3*	
	Blank	DL	Blank	DL	Blank	DL
	(3 α , n = 6)		(3 α , n = 6)		(3 α , n = 6)	
Cd	0.032 ± 0.004	0.012	0.010 ± 0.003	0.010	0.132 ± 0.020	0.060
Cu	0.014 ± 0.004	0.013	0.066 ± 0.030	0.090	0.032 ± 0.005	0.015
Fe	0.201 ± 0.035	0.105	1.560 ± 0.210	0.630	1.932 ± 0.200	0.600
Mn	0.018 ± 0.003	0.010	0.702 ± 0.100	0.300	0.405 ± 0.050	0.150
Pb	0.104 ± 0.028	0.085	0.090 ± 0.023	0.070	0.144 ± 0.025	0.075

note: * see text for definition of steps 1–3.

acetate buffer (1 M, pH 2) is added to prevent re-adsorption processes.

All the reagents were of suprapure grade quality from Merck. Procedural blanks and detection limits are reported in Table II. The accuracy of the procedure was verified by analysing the certified reference material BCR 701 (SM&T Program of European Union).

Sample analysis

Trace elements. To quantify the metals in the solutions obtained after the sample preparation, two atomic spectrometry techniques were used: electrothermal atomization atomic absorption spectrometry (ETAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES).

ETAAS measurements were carried out using a Varian (Springvale, Australia) SpectrAA 300 atomic absorption spectrometer equipped with Zeeman-effect background

corrector and GTA 96 graphite atomizer. Samples were delivered to the furnace using a Varian PSC 56 programmable sample changer, after storing in acid washed polypropylene cups. Pyrolytic graphite coated tubes were used. The temperature programs were optimized in order to get the highest absorbance value and maximum pyrolysis temperature without loss of analyte. Integrated absorbance was measured, exclusively.

The ICP-OES system used was the Varian (Springvale, Australia) Vista PRO. The observation mode is axial-viewing, with an argon counter gas flow through a cone to eliminate the recombination zone at the tip of the plasma. The dispersive system is based on the use of an echelle grating (94 grooves mm^{-1}) with a CaF_2 prism cross dispersion. The echellogramme is sampled by a segmented charge-coupled device, with each segment covering one of the 70 orders of the 2-D spectrum. The total number of pixels is approximately 70 000 with a spectral resolution of 6.9 pm at Mo 202.032 nm emission line. A concentric nebulizer in conjunction with a cyclonic spray chamber was used. Operating parameters were optimized in order to achieve greatest signal-to-background ratios, favourable for ultratrace element determinations.

Nutrients and phytoplankton pigments. Nutrient concentrations were determined by air-segmented continuous flow analyser (Autoanalyzer, Techicon II) according to the classical methodologies of Hansen & Grasshoff (1983). Samples were filtered throughout 0.7 μm Whatman GF/F filters. A carrier solution of 5 g l^{-1} NaCl was used in order to match sample salinities and minimize

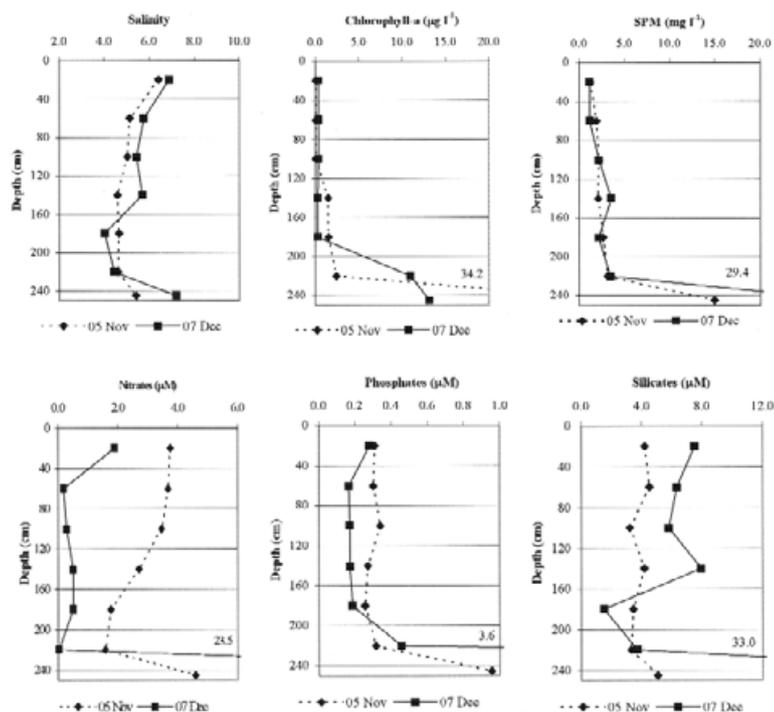


Fig. 2. Vertical profiles of salinity, Chl *a*, SPM and nutrient concentrations within two sea ice cores, collected on 5 November (dashed line) and 7 December (solid line).

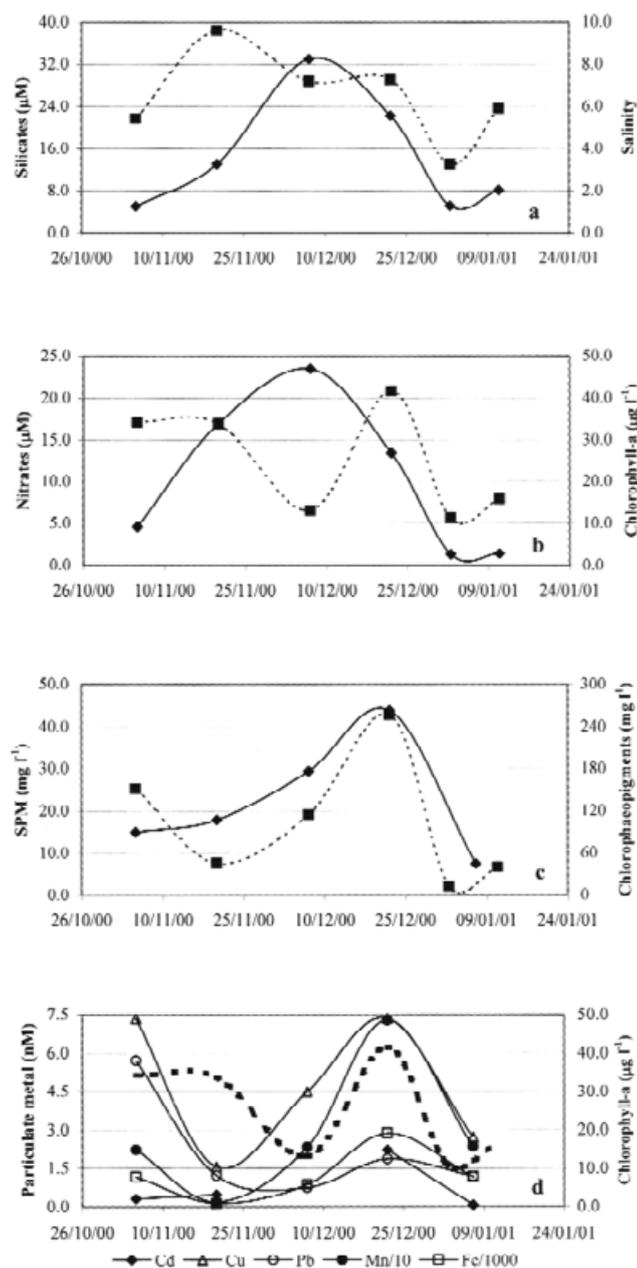


Fig. 3. Temporal evolution of: a. silicates (solid line) and salinity (dashed line), b. nitrates (solid line) and Chl *a* (dashed line), c. SPM (solid line) and chlorophaeopigments (dashed line), d. particulate metals in ice cores at the ice-seawater interface (solid lines) and Chl *a* (dashed line).

refractive index errors.

The concentrations of phytoplankton pigments (chlorophyll *a* and phaeopigments) were determined by spectrofluorimetry (Jasco FP-750/PC), following the methods by Yentsch & Menzel (1963) and Holm-Hansen *et al.* (1965).

Results

Vertical distribution of physical and biological parameters within the sea ice cores

Representative vertical profiles of salinity, chlorophyll *a* (Chl *a*), SPM and nutrient concentrations within two sea ice cores, collected on 5 November and 7 December, are shown in Fig. 2. First, a high spatial and temporal variability may be noted, possibly reflecting the rapid evolution of the physical and biological features of the sea ice (e.g. Ackley & Sullivan 1994, Melnikov 1998, Trevena *et al.* 2000). Salinity values were in the 4–7 range, being higher in the upper layer and particularly at the ice-seawater interface. The decrease in salinity from the surface to the inner part of sea ice agrees with its growth structure and physical properties (Weeks & Ackley 1986). The further increase in salinity at the seawater interface reflects seawater permeation, which becomes more pronounced in the seasonal progression, as temperature warms and ice porosity increases. Chl *a* profiles show that significant biological activity occurred in the lower portion of the ice core, in both considered periods. Chl *a* concentrations at the interface with seawater were 34.2 $\mu\text{g l}^{-1}$ and 13.1 $\mu\text{g l}^{-1}$, at early November and December, respectively. Significant concentrations of Chl *a* may also be observed in the overlying layer (2.40 $\mu\text{g l}^{-1}$ and 10.9 $\mu\text{g l}^{-1}$, at early November and December, respectively) and, for the sea ice collected in November, in the 120–200 cm central portion (1.50 $\mu\text{g l}^{-1}$). Nutrients showed a non-uniform distribution within the ice cores, characterized by significant temporal and vertical variations. In the ice collected in November, silicates and phosphates show a quite homogeneous vertical profile from the surface down to 240 cm depth and higher concentrations in the lowermost 10 cm portion. Differently, a marked concentration minimum in nitrate may be noted at 120–240 cm, corresponding to an increase in biological activity. Consequently, the N/P molar ratio decreases from 10–12 to 5–7.

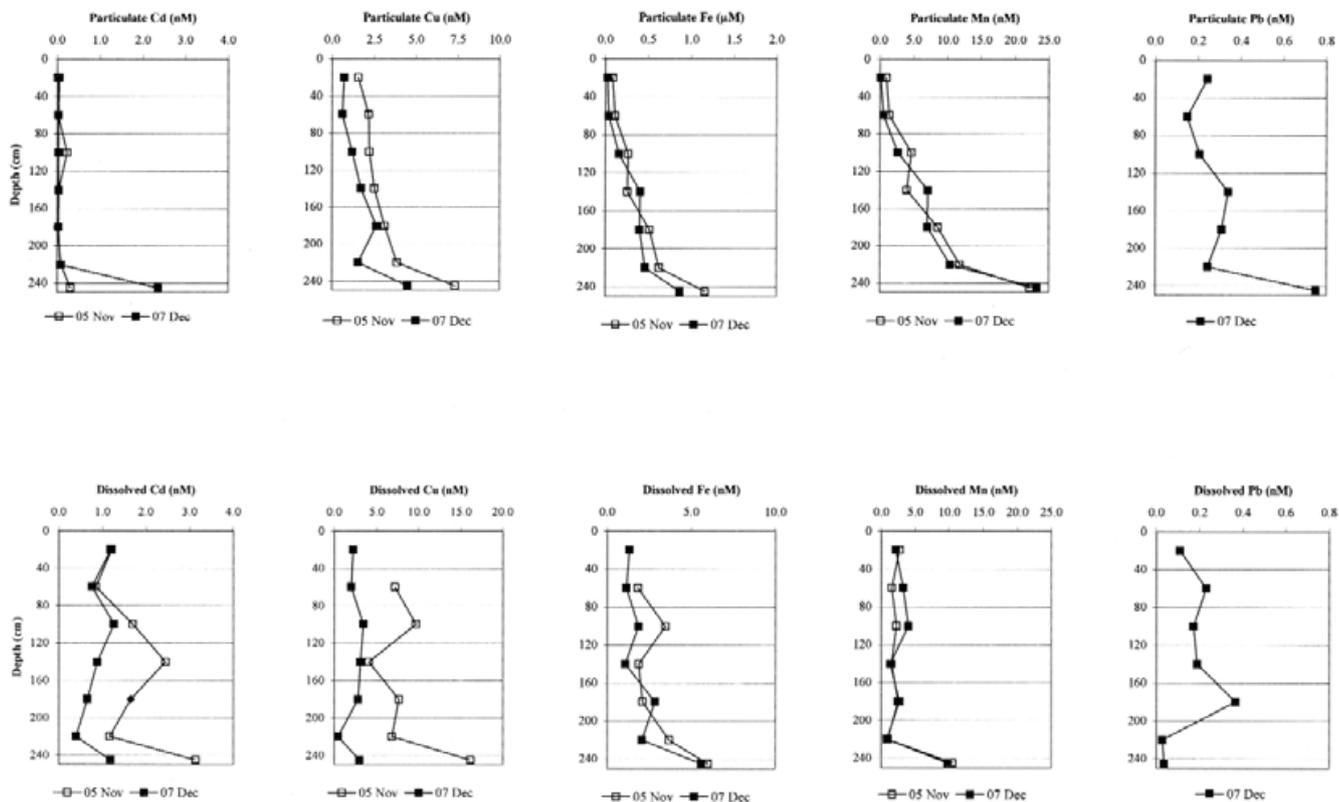
In the sea ice collected one month later, nitrate and phosphate profiles show a concentration minimum in the intermediate portion (40–240 cm), which can be directly ascribed to consumption by phytoplankton only in the 200–240 cm portion, where high Chl *a* concentration (10.4 $\mu\text{g l}^{-1}$) was found. Diffusion of nutrients inside the ice core probably plays a role in determining the spread of concentration minima to the upper portions, where Chl *a* concentration is much lower (0.3–0.4 $\mu\text{g l}^{-1}$). Difference from theoretical N/P ratios may be observed due to the very low nitrate concentrations. Finally, the highest nutrient concentrations at the seawater interface are probably due to input of seawater through the ice pores, since a significant correlation between nutrients and salinity may be observed ($r = 0.58$ for nitrates and phosphates and 0.68 for silicates).

Table III. Dissolved metal concentrations (nM) within the sea ice cores (minimum, maximum and mean values) compared with metal content in underlying seawater and literature data (Martin *et al.* 1990, Grotti *et al.* 2001). Mean values in parentheses.

Sample	Cd	Cu	Fe	Mn	Pb
Sea ice core (except 10 cm lowermost section)	0.394–2.45 (1.18)	0.445–9.67 (4.49)	1.07–3.69 (2.12)	0.840–3.99 (2.13)	0.028–0.365 (0.182)
Sea ice at seawater interface (10 cm lowermost section)	1.18–3.14 (2.16)	2.98–16.2 (9.57)	5.58–5.98 (5.78)	9.76–10.5 (10.1)	(0.036)
Underlying seawater (Terra Nova Bay, 3 m deep)	0.528–0.686 (0.607)	0.596–1.27 (0.932)	0.659–1.51 (1.08)	0.440–4.95 (2.69)	0.074–0.182 (0.128)
Coastal seawater (Terra Nova Bay, water column)	0.080–0.990 (0.556)	0.5–11.6 (2.6)	0.4–4.2 (1.45)	0.08–6.6 (1.24)	0.017–0.104 (0.058)
Coastal seawater (Gerlache Strait)	0.56–0.70 (0.62)	2.09–2.24 (2.16)	4.7–7.4 (6.32)	3.86–5.05 (4.37)	–

Table IV. Particulate metal concentrations (nM) within the sea ice cores (minimum, maximum and mean values) compared with metal content in underlying seawater and literature data (Frache *et al.* 2001, Grotti *et al.* 2001). Mean values in parentheses.

Sample	Cd	Cu	Fe	Mn	Pb
Sea ice core (except 10 cm lowermost section)	0.007–0.225 (0.054)	0.604–3.86 (1.98)	26–627 (279)	0.131–11.8 (4.93)	0.148–0.341 (0.248)
Sea ice at seawater interface (10 cm lowermost section)	0.306–2.37 (1.34)	4.49–7.34 (5.91)	869–1162 (1015)	22.2–23.2 (22.7)	(0.750)
Underlying seawater (Terra Nova Bay, 3 m deep)	0.005–0.017 (0.011)	0.311–0.642 (0.477)	28.1–44.9 (36.5)	0.334–1.05 (0.69)	0.048–0.262 (0.155)
Coastal seawater (Terra Nova Bay, water column)	0.002–0.120 (0.022)	0.04–1.40 (0.33)	1.1–58.5 (18.2)	0.01–0.96 (0.27)	0.001–0.077 (0.037)

**Fig. 4.** Vertical profiles of dissolved and particulate Cd, Cu, Fe, Mn and Pb within the sea ice cores.

Temporal distribution of physical and biological parameters in ice cores at the ice-seawater interface

Temporal changes of physical and biological parameters in ice cores at the ice-seawater interface were further investigated by processing a number of samples collected throughout the spring 2000/01, with a temporal resolution of approximately 14 days. Representative results are shown in Fig. 3a–c. Salinity shows an increase during November, followed by a slight decrease in the seasonal progression. Nutrient concentration trends are highly correlated ($r > 0.8$), showing an initial increase in November, until a maximum value is reached, followed by a decrease due to consumption by phytoplankton. Accordingly, Chl *a* increases with decreasing nutrient concentrations. Finally, the SPM temporal trend is highly correlated with temporal distribution of total pigments (Chl *a* + phaeopigments), suggesting that the major constituent of SPM is organic matter of algal origin.

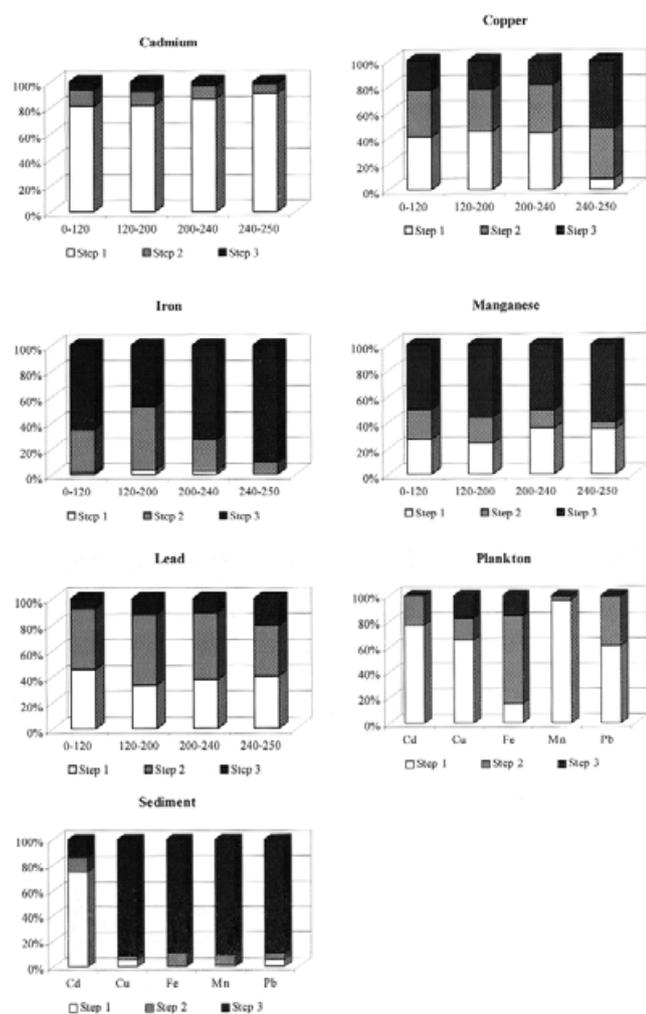


Fig. 5. Solid speciation of Cd, Cu, Fe, Mn and Pb inside the ice core and in plankton and sediment samples (see text for definition of steps 1–3).

Vertical distribution of trace metals within the sea ice cores

Vertical profiles of dissolved and particulate Cd, Cu, Fe, Mn and Pb within the sea ice cores are illustrated in Fig. 4. Raw data are summarized in Tables III & IV, in which concentration ranges (minimum, maximum and mean values) are compared with those found in the underlying seawater and with literature data.

Firstly, it can be seen that the concentration values of dissolved Cu, Fe and Mn within the sea ice core (leaving out the 10 cm lowermost section) are included in the concentration ranges reported for coastal seawater (Martin *et al.* 1990, Frache *et al.* 1997, 2001a, Grotti *et al.* 2001). Dissolved Cd and Pb data exceed the seawater upper limits, by a factor less than 3. Concentrations of dissolved metals at the ice-seawater interface are generally higher than in the overlying layers, particularly for Fe and Mn (see Table III and Fig. 4), with enrichment factors ranging from 1.3 to 5.5.

When comparing concentrations of particulate metals in the sea ice with underlying seawater, a marked difference is observed: concentrations in the lowest 10 cm are 4–5-fold higher than in the other core sections and 1–2 order of magnitude higher than in the underlying seawater. Vertical profiles of particulate metals (Fig. 4) show a slight increase in concentration from the top to the bottom of the ice core for Cu, Mn and Fe, and an homogeneous level, followed by

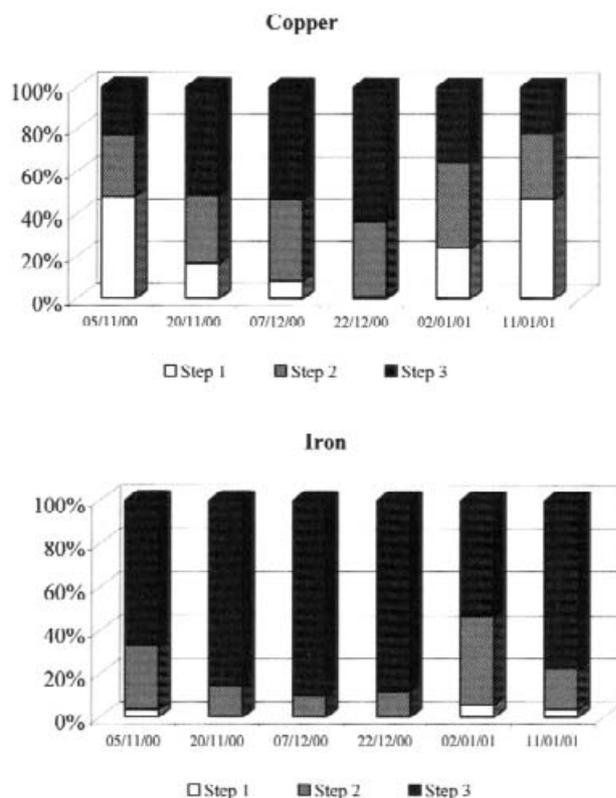


Fig. 6. Temporal variation of solid speciation pattern of Cu and Fe (see text for definition of steps 1–3).

an increase in concentration at the seawater interface, for Cd and Pb.

Temporal distribution of particulate metals in ice cores at the ice-seawater interface

Temporal evolution of particulate metal concentrations in ice cores at the ice-seawater interface is showed in Fig. 3d. It can be seen that concentration trends well agree with Chl *a* variations, especially for Cu, Fe and Mn, suggesting that these metals can be associated with particulate organic matter formed during the phytoplankton blooms.

Solid speciation patterns

The particulate metal speciation was studied by applying the sequential extraction scheme of Rauret *et al.* (2001) summarized in the section on sample preparation. The general speciation pattern is illustrated in Fig. 5, based on the results obtained for the ice core collected in December. In order to better evaluate the results, the data obtained by applying the same procedure to marine sediments collected in the same area and to the certified plankton CRM 414 are also reported.

It can be seen that cadmium is mainly associated with the labile fraction in each ice core section; similar behaviour is observed for both plankton and sediment samples. Copper shows a nearly equal-distribution among the various phases within the ice core (0–240 cm), although in the 10 cm lowermost portion, the labile fraction decreases, while the copper associated with the oxidisable fraction increases. Evidently, at the seawater interface, where the organic matter concentration is much higher, copper is strongly complexed by organic species or associated with algal material. This is the pattern of sediment samples, where copper is principally associated with humic acids (Frache *et al.* 2001b) and is thus expected to be extracted mainly

during the third step of the procedure (Fig. 5).

As expected, iron is essentially present in oxides or bound to the oxidisable fraction. However, its distribution among these phases is not homogeneous within the ice core, since an increase in the percentage of oxidisable iron occurs in the lower part of the sea ice core, revealing, as for Cu, an higher amount of organic matter going towards the sea-ice interface, and, consequently, an association of Fe with this organic material. Manganese shows a quite homogeneous vertical profile and its solid speciation is intermediate between those found in sediment and plankton samples. In fact, a significant fraction of labile manganese is observed within the ice core, which indicates a weak metal association (adsorbed fraction) with particulate matter or an association with labile biological matter similar to that observed in plankton. However, most of the manganese is associated with organic matter or sulphides, as in sediments. Finally, lead is mainly present as labile metal or associated with reducible phases, presenting, as Mn, an intermediate speciation pattern between plankton and sediment speciation, and showing no significant trend within the sea ice core.

Temporal variation of solid speciation at the seawater interface was also investigated. While cadmium, manganese and lead did not exhibit any particular trend, iron and copper displayed a significant variation in their distribution among the SPM phases (Fig. 6). As the season proceeds, the fraction of metal associated with oxidisable fraction increases, reaching a maximum value in December. At the same time, the labile fraction for copper and the reducible fraction for iron decrease. These results indicate that a seasonal incorporation of these metals into the organic particulate matter occurs. The temporal evolution of this process could depend on the temporal variation of organic ligands (e.g. humic acids) concentration inside the sea ice, or the growth of algae at the ice-water interface.

Table V. Comparison between the metal amounts "stored" in sea ice and those found in the 3 m deep underlying layer (sum of particulate and dissolved metal amounts; percentage of particulate metal content in parentheses).

	Cd ($\mu\text{mol m}^{-2}$)	Cu ($\mu\text{mol m}^{-2}$)	Fe ($\mu\text{mol m}^{-2}$)	Mn ($\mu\text{mol m}^{-2}$)	Pb ($\mu\text{mol m}^{-2}$)
Metal amount "stored" in sea ice (November)	4.10 (4.3%)	22.7 (30.4%)	862 (99.3%)	20.4 (72.4%)	–
Metal amount "stored" in sea ice at ice-seawater interface (November)	0.34 (8.9%)	2.35 (31.2%)	117 (99.5%)	3.27 (67.9%)	–
Metal amount in the 3 m deep underlying layer (November)	2.07 (0.7%)	2.72 (34.3%)	137 (98.1%)	4.48 (70.3%)	0.36 (39.4%)
Metal amount "stored" in sea ice (December)	2.50 (13.1%)	9.71 (39.1%)	689 (99.3%)	20.1 (66.9%)	1.11 (60.4%)
Metal amount "stored" in sea ice at ice-seawater interface (December)	0.35 (66.7%)	0.75 (60.1%)	87 (99.4%)	3.30 (70.4%)	0.08 (95.4%)
Metal amount in the 3 m deep underlying layer (December)	1.63 (3.0%)	5.73 (33.6%)	89 (94.9%)	3.40 (29.5%)	1.33 (59.0%)
Metal amount in the 3 m deep underlying layer (February)	0.54 (33.0%)	5.82 (38.1%)	156 (97.5%)	1.71 (70.2%)	0.33 (70.6%)

Discussion

It is widely recognized that iron availability may account for the differences in primary production observed between Antarctic open-ocean and coastal waters (e.g. Martin *et al.* 1990, de Baar *et al.* 1995). The iron sources in the Antarctic marine ecosystem, however, have not been fully elucidated. Sedwick & DiTullio (1997) surmised that both dissolved and particulate iron are released into seawater from the melting sea ice, the metal being derived from atmospheric dust particles which accumulate in snowfall during the winter months. The importance of resuspended sediments as a significant iron source for phytoplankton in the coastal zones has also been recognized (Schoemann *et al.* 1998,

Johnson *et al.* 1999). Fitzwater *et al.* (2000) & Sedwick *et al.* (2000) postulated that annual sea ice may incorporate resuspended shelf sediments during formation over winter when vertical mixing occurs, and then later release the metals with meltwaters. However, the authors remarked that no estimation of the iron concentration in the annual sea ice was available to further support their hypothesis. In this work, concentrations of dissolved and particulate metals in the coastal annual sea ice were evaluated. The absolute values found both along the ice core and at the seawater interface clearly established that annual sea ice may be an important source of trace elements, mainly iron and manganese, for Antarctic coastal seawaters. Moreover, concentration values indicate that the metals are probably introduced into the water column mostly as particulate metals, although direct inputs of dissolved metals cannot be ruled out. This result agrees with the quite complex dissolved/particulate partitioning previously reported (Grotti *et al.* 2001), and may account for the temporal uncoupling between maximum values of particulate and dissolved metals observed in Antarctic coastal surface waters (Grotti *et al.* 2001). In order to evaluate the contribution of sea ice in determining the trace element concentration in surface waters, the absolute amounts of trace elements in sea ice, in sea ice at the ice-seawater interface and in the 3 m deep underlying layer were computed from raw data (Table V). The values are the sum of particulate and dissolved metal amounts for 1 m² wide area. Percentages of particulate metals are also reported. The distribution between the dissolved and particulate phases reflects the peculiar characteristics of the considered elements and it is influenced by the biological activity, which occurred significantly in the lower portion of the ice core, in both considered periods as well as in December in the superficial waters. It can be noted that the amounts of trace elements "stored" in the sea ice are larger than those found in the underlying seawater (except for lead), showing that sea ice is a significant reservoir of trace metals for the superficial waters during the ice coverage period. Moreover, the amount of elements in sea ice at the ice-seawater interface is a significant fraction of the total metal content in the underlying layer. This is particularly evident for manganese and iron in both the studied periods and for copper in November. In those cases, the mass of elements found in the 10 cm foremost layer of sea ice can almost entirely account for the metal content in the 3 m deep underlying layer, despite 300-fold dilution. Finally, by comparing the estimated amounts of metals in the seawater surface layer in February with the ones in the sea ice in November, it is evident that an extra source of metals working over winter have to be considered. Concerning the particulate metals inside the sea ice, both the concentrations and speciation patterns suggest that resuspended sediments are the probable source, in agreement with the hypothesis of Fitzwater *et al.* (2000) and Sedwick *et al.* (2000). In

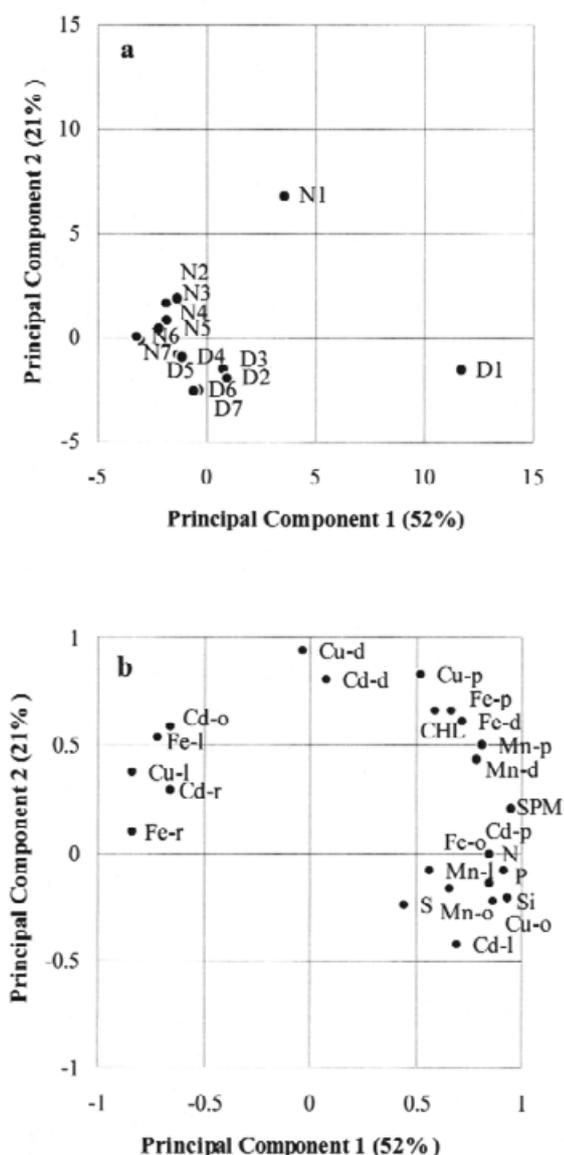


Fig. 7. Principal component analysis results (21%/52%): a. score plot, b. loading plot.

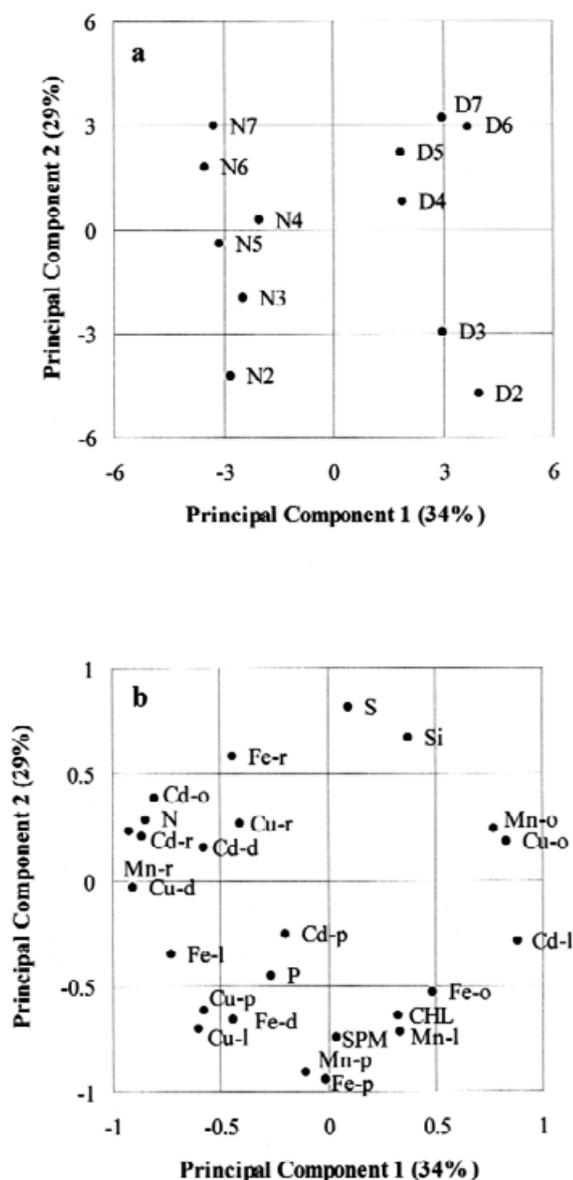


Fig. 8. Principal component analysis results (29%/34%): a. score plot, b. loading plot.

particular, it may be noted that iron speciation in sediments and sea ice particulates (especially at the seawater interface) are very similar (Fig. 5), being characterized by association with the oxidisable fraction and thus probably with organic matter. Iron-complexation by organics should not prevent subsequent removal from seawater by biological uptake, as pointed out by Boye *et al.* (2001), although iron bound in organic particles may not be readily bioavailable.

In order to further investigate the correlation among all the considered parameters, the Principal Component Analysis (PCA) statistical method was employed. In Fig. 7 is reported the PCA that concerns a matrix in which the samples have been considered as *objects* (named N and D, for the samples collected at November and December,

respectively and 1–7 from the bottom to the top of the ice core) and the following parameters as *variables*: salinity (S), nitrate (N), phosphate (P), silicate (Si), Chl *a* (CHL), suspended particulate matter (SPM), particulate metal (Me-p), dissolved metal (Me-d), percentage of metal associated with the labile (Me-l), reducible (Me-r) and oxidisable (Me-o) fractions. Pb data were not inserted due to lacking of data for the samples collected in November (contaminated samples). After autoscaling, two significant components were identified, explaining the 52% and the 21% of the total variance, respectively.

By the analysis of the score plot (Fig. 7a), it can be noted that the ice core portions at the ice-seawater interface (N1 and D1) remarkably differ from the other samples. By considering the loading plot (Fig. 7b), it can be deduced that the ice collected in December (D1) displays the highest values of salinity, nutrients, SPM and particulate metals as well as the highest percentages of iron, copper and manganese associated with the oxidisable fraction and those of cadmium and manganese associated with the labile fraction. This result could indicate the occurring of seawater permeation through the ice pores which supports algal growth and consequent association of trace metals with organic particulate. The sample collected in November (N1) displays high values of Chl *a* as well as of dissolved metals and particulate iron and copper. However, metal incorporation into the organic material shows a different speciation than that found in December, mainly for copper and iron. In fact, by moving from N1 to D1, it can be seen that the percentages of iron and copper associated with the oxidisable fraction increase while decreasing the labile fraction for copper and the reducible fraction for iron. This result was confirmed by further investigating the temporal variation of metal solid speciation. Copper and iron showed significant temporal trends of association with the particles included in the sea ice (Fig. 6). These differences could be ascribed to the temporally-dependent availability of organic ligands within the sea ice, or more likely be the result of processes due to algal or microbial activity. However, additional investigation of the processes occurring in the sea ice and influencing metal speciation is needed in order to clarify the biogeochemical cycling of trace elements and to assess their real bio-availability in the Antarctic coastal environment.

In order to better examine the other samples, N1 and D1 were removed from the dataset and the principal component analysis performed again, identifying two significant components which explain the 34% and the 29% of the total variance, respectively. The object scores and the variable loadings on these components are plotted in Fig. 8. In the score plot, both the vertical profiles and temporal trends can be easily visualized. For both ice cores, by moving from the top (7) to the bottom (2), an increase in SPM, Chl *a*, particulate copper, iron and manganese may be observed together with a decrease in salinity. These trends can be

generally ascribed to transport phenomena occurring along the ice core. Concerning the difference between the sea ice collected in November and December, it should be noted that the discriminant parameters are dissolved copper, cadmium and nitrate, which are lower in December, and the percentages of manganese and copper associated with the oxidisable fraction of SPM, which are higher in December.

A final remark concerns representativeness of the investigated area in comparison to other Antarctic coastal sites. In the framework of PNRA, the coastal area of Terra Nova Bay was systematically investigated by Italian researchers and the main physical and biological features established (Faranda *et al.* 2000). Terra Nova Bay is an 80 x 30 km-wide inlet in the south-western part of the Ross Sea, delimited to the north by the narrow peninsula of Cape Washington and to the south by the Drygalski Ice Tongue. The bay is a continental shelf, with an average depth of about 450 m and greater depths up to 1100 m in the Drygalski basin. The main feature of the region is orography: on the northern side Mount Melbourn is dominant, while to the east the Transantarctic Range is present, which represents the boundary of the polar ice cap and is crossed by outlet glacier reaching the sea. The bay is covered by sea ice for at least nine months of the year. The melting pattern of sea ice reflects that for irradiance: it begins from the south and proceeds towards the north, encountering a certain delay in the coastal zone compared to ice in the open sea. Ice covering dynamic is strongly influenced by the katabatic winds, which form and preserve polynyas persisting during wintertime. The sampling site lays between the coast and the edge of a polynya zone; it is covered from ice approximately until the beginning of January. Finally, dynamic of ice melting influences water column stratification and phytoplankton temporal distribution.

Due to the peculiar characteristic of the site and substantial lack of information on trace element distribution in sea ice at other coastal areas, confident generalization of the results is difficult.

However, the water column depth and closeness to the continental land can be considered common features of Antarctic coastal zones and a certain degree of similarity with respect to trace element distribution and speciation may hence be expected also for other coastal sites.

Finally, results of the environmental monitoring program at the Italian station would exclude significant emission of heavy metals in the atmosphere related to anthropogenic activities (Giuliani *et al.* 2001).

In conclusion, the presented data set can be considered as referred to a natural (uncontaminated) and local situation and it will be fully effective when joined with data sets obtained at other coastal sites.

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