UNIVERSITÀ POLITECNICA DELLE MARCHE
Repository ISTITUZIONALE

Distribution of Cd, Pb and Cu between dissolved fraction, inorganic particulate and phytoplankton in seawater of Terra Nova Bay (Ross Sea, Antarctica) during austral summer 2011-12

This is the peer reviewd version of the followng article:

Original
Distribution of Cd, Pb and Cu between dissolved fraction, inorganic particulate and phytoplankton in seawater of Terra Nova Bay (Ross Sea, Antarctica) during austral summer 2011-12 / Illuminati, S.; Annibaldi, A.; Romagnoli, T.; Libani, G.; Antonucci, M.; Scarponi, G.; Totti, C.; Truzzi, C.. - In: CHEMOSPHERE. - ISSN 0045-6535. - 185:(2017), pp. 1122-1135. [10.1016/j.chemosphere.2017.07.087]

Availability:
This version is available at: 11566/252324 since: 2022-06-01T16:18:37Z

Publisher:

Published
DOI:10.1016/j.chemosphere.2017.07.087

Terms of use:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. The use of copyrighted works requires the consent of the rights' holder (author or publisher). Works made available under a Creative Commons license or a Publisher's custom-made license can be used according to the terms and conditions contained therein. See editor's website for further information and terms and conditions.
This item was downloaded from IRIS Università Politecnica delle Marche (https://iris.univpm.it). When citing, please refer to the published version.

note finali coverpage

(Article begins on next page)

18 April 2024

Distribution of Cd, Pb and Cu between dissolved fraction, inorganic particulate and phytoplankton in seawater of Terra Nova Bay (Ross Sea, Antarctica) during austral summer 2011-12

S. Illuminati*, A. Annibaldi, T. Romagnoli, G. Libani, M. Antonucci, G. Scarponi, C. Totti, C. Truzzi

Dipartimento di Scienze della Vita e dell'Ambiente, Università Politecnica delle Marche, via Brecce Bianche 60131 Ancona

*Corresponding author: Silvia Illuminati, e-mail: s.illuminati@univpm.it

Keywords: metal quotas; metal stoichiometry; seasonal evolution of metals; metal partitioning; phytoplankton; Terra Nova Bay

Abstract

During the austral summer 2011-2012, the metal quotas of Cd, Pb and Cu in the phytoplankton of Terra Nova Bay (TNB, Antarctica) were measured for the first time. Evolution of all the three metal distributions between dissolved and particulate fractions during the season was also evaluated. Metal concentrations were mainly affected by the dynamic of the pack ice melting and phytoplankton activity. In mid-December when TNB area was covered by a thick pack ice layer and phytoplankton activity was very low, all the three metals were present mainly in their dissolved species. When the pack ice started to melt and the water column characteristics became ideal (i.e. moderate stratification, ice free area), the phytoplankton bloom occurred. Cd showed a nutrient-type behaviour with dissolved and particulate fractions mainly influenced by phytoplankton activity. Cd quota showed a mean value of 0.12 ± 0.07nmol L^{-1} (30-100% of the total particulate). Also Cu showed a nutrient-type behaviour, with its quota in phytoplankton varying between 0.08 and 2.1 nmol L^{-1} (20-100% of the total particulate). Pb features the typical distribution of a scavenged element with very low algal content (0.03 ± 0.02 nmol L^{-1}, representing 20-50% of the total particulate). The vertical distribution of this element was influenced by several factors (e.g. pack ice melting, atmospheric inputs), the phytoplankton activity affecting Pb behaviour only partially. Metal:C ratios provide valuable information on the biological requirements for Cd, Pb and Cu, leading us to better understand their biogeochemical cycles.

1. Introduction

The vertical distribution of a metal in Antarctic seawater is related to its biogeochemical cycle, which in turn is influenced by several parameters, i.e. biological activity, atmospheric inputs, mixing and stratification patterns, transport processes, melting of snow and pack ice, glacial input. In this context, marine phytoplankton play a key role. In fact, association with the cycle of growth, sinking and remineralization of phytoplanktonic cells (Collier and Edmond 1984; Morel and Hudson, 1985; Bruland and Lohan, 2003) affects vertical and horizontal distributions of many trace elements in marine systems. Because of its remote location from anthropogenic influence, Antarctica is an ideal site to study the behaviour of trace elements in the environment and the natural processes influencing their distribution between abiotic and biotic components of the marine systems.

Almost all the studies dealing with trace metals and phytoplankton can be classified into two main classes. The first includes studies based on metal-buffered laboratory culture experiments (Morel and Hudson, 1985; Sunda 1989; Santana-Casiano et al., 1995; Sunda and Huntsman, 1998; Sunda and Huntsman, 200; Gonzalez-Davila et al., 2000; Ho et al., 2003; Annett et al., 2008) with the aim to measure trace metal contents–or quotas–of phytoplankton, and to understand the mechanisms of phytoplankton metal uptake, on one hand, and to establish metal toxicity levels on natural phytoplankton community (Echeveste et al., 2014), on the other hand. The second class refers to the metal distribution between dissolved and total particulate fractions. In this case large volumes of seawater were sampled in order to separate the particulate matter, which, therefore, includes both organic and inorganic phases and among the organic one, both phyto- and zoo-plankton (Martin et al., 1976; Bruland et al., 1978; Collier and Edmond 1984; Honda et al., 1987; Bargagli et al., 1996; Dalla Riva et al., 2003). Recently, Twining and co-workers have optimized an alternative approach to measure the composition of individual plankton cells by using the synchrotron X-ray fluorescence microscopy, SXRF (Twining et al., 2003 Twining and Baines 2004; Twining et al., 2011; Twining et al. 2015). They determined cellular quotas of the principal bioactive trace metals (Mn, Fe, Co, Ni, Cu and Zn) in the phytoplankton collected in several oceans worldwide (Twining et al., 2011; Twining et al., 2015).

Despite growing interest in this subject, little is still known about trace metal contents in phytoplankton of the Southern Ocean. This area is considered the largest high-nutrient, low-chlorophyll (HNLC) region in the world, and holds the greatest content of macronutrients in surface waters. Nevertheless, this abundance of macronutrients generally coupled with modest rates of annual net primary productivity, even intense phytoplankton blooms occasionally develop (Arrigo et al., 2004). Generally, an inadequate abundance of trace elements is responsible of this low productivity. Due to its low concentrations in these waters, iron is considered the primary factor limiting phytoplankton productivity in this region (Boyd et al., 2007); on the other hand, an excess of some trace metals, such as Cu or Zn, may inhibit phytoplankton growth, as well (Morel et al., 1994). In addition, this may also affect the distribution of other metals with different biogeochemical behavior and not directly related to biological activity (Capodaglio et al., 1998).

Very few studies reported metal determinations in the organic particulate in Antarctica. Honda et al. (1987) measured metals on planktonic copepods and on krill collected in several sites of the Antarctic and other ocean waters. Bargagli et al. (1996) collected samples of phytoplankton and zooplankton at Terra Nova Bay, by using conical nylon nets with mesh size between 50 µm and 500 µm, determining Cd in the macro-phytoplankton (2.1 ± 0.9 µg g^{-1} dry weight, d.w.). Moreover, Bargagli et al. (1996) and Dalla Riva et al. (2003) reported the metal contents in some species of macro-algae (i.e. *Iridea cordata*, *Phyllophora antarctica*). Twining and Baines (2003) determined by SXRF elemental (P, S, Si, Mn, Ni and Zn) stoichiometries of individual plankton cells collected in the mixed layer of the Pacific sector of the Southern Ocean, evidencing differences in elemental composition for different types of cells (i.e. diatoms were enriched in Mn, Ni, and Zn relative to flagellates).

Here we present trace metal contents (Cd, Pb and Cu) for micro- and nano-phytoplankton collected in the coastal Antarctic area of Terra Nova Bay during the 2011-2012 austral summer, for the first time. In our previous work (Truzzi et al., 2015), we have set-up and optimized an analytical methodology that provides the physical separation of micro- and nano-phytoplankton from the inorganic particulate material, and the subsequent microwave digestion of the algal particulate. The metal distribution between dissolved and particulate fractions was also investigated. Our principal goals were i) to measure the metal quotas of the Antarctic phytoplankton by using a procedure of physical separation set-up by our group; ii) to evaluate the effects of the phytoplankton activity on the metal distribution; and iii) to assess the seasonal evolution of the different metal fractions in the Terra Nova Bay waters.

2. Experimental

2.1. Instrumentation

Laboratory, apparatus, reagents and procedures used in this work were described in detail elsewhere (Truzzi et al., 2015), however a brief summary is reported for the reader.

Clean room laboratories with Class 5 areas (ISO 14644-1, formerly Class 100, US Fed. St. 209e) were available both in Antarctica and in Italy (Illuminati et al., 2015; Illuminati et al., 2016). The voltammetric instrumentation consisted of a Metrohm (Herisau, Switzerland) 746 VA Trace Analyser, equipped with a 747 VA Stand, a Teflon PFA cell, which includes an epoxy-impregnated graphite (Ultra Trace) rotating disk working electrode, an Ag/AgCl/3 M KCl reference electrode (to which all potentials are referred throughout) and a glassy carbon rod counter electrode. A microwave accelerated reaction system (MARS 5) from CEM Corp. (Matthews, NC, USA), equipped with twelve 100-mL HP-500 Plus Teflon PFA (perfluoroalkoxy copolymer) vessels, was used for the mineralization of all samples. A Zeiss Axiovert 25 inverted microscope was used for phytoplankton separation. A Binder (USA) oven model FD 115 was used to dry phytoplankton samples. A Mettler XS205 electronic microbalance (readability 0.01 mg, repeatability SD±0.015 mg) was used for all weighings. The filtration apparatus was Sulfoflo Model 300–4100 from Nalgene (Rochester, New York) equipped with 0.45 µm-pore size membrane-filters (cellulose mixed esters Ø 47 mm, Schleicher & Schuell, Dassel, Germany).

One 20-L GO-FLO bottle from General Oceanics (Florida, USA) was used for seawater collection along the water column. A CTD probe (mod. Ocean Seven 304 from Idronaut, Milan, Italy) and one multi-sensor fluorimetric probe, (mod. C6 from Turner Designs, Sunnyvale, CA, USA) were used to measure temperature, salinity and Chlorophyll a along the water column.

Low-density polyethylene (LDPE) bottles (Kartell, Italy) were used for both storage and subsequent treatments carried out in Italy before voltammetric analysis. LDPE bottles, GO-FLO bottle, cellulose mixed ester filters and all other plastic containers were decontaminated following the procedure reported in Annibaldi et al. (2015) and Illuminati et al. (2015). Briefly, careful and prolonged acid washings were applied using, in sequence, detergent solution, 1:10 diluted analytical grade HNO_3, 1:10 diluted superpure HCl and final storage in 1:1000 diluted superpure HCl until use. Similar acid washings were used for sampling equipment (GO-FLO bottle) and filtration apparatus. Membrane filters were cleaned by soaking twice in 1:10 diluted superpure HCl for one week and stored in 1:1000 diluted superpure HCl. Before use, GO-FLO bottle, filtration apparatus and membrane filters were three-times washed with ultrapure water and in-situ conditioned with seawater before the contact with samples. A procedure similar to LDPE bottles was also used for PFA microwave vessels except for that the final washing was carried out with 5:1 HNO_3/HF solution.

Clean room garments, masks and gloves were worn by the personnel, who followed clean room procedures strictly during all decontamination procedures, sample treatment and analysis phases.

All the reagents used for the sample treatment and storage were of ultrapure grade (UpA from Romil, Cambridge, UK). Ultrapure water was of Milli-Q grade from Millipore (Bedford, MA, USA). Research-grade nitrogen (purity ≥99.999 %) was from Sol (Monza, Italy). Certified reference materials NASS-6 (open ocean seawater) from National Research Council of Canada (NRCC, Ontanio, Canada) and BCR-414 (plankton) from Joint Research Centre (JRC, Bruxelles, Belgium) were used for accuracy tests.

2.2. Field sampling and sample treatment

Terra Nova Bay (TNB) is a wide inlet occupying an area of about 6000 km^2 in the western region of the Ross Sea, along the Victoria Land coast. The bay has one of the deepest continental shelf of the Ross Sea: the mean depth is 450 m, but it is deeper close to the coast and exceeds 1000 m in the central part (Accornero et al., 2003; Cappelletti et al., 2010). The main feature of TNB is a persistent coastal polynya. Katabatic winds, which originate over the Antarctic continental plateau and blow offshore, form the wind-driven flaw polynya as they shift the newly formed ice far from the coasts (Bromwitch and Kurtz 1984). Maximum of both micro-phytoplankton abundances and biomass in late December, followed by a decrease in January and a secondary peak in February characterize this area (Nuccio et al., 2000). The TNB polynya has been intensely investigated by Italian researchers in recent years, studying the plankton community (Nuccio et al., 2000; Saggiomo et al., 2002; Accornero et al., 2003; Arrigo and Van Dijken 2004; Fonda Umani et al., 2005) the physical structure of the water column (Cappelletti et al., 2010); the nutrient and trace element distribution in sea water and in marine organisms (Capodaglio et al., 1989; Capodaglio et al., 1991a; Capodaglio et al., 1991b; Capodaglio et al., 1994; Scarponi et al., 1995; Scarponi et al., 1997; Catalano et al., 1997; Capodaglio et al., 1998; Scarponi et al., 2000; Grotti et al., 2001; Frache et al., 2001; Abollino et al., 2001; Dalla Riva et al., 2003; Corami et al., 2005; Illuminati et al., 2010; Annibaldi et al., 2011a; Rivaro et al., 2012; Illuminati et al., 2016).

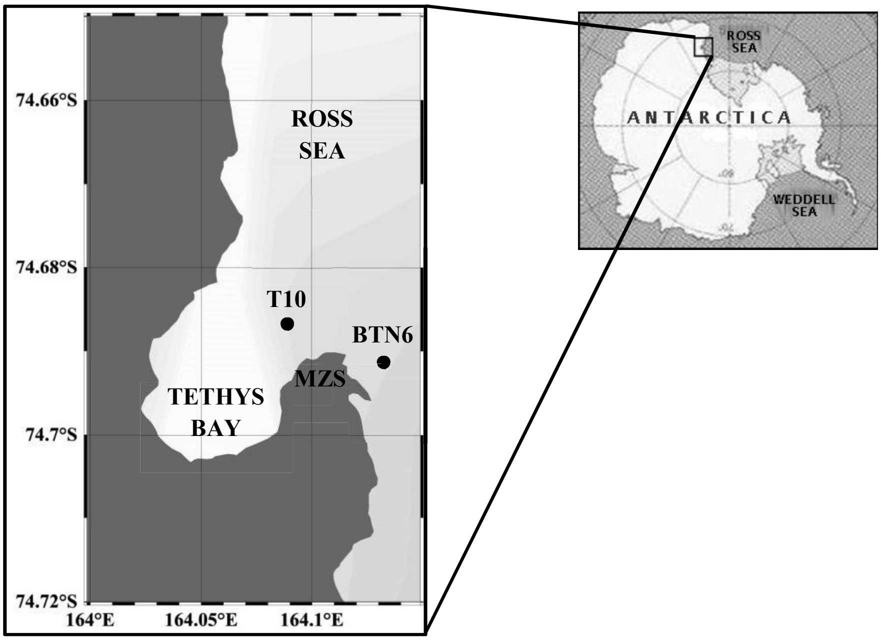


Fig. 1. Map of the Terra Nova Bay area showing the location of the main Italian Station "Mario Zucchelli" (MZ) and the two sampling sites, T10 and BTN6, during the 2011-2012 Antarctic campaign

During the 2011-2012 austral summer, Antarctic sea water samples were collected along the water column in two sites of Terra Nova Bay (Ross Sea, Fig. 1). The first sampling was carried out at mid-summer (December, the 15th, 2011) in a site located at the entry of a TNB cove (called Tethys Bay) close to the Italian Station "Mario Zucchelli" (MZS) nearby to Northern Foothills (site T10, bathymetry 240m, coordinates 74°41'10" S – 164°05'20" E). The other two samplings were carried out at the end of summer (the first in January, the 20th and the second one in February, the 5th, 2012) in the same area, but located in front of MZS (site BTN6, bathymetry 150m, coordinates 74°41'28" S – 164°07'97" E) and very close to the previous site. Seawater samples of mid-December were collected from a hole in the ice, since the presence of the pack-ice which covered most of the TNB area, in this period. The other two samplings were carried out after the pack-ice melting, from the research vessel "R/V Malippo".

Samples were collected by a 20-L GO-FLO bottle at three different depths: 5 m, fluorescence-maximum depth (varying between 8 and 15 m) and 100 m. In Italy, sea water samples were divided in various aliquots (~500 mL) that were subjected to different treatments in order to obtain the different metal fractions. The first aliquot was acidified (raw sample) with ultrapure HCl (2:1000, pH ~2) for the determination of the total metal concentration (M_{tot}). A second aliquot (15-100 mL of the raw sample) was not acidified and subjected to a procedure previously set-up by our group (Truzzi et al., 2015) for the separation of phytoplankton from the "non-living" particulate, in order to determine the metal content–or quota–of phytoplankton (M_{phyto}). A third aliquot (~500 mL) was filtrated through 0.45-µm pore size membrane filter and then acidified with ultrapure HCl (2:1000, pH ~2) for the determination of the dissolved metal content (M_{diss}).

The physical separation of the phytoplankton from the non-living particulate was reported in detail in Truzzi et al., 2015. Briefly, an aliquot of the sample (taken after a complete homogenization) was poured a little at a time in the Ütermohl chamber. After that, the phytoplankton cells were sucked with a modified Pasteur (to have the diameter of the capillary of the same order of magnitude as the micro algal cells) connected to a cell isolator. The diameter of phytoplanktonic isolated cells varied in the range of micro and nano phytoplankton (2-40 µm). For each seawater sample, phytoplankton isolation was performed on three aliquots. To assure the representativeness of the micro and nano phytoplankton community, at least 100 cells were isolated per each aliquot, according to Lund et al. (1958) and Rott et al. (2007). Therefore, volume of seawater sub-samples observed at the inverted microscope for phytoplankton isolation varied from 15 mL to 100 mL.

Before analysis, all the samples were subjected to microwave digestion after the addition of 1:1000 ultrapure H_2O_2, in order to destroy organic matter, to leach bound metals, and to avoid possible adverse effects on the voltammetric determination (Kolb et al., 1992; Truzzi et al., 2015). Samples were irradiated at 100% power (300 W) for 36 min to reach a temperature of 135°C, with a hold time of 2 min, and then they were further irradiated to reach a temperature of 185°C in 18 min, with a hold time of 4 min. A cooling step of 15 min followed the microwave digestion.

Total particulate metal concentrations ($M_{totpart}$) were obtained by difference between the total and the dissolved concentrations. In our previous work (Annibaldi et al., 2011b), we tested the validity of the differential procedure $Me_{tot} – Me_{diss}$, on seawater samples through direct determination of the metal particulate content and comparing the results with the computed one. Results demonstrated the consistence between the total content calculated by summing the dissolved and particulate concentrations and the total content measured directly on the raw sample solution.

Metal stoichiometries were also calculated by normalizing trace metal quotas to carbon, as proxy of the biomass according to Twining et al., 2015. Cellular C was calculated from the bio volume estimate for each cell, using the equation of Menden-Duer and Lessard (2000).

Trace metal concentrations in the non-living particulate fraction (M_{noliv}) were obtained by difference between total computed particulate and phytoplankton concentrations.

2.3. Metal determination

Metals (Cd, Pb and Cu) in seawater and in phytoplankton samples were determined simultaneously, by using the Square Wave Anodic Stripping Voltammetry (SWASV), in background-subtraction mode, according to procedures set-up and optimized in our previous work (Truzzi et al., 2002; Truzzi et al., 2015). Briefly, the thin mercury film electrode (TMFE) was prepared by electrochemical deposition from 6×10^{-5} mol L^{-1} $Hg(NO_3)_2$ and 1.2×10^{-4} mol L^{-1} KCl solution (deposition potential −1000 mV; deposition time 20 min) (Truzzi et al., 2008; Illuminati et al., 2013). Then, using 10-mL sample digested solutions purged with N_2, the metal depositions were carried out at a potential of −950 mV with an electrode rotation of 3000 rpm. After a 30-s quiescent time, the anodic stripping voltammetric scan was carried out from −950 mV to a final potential of −100 mV in SWASV mode with the following instrumental parameters: frequency 100 Hz; square-wave amplitude 25 mV; potential step height 8 mV; step time 100 ms; current sampling time 3 ms. At the end of the scan, the electrochemical cleaning of the mercury film was carried out with the potential held at −150 mV for 5 min and the rotation at 3000 rpm. The background voltammograms to be subtracted were obtained before sample analysis by applying an equilibration potential of −975 mV and an equilibration time of 7.5 s. To verify the sample-to-sample repeatability at least three replicates on each sample were carried out and the mean value was used for the subsequent analysis. The quantification was carried out using the multiple standard addition method with at least three standard additions (and two measurements for each addition). All results were blank-corrected.

2.4. Laboratory blanks and accuracy

Repeated SWASV measurements of the laboratory blank were carried out during the period of work, with deposition times of 20 min. Measurements concerned both the solution of ultrapure HCl 2:1000 diluted with ultrapure water (blank solution) and the digested solution of 2:1000 diluted ultrapure HCl with the addition of 1:1000 diluted ultrapure H_2O_2 after microwave digestion (blank digestion). Results show that generally no voltammetric signals are observed for Cd and Cu, indicating metal contents below the detection limit (LOD) of the technique computed on the basis of the regression equation that fit the standard calibration curve (see for details Truzzi et al., 2014a, 2014b) for 20 min deposition time, i.e. about 1-3 pmol L^{-1}, with the exception of Pb for which an instrumental blank signal of ~10 pmol L^{-1} (Annibaldi et al., 2009; Annibaldi et al., 2011b) was observed.

Phytoplankton separation from inorganic particulate was carried out under microscope and sucking with a Pasteur pipette. Considering that all these manipulations expose samples to possible contamination, further laboratory blank analyses were carried out in order to evaluate a “separation-procedure” blank to be subtracted to the metal concentrations measured in the algal particulate. The blank contributions to the metal concentrations in the isolated phytoplankton represent quite high percentages. In particular, the values, reported as median (interquartile range), are 22% (17–30%) for Cd, 50%(40–70%) for Pb, and 28%(8–45%) for Cu. The highest values referred to the lowest sample concentrations, in particular for Cd and Pb. This result is considered quite normal in the ultra-trace determinations involved in the analyses of the remote samples of this work.

To ascertain accuracy and to assure comparability of data produced during metal determinations, analytical quality control of Cd, Pb and Cu measurements were carried out by analysing the NASS-6 certified reference material

Tab. 1. Accuracy tests on the NASS-6 certified reference material for open sea waters and on the BCR-414 certified reference material for plankton.

	Metal concentrations					
	NASS-6, ng L^{-1}			BCR-414, μg/g		
	Cd	Pb	Cu	Cd	Pb	Cu
Experimental valuses (*n* = 5-7)	30 ± 4	6.0 ± 0.4	270 ± 39	0.39±0.02	3.8±0.2	28.3±0.6
Certified values	31 ± 2[a]	6 ± 2[a]	248 ± 25[a]	0.383±0.014[b]	3.97±0.19[b]	29.5±1.3[b]
Δ%	+4	+0	–9	–2	+4	+4

[a] ±expanded uncertainties

[b] ±half-width of the 95% confidence intervals

(National Research Council of Canada, 1998) for seawater samples and the BCR-414 certified reference material for phytoplankton samples (European Commission, 2007). Certified reference materials were pre-treated and analysed following the same procedures applied to real samples. The results of the systematic measurements carried out on reference materials during the entire period were reported in Table 1. As shown by the table, concentrations of Cd, Pb and Cu measured in the collected samples were in good agreement with certified reference values within the experimental errors, showing a good accuracy of all the measurements.

2.5. Ancillary measurements

2.5.1. CTD data processing

At each sampling site, the physical structure of the water column was profiled from the surface down to 100 m, with a vertical resolution of 0.5 m, using a CTD probe fitted with a fluorometer for the chlorophyll-a vertical distribution.

The salinity is expressed according to the UNESCO practical salinity scale, PSS 1978 (UNESCO, 1981).

Temperature and salinity data obtained from the CTD measurements were used to calculate the density (ρ), and the water column stability. The latter is proportional to the Brunt-Värsälä buoyancy frequency $N^2(z)$, which represents the strength of density stratification and it is defined by the equation

$$\mathrm{N}^2(z) = -\frac{g}{\rho(\mathrm{z})}\frac{\Delta\rho(\mathrm{z})}{\Delta\mathrm{z}}$$

where g is the gravitational acceleration, ρ is the mean density averaged over Δz depth interval, typically, equal to 1 m (Fofonoff and Millard, 1983; Agusti and Duarte 1999; Garcia et al., 2008). The depth at which the Brunt-Värsälä buoyancy frequency was estimated to be maximal represents the Upper Mixed Layer (UML), which also corresponds approximately to the middle of the pycnocline. The value of $N^2(z)$ was also taken as a stability index of the water column (i.e. what it is commonly called pycnocline strength). The depth at the base of the pycnocline corresponds to the top of the winter water and it is considered to be unaffected by the summer dilution or phytoplankton assimilation (Fabiano et al., 1993).

2.5.2. Quali- quantitative analysis of phytoplankton

At each station, discrete samples were collected at different depths for the quali-quantitative analysis of phytoplankton carried out following the Utermöhl method (Edler and Elbrächter, 2010). Immediately after collection seawater samples were preserved in dark glass bottles by adding 0.8% formaldehyde neutralized with hexamethylenetetramine and stored at 4 °C. In Italy, 40-100 mL sub-samples were homogenized, settled in a cylinder-chamber complex and then observed using the inverted microscope. During counting procedure, 30 random fields were examined at 400x magnification. All phytoplankton cells larger than 2 μm were identified and counted. Then the entire chamber was observed at 200x to assess the larger and less frequent organisms. Bio-volume was measured to evaluate the biomass (expressed in μgC L^{-1}) following Menden-Deuer and Lessard (2000).

3. Results

3.1. Environmental parameters.

Data on the master hydrographic variables and phytoplankton community obtained at TNB during the sampling period (austral summer 2011-2012) are showed in Figures 2-3 and Table 2.

3.1.1. Hydrography of the study area

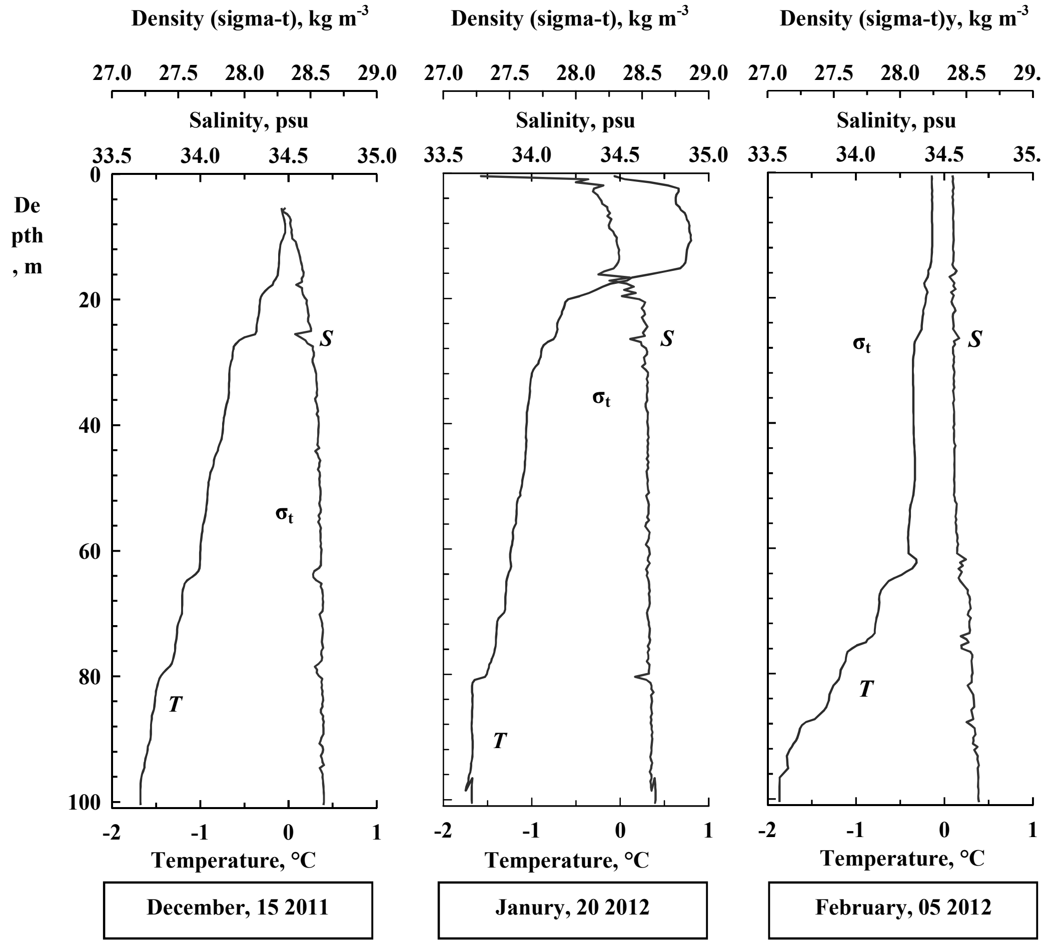
The seawater samples investigated in the present work have different origins in terms of the collection period. In fact, during most of the year, TNB is to a great extent ice covered (Cappelletti et al., 2010). Typically, the thickness of the pack ice is approximately 2 m and it reaches maximum extension in September. During spring and summer the pack ice starts to melt and, generally, from mid-December, TNB area is ice free. The 2011-2012 field campaign was atypical in this respect. The pack ice melted very late in summer (from mid-January) and the area was completely free from ice only at the end of January.

Temperature and salinity varied from −1.90°C to +0.80°C and from 34.38 psu to 34.71 psu, respectively (Fig. 2). Density anomaly computed from temperature and salinity data varied from 27.07 kg m^{-3} to 28.90 kg m^{-3}.

During sampling in mid-December the pack ice covered the most part of Terra Nova Bay. In this period the temperature gradually decreased in the upper 100 m from −0.04°C to −1.68°C, while no stratification of the water column was observed, salinity and density increasing very gradually with depth (Fig. 2).

Wide ice-free areas started to appear from mid-January, with the subsequent increasing of the solar radiation incident in the surface waters. As a result, the surface temperature was warmer (from −0.59°C to +0.63°C) and the salinity (34.25 – 34.47 psu) and density (27.78 – 27.65 kg m^{-3}) were lower, due to sea-ice melting (Fig. 2). Consistent with the higher temperatures and salinities of the surface waters, the water column was stratified with an UML 20-m deep and a quite high strength of the pycnocline ($N^2(z) = 71.6 \times 10^{-4}\ s^{-2}$).

The stratification of the water column following the pack-ice melting is typical of TNB (Scarponi et al., 1997; Catalano et al., 1997; Rivaro et al., 2012) and it persists until February. In the 2011-2012 Antarctic expedition ,seawater temperature reduced to -0.35 ± 0.18°C, and the thermocline extended deeper in the water column down to ~80 m (Fig. 2). Moreover, the UML was deeper (~60 m) than in January, but the pycnoclyne was less strong ($N^2(z) = 39.6 \times 10^{-4}\ s^{-2}$) with salinities and densities quite stable in the water column. By consequence, the water column during the third sampling was less stratified, the conditions becoming to be quite typical of the incoming winter season.



December, 15 2011

Janury, 20 2012

February, 05 2012

Fig. 2. Vertical profiles of temperature (*T*), salinity (*S*) and density (σ_t) measured at Terra Nova Bay (sites T10 and BTN6) during the sampling dates of December, the 15th 2011, January, the 20th 2012, February, the 5th, 2012.

3.1.2. Chlorophyll-a and phytoplankton community

Chlorophyll-a (Chl-a) concentrations measured during the 2011-2012 Antarctic summer ranged from ~0.1 to 4.0 mg m^{-3} (Fig. 3). A clearly defined deep chlorophyll maximum (DCM), which closely followed the thermocline, was observed throughout the sampling period (excepting in December, when the DCM was less pronounced). In mid-December, the Chl-a maximum concentration was high at the DCM (~2.3 mg m^{-3}) and very shallow (8-10 m depth), then in January, it decreased (~1.5 mg m^{-3}) and deepened (~20-m depth). Greatest overall Chl-a content occurred in early February with values 50% higher than in mid-December, and with a deeper extension of the increased Chl-a concentration (down to 50-60 m).

At 100 m-depth, Chl-a decreased to values close to zero, except in mid-December, when a secondary Chl-a peak (mean value 2.2 ± 0.7 mg m^{-3}, as at the surface) was observed (Fig. 3).

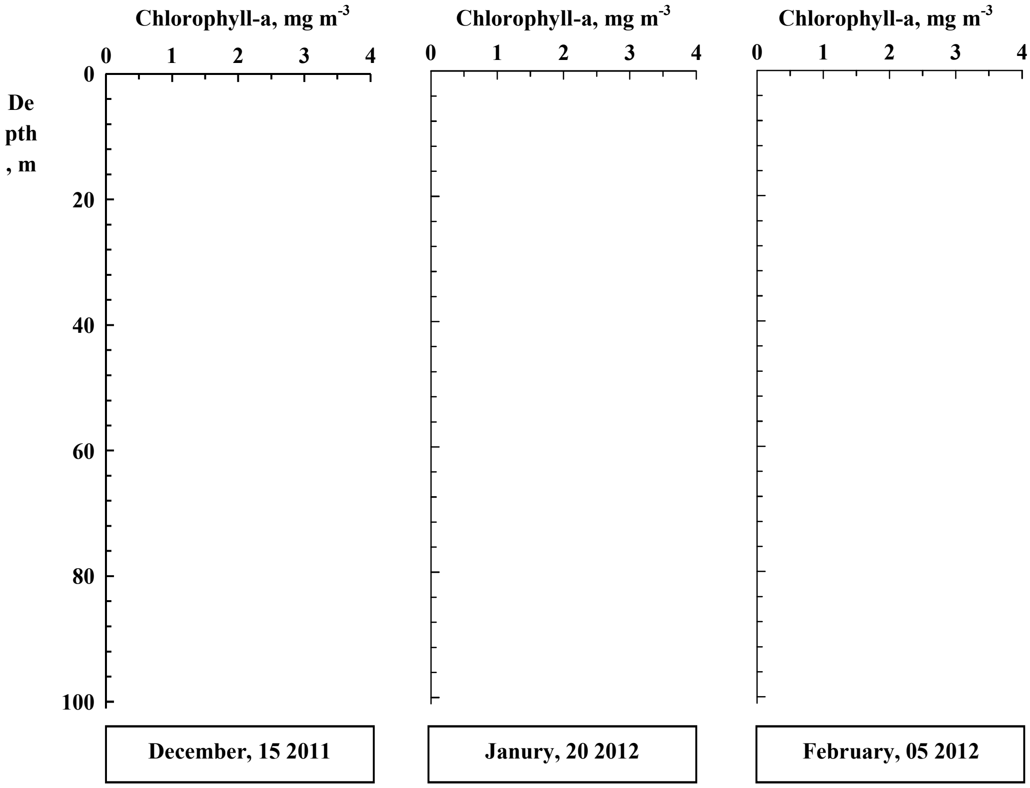


Fig. 3. Vertical profiles of chlorophyll-a (Chl-a) concentrations measured at Terra Nova Bay (sites T10 and BTN6) on December, the 15th 2011, January, the 20th 2012 and February, the 5th, 2012.

From the quali-quantitative analysis of phytoplankton, fifty taxa were identified and were grouped in the major groups of diatoms (Bacillariophyceae), dinoflagellates, phytoflagellates and cyanobacteria. Phytoplankton group abundance and biomass values are reported in Table 2.

Total phytoplankton abundance ranged between 1.6×10^5 cells L^{-1} and 3.6×10^6 cells L^{-1}, with a mean value of 1.8×10^6 cells L^{-1} (Tab. 2). The total phytoplankton abundance showed a general increase in surface waters during the Antarctic summer, with maximum values on early February (~3.4×10^6 cells L^{-1}, Tab. 2).

The most abundant component was diatoms and phytoflagellates. Diatoms represented ~70% of the total abundance ranging between 6.2×10^4 cells L^{-1} and 3.0×10^6 cells L^{-1} (Tab. 2). Among identified diatoms, the most abundant taxa were *Fragilariopisis* cf. *curta, Chaetoceros* spp., *Pseudo-nitzschia subcurvata,* and *Rhizosolenia* spp. In the upper 15 m of the water column, diatom abundance increased during summer, with values that reached a maximum in early February. Considering the vertical distribution, at station T10 (mid-December 2011), an increase of abundance was observed in the deepest waters, the highest values occurring at 100 m. On the contrary, at station BTN6 (January and February, 2012) the highest abundances were observed at the surface (within 15 m), while at the 100-m depth diatom concentrations were two order of magnitude lower.

Phytoflagellates occurred with abundance values ranging from 8.9×10^4 cells L^{-1} to 1.6×10^6 cells L^{-1}, representing on average ~30% of the total phytoplankton abundance (Tab. 1). Phytoflagellates were mainly represented by cryptophyceans, prasinophyceans, silicoflagellates (*Dictyocha speculum* and *Octactis octonaria*) and undetermined phytoflagellates. A seasonal peak of phytoflagellate abundance was observed in January in correspondence of the DCM at 15-m depth, while in February abundance decreased to very low values. Their contribution to the total abundance did not show any marked variation in the three sampling periods.

Dinoflagellates represented a very small fraction (on average ~4%) of the total phytoplankton abundance with values ranging from 2.0×10^3 to 3.5×10^5 cells L^{-1}, the highest value observing in December at the DCM.

Tab. 2. Abundances (× 10^6 cells L^{-1}) and biomass (μg C L^{-1}) of the main phytoplanktonic taxa identified during the austral summer 2011-2012 in the studied sites of Terra Nova Bay (Western Ross Sea). Data are reported as means ± 10% SD for all the phytoplankton taxa.

Sampling station, date and depth (m)	Bacillariophyceae		Dinoflagellates		Phytoflagellates		Total	
	Abundance 10^6 cells L^{-1}	Biomass μg C L^{-1}	Abundance 10^6 cells L^{-1}	Biomass μg C L^{-1}	Abundance 10^6 cells L^{-1}	Biomass μg C L^{-1}	Abundance 10^6 cells L^{-1}	Biomass μg C L^{-1}
T10								
15/12/2011								
5 m	0.19	27	0.007	9.2	0.27	0.90	0.47	37
8 m	0.45	42	0.35	46	0.88	3.7	1.7	92
100 m	0.99	68	0.002	1.1	0.15	0.40	1.1	70
BTN6								
20/01/2012								
5 m	2.0	102	0.026	60	0.45	2.4	2.4	164
15 m	1.8	83	0.064	46	1.6	4.4	3.6	133
100 m	0.062	6.0	0.011	4.7	0.089	0.20	0.16	11
BTN6								
05/02/2012								
5 m	3.0	716	0.10	170	0.27	0.80	3.4	887
15 m	2.8	369	0.076	72	0.26	0.70	3.2	442
100 m	0.066	6.1	0.008	7.6	0.21	0.60	0.28	14

Dinoflagellates were dominated by several *Protoperidinium* spp. and undetermined naked and thecate forms. Maximum abundances occurred at the DCM except in February when highest values occurred at the surface. The main peak of the dinoflagellate abundance was observed in mid-December at the DCM, even if a secondary and small maximum occurred in February (Tab. 2).

A sporadic presence of filamentous cyanobacteria (Oscillatoriales) was also recorded.

Considering the total phytoplankton biomass, a trend similar to that of abundances can be observed, with a more evident increase during summer and a general decrease through the water column (Tab. 2). Also in this case, the large contribution to the total biomass was produced by diatoms, with a proportion varying from ~40% to ~97% of the total. Dinoflagellates represented a variable fraction (from ~2% to ~50%), while phytoflagellates contributed for a few percent (from ~0.2 to ~4%) to the total biomass, even if they represented the most abundant phytoplankton group, after diatoms.

3.2. Metal distribution

Results regarding the total concentrations of metals in seawater and their distribution between dissolved and particulate fractions, and among the latter the distributions between algal and inorganic phases, are reported in Tables 3, 4 and 5. Seasonal variation of the studied metals are reported in Fig. 4, and total, dissolved, inorganic particulate and phytoplankton particulate concentrations measured in December, January and February are given for each element.

3.2.1. Cadmium

Cd showed a total concentration that ranged from ~0.3 to ~0.9 nmol L^{-1} (mean ± SD, 0.55 ± 0.21 nmol L^{-1}, Tab. 3). At the surface (upper 15 m), Cd_{tot} decreased during summer by about 50%, ranging from ~0.6 to ~0.3 nmol L^{-1}. At the depth of 100 m an opposite trend was observed, with values increasing of ~30% in February (from ~0.6 to ~0.9 nmol L^{-1}). Considering the water column, Cd_{tot} was quite constant at mid-December, while in January and February, it showed an increasing trend from DCM to 100-m depth where it reached values 40-70% higher than at the surface (Fig. 4a).

Dissolved Cd represented a remarkable fraction (50-100%) of the total concentration with values ranging from ~0.1 to ~0.9 nmol L^{-1} (0.46 ± 0.27 nmol L^{-1}, Tab. 2). During summer and along the water column, Cd_{diss} followed a trend similar to that of Cd_{tot}. In mid-December, Cd was mainly present in its dissolved forms, representing ~90% of the total. In January and February, at the surface, Cd_{diss} decreased both in absolute and in relative terms, with values that were 40-

60% of the total, while at the depth of 100 m, it increased greatly, reaching concentrations close to that of the Cd_{tot} (Fig. 4a).

Cd in the particulate matter represented a variable fraction of the total content (20-50%) and it was almost totally distributed in the algal fraction, with values ranging between 0.03 and 0.18 nmol L^{-1}. In mid-December, with the presence of the pack ice, particulate Cd was quite low (8-15% of Cd_{tot}) and remained approximately constant with depth. In this period, Cd_{phyto} was ~30% of the total particulate at the surface and increased with depth to values close to $Cd_{totpart}$. In January-February, $Cd_{totpart}$ increased at the surface and it was entirely associated to phytoplankton cells. At the depth of 100 m, $Cd_{totpart}$ was not detectable.

Cd stoichiometry, expressed as Cd:C ratio, ranged between ~15 and ~3 µmol mol^{-1} (Tab. 3). Seasonal variation and vertical gradient in this ratio was observed throughout the field campaign. At the surface, Cd:C remained practically constant with average values of ~13 µmol mol^{-1} until February, where an 80% drawdown of the ratio was recorded. A clear seasonal variation was noticeable also in the Cd:C vertical profile. While during summer, Cd:C remained practically constant within the stratified layer, even at the DCM; in February it increased by ~50% matching the increase in phytoplankton abundance. At 100-m depth no cells were detected, excepting in mid-December, where the Cd:C was slightly lower (~70%) than the surface.

Tab. 3. Cadmium distribution between total concentrations, dissolved, total particulate, inorganic particulate and phytoplankton particulate fractions measured during the austral summer 2011-2012 in the three studied sites of Terra Nova Bay (Western Ross Sea). Cd:C ratios were also reported. Data reported as mean ± SD of at least three measurements.

Sampling station, date and depth (m)		Cd concentration, nmol L^{-1}					Cd:C ratios phytoplankton µmol mol^{-1}.
		Total	Dissolved (% *vs* total)	Total particulate[a] (% *vs* total)	Inorganic particulate[a]	Phytoplankton particulate (% *vs*. Tot part.)	
T10 15/12/2011	5	0.60 ± 0.02	0.51 ± 0.02 (85%)	0.09 ± 0.03 (15%)	0.058 ± 0.03	0.03 ± 0.01 (33%)	11.4 ± 0.5
	8	0.66 ± 0.02	0.58 ± 0.02 (88%)	0.08 ± 0.03 (12%)	<d.l.	0.08 ± 0.01 (100%)	12.2 ± 0.4
	100	0.65 ± 0.02	0.60 ± 0.02 (92%)	0.05 ± 0.03 (8%)	0.006 ± 0.039	0.04 ± 0.01 (~100%)	8.0 ± 0.4
BTN6 20/01/2012	5	0.44 ± 0.03	0.28 ± 0.02 (64%)	0.16 ± 0.04 (36%)	<d.l.	0.18 ± 0.02 (~100%)	15.3 ± 0.4
	15	0.44 ± 0.01	0.28 ± 0.04 (64%)	0.16 ± 0.04 (36%)	0.02 ± 0.04	0.14 ± 0.02 (88%)	14.5 ± 0.4
	100	0.72 ± 0.04	0.72 ± 0.03 (100%)	<d.l. (0%)	<d.l.	<d.l.	<d.l.
BTN6 05/02/2012	5	0.29 ± 0.01	0.12 ± 0.01 (41%)	0.17 ± 0.01 (59%)	<d.l.	0.18 ± 0.04 (100%)	2.8 ± 0.3
	15	0.25 ± 0.02	0.12 ± 0.01 (48%)	0.13 ± 0.02 (52%)	<d.l.	0.17 ± 0.04 (~100%)	5.4 ± 0.3
	100	0.90 ± 0.03	0.90 ± 0.02	<d.l.	<d.l.	<d.l.	<d.l.

	(100%)	(0%)	

[a] ±SD computed as the square root of the sum of variances

3.2.2. Lead

Total Pb concentration ranged from ~0.2 to ~0.5 nmol L^{-1}, with a mean ± SD of 0.31 ± 0.11 nmol L^{-1} (Tab. 4). A general increase of Pb_{tot} was observed during summer, both in surface and deep waters (Fig. 4c). At the beginning of the austral summer, and in presence of a good stability of the water column, Pb_{tot} did not vary with depth. When the pack ice melted, Pb_{tot} decreased in correspondence of the fluorescence maximum of a percentage that increased during summer (from ~25% in January to ~50% at the beginning of February). At the depth of 100 m, values were comparable to those at the surface.

Dissolved Pb showed mean concentrations of 0.21 ± 0.10 nmol L^{-1} and represented a fraction variable between ~40% and ~100% of the Pb_{tot} (Tab. 4). Contrary to the total, dissolved Pb remained almost constant at the surface, during summer, while it increased with depth, excepting in December where Pb_{diss} remained constant along the water column, as well as Pb_{tot} (Fig. 4b). Therefore, the contribution of Pb_{diss} to the total content decreased during summer, and increased with depth. At the 100-m depth all the Pb was present as dissolved species (Tab. 4).

Pb quotas in phytoplankton represented a variable fraction of both the total (10-20%) and the total particulate (20-50%), with concentrations that ranged from values close to the detection limit to 0.06 nmol L^{-1} (mean ± SD, 0.03 ± 0.02 nmol L^{-1}, Tab. 4). At the surface, a general increase of Pb_{phyto} was observed during summer, reaching values which represented ~20% of the Pb_{tot} at the end of the season. Variable vertical gradient of Pb_{phyto} was observed during the sampling period (Fig. 4b). In mid-December, in presence of the pack ice, Pb_{phyto} increased in the upper 10 m, then it remained almost constant down to the 100-m depth, with values being ~10-15% of the total and ~40% of the total particulate. When the pack ice melted (January), Pb_{phyto} showed a maximum both in absolute and in relative terms, at the DCM, while in February Pb quota was quite constant (~0.04 nmol L^{-1}) within the stratified layer, but its percentage to the total particulate increased with depth (from ~19% to ~60%). Both in January and in February, at the depth of 100 m, Pb quotas were not detectable (Tab. 4).

Pb:C in phytoplankton showed low values, ranging from ~0.8 to ~6 µmol mol^{-1}. It showed a peak in January, while it decreased to values close to zero, when the phytoplankton bloom occurred in February. Through the water column, Pb:C ratio generally reached the highest value at the DCM, excepting in December, when, the maximum of Pb:C was observed at the 100-m depth. In January and February, at the depth of 100 m Pb was absent in the phytoplankton cells.

Tab. 4. Lead distribution between total concentrations, dissolved, total particulate, inorganic particulate and phytoplankton particulate fractions measured during the austral summer 2011-2012 in the three studied sites of Terra Nova Bay (Western Ross Sea). Pb:C ratios were also reported. Data reported as mean ± SD of at least three measurements.

Sampling station, date and depth (m)		Pb concentration, $nmol\ L^{-1}$					Pb:C ratio in phytoplankton $\mu mol\ mol^{-1}$
		Total	Dissolved (% *vs* total)	Total particulate[a] (% *vs*. total)	Inorganic particulate[a]	Phytoplankton particulate (% *vs*. Tot part.)	
T10 15/12/2011	5	0.23 ± 0.02	0.19 ± 0.01 (83%)	0.04 ± 0.02 (17%)	0.04 ± 0.02	<d.l.	<d.l.
	8	0.20 ± 0.01	0.15 ± 0.01 (75%)	0.05 ± 0.01 (25%)	0.03 ± 0.01	0.02 ± 0.01 (53%)	3.0 ± 0.5
	100	0.21 ± 0.02	0.14 ± 0.01 (67%)	0.07 ± 0.02 (33%)	0.04 ± 0.02	0.03 ± 0.01 (43%)	6.0 ± 0.4
BTN6 20/01/2012	5	0.44 ± 0.03	0.19 ± 0.01 (43%)	0.25 ± 0.03 (57%)	0.21 ± 0.04	0.04 ± 0.03 (16%)	3.4 ± 0.8
	15	0.33 ± 0.01	0.17 ± 0.01 (52%)	0.16 ± 0.01 (48%)	0.10 ± 0.01	0.06 ± 0.01 (38%)	6.2 ± 0.3
	100	0.45 ± 0.03	0.43 ± 0.02 (98%)	0.02 ± 0.04 (4%)	0.02 ± 0.04	<d.l.	<d.l.
BTN6 05/02/2012	5	0.43 ± 0.01	0.17 ± 0.03 (39%)	0.26 ± 0.03 (61%)	0.21 ± 0.05	0.05 ± 0.04 (19%)	0.79 ± 0.80
	15	0.20 ± 0.02	0.13 ± 0.02 (65%)	0.07 ± 0.03 (35%)	0.03 ± 0.04	0.04 ± 0.03 (57%)	1.3 ± 0.8
	100	0.32 ± 0.04	0.31 ± 0.03 (97%)	0.01 ± 0.05 (3%)	0.01 ± 0.05	<d.l.	<d.l.

[a] ±SD computed as the square root of the sum of variances

3.2.3. Copper

Total Cu concentration ranged from ~3 to ~5 nmol L^{-1} with a mean and standard deviation of 4.0 ± 0.7 nmol L^{-1}(Tab. 5). During summer, Cu_{tot} did not show great variations both at the surface and in deep waters, while it experienced a decrease at the DCM. In particular, in mid-December, with the presence of the pack ice, Cu_{tot} was constant within the upper 10 m and higher by ~20% at 100 m. Then, when the TNB area was free from ice (in January and February), in the correspondence of DCM, Cu_{tot} decreased of about 20% with respect to the surface, while deep waters showed values 15-20% higher than in the surface (Tab. 5, Fig. 4c).

Dissolved Cu was a remarkable fraction (from ~50% to ~90%) of Cu_{tot}, with mean ± SD of 2.8 ± 1.2 nmol L^{-1} (Tab. 5). During the season, a general decrease (~60%) of the surface concentration was observed (Fig. 4c). The contribution of Cu_{diss} to Cu_{tot} also decreased, passing from ~80% of the total in mid-December to ~50% from mid-January. At the depth of 100 m, dissolved concentration remained almost constant during the season. Through the water column, Cu_{diss} showed a trend similar to that of Cu_{tot}, but with a more marked decrease in the surface (Fig. 4c). In mid-December,

Cu_{diss} was constant within the upper 10 m of the water column, while, at the depth of 100 m it was ~30% higher than the surface values. Also the percentage of Cu_{diss} *vs*. Cu_{tot} slightly increased with depth (~75% to 87%). In January and February, within the stratified layer, Cu_{diss} greatly decreased both in absolute and in relative terms with values that were 50% of Cu_{tot}. Conversely, in deep waters Cu_{diss} remained very high in all the season and slightly increased reaching values that were 90% of the total.

Cu quotas showed values ranging between 0.08 nmol L^{-1} and 2.1 nmol L^{-1}, representing a variable fraction of the total and the total particulate (from ~2% to ~50% and from ~20% to 100%, respectively, Tab. 5). At the station T10 (December), particulate Cu was low (~20% of Cu_{tot}) and slightly decreased with depth to values that were ~13% of the total. In this period, Cu_{phyto} was ~40% of the $Cu_{totpart}$ at the surface, but since 10 m, it became the 100% of the total particulate. At the station BTN6 (January and February), $Cu_{totpart}$ increased at the surface and it was almost entirely (90-100%) present into phytoplankton cells. At the depth of 100 m, $Cu_{totpart}$ drastically fell to values that were 7-10% of the Cu_{tot} and it was constituted only for the 20-30% by the fraction associated to phytoplankton cells (Tab. 5).

Cu stoichiometry showed similar values (~150 μmol mol^{-1}) both in December and in January, and remained almost constant with depth (Tab. 5). In February, Cu:C ratio decreased of about 80% in surface waters (~30 μmol mol^{-1}, Tab. 5), whereas at 100-m depth it returned to values similar to those of the previous two samplings.

Tab. 5. Copper distribution between total concentrations, dissolved, total particulate, inorganic particulate and phytoplankton particulate fractions measured during the austral summer 2011-2012 in the three studied sites of Terra Nova Bay (Western Ross Sea). Cu:C ratios were also reported. Data reported as mean ± SD of at least three measurements.

Sampling station, date and depth (m)		Cu concentration, nmol L^{-1}					Cu:C ratio in phytoplankton, μmol mol^{-1}
		Total	Dissolved (% *vs* total)	Total particulate[a]	Inorganic particulate[a]	Phytoplankton particulate (% vs. Tot part.)	
T10 15/12/2011	5	3.9 ± 0.1	2.9 ± 0.1 (76%)	1.0 ± 0.2 (24%)	0.53 ± 0.17	0.42 ± 0.06 (44%)	159 ± 1
	8	3.9 ± 0.1	2.9 ± 0.1 (75%)	1.0 ± 0.1 (25%)	<d.l.	1.0 ± 0.1 (100%)	151 ± 1
	100	5.0 ± 0.1	4.36 ± 0.03 (87%)	0.6 ± 0.1 (13%)	<d.l.	0.71 ± 0.05 (~100%)	142 ± 1
BTN6 20/01/2012	5	4.0 ± 0.1	2.05 ± 0.02 (52%)	1.9 ± 0.1 (48%)	0.17 ± 0.15	1.8 ± 0.1 (91%)	150 ± 1
	15	3.1 ± 0.1	1.7 ± 0.1 (54%)	1.4 ± 0.2 (46%)	0.01 ± 0.23	1.4 ± 0.2 (99%)	147 ± 1
	100	4.7 ± 0.1	4.4 ± 0.1 (93%)	0.33 ± 0.14 (7%)	0.25 ± 0.14	0.08 ± 0.02 (24%)	102 ± 1
BTN6 05/02/2012	5	3.7 ± 0.1	1.7 ± 0.1 (46%)	2.0 ± 0.2 (54%)	<d.l.	2.1 ± 0.2 (~100%)	33.3 ± 0.6
	15	2.9 ± 0.2	1.4 ± 0.1 (48%)	1.5 ± 0.2 (52%)	0.07 ± 0.32	1.4 ± 0.2 (95%)	46.0 ± 0.7
	100	4.7 ± 0.2	4.2 ± 0.2	0.49 ± 0.23	0.36 ± 0.24	0.13 ± 0.08	130 ± 1

	(90%)	(10%)	(27%)

[a] ±SD computed as the square root of the sum of variances

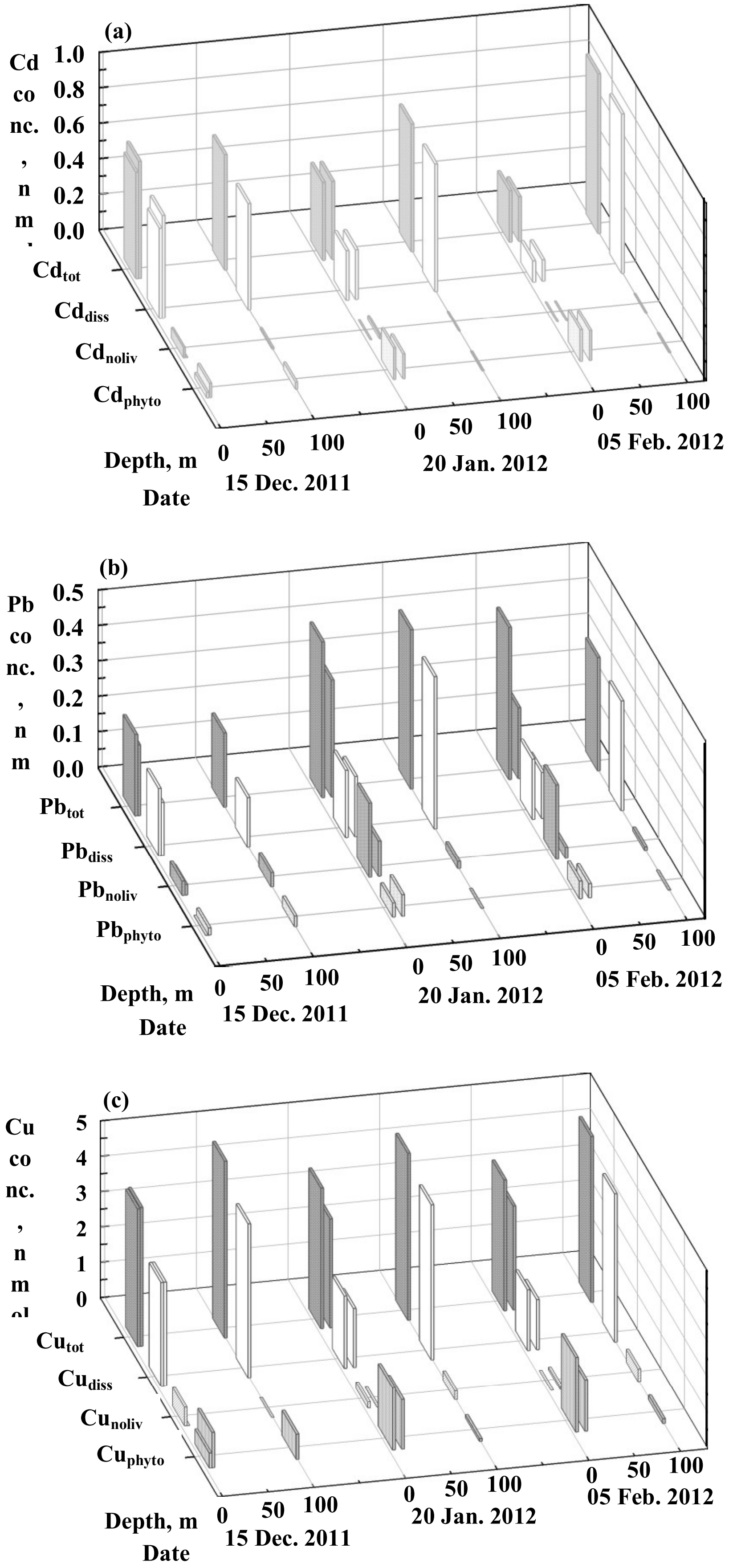


Fig. 4. Distribution between total, dissolved, non-living particulate and phytoplankton particulate fractions of Cd **(a)**, Pb **(b)** and Cu **(c)** in Terra Nova Bay during the austral summer 2011-2012.

4. Discussion

This work presents first direct measurements of metal quotas in the phytoplankton collected from the coastal Antarctic site of Terra Nova Bay (Ross sea, Victoria Land). As stated in previous surveys, metal distributions in the coastal waters of TNB were mainly affected by the dynamic of the pack ice melting and the phytoplankton activity. In particular, surface and subsurface layers are strongly influenced by these two phenomena.

The three metals here investigated have different biogeochemical characteristics in the ocean. Typically, cadmium follows a pattern similar to those of macronutrients, as phosphate and nitrate. Lead has a scavenged-type distribution, showing strong interactions with particles of different origin. This results in a gradual decrease of the dissolved forms with depth, as a consequence of the continual particle scavenging. Copper has a hybrid behaviour, its distribution being influenced by both recycling and relatively intense scavenging processes (Bruland and Lohan., 2003).

The results are discussed below separately for each metal.

Environment

In the austral summer 2011-2012, the TNB polynya experienced a moderate diatom bloom in February, supported by a moderate stratification of the water column.

Typically, the summer evolution of phytoplankton assemblages at TNB had the main peak between December and January, followed by a decrease in January and a secondary peak in February (Nuccio et al., 2000; Arrigo and Van Dijken 2004). During the 2011-2012 field campaign the pack ice melted very late in summer (mid-January) and only at the end of January the characteristics of the water column were ideal for the development of the phytoplankton bloom. This was also confirmed by the lower phytoplankton abundance and biomass values, as well as by chlorophyll-a concentrations observed in December with respect to the literature data (Nuccio et al., 2000; Saggiomo et al., 2002; Fonda Umani et al., 2005).

In February, when the area was completely ice-free, phytoplankton abundance and biomass, as well as Chl-a, increased to values typical of TNB in that period, as reported by previous surveys (Nuccio et al., 2000; Saggiomo et al., 2002; Fonda Umani et al., 2005; Rivaro et al., 2012). Although fluorescence was higher in mid-December than in January, this early peak was not supported by phytoplankton abundance and biomass which both showed low values. In fact, water column characteristics (i.e. absence of stratification) of this period were not favourable to the development of the algal bloom. This discordance is related to the technique here used to measure Chl-a. In fact, Chl-a values were determined by fluorimetric methods which can sometimes overestimate or underestimate the effective Chl-a concentration, due to the superimposition with fluorescence bands of different pigments and/or of degradation products.

Distribution of cadmium

Relatively high vertical and seasonal variability of Cd distribution between dissolved and particulate fractions were observed, which are in good agreement with previous surveys carried out in the same area (Scarponi et al., 1995; Scarponi et al., 1997; Capodaglio et al., 1998; Scarponi et al., 2000; Frache et al., 2001; Abollino et al., 2001; Abollino et al., 2004), in the Ross Sea (Fitzwater et al., 2000; Corami et al., 2005), and in the Weddel Sea (Westerlund and Oehman 1991; Nolting and de Baar 1994).

It is well known that Cd concentrations in the polar regions are subjected to two main phenomena. The first is related to the seasonal evolution of phytoplankton that can actively take up cadmium in productive surface waters. The second process is related to solute dilution, due to the ice melting during the austral summer, and to its concentration, when the pack ice is growing through the winter (Corami et al., 2005). In the present work, a surface summer decrease (both in absolute and in relative terms) of Cd dissolved concentration was observed, with values ranging from ~90% of the total in December, to values that were 40-60% of the total in February. The relationship between Cd concentration and biological activity is emphasized by the comparison of the vertical distribution of dissolved Cd and those of total phytoplankton biomass or abundance. A general negative linear correlation can be observed with biomass ($r = -0.7687$; $p < 0.05$) and with the phytoplankton abundance ($r = -0.8535$; $p < 0.05$). Therefore, Cd was taken up at the surface by phytoplankton which moved the metal from the dissolved fraction to the particulate one.

Through the water column, Cd was released in seawater (dissolved fraction increasing), following the sedimentation of dead phytoplanktonic cells (Bruland and Lohan, 2003). At the same time, the concentration of particulate Cd was high in the surface layer and then it decreased with depth, reaching values close to the detection limit of the technique. It has to be noted that in February the concentration of the algal particulate Cd should be higher than in January, due to the phytoplankton bloom. Conversely, Cd total particulate and, particularly Cd quota in phytoplankton had quite similar concentrations in both January and February.

The Cd:C ratio distribution was subjected to the same surface decrease of the Cd quotas in phytoplankton. As reported in the literature (Sunda and Huntsman, 1998; Sunda and Huntsman, 2000; Ho et al., 2003) a complex set of variables (bioavailability, phytoplankton species, light regime, concentrations of major nutrients and other trace metals) control the Cd content in phytoplankton. As stated in several studies based on culture experiments to assess metal accumulation by marine diatoms, competitions between metals (e.g. Zn^{2+} *vs*. Mn^{2+}) may have as much influence on algal uptake of Cd as do variations in Cd concentrations. In addition, the relationships between metals can be further complicated in Fe-limited regions, such as the Southern Ocean (Sunda and Huntsman, 2000).

Unfortunately, we did not measure neither Zn nor Fe concentrations. Nevertheless, if we consider data reported by Rivaro et al. (2012) in the same area of the present work, we can assert that during summer TNB experiences a Fe limited condition, because of the requirement of this metal for the algal growth. Very few values are reported for Zn, and, in particular for its evolution during the season. In addition, from metal speciation studies reported by Scarponi et al. (1995), we can deduce the concentration of Cd ligands and labile Cd fraction. The latter represents the metal fraction potentially available to the biological uptake and varied greatly during summer, from ~20% of the total Cd content at the phytoplankton bloom to ~70% in presence of low algal abundance (Scarponi et al., 1995). Cd ligand concentrations followed an opposite trend to that of Cd labile fraction. Based on these literature data, we can speculate that a combination of Fe-limited conditions in TNB waters, a labile fraction summer reduction and a simultaneous increase of Zn requirement by phytoplankton could be responsible of the Cd-quota decrease in early February, when the phytoplankton bloom occurred. Additional studies are needed in order to elucidate the dissolved Cd speciation and the interactions between Cd and other competitive metals in modulating phytoplankton requirements for this metal.

The Cd:C ratios reported in the present work are quite similar to those of phytoplankton of the North Pacific (Martine and Knauer, 1973; Martin et al., 1976). They are also in-line with several laboratory studies (Sunda and Huntsman, 1998; Sunda and Huntsman, 2000; Ho et al., 2003). If we reported our Cd algal concentrations per unit of phytoplankton mass as measured by Truzzi et al. (2015), we can compare it to literature data on cellular metal concentrations reported as mass fraction. Even if of the same order of magnitude, our Cd mass fraction values are generally lower than those of Bargagli et al. (1996) who reported Cd concentration of 2.1 ± 0.9 $\mu g\ g^{-1}$ d.w. (dry weight). Nevertheless, this value referred to macro-phytoplankton collected through nylon net with a mesh size of at least 50 μm; a size greater than the phytoplankton here studied (<40 μm). Our data are lower than those of Honda et al. (1987). The authors found Cd values of ~1.3 $\mu g\ g^{-1}$ d.w., but they determined metals in the entire plankton, with particular attention to the zooplankton component (copepods and Antarctic krill).

Distribution of lead

Total Pb concentrations showed a homogeneous distribution through the water column before the pack ice melting. In this period, Pb was dominated by its dissolved fraction, which slightly decreased with depth, while the particulate fraction slightly increased. This is in little contrast with the lead distribution observed in previous surveys at TNB. Both Scarponi et al. (2000) and Frache et al. (2001) reported a homogeneous distribution of dissolved and particulate Pb through the water column, before the beginning of the pack ice melting. In the present work, the little depletion of dissolved Pb at the 100-m depth can be ascribable to the presence of phytoplankton abundance and biomass maximum at this depth, with the subsequent increase of Pb associated to the algal particulate fraction.

From January, Pb experienced a significant surface enrichment in the particulate fraction, whereas Pb in the dissolved fraction remained practically constant over summer. In fact, in this period most of the pack ice which covered TNB during winter and constituted an accumulation site of atmospheric input of pollutants of local and remote origins, broke up and melted, releasing particulate Pb in the seawater (Capodaglio et al., 1989; Frache et al., 2001; Dalla Riva et al., 2003). It should be noted that in February, when TNB area was completely ice-free, particulate lead surface maximum was probably due to the contribution of atmospheric particulate, as already observed by other authors (Frache et al., 2001). Therefore, total Pb concentration increased from December to January, and remained high also in February.

At increasing depths the pack ice and atmospheric effects diminished and, by consequence, also the total particulate Pb which was ~40% and ~70% lower than at the surface, in January and in February, respectively. Moreover, in the correspondence of the DCM (15-m depth) a slight decrease of the dissolved Pb was also recorded. As observed in previous surveys (Scarponi et al., 1997; Frache et al., 2001; Corami et al., 2005), we hypothesised that decrease could be related to the phytoplankton bloom, with the biogenic particles responsible for scavenging dissolved Pb. It has to be noted that Pb is considered a toxic non-essential element with no known physiological requirements (Sunda 1989; Maeda and Sakaguki, 1990). Nevertheless, Pb can be absorbed to algal surfaces or complexed to organic material (e.g. exudates) released by algae at all growth stages (Santana-Casiano et al., 1995).

At 100-m depth, both in January and in February, all the Pb dissolved fraction increased greatly, reaching values double of those at the surface. This Pb distribution is not common. As a scavenging-type element, Pb particulate, and in particular, the inorganic fraction, should increase with depth. Corami et al. (2005) and Scarponi et al. (1997) found a similar behaviour for Pb in other areas of the western Ross Sea. They assumed other local inputs (i.e. hydrothermal vents in volcanic areas, erosion due to glaciers) which could influence the distribution of Pb through the water column. However, further studies are necessary in order to give a better interpretation of this behaviour.

Particulate Pb concentrations are in good agreement with values found in the literature for the same site (Frache et al., 2001; Corami et al., 2005) and for the Ross Sea offshore data (Papoff et al., 1996). Dissolved Pb showed values slightly higher than those reported in the literature (Scarponi et al., 1997; Capodaglio et al., 1998; Scarponi et al., 2000; Dalla Riva et al., 2003). These higher concentrations are probably related to recent increasing anthropogenic activities in the TNB area, following the building of a new South-Korean research station (opening ceremony in February 2014) which is very close to the sampling sites, together with the increased traffic from and to the Italian station "Mario Zucchelli".

Pb stoichiometry showed values lower than the other two metals. Nevertheless, our ratios are higher than the very few data available in the literature for this metal in phytoplankton (Echeveste et al. 2014). It has to be noted that the measured quotas include both intracellular and extracellular elements. Even if extracellular elements may not to be relevant for algal physiology, both fractions should be considered from a biogeochemical perspective. If we reported our Pb algal concentrations per unit of phytoplankton mass as previously done for Cd, we can compare our results to literature data on cellular metal concentrations reported as mass fraction. Our results are lower than data reported in the literature. Honda et al. (1987) found values of 0.46 – 1.67 µg g^{-1} d.w. in the entire plankton, with particular attention to the zooplankton component (copepods and Antarctic krill), while Dalla Riva et al. (2003) found Pb values of 0.25 ± 0.07 µg g^{-1} but they referred to the thallii of two macroalgae (*Iridaea cordata and Phyllophora antarctica*).

Pb:C ratio showed a small peak in January, while in February it decreased to values close to zero, as at the beginning of summer. The distribution of Pb stoichiometry seemed to follow the seasonal variation of pack ice. Therefore, we can hypothesize that the Pb:C peak in January was related to the entrapped phytoplankton cells that adsorbed Pb on their surface and that were released during the melting processes. Along the water column, Pb:C showed a maximum at the DCM, while it was below the detection limit at the depth of 100. The increase of Pb:C ratio at the DCM was probably due to an increase in the number of algal cells that adsorbed the metal on their external surfaces.

Distribution of copper

Total Cu concentration did not show significant variations during the austral summer, whereas dissolved and particulate fractions varied greatly in the same period. Dissolved and total particulate concentrations measured in the present work are in good agreement with values found by several authors in the same site (Capodaglio et al., 1994; Frache et al., 1997; Capodaglio et al., 1998; Grotti et al., 2001; Frache et al., 2001; Abollino et al., 2001; Abollino et al., 2004; Corami et al., 2005) and in other Antarctic coastal areas (Westerlund and Oehman 1991; Fitzwater et al., 2000; Lai et al., 2008). In mid-December in the presence of the pack ice and with low surface values of the phytoplankton biomass (~50 µg C L^{-1}), Cu was mainly present in its dissolved form (~80% of the total). Total particulate Cu showed a surface maximum and a concentration decrease with depth. Even though the phytoplankton abundances were very low in this period, at the depth of ~10 m, the particulate Cu was essentially associated to algal cells.

When the pack ice melted, with the subsequent stratification of the water column and the phytoplankton bloom event (biomass values of 150 µg C L^{-1} on January and ~500 µg C L^{-1} on February), the Cu dissolved proportion decreased in the surface layers by ~50%. Moreover, in February, when the phytoplankton bloom occurred, Cu distribution in seawater showed a nutrient-type profile, with a surface depletion of dissolved Cu and an increase of the particulate fraction, particularly of the algal phase, which represented almost the totality of the particulate matter. As reported by different authors for the same area (Frache et al., 1997; Grotti et al., 2001; Frache et al., 2001) surface maxima of total particulate Cu can be ascribed to various processes. It can be partly released as inorganic particulate by pack ice during the first phases of the melting process, and, partly, taken up by the biological material entrapped in the pack ice, as soon as this started to melt. At the depth of 100 m, a slight increase of the copper inorganic particulate fraction was observed in January and February together with high dissolved Cu, probably due to the release by phytoplankton cells. In mid-December, the particulate fraction of copper was mainly constituted by its algal component, because of the phytoplankton peak at this depth.

Our Cu:C ratios are quite similar to North Atlantic values if we summed Cu stoichiometries calculated for each phytoplankton group by Twining et al. (2015). Nevertheless, they are significantly higher than those found in the Pacific and Southern Oceans by Collier and Edmond (1984), Martin and Knauer (1973), and Martin et al. (1976) and summarized by Bruland et al. (1991).

Cu:C ratios drastically decreased (by ~80%) at the end of summer, while the quota of this metal in phytoplankton remained similar to that of January, as observed for Cd. Also for Cu, we hypothesise a change in copper requirement by algal cells. Cu is a bioactive metal that facilitates many biogeochemically significant processes such as nitrous oxide reduction (Stiefel, 2007), photosynthesis (Peers and Price, 2006), and aerobic ammonia oxidation (Walker et al., 2010). As other trace metal micronutrients (Fe, Cd, Zn), Cu has also the capacity to shape phytoplankton communities and in turn global pattern of primary productivity (Sunda 2012). In natural waters, Cu is typically complexed by two classes of ligands; the first is strong and of organic origin, while the second class of ligand is generally weak and probably made of refractory organic matter. These ligands reduce the Cu free ion concentrations and render it biologically unavailable (Donat et al., 1994). In the coastal area of TNB, dissolved Cu speciation is strongly affected by the concentration of the first ligand, which was generally low and varied greatly during season and with depth. In particular, this ligand increased after the pack ice melting and at the DCM (Scarponi et al., 1994). Therefore, we can assume a change in the Cu speciation, with the reduction of its bioavailability, at the end of summer. We could hypothesize that the first class of ligands comprised dead phytoplankton cells or organic exudates released during the pack ice melting or resulted from the phytoplankton bloom of mid-December, which partially missed because of the prolonged pack ice covering of TNB. Alternatively, we can hypothesise that phytoplankton itself produced copper complexing ligands to detoxify this metal in the environment, as suggested by Donat et al. (2004). Unfortunately, the ambient ligands that bind copper in Antarctic waters have not yet been structurally characterized, making it difficult to discuss this Cu:C ratio distribution, further. At 100-m the influence of the ligands greatly decreased, and Cu was again bioavailable to phytoplankton, which highly required the metal, even the low biomass and abundance.

Conclusions

The distribution of Cd, Pb and Cu in dissolved, inorganic and algal particulate were investigated at Terra Nova Bay from December 2011 to February 2012. Due to the delay in the typical pack-ice melting process (in January instead of mid-December), only at the end of January, water column characteristics were ideal for the phytoplankton bloom, which occurred in February and it was composed largely of diatoms.

Metal distributions in TNB area were mainly affected by the dynamic of the pack-ice melting and the phytoplankton activity.

Metal quotas in phytoplankton as a percentage of the total and total particulate concentrations varied with depth and during the season, the highest values measured at the surface and in presence of the phytoplankton bloom.

A general decrease of the Cd and Cu dissolved metal fractions coupled with the increase of the algal particulate fractions were observed at the surface waters during the austral summer 2011-2012. Cd was dominated by dissolved species and its vertical distribution was mainly controlled by nutrient-like biogeochemical cycling, with a surface phytoplankton uptake of dissolved Cd and a recycling along the water column. Also Cu was mainly dominated by dissolved species with a nutrient-like vertical profile in the presence of the phytoplankton bloom. Pb features the typical distribution of a scavenged element with a surface enrichment of the particulate fraction during summer. However, the vertical distribution of this element may be influenced by several factors (e.g. pack-ice melting, atmospheric inputs), with the phytoplankton activity affected Pb behaviour only partially.

Metal:C ratios in phytoplankton provide valuable information on the biological requirements of trace metals, as well as of nutrients. Our data on metal stoichiometries are broadly similar to those measured in laboratory culture experiments and in other oceans worldwide. Cu and Pb are slightly higher than some literature data, probably because our metal quotas include both intracellular and extracellular metal fractions. Metal:C ratios showed different seasonal and vertical trends. Both Cd and Cu stoichiometries greatly decreased at the end of summer, probably due to a combination of controlling factors (bioavailability changes, competition with other bioactive metals) that occurred simultaneously, reducing and/or modifying the phytoplankton requirements for these metals. Pb:C ratios showed the lowest values, with respect to the other two metals., confirming its nature of non-essential element. Contrary to Cd and Cu, Pb:C was maximum at the end of January, when the pack ice melting released algal cells which could absorb bioavailable Pb onto their external surfaces.

Direct measurements of metal quotas or stoichiometries in natural phytoplankton let us to better understand trace metal distribution between dissolved and particulate fractions along the water column. However, a better resolution of the vertical profiles, as well as a more detailed seasonal sampling strategy coupled with more physical, chemical and biological parameters than temperature and salinity, (i.e. pH, dissolved oxygen, nutrients) would provide a better comprehension of the metal behaviour along the water column. In any case, our data highlight the significant influence of the phytoplankton on the distribution of Cd, Pb and Cu in seawater, showing a determinant role in their biogeochemical cycles.

Acknowledgements

We thank prof. Paolo Povero (Department of Earth, Environment and Life Sciences, DISTAV of the University of Genova) for providing the data on the master hydrographic variables and chlorophyll-a concentrations. This work was financially supported by the Italian Programma Nazionale di Ricerche in Antartide (PNRA) through the project (PdR 2013/AZ1.01) “Assessment and evolution of the chemical contamination by organic and inorganic constituents in Antarctic coastal areas”.

References

Abollino, O., Aceto, M., Buoso, S., La Gioia, C., Sarzanini, C., Mentasti, E., 2004. Distribution of major, minor and trace elements in Antarctic offshore and Coastal seawaters: correlation among sites and variables by pattern recognition. Int. J. Environ. Anal. Chem. 84, 471-492.

Abollino, O., Aceto, M., La Gioia, C., Sarzanini, C., Mentasti, E., 2001. Spatial and seasonal variations of major, minor and trace elements in Antarctic seawater. Chemometric investigation of variable and site correlations. Adv. Environ. Res. 6, 29-43.

Abollino, O., Aceto, M., Sacchero, G., Sarzanini, C., Mentasti, E., 1995. Determination of copper, cadmium, iron, manganese, nickel and zinc in Antarctic seawater. Comparison of electrochemical and spectroscopic procedures. Anal. Chim. Acta 305, 200-206.

Accornero, A., Manno, C., Esposito, F.G.M.C., 2003. The vertical flux of particulate matter in the polynya of Terra Nova Bay. Part II. Biological components. Antar. Sci. 15, 175-188.

Agusti, S., Duarte, C.M., 1999. Phytoplankton chlorophyll a distribution and water column stability in the central Atlantic Ocean. Oceanol. Acta 22, 193-203.

Annett, A.L., Lapi, S., Ruth, T.J., Maldonado, M.T., 2008. The effects of Cu and Fe availability on the growth and Cu:C ratios of marine diatoms. Limnol. Oceanogr. 53, 2451-2461.

Annibaldi, A., Truzzi, C., Illuminati, S., Scarponi, G., 2009. Recent sudden decrease of lead in Adriatic coastal seawater during the years 2000-2004 in parallel with the phasing out of leaded gasoline in Italy. Mar. Chem., 113, 239-248.

Annibaldi, A., Truzzi, C., Illuminati, S., Bassotti, E., Finale, G., Scarponi, G., 2011a. First systematic voltammetric measurements of Cd, Pb and Cu in hydrofluoric acid-dissolved siliceous spicules of marine sponges. Anal. Lett., 44, 2792-2807.

Annibaldi, A., Illuminati, S., Truzzi, C., Scarponi, G., 2011b. SWASV speciation of Cd, Pb and Cu for the determination of the seawater contamination in the area of the Nicole shipwreck (Ancona coast, Central Adriatic Sea). Mar. Pollut. Bull., 62, 2813-2821.

Annibaldi, A., Illuminati, S., Truzzi, C., Libani, G., Scarponi, G., 2015. Pb, Cu and Cd distribution in five estuary systems of Marche, central Italy. Mar. Pollut. Bull., 96, 441-449.

Arrigo, K.R., Van Dijken, G.L., 2004. Annual changes in sea-ice, chlorophyll a, and primary production in the Ross Sea, Antarctica. Deep-Sea Res. II 51, 117-138.

Bargagli, R., Nelli, L., Ancora, S., Focardi, S., 1996. Elevated cadmium accumulation in marine organisms from Terra Nova Bay (Antarctica). Polar Biol. 16, 513-520.

Boyd, P.W., Jickells, T., Law, C.S., Blain, S., Boyle, E.A., Buesseler, K.O., Coale, K.H., Cullen, J.J., de Baar, H.J.W., Follows, M., Harvey, M., Lancelot, C., Levasseur, M., Owens, N.P.J., Pollard, R., Rivkin, R.B., Sarmiento, J., Schoemann, V., Smetacek, V., Takeda, S., Tsuda, A., Turner, S., Watson, A.J. 2007. Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions. Science, 315, 612-617.

Bromwitch, D.H., Kurtz, D.D., 1984. Katabatic wind forcing of the Terra Nova Bay polynya. J. Geophys. Res. 89, 3561-3572.

Bruland, K.W., Knauer, G.A., Martin, J.H., 1978. Cadmium in northeast Pacific waters. Limnol. Oceanogr. 23, 618-625.

Bruland, K.W., Donat, J.R., Hutchins, D.A., 1991. Interactive influences of bioactive trace-metals on biological production in oceanic waters. Limnol. Oceanogr., 36, 1555-1577.

Bruland, K.W., Lohan, M. C., 2003. Controls of trace metals in seawater. In: Elderfield, H., Holland, H. D., Turekian, K. K. (Eds.), Treatise on Geochemistry. Elsevier Science, Vol. 6, Chapt. 6.02, pp. 23-47.

Capodaglio, G., Toscano, G., Scarponi, G., Cescon, P., 1989. Lead speciation in the surface waters of Ross Sea (Antarctica). Ann. Chim. 79, 543-559.

Capodaglio, G., Scarponi, G., Toscano, G., Cescon, P., 1991a. Cadmium complexation in surface seawater of Terra Nova Bay (Antarctica). Ann. Chim. 81, 279-296.

Capodaglio, G., Scarponi, G., Cescon, P., 1991b. Lead speciation in Antarctic Ocean. Anal. Proceed. 28, 76-77.

Capodaglio, G., Toscano, G., Scarponi, G., Cescon, P., 1994. Copper complexation in surface seawater of Terra Nova Bay (Antarctica). Intern. J. Environ. Anal. Chem. 55, 129-148.

Capodaglio, G., Turetta, C., Toscano, G., Gambaro, A., Scarponi, G., Cescon, P., 1998. Cadmium, lead, and copper complexation in Antarctic coastal seawater. Evolution during the austral summer. Int. J. Environ. Anal. Chem. 71, 195-226.

Cappelletti, A., Picco, P., Peluso, T., 2010. Upper ocean layer dynamics and response to atmospheric forcing in the Terra Nova Bay polynya, Antarctica. Antar. Sci. 22, 319-329.

Catalano, G., Povero, P., Fabiano, M., Benedetti, F., Goffart, A., 1997. Nutrient utilization and particulate organic matter changes during summer in the upper mixed layer (Ross Sea, Antarctica). Deep-Sea Res. I 44, 97-112.

Collier, R., Edmond, J., 1984. The trace element geochemistry of marine biogenic particulate matter. Progr. Ocean. 13, 113-199.

Corami, F., Capodaglio, G., Turetta, C., Soggia, F., Magi, E., Grotti, M., 2005. Summer distribution of trace metals in the western sector of the Ross Sea, Antarctica. J. Environ. Monit. 7, 1256-1264.

Dalla Riva, S., Abelmoschi, M.L., Chiantore, M., Grotti, M., Magi, E., Soggia, F., 2003. Biogeochemical cycling of Pb in the coastal marine environment at Terra Nova Bay, Ross Sea. Antar. Sci. 15, 425-432.

Donat, J.R., Lao, K.A., Bruland, K.W., 1994. Speciation of dissolved copper and nickel in South San Francisco Bay: a multi-method approach. Anal. Chim. Acta, 284, 547-571.

Echeveste, P., Tovar-Sanchez, A., Agusti, S., 2014. Tolerance of polar phytoplankton communities to metals. Environ. Pollut. 185, 188-195.

Edler, L., Elbrächter, M., 2010. The Utermöhl method for quantitative phytoplankton analysis. In: Karlson, B., Cusak, C., Bresnan, E. (Eds.), Microscopic and Molecular Methods for Quantitative Phytoplankton Analysis. Intergovernmental Oceanographic Commission of UNESCO, Paris, Chapt. 2, pp. 13-20.

European Commission, Joint Research Centre, Institute for Reference Materials and Mesarurements, 2007. BCR-414, Certified Reference Material for plankton.

Fabiano, M., Povero, P., Danovaro, R., 1993. Distribution and composition of particulate organic matter in the Ross Sea (Antarctica). Polar Biol. 3, 525-533.

Fitzwater, S.E., Johnson, K.S., Gordon, R.M., Coale, K.H., Smith, W.O., Jr., 2000. Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. Deep-Sea Res. II 47, 3159-3179.

Fofonoff, N.P., Millard, J., 1983. Specific volume anomaly and density anomaly of seawater. In: Algorithms for Computation of Fundamental Properties of Seawater. UNESCO technical papers in marine science, Chapt. 3, 15-21.

Fonda Umani, S., Monti, M., Bergamasco, A., Cabrini, M., De Vittor, C., Burba, N., Del Negro, P., 2005. Plankton community structure and dynamics versus physical structure from Terra Nova Bay to Ross Ice Shelf (Antarctica). J.Mar. Syst. 55, 31-46.

Frache, R., Abelmoschi, M.L., Grotti, M., Ianni, C., Magi, E., Soggia, F., Capodaglio, G., Turetta, C., Barbante, C., 2001. Effects of ice melting on Cu, Cd and Pb profiles in Ross Sea waters (Antarctica). Int. J. Environ. Anal. Chem. 79, 301-313.

Frache, R., Baffi, F., Ianni, C., Soggia, F., 1997. Dissolved and particulate metals in the pack ice melting process in the Ross Sea (Antarctica). Ann. Chim. 87, 367-374.

Garcia, V.M.T., Garcia, C.A.E., Mata, M.M., Pollery, R.C., Piola, A.R., Signorini, S.R., McClain, C.R., Iglesias-Rodriguez, M.D., 2008. Environmental factors controlling the phytoplankton blooms at the Patagonia shelf-break in spring. Deep-Sea Res. I 55, 1150-1166.

Gonzalez-Davila, M., Santana-Casiano, J.M., Laglera, L.M., 2000. Copper adsorption in diatom cultures. Mar. Chem. 70, 161-170.

Grotti, M., Soggia, F., Abelmoschi, M.L., Rivaro, P., Magi, E., Frache, R., 2001. Temporal distribution of trace metals in Antarctic coastal waters. Mar. Chem. 76, 189-209.

Ho, T.-Y., Quigg, A., Finkel, Z.V., Milligan, A., Wyman, K., Falkowski, P.G., Morel, F.M.M., 2003. The elemental composition of some marine phytoplankton. J. Phycol., 39, 1145-1159.

Honda, K., Yamamoto, Y., Tatsukawa, R., 1987. Distribution of heavy metals in antarctic marine ecosystem. Proc. NIPR Symp. Polar Biol. 1, 184-197.

Illuminati, S., Truzzi, C., Annibaldi, A., Migliarini, B., Carnevali, O., Scarponi, G., 2010. Cadmium bioaccumulation and metallothionein induction in the liver of the Antarctic teleost Trematomus bernacchii during an on-site short-term exposure to the metal via sea water. Toxicl. Environ. Chem., 92, 617-640.

Illuminati, S., Annibaldi, A., Truzzi, C., Finale, C., Scarponi, G., 2013. Square-wave anodic-stripping voltammetric determination of Cd, Pb and Cu in wine: Set-up and optimization of sample pre-treatment and instrumental parameters. Electrochim. Acta 104, 148-161.

Illuminati, S., Annibaldi, A., Truzzi, C., Libani, G., Finale, C., Mantini, C., Scarponi, G., 2015. Determination of water-soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry after sequential extraction and microwave digestion. J. Electroanal. Chem., 755, 182-196.

Illuminati, S., Bau, S., Annibaldi, A., Mantini, C., Libani, G., Truzzi, C., Scarponi, G., 2016. Evolution of size-segregated aerosol mass concentration during the Antarctic summer at Northern Foothills, Victoria Land. Atmos. Environ. 125, 212-221.

Illuminati, S., Annibaldi, A., Truzzi, C., Scarponi, G., 2016. Determination of heavy metals in Antarctic marine sponges (RossSea) by square wave anodic stripping voltammetry: distribution inorganic and siliceous tissues. Mar. Pollut. Bull., 111, 476-482

Kolb, M., Rach, P., Schaefer, J., Wild, A., 1992. Investigations of oxidative UV photolysis. I. Sample preparation for the voltammetric determination of zinc, cadmium, lead, copper, nickel, and cobalt in waters. Fresenius J. Anal. Chem. 342, 341-349.

Lai, X., Norisuye, K., Mikata, M., Minami, T., Bowie, A.R., Sohrin, Y., 2008. Spatial and temporal distribution of Fe, Ni, Cu and Pb along 140°E in the Southern Ocean during austral summer 2001/02. Mar. Chem. 111, 171-183.

Lund, J.W.G, Kipling, C., Le Cren, F.D., 1958. The inverted microscope method of estimating algal numbers and the statistical basis of estimation by counting. Hydrobiol., 11, 43-170.

Maeda, S., Sakaguki, T., 1990. Accumulation and detoxification of toxic metal elements by algae. In: Akatsuka, I. (Ed.), Introduction to Applied Phycology. Balogh Scientific Books Academic Publishing, Tokyo, pp. 109-136.

Martin, J.H., Knauer, G.A., 1973. The elemental composition of plankton. Geochim. Cosmochim. Acta, 37, 1639-1653.

Martin, J.H., Bruland, K.W., Broenkow, W.W., 1976. Cadmium transport in the California Current. In: Windom, H.L., Duce, R.A. (Eds.), Marine Pollutant Transfer. Lexington Books, Toronto, Chapt. 7, pp. 159-184.

Menden-Deuer, S., Lessard, E.J., 2000. Carbon to volume relationships for dinoflagellates, diatoms, and other protist plankton. Limnol. Oceanogr. 45, 569-579.

Morel, F.M.M., Hudson, R.J.M., 1985. The geobiological cycle of trace elements in aquatic systems: Redfield revisited. In: Stumm, W. (Ed.), Chemical Processes in Lakes. Wiley-Interscience, New York, Chapt. 12, pp. 251-281.

Morel, F.M.M., Reinfelder, J.R., Roberts, S.B., Chamberlain, C.P., Lee, J.G., Yee, D. 1994. Zinc and carbon co-limitation of marine phytoplankton. Nature, 360, 740-742.

National Research Council of Canada. 2010. NASS-6 Seawater Reference Material for Trace metals.

Nolting, R.F., de Baar, H.J.W., 1994. Behaviour of nickel, copper, zinc and cadmium in the upper 300 m of a transect in the Southern Ocean (57° -62°S, 49°W). Mar. Chem. 45, 225-242.

Nuccio, C., Innamorati, M., Lazzara, L., Mori, G., Massi, L., 2000. Spatial and temporal distribution of phytoplankton assemblages in the Ross Sea. In: Faranda, F.M., Guglielmo, L., Ianora, A. (Eds.), Ross Sea Ecology. Springer-Verlag, Heidelberg, Berlin, Chapt. 19, pp. 231-245.

Papoff, P., Bocci, F., Onor, M., 1996. Distribution of macro- and microcomponents in the water column of the Antarctic Ross Sea and in surface Antarctic snow. Int. J. Environ. Anal. Chem. 63, 1-13.

Peers, G., Price, N.M., 2006. Copper-containing plastocyanin used for electroon transport by an oceanic diatom. Nature, 441, 341-344.

Rivaro, P., Luisa Abelmoschi, M., Grotti, M., Ianni, C., Magi, E., Margiotta, F., Massolo, S., Saggiomo, V., 2012. Combined effects of hydrographic structure and iron and copper availability on the phytoplankton growth in Terra Nova Bay Polynya (Ross Sea, Antarctica). Deep-Sea ReS. I 62, 97-110.

Rott, F., Salmaso, N., Hoehn, E., 2007. Quality control of Utermohl-based phytoplankton counting and biovolume estimates - an easy task or a Gordion Knot? Hydrobiol., 578, 141-146.

Saggiomo, V., Catalano, G., Mangoni, O., Budillon, G., Carrada, G.C., 2002. Primary production processes in ice-free waters of the Ross Sea (Antarctica) during the austral summer 1996. Deep-Sea Res. II 49, 1787-1801.

Santana-Casiano, J.M., Gonzalez-Davila, M., Perez-Pena, J., Millero, F.J., 1995. Pb^{2+} interactions with the marine phytoplankton Dunaliella tertiolecta. Mar. Chem. 48, 115-129.

Scarponi, G., Capodaglio, G., Barbante, C., Toscano, G., Cecchini, M., Gambaro, A., Cescon, P., 2000. Concentration changes in cadmium and lead in Antarctic coastal seawater (Ross Sea) during the austral summer and their relationship with the evolution of biological activity. In: Faranda, F., Guglielmo, L., Ionora A. (Eds.), Ross Sea Ecology. Springer-Verlag, Berlin, Heidelberg, Chapt. 43, pp. 585-594.

Scarponi, G., Capodaglio, G., Toscano, G., Barbante, C., Cescon, P., 1995. Speciation of lead and cadmium in Antarctic seawater: comparison with areas subject to different anthropic influence. Microchem. J. 51, 214-230.

Scarponi, G., Capodaglio, G., Turetta, C., Barbante, C., Cecchini, M., Toscano, G., Cescon, P., 1997. Evolution of cadmium and lead contents in Antarctic coastal seawater during the austral summer. Int. J. Environ. Anal. Chem. 66, 23-49.

Stiefel, E.I., 2007. Bioinorganic chemistry and the biogeochemical cycle. In: Bertini, I., Grey, H., Stiefel, E., Valentine, J. (Eds.), Biological inorganic chemistry. University Science Books, pp. 7-30.

Sunda, W.G., 1989. Trace metal interactions with marine phytoplankton. Biol. Oceanogr. 6, 411-442.

Sunda, W.G., Huntsman, S.A., 1998. Control of Cd concentrations in a coastal diatom by interactions among free ionic Cd, Zn, and Mn in seawater. Environ. Sci. Technol. 32, 2961-2968.

Sunda, W.G., Huntsman, S.A., 2000. Effect of Zn, Mn, and Fe on Cd accumulation in phytoplankton: implications for oceanic Cd cycling. Limonol. Oceanogr. 45, 1501-1516.01

Sunda, W.G., 2012. Feedback interactions between trace metal nutrients and phytoplankton in the ocean. Front. Microbiol. 3(204) 1-22.

Truzzi, C., Annibaldi, A., Illuminati, S., Bassotti, E., Scarponi, G., 2008. Square-wave anodic-stripping voltammetric determination of Cd, Pb, and Cu in a hydrofluoric acid solution of siliceous spicules of marine sponges (from the Ligurian Sea, Italy, and the Ross Sea, Antarctica). Anal. Bioanal. Chem. 392, 247-262.

Truzzi, C., Illuminati, S., Finale, C., Annibaldi, A., Lestingi, C., Scarponi, G., 2014a. Microwave-assisted solvent extraction (MAE) of melamine from seafood and analysis by gas chromatography-mass spectrometry: optimization by factorial design. Analyt. Lett., 47, 1118-1133.

Truzzi, C., Annibaldi, A., Illuminati, S., Scarponi, G., 2014b. Determination of proline in honey: Comparison between official methods, optimization and validation of the analytical methodology. Food Chem., 150, 477-481.

Truzzi, C., Lambertucci, L., Gambini, G., Scarponi, G., 2002. Optimization of square wave anodic stripping voltammetry (SWASV) for the simultaneous determination of Cd, Pb, and Cu in seawater and comparison with differential pulse anodic stripping voltammetry (DPASV). Ann. Chim. 92, 313-326.

Truzzi, C., Annibaldi, A., Finale, C., Libani, G., Romagnoli, T., Scarponi, G., Illuminati, S., 2015. Separation of micro-phytoplankton from inorganic particulate in Antarctic seawater (Ross Sea) for the determination of Cd, Pb and Cu: optimization of the analytical methodology. Anal. Method. 7, 5490-5496.

Twining, B.S. Baines, S.B., Fisher, N.S., Maser, J., Vogt, S., Jacobsen, C., Tovar-Sanchez, A., Sanudo-Wilhelmy, S.A., 2003. Quantifying trace elements in individual aquatic protist cells with a synchrotron X-ray fluorescence microprobe. Anal. Chem., 75, 3806-3816.

Twining, B.S., Baines, S.B., 2004. Element stoichiometries of individual plankton cells collected during the Southern Ocean Iron Experiment (SOFex). Limnol. Oceangr., 49(6), 2115-2128.

Twining, B.S., Baines, S.B., Bozard, J.B., Vogt, S., Walker, E.A., Nelson, D.M., 2011. Metal quotas of plankton in the equatorial Pacific Ocean. Deep-Sea Res. II, 58, 325-341.

Twining, B.S., Rauschenberg, S., Morton, P.L., Vogt, S., 2015. Metal contents of phytoplankton and labile particulate in the North Atlantic Ocean. Progr. Ocean. , 137, 261-283.

UNESCO, 1981. Background papers and supporting data on the Practical Salinity Scale 1978. UNESCO Technical papers in marine science, 37, pp. 1-140.

Walker, C.B., de la Torre, J.R., Klotz, M.G., Urakawa, H., Pinel, N., Arp, D.J., Brochier-Armanet, C., Chain, P.S.G., Chan, P.P., Gollagbir,A., Hemp, J., Hügler, M., Karr, E.A., Könneke, M., Shin, M., Lawton, T.J., Lowe, T., Martens-Habbena, W., Sayavedra-Soto, L.A., Lang, D., Sievert, S.M., Rosenzweig, A.C., Manning, G., Stahl, D.A., 2010. *Nitrosopumilus maritimus* genome reveals unique mechanisms for nitrification and autotrophy in globally distributed marine crenarchaea. PNAS 107 (19), 8818-8823.

Westerlund, S., Oehman, P., 1991. Cadmium, copper, cobalt, nickel, lead, and zinc in the water column of the Weddell Sea, Antarctica. Geochim. Cosmochim. Acta 55, 2127-2146.

Woelfl, S., Mages, M., Mercado, S., Villalobos, L., Ovari, M., Encina, F., 2004. Determination of trace elements in planktonic microcrustaceans using total reflection x-ray fluorescence (TXRF): First results from two Chilean lakes. Anal. Bioanal. Chem. 378, 1088-1094.

Tab. 1. Accuracy tests on the NASS-6 certified reference material for open sea waters and on the BCR-414 certified reference material for plankton.

	Metal concentrations					
	NASS-6, ng L^{-1}			BCR-414, µg/g		
	Cd	Pb	Cu	Cd	Pb	Cu
Experimental valuses (*n* = 5-7)	30 ± 4	6.0 ± 0.4	270 ± 39	0.39±0.02	3.8±0.2	28.3±0.6
Certified values	31 ± 2[a]	6 ± 2[a]	248 ± 25[a]	0.383±0.014[b]	3.97±0.19[b]	29.5±1.3[b]
Δ%	+4	+0	–9	–2	+4	+4

[a] ±expanded uncertainties

[b] ±half-widht of the 95% confidence intervals

Table 2
Click here to download Table: Tab.2.docx

Tab. 2. Abundances (× 10^6 cells L^{-1}) and biomass (µg C L^{-1}) of the main phytoplanktonic taxa identified during the austral summer 2011-2012 in the studied sites of Terra Nova Bay (Western Ross Sea). Data are reported as means ± 10% SD for all the phytoplankton taxa.

Sampling station, date and depth (m)	Bacillariophyceae		Dinoflagellates		Phytoflagellates		Total	
	Abundance 10^6 cells L^{-1}	Biomass µg C L^{-1}	Abundance 10^6 cells L^{-1}	Biomass µg C L^{-1}	Abundance 10^6 cells L^{-1}	Biomass µg C L^{-1}	Abundance 10^6 cells L^{-1}	Biomass µg C L^{-1}
T10								
15/12/2011								
5 m	0.19	27	0.007	9.2	0.27	0.90	0.47	37
8 m	0.45	42	0.35	46	0.88	3.7	1.7	92
100 m	0.99	68	0.002	1.1	0.15	0.40	1.1	70
BTN6								
20/01/2012								
5 m	2.0	102	0.026	60	0.45	2.4	2.4	164
15 m	1.8	83	0.064	46	1.6	4.4	3.6	133
100 m	0.062	6.0	0.011	4.7	0.089	0.20	0.16	11
BTN6								
05/02/2012								
5 m	3.0	716	0.10	170	0.27	0.80	3.4	887
15 m	2.8	369	0.076	72	0.26	0.70	3.2	442
100 m	0.066	6.1	0.008	7.6	0.21	0.60	0.28	14

Table 3
Click here to download Table: Tab.3.docx

Tab. 3ankton particulate fractions measured during the austral summer 2011-2012 in the three studied sites of Terra Nova Bay (Western Ross Sea). Cd:C ratios were also reported. Data reported as mean ± SD of at least three measurements.

Sampling station, date and depth (m)		Cd concentration, nmol L^{-1}					Cd:C ratios phytoplankton μmol mol^{-1}.
		Total	Dissolved (% *vs* total)	Total particulate[a] (% *vs* total)	Inorganic particulate[a]	Phytoplankton particulate (% *vs*. Tot part.)	
T10 15/12/2011	5	0.60 ± 0.02	0.51 ± 0.02 (85%)	0.09 ± 0.03 (15%)	0.058 ± 0.03	0.03 ± 0.01 (33%)	11.4 ± 0.5
	8	0.66 ± 0.02	0.58 ± 0.02 (88%)	0.08 ± 0.03 (12%)	<d.l.	0.08 ± 0.01 (100%)	12.2 ± 0.4
	100	0.65 ± 0.02	0.60 ± 0.02 (92%)	0.05 ± 0.03 (8%)	0.006 ± 0.039	0.04 ± 0.01 (~100%)	8.0 ± 0.4
BTN6 20/01/2012	5	0.44 ± 0.03	0.28 ± 0.02 (64%)	0.16 ± 0.04 (36%)	<d.l.	0.18 ± 0.02 (~100%)	15.3 ± 0.4
	15	0.44 ± 0.01	0.28 ± 0.04 (64%)	0.16 ± 0.04 (36%)	0.02 ± 0.04	0.14 ± 0.02 (88%)	14.5 ± 0.4
	100	0.72 ± 0.04	0.72 ± 0.03 (100%)	<d.l. (0%)	<d.l.	<d.l.	<d.l.
BTN6 05/02/2012	5	0.29 ± 0.01	0.12 ± 0.01 (41%)	0.17 ± 0.01 (59%)	<d.l.	0.18 ± 0.04 (100%)	2.8 ± 0.3
	15	0.25 ± 0.02	0.12 ± 0.01 (48%)	0.13 ± 0.02 (52%)	<d.l.	0.17 ± 0.04 (~100%)	5.4 ± 0.3
	100	0.90 ± 0.03	0.90 ± 0.02 (100%)	<d.l. (0%)	<d.l.	<d.l.	<d.l.

[a] ±SD computed as the square root of the sum of variances

Table 4
Click here to download Table: Tab.4.docx

Tab. 4. Lead distribution between total concentrations, dissolved, total particulate, inorganic particulate and phytoplankton particulate fractions measured during the austral summer 2011-2012 in the three studied sites of Terra Nova Bay (Western Ross Sea). Pb:C ratios were also reported. Data reported as mean ± SD of at least three measurements.

Sampling station, date and depth (m)		Pb concentration, nmol L^{-1}					Pb:C ratio in phytoplankton µmol mol^{-1}
		Total	Dissolved (% *vs* total)	Total particulate[a] (% *vs*. total)	Inorganic particulate[a]	Phytoplankton particulate (% *vs*. Tot part.)	
T10 15/12/2011	5	0.23 ± 0.02	0.19 ± 0.01 (83%)	0.04 ± 0.02 (17%)	0.04 ± 0.02	<d.l.	<d.l.
	8	0.20 ± 0.01	0.15 ± 0.01 (75%)	0.05 ± 0.01 (25%)	0.03 ± 0.01	0.02 ± 0.01 (53%)	3.0 ± 0.5
	100	0.21 ± 0.02	0.14 ± 0.01 (67%)	0.07 ± 0.02 (33%)	0.04 ± 0.02	0.03 ± 0.01 (43%)	6.0 ± 0.4
BTN6 20/01/2012	5	0.44 ± 0.03	0.19 ± 0.01 (43%)	0.25 ± 0.03 (57%)	0.21 ± 0.04	0.04 ± 0.03 (16%)	3.4 ± 0.8
	15	0.33 ± 0.01	0.17 ± 0.01 (52%)	0.16 ± 0.01 (48%)	0.10 ± 0.01	0.06 ± 0.01 (38%)	6.2 ± 0.3
	100	0.45 ± 0.03	0.43 ± 0.02 (98%)	0.02 ± 0.04 (4%)	0.02 ± 0.04	<d.l.	<d.l.
BTN6 05/02/2012	5	0.43 ± 0.01	0.17 ± 0.03 (39%)	0.26 ± 0.03 (61%)	0.21 ± 0.05	0.05 ± 0.04 (19%)	0.79 ± 0.80
	15	0.20 ± 0.02	0.13 ± 0.02 (65%)	0.07 ± 0.03 (35%)	0.03 ± 0.04	0.04 ± 0.03 (57%)	1.3 ± 0.8
	100	0.32 ± 0.04	0.31 ± 0.03 (97%)	0.01 ± 0.05 (3%)	0.01 ± 0.05	<d.l.	<d.l.

[a] ±SD computed as the square root of the sum of variances

Table 5
Click here to download Table: Tab.5.docx

Tab. 5. Copper distribution between total concentrations, dissolved, total particulate, inorganic particulate and phytoplankton particulate fractions measured during the austral summer 2011-2012 in the three studied sites of Terra Nova Bay (Western Ross Sea). Cu:C ratios were also reported. Data reported as mean ± SD of at least three measurements.

Sampling station, date and depth (m)		Cu concentration, nmol L^{-1}					Cu:C ratio in phytoplankton, µmol mol^{-1}
		Total	Dissolved (% *vs* total)	Total particulate[a]	Inorganic particulate[a]	Phytoplankton particulate (% vs. Tot part.)	
T10 15/12/2011	5	3.9 ± 0.1	2.9 ± 0.1 (76%)	1.0 ± 0.2 (24%)	0.53 ± 0.17	0.42 ± 0.06 (44%)	159 ± 1
	8	3.9 ± 0.1	2.9 ± 0.1 (75%)	1.0 ± 0.1 (25%)	<d.l.	1.0 ± 0.1 (100%)	151 ± 1
	100	5.0 ± 0.1	4.36 ± 0.03 (87%)	0.6 ± 0.1 (13%)	<d.l.	0.71 ± 0.05 (~100%)	142 ± 1
BTN6 20/01/2012	5	4.0 ± 0.1	2.05 ± 0.02 (52%)	1.9 ± 0.1 (48%)	0.17 ± 0.15	1.8 ± 0.1 (91%)	150 ± 1
	15	3.1 ± 0.1	1.7 ± 0.1 (54%)	1.4 ± 0.2 (46%)	0.01 ± 0.23	1.4 ± 0.2 (99%)	147 ± 1
	100	4.7 ± 0.1	4.4 ± 0.1 (93%)	0.33 ± 0.14 (7%)	0.25 ± 0.14	0.08 ± 0.02 (24%)	102 ± 1
BTN6 05/02/2012	5	3.7 ± 0.1	1.7 ± 0.1 (46%)	2.0 ± 0.2 (54%)	<d.l.	2.1 ± 0.2 (~100%)	33.3 ± 0.6
	15	2.9 ± 0.2	1.4 ± 0.1 (48%)	1.5 ± 0.2 (52%)	0.07 ± 0.32	1.4 ± 0.2 (95%)	46.0 ± 0.7
	100	4.7 ± 0.2	4.2 ± 0.2 (90%)	0.49 ± 0.23 (10%)	0.36 ± 0.24	0.13 ± 0.08 (27%)	130 ± 1

[a] ±SD computed as the square root of the sum of variances

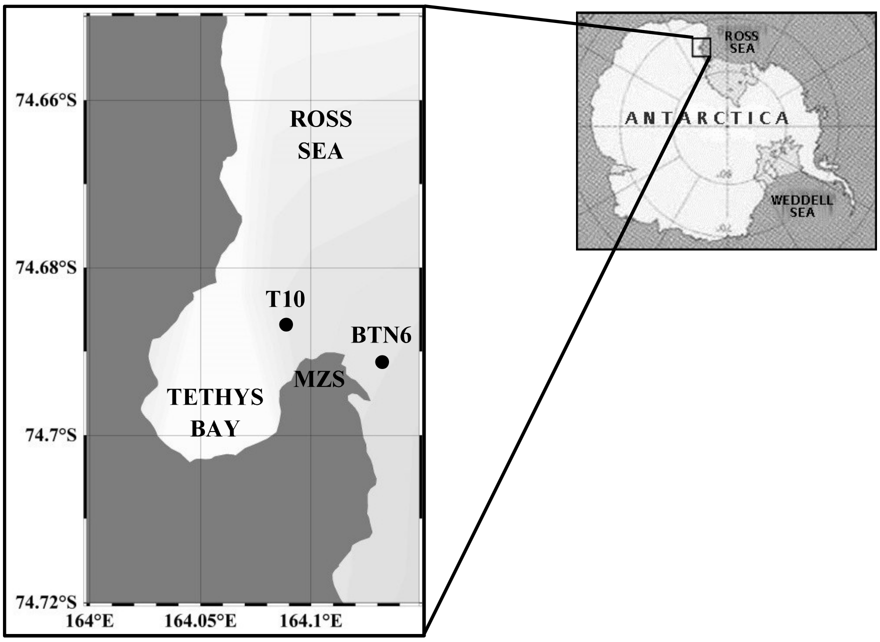

74.66°S
74.68°S
74.7°S
74.72°S
164°E
164.05°E
164.1°E
ROSS SEA
T10
BTN6
MZS
TETHYS BAY
ANTARCTICA
ROSS SEA
WEDDELL SEA

Fig. 1.

Figure 2
Click here to download Figure: Fig.2.pdf

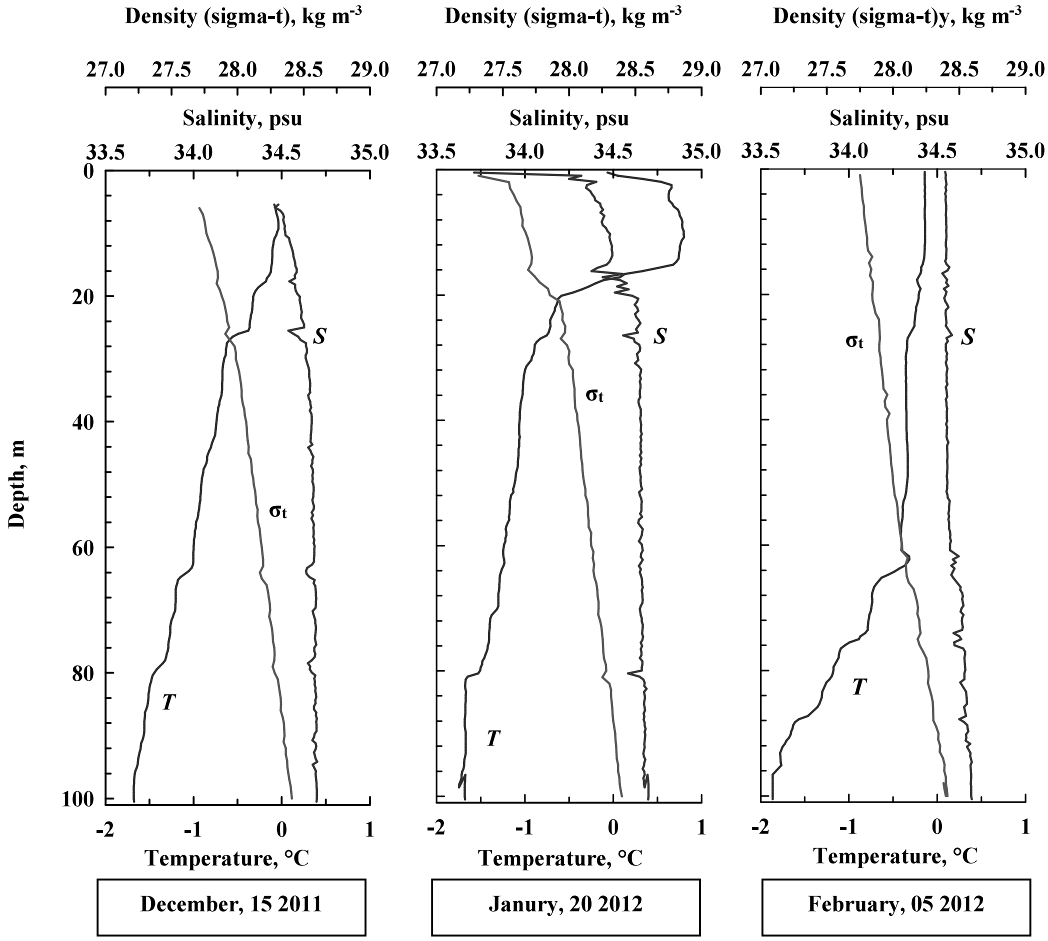


Fig. 2.

Figure 3
Click here to download Figure: Fig.3.pdf

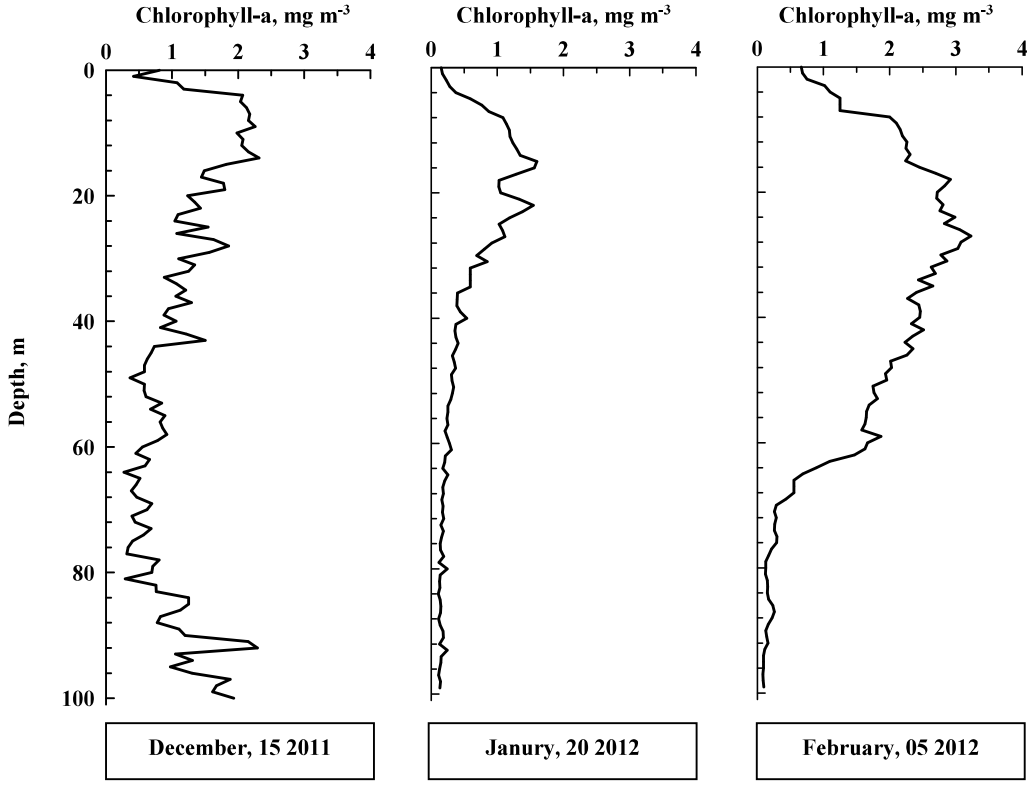


Fig. 3.

Figure 4
Click here to download Figure: Fig.4.pdf

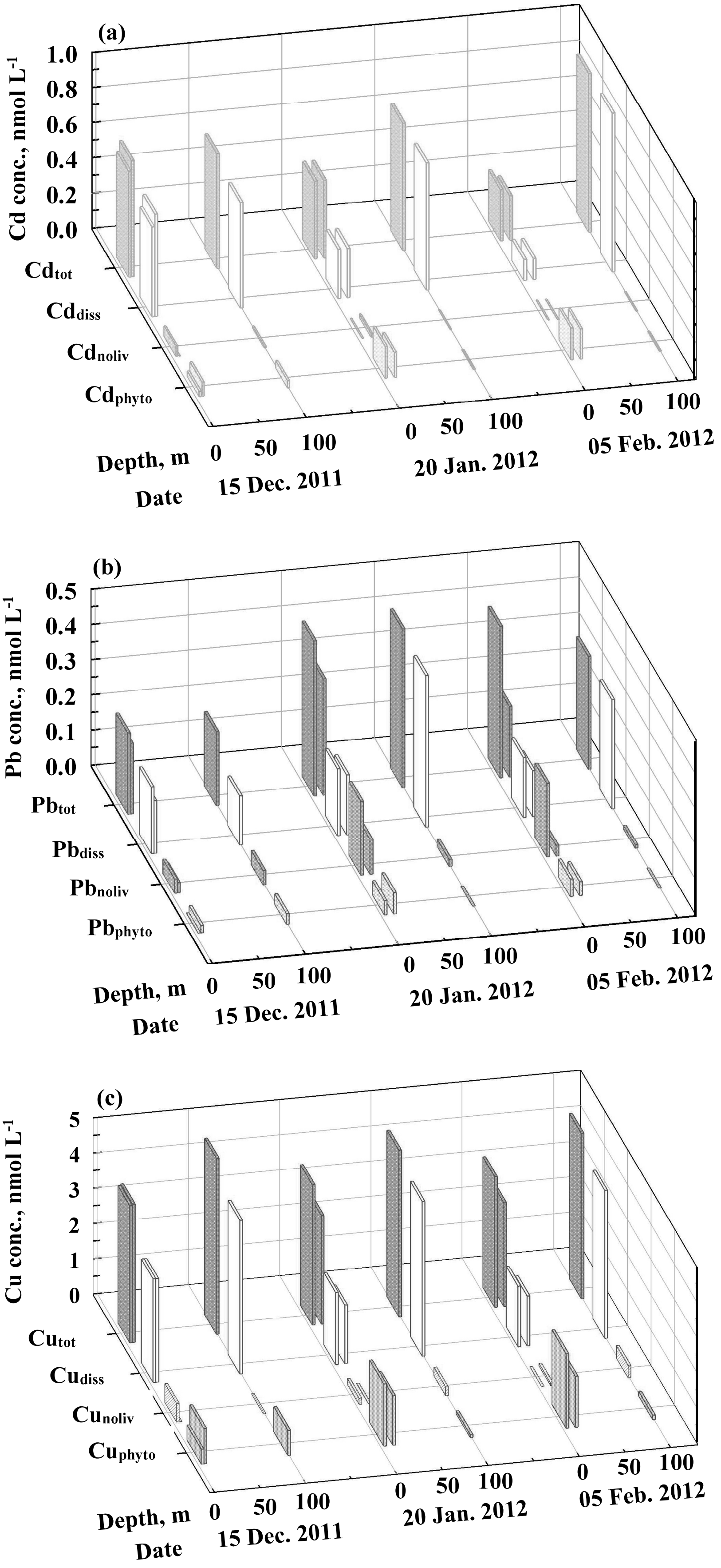


Fig. 4.

FIGURE CAPTIONS

Fig. 1. Map of the Terra Nova Bay area showing the location of the main Italian Station "Mario Zucchelli" (MZ) and the two sampling sites, T10 and BTN6, during the 2011-2012 Antarctic campaign

Fig. 2. Vertical profiles of temperature (*T*), salinity (*S*) and density (σ_t) measured at Terra Nova Bay (sites T10 and BTN6) during the sampling dates of December, the 15th 2011, January, the 20th 2012, February, the 5th, 2012.

Fig. 3. Vertical profiles of chlorophyll-a (Chl-a) concentrations measured at Terra Nova Bay (sites T10 and BTN6) on December, the 15th 2011, January, the 20th 2012 and February, the 5th, 2012.

Fig. 4. Distribution between total, dissolved, non-living particulate and phytoplankton particulate fractions of Cd **(a)**, Pb **(b)** and Cu **(c)** in Terra Nova Bay during the austral summer 2011-2012.