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Summer distribution of trace metals in the western sector of the Ross Sea, Antarctica

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The more important water masses generated by the interaction of Circumpolar Deep Water and the shelf waters in the western sector of the Ross Sea are characterized for trace element contents. The distribution of cadmium, lead, copper, zinc, iron, manganese and chromium during the austral summer is analysed and discussed according to the physical, chemical and biological processes which affect the composition of the water masses. The Cd concentration is found to have a relative high variability that can be related to biological activity and the water mass age, MCDW presents a mean dissolved concentration (SD) of 0.77 (0.07) nmol kg^{-1}, while the HSSW and AASW have a mean concentration of 0.63 (0.06) and 0.61 (0.16) nmol kg^{-1}, respectively. Lead features the typical distribution of a scavenged element with a surface maximum ranging between 22 and 130 pmol kg^{-1} decreasing to 11 pmol kg^{-1} in deep waters. However, the vertical distribution in the shelf area features a maximum concentration in intermediate/deep waters and we can hypothesize that the distribution may be influenced by more than one source. The surface dissolved concentration of zinc and copper were un-homogeneously distributed, the mean (SD) values were 5.25 (2.92) and 1.99 (1.49) nmol kg^{-1} for zinc and copper, respectively and increased with depth for both the elements. We may therefore hypothesize enrichment in the dissolved phase deriving from recycling in deep waters. 95% of the chromium was in dissolved form and showed a superficial depletion; the mean concentrations were 1.6 ± 0.2 and 2.6 ± 0.8 nmol kg^{-1} for surface and deep waters respectively. The vertical distribution of dissolved manganese was quite homogeneous with a mean concentration 0.96 ± 0.7 nmol kg^{-1}. The particulate iron and manganese concentration trends are similar and feature a significant bottom increase implying a significant input from resuspension; the mean concentration of particulate ranged between 1.4 and 7.4 nmol kg^{-1} for iron and ranged between 0.072 and 0.29 nmol kg^{-1} for manganese.

1. Introduction

The Ross Sea makes an important contribution to the formation of Antarctic Bottom Water[1,2] and features some of the highest primary production and phytoplankton biomass in the Southern Ocean:[3,4] the physical, chemical and biological processes taking place there define the composition of water masses; on the other hand, the differences observed in the composition may affect their plankton ecology.

The plankton community may affect the water concentration of major and minor nutrients by metabolic and catabolic activities, indeed it is well known that some trace metals co-vary with major nutrients and there is also evidence that they may influence plankton productivity and hence community structure.[5–7] Trace elements, such as iron, copper and zinc, are recognized as micronutrients because they play an essential biological role and some of them assume the typical nutrient-type vertical distribution.[8–10] Iron, due to its low concentration in the so-called high nutrient low chlorophyll areas (HNLC) is deemed the limiting factor for the primary production of phytoplankton; on the other hand, an excess of some of them, such as copper or even zinc, may inhibit phytoplankton growth.[11,12] The distribution of other metals with different geochemical behaviour, although not directly related to biological activity, may also be affected by it throughout the particulate cycle.[13]

Trace metal distribution in the Ross Sea shows a remarkable variability of concentration and dissolved/particulate partition, the variability being observed in relation to time and space, both horizontal and vertical. Concentration in the dissolved phase is substantially different in the shelf area and offshore; the surface water concentration of micronutrient elements shows a significant depletion going from north to south due the high primary production observed in inshore water. It should be noted that the Ross Sea features one of the largest HNLC areas, so iron may play a key role in controlling phytoplankton bloom.[14,15] The seasonal cycle of plankton blooms and the pack ice formation in the Southern Ocean are also responsible for the remarkable variability in the concentration of trace metals and the dissolved/particulate partition in coastal areas, where the strongest spring/summer plankton bloom is observed and the cycle of pack ice formation/melting considerably changes the composition of the water.[13,16] Sediment resuspension is also hypothesized to contribute to the trace metal concentration in water.[14]

Study of the distribution of trace metals may therefore improve the understanding of processes occurring in different parts of the Ross Sea, in relation to their hydrological regime. Although different areas have been investigated in the Southern Ocean our knowledge of the distribution and speciation of trace elements in this geographical area is only partial.[13–15,17–19] Moreover, the distribution of some important elements, including chromium, is practically unknown and for other elements such as manganese, which affects the vertical distribution of microcomponents, very few data are available.

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In the framework of the Italian Research Program in Antarctica (PNRA), the Ross Sea was investigated during the austral summer 2000/01. The aim of the research was to study the distribution of dissolved and particulate cadmium, lead, copper, zinc, iron, manganese and chromium in the western sector of the Ross Sea during the austral summer. Results will be considered and discussed in relation to the different water masses that characterize this oceanic region.

2. Description of the area

Large seasonal variations in winds, ice cover, phytoplankton biomass and sedimentation of particulate matter characterize the Ross Sea.[20] Due to the occurrence of several significant water masses, the Ross Sea plays an important role in the circulation of the Southern Ocean and the composition of the other oceans as well. The position in the western sector of the main water masses that can be recognized in the Ross Sea is schematically reported in the frame included in Fig. 1: Antarctic Surface Water (AASW), Modified Circumpolar Deep Water (MCDW), High Salinity Shelf Water (HSSW) and Iced Shelf Water (ISW).[1] Antarctic Surface Water (AASW) broadens from the Polar Front to the continental margins of Antarctica with rather variable properties: the temperature ranges between −1 and +0.5 °C, as a function of solar irradiation, and salinity may vary from 33 up to 34.4‰, as a function of the contribution of thawed pack ice and continental ice. Usually close to the continental shelf break, below AASW, there is a warm, saline water mass, which derives from the intrusion of Circumpolar Deep Water (CDW). CDW occupies most of the deep layers of the Antarctic Circumpolar Current, assuming different names according to different values of density and depth. In the Ross Sea, CDW develops into several new water masses on and near the Antarctic continental shelves and it is characterized by a temperature value of around +1 °C and a salinity value of around 34.7‰. Modified CDW, referred to as a Warm Core in the Ross Sea, derives from the mixing of CDW and shelf waters near the continental shelf break and is typified by considerable variability of temperatures and a relatively constant salinity. In the western sector, it intrudes on the continental shelf at an intermediate depth. HSSW constitutes one of the more important water masses in the western sector of the Ross Sea and its presence is related to winter processes in the Ross Sea polynia. During the austral winter, the pack ice formation and its northward drift yields high salinity water (HSSW), which, due to its density, sinks. Therefore, the volume of HSSW will depend on the volume of pack ice produced on the continental shelf during the winter. It flows partially northward, following canyons, and southeastward, under the Ross Sea Ice Shelf, taking part in the formation of ISW, which is characterized by a potential temperature below freezing point. Due to their density, ISW and HSSW sink to the bottom and contribute to the development of the Antarctic Bottom Water (AABW).[21] The Ross Sea polynia starts broadening in October, due to the katabatic winds and ice melt and thanks to the energy imparted by solar radiation and sporadic heat inputs from ACC, which is up-welled onto the shelf. At the end of December the ice coverage in the Ross Sea is for the most part disappearing and by late January ice largely fades out from the continental shelf region. In early March surface waters begin freezing again. Phytoplankton biomass starts blooming in late October, achieving its seasonal maximum in late December and diminishing thereafter.[3,20] There is evidence that in coastal areas a second bloom may occur at the end of January.[22] Productivity seems to have a similar seasonal pattern, characterized by elevated production occurring in November and early December, although productivity lessens much faster than biomass does.[3,23]

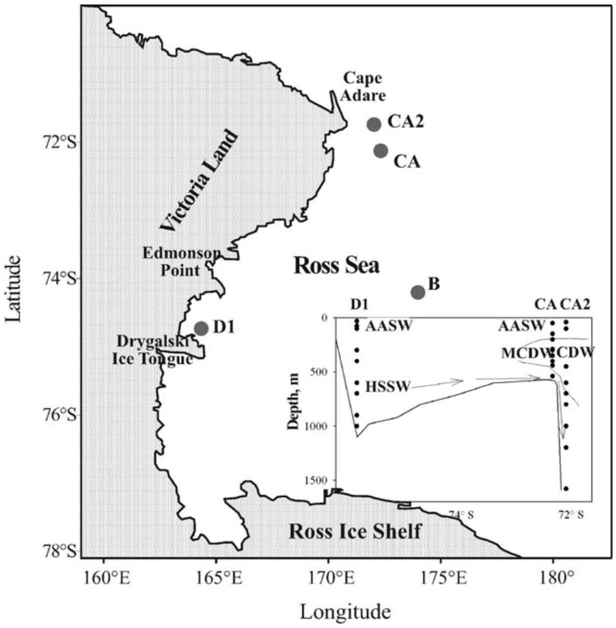

Fig. 1 Sampling sites in the western sector of the Ross Sea. The enclosed frame represents the schematic distribution of the water masses in the sampling area.

Studies carried out in the Ross Sea indicate three biogeochemical regimes differentiated on the base of primary production and phytoplankton species. In particular the south/western sector examined in this study was characterized by high production dominated by diatom growth, while the northern area around the shelf break is characterized by lower and more variable production. The low primary production in the latter area was hypothesized due to micronutrient deficiency in addition to prolonged ice coverage.[24] Differences were also observed in the nutrient distribution. Measurements of nitrate and phosphate were carried out in the same areas as those examined in this study; results showed a higher depletion of phosphate for AASW in the permanent polynia area and the Joides Basin platform compared with Cape Adere, while the difference was reduced, although significant, for nitrate. The mean surface concentrations of phosphate were 1.08, 1.20 and 1.75 μmol kg^{-1} for the three areas respectively, while in the same sites the mean surface concentrations of nitrate were 23.2, 23.3 and 25.3 μmol kg^{-1}.[25] Differences were also observed for the characteristics of sediment as a consequence of rock composition, transport and deposition processes. The sediment on the external platform along the Joides Basin is comprises very fine sediments with a high content of Cr, Ni, V Cu, Zn, Si and L.O.I. Thus, also in consideration of the fact that in the sediment there is a large content of biogenic Si, the sedimentation is related to biological processes.[26,27]

As a consequence of the energy level, the sediment along the Drygalski Basin presents an unhomogeneous granulometric distribution and a metal composition related to the McMurdo volcanic rock.[26] The metal distribution in the Ross Sea is also affected by the geological characteristics: the Ross Sea is influenced by the West Antarctic Rift System, by active volcanoes (Mts Erebus and Melbourne) and hydrothermal vents; indeed the coastal area around Edmonson Point presents hydrothermal activity which is related to the structure of Mt Melbourne.[28]

3. Experimental

3.1 Sampling

Seawater samples were collected in the western Ross Sea (Southern Ocean, Antarctica) during the 2000–01 Italian expedition (sampling dates are reported on Table 1), on board the RV Italica. Samples were gathered along the water column

Table 1 Coordinates, physical and chemical parameters, fluorescence and particulate content characterizing samples collected in the western sector of the Ross Sea at the date indicated

Site	Latitude	Longitude	Depth/m	Salinity (‰)	Temp./°C	O_2/μmol kg^{-1}	Fluores.	Particul./mg kg^{-1}
D1	75°9′ S	164°29′ E	30	34.49	−1.42	244	1.68	0.43
17 Jan 2001			75	34.72	−1.86	211	0.28	0.10
			100	34.73	−1.87	210	0.17	0.10
			300	34.76	−1.90	206	0.02	0.20
			400	34.78	−1.90	206	0.01	0.18
			600	34.82	−1.91	209	0.01	0.29
			700	34.82	−1.92	208	0.01	0.12
			900	34.83	−1.92	207	0.01	0.11
			1000	34.83	−1.92	207	0.01	0.13
CA	72°12′ S	172°58′ E	50	34.15	−1.37	239	0.31	0.76
21 Jan 2001			150	34.48	−0.28	176	0.03	0.28
			200	34.57	0.32	164	0.02	0.20
			290	34.64	0.67	150	0.01	0.12
			300	34.64	0.56	152	0.01	0.08
			350	34.66	0.24	157	0.01	0.15
			400	34.67	0.03	163	0.01	0.30
			440	34.70	−0.98	175	0.01	0.34
			540	34.71	−0.75	177	0.01	0.39
CA2	71°57′ S	172°30′ E	40	34.14	−1.30	235	0.28	0.62
26 Jan 2001			100	34.27	−1.25	224	0.28	0.47
			450	34.63	0.55	157	0.02	0.10
			600	34.67	0.64	149	0.01	0.07
			700	34.69	0.45	151	0.01	0.19
			800	34.69	0.41	151	0.01	0.10
			1000	34.70	0.11	156	0.01	0.26
			1200	34.69	−0.25	162	0.01	0.19
			1580	34.70	−0.06	156	0.01	0.09
B	74°00′ S	174°26′ E	20	34.19	0.68	260	0.55	0.89
6 Feb 2001			60	34.19	0.67	261	0.55	0.79
			80	34.58	−0.70	195	0.25	0.83
			150	34.59	−0.86	185	0.04	0.27
			200	34.60	−1.51	194	0.03	0.12
			250	34.63	−1.85	201	0.02	0.04
			300	34.66	−1.88	205	0.02	0.08
			400	34.73	−1.90	203	0.02	0.06
			450	34.76	−1.91	203	0.02	0.08
			500	34.76	−1.91	203	0.02	0.17

at ten different depths, according to temperature, dissolved oxygen, salinity and fluorescence profiles, using Teflon coated GO-FLO bottles (General Oceanics, USA) mounted on a Kevlar line and triggered by Teflon messengers. Sampling at each site was completed within 12 hours of the ship positioning; 2 or 3 bottles were dipped at the same time; in Table 1 are reported the mean coordinate for each sampling site; the constancy of water vertical structure during the sampling was checked by CTD profile at the beginning and the end of sampling. To verify the representativity of results, occasionally, two samples were collected at the same depth. Four sites (Fig. 1) were chosen, in order to evaluate the relevant water masses present in the western sector of the Ross Sea. Two sites, CA and CA2, are in the Cape Adare area, where the HSSW sinks towards the deep sound of the Ross Sea contributing to form the AABW, and where the CDW intrudes around 200–600 m producing MCDW. Site D1 is in the Drigalsky Basin, close to the ice tongue, where the small permanent polynia is located and contributes to the HSSW formation. Site B is in the Joides Basin, characterized by reduced horizontal transport and an efficient sedimentation process.[29]

3.2 Analytical procedure

The water samples were immediately filtered on board through polycarbonate membrane filters (0.4 μm) and collected in 2 L FEP bottles; both the filtered water sample and the membrane with the particulate were stored frozen at −20 °C until analysis. The entire 20 L bottle content was filtered to obtain enough particulate matter for analysis and to avoid the effect of non-homogeneous particle distribution inside the sampling bottle. To prevent sample contamination all the precautions and material treatments previously described were applied.[30] Briefly all materials were cleaned applying one multi-step protocol beginning with a heated detergent bath solution for 2 weeks, 2 steps in a heated acid bath (10% HNO_3, suprapure grade-65% Merck, Darmstadt, Germany) for 2 weeks; the bottles were then filled for two weeks with a 0.1% solution of ultrapure concentrated HNO_3 (Romil Pure Chemistry-Romil Ltd, Cambridge, GB). This step was repeated twice, the bottles were filled with a 0.01% ultrapure HNO_3 solution and sealed in double polyethylene bags until use; between each step the materials were rinsed with ultrapure water (ELGA-Vivendi Water Systems, Bucks, UK). The GO-FLO bottles, were repeatedly washed using ultrapure water and 0.1% ultrapure HCl (Romil Pure Chemistry, Romil Ltd, Cambridge, GB) and were finally rinsed with ultrapure water to avoid contamination before sampling. Tests to check the cleanliness were performed on the rinse water.

Treatments and analytical measurements were performed in clean laboratories, where the working area was in a class 100 laminar flow area. Dissolved trace metal measurements were performed by HR-ICP-SFMS (Element2, Finnigan-MAT, Bremen, Germany), as previously described by Turetta *et al.*[31] Intensity optimization was carried out daily, using a tuning solution of indium in ultra pure water, 1 ng ml^{-1}. Before beginning the analyses, an accurate mass calibration was performed in low, medium and high resolution modes using a solution containing elements with m/z values covering the whole mass range of interests. Cd and Pb were determined in low-resolution mode ($m/\Delta m$ = 400), while Cr, Cu, Mn and Zn were determined in medium resolution mode ($m/\Delta m$ = 4000). Two sample introduction systems were used. The first employed direct introduction by a μ-flow nebulizer (Elemental Scientific, 100 μl min^{-1}) with a Teflon spray chamber to determine Cr, Mn and Zn; the second, used to determine Cd and Pb, was by direct introduction *via* a μ-flow nebulizer (Elemental Scientific, 100 μl min^{-1}) coupled with a desolvation unit (Aridus, Cetac Technologies, Omaha, NE, USA). The two introduction systems were coupled with an ASX-100 autosampler (Cetac Technologies, Omaha, NE, USA). Details of operating parameters for the ICP-SFMS and desolvation unit are reported in the original paper.[31] The sample introduction system, the desolvation unit and the autosampler were kept and handled under a laminar flow hood. Each sample was diluted 10-fold using ultra pure water and acidified with HNO_3 (1 : 10 v : v) UPA grade (ROMIL, UK) and an internal standard solution of In, Sc, Y and W (1 ng ml^{-1}) was added. The accuracy of the measurements was determined using a certified reference material (NRCC-NASS 5); the measured values were in good agreement with certified values for the available data: for the determined elements the mean difference between the measured and certified value was 5% of the certified value and always within the certified tolerance interval. The quantification of trace elements was carried out by a matched calibration method. Five aliquots of one sample were spiked with a multi-element standard solution (5, 10, 50, 100, 200 pg ml^{-1}) to quantify the trace element contents. Blank tests were performed for each analytical session by analysis of a solution obtained from ultrapure water acidified by HNO_3 10%. Where internal standard and reagents used for analyzing samples were added, the blank concentration compared with the mean sample concentration ranged between 7% for lead and less than 1% for manganese. The blank contribution was subtracted from the concentration of acidified and diluted samples.

The particulate was solubilized with 8 M HNO_3 (suprapur grade quality, Merck), using a microwave digestion system (CEM DS2000). Multi-element determinations in the extracts were performed by inductively coupled plasma optical emission spectrometry with a simultaneous CCD detection system (Varian Vista PRO). The quantification was carried out by working standard solutions prepared daily by proper dilution of stock standard solution (1 mg mL^{-1}, Merck, Darmstadt, Germany) with Milli-Q water (Millipore, USA). The accuracy of analytical procedures was tested by certified reference material BCR 414 (SM&T Program of European Union). The blank contribution was evaluated on 5 membranes that were not used on-board and that were handled, stored and analyzed in the same way as the samples; the blank contribution ranged between 3 and 25% of the mean value (obtained by digesting filters containing the particulate samples) depending on the element and the particulate content. The difference in the particulate content for the replicate samples was meanly 20%.

4. Results and discussion

The coordinates of sampling sites, data of salinity, temperature, biomass measured as fluorescence and particulate content are reported in Table 1. The trace element concentrations in dissolved and particulate form are reported in Table 2.

The potential temperature–salinity properties of samples are reported in Fig. 2. Samples collected deeper than 400 m at site D1 and deeper than 450 m at site B can be identified as HSSW. Waters at a depth of between 200 and 350 m at site CA and waters at a depth of between 450 and 1000 m at site CA2 presented characteristics of salinity and potential temperature corresponding to MCDW. The upper layer of 50–100 m presented variable temperature and salinity corresponding to AASW. A relatively low depth characterizes the sites CA and B that showed enrichment of particulate matter in surface and bottom waters. Particulate in the surface layers of these two sites is mostly related to biological activity, while we may hypothesize that particulate matter in the bottom layers derives from sediment resuspension. Indeed the CA site (Cape Adere area) is characterized by high hydrodynamic energy as confirmed by the granulometric distribution of sediment,[26] that justify the particularly evident enrichment in particulate matter observed. The overflow of bottom waters, enriched in particulate matter, from the shelf was also visible in the CA2 profile (depth of between 700 and 1200 m). The D1 profile shows a deep-water higher in particulate (depth of 300–700 m). Considering the presence of the Drigalsky Ice Tongue, we can hypothesize that this originates from the detritical matter transported by the base of the David Glacier feeding the ice tongue.

4.1 Cadmium

The dissolved cadmium concentration ranged between 0.3 and 0.9 nmol kg^{-1} and showed general agreement with the concentrations observed in the Weddel Sea[32,33] and in the Ross Sea.[16,17,34] Relatively high vertical and horizontal variability were observed. Two phenomena may change Cd concentration in polar areas: biological processes, since phytoplankton take up cadmium as a micronutrient, and physical processes. The latter are dilution, due to the ice melting during the austral summer, and concentration, when the pack ice is growing through the winter. In all the sampling sites the particulate Cd showed a surface maximum. A substantial decrease of Cd concentration in the dissolved phase and an increase in the particulate phase in coastal areas of the Ross Sea in relation to phytoplanktonic blooms were highlighted during the austral summer.[13,16,34] The relationship between Cd concentration and biological activity is emphasized by the comparison of the vertical distribution of Cd at the four sites and that of biomass, evaluated by fluorescence measurements. The vertical profiles showed a minimum value of dissolved Cd concentration in the surface layer, in relation to maximum values of fluorescence. This was particularly pronounced in the sites D1 and B, where the highest values of fluorescence were determined. On the other hand, the concentration of particulate Cd is higher in the surface/subsurface layers and it decreases along the water column (see Fig. 3a). The variable surface distribution of cadmium in the Ross Sea, in both the dissolved and particulate phase, may be related to the non-homogenous distribution of phytoplankton activity during the austral summer, as highlighted in previous studies,[6,7] which implies differences in concentrations of major nutrients and of the trace elements whose distribution is controlled by biological activity. Therefore, the depletion in the surface layer and the regeneration of Cd in deep waters observed at site B may be related to the efficient sedimentation process of biogenic particles that characterizes the Joides Basin. An independent study carried out to evaluate the nutrient distribution in the same area during the campaign, it showed a similar trend for phosphate concentration.[25] Although the relationship observed between the impoverishment of dissolved cadmium and fluorescence may support the hypothesis of a vertical nutrient-like distribution for this element, it cannot provide a thorough explanation of the differences in the mean concentrations observed in the deep

Table 2 Metal concentrations in dissolved and particulate form (nmol kg^{-1})[a]

		Cd		Cr		Cu		Fe	Mn		Pb		Zn	
Site	Depth/m	Diss.	Part.	Diss.	Part.	Diss.	Part.	Part.	Diss.	Part.	Diss.	Part.	Diss.	Part.
D1	30	0.48	97.5	1.4	0.123	1.6	0.652	1.8	0.35	59	0.045	15.1	8.2	0.81
	75	0.62	12.8	4.2	0.087	2.3	0.0516	2.5	0.41	120	0.027	7.8	6.1	0.20
	100	0.53	30.9	3.0	0.076	2.1	0.083	5.9	0.81	198	0.014	12.2	5.5	0.17
	300	0.59	3.79	6.2	0.064	4.1	0.072	6.0	0.90	337	0.204	14.1	24.1	0.28
	400	0.66	2.23		0.078	2.0	0.047	4.5		321	0.053	15.5	6.7	0.25
	600	0.64	2.30		0.176	2.6	0.164	3.9		286	0.026	10.8	4.9	0.60
	700	0.54	3.24	1.5	0.176	2.6	0.067	3.7	0.96	240	0.023	8.6	8.6	0.21
	900	0.69	1.49	1.8	0.106	1.9	0.132	3.1	0.97	205	0.003	7.0	7.3	0.14
	1000	0.63	0.60	2.4	0.033	2.0	0.0185	3.9	1.14	139	0.021	6.8	2.3	0.15
CA	50	0.73	45.5	1.3	0.113	0.43	0.097	1.2	0.76	31	0.057	17.2	2.3	0.63
	150	0.72	11.5	1.3	0.102	1.6	0.085	1.0	0.92	51	0.043	11.1	8.0	0.38
	200	0.90	6.3	3.0	0.165	1.9	0.100	1.2	0.58	24	0.035	11.2	7.6	0.28
	290	0.72	1.3	2.9	0.102	2.4	0.101	2.2	0.92	52	0.082	8.6	7.1	0.26
	300	0.76	1.7	3.1	0.088	2.1	0.088	1.8	1.3	96	0.042	7.0	7.3	0.11
	350	0.85	2.9	2.3	0.131	1.7	0.136	3.3	0.33	142	0.031	13.4	6.5	0.43
	400	0.65	2.1	4.9	0.107	26.5	0.126	4.1	1.0	190	0.034	8.8	11.9	0.36
	440	0.59	2.7	3.0	0.097	4.1	0.107	5.5	1.2	208	0.031	7.2	8.1	0.26
	548	0.89	1.8	1.5	0.127	3.2	0.076	3.1	0.88	105	0.021	19.6	11.2	0.17
CA2	40	0.59	11.1	1.7	0.099	1.2	0.187	1.5	0.33	94	0.022	26.0	3.2	0.58
	100	0.53	24.3	1.8	0.118	3.3	0.112	0.75	0.66	19	0.016	14.0	5.1	0.42
	450	0.73	1.7	2.8	0.106	3.1	0.067	1.0	0.58	26	0.017	9.1	5.0	0.14
	600	0.73	1.4	2.1	0.053	2.6	0.058	0.67	0.85	36	0.013	10.8	6.8	0.26
	700	0.67	0.86	2.5	0.044	2.6	0.056	0.57	0.90	51	0.012	19.3	6.4	0.16
	800	0.72	2.4	2.4	0.118	3.4	0.066	2.0	1.1	56	0.010	20.1	5.4	0.09
	1000	0.84	0.85	1.9	0.084	2.6	0.070	0.91	0.68	46	0.013	18.9	6.1	0.10
	1200	0.69	2.6	3.4	0.108	3.5	0.058	3.2	2.3	187	0.017	10.5	6.2	0.09
	1580	0.75	1.7	2.7	0.067	2.3	0.048	1.3	4.1	91	0.016	16.7	7.5	0.35
B	20	0.34	79.9	1.4	0.210	1.0	0.7334	3.3	0.45	92	0.127	13.6	2.2	1.20
	60	0.86	13.4	1.6	0.284	1.6	0.128	1.0	1.2	60	0.078	11.1	3.5	0.44
	80	0.85	54.1	1.7	0.140	2.1	0.151	1.2	0.57	25	0.044	21.6	3.6	0.79
	150	0.70	4.9	2.7	0.120	2.1	0.069	2.5	0.68	208	0.038	13.7	4.1	0.24
	200	0.67	4.2	1.8	0.108	1.6	0.094	2.7	0.36	147	0.028	7.0	4.4	0.31
	250	0.75	3.4	2.0	0.065	3.6	0.042	3.1	0.84	199	0.030	8.7	5.4	0.12
	300	0.71	5.2	1.9	0.098	2.2	0.057	2.1	0.63	207	0.018	9.3	3.8	0.18
	400	0.86	4.7	2.2	0.078	1.8	0.056	11.3	0.58	306	0.098	10.1	5.0	0.27
	450	0.56	5.5	2.0	0.058	1.8	0.054	12.3	0.81	345	0.053	11.1	5.1	0.21
	500	0.70	8.0	2.2	0.061	3.5	0.071	16.6	1.7	538	0.031	16.4	5.8	0.31

[a] Concentration of particulate Cd and Pb in pmol kg^{-1}.

waters, going from the coastal zone (site D1, mean concentration 0.62 nmol kg^{-1}) to the shelf break down (sites CA and CA2, mean concentration 0.78– 0.75 nmol kg^{-1}) (see Table 2). Dilution phenomena and biological activity may justify the low content of cadmium in AASW. However, they cannot explain the lower concentration observed in the HSSW compared with the MCDW. Taking into account the age of formation of the water masses, a likely explanation may be that higher concentrations were determined in relatively older water masses (the mean concentration in MCDW at sites CA and CA2 was 0.77 ± 0.07 nmol kg^{-1}) than in younger waters (HSSW at site D1 had a mean concentration of 0.63 ± 0.06 nmol kg^{-1} and the mean concentration of AASW in the region was 0.61 ± 0.16 nmol kg^{-1}). Both the AASW and the HSSW waters are of recent formation. The first is formed during the austral summer, while the second is generated during the austral winter along the coastal areas of the Ross Sea, where in the previous summer a phytoplankton bloom took place, producing a substantial decrease of cadmium.[34,35] Hence we can hypothesize that the composition of the HSSW was affected and partially maintained the assets acquired by the processes which occurred during the previous Antarctic summer. That indicates that about 20% of particulate cadmium is regenerated in a time longer than one annual cycle. Indeed, the cadmium concentra-

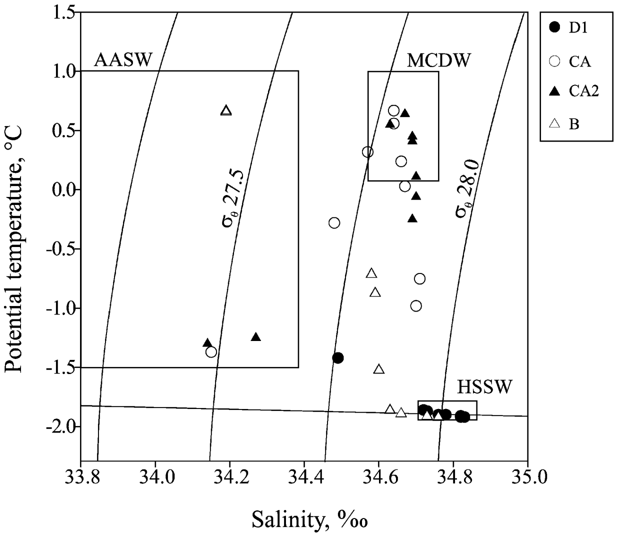

Fig. 2 Potential–salinity (*Θ vs. S*) plot for the samples collected at the 4 sites.

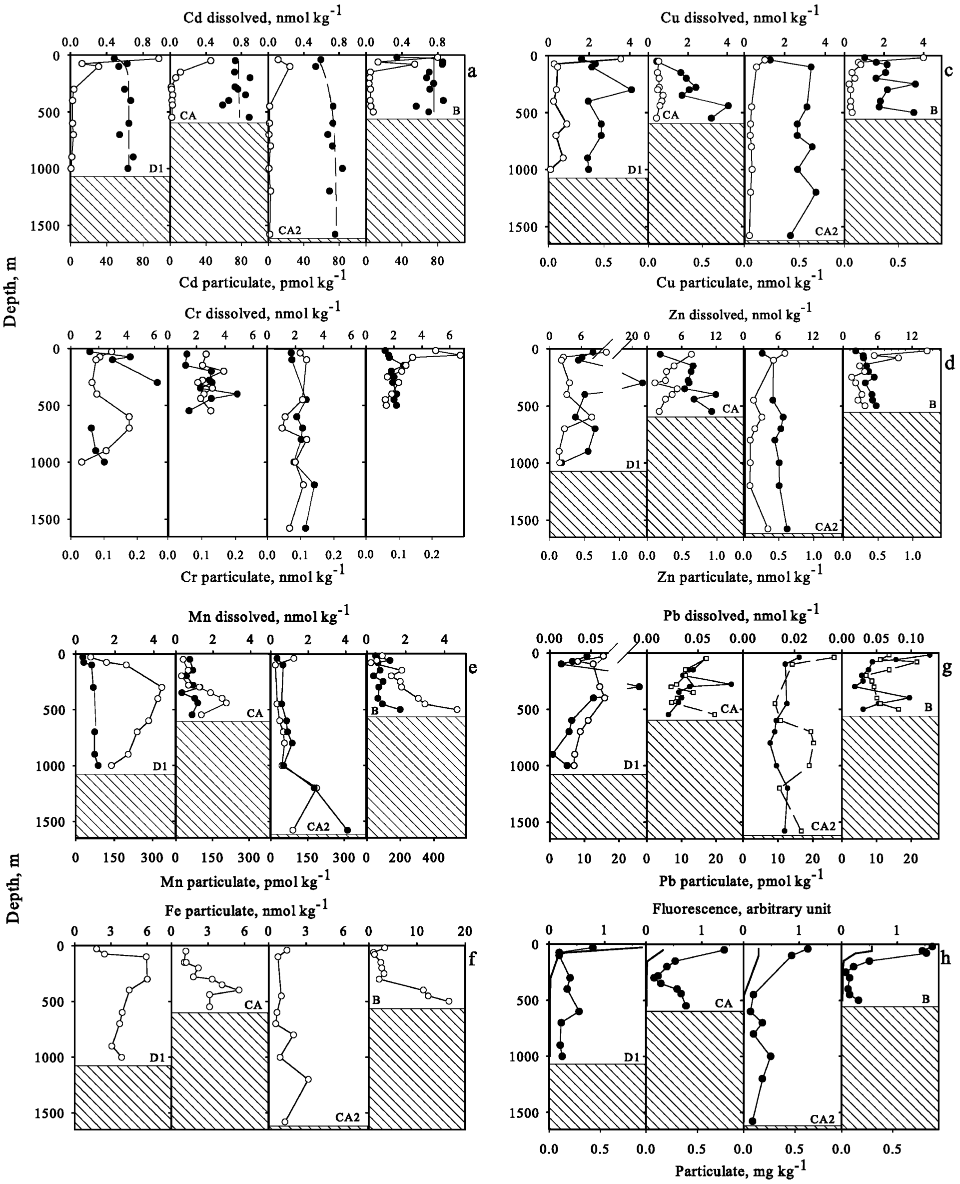

Fig. 3 Dissolved (○) and particulate (●) metal distribution at the four sampling sites: (a) Cd, (b) Cr, (c) Cu, (d) Zn, (e) Mn, (f) Fe, (g) Pb; (h) particulate matter content (●) and fluorescence measurement (—).

tion in the sediment of the polynia area is considerably higher than the mean concentration in the western Ross Sea: the mean concentration determined in the D1 area was 0.32 µg g^{-1} and the mean value detected in the western Ross Sea (Drygalsky Basin) was 0.13 µg g^{-1}.[26]

4.2 Lead

The results showed a significant surface enrichment of dissolved and particulate lead, which seems to differ according to the studied areas. The surface concentration of the dissolved fraction ranged between 22 and 127 pmol kg^{-1} (Table 2). Particulate Pb concentration ranged between 14 and 26 pmol kg^{-1} and showed an almost constant surface concentration in the shelf region (14–17 pmol kg^{-1} in D1, CA and B), while it was almost double in CA2. A surface enrichment of lead concentration is consistent with previous studies carried out in oceanic regions and reflects the atmospheric input and the short residence time of this element.[36,37] Previous studies carried out in coastal areas of the Ross Sea emphasized that Pb concentration may vary in relation to the geographical position and to the season.[13,34] At the end of summer in Wood Bay, the lead concentration was depleted along the entire water column by about 30% of the initial value, reaching a final 10 pmol L^{-1}.[34] In the Gerlache Inlet the concentration decreased from an initial value of 0.1 nmol kg^{-1} to 0.04 nmol L^{-1}.[13] In both the studies it was observed that the decrease was related to phytoplanktonic bloom and it was hypothesized that the biogenic particles were responsible for scavenging the dissolved Pb.

In this study deep-water concentration was about 30–50% of surface concentration and the minimum was reached in the CA2 profile, in correspondence with the MCDW; the mean value was the same as that detected in Wood Bay at the end of the summer (0.013 nmol kg^{-1}). However, all the profiles in the shelf area, D1, CA and B, showed a maximum value of dissolved Pb at intermediate depths (250–400 m), with concentrations ranging between 100 and 210 pmol kg^{-1} (Fig. 3f). Hence, it may be assumed that other local inputs, different from the atmospheric particulate, might rule the distribution of lead along the depth in this area. Flegal *et al.*,[36] who studied lead distribution in the Ross Sea, drew attention to the fact that hydrothermal vents in volcanic areas represent a significant source of Pb in the Southern Ocean. The coastal area of the western Ross Sea presents some active hydrothermal zones. In addition, the area of permanent polynia (site D1) is close to the Drigalsky Ice Tongue fed by the David Glacier. Hence, erosion due to glaciers, which carry a considerable amount of detritus particles, may be a substantial factor for trace metal distribution in this basin.[35,38] However, further studies are necessary to verify the significance of this maximum in intermediate shelf waters.

Profiles of CA and B, which are characterized by a relatively low depth, showed an enrichment of particulate Pb in surface and bottom waters. The sites showing the higher surface concentration of particulate matter showed a lower content of dissolved Pb, emphasizing the role of scavenger of biogenic particles, as previously hypothesized in coastal areas and discussed above. The bottom enrichment may derive from sediment resuspension and this was evident at site CA where the hydrodynamic is characterized by a flow of bottom water. Sediment resuspension increased the particulate lead in the bottom waters, but no effects were detectable for the dissolved metal. Therefore, particulate matter seems to be constituted by inert matter not releasing Pb. Thus, more than one factor may be affecting the distribution of this element in the Ross Sea.

4.3 Copper

Dissolved copper concentration in surface water ranged between 0.4 nmol kg^{-1} and 1.6 nmol kg^{-1}, in agreement with literature data for the Southern Ocean;[13,14,17,18] the concentrations are consistent with near shore waters or high atmospheric delivery.[39] In deep water its dissolved concentration ranged between 1.7 nmol kg^{-1} to 3.5 nmol kg^{-1}. The concentration is in excellent agreement with the general deep-water circulation and the residence time (about 1000 y) reported by Bruland.[39] The deep-water concentration is intermediate between concentrations in the Atlantic Ocean and Pacific Ocean. We can observe a surface depletion of dissolved copper corresponding to an increase of concentration in the particulate fraction and possibly related to biomass content. Hence, in agreement with its behaviour as an essential micronutrient, the surface concentration of copper seems to be ruled by phytoplankton uptake. It is necessary for the correct functioning of certain enzymes, relevant for the cellular metabolisms.[40,41] In oceanic oligotrophic waters the vertical distribution is intermediate between the nutrient-type and that of a scavenged element; it shows paucity in the surface waters and an enhancement in the intermediate and deep waters. The vertical profiles at sites CA and B show a general increase of concentration in bottom compared with intermediate waters, indicating a flux from the sediments caused by an earlier diagenesis (Fig. 3c). However, the distribution of the particulate fraction of total Cu was nearly constant at the sites studied (Fig. 3c). Therefore, we may hypothesize enrichment in the dissolved phase deriving from recycling at the sediment level without a resuspension of particulate containing copper. Hence, the vertical distribution seems to be controlled by the general processes highlighted by Bruland[39] for oceanic areas; it is scavenged *in situ* within the surface-intermediate waters and a significant part of particulate copper is regenerated back into the deep waters from diagenesis at the water/sediment interface.[42] Like most of the analyzed elements, intermediate waters at the site of permanent polynia (D1) showed a maximum value of dissolved Cu.

4.4 Zinc

The results of dissolved and particulate zinc concentration are reported in Table 2. In agreement with its characteristics as a nutrient-type element surface depletion was observed; however the reduction was small and not comparable to the concentration decrease detected in the surface waters of oligotrophic areas of the Pacific Ocean (0.05 nmol L^{-1}). The sub-surface concentration was about half to one third of the value detected in deep water (2.6 and 6.5 nmol kg^{-1}, respectively); only the samples collected in the polynia showed noticeably higher concentration than the mean value detected in the deeper layers. Since we do not have enough evidence to say whether the value was significant or the sample was subjected to weak contamination from the ship, the latter problem always represents a risk for this element, follow-up studies are necessary to validate the value. The dissolved concentration is consistent with deep waters in the Pacific Ocean[8] and the Southern Ocean.[18,33] The concentration along the water column of site B (the Joides Basin) is significantly lower than that detected at the other sites (the mean concentrations were 4.6, 6.1, 8.8, 6.2 nmol kg^{-1} for sites B, D1, CA, and CA2, respectively), however the vertical distribution highlighted bottom enrichment (Fig. 3d). In view of the fact that site B features an efficient sedimentation of biogenic particles rich in silicate, the correlation of Zn and Si in sediments[26,27] observed in the same area and the correlation of Zn and Si reported in studies carried out in oceanic oligotrophic areas,[8] we may hypothesize that the vertical distribution is ruled by surface uptake by plankton and by slow recycling along the water column towards the bottom. Indeed, the dropping off of its surface concentration in the dissolved phase was always accompanied by an increase in the particulate phase.

The distribution coefficient (the ratio between Zn concentration in dissolved and in particulate form) is at its minimum in surface layers (about 2) and increases by about one order of magnitude with depth (about 20), thus highlighting its recycling with depth.

4.5 Chromium, manganese and iron

The results of dissolved chromium show a homogeneous surface distribution in the studied area (see Table 2). It ranged between 1.4 nmol kg^{-1} (site B, in the Joides Basin) and 1.9 nmol kg^{-1} (site D), with a mean concentration of 1.6 ± 0.2 nmol kg^{-1}. The concentration for intermediate/deep waters was significantly higher than for the surface layer, varying from 1.9 nmol kg^{-1} (site B) up to 5.0 (site CA), and the mean concentration was 2.6 ± 0.8 nmol kg^{-1}. As for the other elements the intermediate water at site D showed a significantly higher concentration than that determined in the western Ross Sea. No data are available at present for chromium concentration in the Southern Ocean, but the results of this study are in agreement with concentration expected in oceanic areas, such as the Northeastern Pacific Ocean,[43] and lower than the concentration detected in the Atlantic Ocean[44] following the trend emphasized by Sirinawin and coworkers.[45]

The expected oceanic distribution of chromium is related to the biological activity, though it can be complicated by oxidation-reduction processes in anoxic waters. The vertical profiles of dissolved Cr for the four sites studied showed a general increase with depth (Fig. 3b); however, the surface depletion was not pronounced enough, the surface depletion ranging between 25 and 55% compared to intermediate water, confirms the results obtained in the Atlantic Ocean.[45] The particulate Cr fraction, in agreement with the results of previous studies, represents only a small fraction of the total metal, varying from 2% to 13% at the four sites studied. However, it showed surface enrichment, which suggests intermediate recycling (Fig. 3b). Therefore, there is some evidence of a nutrient-like behaviour of chromium, although this is not fully clarified and deeper studies are necessary. In this context, the evaluation of chromium speciation is particularly important and should be considered. In oxygenated water Cr(IV) is the dominant oxidation state. Therefore, considering that the analyzed water masses are not anoxic (see the oxygen concentration in Table 1), chromium should assume this form. However, because the slow oxidation rate of Cr(III) could allow the presence of this form also in oxygenated waters, in shelf areas close to the sediment the reduced form cannot be excluded.[45] We can speculate that Cr(III) may play a significant role in chromium cycling, which can justify the relatively lower concentration detected in the bottom sample collected at the CA site only few metres from the bottom.

The concentrations of dissolved and particulate manganese are reported in Table 2. The distribution in the Ross Sea area was quite homogeneous: the dissolved concentration in the mixed layer ranged from 0.33 nmol kg^{-1} (site CA2) to 0.76 nmol kg^{-1} (site CA) and in the intermediate waters from 0.36 nmol kg^{-1} (site B) to 1.3 nmol kg^{-1} (site B) with a mean value of 0.94 ± 0.67 nmol kg^{-1}. A weak increase of concentration was observed with depth; this was evident in profile CA2, where we detected the maximum value of 4.1 nmol kg^{-1} on the bottom (Fig. 3e). A homogeneous vertical distribution of this element in surface/intermediate water was also highlighted by Bucciarelli[46] in the Indian sector of the Southern Ocean; on the basis of data reported by these authors, the concentration reported here can be considered characteristic of shelf water or open ocean affected by upwelling/coastal water. The only significant data of dissolved manganese in the Ross Sea are those reported by Sedwick *et al.*[47] They emphasized different concentrations and vertical distributions during the spring and summer. The concentration level agrees to a great extent with the results reported here. Specifically, the concentration detected in bottom waters agrees with the spring concentration determined in the polynia region. The dissolved concentrations are in excellent agreement with those detected in the Weddel Sea.[32]

The concentration of particulate Mn increased between three to five times with depth, according to the site studied. The concentration was 30–90 pmol kg^{-1} in the mixed layer and ranged between 200 and 500 pmol kg^{-1} in bottom waters; this increase was largely evident at sites B and CA, while it was extremely low at the CA2 site. The concentration of particulate manganese was in excellent agreement and showed the same vertical distribution as those detected in the Indian Sector of the Southern Ocean,[46] in the Ross Sea[14] and the Weddell Sea.[48] Fitzwater *et al.* detected particulate manganese in samples collected along two transects in the Ross Sea: they investigated only the distribution in the first 200–300 m and reported surface concentrations substantially higher than our results; however the concentrations detected in intermediate water were in excellent agreement with our results. To explain this higher concentration compared with the continental contribution they hypothesize a significant resuspension of shelf sediments enriched with Mn and Fe oxides.[14] In agreement with this hypothesis we observed that concentration increases with depth reaching its maximum close to the bottom.

The concentration of particulate iron (Fig. 3f) is one order of magnitude higher than that of manganese. It may be observed that the particulate concentration of this element is influenced by the characteristics of the sampling site. The highest Fe concentration in surface water was observed in the Joides basin (site B, 3.4 nmol kg^{-1}). Moreover, samples collected in the shelf area generally showed higher concentrations than the values detected in open ocean. Similarly to the trend of the particulate Mn fraction, the particulate Fe fraction in intermediate and deep waters showed considerable differences of concentration between shelf area and open ocean: the mean concentration ranged between 2.8 nmol kg^{-1} at site CA and 7.4 nmol kg^{-1} in the Joides Basin (Site B), while it was 1.4 nmol kg^{-1} at site CA2. Though a weak surface increase was observed in some profiles, coincident with a maximum of fluorescence that was always not significant, we must consider that the input of iron in the shelf region is related to local sources, such as the presence of the Drigalsky Ice Tongue at site D, resuspension at site B and possibly a hydrothermal vent at site CA. The relative maximum at a depth greater than 700 m at the CA2 site may be related to the flow of bottom waters from the shelf area. An analogous maximum was also observed for Mn (see Fig. 3e). The trend of the concentration in intermediate-deep water obtained by Fitzwater *et al.* in the Ross Sea and the results reported here are in excellent agreement; while the results of surface concentration reported here are higher than the values reported by Fitzwater.[14]

5. Conclusions

The mean concentrations of trace metals in dissolved and particulate matter detected in the water masses identified in the Ross Sea in the austral summer are reported in Table 3.

Their different compositions, together with the different geophysical features of the sites studied, seem to affect the distribution of dissolved cadmium and chromium concentration. Statistical tests were carried to verify the hypothesis of differences of concentration between HSSW and MCDW, the results showed that the difference was significant at the 5% level. The distributions of the other trace elements studied seem not to be greatly affected by the different features of the water masses present in the Ross Sea. Lead distribution in the shelf area may be influenced by more than one factor. The significant surface enrichment of about 50% compared with the deep water indicates an atmospheric contribution to the lead concentration. However, the maximum concentration present in intermediate water suggests a local input, such as hydrothermal vents and volcanic activity; the latter evidence needs to be confirmed by other studies. In areas of greater productivity, the vertical distribution of dissolved Cu in the Ross Sea was ruled for the most part by scavenging within the surface-intermediate waters, coupled with a recycling process towards the intermediate waters by early diagenesis at the water/sediment interface. However, insignificant differences of concentration were observed in the water masses that characterize the study area. The vertical distribution of total Zn was mainly influenced by surface planktonic uptake and by slow recycling along the water column towards the bottom; the lessening of its surface concentration in the dissolved phase was always coupled with an increase in the particulate phase. However, the biological activity in the shelf area of the Ross Sea exerts an overall effect on the vertical distribution of particulate micronutrients, as well as cadmium, copper and zinc; the difference between the mean values reported in Table 3 for AASW waters and intermediate-deep waters (HSSW and MCDW) for these ele-

Table 3 Trace metal mean concentration (SD) for water samples with characteristics corresponding to the main water masses present in the study area

	Cd/nmol kg^{-1}	Cr/nmol kg^{-1}	Cu/nmol kg^{-1}	Fe/nmol kg^{-1}	Mn/nmol kg^{-1}	Pb/pmol kg^{-1}	Zn/nmol kg^{-1}
	Dissolved						
AASW	0.62 (0.17)	1.45 (0.21)	1.99 (1.49)		0.70 (0.31)	54 (35)	5.25 (2.92)
HSSW	0.63 (0.06)	1.96 (0.36)	2.32 (0.62)		1.12 (0.35)	30 (18)	5.80 (2.01)
MCDW	0.77 (0.07)	2.55 (0.42)	2.49 (0.53)		0.81 (0.30)	29 (23)	6.47 (0.86)
	Particulate						
AASW	0.040 (0.035)	0.15 (0.07)	0.28 (0.28)	1.5 (0.9)	0.06 (0.03)	15 (5)	0.64 (0.29)
HSSW	0.003 (0.003)	0.10 (0.06)	0.08 (0.05)	6.9 (5.4)	0.30 (0.13)	11 (4)	0.27 (0.16)
MCDW	0.002 (0.002)	0.10 (0.04)	0.08 (0.03)	1.5 (0.9)	0.06 (0.04)	13 (5)	0.20 (0.11)

ments was always significant. About 95% of chromium is in dissolved form and its vertical distribution highlights an increase with depth, though this is not pronounced. The dissolved distribution is coupled to a surface enrichment in the particulate fraction, that suggests an intermediate recycling that must be verified by further studies. The dissolved Mn fraction showed an unvarying surface/intermediate vertical distribution, while the total particulate Mn fraction showed an increase along the water column, inferring a significant input from resuspension and a limited relation to biological activity in the area; the trend of the particulate Fe fraction follows that of Mn. In agreement with studies carried out in the same area,[14] the high concentration of particulate Mn and Fe compared with the concentration normally detected in oceanic water strengthens the significant contribution from the resuspension.

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