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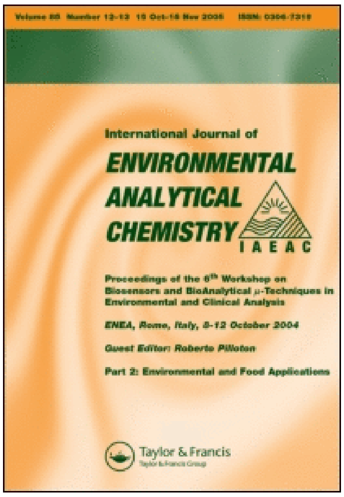

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Distribution of major, minor and trace elements in Antarctic offshore and Coastal seawaters: correlation among sites and variables by pattern recognition

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DISTRIBUTION OF MAJOR, MINOR AND TRACE ELEMENTS IN ANTARCTIC OFFSHORE AND COASTAL SEAWATERS: CORRELATION AMONG SITES AND VARIABLES BY PATTERN RECOGNITION

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The composition of seawater in the Ross Sea (Antarctica) was investigated. The distribution of heavy metals (Cd, Cu, Fe, Mn, Ni), minor and trace (B, Ba, Li, Sr, Si) and major (Na, K, Ca, Mg) elements in coastal and offshore sites was determined. The samples were collected during the XIII Campaign of the Italian "National Programme of Research in Antarctica", PNRA, at different depths and different stages of the Antarctic summer. In the subsequent campaign the concentrations in the water top micro-layer, and just below it, were compared. Results are also given for the data treatment by pattern recognition.

Keywords: Seawater; Chemometrics; Heavy metals; Traces

INTRODUCTION

The composition of seawater is the result of the interaction of chemical, biological, physical and geological processes, which together give rise to the biogeochemical cycle. The main input mechanism in the cycle is from rivers, but atmospheric deposition, human activities, hydrothermal circulation, subsurface volcanoes and tectonics also play important roles. Material removal takes place through sedimentation, hydrothermal circulation and emission into the atmosphere by sea-spray. In the sea great influence is exerted by water currents and by the action of living organisms, which accumulate elements during their lifetime and release them after death [1–5].

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The Antarctic seawaters are involved in such a cycle, which in turn is influenced by the formation, presence and melting of pack ice, by the low temperature and by the absence of light for several months of the year. These processes influence the biological activity, which is restricted to a few months [1,3,5]. Moreover direct anthropogenic contributions are virtually absent, so the influence of natural phenomena and processes is more evident [4,5].

The composition of seawater around Antarctica has been studied less extensively than in other parts of the world, e.g., the Mediterranean Sea or the Atlantic Ocean, owing to the obvious difficulties in reaching the area and the harsh climatic conditions. Nonetheless, several studies were carried out in different areas of the Southern Ocean, particularly from 1990, and series of analytical data are now available.

With regard to heavy metals, much attention has been devoted to the distribution of iron, and it is now generally accepted that Fe is the main trace element limiting primary production in the so-called high-nutrient-low-chlorophyll (HNLC) regions, such as many areas of the Southern Ocean [6–12]. *In situ* fertilization studies, such as the Southern Ocean Iron Release Experiment (SOIREE) [13,14] demonstrated that iron supply controls phytoplankton processes. The other bioutilized trace metals, Cu, Ni, Zn or Cd, did not show co-limitation with Fe on phytoplankton growth [12].

In this framework, the depth profiles of several heavy metals (Cd, Cu, Fe, Ni, Pb and Zn) in the Weddell Sea were studied [15,16]. The distribution of Cd [17], Ni, Cu and Zn [18] and their relation to nutrients in the Southern Ocean were investigated. Sedwick *et al.* [19] determined the concentrations of Fe and Mn in the Australian sub-Antarctic region. Fitzwater *et al.* [11] measured the levels of dissolved Fe, Zn, Cd, Co, Cu and Ni and of particulate Fe, Mn and Al in the Ross Sea. Part of the US Antarctic Environment and Southern Ocean Process Study (AESOPS) was devoted to the Ross Sea continental shelf; AESOPS in turn is a part of the international Joint Global Ocean Flux Study (JGOFS), whose aim is to evaluate the magnitude of the organic matter flux from the ocean surface to depth, identify the processes that regulate this flux and develop a capacity to predict how future global changes will influence it [20,21]. Six cruises collected a variety of data from October 1996 through February 1998 in order to study the processes that contribute to making this one of the Antarctic's most productive seas.

Data on heavy metal content and behaviour in the Ross Sea were collected also within the Italian PNRA activities. The distributions of Cd, Cu, Fe, Mn, Ni and Zn [22,23] as well as the speciation of Cd, Cu and Pb [24] were investigated.

We have been studying the distribution of heavy metals and other elements in the Antarctic ecosystem since 1987, in both earth (lake waters, algae, sediments, soil) and marine environments within the above mentioned PNRA. As to the Ross Sea, after the optimization of analytical techniques [25,26], we investigated the effect of sampling depth, time and location [27–29]. In particular, we observed a decrease in dissolved concentrations after pack-ice melting, due to both water dilution and phytoplankton bloom.

This paper reports the results obtained from the analysis of samples collected during the 1997–98 and 1998–99 Expeditions. Heavy metals, trace, minor and major elements were determined. The "qualitative" conclusions drawn by examining the data obtained were compared with the results of statistical elaborations by pattern-recognition techniques.

EXPERIMENTAL

Apparatus and Reagents

An Autolab PGSTAT10 software-driven voltammetric analyser connected to a 663 VA Metrohm stand was used for Cd, Cu, Fe and Ni determinations. The stand carried a hanging mercury drop electrode, a glassy carbon counter electrode and an Ag/AgCl reference electrode.

Manganese enrichment was performed with a Perkin-Elmer Flow Injection Atomic Spectrometry (FIAS) apparatus provided with two peristaltic pumps and a four-way valve. Its determination was carried out with a Perkin-Elmer 5100 atomic absorption spectrometer equipped with Zeeman-effect background correction, an HGA-600 graphite furnace, an AS-60 autosampler and interfaced to a personal computer.

A software-driven Varian Liberty 100 inductively coupled plasma-atomic emission spectrometer (ICP-AES) was employed for the determination of major, minor and trace elements, namely B, Ba, Ca, K, Li, Mg, Na, Si and Sr.

A Mettler Delta 320 pH meter equipped with a combined glass–calomel electrode was used for pH measurements.

Metal standard solutions were obtained by dilution of concentrated stock solutions (Merck Titrisol) in 0.01 M HNO_3, 0.1 M HCl (for Mn), or 0.01 M HCl–1 mM hydroxylammonium chloride (for Fe).

Boric acid, 1-nitroso-2-naphthol (1N-2N) and hydroxylammonium chloride were purchased from Merck. 4-(2-hydroxyethyl)piperazine-1-ethanesulphonic acid (HEPES), piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES) and 8-hydroxyquinoline were Fluka products, dimethylglyoxime (DMG) was obtained from Aldrich. Ammonium acetate buffer was obtained by mixing the volumes of purified acetic acid and ammonia required to obtain the desired pH.

Sample Collection and Handling

During the 1997–98 Expedition seawater samples were collected with acid-cleaned PTFE-coated Go-flo bottles connected to a Kevlar cable. The bottles were repeatedly rinsed with Milli-Q water after each sample collection. Coastal seawater was collected from the prow of a small boat; offshore samples were taken from the ship after stopping the engines: the depth of collection was at least 25 m, so the contamination caused by the ship can be considered negligible.

The sampling of top and sub-surface layers in the subsequent Campaign was performed with a Multi Use Micro-layer Sampler (MUMS) equipped with a rotating glass cylinder placed on a floating stand [30].

All samples were immediately pressure-filtered through 0.45-μm membrane filters, stored in pre-cleaned polyethylene bottles and kept frozen. They were unfrozen in our laboratory and acidified with purified nitric acid (1 mL per liter) at least one day before analysis.

In order to avoid contamination, heavy metal determinations were carried out in a controlled atmosphere laboratory provided with filtered air and laminar flow hoods, under which sample and reagent handling was performed. Acids and ammonia were purified by sub-boiling distillation in a quartz still (K. Kurner) and Milli-Q high-purity water was used. When necessary, buffers and hydroxylammonium chloride were purified by contact with Chelex-100 (Bio-Rad) chelating resin.

Procedures

Analyses were performed according to previously developed procedures [25–29].

Cadmium, copper, iron and nickel were determined by adsorptive cathodic stripping voltammetry (ACSV) after complexation with the proper ligand in the following conditions: (a) cadmium and copper: pH 7.70 (HEPES/NH_3 buffer), 8 hydroxyquinoline, deposition at -0.30 V for Cu and -1.10 V for Cd (start potential -0.30 V), accumulation time 120 s for copper and 240 s for cadmium; (b) iron: pH 6.90 (PIPES/NH_3 buffer), 1-N-2-N, hydroxylammonium chloride, deposition at -0.20 V for 180 s; (c) nickel: pH 8.30 (boric acid/NH_3 buffer), DMG, deposition at -0.70 V for 120 s.

Manganese was determined by atomic spectroscopy after preconcentration. Enrichment was carried out with a FIAS apparatus [29]. The samples were mixed on line with the ammonium acetate buffer (final pH 9.0) and 8-hydroxyquinoline and driven through a microcolumn packed with reversed-phase C_{18}-silica. The sorbed complex was eluted with a small volume of 0.1 M HCl and the eluate was analysed by atomic absorption spectrometry (FIAS/ETAAS). Three 30-μL injections of such eluate in a graphite tube fitted with L'vov platform permitted a good sensitivity of response.

The other elements were determined by ICP-AES. The samples were diluted 1 : 1000 for Na determination and 1 : 100 for K, Ca and Mg determination; they were analysed undiluted for B, Ba, Li, Si, and Sr.

All concentrations were evaluated using the standard addition method and are the average of at least three replicates. The relative standard deviations were typically 10% for Cd, Cu, Ni, 5% for Mn, 15% for Fe and 3% or lower for all other analytes. Blank values and detection limits are reported in Table I. The accuracy of the procedures for Cd, Cu, Fe, Ni determination had been tested in previous work on

TABLE I Blanks and detection limits for the 14 elements investigated

Element	*Blank*[a]	*Detection limit*[a,b]
Cd	0.09	0.06
Cu	0.71	0.33
Fe	0.93	0.57
Mn	0.24	0.15
Ni	0.75	0.16
Na	0.26	0.06
Ca	<0.15	0.15
K	<0.51	0.51
Mg	0.03	8×10^{-3}
Ba	8×10^{-4}	5×10^{-4}
B	6.01	1.09
Li	<0.09	0.09
Si	0.25	0.18
Sr	3×10^{-4}	2×10^{-4}

[a] Values are in nM for Cd, Cu, Fe, Mn, Ni and in μM for the remaining elements.
[b] Detection limits were calculated as three times the standard deviation of the blanks, except for Ca, K, Ba, Li, Si, Sr. For these elements the detection limit coincides with the instrumental limit.

Antarctic seawater [28] in which the same sample had been analysed by both ACSV and FIAS/ETAAS: the results obtained were similar, differing by no more than 10%. The accuracy of the procedures for iron and manganese had also been tested by analysis of certified seawater (NASS-2, NASS-3) [31,32].

Multivariate Techniques

Two unsupervised (Hierarchical Cluster Analysis and Principal Component Analysis) and one supervised (Discriminant Analysis) pattern recognition techniques [29,33] were applied to the results, considering the data from each Campaign separately.

Hierarchical Cluster Analysis (HCA) was run, applying Ward's method [33] of agglomeration and squared Euclidean distance as the similarity measure. All variables were standardized transforming data values into Z-scores (i.e. $(x-\bar{x})/\sigma$). A dendrogram was obtained.

In Principal Component Analysis (PCA) the first three principal components were extracted and utilized in bivariate plots; loadings plots were also considered.

Discriminant Analysis (DA) was used to verify *a priori* hypotheses. Univariate ANOVA was used to calculate F-ratios and to find variables with higher discriminating power. One canonical discriminant function was obtained and probabilities of class membership were calculated for all samples.

RESULTS AND DISCUSSION

Fourteen analytes were determined, namely heavy metals (Cd, Cu, Fe, Mn and Ni), minor and trace elements (B, Ba, Li, Sr and Si) and major ones (Na, K, Ca and Mg). Table II reports the location and date of collection for each sample. During the 1997–98 Expedition, seawater was sampled at different depths and periods of the Antarctic summer in order to study the effect of these two parameters on its composition. Nine sites close to the coast or in offshore waters were studied. Three stations (coded B2, B3, B4) are located in Gerlache Inlet, a small bay NE of the Italian station in Antarctica; four sample collections (B2-1, B2-2, B2-3, B2-4) were performed at station B2 from November 1997 to February 1998. In all cases one sample was collected under the surface (2 m) and another in deeper waters (380 m); in the second half of November and in February (series B2-2 and B2-4) water was also collected from intermediate depths. Sites B3 and B4 are located NE and SW of B2 respectively: here one sampling was performed in the second half of November at depths of 4 and 100 m. The other six sites (Y1–Y6) are in the open Ross Sea: three samples were collected from each site at increasing depths between 25 and 250 m between 23 November 1997 and 15 January 1998. Finally, seawater was also collected at a depth of 200 m close to station Y1. In total, 38 samples were made available during the 1997–98 Expedition.

In the 1998–99 Campaign (January 1999) the concentrations in the uppermost layers of the sea and immediately below were compared. Four pairs of sub-surface water (50 cm below sea surface) and of the top superficial microlayer water (the first layer of 150-μm nominal thickness) were collected from site B2.

The analyte concentrations in B-series samples are reported in Table III for heavy metals and Table IV for the other elements. The corresponding values for Y-series

TABLE II Geographical location, sampling date and sea depth for seawater collected during the Italian expedition to Antarctica in 1997–98

Sampling code	*Date of sampling*	*Place of sampling*	*Latitude*	*Longitude*	*Sea depth* (m)
B2	11-13-1997 (B2-1) 11-27-1997 (B2-2) 12-19 to 22-1997 (B2-3) 02-11-1998 (B2-4)	Gerlache Inlet	74° 41′ 632″ S	164° 11′ 178″ E	430
B3	11-21-1997	Gerlache Inlet	74° 40′ 036″ S	164° 13′ 882″ E	420
B4	11-16-1997	Gerlache Inlet	74° 42′ 137″ S	164° 09′ 149″ E	220
Y1	11-23-1997 to 01-15-1998	Polynya (Drygalski Basin)	75° 04′ S	164° 13′ E	950
Y1b	11-23-1997 to 01-15-1998	Polynya (Drygalski Basin)	74° 52′ 84″ S	164° 02′ 97″ E	718
Y2	11-23-1997 to 01-15-1998	Ross Bank	76° 09′ S	179° 57′ W	319
Y3	11-23-1997 to 01-15-1998	Challenger Basin	75° 54′ 20″ S	177° 34′ 44″ W	628
Y4	11-23-1997 to 01-15-1998	Challenger Basin Slope	75° 06′ S	176° 50′ W	515
Y5	11-23-1997 to 01-15-1998	Joides Basin	74° 00′ 45″ S	174° 48′ 72″ E	582
Y6	11-23-1997 to 01-15-1998	Cape Adare	72° 02′ S	172° 15′ E	415

TABLE III Heavy metal concentrations (nmol/L) in Gerlache Inlet samples

Sample[a]	*Cd*	*Cu*	*Fe*	*Mn*	*Ni*
B2-1-2	0.46	4.2	0.6	1.4	6.1
B2-1-380	0.20	1.4	1.1	0.9	3.7
B2-2-2	0.43	1.9	0.8	1.9	5.8
B2-2-10	0.58	4.1	0.9	0.8	5.6
B2-2-25	0.45	1.7	0.9	0.8	5.2
B2-2-50	0.50	1.7	0.7	1.0	5.8
B2-2-100	*	2.2	0.6	0.5	6.8
B2-2-200	0.43	2.2	1.1	0.5	5.9
B2-2-380	0.41	1.6	0.6	1.0	5.2
B2-3-2	*	*	5.9	*	11.5
B2-3-380	0.53	2.9	2.3	1.2	7.6
B2-4-4	0.19	2.4	0.6	0.1	5.0
B2-4-25	0.12	2.6	2.8	2.0	5.5
B2-4-100	0.10	2.4	0.7	0.8	4.5
B2-4-380	0.54	3.2	1.0	2.5	5.1
B3-1-4	0.25	3.0	1.7	1.1	6.4
B3-1-100	0.58	2.3	*	1.2	6.3
B4-1-2	0.38	1.2	0.3	0.9	3.5
B4-1-100	0.58	1.7	0.7	1.1	6.4

*Elements for which contamination could be present.

[a] The final figure is the depth (in meters) at which the sample was taken.

TABLE IV Major and minor element concentrations in Gerlache Inlet samples

Sample[a]	*Na*	*Ca*	*K*	*Mg*	*B*	*Ba*	*Li*	*Si*	*Sr*
B2-1-2	444.5	9.41	8.70	50.10	0.41	69	24	45	80
B2-1-380	495.4	11.55	11.82	60.67	0.49	112	24	50	95
B2-2-2	463.2	10.43	10.23	55.90	0.38	78	26	53	84
B2-2-10	456.7	10.38	10.49	58.37	0.45	78	23	76	87
B2-2-25	450.2	10.83	10.95	58.91	0.39	70	24	50	88
B2-2-50	441.5	10.10	9.77	56.93	0.39	89	23	46	88
B2-2-100	447.1	10.48	10.56	55.99	0.42	84	30	53	86
B2-2-200	460.6	10.63	11.59	56.81	0.46	87	27	63	83
B2-2-380	459.3	10.08	9.64	54.79	0.38	79	24	57	80
B2-3-2	414.9	9.88	9.95	52.20	0.44	87	26	48	77
B2-3-380	452.8	10.75	11.18	58.37	0.41	84	33	69	90
B2-4-4	436.3	10.50	10.38	56.40	0.39	94	27	61	86
B2-4-25	454.1	10.18	10.28	54.75	0.37	62	22	52	80
B2-4-100	482.4	10.60	11.30	57.63	0.38	80	23	55	90
B2-4-380	488.0	10.85	12.15	59.52	0.42	74	29	54	89
B3-1-4	493.3	10.45	10.10	57.22	0.43	102	24	54	89
B3-1-100	483.7	10.33	10.77	57.18	0.40	92	23	73	86
B4-1-2	479.3	10.35	10.33	56.73	0.36	70	24	59	87
B4-1-100	479.3	10.33	10.41	56.52	0.39	85	32	62	87

Values in mmol/L for Na, Ca, K, Mg, B, in μmol/L for Li, Si, Sr, and in nmol/L for Ba.

[a] The final figure is the depth (in meters) at which the sample was taken.

TABLE V Heavy metal concentrations (nmol/L) in the open Ross Sea samples

Sample[a]	*Cd*	*Cu*	*Fe*	*Mn*	*Ni*
Y1-25	0.60	2.9	1.5	0.7	5.5
Y1-80	0.80	3.9	*	1.4	9.0
Y1-250	0.75	2.6	0.6	1.3	6.0
Y1b-200	0.73	1.7	0.8	0.7	5.2
Y2-25	0.42	2.9	0.9	0.7	7.4
Y2-100	0.69	2.9	5.5	0.4	6.2
Y2-250	0.60	1.9	*	1.5	6.2
Y3-25	0.64	5.4	2.7	1.8	9.4
Y3-140	0.44	3.6	0.9	1.1	7.8
Y3-250	0.65	2.3	1.3	2.0	7.4
Y4-25	0.78	3.4	0.9	1.9	8.4
Y4-100	0.79	2.5	1.3	1.5	7.3
Y4-250	0.72	2.3	*	1.0	6.7
Y5-25	0.49	2.9	0.9	0.5	9.2
Y5-90	0.44	1.6	1.1	0.7	6.5
Y5-250	0.61	2.7	1.0	0.5	6.2
Y6-25	0.54	1.2	0.7	0.2	6.0
Y6-70	0.49	1.8	0.4	1.3	7.4
Y6-200	0.66	2.0	0.9	0.4	7.3

*Elements for which contamination could be present.

[a] The final figure is the depth (in meters) at which the sample was taken.

TABLE VI Major and minor element concentrations in the open Ross Sea samples

Sample[a]	*Na*	*Ca*	*K*	*Mg*	*B*	*Ba*	*Li*	*Si*	*Sr*
Y1-25	474.1	10.78	11.25	58.37	0.37	84	23	57	88
Y1-80	474.0	10.58	10.23	56.89	0.35	93	27	62	89
Y1-250	460.6	10.55	10.90	56.97	0.42	87	27	65	87
Y1b-200	464.6	10.48	9.87	56.31	0.42	87	27	65	87
Y2-25	467.2	10.73	12.12	58.58	0.44	95	39	80	89
Y2-100	470.6	10.08	10.43	55.04	0.42	83	27	58	83
Y2-250	497.6	10.30	10.77	56.73	0.35	82	23	75	86
Y3-25	468.5	9.83	10.43	54.59	0.42	82	20	40	84
Y3-140	459.8	10.43	10.97	56.36	0.52	102	24	59	86
Y3-250	475.4	10.58	10.84	57.88	0.49	113	32	51	85
Y4-25	485.4	10.23	9.34	55.61	0.48	92	27	73	83
Y4-100	478.5	10.28	10.23	55.78	0.39	90	20	69	82
Y4-250	478.9	10.20	9.90	55.00	0.34	56	16	58	83
Y5-25	468.5	10.50	10.03	56.15	0.36	84	32	64	87
Y5-90	481.1	10.60	10.46	57.84	0.46	82	20	58	90
Y5-250	492.4	10.58	9.72	55.99	0.36	90	23	77	86
Y6-25	488.0	10.38	10.33	55.86	0.42	57	23	77	83
Y6-70	489.3	10.23	10.69	55.16	0.42	71	32	62	84
Y6-200	506.3	10.65	10.15	56.19	0.43	84	24	72	85

Values in mmol/L for Na, Ca, K, Mg, B, µmol/L for Li, Si, Sr, and in nmol/L for Ba.

[a] The final figure is the depth (in meters) at which the sample was taken.

samples are reported in Tables V and VI. The last number of the sample code corresponds to the depth of collection.

Among the investigated parameters, heavy metals give the most useful information from the environmental point of view; however, the concentrations of the other elements considered in this study are also of interest because of their involvement in the global biogeochemical cycle and because they help characterize the seawaters under study: in fact, owing to the relative scarcity of information on Antarctica, even data on major and minor elements may increase our knowledge on this remote continent and enable us to make comparisons with seawaters from other parts of the world. Data on salinity are not available for these samples, but its relative variations can be deduced from the concentrations of major metals, especially sodium, which are reasonably proportional to this parameter.

Among the minor elements, the behaviour of Si and Ba is of particular interest. The Ross Sea appears to have two main phytoplankton assemblages, which are often spatially distinct, the first being dominated by diatoms, and the second by the colonial haptophyte *Phaeocystis antarctica* [19,20]. The concentration of Si is of particular importance in the areas where diatoms prevail, since significant depletions were observed because of algal growth. Nelson and Smith [34] found that the depletion of dissolved silicic acid at the western Ross Sea ice-edge was matched almost exactly by the accumulation of biogenic particulate silica. On the other hand, a small decrease in the level of silicic acid was found in a site dominated by *Phaeocystis antarctica* [20]. Evidence of Si–Fe co-limitation of primary productivity was found in low-Si waters [20,35,36].

Barium is a bio-intermediate element, whose distribution is influenced both by its involvement in biological processes and by the equilibrium between the dissolved form and barite crystals; the content of barium is also of interest in paleo-oceanographic studies [37].

Examination of the data allowed us to identify some trends that are discussed below.

Coastal Seawater Samples

The coastal area under study is characterized by high biomass production [38]. The melting of sea-ice takes place approximately at the end of December and in the first half of January.

The level of heavy metals at station B2 was higher near the surface than at a depth of 380 m from November to the end of December. The trend is reversed in February (samples B2-4). This behaviour is probably due to the biological activity occurring during the Antarctic summer [38], which involves uptake of nutrients from the surface and their release into deeper waters owing to the death of living organisms [1,11]. The results obtained in JGOFS for the Ross Sea confirm this trend: nutrient concentrations reflected phytoplankton uptake, and reached their seasonal minimum in early February [20].

A concurrent depletion of Si between November and February was not observed in the present study, even if diatoms are prevalent in this area: the consumed silicon might have been replaced by an input from other sources, e.g., melted sea ice.

As to major elements, concentrations are generally higher at a depth of 380 m (with the exception of B2-2) and a surface depletion from November to February is not observed, probably because the amounts of Na, K, Ca and Mg are not significantly decreased by biological uptake. The behaviour of Sr is similar to that of Ca and Mg, as could be expected because of their similar chemical properties. On the other hand Ba, which is also an alkaline earth metal, has an opposite trend. Non-regular behaviour is evident for B and Si.

Vertical profiles of series B2-2 (7 points) and B2-4 (4 points) have a complex behaviour, but some regular trends can be identified.

In B2-2 samples, dissolved iron and nickel concentrations are relatively homogeneous throughout the profile, except for maxima at 200 m and 100 m, respectively. A decrease from 200 to 380 m is observed also for cadmium and copper, which are characterized by a distinctly high concentration at 10 m. The concentration of manganese is highest at the surface, decreases at intermediate depth, with a minimum in the range 100–200 m, then increases again.

The present profiles are similar to the ones observed by Löscher [18] in the southern Antarctic Circumpolar Current area: the vertical distribution of dissolved nickel and copper was characterized by subsurface maxima between 50 and 200 m depth, which were attributed to leaching of sea-ice diatoms sedimented from the sea-ice. The behaviour of Fe is in agreement with the findings of Sohrin *et al.* [10] for the Australian sector of the Southern Ocean: they observed an increasing trend for iron from surface to deep waters and local subsurface maxima attributed to the combination of nutrient-like behaviour with the effect of water circulation and local sources, such as redissolution from sediments and hydrothermal vents. Elevated surface layer concentrations of Mn, due primarily to photoreductive dissolution and aeolian inputs, are typically present in the Atlantic and Pacific Oceans [39].

Common features of major metal profiles in B2-2 samples are a slight decrease from 25 to 50 m, an increase between 100 and 200 m and a further decrease below 200 m. The point at 50 m, characterized by a low concentration of all major metals, and in particular of sodium, could be affected by local currents. The decrease from 200 to 380 m is found also for all minor and trace elements. Low concentrations at 50 m (even if not always corresponding to the minimum value in the profile) are also observed for B, Li and Si. It is interesting to note the similarity among the profiles of Si, B and Cu. Lithium has a maximum at 100 m, whereas its concentrations at the other depths vary in a narrow range.

Other researchers have reported that the vertical distribution of Fe and Mn in intermediate and deep waters was characterized by a substantially constant profile until January; then, an increase in particulate metal concentration with depth was observed along with a corresponding decrease in dissolved concentrations. This trend is typical of elements which are removed by particulate matter during the sinking process [23].

The element distribution changes between November and February. In the B2-4 series there are more similarities among groups of elements. The profiles of Cu, Fe, Mn and Ni have the same shape, whereas cadmium differs at intermediate depth. In all cases, the concentrations increase below 100 m, the most relevant rise being shown by cadmium, probably for biological reasons, as discussed above. It is possible that at this depth the effect of redissolution of sinking debris starts to be observed.

The profile of Fe concentration in the water column appears to follow the behaviour described by de Baar *et al.* for the Pacific waters of the Southern Ocean [36] with a generally increasing trend with depth.

The profiles of K, Ca and Mg are also very similar, while sodium differs only in the behaviour at 25 m. The levels of K, Mg and Ca increase from top to bottom, except between 4 and 25 m, whereas Na concentrations always increase with depth. Ba, Si and Sr have a similar trend, the greatest difference being concentration maxima at 4 m for Ba and Si; their profile is also analogous to the one of the major metals, except for a small decrease in concentration from 100 to 380 m. The profiles of B and Li are also alike.

With respect to all these observations, one has to bear in mind that the Ross Sea is characterized by the presence of the Antarctic Circumpolar Current which divides into several currents and water masses, e.g., the Circumpolar Deep Water, the Antarctic Bottom Water and the High Salinity Shelf Waters, whose mixing gives rise to new waters [40]; such currents and masses have remarkably different values of density, salinity and temperature, thus influencing chemical and biological processes [18] and consequently the distribution of metals in the various depths and positions where such flowing masses mix and interact.

The five investigated heavy metals have different biogeochemical characteristics. They have been classified [41] as nutrient-type or recycled (Cd, Ni), scavenged (Mn), or both recycled and scavenged (Cu, Fe). Moreover, the behaviour of Mn and Fe is strongly influenced by their chemical properties, such as the tendency to form oxides and hydroxides and to exist in different redox states.

The increase in concentration in deeper waters for B2-4 samples is in agreement with this classification for Cd, Ni, Cu and Fe, whereas the surface depletion expected for nutrient-type and recycled and scavenged elements does not always take place.

In general, the variability of the observed trends is due to the complexity and large number of factors influencing the distribution of the elements. The particular geographical location of Antarctica suggests that the climatic conditions (low temperatures, formation and melting of pack ice, light limitation) and the dynamics of currents have the greatest influence on seawater composition [38]. These two factors in turn influence and interact with the other phenomena acting in the biogeochemical cycle, i.e., the bioaccumulation of heavy metals by living organisms and their release after death; atmospheric deposition; sedimentation; adsorption/desorption equilibria on suspended particles (strongly dependent on the chemical properties of each element); the mixing action of wind and the erosion of the coasts by ice [1–3]. Grotti *et al.* [23] found that metal concentrations in the surface layers in the Ross Sea were mainly affected by the dynamic of the pack-ice melting and phytoplankton activity. The first process influences both the input of metals from melt-waters and the covering of the seawater surface, allowing atmospheric dust input only when all ice has been melted or removed. Direct release from ice of particulate Fe and Cu were clearly shown by surface concentration peaks and by the high concentrations of suspended particulate matter and particulate metals detected in the ice-core section interfaced with the seawater. In the absence of pack ice, there is evidence of a further input of Fe and Mn due to atmospheric dust brought into the water column through the marine microlayer. This picture is complicated by phytoplankton activity, which removes micronutrients like Fe and Cu from water, incorporating them into organic particulate matter.

Open-sea Samples

Open seawater in the Ross Sea is characterized by lower biomass production than in the coastal area [11,38].

Samples from Y stations came from a broader area than B ones, and were taken at various times. The different characteristics of the samplings are reflected in the differing trends in the concentrations from site to site. There is no common variability in element content as a function of depth. However, some regularities may be observed for sites and analyte types.

For instance, the concentrations of Cd, Cu, Mn and Ni in Y1 increase from 25 to 80 m and decrease again down to 250 m. On the other hand, a decrease from 25 to 140 m is observed for all heavy metals in station Y3. Cu, Mn and Ni concentrations always decrease in site Y4. If each metal is considered, the same shape in the profiles is observed for Mn in stations Y2 and Y3, Cu in Y3 and Y4, Cd in Y1–Y2 and Y5–Y6, Ni in Y3, Y4 and Y5.

For major elements, a decrease from 80 to 250 m is found for Na and Ca in Y1. The behaviour of Ca, K and Mg is similar in site Y2, with a distinct maximum at 25 m and an increase below 100 m. A similar increase is present for sodium. The profiles of calcium and magnesium are also similar, inside each station, in Y3, Y4, Y5 and Y6. The same trend for K, with a maximum at intermediate depth, is observed in sites Y3, Y4, Y5 and Y6.

The previously noted decrease in concentration below 80 m in Y1 is also present for Sr and Ba. A common feature of minor and trace elements in site Y2 is the decrease from 25 to 100 m, which is also observed for Mn, Ni, Ca, K and Mg. The concentrations of B, Ba, Li, Si and Sr have a maximum at 25 m, like those of Ca, Mg and K. The content of minor and trace elements also decreases from 25 to 100 m in station Y4. The decrease continues down to 250 m for B, Ba, Li and Si. In site Y5 there are similarities among Ba, Li and Si and between Sr and B. The concentrations of B, Ba, Si and Sr increase from 70 to 200 m in Y6. Similar findings have been reported by other authors [42].

We also plotted analyte concentrations in open-sea samples *vs.* longitude or latitude, for each depth; there was no meaningful trend or regularity in the concentrations with reference to the spatial distribution of the sampling stations. Probably the investigated area is too small to allow us to detect any meaningful influence of the sampling geographical position. Moreover, the samples were collected over a relatively long period, so that it is hard to distinguish between spatial and temporal variability.

The differences from site to site may be due to the factors cited in the previous section and also to the “patchiness” in the distribution of blocks of pack-ice. A patchiness in the distribution of dissolved elements in the Southern Ocean has been observed by other authors [8,10]. In fact, waters surrounding Antarctica are not considered as a single functional unit but rather as a mosaic of subsystems [20,38].

Finally, it must be kept in mind that the data are affected by an analytical uncertainty, mainly due to the risk of contamination during collection and pretreatment: for instance, an uncertainty of 20–30% can be estimated for the determination of dissolved iron [19,23].

Subsurface and Microlayer Samples

The concentrations in the samples collected during the 1998–99 Campaign are reported in Table VII (heavy metals) and VIII (major, minor and trace elements). The letters “S” and “M” in the sample codes refer to subsurface and microlayer samples, respectively; the numbers 1–4 represent the sample couples. As can be seen, the concentrations of Cd, Cu, Mn and Ni are higher in the microlayer than in the water below, with

TABLE VII Heavy metal concentrations (nmol/L) in subsurface (S) and microlayer (M) seawater from Gerlache Inlet

Sample	*Cd*	*Cu*	*Fe*	*Mn*	*Ni*
B2-S1	0.14	2.7	1.6	0.5	3.8
B2-M1	0.18	4.2	2.3	0.6	4.5
B2-S2	0.33	2.2	2.4	0.9	3.2
B2-M2	0.20	2.9	2.1	0.4	2.4
B2-S3	0.14	1.9	1.7	0.2	2.6
B2-M3	0.18	2.9	1.3	0.6	3.0
B2-S4	0.18	1.7	4.0	0.5	3.0
B2-M4	1.49	2.9	2.3	0.8	3.8

TABLE VIII Major and minor element concentrations in subsurface (S) and microlayer (M) seawater from Gerlache Inlet

Sample	*Na*	*Ca*	*K*	*Mg*	*B*	*Ba*	*Li*	*Si*	*Sr*
B2-S1	499.9	9.61	10.36	54.84	0.32	69	24	31	81
B2-M1	514.4	10.13	10.11	58.05	0.35	79	25	44	81
B2-S2	449.6	8.54	8.04	49.19	0.33	76	23	24	71
B2-M2	448.6	9.27	8.86	52.64	0.39	85	24	24	76
B2-S3	477.9	10.26	10.32	58.04	0.43	86	27	36	83
B2-M3	486.3	9.92	9.59	55.93	0.39	81	22	28	78
B2-S4	427.3	8.58	9.06	48.53	0.35	76	20	31	73
B2-M4	434.0	8.78	8.13	50.23	0.34	92	19	29	73

Values in mmol/L for Na, Ca, K, Mg, B, μmol/L for Li, Si, Sr and nmol/L for Ba.

the exception of sample-couple 2. The most significant difference is found for Cd in the sample-couple 4. Iron differs from the other heavy metals because it almost always has higher levels under the surface. As to the other elements, in some cases the concentrations are higher in the microlayer, while in other cases the reverse is true or similar concentrations are observed.

Enrichment factors from subsurface to microlayer water (when such enrichment is observed) are between 1.02 and 1.16 for trace, minor and major elements and between 1.21 and 3.62 for heavy metals. A value of 1.43 was found for Si in sample-couple 1.

The microlayer environment is of particular interest for its chemical composition, as it is the interface between atmosphere and bulk seawater. A remarkable increase in concentrations in the microlayer was expected, according to literature data [30], especially for heavy metals, because of the higher level of organic substances with surface-active properties. The limited enrichment found in these samples could be due to partial dilution with the water below during the sampling. It is also possible that the highest degree of enrichment takes place only in the nanolayer ($< 1\,\mu m$). Moreover, the analytical methods employed for heavy metals allow us to detect only the amount complexed by the analytical ligands. Such ligands form very stable complexes with the metals of interest, so that it can be assumed that in clean water the total concentrations are found. It is possible that in the presence of high concentrations of organic matter a fraction of strongly bound metal is not detected. An increase in concentrations might be found after decomposition of the organic matter, e.g., by UV degradation. However it can be presumed that such increase would not be very high, since it was observed that, using the standard addition method, the sensitivity of the response to the added concentrations in microlayer samples was similar to the one in surface samples and in the samples of the previous campaigns.

The small degree of enrichment could also be explained by competition for binding sites on the organic matter from alkaline earth elements, which are present in large excess with respect to heavy metals.

Concentration Ranges

The measured heavy metal concentrations are generally higher in the open sea than in Gerlache Inlet, as remarked for previous campaigns [29], whereas the other analytes have comparable concentrations; therefore any contribution of dissolved elements from rock weathering to coastal waters should be very limited. Since Gerlache Inlet is close to the Italian station in Antarctica, the activities of the latter did not cause contamination in seawater, at least from the point of view of the investigated parameters. An opposite scenario was observed in other areas of the Southern Ocean. For instance, the concentrations of dissolved Fe, Mn, Co, Cu, Cd and Zn found in the neritic Gerlache Strait were much higher than in the off-shore sites, probably because of the input of atmospheric dust from land [6,11,23].

Comparison with our previous data shows that no meaningful variations have taken place in heavy metal concentrations in the investigated area since 1987, as shown in Table IX. Most of the results of the present study are in good agreement with the concentrations measured by Fitzwater *et al.* [11] in two areas of the Ross Sea close to our sampling points (two transects located along 76°30′ S and 72°30′ S); the main differences lie in the upper limits of our data, above those reported by Fitzwater *et al.* (see Table IX). It can be presumed that the content of Fe in the investigated area does not limit phytoplankton growth; in fact the concentration of Fe in an area of low productivity of the Ross Sea was lower than 0.15 nM [11]. Moreover, according to de Baar *et al.* [36], mean surface water levels at 0.31 or 0.49 nM are adequate to sustain a low and constant phytoplankton biomass but insufficient for bloom development.

Table IX also shows that the measured values are in agreement with the ranges found in other studies for the Weddell Sea, other areas of the Southern Ocean and the Arctic Ocean. For instance, copper concentrations observed in our samples can be compared with the similar ranges reported for total dissolvable Cu in the Wasa shelf [16] (1.7–2.1 nM), the Scotia Sea (1.9 nM) and the Weddell/Scotia Confluence (2.0–3.5 nM) [45]. In the completely ice-covered Weddell Sea, Cu concentrations up to 4.2 nM were also found [45]. Also for Ni, we found comparable data with those

TABLE IX Concentrations in Antarctic and Arctic seawaters, in the Ross Sea and typical concentrations for seawater (nmol/L)

Seawater	*Cd*	*Cu*	*Fe*	*Mn*	*Ni*	*Ref.*
Arctic Ocean	0.28–0.66	1.8–4.1	–	0.51–2.11	3.1–5.5	[43]
Weddell Sea	0.40–0.80	2.0–5.3	1.0–8.2	0.1–2.2	6.0–7.0	[7,15,16]
Southern Ocean	0.15–1.31	0.9–3.4	0.04–3.8	–	3.7–8.2	[8,17,18,44]
Ross Sea	0.07–0.98	0.5–4.8	0.6–7.6	0.1–2.2	1.5–9.0	[25–29]
Ross Sea	0.04–0.80	1.23–2.43	< 0.05–1.13	–	4.78–6.88	[11]
Typical range	0.001–1.1	0.5–6	0.1–2.5	0.2–3	2–12	[1,41]
Typical mean	0.7	4	1	0.5	8	[1,41]

reported by Löscher [18] during consecutive transects at the 6° W meridian (3.1–7.5 nM) and by Nolting and De Baar [45] for the Scotia Sea and the Weddell/Scotia Confluence (4.6–8.3 nM). Also the total dissolvable Ni concentration (5.5–6.8 nM) for the Wasa shelf [16] may be compared with our data.

It is interesting to note that the measured heavy metal levels are not significantly different from typical oceanic concentrations, reported in Table IX for comparison. Moreover, it was found that several heavy metals such as Cd, Cu, Ni and Zn occur at high concentrations in the Southern Ocean compared to the low concentrations found in remote regions such as the North Pacific gyre and in particular the equatorial Pacific [10,11]. On the other hand, heavy metal concentrations in the Antarctic continent, e.g., in soils or lake waters, are lower than typical ones [46] for corresponding environmental compartments, owing to the virtual absence of anthropogenic activities. This happens because the water circulation and the biogeochemical cycle described above ensure approximately similar levels of solutes in seawaters. In fact it must be recalled that Antarctic waters are not isolated from the rest of the oceans. The presence of thermohaline circulation and other oceanic currents, together with other mixing mechanisms, cause ocean waters to mix in a time range of about 10^3 years. From the environmental point of view, water motion obviously has the effect of transporting pollutants to areas far away from the point of input. Therefore, even if Antarctica is not directly affected by anthropic activities, it is not free from the risk of pollution.

A feature of the area studied is the presence of Ross Ice Shelf, which is a source of cold water that is then transported to lower latitudes. From the available data it is impossible to evaluate the effect of such water flow, and of the other hydrological characteristics of the area, on the element distribution found in this study. The sea-depth in the sampling stations varies from 220 to 950 m, with most stations ranging from 300 to 600 m: no apparent relationship was found between this parameter (which in turn influences water circulation) and analyte concentrations.

Also major and minor element concentrations agree with the values expected for seawater, reported in Table X, with the exception of Si, and with the ones found by other authors in the Ross Sea [42]; however, the concentrations of Si reported by other researchers [10,17] for the Southern Ocean are similar to ours. For instance, the values measured in the Ross Sea (32.0–93.7 μM) [11] are in very good agreement with our data (40–80 μM for 1997–98 samples). These levels of Si are presumably high enough to sustain phytoplankton growth, since silica-limitation was found to occur at concentrations below about 5 μM [11,47].

Major elements have a conservative behaviour and the ratios among their concentrations, which essentially depend on physical phenomena [1], are generally constant regardless of the variations of the single values. This behaviour was also observed for these samples, in which the ratios do not significantly change either with depth or with site location. The average molar ratios are 44.9 (Na/K), 45.2 (Na/Ca),

TABLE X Typical concentrations of major and minor elements in seawater

Na	*Ca*	*K*	*Mg*	*B*	*Ba*	*Li*	*Si*	*Sr*
460	10	10	53	0.4	100	25	100	90

Data from Refs. [1,5].
Values in mmol/L for Na, Ca, K, Mg, B, μmol/L for Li, Si, Sr, and nmol/L for Ba.

8.33 (Na/Mg), 1.01 (K/Ca), 0.19 (K/Mg), 5.42 (Mg/Ca), with standard deviations from 1 to 7%. The deviations were higher (up to 20%) in seawater samples collected in previous years [29] where the contribution of pack melting was probably more strongly felt and caused a bias in a purely conservative behaviour.

An attempt was made to compare the behaviour of heavy metals and major elements, by testing the extent of their variations. The ratio of the sum of Na, K, Ca and Mg concentrations to the concentration of each heavy metal was computed for every sample. The averages of such ratios (calculated for coastal and open seawater separately) have large relative standard deviations, typically from 30 to 75%: as a first approximation it can be confirmed that the metals are influenced by different factors than major elements, and their behaviour is far from the conservative one, since their variations from sample to sample do not seem to follow the same trend as major elements.

Chemometric Investigation

Principal Component Analysis (PCA) allows an easy representation of samples in a two- or three-dimensional diagram, where similarities and differences among groups of samples and correlations among variables can be identified. Fig. 1 shows the biplot of scores and loading for the first three principal components (PCs) for the 1997–98 Campaign.

If PC1 is plotted *vs.* PC2 (Fig. 1a), no clear distinction can be observed among the samples, as a function of either location or sampling date or depth. Samples B2-3-2, B2-1-2 and B2-1-380 are placed far from the other ones in the bivariate plot, because of the low (B2-1-2, B2-3-2) or high (B2-1-380) content of major elements and the high nickel concentration (B2-3-2).

The plot of PC1 *vs.* PC3, (Fig. 1b) allows us to make a more clear distinction between two groups formed by B and Y series samples. The "anomalous" points B2-3-2, B2-1-2 and B2-1-380 are again apart from the other ones, even if they are in the section of the plot associated with the B-series. No classification as a function of sampling depth is apparent. Most Y samples have higher PC3 scores than do B samples. A three-dimensional plot of the three PCs does not add any additional information.

As to variable loadings, Fig. 1a shows that there are correlations among Ca, Mg and Sr, among Cd, Cu, Fe and Ni, and among B, Ba and Li. K is more similar to alkaline earth metals than to alkali ones, whereas Na is not correlated to any other metal but only to Si. The similarity among calcium, magnesium and strontium is probably due to their similar chemical properties.

Barium has a different behaviour, probably because of its low concentration, which is therefore more strongly influenced by bioaccumulation and remineralization, and the low solubility of barite. The correlation between Ba and Si described by Jeandel *et al.* [37] was not observed in this study; in any case, they also observed that the two elements were poorly correlated in the Upper Circumpolar Deep Waters. Cu and Si were found to be correlated by some authors [18] but not by others [7]; no correlation was found in the present study.

The position of heavy metals in the plot shows that their concentrations are influenced by different factors from the other elements. In particular heavy metals are strongly influenced by the biological processes occurring in seawater, whereas alkali and alkaline earth elements are more affected by physical factors such as currents. The correlation between Si and Na suggests that such factors, and not only the

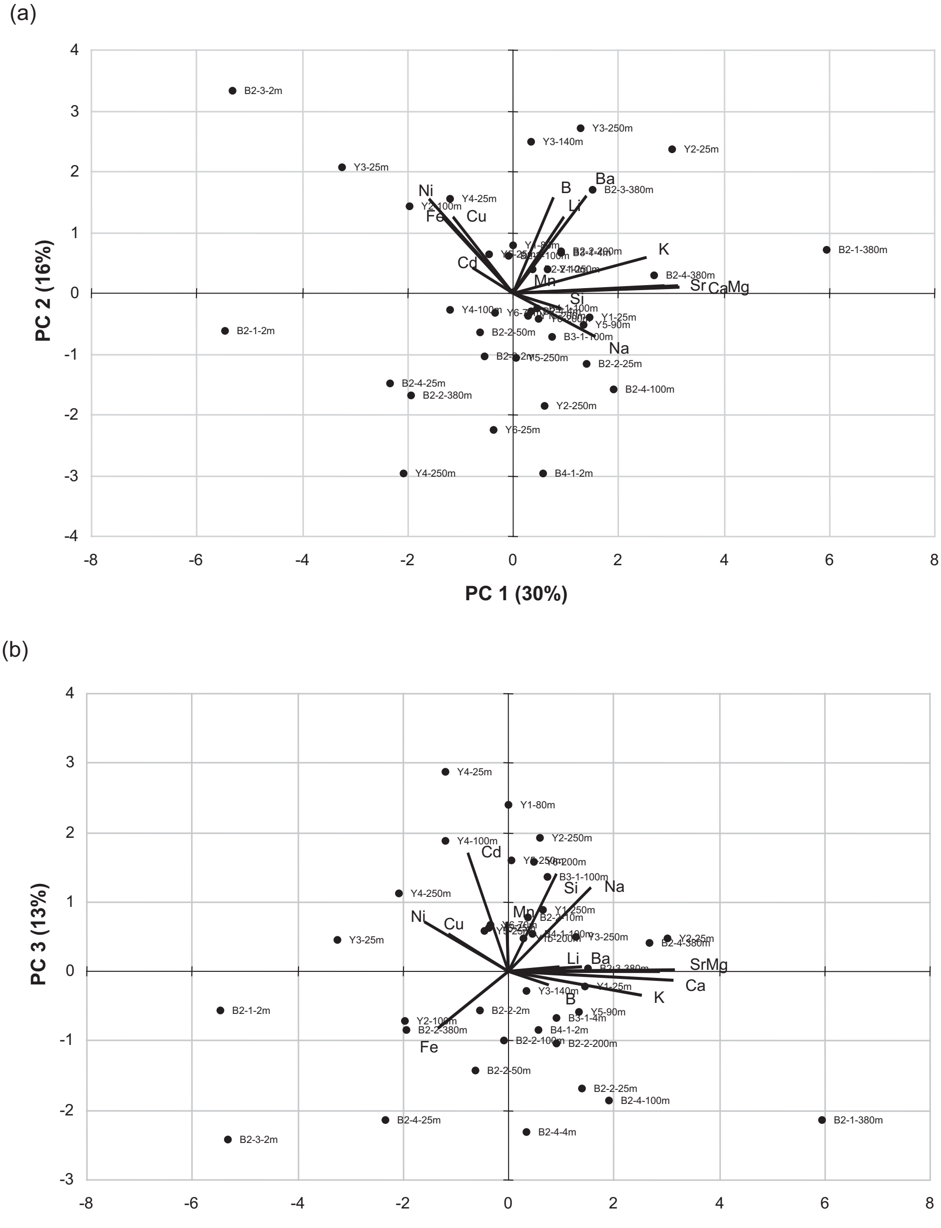

FIGURE 1 Combined plot of scores and loadings obtained by PCA for 1997–98 samples: (a) PC1 *vs.* PC2; (b) PC1 *vs.* PC3.

nutrient-type behaviour, influence the concentration of silica: this might explain why a depletion of Si in B2-4 samples, as remarked above, was not observed. A correlation between silicate and salinity was found also in the Scotia Sea [45]. Finally, some of the correlations found with these samples were also observed in the treatment of data from previous expeditions [29]. PC1 is heavily influenced by alkaline earth elements and partly by alkali metals, so it seems to be connected to physical or chemical factors. PC2 is related to heavy metals and B, Li and Ba, so it could reflect the dependence of concentrations on biological factors. If the waters were polluted, PC2 could have been supposed to be related also to site contamination, but this is not the case. HCA did not allow us to identify meaningful sample clusters. This is probably due to the different sample origins as to the depth and time. DA showed that it is possible to classify samples as belonging to the B and Y series respectively with 89.5% and 100% probability. Table XI reports univariate *F*-ratios for all elements (reference value at $P = 0.95$ with 1 and 36 degrees of freedom is 4.11). The variables with the highest discriminating power were Cd, Ni, Si and Na. It must be pointed out that Cd, Na, Ni and Si are the variables with highest loadings on PC3, i.e., the component along which the two groups of samples are also distinguished.

The statistical results discussed in this section and the "qualitative" observations reported in the previous ones complement each other, because the former cannot distinguish among some patterns identified by examination of the data, such as the similarities in the profiles, at least with the available number of results. The applied statistical techniques give a picture of the whole data set and do not allow the detection of local, subtle behaviours, which a careful observer can notice. On the other hand multivariate procedures help find correlations which would not be so evident, such as the dependence on more variables at a time and similarities among groups of samples.

The same statistical procedures were applied to the 1998–99 results, even if the small data set is a drawback for this kind of treatment and few meaningful results are expected. The results obtained with PCA are reported in Fig. 2. The scores, when all variables were considered, did not allow us to make a clear distinction between M and S samples. However some regular trends are present, such as the positive PC3 value for all microlayer samples and the negative one for subsurface water, with the exception of S3. No further trends are observed if the data on heavy metals and on the other parameters are considered separately. Figure 2a shows that Mg, Ca and Sr are again correlated, as found for the 1997–98 samples, and the heavy metals are far from the other analytes. Barium is anticorrelated to the other alkaline earth elements. PC1 is strongly related to the alkali and alkaline earth metal content of the waters.

TABLE XI Univariate *F*-ratios for the investigated elements

Variable	*1997–98*	*1998–99*
B	0.128	0.095
Ba	0.245	2.78
Ca	0.067	0.288
Cd	21.4	0.898
Cu	0.937	8.309
Fe	0.0101	0.498
K	0.174	0.148
Li	0.0025	0.250
Mg	0.0996	0.298
Mn	0.123	0.158
Na	7.47	0.0875
Ni	6.52	0.272
Si	6.37	0.0241
Sr	0.0098	0.0023

Reference values: 4.11 and 5.99 respectively for the two Campaigns at a confidence level of 95%.

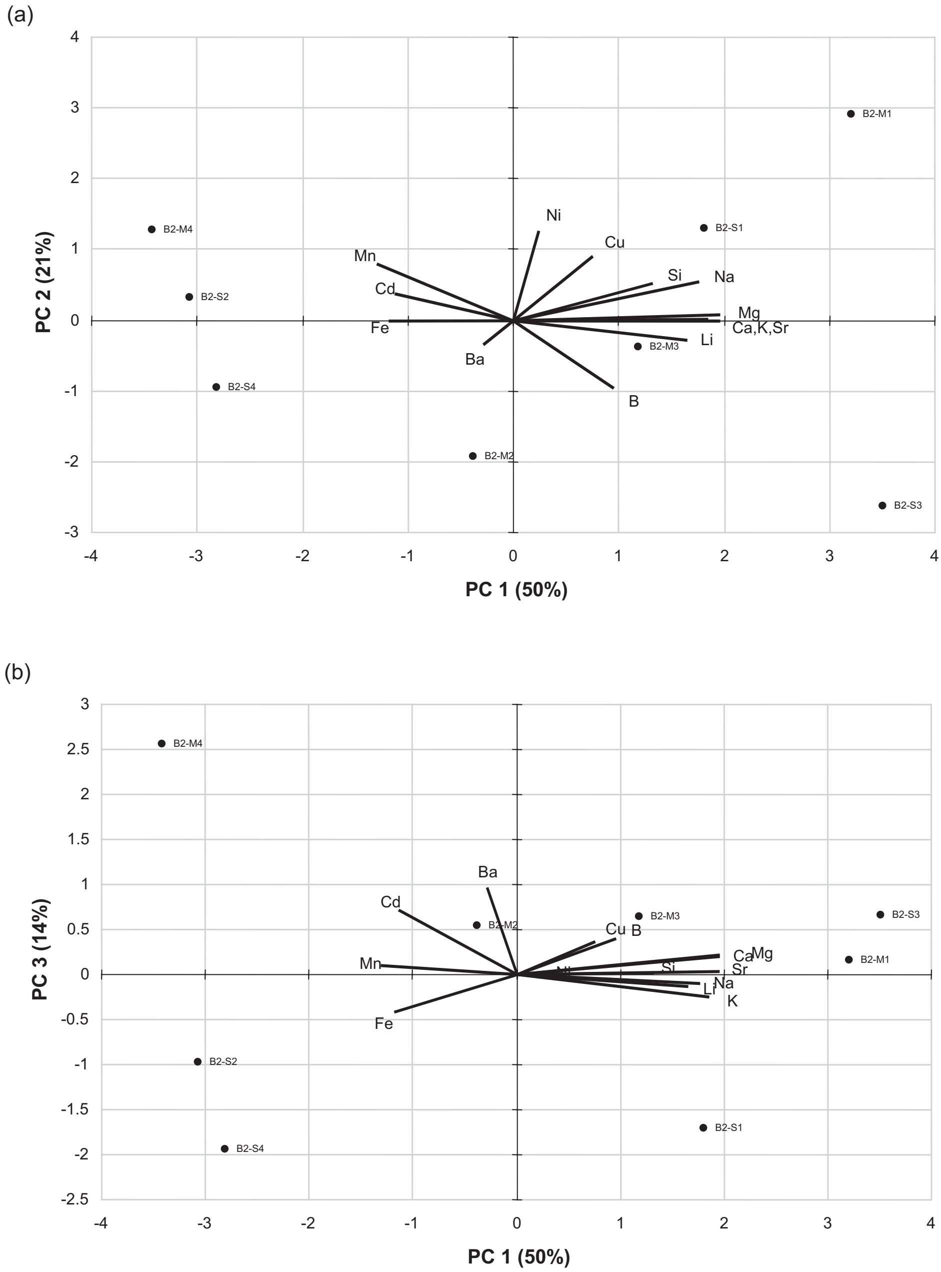

FIGURE 2 Combined plot of scores and loadings obtained by PCA for 1998–99 samples: (a) PC1 *vs*. PC2; (b) PC1 *vs*. PC3.

No analyte was found to have a discriminating power between the two kinds of samples in DA. On the other hand, HCA revealed a certain degree of similarity among samples collected in the same day (S1/M1, S3/M3, S4/M4), as shown in Fig. 3.

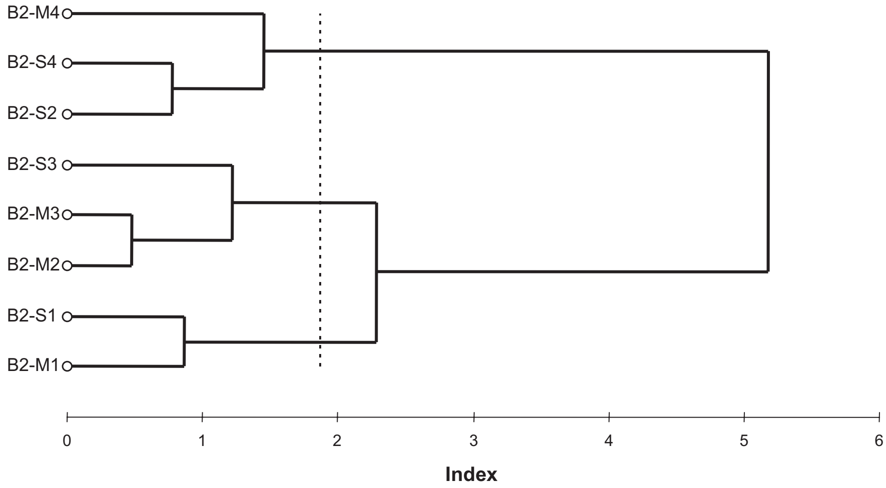

FIGURE 3 Dendrogram (Ward's method) for 1998–99 samples.

Probably the number of available results is not high enough to reveal other similarities among samples. Other statistical examinations may be proposed in order to extract information from the data.

CONCLUSIONS

The use of statistical techniques, together with the examination of data for individual elements, allows us to identify some trends in element concentrations as a function of collection time or depth. For instance, heavy metal concentrations are higher on the surface at the beginning of the Antarctic summer, whereas a phenomenon of surface depletion and deep-water enrichment is observed toward the end of the season. The depth profiles of the elements have a complex behaviour, dependent on chemical as well as biological and physical factors. The typical nutrient-type profile was not observed, in agreement with the findings of other studies [7,12,17,18].

The sites investigated during the 1997–98 Campaign could be classified with chemometric techniques according to the their location, but no subdivision as a function of collection depth was observed. Variables with similar properties, such as alkaline earth elements or heavy metals, were found to be correlated. In general, statistics and "common sense" examination of results provide complementary information in order to characterize the analyte behaviour in the samples.

As to the difference between microlayer and subsurface water, a certain degree of enrichment, especially of heavy metals, was present in the former. Such enrichment was smaller than expected, as discussed above.

The measured heavy metal ranges and mean concentrations are in agreement with the ones reported for different areas of the Southern Ocean and those found in the previous campaigns in the Ross Sea, therefore there seem to be no phenomena of accumulation or decrease.

Anthropic influence can alter the natural equilibria in many ways, not only by direct waste dumping but also as a result of river and runoff input, atmospheric deposition, soil dredging, oil drilling and shipping. Besides inorganic and organic contaminants, an increase in particulate input also alters natural biogeochemical equilibria.

Antarctica has the unique advantage that direct anthropogenic influences are virtually absent, so it is possible to study natural phenomena with little perturbation. Anyway it must be born in mind that any hypothetical increase in the pollutant content of seawater will eventually affect the Antarctic Ocean as well because of its involvement in the global water circulation.

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