

Distribution of major, minor and trace elements in lake environments of Antarctica

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Abstract: The concentrations of major, minor and trace metals were measured in water samples collected from five shallow Antarctic lakes (Carezza, Edmonson Point (No 14 and 15a), Inexpressible Island and Tarn Flat) found in Terra Nova Bay (northern Victoria Land, Antarctica) during the Italian Expeditions of 1993–2001. The total concentrations of a large suite of elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Gd, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sc, Si, Sr, Ta, Ti, U, V, Y, W, Zn and Zr) were determined using spectroscopic techniques (ICP-AES, GF-AAS and ICP-MS). The results are similar to those obtained for the freshwater lakes of the Larsemann Hills, East Antarctica, and for the McMurdo Dry Valleys. Principal Component Analysis (PCA) and Cluster Analysis (CA) were performed to identify groups of samples with similar characteristics and to find correlations between the variables. The variability observed within the water samples is closely connected to the sea spray input; hence, it is primarily a consequence of geographical and meteorological factors, such as distance from the ocean and time of year. The trace element levels, in particular those of heavy metals, are very low, suggesting an origin from natural sources rather than from anthropogenic contamination.

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Introduction

Antarctica is one of the most pristine places on earth, where natural background levels of major, minor and trace elements can still be determined. The distribution of trace elements in the separate components of the Antarctic ecosystem represents the result of natural processes. Natural background levels of trace elements, particularly the potentially toxic heavy metals, need to be determined before we can assess the level and extent of global environmental pollution. The identification of possible sources and pathways of major, minor and trace metals in Antarctica is particularly useful for the definition of baseline concentrations in the pristine Antarctic environment. Nevertheless, human activities in Antarctica, particularly in the vicinity of research stations such as Terra Nova Bay, in Victoria Land, and possibly an increase in global contamination over the last decades might have contributed substantially to the trace metal budget of some Antarctic ecosystems. For this reason a comparison of results obtained over a relatively long period of time is necessary to detect the effect of pollution from human activities or, conversely, to confirm the absence of local and/or global anthropogenic contamination in the Antarctic areas investigated.

The lacustrine Antarctic ecosystems of the Terra Nova

area in Victoria Land have been studied since 1985 within the framework of the Italian National Antarctic Research Program. Results for the period 1985–94 have already been published (Cremisini *et al.* 1991a, 1991b, Aceto *et al.* 1994, Caprioli *et al.* 1994, Abollino *et al.* 1996, Mentasti *et al.* 1998). In this study, we have examined the distribution of a series of metals in freshwater collected in five Antarctic lakes (Carezza, Edmonson Point Lakes 14 and 15a, Inexpressible Island and Tarn Flat), during the Italian Expeditions carried out in the period 1993–2001.

The concentrations of thirty-six elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Gd, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sc, Si, Sr, Ta, Ti, U, V, Y, W, Zn and Zr) were determined in the lake waters. The water samples were analysed by atomic emission, atomic absorption spectroscopy and ICP mass spectroscopy depending on the metal concentration level. The data obtained were analysed by Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) to show possible correlations among the elements determined and the similarities and differences present among the different sampling campaigns.

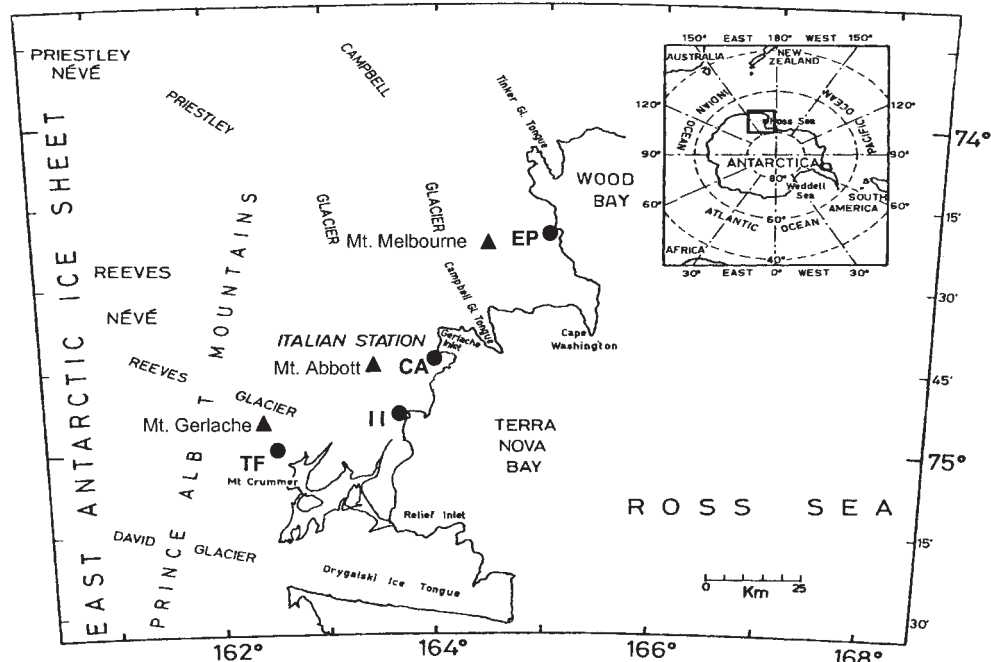


Fig. 1. Map of Terra Nova Bay, showing the investigated lakes: Carezza Lake (CA), Inexpressible Island (II), Tarn Flat (TF) and Edmonson Point (EP). The grey area in the inset map indicates the study site.

Location and setting

Terra Nova Bay is a large inlet, approximately 80 x 30 km wide, delimited by the Aviator Glacier (73°55'S, 165°20'E) to the north and the Drygalski Ice Tongue (75°20'S, 162°50'E), a floating ice strip generated by the Davis Glacier, which advances into the Ross Sea for *c.* 60 km, to the south (Fig. 1). Terra Nova Bay is part of the Ross Sea, and is relatively ice-free in summer. The Terra Nova Bay coasts are generally high, rocky, with numerous deep inlets, sometimes with some beaches as in the Edmonson Point and Inexpressible Island areas.

The geological basement of Terra Nova Bay is lithologically very variable, with several suites of granites, diorites, schists, amphibolites, basic and acid dykes, basalts and other volcanic rocks (Gragnani & Torcini 1991).

The lakes selected for this study are frozen in winter but completely ice-free during the summer months. They do not have defined inflow and outflow channels, and their only input is from snow and ice melt. The lake locations are shown in Fig. 1 and the geographic characteristics of the sampling points and the sampling dates are presented in Table I.

The lakes considered in this study are small and shallow. Carezza and Tarn Flat Lakes are situated on granitic soil (syenogranites and biotite granodiorites). Among the lakes sampled for this study, Carezza Lake is the nearest to the Italian Antarctic station, while Tarn Flat Lake is located in a basin, in the proximity of Mount Gerlache. The two lakes at Edmonson Point are close to Mount Melbourne, an active volcano, and their basement consists of Quaternary, basaltic volcanic soil. The lake at Inexpressible Island is the closest to the sea, and lies in an area mainly characterized by Jurassic tholeiites.

The Inexpressible Island area, which is almost completely free from glaciers and culminates at 390 m, is characterized by ice-cored moraine and disintegration moraine, with isolated conical reliefs and circular depressions accommodating shallow lakes. The mineralogical species detected by XRD in regoliths close to the borders of this lake are quartz, feldspars, amphiboles, biotite, chlorite and muscovite.

The Tarn Flat area, included between Larsen Glacier and Reeves Glacier, is almost completely ice-free and rich in shallow lakes and ponds. Eskers, constituted by gravels and

Table I. Geographical position of the investigated lakes at Terra Nova Bay and corresponding sampling periods.

Ref. No	Lake	Coordinates	Altitude m (a.s.l.)	Distance from the sea (km)	Samplings
3	Carezza Lake	74°43'S; 164°01'E	175	1	1993–94, 1994–95, 1995–96, 1997–98, 2000–2001
10b	Inexpressible Island	74°53'S; 163°43'E	30	~0.8	1993–94, 1994–95, 1995–96
20	Tarn Flat	74°59'S; 162°33'E	-70	35	1993–94, 1994–95, 1995–96, 1997–98
14	Edmonson Point	74°20'S; 165°07'E	20	~0.5	1995–96
15a	Edmonson Point	74°19'S; 165°04'E	0	~0.5	1997–98

Table II. Major and minor elements concentrations and corresponding standard deviations determined in lake water samples by ICP-AES (all values in $\mu\text{mol/L}$ with the exception of Ba expressed in nmol l^{-1}).

	Ba	Ca	K	Mg	Na	Si	Sr	Mg/Ca	Na/Na + Ca
CA 01/15/94	5.75 ± 0.58	175 ± 1	15.60 ± 0.26	70.77 ± 0.41	444 ± 0.4	81.18 ± 0.00	0.67 ± 0.002	0.40	0.72
CA 02/02/94	2.04 ± 0.51	159 ± 1	19.69 ± 0.51	103 ± 0.4	587 ± 4	118 ± 1	0.74 ± 0.003	0.65	0.79
CA 12/15/94	0.29 ± 0.03	124 ± 2	41.18 ± 1.02	38.67 ± 0.41	483 ± 2	63.38 ± 2.14	0.16 ± 0.001	0.31	0.80
CA 01/26/95	0.51 ± 0.07	189 ± 1	49.62 ± 0.26	69.12 ± 0.41	496 ± 8	115 ± 4	0.22 ± 0.003	0.37	0.72
CA 01/18/96	7.50 ± 0.95	249 ± 2	97.19 ± 2.56	160 ± 0.4	1562 ± 36	111 ± 1	0.88 ± 0.03	0.64	0.86
CA 12/31/98	1.38 ± 0.22	251 ± 2	91.05 ± 1.79	246 ± 0.4	2089 ± 19	98.63 ± 0.36	0.78 ± 0.003	0.98	0.89
CA 01/29/2001	5.68 ± 0.29	187 ± 1	112 ± 41	144 ± 9	2079 ± 38	89.73 ± 0.71	0.73 ± 0.002	0.77	0.92
II 01/05/94	9.47 ± 0.29	332 ± 1	111 ± 0.5	1041 ± 3	4611 ± 43	104 ± 0.1	1.59 ± 0.01	3.14	0.93
II 01/23/95	11.00 ± 0.07	931 ± 2	1460 ± 29	2905 ± 5	16181 ± 391	241 ± 4	1.55 ± 0.01	3.12	0.95
II 01/21/96	14.49 ± 0.65	778 ± 17	719 ± 13	1930 ± 28	26359 ± 478	238 ± 4	3.12 ± 0.02	2.48	0.97
TF 01/08/94	23.30 ± 0.07	479 ± 2	24.04 ± 0.26	323 ± 1	896 ± 4	258 ± 2	0.86 ± 0.001	0.67	0.65
TF 01/28/95	7.35 ± 0.07	566 ± 2	106 ± 3	366 ± 1	1296 ± 15	449 ± 4	0.31 ± 0.002	0.65	0.70
TF 01/21/96	11.07 ± 0.29	414 ± 4	85.94 ± 3.84	290 ± 3	1718 ± 70	220 ± 0.2	0.56 ± 0.01	0.70	0.81
TF 01/09/98	22.57 ± 0.36	594 ± 2	98.47 ± 2.05	381 ± 2	2525 ± 25	184 ± 1	0.73 ± 0.006	0.64	0.81
TF 01/29/98	21.12 ± 0.07	672 ± 5	119 ± 0.06	434 ± 2	2774 ± 41	221 ± 1	0.82 ± 0.002	0.65	0.80
EP 14 01/19/96	1.60 ± 0.29	139 ± 0.7	243 ± 4	356 ± 2	4654 ± 130	105 ± 1	0.40 ± 0.003	2.57	0.97
EP 15a 01/11/98	0.73 ± 0.07	17.96 ± 0.50	9.46 ± 0.26	23.04 ± 0.00	273 ± 6	11.39 ± 0.71	0.023 ± 0.0002	1.28	0.94
EP 15a 02/02/98	0.73 ± 0.07	19.96 ± 0.25	11.51 ± 0.77	25.10 ± 0.00	301 ± 5	40.23 ± 0.36	0.024 ± 0.001	1.26	0.94
Calibration blank	1.14	0.090	1.57	0.006	0.145	10.06	0.0001		

sands of glacial contact, are common in the area. Generally speaking, the landscape is characterized by glacial erosion, with wide extensions of bare rock smoothed or modelled in undulating surfaces. The undulations culminate in wide hilly reliefs and, sometimes, form depressions such as closed basins. Tarn Flat Lake lies in one of these depressions, which has been preserved due to the particularly dry climate and wind action that prevent snow accumulation. Tarn Flat Lake is about 35 km from the sea. It has a surface of about 17700 m² and a maximum depth of 3.9 m. Meltwater is supplied from a drainage area of 2 km² and from a glacier of 0.3 km². The mineralogical species detected by XRD in the regolith close to the borders of this lake are quartz, feldspars, amphiboles, chlorite, muscovite, calcite and fluorite (Orombelli 1986, Libera 1997, Bertelle *et al.* 1998).

The weather conditions along the coast of Terra Nova Bay are largely influenced by strong late evening to early morning katabatic winds blowing seaward from the plateau, mainly along the direction of the glaciers. These persistent katabatic winds result in these shallow lakes being well-mixed, particularly during summer, when most of the lakes are unfrozen for more than two months (Cremisini *et al.* 1991a, 1991b, Gragnani & Torcini 1992, Gasparon *et al.* 2001).

Experimental

Sampling and procedures

The Antarctic lacustrine waters contain very low concentrations, at the level of nmol l^{-1} , of trace elements of environmental significance such as Pb and Cd. It is therefore imperative that sampling, storage and analysis be done with extreme care to avoid false positive results or

high blanks. All water samples were taken with a one litre polyethylene bottle which had been rinsed several times with ultrapure water and then rinsed with the water sample before collection. The appropriately modified Millipore pressure system, in which all the steel parts had been replaced by Teflon, was also subjected to the same washing procedure (prior to use). The water samples were immediately filtered through acid washed 0.45 μm cellulose acetate filters into pre-cleaned polyethylene bottles and frozen at -24°C . All samples were maintained at -24°C during all stages of storage and transportation to our laboratory.

Samples were processed in a clean environment under a Class-100 laminar flow bench-hood. The water samples were acidified with purified nitric acid after melting and analysed by atomic emission, atomic absorption spectroscopy or mass spectroscopy depending on the metal concentration level. The sample blanks were prepared similarly to samples in the laboratory, but without the field sampling step. Because the difference between the sample blanks and the calibration blanks was always lower than the detection limit of the instrument used, the calibration blank, made in connection with instrumental calibration and prepared daily, was subtracted from the sample concentration. Also the standard solutions for the instrumental calibration were prepared in aliquots of calibration blank. The values of calibration blanks for the elements analysed are shown in Tables II–IV. In atomic absorption spectroscopy, it was necessary to use the multiple standard additions method to determine all elements. Moreover, matrix modifiers were employed to analyse Al (0.2 mg of $\text{Mg}(\text{NO}_3)_2$), Cd (0.2 mg of $(\text{NH}_4)_2\text{PO}_4$ + 0.01 mg of $\text{Mg}(\text{NO}_3)_2$), Co (0.05 mg of $\text{Mg}(\text{NO}_3)_2$) and Pb (0.2 mg of $(\text{NH}_4)_2\text{PO}_4$ + 0.01 mg of $\text{Mg}(\text{NO}_3)_2$).

Table V. Mean, 1% and 99% percentiles for element concentrations in lake water samples collected during the Italian expeditions from 1993/94 to 2000/01.

	Mean	1% percentile	99% percentile
Al	527	41.12	1.47 x 10 ³
As	10.95	1.94	27.82
Ba	8.14	0.33	23.18
Ca	3.49 x 10 ⁵	1.83 x 10 ⁴	9.05 x 10 ⁵
Cd	0.12	< 0.009	0.53
Ce	0.10	0.008	0.45
Co	1.70	0.22	5.48
Cr	10.07	0.42	120
Cs	0.037	< 0.007	0.20
Cu	11.84	0.23	27.54
Fe	357	13.68	848
Ga	0.13	< 0.029	0.59
Gd	0.013	< 0.006	0.030
K	1.90 x 10 ⁵	9.81 x 10 ³	1.33 x 10 ⁶
La	0.090	0.008	0.43
Li	1.52 x 10 ³	29.26	4.68 x 10 ³
Mg	4.95 x 10 ⁵	2.34 x 10 ⁴	2.74 x 10 ⁶
Mn	71.25	9.16	269
Mo	32.99	4.56	147
Na	3.85 x 10 ⁶	2.78 x 10 ⁵	2.46 x 10 ⁷
Nd	0.045	0.007	0.19
Ni	8.75	0.63	62.70
Pb	0.73	0.041	4.56
Pr	0.016	< 0.007	0.047
Rb	17.79	2.56	111
Sc	13.03	0.11	40.12
Si	1.53 x 10 ⁵	1.63 x 10 ⁴	4.17 x 10 ⁵
Sr	790	20	2.86 x 10 ³
Ta	0.082	0.007	0.22
Ti	16.42	0.29	78.22
U	2.05	0.004	9.28
V	58.07	24.82	95.71
Y	0.080	0.011	0.24
W	3.75	0.31	16.13
Zn	21.41	3.16	107
Zr	0.42	0.049	0.88

Antarctic lacustrine waters data were analysed by Principal Component Analysis and Cluster Analysis with XIStat 4.4 software package. When concentrations were below the detection limit, a random value between zero and that limit was inserted in order to be able to thoroughly apply PCA and HCA without losing any data.

Apparatus and reagents

A Varian Liberty 100 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) was used to determine major (Ca, K, Mg, Na and Si) and some minor (Ba, Sr) elements, because their concentrations were higher than the detection limits of the instrument. The spectrometer is provided with a Czerny-Turner monochromator, a Sturman-Masters spray chamber, a V-groove nebuliser and a radio frequency (RF) generator at 40.68 MHz. The instrumental conditions were: plasma power 1.0 kW; nebuliser pressure 150 kPa; sample aspiration rate 15 rpm (~2 ml m⁻¹); argon

Table VI. Concentrations of major, minor and trace elements (nmol l⁻¹) in freshwaters, ocean waters and Ross Sea.

	Freshwaters	Ocean Waters	Ross Sea
Al	< 1112 ^a	4.82–40.77 ^c	-
As	26.69 ^a	14.95–24.96 ^c	-
Ba	72.82 ^a	31.97–150 ^c	50.97–160 ^d
Ca	44.99 x 10 ³ –1230 x 10 ³ ; 330 x 10 ³ ^b	10.28 x 10 ⁶ ^c	6.76 x 10 ⁶ –13.25 x 10 ⁶ ^d
Cd		8.9 x 10 ⁻⁴ –1.07 ^c	0.035–0.98 ^{d,e}
Co	0.85 ^a	0.010–0.10 ^c	0.005–0.034 ^c
Cr	9.62 ^a	1.92–50.00 ^c	-
Cu	28.33 ^a	0.47–5.98 ^c	0.47–4.88 ^{d,e}
Fe	< 537 ^a	0.10–2.51 ^c	0.05–7.52 ^{d,e}
K	12.99 x 10 ³ –100 x 10 ³ ; 30.00 x 10 ³ ^b	10.20 x 10 ⁶ ^c	6.47 x 10 ⁶ –14.12 x 10 ⁶ ^d
Li	144 ^a	25.07 x 10 ³ ^c	12.97 x 10 ³ –29.97 x 10 ³ ^d
Mg	33.00 x 10 ³ –620 x 10 ³ ; 150 x 10 ³ ^b	53.07 x 10 ⁶ ^c	37.03 x 10 ⁶ –72.82 x 10 ⁶ ^d
Mn	< 91.01 ^b	0.18–2.91 ^c	0.20–2.18 ^d
Mo	10.42 ^a	110 ^c	-
Na	50.02 x 10 ³ –1600 x 10 ³ ; 2 30 x 10 ³ ^b	468 x 10 ⁶ ^c	429 x 10 ⁶ –478 x 10 ⁶ ^d
Ni	5.11 ^a	2.04–11.93 ^c	1.87–9.37 ^{d,e}
Pb	0.96 ^a	0.005–0.19 ^c	0.05 ^{f,g}
Rb	-	1404 ^c	-
Si	190 10 ³ ^c	< 1.00 10 ³ –180 10 ³ ^c	37.99 10 ³ –73.99 10 ³ ^d
Sr	570 ^a	90.00 10 ³ ^c	60.00 10 ³ –107 10 ³ ^d
U	2.10 ^a	13.86 ^c	-
V	17.67 ^a	19.63–35.33 ^c	-
Zn	7.65 ^a	0.046–9.02 ^c	0.30–7.03 ^c

^a trace element concentration in freshwaters (Förstner & Wittmann 1983)

^b 1% and 99% percentile levels for global rivers (Meybeck 1981) and the global average for freshwaters (Bernier & Bernier 1987)

^c Libes 1992

^d Abollino *et al.* 2001

^e Fitzwater *et al.* 2000

^f Scarponi *et al.* 1997

^g Capodaglio *et al.* 1998.

auxiliary flow 1.5 l m⁻¹.

Metal concentrations close to or lower than the detection limits for ICP-AES were determined with a Perkin Elmer 5100 Graphite Furnace Absorption Spectrometer (GF-AAS) equipped with a Zeeman-effect background correction, a HGA 600 graphite furnace and an AS-60 autosampler interfaced to a personal computer for the execution of analysis and data collection. Pyrocoated graphite tubes with L'Vov platform were used throughout.

Hollow cathode lamps (Perkin-Elmer) were used for Al, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb and Zn and a electrodeless discharge lamp (Perkin-Elmer) was used for As. The volume sampled into the graphite tube was 20 µl for the test sample and calibration solutions. The volume of the matrix modifier, when added into the solution, was 10 µl with the exception of Pb (15 µl). The graphite furnace temperature program for each analyte was optimized before analysing the freshwater samples.

An X5 ICP-MS instrument (Thermo Elemental, Winsford, UK), equipped with an ASX-500 autosampler (CETAC, Omaha, USA) was used for ICP-MS analysis.

Table VII. Concentrations of major, minor and trace elements (nmol l⁻¹) in water samples collected in Carezza Lake, Inexpressible Island, Edmonson Point and Tarn Flat during the Italian expeditions from 1985/86 to 1991/92, in McMurdo Dry Valleys lakes (Antarctica), in Larsemann lakes (Antarctica), in Lake Hayes (New Zealand) and in Lapland lakes (Finland).

	Italian expeditions 1985/86–1991/92	McMurdo Dry Valleys lakes	Larsemann lakes	Lake Hayes	Lapland lakes
Al	519 ^a	-	10.64–6609 ^d	-	593–5449; 2335 ^g
As	12.01 ^a	-	1.71–139 ^d	-	1.60–5.47; 2.27 ^g
Ba	3.64–33.50; 12.16 ^a	-	1.59–40.88 ^d	-	-
Ca	3.74 x 10 ³ –4042 x 10 ³ ; 501 x 10 ^{3 a, b}	0.028 x 10 ⁶ –6.58 x 10 ⁶ ; 2.21 x 10 ^{6 c}	7.48 x 10 ³ –314 x 10 ^{3 e}	600 x 10 ^{3 f}	-
Cd	0.018–0.62; 0.17 ^{a, b}	< 0.009–1.12; 0.39 ^c	0.018–16.19 ^d	< 0.04 ^f	0.18–0.36; 0.18 ^g
Ce	-	0.004–11.2; 1.66 ^c	0.007–0.28 ^d	-	-
Co	0.044–2.17; 0.81 ^{a, b}	< 0.34–1.56; 0.38 ^c	0.20–3.73 ^d	-	-
Cr	0.63–7.69; 2.21 ^a	-	6.35–17.62 ^d	-	1.54–12.69; 4.62 ^g
Cu	0.31–20.93; 9.13 ^{a, b}	< 0.75–121; 19.28 ^c	4.36–31.14 ^d	1.62 ^f	2.05–8.97; 4.41 ^g
Fe	2.33–874; 210 ^{a, b}	< 1.79–17190; 1160 ^c	-	-	304–13250; 1558 ^g
Gd	-	0.007–0.76; 0.20 ^c	0.000–0.019 ^d	-	-
K	5.11 x 10 ³ –5499 x 10 ³ ; 389 x 10 ^{3 a, b}	0.002 x 10 ⁶ –8.00 x 10 ⁶ ; 1.54 x 10 ^{6 c}	3.32 x 10 ³ –194 x 10 ^{3 e}	33.6 x 10 ^{3 f}	-
La	-	0.005–4.73; 1.49 ^c	0.007–0.26 ^d	-	-
Li	144 -	-	-	-	-
Mg	16.46 x 10 ³ –19008 x 10 ³ ; 1074 x 10 ^{3 a, b}	0.002 x 10 ⁶ –12.9 x 10 ⁶ ; 2.85 x 10 ^{6 c}	18.10 x 10 ³ –1498 x 10 ^{3 e}	126.3 x 10 ^{3 f}	-
Mn	17.98–1747; 148 ^{a, b}	12.74–68896; 17219 ^c	-	-	91.01–564; 273 ^g
Mo	1.46–93.81; 13.65 ^b	-	0.24–4.23 ^d	-	-
Na	180 x 10 ³ –100000 x 10 ³ ; 8612 x 10 ^{3 a, b}	0.083 x 10 ⁶ –129 x 10 ⁶ ; 27.09 x 10 ^{6 c}	196 x 10 ³ –10744 x 10 ^{3 e}	133 x 10 ^{3 f}	-
Nd	-	0.01–3.63; 1.12 ^c	0.000–0.26 ^d	-	-
Ni	0.31–24.94; 5.25 ^{a, b}	< 0.34–100; 24.67 ^c	3.22–17.75 ^d	-	1.70–8.86; 4.26 ^g
Pb	0.048–6.18; 0.48 ^{a, b}	-	0.010–1.20 ^d	< 0.2 ^f	0.43–3.28; 1.21 ^g
Rb	-	-	0.63–27.25 ^d	-	-
Si	-	-	-	17 x 10 ^{3 f}	-
Sr	37.66–1689; 852 ^a	-	17.69–1894 ^d	1720 ^f	-
U	-	-	0.004–0.59 ^d	-	-
V	0.19–47.11; 12.07 ^b	-	6.54–213 ^d	-	-
Y	-	0.02–7.66; 2.45 ^c	0.011–0.65 ^d	-	-
Zn	2.45–65.76; 13.07 ^{a, b}	-	13.76–12158 ^d	0.89 ^f	11.16–57.50; 28.14 ^g

^a concentration ranges and averages (Aceto *et al.* 1994, Abollino *et al.* 1996, Mentasti *et al.* 1998)

^b concentration ranges and averages (Cremisini *et al.* 1991a, 1991b, Gagnani & Torcini 1991, 1992, Caprioli *et al.* 1994)

^c concentration ranges and averages (De Carlo & Green 2002, Green *et al.* 1988, 1989)

^d concentration ranges (Gasparon & Burgess 2000)

^e concentration ranges (Gasparon *et al.* 2001)

^f mean metal concentrations and reactive SiO₂ (Reid *et al.* 1999)

^g 1% and 99% percentile levels and median (Mannio *et al.* 1995)

Data acquisition and processing were performed using the PlasmaLab 2.01 software (Thermo Elemental). With the instrumental configuration described, oxide and doubly-charged species formation was found to be < 2%. The instrument was tuned daily with a solution containing 10 µg l⁻¹ of Li, Y, Ce and Tl.

The reagents used were all of analytical purity. The nitric acid, used to acidify the samples before analysis, was further purified by sub-boiling distillation in a quartz apparatus. Water was purified in a Milli-Q system, resulting in water with a resistivity of 18 MΩ cm.

Standard metal solutions were prepared from concentrated stock solutions (Merck Titrisol).

Results and discussion

The concentrations of the major, minor and trace elements in the waters of the five Antarctic lakes sampled in the period 1993–2001 are reported in Tables II–IV, in addition the mean and 1% and 99% percentile levels of the elements

considered are reported in Table V. For comparison, Table VI shows the distribution of major, minor and trace metals in freshwaters, ocean waters and the Ross Sea. Table VII compares the metal distributions in the five lakes with data from the Antarctic lakes of the McMurdo Dry Valleys, the Larsemann Hills, Lake Hayes (New Zealand) and 36 lakes in Lapland (Finland).

Major components

Na is the most abundant cation in the Antarctic lake waters, followed by Mg, Ca and K (Table II). By comparison with major metal concentrations in freshwaters reported in Table VI, Antarctic lakes of Terra Nova Bay are characterized by a higher salt content. The major metals content of these lakes is similar to the upper limit of the concentration range reported for freshwaters. The most saline lake considered in this study was found to be Inexpressible Island, and its Ca, K, Mg, Na and Sr content largely exceeds the maximum values encountered both in

freshwaters and in the Antarctic lakes of the Larsemann Hills. The Mg/Ca ratio values (Table II) range from 0.31 to 3.14, with an average of 1.18 and decrease in the following order: Inexpressible Island > Edmonson Point > Tarn Flat > Carezza Lake. Na/(Na + Ca) ratio values range from 0.65 to 0.97, with an average of 0.84, and decrease in the order: Inexpressible Island = Edmonson Point > Carezza Lake > Tarn Flat. These values suggest that sea spray influences the water chemistry of some of the lakes investigated. The extent of this influence varies considerably from area to area as a function of both the distance from the sea and the different geomorphological conditions, such as the presence of surface melt water or shallow level ground water flowing into the lakes from the nearby glacier, especially during the summer. In fact, the lakes nearest to the sea (Lake 10b at Inexpressible Island and Lakes 14 and 15a at Edmonson Point) are characterized by higher Mg/Ca and Na/(Na+Ca) values (the second, being higher than 0.90, is very close to the value of 0.98 found in the Ross Sea (Abollino *et al.* 2001)) and, hence, by a stronger marine contribution.

There are, however, some substantial differences among lakes situated at almost the same distance from the sea (Inexpressible Island and Edmonson Point), as well as between lakes very close to each other (Lakes 14 and 15a at Edmonson Point) or for different elements within the same lake (Inexpressible Island). In fact, even though the chemical composition of Inexpressible Island and of Edmonson Point lakes is strongly influenced by sea spray, the major metal concentration in Inexpressible Island is higher than that found in Edmonson Point lakes, probably because the latter are situated on the slopes of Mount Melbourne: the input of low salinity water from fresh snow and condensate of the fumaroles of the Mount Melbourne volcano at 2700 m a.s.l. determines a dilution of the major cation content in Lakes 14 and 15a (Gragnani & Torcini, 1991). Differences between Lakes 14 and 15a could be due to their different position, or possibly to their different altitudes.

Instead, Tarn Flat and Carezza Lake show lower Na/(Na+Ca) values (0.75 and 0.81 respectively). The major metal content present in these lakes varies in the following order: Ca > Mg > K.

Among the Antarctic lakes considered in this study, Tarn Flat Lake is the most distant from the sea, and this may explain its low Na/(Na+Ca) and Mg/Ca values. It should, however, be noted that such low values are due to a high Ca concentration and not to a low Na or Mg content. The high Ca input is likely to be due to the position of the lake, which is situated in a zone below sea level with noticeable inflowing water that comes from Mount Gerlache and reaches the lake after crossing snow-free areas. Part of the magnesium and calcium present in the lake, therefore, could derive from the leaching of biotite-rich granites extensively present in this area. Similar leaching processes were also observed by Claridge & Campbell (1977) in other Antarctic

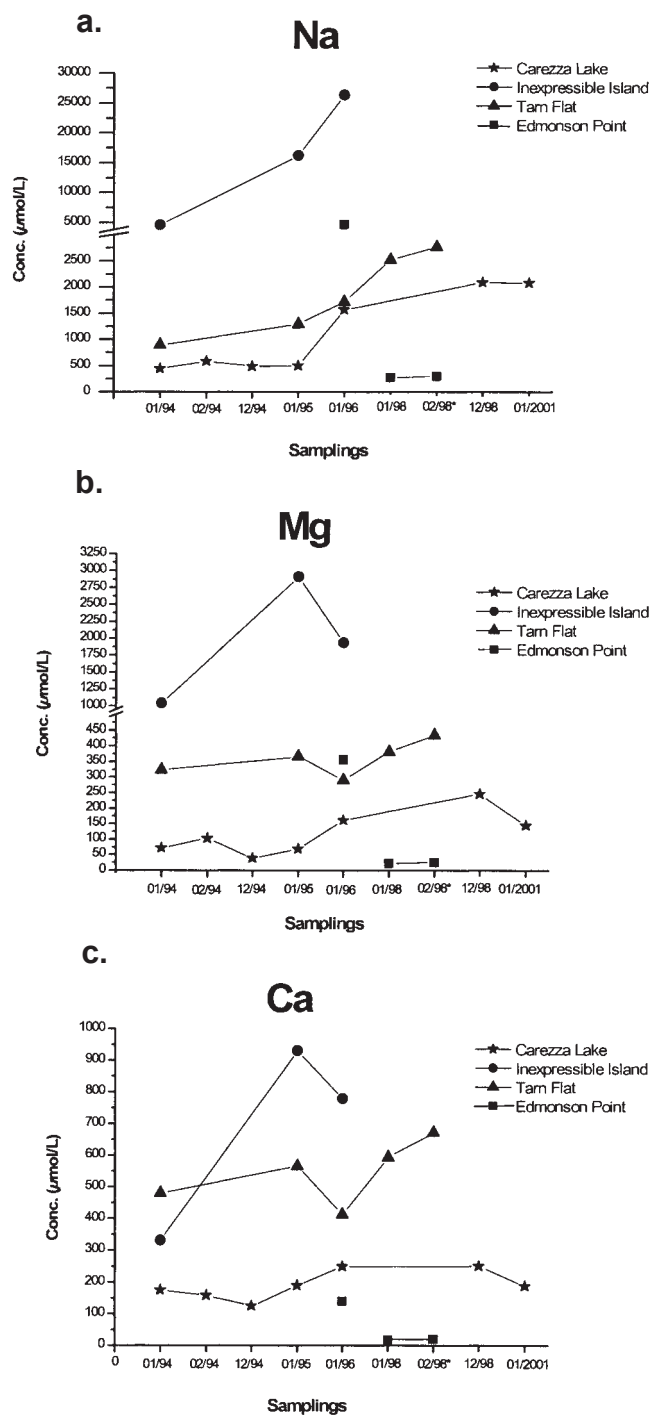


Fig. 2. Trends of **a.** Na, **b.** Mg, **c.** Ca over time. Time is expressed as sampling dates. 02/98* includes TF 01/29/98 and EP 02/02/98.

areas. Carezza Lake, although near the coast, has low Na/(Na+Ca) and Mg/Ca ratios because the influx of sea spray is partly balanced by dilution with surface melt water and shallow level ground water that flow into the lake from the nearby glacier.

For a given lake, the concentrations of Ca, K, Mg, Si and

Sr are higher at the end of January or at the beginning of February, when the lakes are almost completely ice-free, than at the start of the summer season, when the surface ice starts shrinking and the air and water temperatures are considerably lower. This is evident in the first sampling campaign (1993–94) for Carezza Lake, with the exception of Ca content, and in the sampling campaign (1997–98) for Tarn Flat and Edmonson Point, i.e. in the expeditions in which sampling was conducted in different periods of same year (Table II and Fig. 2). This trend was also found by Caprioli *et al.* (1994) in the same lakes for salinity and by Gasparon *et al.* (2001) in the Larsemann Hills and is due to the chemical stratification of the water column in winter and its subsequent homogenization in summer when the lakes are not frozen and their waters well-mixed by the intense action of the katabatic winds. The effectiveness of this mixing is a function of the climatic conditions, the lake dimensions, the depth of the water column and, indirectly, the input of streams derived from snow melting or glacial runoff. The water column is well-mixed because the lakes have shallow depth (the maximum depth is 3.5 m in Tarn Flat), small size, and are exposed to wind action. Moreover, the observed differences between early and late summer are not great. This is due to the absence of sizable inflows and outflows for the metals deriving from processes of rock weathering and to the short period in which the lake system is not insulated from atmosphere, and therefore from sea spray, whereas during most of the year the lake surface is covered by ice. The largest difference was observed for Tarn Flat, which is subject to more intense wind action than Carezza Lake and Edmonson Point, and therefore becomes ice-free earlier and receives a greater flow of water from the nearby glacier. A similar trend was observed for Inexpressible Island, where the concentrations of Ca, Mg, K and, in part, Si increase from the first (II 01/05/94) to the second (II 01/23/95) expedition and slightly decrease from the second to the third (II 01/21/96), i.e. they are higher at the end than at the beginning of January. It must be pointed out that the variability observed for Inexpressible Island is higher than for the other lakes, because the samples were collected in different years.

Na contents increase from year to year in all investigated lakes (Fig. 2a). This trend is due principally to the influence of sea spray, to the absence of substantial outflows and to evaporation and sublimation in this arid climate, with a consequent variation of the lake hydrologic balance. In fact, evaporation and sublimation can occur, as elsewhere in Antarctica, through ice sublimation balanced by freezing of the lake water with consequent volume shrinkage (Green *et al.* 1988), or during the short summer period, when the lakes are partially ice-free. This increase is not so great and so constant in the years because probably the stratification of the water column during freezing produces an increase of the salinity on the bottom waters and, consequently, sodium may precipitate out of solution during early freezing. This

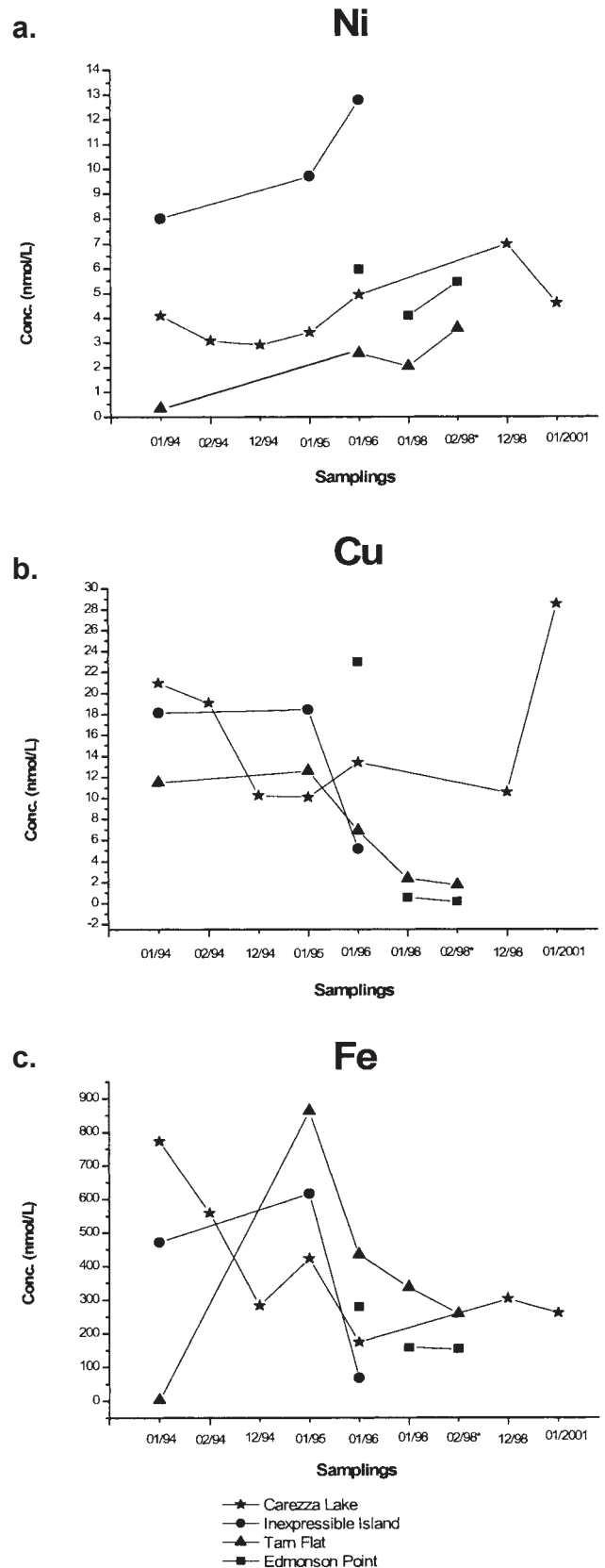


Fig. 3. Trends of a. Ni, b. Cu, c. Fe over time. Time is expressed as sampling dates. 02/98* includes TF 01/29/98 and EP 02/02/98.

effect was also observed by other researchers (e.g. Schmidt *et al.* (1991)) who studied the changes throughout the year in the physical and chemical characteristics of the water of two lakes situated at Cape Evans, Ross Island. The behaviour of sodium in Inexpressible Island Lake is very different from that observed in the other lakes, since its concentration greatly increases from one year to another. This trend cannot be explained simply by an interaction between the lake system and the atmosphere, and therefore with sea-spray; but it might depend on several concomitant factors, for example an anomalously high wind action, not completely verifiable at the moment. Finally, by comparing our data with those of other surface waters in the McMurdo Dry Valleys, Antarctica, it is again evident that the influence of sea-spray is strong along the coast of Terra Nova Bay (Green *et al.* 1988).

Lastly, it is evident that the trends of Mg and Ca in the investigated period are very similar. This suggests that the Mg content in the lakes does not originate only from the input of sea spray but also from rock weathering. The influence of rock weathering on the elemental content of the waters is confirmed by the high Si concentrations found in most lakes; this effect is more evident in Tarn Flat and less apparent in Edmonson Point.

Minor and trace components

The minor and trace metals content is reported in Tables III & IV. The highest concentrations of chromium, lithium, scandium, vanadium, uranium and tungsten were observed in Tarn Flat Lake. Inexpressible Island Lake is characterized by relatively high concentrations of lithium, molybdenum and rubidium and by low aluminium content. The high uranium content in Tarn Flat Lake is particularly interesting. Uranium is not usually introduced into the environment as a result of human activities (with the exception of nuclear waste). Therefore, it most probably derives from sea-spray or from sediment- and rock-water interactions. Since Tarn Flat Lake is distant from the coast, it is very likely that the high uranium content is due to leaching of sediments containing relatively high concentrations of U-bearing minerals such as fluorite. In Inexpressible Island, the sea-spray might be the major source of uranium; while the rubidium content, as well as the K content, might derive from the weathering of biotite present in the regoliths close to the borders of the lake (Bertelle *et al.* 1998). At Edmonson Point, Lake 14 shows a higher content of almost all metals compared to Lake 15a. Finally, Carezza Lake is characterized by high Pb and Co concentrations.

In Fig. 3 the trends for nickel, copper and iron are reported as a function of the sampling period. As for the major metals, nickel concentrations are higher in the samples collected at the end of the Antarctic summer, with the exception of the first sampling campaign (1993–94) for Carezza Lake. As already noted by Caprioli *et al.* (1994),

nickel concentrations increase from one year to the next in all investigated lakes. Unlike nickel, copper and iron concentrations decrease with time within the same expeditions with few exceptions. The concentration of these elements is lower at the end of January or at the start of February, i.e. during the warm period, when algal growth takes place. These elements are essential for life, and therefore can be absorbed by organic matter in the lakes. Such phenomena were evidenced in some of our previous articles about Antarctic lakes and they are widely described in the literature. Several vegetal and animal organisms (especially aquatic) are able to accumulate metals owing to the presence of groups with complexing properties in their tissues (Merian 1991, Aceto *et al.* 1994, Stumm & Morgan 1996, Mentasti *et al.* 1998). This is a possible explanation of the seasonal trends observed for these metals in the lakes of Terra Nova Bay. Copper and iron contents also decrease from one year to the next in all investigated lakes, although this trend is less obvious and consistent because of possible cyclic bioaccumulation and remobilization of these elements by living organisms. Copper concentrations were lower in samples collected during the 1997–98 campaign (Table III and Fig. 3b). The water temperatures during the 1997–98 sampling period were relatively high, and this may have induced a higher algal growth and a consequent decrease in the content of essential elements in the lake waters. These samples are also characterized by lower iron content.

The other analysed trace and minor metals do not show well defined trends because their content varies very little with time in all examined lakes. This phenomenon could be due to the combined effect of the processes that determine the solubilization or the removal of these elements in the Antarctic lakes making their concentration to appear constant over time.

The following conclusions can be drawn from the comparison of our results with the values reported in Table VI & VII. Minor and trace metal concentrations are generally similar to those reported for freshwaters. In some cases, higher concentrations of Al, Co, Cu, Fe, Li, Mn, Mo, V and Zn are probably due to the presence of higher geochemical background. This is particularly obvious when comparing the concentrations of these elements in the lakes with those reported for open sea water and for the Ross Sea. The content of minor and trace elements in the lakes of Terra Nova Bay falls in the range of concentration reported for the Larsemann Hills, with the exception of Mo (all lakes), Rb (Inexpressible Island and Lake No 14 of Edmonson Point), and U (Inexpressible Island and Tarn Flat) concentrations. The higher concentration of these elements is due either to a higher input of sea-spray (this is the case for Inexpressible Island) or, more likely, to the presence of rocks and sediments more easily weathered and containing higher proportions of U-rich and Rb-rich minerals such as muscovite, biotite and fluorite. Finally the

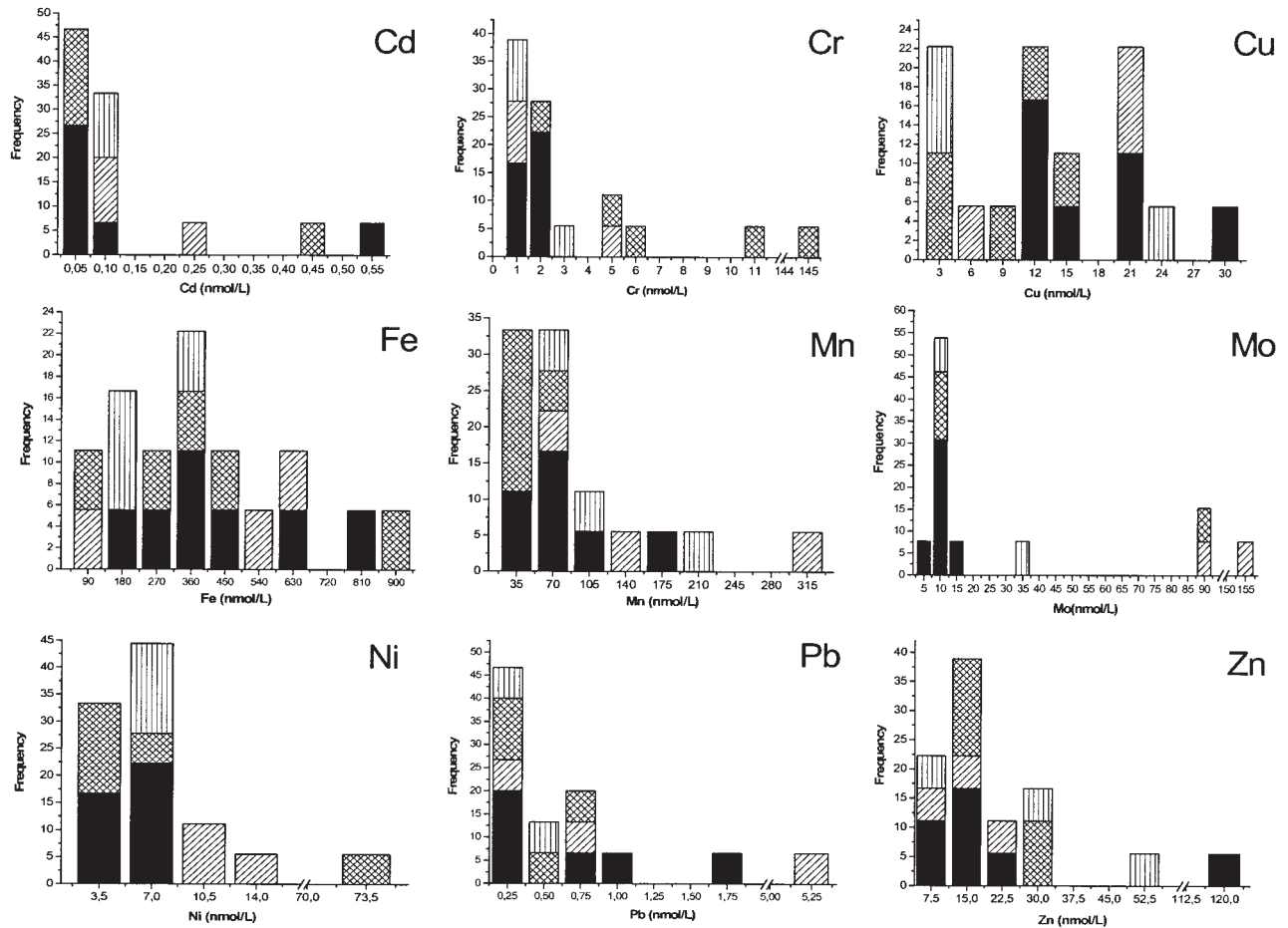


Fig. 4. Frequency histograms for Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn. Solid = Carezza Lake, diagonal lines = Inexpressible Island, cross-hatching = Tarn Flat, vertical lines = Edmonson Point.

concentrations of minor and trace elements in the samples are similar to the metal distribution found in the same lakes in the previous Italian Expeditions (Cremisini *et al.* 1991b, Gragnani & Torcini 1991, 1992, Aceto *et al.* 1994, Caprioli *et al.* 1994, Abollino *et al.* 1996, Mentasti *et al.* 1998), with a few exceptions. As might be expected, they are often lower than values reported for the deep, permanently stratified McMurdo Dry Valleys Lakes, where metal concentrations at redox boundaries can be elevated. This is especially evident for Fe and Mn concentrations (Green *et al.* 1988, 1989, De Carlo & Green 2002). These observations suggest that the lacustrine Antarctic ecosystem under investigation can be considered as uncontaminated either by human activity at Terra Nova Bay station or by atmospheric global circulation.

The frequency histograms for the concentrations of some minor and trace elements determined in the water samples are reported in Fig. 4.

Cadmium concentrations in about 50% of the samples are lower than $0.040 \text{ nmol l}^{-1}$, therefore lower than the Cd content in freshwaters and Ross Sea, indicating again the absence of anthropogenic contamination.

About 60% of the samples show chromium concentration levels lower than 1.50 nmol l^{-1} , which are similar to values encountered in freshwaters and below the lower limit of the range reported for the waters of the lakes in Larsemann Hills and ocean waters. Higher chromium concentrations were found in Tarn Flat Lake which might be due to the greater input of metals deriving from processes of rock weathering. The water collected during the 1994–95 expedition had high chromium and nickel concentrations, indicating a certain degree of natural temporal variability, although sample contamination during collection or instrumental analysis cannot be ruled out.

More than 70% of the samples show Fe concentration lower than 500 nmol l^{-1} , the value reported for freshwaters. The iron content is much higher than the maximum value encountered in ocean waters and the Ross Sea because of its heavy dependence on rock leaching processes.

For Mn, more than 60% of the samples fall into the 7.00 to $70.00 \text{ nmol l}^{-1}$ range, therefore lower than the value in freshwaters. A higher Mn concentration was found in lakes of Edmonson Point and Inexpressible Island. The higher variability in the Fe and Mn content is probably due to the

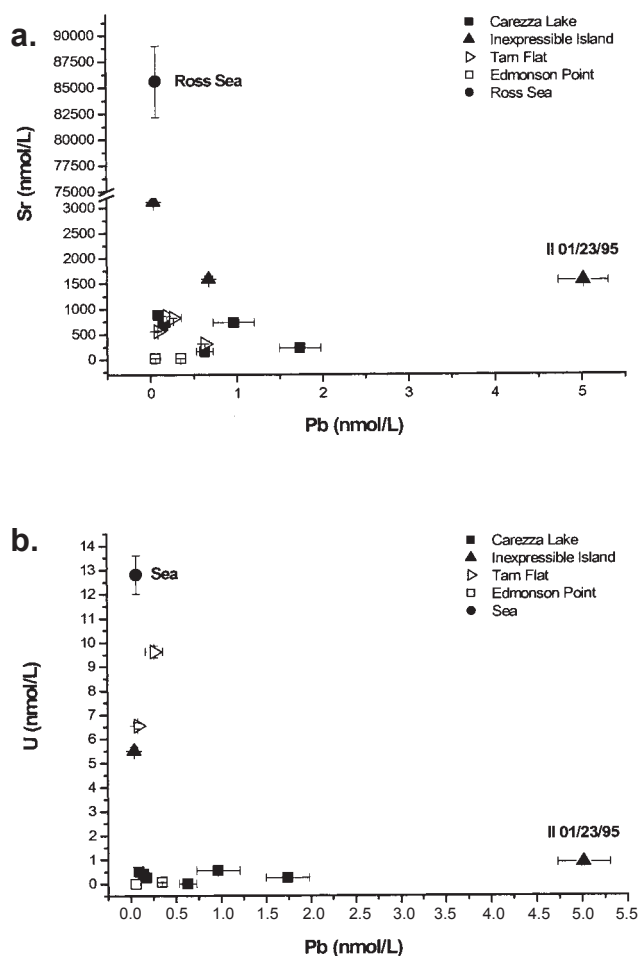


Fig. 5. Lead concentrations as a function of a. strontium, and b. uranium for all lakes.

fact that their geochemical mobility is strongly influenced by the pH–Eh conditions of the waters and their availability in the water–soil system is largely governed by the supply of H^+ ions and electrons, which reduce the higher oxidation states to a more labile divalent form (Fe(II) and Mn(II)) (Smith 1990, Aldrich *et al.* 2001). The concentrations of these two elements in the filtered samples can correspond to both the dissolved and colloidal ($< 0.45 \mu m$) fractions (Sigg *et al.* 1991).

Molybdenum content is highly variable because Mo is one of the trace elements with the highest geochemical mobility. Mo concentrations in about 60% of the samples range between 1.00 – $10.00 \text{ nmol l}^{-1}$, and exceed $5 \mu g \text{ l}^{-1}$ in some samples, notably Inexpressible Island, mainly due to sea-spray input that heavily influences the metal distribution in this lake. The sample collected in Tarn Flat Lake during the 1994–95 expedition is also characterized by a high Mo content (Fig. 4). Mo^{4+} ions can substitute Al^{3+} and other elements in micas and feldspars, and are often associated to fluorite (Jones *et al.* 1990). It is possible that TF 01/28/95 was collected at shallow level near the shore of

the lake at a time when the interactions between sediments and the water column were particularly strong.

About 70% of the samples have Ni concentrations lower than 6.00 nmol l^{-1} . These data are in good agreement with the lower value indicated for freshwaters, the concentration range of the Larsemann Hills, ocean waters, and the Ross Sea. As for Mo, TF 01/28/95 shows a very high Ni content and is characterized also by a high concentration of Cd, Co, Fe, Mn, Mo, Pb and Si: contamination cannot be ruled out for this sample.

More than 65% of the samples show Zn concentrations varying from 3.00 to $16.00 \text{ nmol l}^{-1}$. These values are in good agreement with the concentrations reported for freshwaters, and generally lower than the minimum value of the range of the lakes in Larsemann Hills. This indicates the absence of evident ongoing contamination processes and the moderate geochemical mobility of zinc. The high Zn concentration found in CA 12/31/98 sample is likely to be attributed to contamination. The sample was collected at the end of December, when the lake surface is not completely free from ice, so that it was probably necessary to perforate the surface layer of ice; this operation can lead to sample contamination (e.g. Gagnani & Torcini 1991).

For lead, about 50% of the samples show concentrations lower than 0.24 nmol l^{-1} , which fall in the range of the ocean waters and are much lower than the value in freshwaters. Some of the lakes of Terra Nova Bay are characterized by higher Pb concentration than those of the Larsemann Hills. This difference may be due to differences in basement lithologies and the lack of silt- and clay-size sediments, acting as a sink for Pb and other trace metals, in the lakes of Terra Nova Bay. Sample II 01/23/95 is characterized by a very high Pb content. This is unlikely to be due to contamination, as this sample also contains high Al and rare-earth elements (REE) levels. These elements are generally enriched in groundwater and cannot be derived from sources other than the basement lithologies. Thus, high levels of Al and REE may result from groundwater influx.

Figure 5a & b shows Pb concentration as a function of Sr and U concentrations, respectively. Lead can be considered an indicator of anthropogenic contamination because its concentration in sea water is low and it is an ubiquitous pollutant. In addition, lead is relatively abundant in fuels used by all the research stations. Unlike Pb, U and Sr are not usually introduced into the environment as a result of human activities and, therefore, the most probable sources of these elements in lacustrine waters are sea-spray and/or weathering of silicate rocks or dissolution of calcium carbonate, i.e. only natural processes. As a consequence, high Pb/U or Pb/Sr values indicate anthropogenic contamination. Lakes 14 and 15a at Edmonson Point are characterized by low concentrations of Pb, U and Sr (Fig. 5a & b). In contrast, Tarn Flat shows high concentrations of uranium but low lead and strontium contents. The low Sr

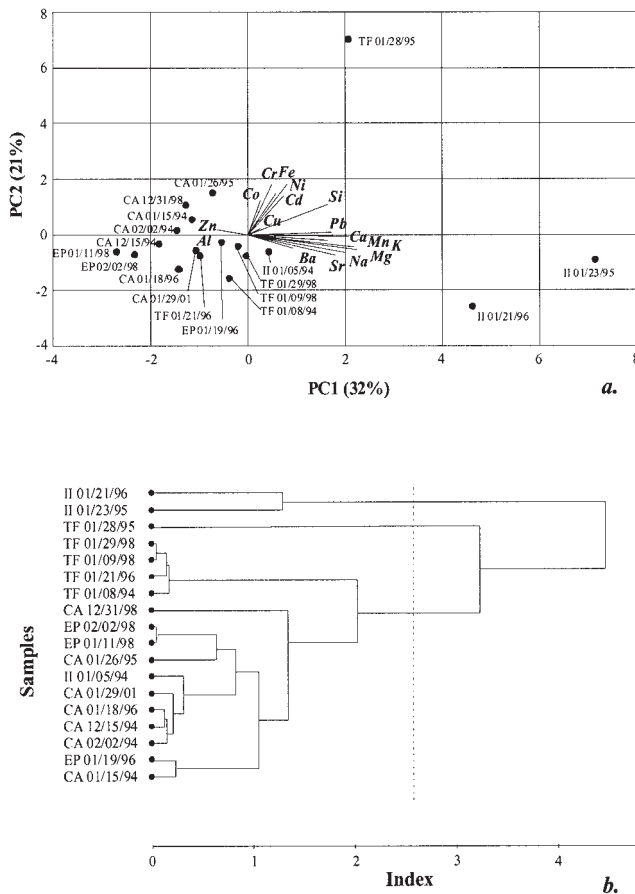


Fig. 6. Major, minor and trace metal concentrations: **a.** combined plot of scores and loadings on PC1–PC2, and **b.** dendrogram obtained by HCA.

levels show that sea-spray is not the main source of metal input, and therefore U can derive not only from sea-spray input but also from water-sediment and water–bedrock interactions. Sample II 01/23/95 is characterized by a high Pb concentration, as discussed above, whereas the other samples of Inexpressible Island are characterized by high U and Sr contents, in line with a strong sea-spray influence. Finally samples from Carezza Lake also show relatively high Pb concentrations. This might be due both to a higher input of trace metals from shallow-level groundwater and surface water, whose composition is dominated by rock weathering processes, and to the lack of silt- and clay-size sediments in the lake.

These results demonstrate that the minor and trace metal composition of the Terra Nova Bay lakes is mainly controlled by natural water-sediment and water–bedrock interaction and by shallow-level groundwater and surface water input and is virtually unaffected by anthropogenic contamination.

Where comparisons are possible (as in the case of Y, La, Ce, Pr and Nd) between our REE values and those obtained recently by De Carlo & Green (2002) for Lake Vanda in the

McMurdo Dry Valleys, the lakes in our study have significantly higher REE concentrations. For example, the ratio of Carezza waters to shallow Lake Vanda waters (25m) is as follows: Y = 2.0; La = 6.8; Ce = 24.5; Pr = 10 and Nd = 10. We attribute these values to differences in lithology and to possible groundwater influences.

Principal components analysis and hierarchical cluster analysis

A chemometric study on the analytical data was carried out to obtain a visual representation of the metal distribution in the Antarctic lake waters and to find out similarities and correlations among variables which would be more difficult to identify only by the number in the tables.

The Principal Components Analysis (PCA) is an unsupervised multivariate technique in which new variables are calculated as linear combinations of the old ones (metal concentrations in this case); the new variables, called principal components (PC), have two main features:

- they are totally uncorrelated between themselves,
- the first PCs keep the main part of the variance of the original dataset.

In this way, it is possible to show a greater part of information by plotting the first two or three PCs. Though visualized data represent a fraction of the total variance, combined plot of scores (coordinates of the objects on the new variables) and loadings (weights of original variables on the linear combination PCs are built from) allows the similarities of the samples and the existing correlations among the original variables and between samples and variables to be shown.

The Hierarchical Cluster Analysis (HCA) is an unsupervised method in which the samples are considered as objects in an n -dimensional hyperspace (with n = number of variables), described by n -components vectors. Different techniques can be used to evaluate similarities among samples: in this case the agglomerative hierarchical clustering procedure was used. The whole procedure can be represented in a dendrogram, in which correlations among samples can readily be seen. This technique is complementary to PCA; the total information is shown in the dendrogram.

Figure 6a shows the combined plot obtained by PCA for the following metals: Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Sr and Zn that have a greater environmental significance and were analysed in most water samples collected in Antarctic lakes. In general, even if no neat grouping is present, most samples from the same lake are in the same area of the plot and, therefore, it is possible to identify the following groups:

- all samples from Carezza Lake,
- samples taken in Tarn Flat Lake with the exception of

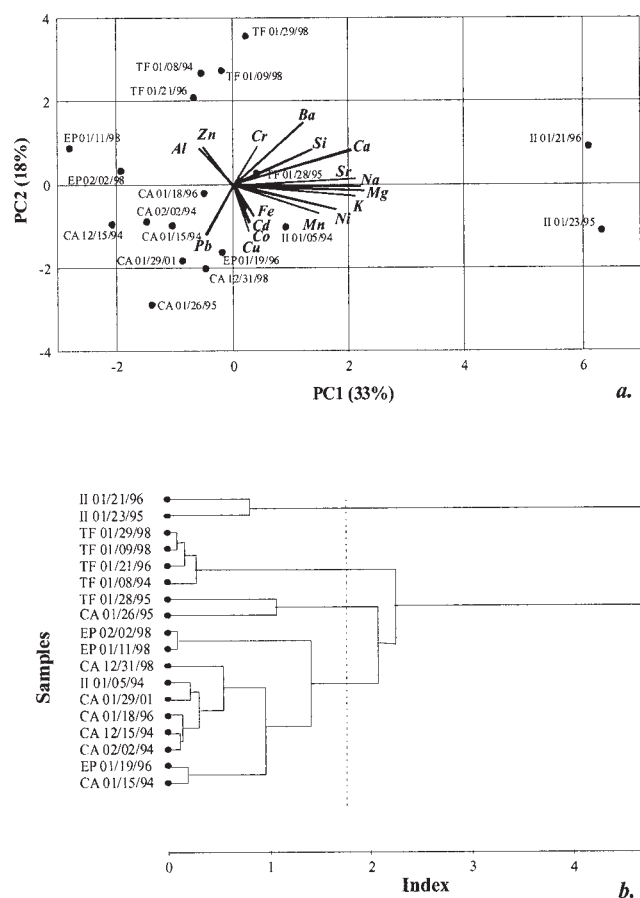


Fig. 7. Major, minor and trace metal concentrations of only uncontaminated samples: **a.** combined plot of scores and loadings on PC1–PC2, and **b.** dendrogram obtained by HCA.

TF 01/28/95 due to its higher content of nickel and chromium,

iii) EP 01/11/98 and EP 12/15/94,

iv) Inexpressible Island with the exception of II 01/05/94 that was collected at the beginning of January, when the lake surface was not completely free from ice and the homogenization of the water column had not taken place.

Sample EP 01/19/96 was taken from Lake 14 at Edmonson Point. Compared with Lake 15a, Lake 14 is subjected to stronger sea-spray input, and this accounts for its position in Fig. 6a.

The dendrogram reported in Fig. 6b confirms the differences and similarities visible in PCA plot, and in particular allows us to distinguish the TF 01/28/95 and CA 12/31/98 samples from the others.

Relative to variables in the PCA plot, a clear correlation between alkaline and alkaline-earth metals is evident, suggesting a common origin due to the input of sea salts. This is confirmed by the presence of a similar correlation in the waters from the Ross Sea (Abollino *et al.* 2001). Pb and

Mn are correlated with Ba, Ca, K, Mg, Na and Sr for different reasons. The behaviour of manganese is determined by its geochemical mobility, and is heavily influenced by the pH–Eh conditions of the waters, while the position of lead in the plot is due to its high concentration in sample II 01/23/95. The correlation between most heavy metals and, more exactly, between Cd, Co, Cr, Fe and Ni is the result of the combination of effects related both to their origin (principally rock and sediment leaching) and their chemical properties. Finally, the strong correlation between Al and Zn cannot be clearly explained in terms of chemical properties, origin, or biological function.

With the exception of samples collected in Inexpressible Island and TF 01/28/95, most samples are not strongly influenced by the variables identified by the vectors in Fig. 6a. This may be due to contamination in CA 12/31/98, II 01/23/95 and TF 01/28/95. For this reason we repeated Principal Component Analysis and Hierarchical Cluster Analysis (Fig. 7a & b) inserting, for these samples, a random value between the minimum and the maximum concentration found in the water samples collected in the same lake.

Figure 7a shows that the groups identified in Fig. 6a are clearly defined. EP 01/19/96 and II 01/05/94 still plot in separate fields for the reasons discussed. With respect to the other samples collected in Tarn Flat lake, TF 01/28/95 is closely aligned with the direction of the Fe, Cd, Co and Cu vectors, due to the higher concentration of these elements in this sample. The positions of the Carezza Lake and Tarn Flat samples reflect their basement lithologies and catchment characteristics. Sediments of Tarn Flat differ from those of the others lakes in Terra Nova Bay because they contain calcite and fluorite and have a substantially different silicate composition (Bertelle *et al.* 1998). This results in high Ca, Ba, Si, Al and Cr content. Carezza Lake is characterized by a high Pb content, but Co, Cu, Cd and Fe values are also higher than in the other samples. We suggest that these elements derive from groundwater input, and remain in solution in the water column because the lake sediments are relatively coarse-grained and therefore unable to adsorb these metals effectively. Lastly, the correlation between Sr, Na, Mg and K, and Ni confirms that the geochemical behaviour of Ni is similar to that of Na, Mg and Ca. The correlation among Mn and K, Mg, Na and Sr cannot be clearly explained in terms of chemical properties, origin or biological function.

The groups identified in the PCA plot are clearly visible also from the dendrogram in Fig. 7b. The only difference consists in the similarity between TF 01/28/95 and CA 01/26/95, due to the relatively high Pb and Cd content of these samples.

Conclusions

The elemental composition of lake waters in Terra Nova

Bay is mainly dominated by sea-spray input and to some extent by shallow-level groundwater and surface water input and, hence, by rock- and sediment-water interaction processes. No evidence was found for contamination from human activities in the research stations or from global air circulation.

The extent of the sea-spray influx is essentially a function of geographic factors, such as distance from the shore and exposure to winds carrying the sea spray. Other factors are the weather conditions (for example the possible stratification of the water column in the cold periods) and the lake dimensions. The major metal content in the lake waters is principally regulated by sea-spray input while the concentrations of trace elements seem to be more conditioned by rock and sediment weathering (groundwater and surface water input). The effects of rock and sediment weathering are difficult to evaluate because the hydrogeology of individual lakes is poorly known and the sediment and groundwater composition and the input of streams derived from snow melting or glacial runoff vary from lake to lake.

The differences observed among the water samples collected during the Italian expeditions are well within the natural variability observed in other Antarctic lakes and generally in freshwaters. This study demonstrates that a single sampling campaign is not sufficient to characterize elemental chemistry of Antarctic lakes, as element concentrations vary seasonally and from one year to the other. The degree of natural variability, both temporal and spatial, is substantial - up to several orders of magnitude for most metals - and appears to be larger than any changes due to anthropogenic input. The rate of change in element concentration can be extremely rapid, and reflects extreme weather conditions and the small size of the lakes.

The chemometric study enabled us to show similarities and differences among the Antarctic lakes examined and correlations and anticorrelations among variables that were not clearly visible from an examination of the analytical data in the tables. For instance, samples from the same lake showed a similar chemical composition and alkali and alkaline-earth metals were found to be correlated, suggesting a common origin due to the input of sea salts.

Acknowledgements

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References

- ABOLLINO, O., ACETO, M., SACCHERO, G., SARZANINI, C. & MENTASTI, E. 1996. Distribution of minor and trace metals in lake and sea environments (Antarctica). *Annali di Chimica*, **86**, 229–243.
- ABOLLINO, O., ACETO, M., LA GIOIA, C., SARZANINI, C. & MENTASTI, E. 2001. Spatial and seasonal variations of major, minor and trace elements in Antarctic seawater. Chemometric investigation of variable and site correlations. *Advances in Environment Research*, **6**, 29–43.
- ACETO, M., SARZANINI, C., ABOLLINO, O., SACCHERO, G. & MENTASTI, E. 1994. Distribution of minor and trace metals in Carezza Lake (Antarctica) ecosystem. *International Journal of Environmental Analytical Chemistry*, **55**, 165–177.
- ALDRICH, A.P., VAN DEN BERG, C.M.G., THIES, H. & NICKUS, U. 2001. The redox speciation of iron in two lakes. *Marine and Freshwater Research*, **52**, 885–890.
- BERNER, E.K. & BERNER R.A. 1987. *Global water cycle: geochemistry and environment*. Englewood Cliffs, NJ: Prentice-Hall, 397 pp.
- BERTELLE, M., LEOTTA, G., CALOGERO, S. & ODDONE, M. 1998. Characterization of sediments of the lake of Tarn Flat (Antarctica). *International Journal of Environmental Analytical Chemistry*, **71**, 227–244.
- CAPODAGLIO, G., TURETTA, C., TOSCANO, G., GAMBARO, A., SCARPONI, G. & CESCONE, P. 1998. Cadmium, lead and copper complexation in antarctic coastal seawater. Evolution during the austral summer. *International Journal of Environmental Analytical Chemistry*, **71**, 195–226.
- CAPRIOLI, R., FALCHI, G., GRAGNANI, R. & TORCINI, S. 1994. Variations of major and trace elements in some of the lakes at Terra Nova Bay (Antarctica), December 1990–February 1991. *International Journal of Environmental Analytical Chemistry*, **55**, 179–195.
- CLARIDGE, G.G.C. & CAMPBELL, I.B. 1977. The salts in Antarctic soils, their distribution and relationship to soil processes. *Soil Science*, **123**, 377–384.
- CREMISINI, C., GIANELLI, G., MUSSI, M. & TORCINI, S. 1991a. Geochemistry and isotope chemistry of surface waters and geothermal manifestations at Terra Nova Bay (Victoria Land, Antarctica). *Memorie della Società Geologica Italiana*, **46**, 463–475.
- CREMISINI, C., ORLANDI, C. & TORCINI, S. 1991b. Major, minor and trace elements in the surface waters at Terra Nova Bay (Antarctica). Data collected during the II, III and IV Italian expeditions (1986–1989). *Annali di Chimica*, **81**, 563–577.
- DE CARLO, E.H. & GREEN, W.J. 2002. Rare earth elements in the water column of Lake Vanda, McMurdo Dry Valleys, Antarctica. *Geochimica et Cosmochimica Acta*, **66**, 1323–1333.
- FITZWATER, S.E., JOHNSON, K.S., GORDON, R.M., COALE, K.H. & SMITH JR, W.O. 2000. Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. *Deep-Sea Research II*, **47**, 3159–3179.
- FÖRSTNER, U. & WITTMANN, G.T.W. 1983. *Metal pollution in the aquatic environment*. Berlin: Springer, 86–87.
- GASPARON, M. & BURGESS, J.S. 2000. Human impacts in Antarctica: trace-element geochemistry of freshwater lakes in the Larsemann Hills, East Antarctica. *Environmental Geology*, **39**, 963–976.
- GASPARON, M., LANYON, R., BURGESS, J.S. & SIGURDSSON, I.A. 2001. The freshwater lakes of the Larsemann Hills, East Antarctica: chemical characteristics of the water column. *ANARE Research Report*, **147**, 28 pp.
- GRAGNANI, R. & TORCINI, S. 1991. Geochemistry of trace elements in the surface waters of Terra Nova Bay (Antarctica). *Memorie della Società Geologica Italiana*, **46**, 477–493.
- GRAGNANI, R. & TORCINI, S. 1992. Major, minor and trace element distributions in surface water in Terra Nova Bay, Antarctica. *The Science of the Total Environment*, **125**, 289–303.
- GREEN, W.J., ANGLE, M.P. & CHAVE, K.E. 1988. The geochemistry of Antarctic streams and their role in the evolution of four lakes of the McMurdo Dry Valleys. *Geochimica et Cosmochimica Acta*, **52**, 1265–1274.

- GREEN, W.J., FERDELMAN, T.G. & CANFIELD, D.E. 1989. Metal dynamics in Lake Vanda (Wright Valley, Antarctica). *Chemical Geology*, **76**, 85–94.
- JONES, K.C., LEPP, N.W. & OBBARD, J.P. 1990. Other metals and metalloids. In ALLOWAY, B.J., ed. *Heavy metals in soils*. Glasgow: Blackie & Son Ltd, 291–298.
- LIBERA, V. 1997. Physical observations and monitoring on small lakes connected with Tarn Flat Glacier. *Terra Antartica Reports*, **1**, 47–49.
- LIBES, S.M. 1992. *An introduction to marine biogeochemistry*. New York: John Wiley & Sons Inc, 36, 68–73, 683.
- MANNIO, J., JÄRVINEN, O., TUOMINEN, R. & VERTA, M. 1995. Survey of trace element in lake waters of Finnish Lapland using the ICP-MS technique. *The Science of the Total Environment*, **160/161**, 433–439.
- MENTASTI, E., ABOLLINO, O., ACETO, M. & SARZANINI, C. 1998. Distribution and statistical correlations of major, minor and trace metals in lake environments of Antarctica. *International Journal of Environmental Analytical Chemistry*, **71**, 245–255.
- MERIAN, E. 1991. *Metals and their compounds in the environment*. Weinheim, Germany: VCH Verlagsgesellschaft, 418–448, 893–908, 945–958.
- MEYBECK, M. 1981. Pathways of major elements from land to ocean through rivers. In MARTIN, J.M., BURTON, J.D. & EISMA, D., eds. *River inputs to ocean systems*. New York: UNEP, IOC, SCOR, 18–30.
- OROMBELLI, G. 1986. La prima spedizione del Programma Nazionale di Ricerche in Antartide—Osservazioni geomorfologiche. *Rivista Geografica Italiana*, **93**, 129–169.
- REID, M.R., KIM, J.P. & HUNTER, K.A. 1999. Trace metal and major ion composition of Lakes Hayes and Manapouri. *Journal of the Royal Society of New Zealand*, **29**, 245–255.
- SCARPONI, G., CAPODAGLIO, G., TURETTA, C., BARBANTE, C., CECCHINI, M., TOSCANO, G. & CESCONE, P. 1997. Evolution of cadmium and lead contents in Antarctic coastal seawater during the austral summer. *International Journal of Environmental Analytical Chemistry*, **66**, 23–49.
- SCHMIDT, S., MOSKAL, W., DEMORA, S.J., HOWARD-WILLIAMS, C. & VINCENT, W.F. 1991. Limnological properties of Antarctic ponds during winter freezing. *Antarctic Science*, **3**, 379–388.
- SIGG, L., JOHNSON, C.A. & KUHN, A. 1991. Redox conditions and alkalinity generation in a seasonally anoxic lake (Lake Greifen). *Marine Chemistry*, **36**, 9–26.
- SMITH, K.A. 1990. Manganese and cobalt. In ALLOWAY, B.J., ed. *Heavy metals in soils*. Glasgow: Blackie & Son Ltd, 197–221.
- STUMM, W. & MORGAN, J.J. 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*. New York: John Wiley & Sons Inc, 614–671.