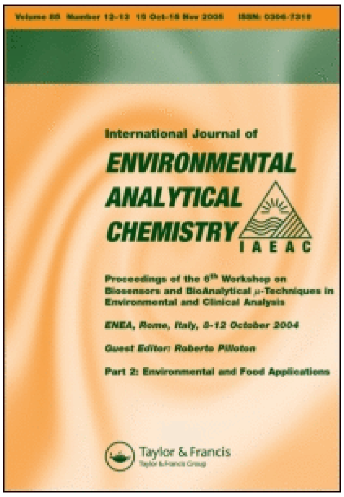

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Distribution and Statistical Correlations of Major, Minor and Trace Metals in Lake Environments of Antarctica

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DISTRIBUTION AND STATISTICAL CORRELATIONS OF MAJOR, MINOR AND TRACE METALS IN LAKE ENVIRONMENTS OF ANTARCTICA

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This paper reports the distribution of minor and trace metals determined in water, algae, soil and sediment collected in different lakes in Antarctica, during the Italian Expedition in the austral summer 1993/94. The determination of the total concentration of the following metals was performed: Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Zn. These have been determined in Carezza Lake (two temporally separate samplings) in Tarn Flat Lake and in Inexpressible Island Lake.

The analytical results have been discussed with reference to their different meaning for matrices such as soil and sediment. Bivariate plots obtained with the factorial analysis for principal components have been obtained and discussed for lake water samples collected in the 1993/94 campaign and the previous ones (1989–1993). In addition a *t*-test correlation method showed that soil samples collected around the lakes and sediments sampled at the bottom of the lakes have equal composition with a coefficient correlation of 0.988 (95% confidence level).

Keywords: Antarctica lakes; lake water; metal ions; sediments; algae; metal speciation

INTRODUCTION

The activity of the present operative unit in Antarctica has been directed also for the 1993/94 campaign to the analysis of metal ions in a group of samples covering lake water, soil collected from the surroundings of the lakes, lake sediments and algae collected in the same lacustrine systems. [1,2,3]

Major, minor and trace metal species have been taken into consideration in such matrices. Determinations have been performed, as for the previous cam-

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paigns, for alkali, alkali earth metals and other elements, in particular Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Zn.

Four different series of lacustrine samples have been analyzed, namely two series of samplings, for water, algae, sediment and soil, from Carezza lake, and one series of samplings from Tarn Flat lake, and Inexpressible Island lake. The relevant sampling data are the following : Carezza Lake no. 3, lat. 74° 43' S, long. 164° 01' E (two samplings completed on January 15, 1994, and February 2, 1994); Tarn Flat Lake no. 20, lat. 74° 59' S, long. 162° 33' E (one sampling completed in January 8, 1994); Inexpressible Island Lake no. 10b, lat. 74° 53' S, long. 163°, 43' E (one sampling completed in January 5, 1994).

The data obtained for the 1993/94 campaign fit well in the whole, within a certain degree of variation, with the corresponding (1989–93) expecially for the solid samples (sediments, soils and algae); a higher variation is shown for metal content in lake water.

In agreement with the previous findings,[1,2,3] again it has been found that the data have a temporal variability rather high and that it appears difficult to make comparisons between different campaigns or to point out historical trends from which to extract general considerations.

Probably the variability within the various substrates is higher than the one which can be reasonably observed from year to year as a consequence of atmospheric phenomena or of anthropogenic contaminations.

It should be necessary to analyze a higher number of subsamples relative to each substrate for being able to extract a more accurate characterization.

EXPERIMENTAL

All the samples were frozen at −24 °C immediately after sampling.

Water samples were filtered through 0.45 μm cellulose disks and kept in properly cleaned[2,3] polyethylene containers. All of the samples were maintained at −24 °C during all stages of storage and transportation to our laboratory at the University of Torino.

All sample manipulations and treatments were performed under a Class-100 laminar flow bench-hood, and all reagents utilized were purified with a quartz sub-boiling apparatus,[4] in order to minimize all metal contaminations, expecially for water samples in which the concentration of several trace components are below ppb level. Other non-volatile chemicals were purified according to described procedures.[5]

High purity water produced with a Millipore Milli-Q system was used throughout.

For metal determinations, the following instrumental techniques were utilized:

- A Perkin-Elmer 5100 Atomic Absorption spectrometer with graphite furnace electrothermal atomization GF-ETA-AAS, and Zeeman effect background correction;
- A Varian Liberty 100 Inductively Coupled Plasma Atomic Emission Spectrometer ICP-AES;
- A microwave oven (WI 40, White Westinghouse, full power 1.35 kW) was used throughout for the attack of the samples.

In all cases the determination of each metal was been performed using the standard addition method.

All analyses were performed in triplicate for three independent samples. So that three sets of triplicate data were available. Since the standard deviations within the average for each independent sample were equal or better to those for the replicates, the nine analytical results obtained for each sample were considered as a whole.

PROCEDURES AND RESULTS

Sample treatment

Lake Algae

Algae samples have been treated according to the procedure optimized in the previous years:[2,3] it included lyophilization of the wet mass and acid digestion of the dried sample in a microwave oven, with nitric acid or with a mixture of nitric acid/hydrofluoric acid, in the case they inglobated inorganic silicate micro-fragments.

The concentration of a series of elements determined with inductively coupled atomic emission spectroscopy (ICP-AES) and with electrothermal atomic absorption specroscopy with graphite furnace (GF-AAS) are collected in the following Table I.

In the same table the enrichment factors of the various elements in algae, compared to the concentrations of the same elements in lake water (see below) are reported. As one may notice, these enrichment factors are rather high and confirm that these organisms act as strong concentrators for metal ions[6,7,8] from the surrounding environment; this occurs also in the lacustrine systems that we have studied, *i.e.* under conditions in which metal ions concentrations lie well below their toxicity threshold for every living species.

TABLE I Determination of a series of metals in algae collected from different lakes. *a*, ICP-AES; *b*, GF-AAS

	mg/kg on lyophilized solid ± *s.d.*			*Enrichment factor* (C_{algae}/C_{water})		
	Carezza Lake	*Tarn Flat*	*Inexpr. Island*	*CL II*[c]	*T. F.*	*In. Isl.*
Al[a]	25600 ± 400	50300 ± 400	58400 ± 200	*d*	*d*	*d*
Ba[a]	145 ± 1	210 ± 2	350 ± 19	5.2×10^5	6.6×10^4	2.7×10^5
Ca[a]	29100 ± 700	18300 ± 100	9470 ± 50	4.6×10^3	9.5×10^2	7.1×10^2
Cd[b]	0.110 ± 0.003	0.175 ± 0.011	0.435 ± 0.017	3.7×10^4	8.8×10^4	4.4×10^4
Co[b]	12.5 ± 0.1	13.2 ± 0.3	19.0 ± 0.3	1.5×10^5	1.3×0^6	3.8×10^5
Cr[b]	27.2 ± 0.1	38.0 ± 0.4	81.4 ± 0.5	8.2×10^5	5.4×10^5	2.1×10^6
Cu[b]	19.3 ± 0.4	41.1 ± 0.5	33.9 ± 0.3	1.6×10^4	5.7×10^4	2.9×10^4
Fe[a]	20400 ± 400	32800 ± 700	36200 ± 1000	6.5×10^5	2.4×10^8	1.4×10^6
K[a]	13100 ± 1300	19300 ± 400	29500 ± 1200	1.7×10^4	2.1×10^4	6.8×10^3
Mg[a]	9100 ± 100	8700 ± 100	11500 ± 100	3.6×10^3	1.1×10^3	4.5×10^2
Mn[a]	567 ± 10	579 ± 6	585 ± 7	5.7×10^5	4.5×10^5	2.7×10^5
Na[a]	6500 ± 200	5270 ± 230	15300 ± 500	4.8×10^2	2.6×10^2	1.4×10^2
Ni[b]	17.0 ± 0.3	15.8 ± 0.5	35.4 ± 0.3	9.3×10^4	8.8×10^5	7.5×10^4
Pb[b]	13.1 ± 0.4	19.8 ± 0.1	36.5 ± 0.4	4.5×10^5	4.6×10^5	2.7×10^5
Sr[a]	147 ± 3	101 ± 1	169 ± 10	2.3×10^3	1.3×10^3	1.2×10^3
Zn[a]	56.9 ± 1.8	99.6 ± 0.3	91.3 ± 10.0	7.5×10^4	1.4×10^5	1.6×10^5

[c] = Carezza Lake, 2nd sampling.
[d] = not determined in corresponding lake water sample

Algal sample taken from Inexpressible Island Lake surely contained inorganic fragments, as it may be noticed by the high Al, Fe, K and Na content and in agreement with the very different macroscopic appearance of the sample, compared with the other algal samples.

Lake Sediments

Lake sediment samples were treated under controlled conditions (laminar flow bench hoods, ultrapure reagents, teflon and polypropylene labware) in order to minimize contaminations.

Samples were unfrozen and dried overnight at 120 °C. After this treatment all sediment and soil samples appeared as a mixture of solid particles with sizes ranging between 2 cm and few tenth of mm.

In order to select more representative subsamples, they were sieved through a 2 mm path sieve (the sieve was prepared from polymethacrylate bars and 1 mm diam. nylon wire, previosly cleaned with HCl, HNO_3 or 0.1 M acetic acid when appropriate).

Sediment samples have been treated according to the previously developed procedure[2,3]: they were ground to powder in an agata mortar and then subjected to analysis: The attacks were conducted in teflon bombs, inside a microwave oven, using a mixture of 8.0 ml of conc. HF, 1.5 ml of conc. HCl and 0.5 ml of conc. HNO_3 for 500 mg of powdered sediment.[3]

In order to determine also elements at particularly low concentration, we completed two separate acid attacks on each sample, with final concentration of 1 g/l and 5 g/l. The results are reported in the following Table II.

TABLE II Determination of a series of metals in different lake sediments. Results are expressed as mg/kg (on dried solid) ± s.d. *a*, ICP-AES; *b*, GF-AAS

	Carezza Lake	*Tarn Flat*	*Inexpr. Island*
Al[a]	69300 ± 900	66400 ± 2200	65500 ± 800
Ba[a]	386 ± 19	311 ± 5	251 ± 20
Ca[a]	8020 ± 100	9910 ± 190	8300 ± 30
Cd[b]	0.051 ± 0.005	0.042 ± 0.003	0.063 ± 0.004
Co[a]	8.3 ± 0.4	8.3 ± 0.2	10.6 ± 0.1
Cr[a]	37.4 ± 2.2	19.9 ± 0.4	68.1 ± 1.5
Cu[a]	6.1 ± 0.3	10.9 ± 0.1	9.2 ± 0.1
Fe[a]	21300 ± 2.8	16800 ± 10	27000 ± 700
K[a]	46000 ± 800	33100 ± 600	33200 ± 600
Mg[a]	5120 ± 160	3350 ± 60	5040 ± 40
Mn[a]	371 ± 16	367 ± 37	655 ± 10
Na[a]	17300 ± 1000	18700 ± 280	20300 ± 400
Ni[a]	7.93 ± 0.06	8.8 ± 0.3	12.5 ± 0.1
Pb[b]	13.6 ± 1.4	44.1 ± 1.6	27.7 ± 3.6
Sr[a]	157 ± 3	200 ± 10	166 ± 2
Zn[a]	20.6 ± 1.7	32.5 ± 6.2	56.0 ± 0.7

Soil sampled around the lakes

Soil samples have been treated according to the same procedure developed for sediments. The results have been reported in Table III; the similarity of the data with the ones for the corresponding sediments is evident.

TABLE III Determination of metals in a series of soils collected around the investigated lakes. Results are expressed as mg/kg (on dried solid) ± s.d. a, ICP-AES; b, GF-AAS

	Carezza Lake	*Tarn Flat*	*Inexpr. Island*
Al[a]	62100 ± 1000	66200 ± 1700	69100 ± 700
Ba[a]	219 ± 1	333 ± 33	168 ± 25
Ca[a]	9310 ± 400	9470 ± 630	7070 ± 100
Cd[b]	0.136 ± 0.010	0.050 ± 0.004	0.207 ± 0.014
Co[a]	10.8 ± 0.2	8.6 ± 0.4	7.0 ± 0.1
Cr[a]	48.3 ± 1.8	18.0 ± 0.2	44.6 ± 1.5
Cu[a]	10.6 ± 0.2	10.6 ± 0.2	10.2 ± 0.1
Fe[a]	26800 ± 400	16200 ± 300	37400 ± 400
K[a]	38100 ± 1700	37400 ± 2200	41100 ± 1000
Mg[a]	5370 ± 40	3500 ± 40	3570 ± 260
Mn[a]	571 ± 10	349 ± 10	1040 ± 15
Na[a]	15800 ± 300	20100 ± 600	29800 ± 800
Ni[a]	11.9 ± 0.1	8.54 ± 0.34	9.27 ± 0.28
Pb[b]	7.54 ± 0.40	35.2 ± 4.4	23.6 ± 0.6
Sr[a]	141 ± 3.0	213 ± 10	105 ± 7
Zn[a]	45.3 ± 0.5	30.2 ± 3.0	117 ± 5

The data relative to sediments and soils collected during the expeditions 1989–90. 1990–91 and 1993–94 have been grouped in Table IV for pointing out that such similarity holds over the three campaigns investigated. A comparison among data, to which the correlation method by a *t*-test has been applied,[9] has shown that the two substrates appear as equal with a correlation coefficient of 0.988 (95% confidence level).

Lake water

Lake water samples have been analyzed without any pretreatment in order to avoid contamination. All samples have been filtered immediately after sampling through 0.45 μm cellulose filters. The results for the determined metals are reported in the following Table V.

TABLE IV Concentration of metals (mg/kg) in sediments and soils sampled from Carezza Lake in different campaigns

	Sediment			*Soil*		
	1993–94	*1990–91*	*1989–90*	*1993–94*	*1990–91*	*1989–90*
Cd	0.051	0.024	0.371	0.136	0.02	0.38
Co	8.25	1.740	14.6	10.8	1.77	13.6
Cr	37.4	16.100	28.5	48.3	29.700	28.6
Cu	6.09	2.32	9.88	10.6	4.13	13.4
Fe	21300	22500	23300	26800	21700	22300
Mn	371	410	323	571	502	330
Ni	7.93	1.86	16.3	11.9	3.16	17
Zn	20.6	54.6	25.8	45.3	49	27.5

TABLE V Determination of major, minor and trace metals on filtered lake water by ICP-AES *(a)* and by GF-AAS *(b)*. All samplings refer to the campaign 1993–94. Concentrations are expressed in mg/L *(c)* or µg/L *(d)* on filtered samples ± s.d

	Carezza L. I^e	*Carezza L. II*^{f}	*Tarn Flat*	*Inexpr. Island*
Ca^{a,c}	7.02 ± 0.04	6.39 ± 0.10	19.2 ± 0.1	13.3 ± 0.1
K^{a,c}	0.608 ± 0.02	0.772 ± 0.020	0.937 ± 0.012	4.36 ± 0.02
Mg^{a,c}	1.72 ± 005	2.51 ± 0.02	7.86 ± 0.04	25.3 ± 0.1
Na^{a,c}	10.2 ± 0.1	13.5 ± 0.1	20.6 ± 0.1	106 ± 1
Ba^{a,d}	0.79 ± 0.08	0.28 ± 0.07	3.20 ± 0.01	1.30 ± 0.04
Sr^{a,d}	58.8 ± 0.2	64.7 ± 0.3	75.0 ± 0.5	139 ± 1
Si^{b,c}	2.28 ± 0.05	3.31 ± 0.02	7.24 ± 0.05	2.92 ± 0.03
Cd^{b,d}	0.009 ± 0.002	0.003 ± 0.001	0.002 ± 0.001	0.010 ± 0.002
Co^{b,d}	0,117 ± 0.016	0.083 ± 0.016	0.010 ± 0.004	0.050 ± 0.002
Cr^{b,d}	0.055 ± 0.005	0.033 ± 0.004	0.071 ± 0.007	0.038 ± 0.005
Cu^{b,d}	1.33 ± 0.07	1.21 ± 0.13	0.727 ± 0.100	1.15 ± 0.16
Fe^{b,d}	43.1 ± 0.5	31.2 ± 0.7	0.138 ± 0.005	26.3 ± 1.6
Mn^{b,d}	7.81 ± 0.08	0.988 ± 0.010	1.28 ± 0.03	2.19 ± 0.02
Ni^{b,d}	0.236 ± 0.020	0.182 ± 0.016	0.018 ± 0.009	0.47 ± 0.02
Pb^{b,d}	0.029 ± 0.007	0.036 ± 0.007	0.043 ± 0.007	0.136 ± 0.015
Zn^{b,d}	1.00 ± 0.02	0.763 ± 0.010	0.699 ± 0.030	0.570 ± 0.010

^{e} = Carezza Lake, 1st sampling; ^{f} = Carezza Lake, 2nd sampling.

From the comparison of the data for the different lakes it appears evident a much higher salinity for the sample collected from Inexpressible Island Lake (see Na, K and Mg) in comparison with Tarn Flat and Carezza Lakes. This finding appears as fully justified by the closeness of Inexpressible Island Lake to the Terra Nova Bay coast, therefore this lake receives salt incomes from the Antarctic Ocean in form of aerosol tranport.

Comparison within the data obtained in the period 1989–94

As prevously observed, it is extremely difficult to extract historical series or tendencies ascribed to a definite origin, among the data obtained from the samples collected during the campaigns completed in the period 1989–94. Again it comes out very clear that the considered matrices should be characterized as much as possible, performing a higher number of samplings, expecially for what regards solid samples, such as algae, sediments and solis.

The time period considered (five years) is perhaps too short in order to point out clearly significant variations induced by external origins. The presence, in the vicinity of the lakes of the Italian base of Terra Nova Bay, active from 1986, is a potential factor of alteration for the equilibrium of the lacustrine systems considered, although this consideration could be confirmed performing a comparison with reference data relative to the period precedent to the base construction (before 1985) and checking in continuous the trend of the analytical data for a longer period.

In addition to the effects of contamination on a shorter scale, the possibility of external contributions from long and very long distance must be considered, or the income of pollutants coming from other zones of the globe and transported by the atmosphere in different ways (see for example the presence of sulphur containing compounds produced during volcanic eructions which took place at distances of thousands of kilometers). Also in these cases it is necessary to monitor a longer period of time.

A simple consideration that one can advance is the fact that sediments and soil samples from the same lakes gave analytical concentration values almost always very close. The obvious conclusion is that these two substrates indeed originate from the same matrix, whose composition is not being altered by the interaction with the surrounding system (water-ice-living organisms). It should be mentioned that these lakes, and in particular Carezza Lake, exist really only few months in the year, therefore, for a very long period the income of compounds from the outside of their system, and the occurrence of sedimentation process, are hindered by the presence of ice. These data, in our opinion, point out that such lacustrine systems are virtually uncontaminated.

For effecting a complete comparison over the period 1989–1994 using the data in our hands, we decided to refer to the data relative to Carezza Lake, and in particular to the results concerning lake water samples since this group of data is available for 15 analytes and for four sampling campaigns (1989–90, 1990–91, 1991–92 and 1993–94).

It should be remarked, obviously, that all analyses have been effected using always the same procedures, either for the pretreatment of the samples or for the analytical techniques.

Carezza Lake – Period 1989–94

In the following Table VI the data referring to a series of metals in lake waters collected in the Antarctic campaigns 1989–90, 1990–91, 1991–92 and 1993–94 are reported. From the data of Table VI a bivariate plot obtained with the factorial analysis for principal components is reported.[10]

TABLE VI Concentration of metals in lake water sampled from Carezza Lake in different campaigns

	1993–94	*1991–92*	*1990–91*	*1989–90*
Ba (μg/L)	0.79	0.81	2.15	4.6
Ca (mg/L)	7.02	8.3	10.6	10.1
Cd (μg/L)	0.009	< 0.05	< 0.05	0.07
Co (μg/L)	0.117	< 0.5	< 0.5	< 0.5
Cr (μg/L)	0.055	0.12	0.25	0.21
Cu (μg/L)	1.33	0.76	0.840	1.26
Fe (μg/L)	43.1	16.2	16.8	48.8
Mg (mg/L)	1.72	2.3	3.4	4.44
Mn (μg/L)	7.81	16.9	6.500	4.2
Na (mg/L)	10.2	17.1	25.6	41.2
Ni (μg/L)	0.236	0.31	0.23	0.57
Pb (μg/L)	0.029	< 0.2	< 0.2	0.43
Si (mg/L)	2.28	2.3	2.400	2.2
Sr (μg/L)	58.8	50.3	75.3	74.2
Zn (μg/L)	1.00	0.16	0.76	1.3

In the plot, the loadings relative to the variables (in these cases the metals determined) have been plotted in such a way that the correlations among the various analytes for the investigated period are made more evident.

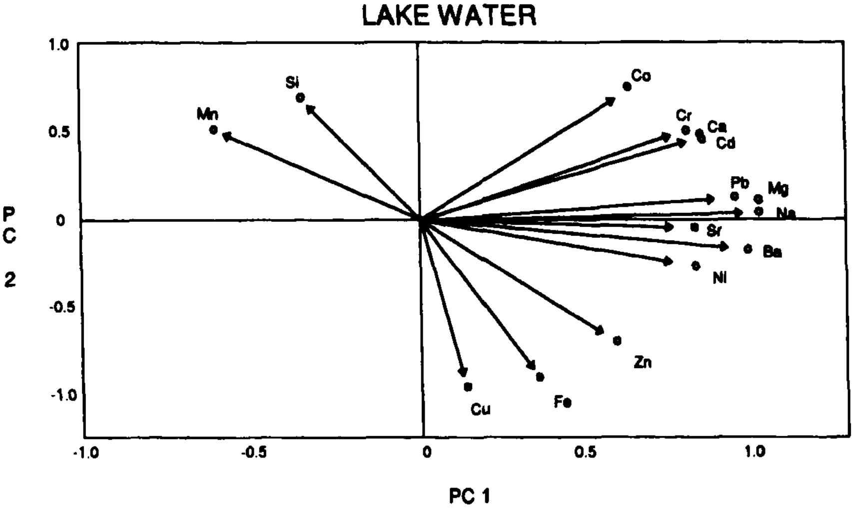

FIGURE 1 Bivariate plot obtained with factorial analysis for principal components on the data for metal content in Carezza Lake water sampled in the period 1989–1994 (see table VI)

The bivariate plot points out some correlations existing between various groups of elements (Fe -Cu, Ca-Cd-Cr, et c.).

On the contrary, an anticorrelation behaviour is shown by Mn and Si, whose concentrations do not parallel those of trace heavy metals. In particular, Fe and Cu seem to behave as the less correlated metal species with more structural elements such as Si and Mn.

The opposite dependence of alkali and alkali earth elements, on one side, and crustal structural elements such as Mn and Si, on the other, seems to point out that the origin of the first group of elements may be ascribed to a marine contribution through aerosol transportation by the winds.

As said before, it is difficult to state that variability from year to year in metal concentrations be due to well defined causes (atmospheric or anthropogenic influences), since the intrinsic variability of the substrates studied seems to have a higher weight.

In conclusion, the availability of a higher number of data could make it possible to characterize the systems considered with increased accuracy. Moreover it is possible that combinations of variables (*i.e.* concentration ratios) be more meaningful than single variables; this can be revealed by a chemometric approach, given the availability of a sufficiently high data set. It appears superfluous to underline that the mathematical applications utilized in this paper are just an example of what can be done; results obtained should be strengthened in the following years with additional data.

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