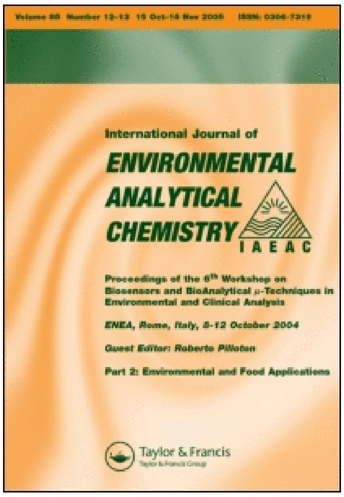

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Distribution of Minor and Trace Metals in Carezza Lake (ANTARCTICA) Ecosystem

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DISTRIBUTION OF MINOR AND TRACE METALS IN CAREZZA LAKE (ANTARCTICA) ECOSYSTEM

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This paper reports the distribution of a series of metals in natural samples collected at Carezza Lake in Antarctica, during the Italian Expedition in the austral summer 1989/90. The considered elements are: water, sediments and soil sampled from the surroundings of the lake and algae. The determination of the total concentration of the following metals was performed: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Zn. In addition, for sediment and soil samples, a speciation study was performed for some metals, namely Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn, using the Tessier procedure.

KEY WORDS: Antarctica lakes, lake water, sediments, algae, metal speciation.

INTRODUCTION

In the present investigation we have determined the distribution of a series of metals in natural samples collected at Carezza Lake in Antarctica, in the austral summer 1989/90.

This lake, located a few kilometers from Terra Nova Bay (lat. 74° 43′ S, long. 164° 01′ E), represents an ecosystem which is almost uncontaminated by anthropic influences[1,2]. Therefore, the distribution of minor and trace metals within the various components should result almost entirely from the interactions and equilibria among the elements themselves, such as, *e.g.*, water, sediments, soil and living organisms such as algae.

However, the presence of some logistic bases nearby Terra Nova Bay, and consequently the relative human activities, could render the above hypothesis erroneous[3].

In order to verify the environmental impact effects, a comparison of the results obtained from the analysis of samplings performed over the years will be very helpful.

The elements which have been considered are:

- Water samples from the lake (the lake is completely unfrozen in the austral summer, has an average surface of ca. 8000 m^2 and its maximum depth is around 1 m);

- — Lake bed sediments;
- — Soil samples from the area surrounding the lake;
- — Algae collected from the lake edge.

The determination for the total concentration of the following metals was performed on all samples: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Zn. In addition, for sediment and soil samples, a speciation study was performed for some metals, namely Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn, according to the Tessier procedure which involves a series of selective sequential extractions on the solid sample[4].

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[5] 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[6], in order to minimize all metal contaminations, especially 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[7]. 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;
- — An Allied Analytical Systems 300 inductively coupled plasma Atomic Emission Spectrometer ICP-AES;
- — A laboratory-modified LDC Milton Roy Elemental mercury detector based on cold vapour atomic absorption spectrophotometry CV AAS for the determination of Hg in lake water;
- — Some data was cross-checked using an Amel Voltammetric Analyzer mod. 433 equipped with a hanging mercury drop electrode.

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

Determination of metal concentrations in sediment and soil samples

Sample treatment All sample treatments were performed 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, previously cleaned with HCl, HNO_3 or 0.1 M acetic acid when appropriate).

In order to verify the suitability of the adopted sampling and sieving method, analyses were performed on two series of samples:

— Fine sediment (FS) and fine soil (FG), subsamples obtained by grinding the samples obtained from the nylon sieve to a powder in an agata mortar.

— Coarse sediment (CS) and coarse soil (CG) subsamples obtained directly from the nylon sieve.

It is logical to expect a large scattering in the data obtained from the coarse samples and a better precision in that obtained for the fine samples. These results were confirmed by the analytical results.

Sample dissolution For the determination of the total concentration of metals, an acid digestion in a microwave oven was chosen as the dissolution procedure.

With the optimized procedure, a sample aliquot was treated with a mixture of acids in a gas tight teflon bomb which is then inserted in the oven and subjected to a series of heating cycles. In this way, the metals present in the samples are extracted and brought into solution.

The choice of the acids used for digestion was based on the nature of the samples. In the present cases, we adopted a ternary mixture of HCl, HNO_3 and HF, in order to ensure a sufficient oxidant attack together with the complete dissolution of silicates, present in large amounts in our samples.

The dissolution used procedure was the following: 500 mg of powdered subsample were introduced into the teflon bomb and made to react with 8.0 ml of conc. HF, 1.5 ml of conc. HCl and 0.5 ml of conc. HNO_3.

The sealed container was then subjected to the following heating program: 5 heatings for 3 minutes each at a 40 % power (full power 1.35 kW) followed by 5 heatings for 3 minutes at 50 % power. A 5 min. pause seemed convenient in order to allow the reactants to cool between cycles. At the end of the full treatment, the sample appeared completely dissolved. At this stage, 10 ml of a 10 % H_3BO_3 were added in order to obtain the formation of volatile tetrafluoborate which was easily removed together with volatile SiF_4. The resulting solution was then brought to mark in a 100 ml polyethylene flask with ultrapure water.

The solution was directly employed for the ICP-AES and GF-AAS analysis.

The procedure was applied, in parallel, to three equal portions of each sample, in order to check the precision of the method.

Results As can be noted from the analytical data reported in Table 1, the sediment sampled at the center of the lake bed and the soil taken from around the lake, show a composition very similar, even as regards minor and trace elements: these results appear very reasonable, since water is only present in the basin that forms Carezza Lake a few months during the year, and alteration of such samples by differential humification processes involving soil and sediments appears almost completely inactive[8].

It is therefore easy to affirm that the two different samples are almost identical, either from a compositional point of view or from a mineralogical point of view.

This identity in composition also proves the absence of interaction of these substrates with elements which do not belong to the natural system, or, in other words, it proves the absence of anthropogenic contaminations[1,2,8,9].

Speciation of metals using sequential extraction on lake sediment and soil samples

Sequential extraction procedure The speciation of a series of metals was performed on lake sediment samples (7 LS) and samples of soil surrounding the lake (7 TR), according to the scheme suggested by Tessier *et al.*[4].

The procedure involves the sequential extraction of five fractions obtained by shaking the solid sample with 5 solutions used to modify some chemical characteristics of the sample. Other slightly different procedures have also been used and described for the speciation of Antarctic sediment and soil samples[10,11,12,13]. The procedure for the sequential extractions is reported in Figure 1 and involves the following steps:

— 1. *Exchangeable fraction*: By placing the sample in contact with a high ionic strength solution, sorption-desorption superficial processes, involving ion-exchange interactions, may be altered. In this way the so-called exchangeable fraction of metal traces may be released. This is due to the competition for the adsorption sites on the surface of the sediment (or soil).

— 2. *Fraction bound to carbonates*: The fraction of metal traces bound to carbonates, present in a sample, may be labilized selectively by varying the pH of the sample itself with a slightly acidic extraction solution. This procedure simulates the possible metal release after pH lowering in natural waters.

— 3. *Fraction bound to iron and manganese oxides*. Fe and Mn oxides act as cohesive matter among the particles or as a covering layer; in their nodules a certain fraction of metal traces may be retained. This fraction may be labilized in anoxic conditions (for example with a reducing agent at high temperature).

— 4. *Fraction bound to organic matter and to sulfides*: It is well known that many compounds of natural origin (but also synthetic compounds) are able to complex metal traces. If organic matter residues are present in a sample, the fraction of metals bound in the form of complexes to these residues may be released by treating the sample itself with an oxidant treatment.

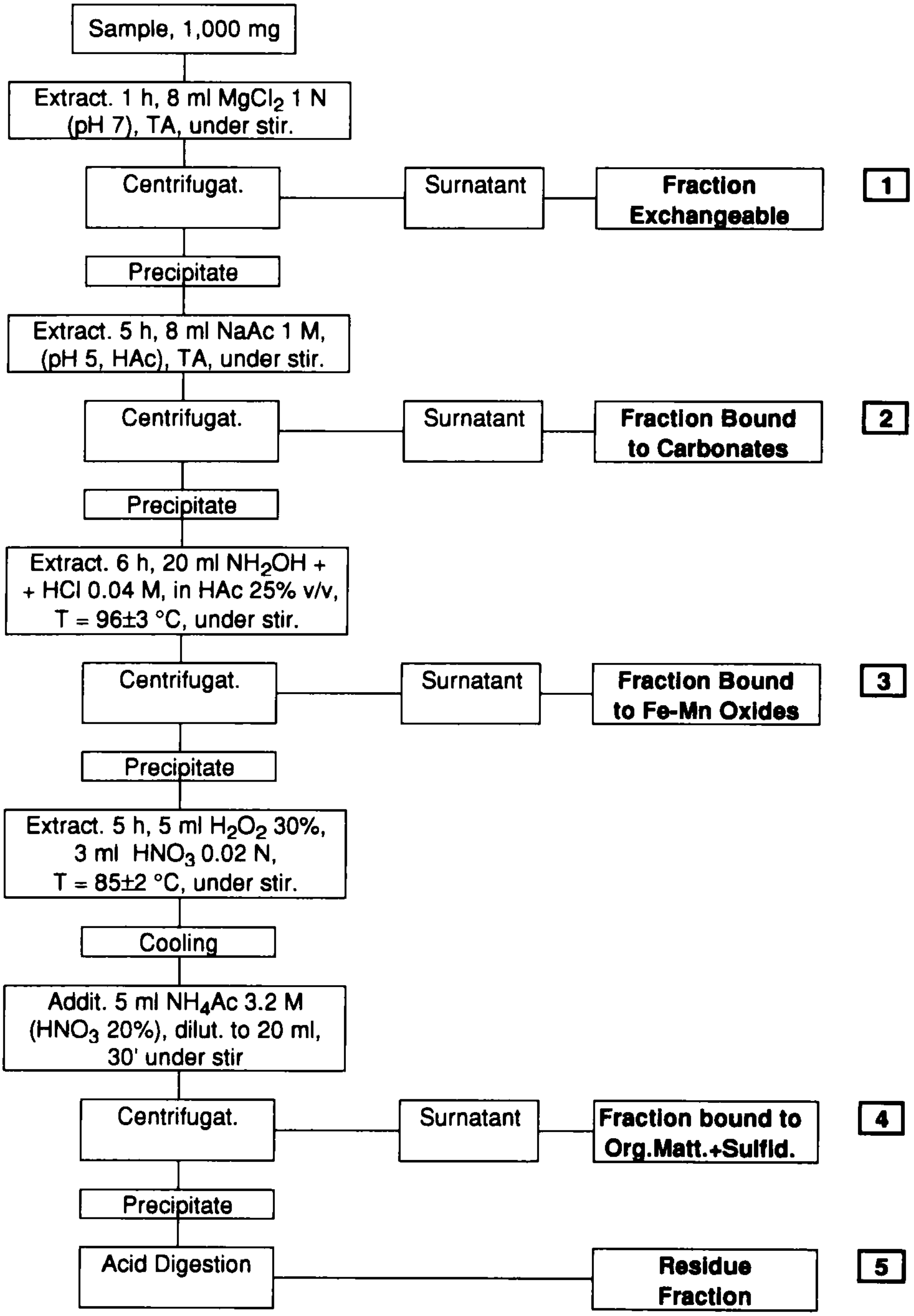

Figure 1 Diagram of the sequential extraction of sediments

Table 1 Lake sediment (Sample 7LS) and soil (Sample 7 TR)
1° value: mean concentration in samples (mg/Kg on solid) computed on 9 determinations
2° value: standard deviation.
3° value: relative standard deviation (%).

Determination using ICP-AES:

	Al	*Ca*	*Fe*	*Mg*	*Mn*	*Na*	*Cr*	*Zn*
FS	31300	657	23300	774	323	9880	28.5	25.8
	5810	82	641	120	5	2670	1.96	4.0
	18.6	12.5	2.8	15.5	1.5	27.0	6.9	13.1
CS	44100	621	13300	534	235	8080	13.4	8.02
	8380	268	5940	216	119	511	4.87	1.71
	19.0	43.2	44.5	40.4	50.6	6.3	36.1	21.3
FG	39800	1140	22300	614	330	9070	28.6	27.5
	1930	125	784	80	12	332	1.04	1.9
	4.8	11.0	3.5	13.0	3.6	3.7	3.6	6.9

Determination using GF-AAS:

	As	*Cd*	*Co*	*Cu*	*Ni*	*Pb*
FS	1.08	0.371	14.6	9.88	16.3	17.9
	0.070	0.016	0.417	0.190	1.22	1.98
	6.5	4.3	2.9	1.9	7.5	11.1
CS	0.681	0.176	9.71	5.93	8.69	36.8
	0.267	0.072	3.85	1.06	2.96	8.80
	39.2	40.9	39.6	17.8	34.1	23.9
FG	1.06	0.380	13.6	13.4	17.0	21.3
	0.058	0.015	1.59	0.227	0.06	2.55
	5.5	3.9	11.7	1.7	0.4	12.0

FS = fine sediment; CS = coarse sediment: FG = fine soil.

— 5. *Residue fraction*: The most consistent fraction of metal traces is present as scatter within the crystal lattice of the rocks and minerals which constitute the sediment or the soil. This fraction is extracted with an acid digestion treatment in a microwave oven. It appears evident that such a fraction would not be released to the environment in normal natural conditions.

It is worth mentioning that the distribution of metals among the various fractions is defined, from an operative point of view, by the extraction procedure, and does not necessarily reflect the relative affinity of the various geochemical phases of the sediment (or of the soil) for the investigated metal traces. Nevertheless, the sequential extraction procedure allows the simulation, to a certain extent, of some environmental conditions to which the sediment may be exposed, and in which a certain metal release may occur.

The overall procedure was applied to sediment sample 7 LS and to soil sample 7 TR. 1,000 mg of subsample, sieved and ground according to the previously described procedure, was shaken, in consecutive subsequent steps, with five extraction solutions. At the end of each extraction, the surnatant was separated by means of centrifugation, from the solid residue. The solid residue was in turn washed with few mls of water and subjected to the following extractions. The surnatant solutions, which, after each extraction, represent the fraction 1–5, was analyzed for the investigated metal traces with the described analytical procedures.

The residue, obtained after the fourth extraction, was digested with acids in a microwave oven, with the same procedure, described above, for the determination of the total concentration of metals.

The determination of the concentration of the following metals was performed on the five fractions obtained: Cd, Co, Cr, Cu, Ni (with GF-AAS) and Fe, Mn, Zn (with ICP-AES). The results of the determinations are reported in the Tables 1, 2, 3, 4 and 5.

Results The results reported in the Tables point out the following observations: the exchangeable fraction (F1) contains negligible concentrations of almost all of the metals

Table 2 Lake sediment (Sample 7 LS)
Metal determination with GF-AAS in fractions F1/F5 obtained from sequential extraction according to Tessier.
1° value: mean concentration in samples (μg/Kg on solid) computed on 9 determinations
2° value: standard deviation.
3° value: relative standard deviation (%).
Total: sum of the determined fractions (μg/Kg)
Tot.a.d.: total metal content determination after acid digestion with HCl-HNO_3-HF mixture in microwave oven (μg/Kg)

Cd	F1	F2	F3	F4	F5	Total	Tot.a.d.
Mean	n.d.[1]	n.d.[1]	26.0	7.08	69.6	102	371
Std. Dev.			3.86	2.00	6.13		
Rel.std.Dev.			14.8	28.2	8.8		
Co	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	190	1560	657	7540	9950	14600
Std.Dev.		29.5	206	78.4	918		
Re.std.Dev.		15.5	13.2	11.9	12.2		
Cr	**F1**	**F2**	**F3**	**F4**	**F5[2]**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	166	967	1670	25300	28100	28500
Std.Dev.		45.0	70.4	485	1500		
Rel.Std.Dev.		27.1	7.3	29.0	5.9		
Cu	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	675	2920	1480	5070	10200	9880
Std.Dev.		67.1	532	122	747		
Rel.std.Dev.		9.9	18.2	8.2	14.7		
Ni	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	779	3910	1250	9040	15000	16300
Std.Dev.		118	368	189	1010		
Rel.std.Dev.		15.1	9.4	15.1	11.1		

[1] below the detection limit

[2] determination performed using ICP-AES

considered; this proves, on one hand, that surface activity for the absorption of metals on sediments and soil is very low and, on the other, that anthropic alteration, if present, is very low. In addition, the comparison of the analytical results obtained for lake sediments and surrounding soil are not only very similar, but are also distributed among the fractions with very similar relative yields.

Determination of metals in lake water

Sample handling Even in this case, all possible procedures in order to reduce sample alteration were adopted. Each sample, filtered during sampling through 0.45 μm cellulose membranes, was unfrozen before analysis and acidified to pH 2.0 by the addition of ultrapure HCl. The results are reported in Table 6. As can be seen, the concentrations are very low and fit below the values generally reported for corresponding environmental samples interested by a low pollution index[2,8,9].

Table 3 Soil (Sample 7 TR)
Metal determination with GF-AAS in fractions F1/F5 obtained from sequential extraction according to Tessier.
1° value: mean concentration in samples (μg/Kg on solid) computed on 9 determinations
2° value: standard deviation.
3° value: relative standard deviation (%).
Total: sum of the determined fractions (μg/Kg)
Tot.a.d.: total metal content determination after acid digestion with HCl-HNO_3-HF mixture in microwave oven (μg/Kg)

Cd	F1	F2	F3	F4	F5	Total	Tot.a.d.
Mean	n.d.[1]	n.d.[1]	25.6	n.d.[1]	60.0	85.6	380
Std. Dev.			5.35		4.59		
Rel.std.Dev			20.9		7.7		
Co	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	945	1360	668	6270	9240	13600
Std.Dev.		72.4	236	62.1	705		
Rel.std.Dev.		7.7	17.4	9.3	11.2		
Cr	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	225	2570	1620.	18400	22800	28600
Std.Dev.		33.2	594	158	681		
Rel.std.Dev.		14.8	23.1	9.8	3.7		
Cu	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	2710	4200	2490	5450	14800	13400
Std.Dev.		603	226	177	652		
Rel.std.Dev.		22.3	5.4	7.1	12.0		
Ni	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	1220	4490	1020	11100	17900	17000
Std.Dev.		480	187	63.7	554		
Rel.std.Dev.		39.3	4.2	6.2	5.0		

[1] below the detection limit
[2] determination performed using ICP-AES

Table 4 Lake sediment (Sample 7 LS)
Determination of metals with ICP-AES (mg/Kg, unless otherwise specified)
Metal Determination in fractions F1/F5 obtained from sequential extraction according to Tessier
1° value: mean concentration in samples (mg/Kg on solid) computed on 9 determinations
2° value: standard deviation.
3° value: relative standard deviation (%).
Total: sum of the determined fractions (mg/Kg)
Tot.a.d.: total metal content determination after acid digestion with HCl-HNO$_3$-HF mixture in microwave oven (mg/Kg)

Fe	F1	F2	F3	F4	F5	Total	Tot.a.d.
Mean	n.d.[1]	71.2	2050	985	17000	20100	23300
Std. Dev.		3.75	24.0	39.0	770		
Re.std.Dev.		5.3	1.2	4.0	4.5		
Mn	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	1.08	2.35	25.7	13.1	267	310	323
Std. Dev.	0.18	0.18	0.59	0.51	7.26		
Rel.std.Dev.	16.7	7.7	2.3	3.9	2.7		
Zn (μg/Kg)	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	n.d.[1]	3750	3700	12100	19500	25800
Std. Dev.			646	310	5350		
Rel.std.Dev.			17.2	8.4	44.2		

[1] below the detection limit

Table 5 Soil collected around Carezza Lake (Sample 7 TR)
Determination of metals using ICP-AES (mg/Kg, unless otherwise specified)
Metal Determination in fractions F1/F5 obtained from sequential extraction according to Tessier.
1° value: mean concentration in samples (mg/Kg on solid) computed on 9 determinations
2° value: standard deviation.
3° value: relative standard deviation (%).
Total: sum of the determined fractions (mg/Kg)
Tot.a.d.: total metal content determination after acid digestion with HCl-HNO$_3$-HF mixture in microwave oven (mg/Kg)

Fe	F1	F2	F3	F4	F5	Total	Tot.a.d.
Mean	n.d.[1]	141	2410	1080	15000	18600	22300
Std.Dev.		5.38	67.6	30.0	202		
Rel.std.Dev.		3.8	2.8	2.8	1.3		
Mn	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	4.67	32.9	36.5	15.1	206	296	330
Std.Dev.	0.15	0.66	1.00	0.14	5.93		
Rel.std.Dev.	3.2	2.0	2.7	0.9	2.9		
Zn (μg/Kg)	**F1**	**F2**	**F3**	**F4**	**F5**	**Total**	**Tot.a.d.**
Mean	n.d.[1]	4530	8620	3360	31800	48300	27500
Std. Dev.		105	145	54.5	52.1		
Re.std.Dev.		2.3	1.7	1.6	1.6		

[1] below the detection limit

Table 6 Lake water (Sample 7 LW). Analytical data for minor and trace metals

Element	Conc.±std.dev.	Unit	Instrum. techn.
Ca	10.1 ± 1.2	mg/l	ICP-AES
Mg	4.44 ± 0.08		
Na	41.2 ± 0.6		
Si	2.20 ± 0.09		
Al	14 ± 3	µg/l	GF-AAS Zeeman
As	0.9 ± 0.1		
Ba	4.6 ± 2.3		
Cd	0.07 ± 0.03		
Co	≤ 0.5		
Cr	0.21 ± 0.05		
Cu	1.26 ± 0.50		
Fe	48.8 ± 4.4		
Mn	4.20 ± 0.83		
Ni	0.57 ± 0.09		
Pb	0.43 ± 0.05		
Sr	74.2 ± 3.2		
Zn	1.3 ± 0.6		
Hg	20 ± 3	ng/l	CV-AAS

Determination of metals in algae

Algae interaction with metallic species In the analysis of metal content in algae samples, the determination of heavy metals is very interesting for the verification of the occurrence of bioconcentration effects[9].

Such phenomena are widely described in literature: several vegetable and animal organisms (especially aquatic) are able to accumulate metals and other chemical species which are not part of their feeding chain[8,9,14,15].

These species may be concentrated in various organs and, in particular, in the biopolymers of lipidic and glycidic nature which form cellular walls.

As regards metal enrichment, the phenomenon is probably due to the presence, in the above biopolymers, of functional groups capable of coordinating metal ions (it must be pointed out that this occurs in both living and dead cells). Moreover, very often metal ions are bound in a chemical form different from the primitive one, since organisms, in which bioaccumulation occurs, are able to transform metals into species with reduced toxicity for their metabolic activity, or escrete them more easily.

A very common example is the biomethylation of mercury[15].

Sample dissolution procedure In order to optimize the significance of the subsamples and the reproducibility of the analytical results, the following procedure was adopted. The sample was composed of a solid and a liquid impregnated phase. They were isolated by means of a 200 mesh teflon net. Part of the solid algal sample was liophilized, and then ground to powder.

The sample dissolution procedure was analogous to the one adopted for the analysis of sediments and soil; also in this case an acid digestion was performed in a microwave oven. The addition of HF was not necessary here since the samples did not contain silicates. Since the matrix had a prevailing polysaccaride and lipid structure, the main problem involves the breaking of the glycosidic bonds that constitute the polymeric chains of cellulose and micropolysaccarides. Conc. HNO_3 was sufficient for this purpose.

The unfrozen sample was subjected directly to acid digestion.

The algal sample obtained after sieving was approx. 47 % w/w of the starting material. The two successive portions, the liophilized portion and the untreated one, were subjected to direct acid digestion.

For the acid digestion and the subsequent analysis steps, 100 mg of sample was made to react in a teflon bomb with 10 ml of 12 M HNO_3, the dissolution was performed by heating in a microwave oven for 30 min at 40 % power. After cooling, the clear solution was brought to 100 ml with ultrapure water and analyzed by ICP-AES or GF-AAS.

In order to compare the data obtained for the liophilized and unliophilized algae, concentrations were referred to the original solid weight, taking the liophilization yield into account.

Table 7 reports the analytical data thus obtained for each of the two samples.

Results As can be seen from the data reported in Table 7, the enrichment factor values (E.F., last rows in the Table) (ratio between the concentration of a metal in the algae and that in the lake water) are rather high, even if algae are inserted in a system characterized by a low content of heavy metals. This feature points out the extent of the phenomenon of bioaccumulation.

DISCUSSION

Sediments and soil

The data reported in Table 1 show that there is a very slight and insignificant difference between the analytical data of sediment and soil. This points out that anthropogenic effects, and/or natural alteration by humifying agents of these samples is not present or, at least, is very limited.

The data on coarse and fine samples also shows that the grinding procedure does not alter or significantly affect the composition, and that the treatment noticeably improves the precision of the measurements.

The speciation procedure (see Tables 2–5) points out that the exchangeable fraction (fraction 1 of Tessier scheme) is very limited; the fraction of metals behaving as bound to carbonates (2), to organic matter + sulfides (4), to Fe-Mn oxides (3) increases in that order.

The main fraction is the residual fraction (5), again pointing out a very reduced disgregation of the samples.

Table 7 Analysis of algae from Carezza Lake (sample 7 AG)
1° value: mean concentration in the samples (mg/Kg solid) computed on 9 determinations.
2° value: standard deviation.
3° value: relative standard deviation (%)
E.F., Enrichment Factor C_{algae}/C_{H2O}

Determination of metals using ICP-AES:

	Al	*Ca*	*Fe*	*Mg*	*Mn*	*Na*	*Cr*	*Zn*
	5580	67200	11100	11100	479	1040	13.2	27.2
Algae	413	2840	338	266	7.36	31.8	1.51	2.10
Liophil	7.4	4.2	3.0	2.402	1.5	3.1	11.38	7.7
	6224	66700	11300	10900	421	1011	12.9	25.4
Algae	2410	10200	2950	3010	64.9	109	3.14	7.85
Not Lioph.	38.7	15.3	26.1	27.6	15.4	10.8	24.3	30.9
E.F.	4×10^5	7×10^3	2×10^5	2×10^3	1×10^5	2×10^1	6×10^4	2×10^4

Determination of metals using GF-AAS:

	As	*Cd*	*Co*	*Cu*	*Pb*
	8.31	0.277	2.05	23.9	4.98
Algae	0.133	0.022	0.536	2.72	0.650
Liophil.	1.6	7.9	26.1	11.4	13.1
	6.15	0.316	2.91	20.6	5.21
Algae	0.413	0.046	0.393	5.65	1.60
Not Lioph.	6.7	14.6	13.5	27.4	30.7
E.F.	9×10^3	4×10^3	$>10^5$	2×10^4	1×10^4

Lake water

The analytical data (see Table 6) once again emphasize very low concentrations for transition metal species, in agreement with the hypothesis of a low alteration of the geochemical equilibria which govern the distribution of metal species.

Algae

As can be seen from the standard deviation estimates reported in Table VII, the liophilization treatment and the following grinding procedure make the algal samples more homogeneous. The relative values are always better than 8 % (11.4 for Cr) as compared to values typically ranging between 10 % and 38 % for the non liophilized samples.

Remarkably high enrichment factors, ranging between 10^3 and 10^5, were observed for the bioaccumulation of transition metal species in algae from lake water. Alkali earth elements, such as Ca and Mg, and Na are also concentrated to a considerable extent.

This feature has been suggested as the basis for the use of algal substrates for analytical enrichment, also in the form of immobilized specimens (Schwartz, 1991).

The availability of other samples collected in successive years from the same ecosystem, and from other Antarctic Lakes will allow a better interpretation and a more clearcut understanding of the present observations.

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