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Recent trends in chemistry and mass budget of a high altitude lake in the southern Alps (Laghetto Inferiore, Canton Ticino, Switzerland)

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ABSTRACT

Since 1980, surveys have been performed every three years on about 50 small high-altitude Alpine lakes located in the Swiss part of the Lago Maggiore watershed (Southern Central Alps). Since 1996 one of these lakes, Laghetto Inferiore (LI) has been included in the Mountain Lakes Research (MOLAR) program, an extensive European co-operative research project with 23 partners. Laghetto Inferiore, situated at 2074 m a.s.l., has a watershed mainly composed of crystalline silicic rocks, a maximum depth of 33 m and a theoretical renewal time of 41 days. The watershed includes a second lake, Laghetto Superiore (LS), located at 2128 m a.s.l. The surface water pH of LI is around 6.6, while alkalinity is about 30 µeq l^{-1}, increasing to 90 µeq l^{-1} at the maximum depth. Calculated inputs from atmospheric deposition and the main tributary streams were compared with changes in the lake concentration, and outflow fluxes on a monthly basis. Weathering ranged between 90-130 meq m^{-2} of alkalinity using a mass budget approach, of which 50% was consumed by the actual (H^+) and potential (NH_4^+) atmospheric acidity. Chemical trends over the period 1985-1998 show an increase in alkalinity and a decrease in sulphate, due to a reduction in the deposition of atmospheric acidity, and a decrease in nitrate, probably because of increased lake productivity.

Key words : Alpine lakes, hydrochemistry, acidification, deposition chemistry, trends, weathering

1. INTRODUCTION

Over the past 20 years the Environmental Studies Laboratory (LSA) has conducted limnological studies at high altitude Alpine lakes located on the southern side of the Central Alps (Canton Ticino), (Barbieri & Righetti 1987; Boggero *et al*. 1996). Many of these studies have been in collaboration with the Italian Institute of Hydrobiology of the C.N.R. (National Research Council), which works on Alpine lakes in the Ossola Valley, bordering on the Canton Ticino (Marchetto *et al*. 1991, 1995; Mosello *et al*. 1994). Studies of lake water chemistry have concentrated mainly on acidification problems, as the geological characteristics of the area result in sensitive lakes with low buffering capacities.

Since 1980 lake chemistry studies have taken the form of six surveys, carried out at approximately three-year intervals on a group of 21 lakes, and occasionally on a larger group of 50 lakes. The results are summarised by Boggero *et al*. (1996). In June 1996 a detailed limnological study was begun on Laghetto Inferiore (LI) and Laghetto Superiore (LS), which are located on the southern side of the Central Alps, in the Canton Ticino, in the watershed of the River Maggia (Fig. 1). Biological studies comprised research on phyto- and zooplankton, fish fauna and littoral benthos (Barbieri *et al*. 1999; Simona *et al*. 1999). Data from these two lakes were included and co-ordinated in a wider European project, Mountain Lakes Research (MOLAR), which aimed to evaluate the susceptibility of remote mountain ecosystems to acid (sulphur plus nitrogen) deposition, and to measure and model their temporal responses to climate variability (Patrick *et al*. 1998). In the particular case of LI, an additional objective was to assess chemical trends using the results of previous studies (Boggero *et al*. 1996) and relating them to trends in atmospheric deposition chemistry. Atmospheric loads were also calculated, to provide a chemical budget for the lakes during the period July 1996 to July 1997.

In this paper we evaluate these chemical results, which provide the basis of a large scale comparison with other lakes studied in the MOLAR project.

2. STUDY AREA

The study area is located in the Maggia Valley, in the Lago Maggiore watershed, on the southern side of the Central Alps (Fig. 1). This catchment area contains two small lakes: Laghetto Inferiore (LI), situated 2074 m a.s.l. in Val Maggia, and Laghetto Superiore (LS), situated 2128 m a.s.l., the outflow of which flows into LI. The morphometric and geographic characteristics of the catchment areas and the lake basins are given in table 1.

The basin of LI is of glacial origin and is roughly triangular in shape; it is surrounded mainly by crystalline rocks and stony detritus (86%), and by pasture land and shrubs (7%). There are some small areas with limno-lacustrine deposits of mud on the shore of the lake (Boggero 1996).

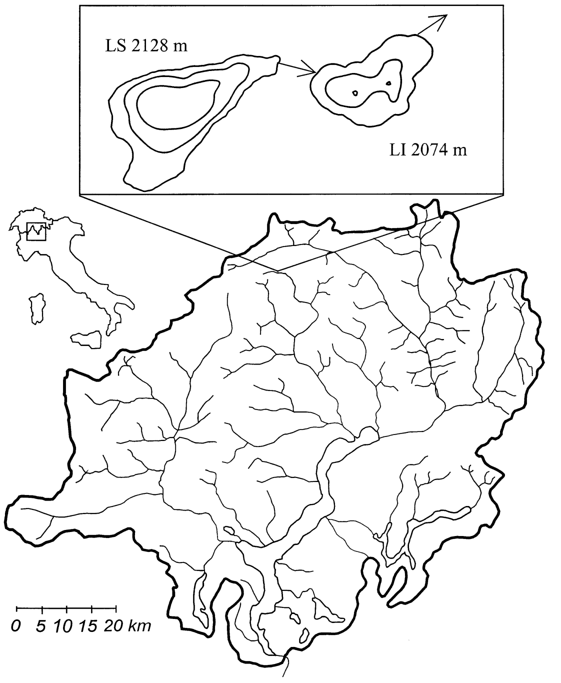

Fig. 1. Location of Laghetto Inferiore (LI) and Laghetto Superiore (LS) in the watershed of Lake Maggiore.

Tab. 1. Geographic and morphometric characteristics of Laghetto Inferiore (LI) and Laghetto Superiore (LS) and watersheds. (1) includes the watershed of Laghetto Superiore. (2) net waterflux through the soil.

		LI	LS
Longitude		08°35'38"	08°35'08"
Latitude		46°28'37"	46°28'36"
Altitude	m	2074	2128
Altitude max watershed	m	2648	2648
Lake area (a)	km^2	0.048	0.080
Watershed area (b)	km^2	1.78(1)	1.22
b/a rate		36	15
Maximum depth	m	33	29
Mean depth	m	10.6	12.7
Volume	$m^3\ 10^6$	0.51	1.01
Mean precipitation (prec)	$mm\ y^{-1}$	2416	2416
Precipitation surplus	$mm\ y^{-1}$	2000(2)	2000
Mean residence time	days	51	150
Origin		glacial circle	glacial circle
Soil cover bedrock		86%	88%
pasture		7%	6%
lake		7%	6%

From the lithological point of view the lakes are located in the Penninic nappes, bordering with the Gotthard Massif and the Helvetic and Ultrahelvetic sediments (Cotti *et al.* 1990). The lithotype present in the watershed of LI (Fig. 2) is formed by striped gneisses (from alkali feldspars to oligoclase, from granitic to quartz dioritic), with some biotite and brown plagioclase gneiss up to micaschists. Also present are amphibolite with aplitic veins, marbles and talus material (Boggero *et al.* 1996). Moraines are composed of chaotic accumulations of medium to large size clasts.

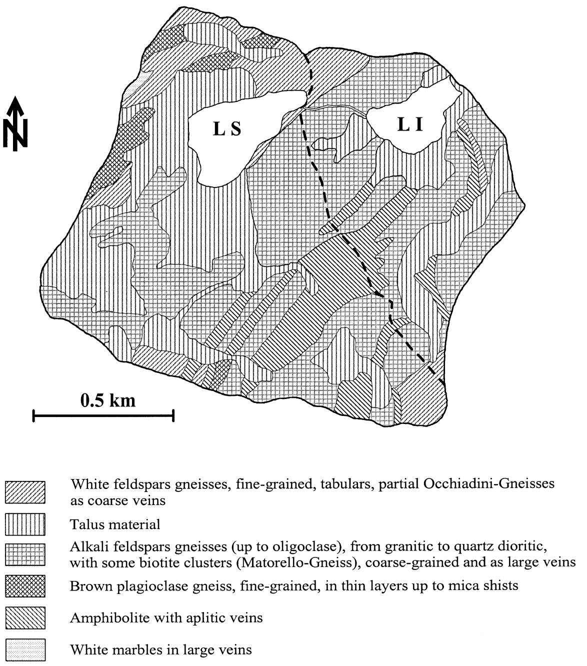

Fig. 2. Litology of the drainage basins and of the two lakes.

On the lake shore there are some small lacustrine mud deposits, of dark grey colour due to the presence of organic material. Shrubs and pastures are present in the catchment and on the mountainside to the north, not far from a snowfield. Most of the lake shore is formed of massive rocks, shaped by atmospheric events.

The bathymetric maps of the two lakes and their respective hypsographic curves are shown in figure 3.

3. MATERIALS AND METHODS

Atmospheric deposition was sampled weekly from May to October during 1996-1997, using a wet-only sampler. Winter precipitation from October 1996 to April 1997 was estimated by sampling a snow core; the column was subdivided into five fractions corresponding to the five heaviest snowfalls of the winter on the basis of their stratification (thickness, density and water equivalent). Sampling from LI, taken at the point of maximum depth (33 m), was concentrated in the lake's ice-free season (June - October) during the two years of the cycle. The lake waters were sampled on two other occasions (March 1997 and February 1998), under a layer of ice and snow about 2 metres thick. At the time of sampling, measurements of temperature, pH, light transmittance, dissolved oxygen and conductivity were made every 0.5 m using a multiprobe, Idronaut mod. Ocean seven 316. Samples for chemical analysis were taken every 2.5 m in the water column. The dissolved oxygen concentration was also measured at these depths using Winkler's method (A.P.H.A, AWWA & WEF 1995).

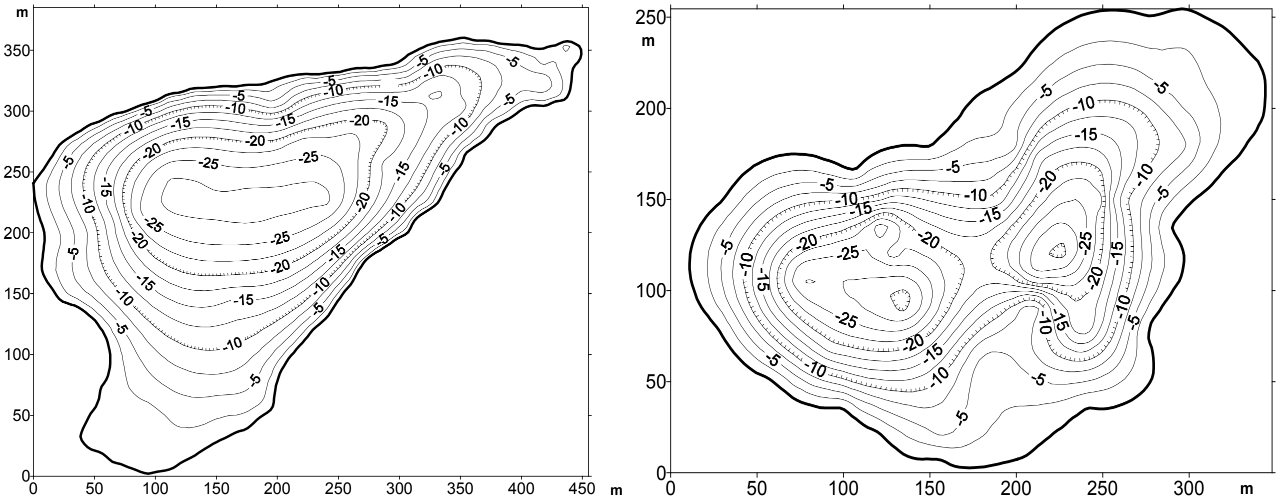

Fig. 3. Bathimetric maps of Laghetto Superiore (left) and Laghetto Inferiore (right).

Tab. 2. Analytical methods, working ranges and limits of quantification (L.O.Q.). IC: Ion chromatography; AM: automated colorimetric method.

Parameter	Method	References	Unit	Working range	L.O.Q.
Alkalinity (Alk)	Potentiometric titration, two end points 4.5 and 4.2	A.P.H.A., 1971 Rodier, 1971	µeq l^{-1}	1-250	3
Conductivity (cond)	Kolrausch bridge 20°C	APHA-AWWA-WPCF, 1995	µS cm^{-1}	0.2-100	0.5
Oxygen (O_2)	Volumetric titration, Winkler method	A.P.H.A., 1971,	mg l^{-1}	0.5-15.0	0.5
Sulphate (SO_4)	IC	A.S.T.M., 1984, A.P.H.A., 1985, Weiss, 1986	mg l^{-1}	0.25-4.00	0.045
Chloride (Cl)	IC	A.S.T.M., 1984, A.P.H.A., 1985, Weiss, 1986	mg l^{-1}	0.05-0.80	0.018
Calcium (Ca)	IC	Weiss, 1986	mg l^{-1}	0.10-4.00	0.03
Magnesium (Mg)	IC	Weiss, 1986	mg l^{-1}	0.02-0.80	0.007
Sodium (Na)	IC	Weiss, 1986	mg l^{-1}	0.05-2.00	0.013
Potassium (K)	IC	Weiss, 1986	mg l^{-1}	0.05-2.00	0.02
Ammonium (NH_4-N)	AM	APHA-AWWA-WPCF, 1995	mg l^{-1}	0.014-0.140	0.020
Nitrite (NO_2-N)	AM	APHA-AWWA-WPCF, 1995	µg l^{-1}	2-20	0.55
Nitrate (NO_3-N)	AM	APHA-AWWA-WPCF, 1995	mg l^{-1}	0.050-1.500	0.015
Phosphate (PO_4-P)	AM	APHA-AWWA-WPCF, 1995	µg l^{-1}	6-60	4.3
Silica (SiO_2)	AM	APHA-AWWA-WPCF, 1995	mg l^{-1}	0.3-4.0	0.035

Three samples were taken from the LS depth profile in summer 1997, using the same methods as for LI. To calculate the chemical budget of the lakes, their outflows were also sampled weekly from June to October 1996 and monthly during the same period in 1997.

The chemical variables considered and the methods used are listed in table 2, which also specifies the measurement range as well as the LOQ (Lower quantification limit, following the IUPAC definition (Tartari & Mosello 1997)). The LSA participates regularly, with good results, in intercalibration exercises for analytical methods, both on rainwater and surface water samples, in the framework of the EU programme AQUACON (Analytical Quality Control and Assessment Studies in the Mediterranean Basin, Mosello *et al.* 1998a, b) and of ICP Assessment and monitoring of acidification of rivers and lakes (Hovind 1997, 1998).

The results obtained in this study were validated on the basis of the ionic balance and the comparison between measured conductivity and that calculated from the ionic concentrations multiplied by the respective conductivity equivalents, following the methods adopted in the MOLAR programme (Mosello & Wathne 1997).

To evaluate the trend of the lake concentrations we used the data collected from 1983 to 1997. The comparability of the results obtained in different years in relation to changes in the analytical methods used was examined by Boggero *et al.* (1996, 1998).

The water density profile in LI is shown as density anomaly, defined as the difference between the actual density of the lake water (ρ, g cm^{-3}) and the density of pure water at 3.98 °C, assumed as 1 g cm^{-3}. ρ is calculated from the temperature and using the table of absolute density of water (Weast 1970) and from the solute concentrations (mg l^{-1}) of Ca, Mg, Na, K, SO_4, NO_3, Cl, NH_4 and SiO_2.

The annual hydrological balance of the lake was evaluated on the basis of measurements of the amount of deposition, performed in the meteorological station of Robiei, about 7 km from the sampled lakes. The approach used was that proposed for the Swiss Alps by Rihm *et al.* (1994).

The mass balance calculation is based on the continuity equation. Such equation can be differently formulated but the common concept is condensed in the statement that the sum of all (positive and negative) fluxes of given substances M equals zero, i.e.:

$$\sum_1^r m_r = 0$$

Another form of the same statement may be written as (Vollenweider 1975):

$$\frac{d(M)content}{dt} + \frac{d(M)input}{dt} + \frac{d(M)output}{dt} + \frac{d(M)exchange}{dt} = 0$$

This second equation makes it easy to distinguish between non-conservative and conservative substances; for the latter, the exchange term becomes zero.

4. RESULTS AND DISCUSSION

4.1. Atmospheric deposition chemistry

Volumes of precipitation in the two study years (Fig. 4) show marked variability in the monthly distribution of the wet deposition, with extreme values ranging from 0 to 500 mm. A comparison with the pluriannual mean (1991-1996) reveals an appreciable difference in the mean monthly values. Nevertheless, the volume collected is the same for both years (2280 mm y^{-1}), and is fairly close to the mean annual volume of the period 1991-1996 (2467 mm y^{-1}).

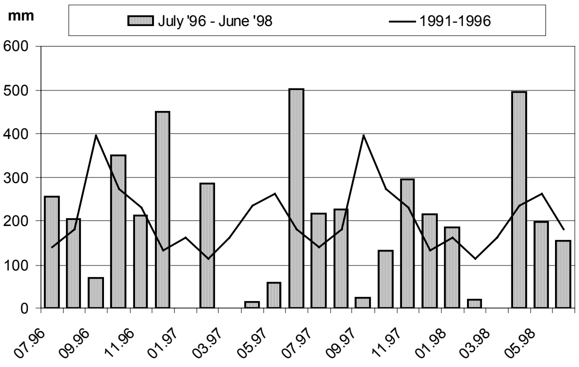

Fig. 4. Monthly precipitation (1996-1998) compared to the average 1991-1996 at Robiei.

The mean monthly values of acidity (Tab. 3) are slightly higher in summer (June-October: pH 4.8-5.2) than in winter deposition (November-May: pH 5.2-5.6); the concentrations of the other solutes, in particular sulphate, nitrate and ammonium, are also higher in summer than winter. Alkalinity, assumed to be entirely due to HCO_3^-, and calcium are present in high values only in May (Tab. 3), coinciding with precipitation containing sand from the Sahara, which left unmistakable coloured dust during filtration. These variations also emerge noticeably in the mean rain and snow concentrations (Fig. 5). The marked differences between them reflect the greater influence of the air masses coming from the south-south-west, which are more frequent from April to October, when the layer of the atmosphere in circulation is above 2000 m a.s.l., than in winter, when the atmosphere is stratified below an altitude of 800-1200 m. The different composition of ions in precipitation from the south is mainly reflected in the concentrations of sodium, chloride and magnesium of marine origin, which are higher in summer and almost absent in winter. Taking into account the fact that the deposition volumes of rain and snow are similar (respectively 1232 and 1196 mm), we calculated a mean concentration of atmospheric deposition and compared this with the lake water concentrations (Tab. 3). The results show a mean annual total ionic concentration of 80 µeq l^{-1}, compared with that of the lake water (200 µeq l^{-1}) and very different ionic composition:

rain: $SO_4^{2-} > NH_4^+ \geq NO_3^- > Ca^{2+} > H^+ > Mg^{2+} \geq Na^+ \geq Cl^- > K^+$

lake: $Ca^{2+} > SO_4^{2-} \geq Alc^- > NO_3^- > Na^+ > K^+ > Mg^{2+} > Cl^-$

4.2. LI temperature and chemistry

During each summer (July-August) the surface water temperature varies between 14 °C and 18 °C, and the water is warmed to a depth of 15 m. During the cold period (September-June) the temperature of the surface layers falls from around 8 °C in September to 4 °C in October (Fig. 6), and reaches values between 4 °C and 0 °C in the winter, rising to around 4 °C again in June. The temperatures of the deepest layers (between 15-32 m) remain close to 4.2 °C throughout the year. The period of ice-cover is from mid-October to June.

Over the two years of the study, dissolved oxygen (Fig. 7) was always well saturated (90-100%), with a relative maximum in August at a depth of around 15 m.

The lake water chemistry (Tab. 4) is considerably affected by the atmospheric deposition, which is largely responsible for the nitrate and sulphate concentrations (Boggero *et al.* 1996). On the other hand, weathering phenomena neutralise atmospheric acidity, in its free form (hydrogen ion) and in the form freed by the oxidation of ammonium (Van Breemen *et al.* 1984). Concentrations of the latter ion, which is important in atmospheric deposition, are in fact almost negligible in the lake waters.

Weathering produces a small reserve of alkalinity, with values always above 30 µeq l^{-1} and increasing with depth (from 30 to 90 µeq l^{-1}, Fig. 8). In June 1997 a very heavy rainfall, occurring after the end of the snowmelt in the watershed, brought about an almost complete cir-

Tab. 3. Monthly weighted means of the precipitation (mm), values of pH, conductivity (μS cm^{-1}), acidity (H^+) and ions concentrations (μeq l^{-1}) in the period July 1996 – June 1998.

	prec	pH	cond	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	SO_4^{2-}	NO_3^-	Cl^-	Anions	Cations
Jan	93	5.65	2.7	2.2	10.9	1.5	2.1	0.6	0.0	3.0	4.4	5.0	2.1	14.5	17.3
Feb	154	5.10	4.1	7.8	1.4	0.1	0.1	0.1	2.9	0.0	4.3	5.7	0.1	10.0	12.4
Mar	0														
Apr	254	5.14	5.5	7.8	11.1	2.1	1.9	0.5	0.5	0.0	9.2	10.4	1.2	20.8	23.9
May	127	5.38	13.6	2.7	53.2	6.5	10.9	1.7	52.5	24.0	47.4	27.8	6.2	105.3	127.5
Jun	328	5.18	10.3	11.7	10.5	1.4	3.5	0.6	25.5	1.1	27.8	19.1	2.3	50.3	53.2
Jul	236	5.08	10.8	14.4	17.6	5.9	5.0	1.8	20.2	0.5	57.0	17.9	7.4	82.9	65.0
Aug	215	5.10	8.8	11.8	9.9	4.7	2.6	0.5	24.4	0.1	32.0	12.9	4.5	49.5	53.8
Sep	46	5.16	10.2	8.8	19.2	9.9	2.5	0.6	24.1	0.5	34.2	25.3	3.5	63.5	65.2
Oct	241	4.80	10.3	15.8	7.3	3.3	5.3	1.1	19.1	0.0	25.4	25.8	2.5	53.7	52.0
Nov	254	5.28	3.7	5.2	5.6	0.8	0.7	0.5	2.7	0.0	5.7	6.1	1.6	13.3	15.5
Dec	333	5.26	3.4	5.9	3.8	0.4	0.5	0.3	1.2	0.0	2.6	5.0	0.7	8.3	12.0
mean	2279	5.19	7.4	9.2	11.4	2.6	2.9	0.7	14.2	1.7	21.4	13.7	2.7	39.6	41.1

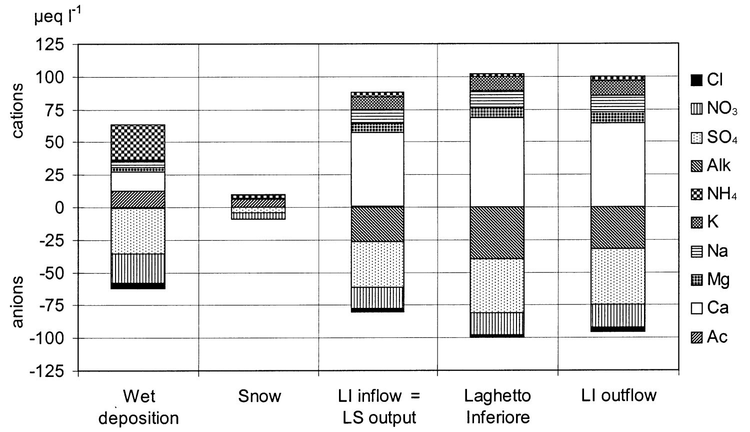

Fig. 5. Chemical characteristics in: atmospheric depositions (rain and snow), inflow and outflow, Laghetto Superiore and Laghetto Inferiore.

culation and lake turnover, also causing a temporary decrease of alkalinity in the water column (from 41 to 29 μeq l^{-1}). The pH values (Fig. 9) are always over 6.4, with a range of variation from 6.4-7.0; the highest values (>6.8) are found in August-September, in the deepest layers (15-20 m), coinciding with the oxygen maxima. Calcium (70 μeq l^{-1}) dominates the cations, followed by sodium and potassium (respectively 14 and 11 μeq l^{-1}; Tab. 4); sulphate concentrations are very similar to alkalinity values. The total solute concentration in LI is on average low (*ca* 200 μeq l^{-1} ±10%) with a mean conductivity value of 12.5 μS cm^{-1} at 20 °C.

The other main chemical variables in solution also show variations similar to that described for alkalinity, with concentrations increasing with depth between 60 and 120 μeq l^{-1} for Ca, between 30 and 80 μeq l^{-1} for SO_4, 15 and 18 μeq l^{-1} for NO_3 and between 10 and 20 μmole l^{-1} for SiO_2. The total solute concentration increases progressively with depth, showing values of 180 μeq l^{-1} at the surface and 300 μeq l^{-1} at 25 m depth.

As regards nutrients (Tab. 4), reactive and total phosphorous were below the LOQ (Tab. 2) in lake water, but were quantifiable as particulate P (1-2 μg P l^{-1}), obtained by filtering 1 litre of water. Nitrate was the dominant form of dissolved nitrogen (16 μeq l^{-1}) showing only small seasonal variation. Total nitrogen averaged 340 μg l^{-1} (24.4 μmol l^{-1}), indicating an organic fraction of 118 μg l^{-1} (8.4 μmol l^{-1}), of which 21 μg l^{-1} (1.5 μmol l^{-1}) was particulated organic N.

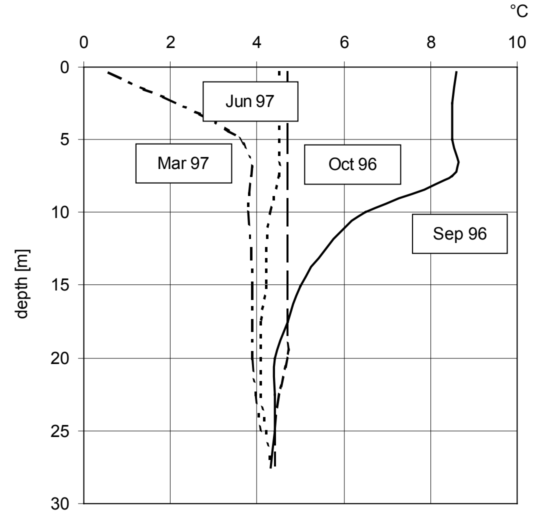

Fig. 6. Seasonal profiles of temperature in Laghetto Inferiore.

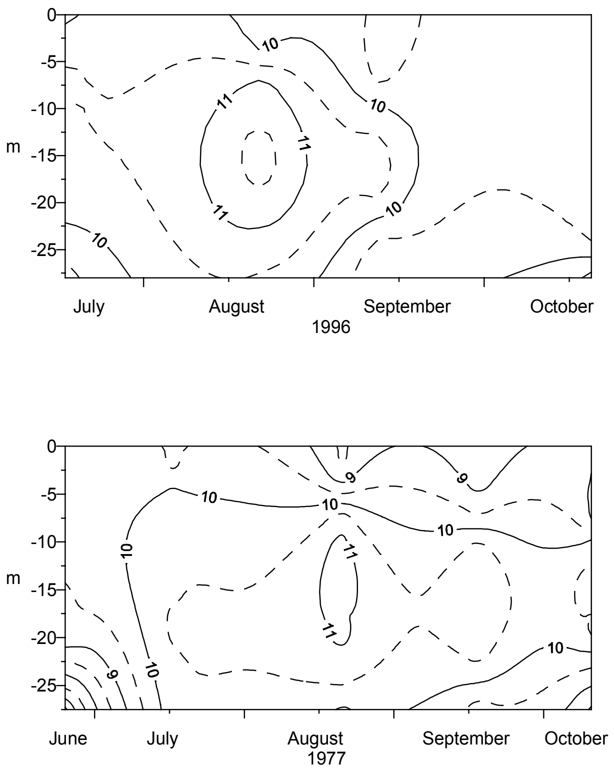

Fig. 7. Seasonal variations of oxygen (mg l^{-1}) in Laghetto Inferiore during 1996 and 1997.

Tab. 4. Weighted mean values of temperature, pH, oxygen (mg l^{-1}), conductivity (µS cm^{-1}), ion concentrations (µeq l^{-1}), reactive phosphorus and silica (µg l^{-1}), particulated phosphorus and nitrogen (µg l^{-1}), total phosphorus and nitrogen (µg l^{-1}) of Laghetto Inferiore (1996-1999).

	16.7.96	18.10.96	18.3.97	9.10.97	19.2.98	22.7.98	15.2.99
Temperature	7.18	4.54	3.01	7.39	3.18	6.28	3.09
Dissolved oxygen	10.00	9.54	9.38	9.25	-	9.04	8.38
pH	6.34	6.21	6.39	6.39	6.26	6.43	6.26
Conductivity, 20°C	12.3	13.8	14.2	11.1	12.4	11.1	12.2
Calcium	60.2	74.6	76.7	67.8	72.6	60.72	81.1
Magnesium	7.2	8.8	9.2	9.2	9.5	8.0	10.1
Sodium	13.0	13.6	13.2	12.2	15.1	12.0	17.2
Potassium	10.3	11.5	11.5	11.0	12.3	10. 5	12.7
Alkalinity	32.1	46.9	47.0	33.0	39.6	33.3	45.3
Sulphate	39.6	43.1	46.5	39.4	43.3	37.6	44.3
Chloride	2.9	2.5	2.3	1.9	3.2	3.1	2.8
Ammonium	1.2	2.9	0.4	0.3	0.1	1.9	0.1
Nitrite	0.1	0.2	0.0	0.1	0.0	0.1	0.1
Nitrate	15.5	16.2	17.4	14.7	16.5	16.6	19.7
Anions	90.2	109.0	115.0	89.1	104.2	90.7	112.1
Cations	91.9	111.5	114.2	100.5	111.7	93.0	122.7
Particulted nitrogen	13	20	14	21	30	13	-
Total nitrogen	252	356	-	364	-	392	-
Reactive phosphorus	1.8	1.4	2.1	0.5	-	0.6	-
Particulated phosphorus	1.5	0.9	2.0	1.9	1.3	0.9	-
Total phosphorus	2.8	4.6	-	10.4	-	0.6	-
Reactive silica	648	713	802	628	740	664	860

The inflowing water to LI displays characteristics which are somewhat different from those of the atmospheric deposition (Fig. 5): acidity has completely disappeared and alkalinity (around 25 µeq l^{-1}) is present. Also the inflowing water shows a total absence of ammonium, while nitrate concentrations remain at the same level as those in atmospheric deposition. The ionic concentration of LI waters is slightly higher than in the inflowing water, mainly because of the increase of calcium and alkalinity.

4.3. LI water density

The profile of water density anomaly in LI (Fig. 10) in the upper 15 m is regulated by temperature (Fig. 6). In fact, during the summer the surface water is warmed and its density decreases, stabilising the water column. In contrast, during the frosty period (October-June) the surface layers cool, and when the temperature falls below 3.98 °C the water density decreases; in this case too the water column is stabilised. On the other hand the density of the water layer below 20 m, which shows slight variations in temperature, is mainly regulated by ion content. The most favourable time for the circulation is during the periods of homothermia, which are however very short. In these situations, too, the vertical saline gradient seems to be able to stabilise the deep layers of the column, and only the occurrence of extreme meteorological and/or hydrological situations appears to be able to destabilise the vertical stratification. For example, a particularly intense (more than 500 mm) rainfall event occurring at the end of June 1997 (Fig. 4), when the lake was still in a condition of homothermia, caused a partial mixing and a dilution of the water, reducing the mean ionic concentration from 205 to 170 µeq l^{-1}. After this phenomenon the vertical saline gradient quickly recovered, and by July the lake had returned to its previous condition of stability (Fig. 10).

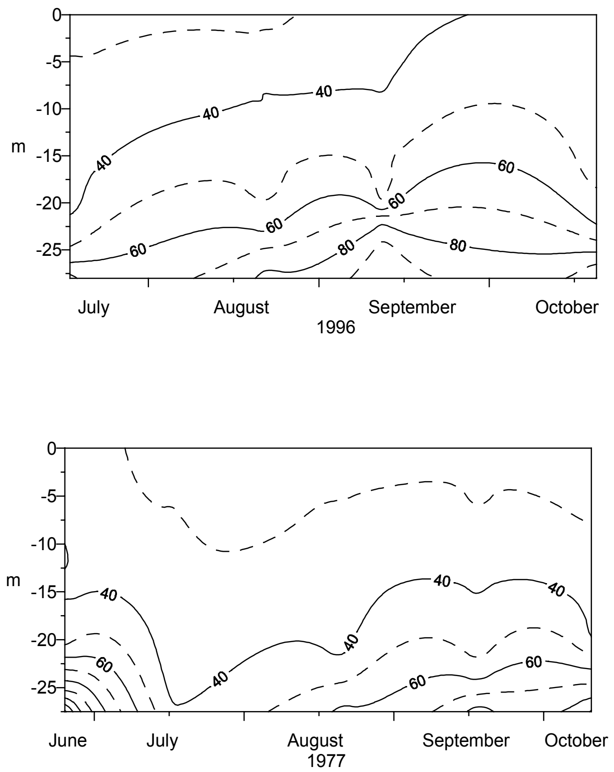

Fig. 8. Seasonal variations of alkalinity (μeq l^{-1}) in Laghetto Inferiore during 1996 and 1997.

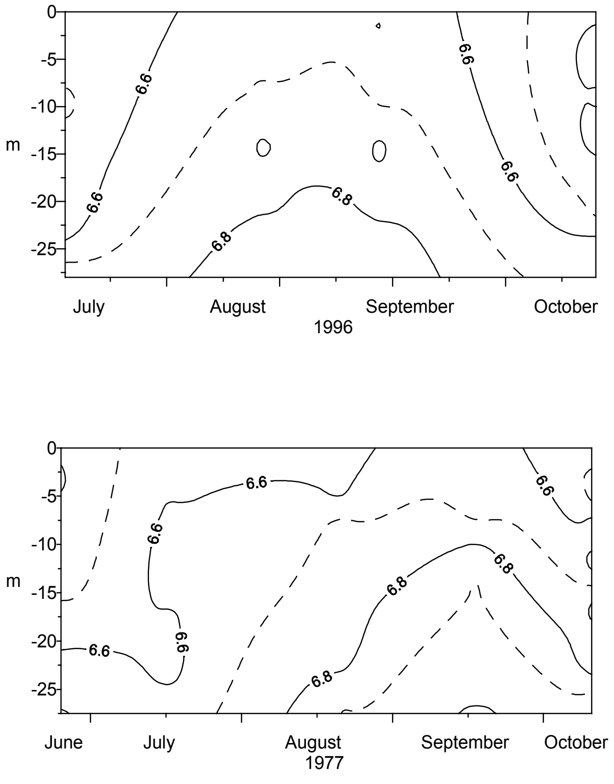

Fig. 9. Seasonal variations of and pH in Laghetto Inferiore during 1996 and 1997.

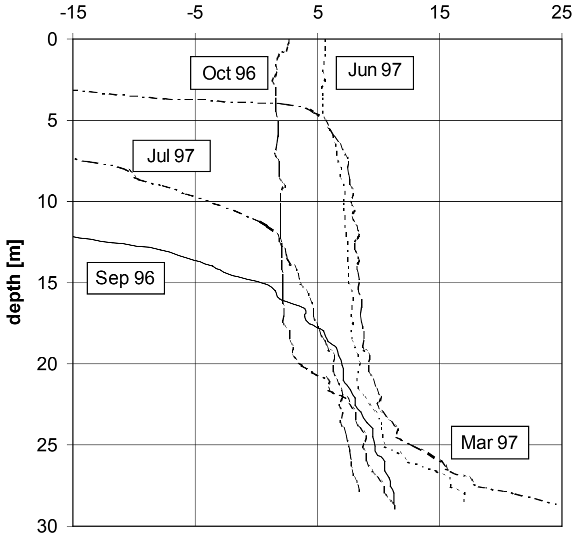

Fig. 10. Seasonal profiles of density anomaly (mg l^{-1}) in Laghetto Inferiore

4.4. Chemical budget and weathering

The mass budget has been calculated on the basis of the continuity equation, which takes account of the atmospheric input and the contribution from the outflow of LS. In the study period the variations in the total ionic content of the water were ±14% (Tab. 4). In both lake catchments the weathering rates were similar, showing an appreciable increase in basic cations, alkalinity, sulphate and silica (Tab. 4). Chloride and nitrate did not show significant variations between input and output.

The flux of ions in the LS and LI catchments is shown in table 5 and figure 11. The overall flux of ions deriving from deposition is 147 meq m^{-2} y^{-1}, while the flux leaving LI, that is, including weathering, is slightly more than 390 meq m^{-2} y^{-1}. The most marked variations are those of the disappearance of acidity and ammonium and the presence of alkalinity in the outflowing waters.

Altogether the weathering processes in the watershed of LS are able to neutralise an acidity of 18 meq m^{-2} y^{-1}, to which must be added the acidity deriving from the transformations of the ammonium ion falling in atmospheric deposition (24 meq m^{-2} y^{-1}). This may vary from 1 to 2 moles of acidity produced per mole of ammonium consumed, according to whether the transformation is caused by uptake from the vegetation crop in the watershed (1 mole), or from oxidation to nitrate (2 moles) (Schuurkes & Mosello 1988; Van Breemen *et al.* 1984).

The overall quantity of neutralised acidity thus ranges between 42 and 66 meq m^{-2} y^{-1}. To this quantity must be added the alkalinity in the water flowing from LS (52 meq m^{-2} y^{-1}) and from the LI system (64 meq m^{-2} y^{-1}), which brings the overall quantity of potentially

Tab. 5. Fluxes balance of Laghetto Superiore (LS) and Laghetto Inferiore (LI); ions (meq m^{-2} y^{-1}) silica (mmole m^{-2} y^{-1}).

	Input		Output		Input-Output	
	Rain	Snow	LS	LI	LS	LI
Acidity	13.1	5.8	1	1	-18	-18
Calcium	14.7	1.0	113	128	97	113
Magnesium	4.0	0.0	15	16	11	12
Sodium	4.5	0.0	21	25	17	20
Potassium	1.0	0.0	19	24	18	23
Ammonium	27.4	2.9	6	7	-24	-24
Alkalinity	0.6	0.0	53	65	52	64
Sulphate	35.9	3.9	70	85	30	45
Nitrate	23.1	4.9	32	35	4	7
Chloride	3.9	0.0	6	7	2	3
Cations	64.8	9.7	175	200	101	125
Anions	63.5	8.8	161	191	88	119
Reactive silica	0.0	0.0	18	21	18	21

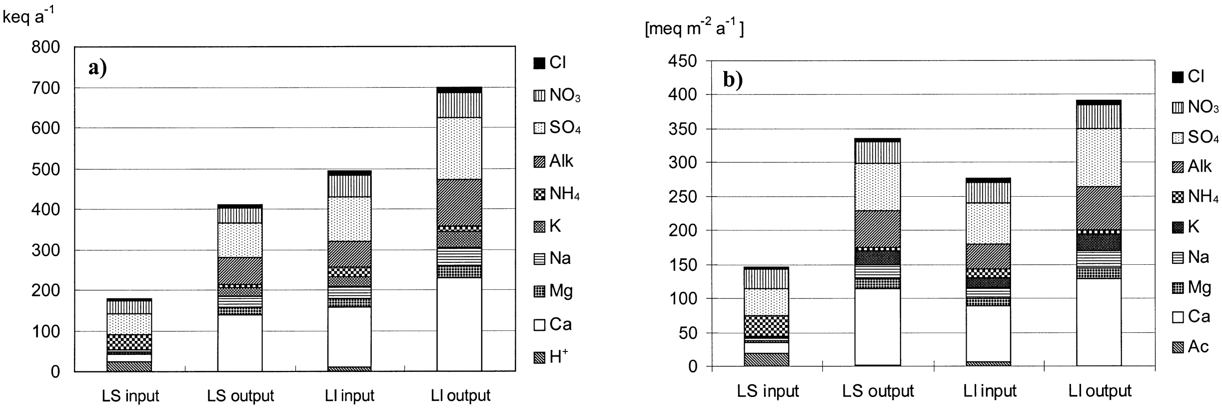

Fig. 11: Mass balance (**a**) and fluxes (**b**) of ions in the system LS and LI. LS input: atmospheric load to the watershed of LS; it does not include weathering. LI input: includes LS output and atmospheric loads to the watershed of LI: it does not include weathering of LI watershed. LS and LI output: loads leaving the lakes through the outlets.

neutralisable acidity to values of 94-118 meq m^{-2} y^{-1} for LS and 106-130 meq m^{-2} y^{-1} for LI.

This means that at least 50% of the potential alkalinity that the rocks in the watershed can release has been consumed by atmospheric deposition acidity.

4.5. Long-term trend

The long-term trend in the chemical components of LI provides an insight into the extent of recovery from the impact of acidification on Alpine lakes. The main chemical parameters of LI, measured since 1985, show an increase in pH and alkalinity values, while there is a decrease in sulphate and nitrate (Fig. 12). However, these results refer to samples taken near the surface (-1 m) towards the end of the summer, when the neutralising action of the weathering has reached its maximum. Compared with a series of 21 Alpine lakes sampled at three-yearly intervals in the Maggia valley (Boggero *et al.* 1996), LI shows a slightly increasing trend of pH and alkalinity, contrasted with a decreasing trend of nitrate and sulphate. These trends are justified by similar variations found in atmospheric deposition in Ticino (Boggero 1998; Barbieri 1999); while these refer to stations located at low altitudes, they suggest that the decrease of deposition acidity has also affected higher altitudes. The decrease in the deposition has not affected the loading of inorganic nitrogen; the decrease which, in contrast, is observable in the water of LI is probably the effect of a greater nitrogen consumption by in-lake processes and/or by vegetation uptake in the catchment. A similar decline in nitrate in high-altitude lakes has been found in the nearby Ossola Valley (Boggero *et al.* 1996) and constitutes a general trend on a European scale (Mosello *et al.* 1999), with particular reference to high-altitude lakes (The MOLAR Water Chemistry Group 1999).

5. CONCLUSIONS

Despite the high loading of acidifying pollutants to LS and LI catchments, weathering processes are sufficient to completely neutralise these inputs. The deposition of pollutants occurs mainly in late spring and summer, with snow having the lowest pollutant concentrations. This is due to stratification of the atmosphere, which greatly limits the transport of pollutants from the plain during the winter.

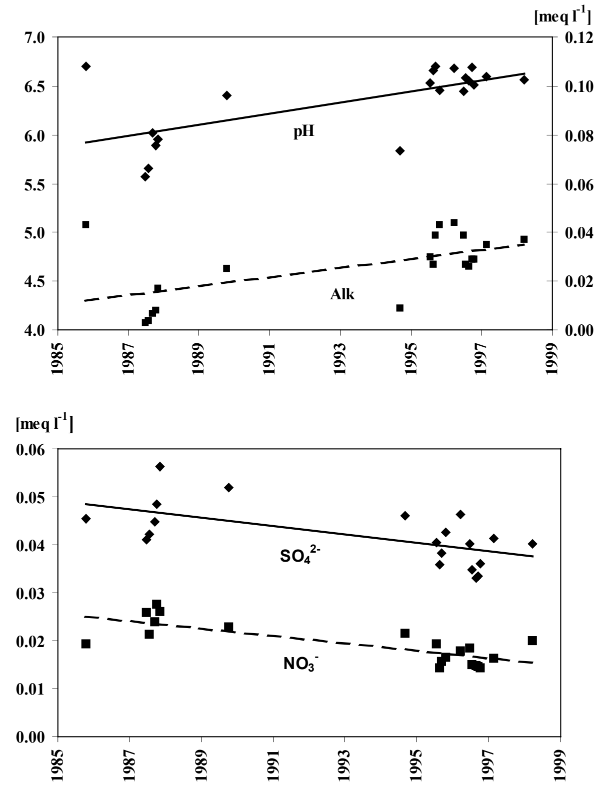

Fig. 12. Trends of pH, alkalinity, sulphate and nitrate in Laghetto Inferiore (-0.4 m depth).

A considerable contribution to acid deposition also derives from ammonium, which is one of the main ions in the atmospheric deposition, though almost absent in the lake waters. Taking account of the total acidity of the deposition, and the alkalinity which is finally present in the lake waters, we estimated that an alkalinity value of 94 - 130 meq m^{-2} y^{-1} is released by weathering from the rocks of the watershed; more than 50% of this alkalinity is neutralised by the acidity of the deposition.

A study of the stratification of the lake reveals a solute gradient which could be stable over a period of months. The density profile of LI is determined mainly by temperature, which results in a relatively stable water column. The mixing of the lake water may be heavily influenced by intense precipitation events (400-500 mm) during the short periods of homothermia (2-3 weeks a year). However, on these occasions the saline gradient, a characteristic of the bottom layer, is able to inhibit a complete circulation. On the other hand, the nutrient concentrations and higher alkalinity of the deep waters may considerably affect algal production, which in Alpine lakes is highest close to the bottom, if it gets enough light.

These results highlight the need for more detailed studies on the physics of Alpine lakes, especially those with a maximum depth greater than 20-30 m, or which, owing to the configuration of the watershed, are particularly sheltered from the wind. The homogenisation of the water is in fact an important process which allows the redistribution of both algal nutrients and other ions present in the water.

The decreased impact of acidic atmospheric depositions may have far-reaching ecological consequences. An important line is that of possible variations in plankton populations, which have already been a focus of study in recent years (Simona *et al.* 1999). But it is in the study of the effects of climatic variations on aquatic ecosystems, and more generally on the Alpine environment, that Alpine lakes, especially those for which we have a large amount of information, can be particularly useful, thanks to their sensitivity to environmental factors and the low human impact to which they are exposed. Continuous monitoring is therefore vital, as is more detailed study of the phenomena which are most likely to be sensitive to variations in the atmospheric temperature, such as the weathering of ions in the watershed, and the biological processes both in the lakes and in the vegetation covering the watershed.

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