

Acidification and weathering processes in high mountain lakes in Southern Alps

Aldo Marchetto¹, Alberto Barbieri², Rosario Mosello¹ & Gabriele A. Tartari¹

¹CNR Istituto Italiano di Idrobiologia, I-28048 Verbania Pallanza, Italy; ²Laboratorio di Studi Ambientali, Dipartimento Acque, Cantone Ticino, CH-6502 Bellinzona, Switzerland

Key words: acidification, weathering, mountain lakes

Abstract

About 200 lakes in Southern Alps (Italy and Switzerland) were studied in order to quantify their acidification. Although samplings were carried out in summer, long after the acid shock caused by snowmelt, some lakes were found to be acidic and 47% of them show alkalinity values of below $50 \mu\text{eq l}^{-1}$. Losses in alkalinity (acidification levels) were evaluated using a titration model with variable F-factor.

Factor analysis shows that the main factors influencing water chemistry are related to rock weathering and nitrate uptake by vegetation. In watersheds containing carbonatic rocks the weathering of calcite is responsible for the most of the alkalinity production. We therefore focused on a set of 19 low-alkalinity lakes in the Maggia Valley lying in watersheds containing mainly acidic rocks. Results show that the weathering of silicate and calcite (present in small quantities, but highly soluble) and nitrate uptake account for most of the alkalinity production. Other watershed and in-lake processes may be important in some cases, but they never account for more than 27% of the alkalinity production in these lakes.

Introduction

Over the last ten years Alpine lakes have been studied with regard to the problem of acidification, and the implications of the long-range transport of pollutants. These lakes vary greatly in shape, size and lithological and hydrological features, and therefore show a wide range of chemical characteristics: previous surveys (Mosello, 1984) have revealed conductivity values ranging from 7 to $1265 \mu\text{S}_{18} \text{cm}^{-1}$, pH values as low as 4.5 and 50% of the alkalinity values lower than $200 \mu\text{eq l}^{-1}$. Furthermore, acidification (loss of alkalinity) was estimated to be $40 \mu\text{eq l}^{-1}$ (Mosello *et al.*, 1988) for the Southern and $55 \mu\text{eq l}^{-1}$ (Psenner *et al.*, 1988) for the Austrian

Alps on the basis of Henriksen's (1980) model.

Atmospheric deposition show higher pH values at elevations between 1500 and 2200 m a.s.l. (pH 4.8–5.4 as annual volume weighted mean) than in the subalpine area, at altitudes between 200 and 900 m (pH 4.3–4.5) (Gruppo di Studio, 1987).

This paper focuses on a set of lakes located in the Southern Alps in order to improve the estimate of the number of acidified and acid sensitive lakes and their level of acidification, to compare the chemical properties of lake and atmospheric deposition and to single out the principal processes determining the sensitivity of lakes to acid deposition.

Description of the study area

The Alpine lakes studied are located in the Southern (Pennine and Lepontine) Alps in Piedmont (Italy) and in Canton Ticino (Switzerland), in an area (Fig. 1) of about 4200 km² which receives a high amount of orographic precipitation (1100–2700 mm y⁻¹, Carollo *et al.*, 1985).

During the present study 188 lakes and 20 reservoirs were sampled: 27 in the Valley of the River Sesia (Italy), 105 in the Valley of the River Toce (Ossola Valley: 98 lakes in Italy and 7 in Switzerland) and 76 in the Valley of the River Ticino (72 lakes in Switzerland and 4 in Italy). The sampled lakes are situated at altitudes ranging between 1073 and 2915 m a.s.l., and have surface areas ranging between 0.001 and 1.35 km². Nearly all the major lakes were sampled.

Methods

Studies on the chemistry of atmospheric deposition have been carried out since 1981 at Lake

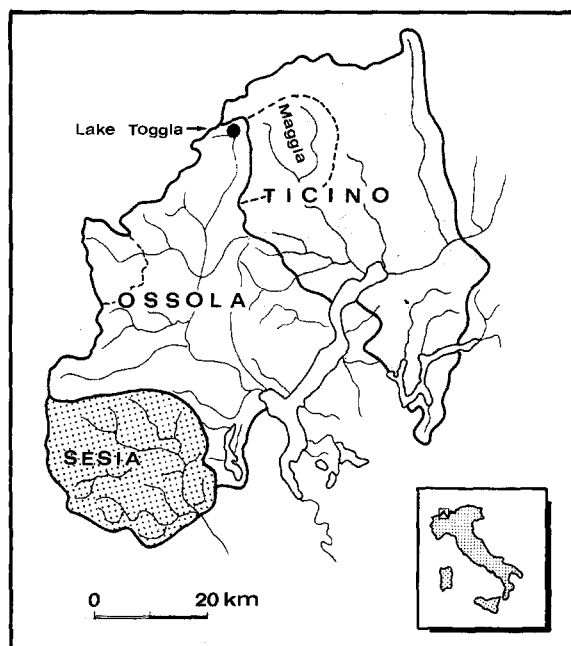


Fig. 1. Study area and geographic distribution of the lakes sampled.

Toggia, a hydroelectric reservoir located near the Alpine divide at an altitude (2160 m a.s.l.) similar to that of the lakes sampled. This station is equipped with bulk sampler consisting of a 20 l polyethylene container and a funnel, surface area 0.12 m², the mouth of which stands about 1.5 m above the ground. Deposition was collected monthly in 1981–82 and then weekly.

Lake samples were collected at the outflow in polyethylene bottles, in summer and autumn 1979–89, well after the snowmelt had finished. Samples were stored at 4 °C in the dark and analysed within 3 days. To have information on the seasonal variations, some lakes were sampled throughout the ice-free season (June–October). To obtain a homogeneous sample for the statistical description of the lake population, one sample was chosen for each lake, normally the last autumn analysis unless excluded by quality control.

Analytical methods are reported by Mosello (1984) and Mosello *et al.* (1991) for atmospheric deposition and Italian lakes and from Barbieri & Righetti (1987) for Swiss lakes. Variations in the analytical methods employed during the period mean that the sulphate concentrations measured after 1984 (by ionic chromatography and the barium chlorinate method in the Italian and Swiss laboratories, respectively) are more accurate than those measured prior to this date (by conductometry or turbidimetry). The sulphate and chloride concentrations of atmospheric deposition and of 71 lakes sampled in 1979–1983 were not used in this study.

The results for each lake were validated by excluding analyses with a difference between the sum of anion and cation concentrations of over 10% of the total ionic content. Quality control performed on the chemical results led to the exclusion of 12 lakes.

Results

The mean amount of precipitation in 1981–88 was 1254 mm, very close to the historical mean (1264 mm). The volume-weighted average of ionic concentrations are shown in Table 5. Main an-

ions are sulphate and nitrate, in the equivalent ratio 2:1. Mineral acidity is low because it is partly buffered by the ammonium ion. However, ammonium oxidation can produce further acidity in the lakes. Taking into account this reaction, mean weighted potential acidity will result $57 \mu\text{eq l}^{-1}$, corresponding to a pH value of 4.24. Episodic deposition of HCO_3 released from Saharian dust amounted to $4.1 \mu\text{eq m}^{-2} \text{y}^{-1}$, as an average for the nine-year period, and this can neutralize 34% of the free mineral acidity.

If these episodes are excluded, weighted mean acidity increases to $15 \mu\text{eq l}^{-1}$ (pH = 4.8).

The ionic concentrations of the lakes are generally low (Table 1). Calcium is usually the main cation, followed by magnesium, but the four lakes with watersheds composed entirely of ultrabasic rocks show a higher concentration of magnesium than of calcium, as might be expected because of the weathering of these rocks. In lakes lying in watersheds composed only of acidic or ultrabasic rocks, the main anion is sulphate, while in the other lakes the anionic composition is dominated by bicarbonate ion which represents most of the alkalinity. Chloride concentrations are below $10 \mu\text{eq l}^{-1}$ in 83% of the cases, indicating a negligible sea-salt contribution to the ionic concentrations.

To arrive at the number of acid and acid-sensitive lakes on a statistical basis, we considered alkalinity and pH distribution (Fig. 2), their variability in a single year, due to seasonal (ex-

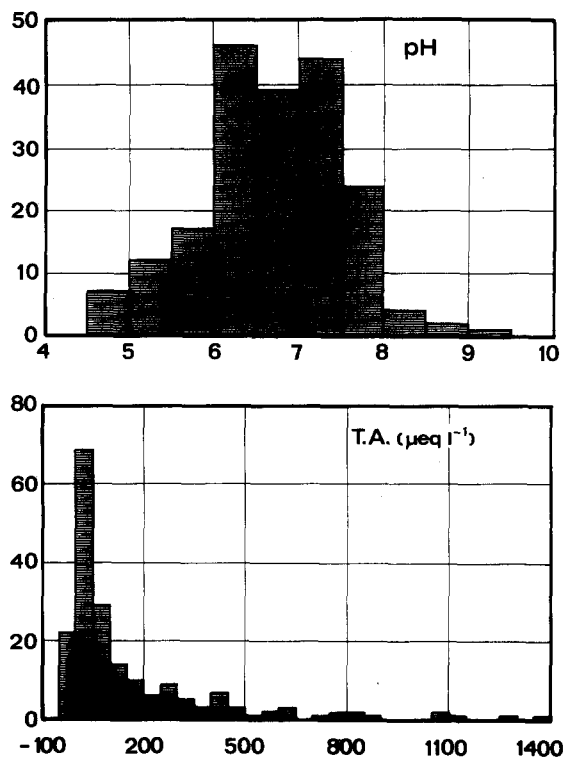


Fig. 2. Frequency distribution of pH and total alkalinity ($\mu\text{eq l}^{-1}$).

cluding the period immediately after the snow-melt), hydrological and random causes, using 40 lakes sampled 3 or more times throughout the year, and their variability in different years using 11 lakes sampled in 5 or more different years.

The alkalinity value of $200 \mu\text{eq l}^{-1}$ is generally assumed to be the threshold indicating suscepti-

Table 1. Ionic composition of the lakes sampled.

Variable	Unit	No.	Average	Min	P25	Median	P75	Max
Conductivity	$\mu\text{S}_{18} \text{ cm}^{-1}$	196	29	5.2	11.7	16.3	31	248
pH		196	6.69	4.64	6.18	6.70	7.27	9.14
Alkalinity	$\mu\text{eq l}^{-1}$	196	171	-23	19	63	230	1372
Ca^{2+}	$\mu\text{eq l}^{-1}$	196	236	15	65	105	268	2295
Mg^{2+}	$\mu\text{eq l}^{-1}$	196	43	0	10	19	141	592
Na^+	$\mu\text{eq l}^{-1}$	196	12	0	9	13	19	69
K^+	$\mu\text{eq l}^{-1}$	196	12	0	6	9	14	123
NH_4^+	$\mu\text{eq l}^{-1}$	196	3	0	1	1	2	71
SO_4^{2-}	$\mu\text{eq l}^{-1}$	125	110	17	45	60	76	1976
NO_3^-	$\mu\text{eq l}^{-1}$	196	19	0	12	17	24	64
Cl^-	$\mu\text{eq l}^{-1}$	125	7	1	4	5	7	60
Reactive Si	$\mu\text{mol l}^{-1}$	183	25	1	14	23	36	110

Table 2. Estimate of the number of lakes sensitive to acidification.

Threshold	No.	%	95% confidence interval	
			No.	%
T.A. $\leq 200 \mu\text{eq l}^{-1}$	142	73%	138–147	71–76%
T.A. $\leq 50 \mu\text{eq l}^{-1}$	92	47%	62–101	32–52%
H ≤ 6.0	35	18%	18–36	9–18%
pH ≤ 5.3	11	6%	1–30	0.5–15%

bility to acidification (e.g. Goldstein & Gherini, 1984). This value may ensure that in spring total alkalinity values do not fall below zero. Recently a threshold of $50 \mu\text{eq l}^{-1}$ has been proposed (e.g. Sullivan *et al.*, 1990) and this value is closer to the loss of alkalinity calculated for Alpine lakes in this and other studies (Mosello *et al.*, 1988; Psenner *et al.*, 1988).

The numbers of lakes with total alkalinity values of below 200 and $50 \mu\text{eq l}^{-1}$ are reported in Table 2 with their 95% confidence interval, showing that about two thirds of the lakes considered can be regarded as sensitive to acidification.

Conditions of acute acidification are reached when the lake pH drops below 5.3 and the acid-base equilibrium no longer depends on the buffer effect of bicarbonate ions, but on the various forms of aluminium (Wright, 1983). In these lakes the toxic effects are induced both by low pH and a high level of aluminium (Baker & Schofield, 1982). However, the effects of acidification on organisms begin at pH values of about 6 (Psenner & Zapf, 1990).

The number of lakes with pH values below 5.3 and below 6 are also reported in Table 2 with their 95% confidence interval; pH values below 5.0 were also found in 31 out of 806 total analyses (4%).

Factors affecting lake chemistry

Relations between chemical variables were defined using factor analysis on standardized concentrations, excluding pH because it is not truly

Table 3. Varimax rotated factor matrix.

Factor	1	2	3	4
Accounted variance	38.3%	18.9%	10.8%	9.8%
Ca ²⁺	0.91	0.04	0.15	-0.24
Mg ²⁺	0.89	0.10	0.09	0.01
Alkalinity	0.73	-0.02	-0.05	0.14
SO ₄ ²⁻	0.88	0.13	0.02	0.19
Na ⁺	-0.07	0.83	0.16	0.12
Reactive Si	0.27	0.75	0.28	-0.41
K ⁺	0.32	-0.05	0.76	-0.06
Cl ⁻	-0.08	0.31	0.78	0.19
Inorganic N	-0.07	0.06	0.11	0.93

independent of the other variables, and considering nitrate and ammonium together to take into account the redox processes that can transform them into each other.

The results show that the first 4 factors account for 77.8% of the total variance. Their loadings, after Varimax rotation, are showed in Table 3. We consider the first factor, loading on Ca, Mg, sulphate and alkalinity, and the second, loading on Na and silica, as weathering factors, for carbonatic and acidic rocks, respectively. So weathering accounts for more than one half of the total variability. The first two factors are both significantly related to the lithology of the watersheds, as shown by Kendall rank correlation analysis performed between factor scores and a semiquantitative lithological description in which lower values are assigned to acidic rocks and higher values to carbonate rocks (Mosello *et al.*, 1991).

For the third factor, loading on K and chloride, the interpretation is less simple. It is significantly related to the amount of vegetation in the watershed and, inversely, to its surface. It may be an evapotranspiration and ionic exchange factor.

The last factor, directly related to total nitrogen and inversely related to the amount of vegetation in the watershed, represents the nitrogen uptake by the watershed vegetation.

Only the first and fourth factors are related to alkalinity, indicating that the latter is mainly controlled by carbonate weathering and nitrogen uptake.

Level of acidification

The preacidification value of total alkalinity, TAO, was estimated from pristine base cation concentrations, $(Ca + Mg)_o$, on the basis of the empirical relationship (Wright, 1983):

$$TAO = 0.91 (Ca + Mg)_o$$

Sea-salt correction of ionic concentrations is omitted, because of the low chloride level.

Pristine base cation concentrations can be estimated from present values assuming no change in weathering rate (Wright, 1983) or an increase in weathering and cation desorption caused by the deposition of strong acid. In this case it would be buffered by the increase in base cation concentrations, $\Delta(Ca + Mg)$, related to those of strong acid anions, in our case $\Delta(SO_4 + NO_3)$, through the variable F-factor (Brakke *et al.*, 1990):

$$F = \frac{\Delta(Ca + Mg)}{\Delta(SO_4 + NO_3)}$$

$$= \sin\left(90^\circ \frac{(Ca + Mg)}{S}\right),$$

where S was set to 200–400 $\mu\text{eq l}^{-1}$ depending on the acid loading. If the base cation concentrations exceed S , the acid input will be completely buffered by the watershed weathering.

The maximum value of F can be estimated by assuming that the initial base cation concentration was zero and that the background sulfate (and nitrate) concentration is about 8–15 $\mu\text{eq l}^{-1}$ (Brakke *et al.*, 1990) or negligible: in this case F will be smaller than $(Ca + Mg)/(SO_4 + NO_3)$.

Table 4. Loss of alkalinity ($\mu\text{eq l}^{-1}$) for lakes with base cation concentration below S ($\mu\text{eq l}^{-1}$), assuming different values of S .

Values of S assumed	200	400	∞
No. of lakes	42	55	125
25th percentile	9	21	38
Median	18	32	56
75th percentile	26	40	73
Average	17	30	89

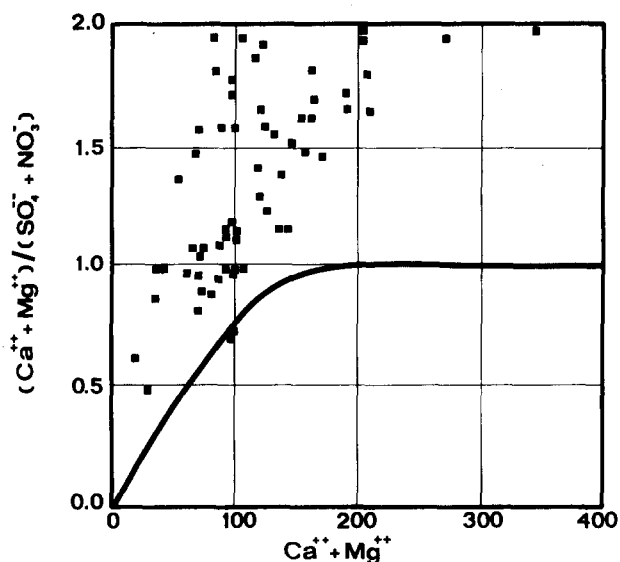


Fig. 3. Ratio of base cation concentration $(Ca + Mg)$ to those of strong acid anion $(SO_4 + NO_3)$ plotted versus base cation concentration $(Ca + Mg)$ and compared with calculated F values, assuming $S = 180$. Unit: $\mu\text{eq l}^{-1}$.

With this set of data, the minimum S value is about 180 (Fig. 3), confirming Brakke's approach.

The acidification levels (losses of alkalinity) calculated assuming $S = 200$ and $S = 400$ are compared with the values obtained by assuming no change in weathering rate (S set to ∞) in Table 4.

Quantification of processes leading to alkalinity production

For lakes lying in watersheds formed of carbonatic rocks, carbonate weathering accounts for nearly all the production of alkalinity, but in lakes with watersheds completely formed of acidic rocks, silicate weathering and nitrate uptake may play a major role.

To find out whether the above-mentioned processes can account for all the alkalinity production, we focused on nineteen lakes in the Maggia Valley, Switzerland, sampled five times during summer 1988. Since the valley is located only 10 km east of the atmospheric deposition sampling station of lake Toggia (Fig. 1), these lakes are suitable for a comparison between atmospheric deposition and lake chemistry. In order to

avoid episodic fluctuations, the ionic composition of each lake was obtained by choosing the median concentration of each solute. The Maggia Valley is one of the most acid-sensitive areas in the Alps, so these lakes are not representative of the whole set of lakes studied, lying as they do mainly on granitic bedrock: their alkalinity is below $50 \mu\text{eq l}^{-1}$, with a median value of $2 \mu\text{eq l}^{-1}$.

Table 5 shows a comparison between lake chemistry and atmospheric deposition, corrected for evapotranspiration by multiplying for the factor precipitation/runoff of 1.4 proposed for this area by Giovanoli *et al.* (1988).

On this basis, we calculated the alkalinity for each lake on the basis of the following assumptions:

- sulphate and sulphide production is of minor importance, as they produce less than $5 \mu\text{eq l}^{-1}$ of sulphate in 72% of the lakes;
- the alkalinity produced by in-lake processes is negligible;
- ammonium is completely oxidised to nitrate, producing two equivalents of acidity, or ammonium is in part taken up producing one equivalent: because of an equivalently lower uptake of nitrate, there is no variation in the resulting alkalinity production and the calculation is also valid for all intermediate situations;

Table 5. Comparison between atmospheric deposition and lake chemistry (unit: $\mu\text{eq l}^{-1}$), silica in $\mu\text{mol l}^{-1}$.

Variable	Bulk deposition	Deposition corrected	Lake range	Lake median
pH	4.88	-	4.82-6.73	5.86
H ⁺	13	18	0-15	1
T.A.	-13	-18	-15-49	2
NH ₄ ⁺	22	30	1-3	1
Ca ²⁺	20	28	38-92	55
Mg ²⁺	5	7	4-15	14
Na ⁺	5	7	8-24	14
K ⁺	2	3	3-13	6
SO ₄ ²⁻	33	46	31-60	50
NO ₃ ⁻	19	27	14-39	23
Cl ⁻	7	10	5-8	5
R. Si	0	0	16-52	28

- nitrate uptake from vegetation produces one equivalent of alkalinity;
- silica losses through sedimentation of diatoms are negligible, because oligotrophy and high runoff limit primary production, and pulses of low silica concentration caused by chrysophycean uptake were avoided during data screening;
- silicate minerals are weathered to gibbsite, producing alkalinity: alkalinity production can be evaluated from 0.6 equivalent (plus 0.08 equivalent of Ca) as calculated for rocks in the same area by Giovanoli *et al.* (1988) to 1 equivalent, as proposed by Zobrist *et al.* (1987). The first value was chosen because it provides a more prudent estimate of alkalinity production;
- the remaining increase in Ca is due to the weathering of calcite, which is present in small quantities, but highly soluble, and produces one equivalent of alkalinity;
- the apparent chloride sink is due to slight contamination of snow samples.

In each lake, alkalinity is then calculated as:

$$\begin{aligned} \text{Alk} = & -1.4 [\text{H}^+]_{\text{deposition}} + \\ & + (1.4 [\text{NO}_3^-]_{\text{deposition}} - [\text{NO}_3^-]_{\text{lake}}) - \\ & - (1.4 [\text{NH}_4^+]_{\text{deposition}} - [\text{NH}_4^+]_{\text{lake}}) + \\ & + 0.6 [\text{Si}]_{\text{lake}} + ([\text{Ca}^{++}]_{\text{lake}} - 0.08 [\text{Si}]_{\text{lake}} - \\ & - 1.4 [\text{Ca}^{++}]_{\text{deposition}}) \end{aligned}$$

The differences between observed and calculated alkalinities (Fig. 4) represent the alkalinity produced by other processes, such as ionic exchange, in-lake production, Mg-carbonate weathering and aluminium hydroxide dissolution. They range between -1 and $21 \mu\text{eq l}^{-1}$, with 90% of the values below $12 \mu\text{eq l}^{-1}$ (17% of the total alkalinity production). However, in two out of the 19 lakes, Lower and Upper Laghetto, unexplained alkalinity production reaches 21 and 27% respectively. They have longer renewal time (about one year) than typical values for Alpine lakes in this area (a few weeks): losses in silica caused by diatom sedimentation may therefore play an important role, causing an underestimate of silicate mineral

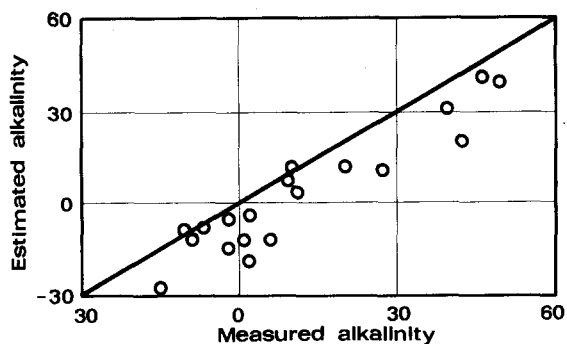


Fig. 4. Differences between measured alkalinity and the value calculated considering only watershed processes. Unit: $\mu\text{eq l}^{-1}$

weathering that may account for half of the unexplained alkalinity production.

The oxidation of the ammonium deriving from atmospheric deposition is an important source of acidity, and can contribute up to 62% of the acidifying capacity of deposition itself.

Conclusions

In spite of the episodic deposition of Saharian dust, Alpine lakes in the Southern Alps receive an atmospheric input of pollutants, mainly sulphate, nitrate and ammonium, which cause acidification processes. Along with acid loading, ammonium oxidation is an important source of lake acidity.

Calcite and silicate weathering and nitrogen uptake from vegetation are the main sources of alkalinity buffering the atmospheric acid loading. In carbonate watersheds, weathering is the main source of alkalinity, but calcite weathering is also present in acidic watersheds and watershed alkalinity production accounts typically for 89% or more of the total production. However, in some lakes other processes may contribute up to 27% of the alkalinity.

The alkalinity produced is not enough to avoid acidification processes, as 11 lakes show summer pH of below 5.3 and 18% of the pH values measured were lower than 6.0. In front of a deposition potential acidity of $57 \mu\text{eq l}^{-1}$, summer acidification levels of below $60 \mu\text{eq l}^{-1}$ were calculated for acid-sensitive lakes using a titration model

with variable F-factor with median values ranging from 18 to $32 \mu\text{eq l}^{-1}$, depending on parameter setting.

References

- Barbieri, A. & G. Righetti, 1987. Chimica delle deposizioni atmosferiche nel Cantone Ticino ed effetti sulle acque dei laghi alpini d'alta quota. *Documenta Ist. ital. Idrobiol.* 14: 19-34.
- Baker, J. P. & C. L. Schofield, 1982. Aluminium toxicity to fish in acidic waters. *Wat. Air Soil Pollut.* 18: 289-309.
- Brakke, D. F., A. Henriksen & S. A. Norton, 1990. A variable F-factor to explain changes in base cation concentrations as a function of strong acid deposition. *Verh. int. Ver. Limnol.* 24: 146-149.
- Carollo, A., F. Contardi, V. Libera & A. Rolla, 1985. Hydroclimatic cartography of the Lake Maggiore drainage basin. *Mem. Ist. ital. Idrobiol.* 42: 1-4.
- Giovanoli, R., J. L. Schnoor, L. Sigg, W. Stumm & J. Zobrist, 1988. Chemical weathering of crystalline rocks in the catchment area of acidic Ticino lakes, Switzerland. *Clays and Clay Minerals* 36: 521-529.
- Goldstein, R. A. & S. A. Gherini (eds), 1984. The integrated lake-watershed acidification study. Report EPRI EA-3221.
- Gruppo di Studio, 1987. Depositioni atmosferiche nel Nord Italia. Rapporto finale anni 1983-84. *Quaderni Ingegneria Ambientale* 6: 5-63.
- Henriksen, A., 1980. Acidification of freshwater. A large scale titration. In D. Drablos and Tollan, A. (eds), *Proc. Int. Conf. on Ecol. Impact of Acid Precipitation*. As, Norway: 68-74.
- Mosello, R., 1984. Hydrochemistry of high altitude alpine lakes. *Schweiz. Z. Hydrol.* 46: 86-99.
- Mosello, R., A. Marchetto, G. A. Tartari & L. Guzzi, 1988. Acidificazione e acidificabilità delle acque lacustri italiane. *Documenta Ist. ital. Idrobiol.* 15: 1-80.
- Mosello, R., A. Marchetto, G. A. Tartari, M. Bovio & P. Castello, 1991. Chemistry of Alpine lakes in Aosta Valley (N. Italy) in relation to watershed characteristics and acid deposition. *Ambio* 20: 7-12.
- Psenner, R., K. Arzet, A. Brugger, J. Franzoi, F. Heisberger, W. Honsig-Erlenburg, F. Horner, U. Nickus, P. Pfister, P. Schaber & F. Zapf, 1988. Versauerung von Hockgebirgsseen in Kristallinen Einzugsgebieten Tirols und Kaerntens. *Bundesministerium fuer Land- und Forstwirtschaft, Wien*, 335 pp.
- Psenner, R. & F. Zapf, 1990. High mountain lakes in the Alps: peculiarity and biology. In: M. Johannessen, R. Mosello and H. Barth (eds), *Acidification processes in remote mountain lakes*. Guyot, Brussels: 22-38.
- Sullivan, T. J., D. F. Charles, J. P. Smol, B. F. Cumming, A. R. Selle, D. R. Thomas, J. A. Bernert & S. S. Dixit, 1990. Quantification of changes in lakewater chemistry in response to acidic deposition. *Nature* 345: 54-58.
- Wright, R. F., 1983. Predicting acidification of North American lakes. EPA, Corvallis, Oregon: 165 pp.
- Zobrist, J., Sigg, L., Schnoor, J. L. & W. Stumm, 1987. Buffering mechanism in acidified Alpine lakes. In: Barth, H. (ed.), *Reversibility of acidification*. Elsevier, London: 95-103.