Journal of Paleolimnology 15: 245–264, 1996.

The environmental history of a mountain lake (Lago Paione Superiore, Central Alps, Italy) for the last *c.* 100 years: a multidisciplinary, palaeolimnological study

P. Guilizzoni[1], A. Marchetto[1], A. Lami[1], N. G. Cameron[2], P. G. Appleby[3], N. L. Rose[2], Ø. A. Schnell[4], C. A. Belis[5], A. Giorgis[1] & L. Guzzi[6]
[1]*C.N.R. Istituto Italiano di Idrobiologia, 28048 Verbania, Pallanza, Italy*
[2]*Environmental Change Research Unit, Dept. of Geography, University College London, 26, Bedford Way, London WC1H 0AP, UK*
[3]*Dept. of Applied Mathematics and Theoretical Physics, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK*
[4]*Zoologisk Institutt, University of Bergen, Allégt 41, N-5007 Bergen, Norway*
[5]*Instituto de Limnologia 'Dr R. A. Ringuelet', CC 712, 1900 La Plata, Argentina*
[6]*ENEL-CRAM, Via Rubattino 54, 20134 Milan, Italy*

Received 20 February 1995; accepted 7 August 1995

Key words: palaeolimnology, acidification, diatoms, chrysophytes, pigments, chironomids, temperature, Alps, Italy

Abstract

A palaeoecological study of an oligotrophic alpine lake, Paione Superiore (Italy), provided a record of historical changes in water quality. Historical trends in lake acidification were reconstructed by means of calibration and regression equations from diatoms, chrysophycean scales and pigment ratios. The historical pH was inferred by using two different diatom calibration data sets, one specific to the alpine region. These pH trends, together with the record of sedimentary carbonaceous particles and chironomid remains, indicate a recent acidification of this low alkalinity lake.

Concentration of total organic matter, organic carbon, nitrogen, biogenic silica ($BSiO_2$), chlorophyll derivatives (CD), fucoxanthin, diatom cell concentration and number of chironomid head capsules increased during the last 2–3 decades. When expressed as accumulation rates, most of these parameters tended to decrease from the past century to *c.* 1950, then all except P increased to the present day. A marked increase in sedimentary nitrogen may be related to atmospheric pollution and to the general increases in output of N in Europe. High C/N ratios indicate a prevailing allochthonous source of organic matter.

Finally, the increase in measured air temperature from the mid-1800's appeared to be related to lake water pH before industrialization: cold periods generally led to lower pH and *vice-versa*. The more recent phenomenon of anthropogenic acidification has apparently decoupled this climatic-water chemistry relationship.

Introduction

High altitude lakes are particularly sensitive to acidification and their acidification has been widely studied in Europe and North America (Battarbee & Charles, 1986; Mosello *et al.*, 1992a; Charles *et al.*, 1989 and 1990; Fott, 1994). Following the success of the palaeolimnological approach in the study of acid lakes, the analysis of lake sediment cores became one of the main objectives of the AL:PE programme (*Acidification of Mountain lakes: Palaeolimnology and Ecology*, a project supported by the Commission of the European Community; Wathne & Patrick, 1994), of which the present study is one part. The aims of this paper are to assess the degree of atmospheric contamination by analyzing carbonaceous particles in lake sediments and to determine the extent of acidification from photosynthetic pigment ratios and from the remains of diatoms,

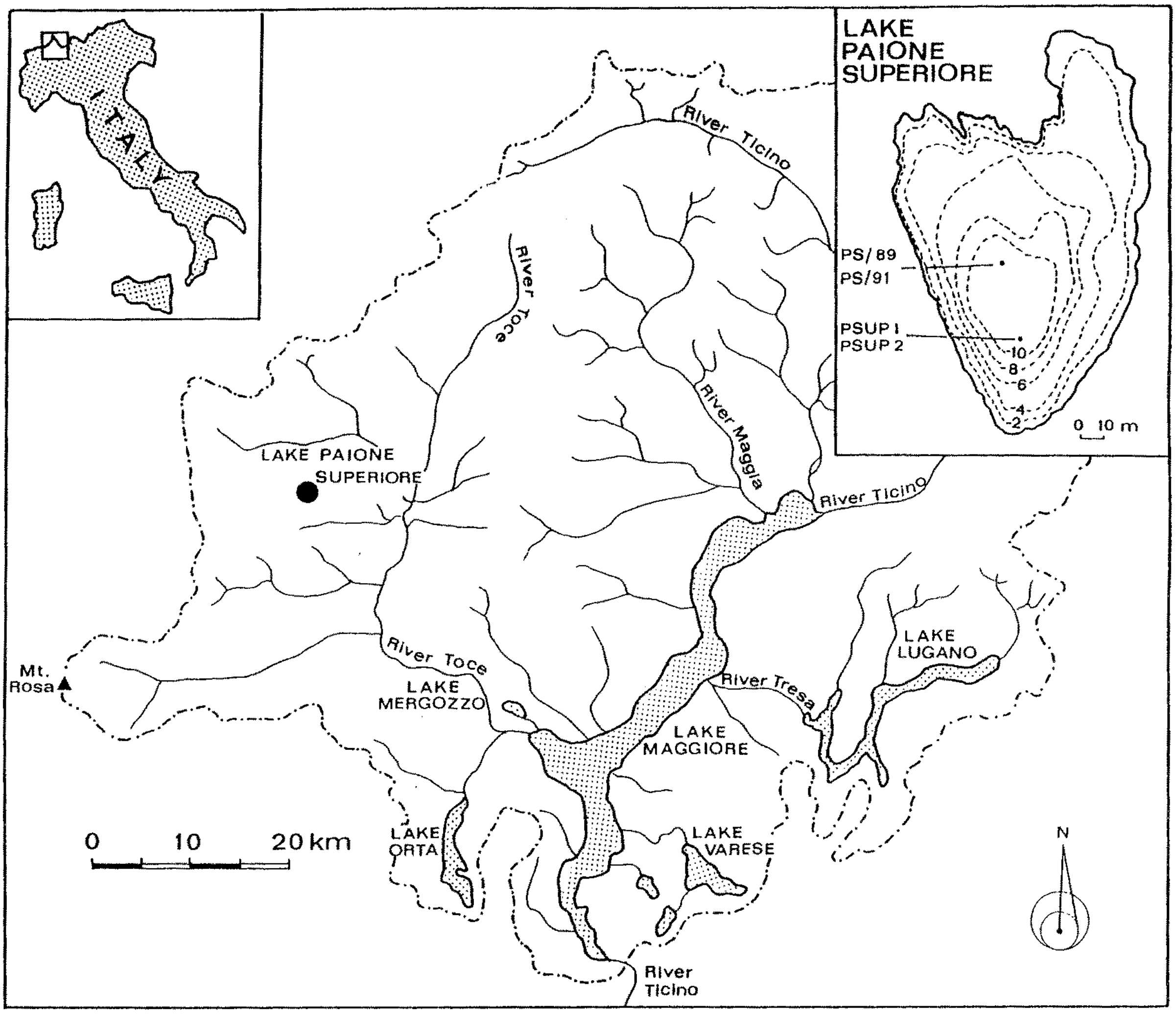

Fig. 1. Location and bathymetric map (showing approximate sampling points) of the alpine lake, Lago Paione Superiore in the watershed of Lago Maggiore.

chrysophytes and chironomids. In addition, this assessment establishes baseline conditions for the long-term evaluation of major changes in trophic state, productivity, as well as climatic change, and to attempt to interpret the most important causative processes. This particular study takes advantage of the fact that two teams of researchers sampled and analysed cores from the same lake relatively independently, and from several points-of-view. Thus, comparison of the historical reconstructions allows us to assess the similarities and differences that result from different palaeolimnological techniques and laboratories.

Site description

Lago Paione Superiore, (2269 m a.s.l; Fig. 1), is located above the timberline. By selecting this remote lake it was hoped that any direct influence of human activity on the catchment and on water quality would be minimal. However, precipitation to the lake is acidic and relatively rich in sulphate, nitrate and ammonium (Mosello *et al.*, 1993a). The first limnological study of Lago Paione Superiore was published in 1947 (Tonolli, 1947). More recent investigations have been mainly concerned with water chemistry (Mosello, 1984; Pugnetti *et al.*, 1993; Mosello *et al.*, 1993a). Some of the main morphometric characteristics of the lake are given in Table 1. The lake was clear and the bottom

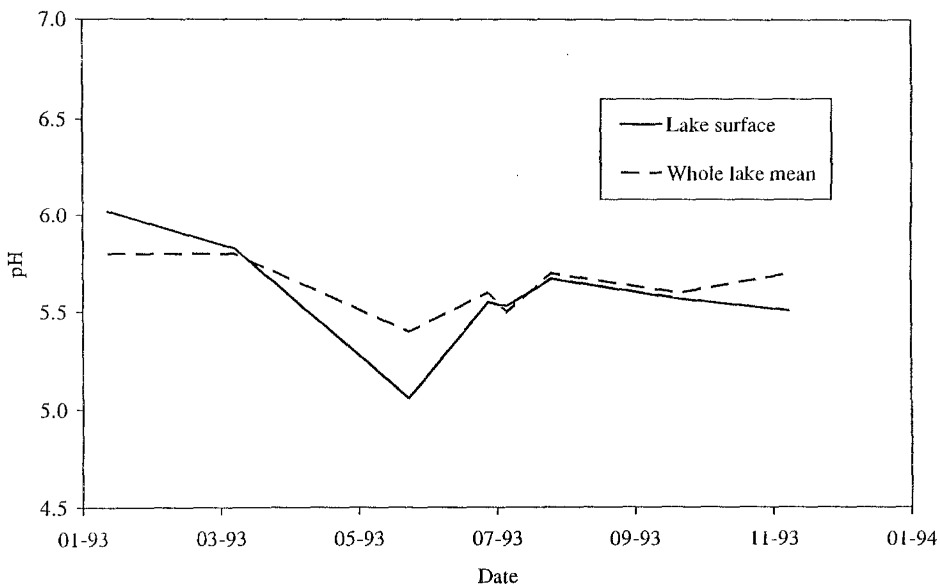

Fig. 2. Seasonal variation of pH values in Lago Paione Superiore (redrawn from Mosello *et al.*, 1994b).

is always visible, even at the point of maximum depth (11.7 m). From July 1991 to October 1992 twelve samplings were performed, also during the *c.* 9 months of ice cover. Lake water samples were collected at the maximum depth at 0, 2.5, 5, 10 m. Ionic composition of the lake is dominated by sulphate, nitrate, calcium and ammonium (Table 1). Total and reactive phosphorus concentrations are very low ($<3\ \mu g\ l^{-1}$). Carbonate buffering is poor, as alkalinity ranges between -2 and $2\ \mu eq\ l^{-1}$, and the lake is slightly acid (Table 1). Seasonal variability in lake pH (measured in the laboratory) is evident (Fig. 2). From 1992 up to the present day, chemical water characteristics are not changed significantly (Mosello, pers. com.). The watershed bedrock consists of clear-banded orthogneisses and grey gneisses with potassium feldspar and epidote. Land cover, mainly hay meadows, is restricted to small areas. Additional characteristics of the catchment area (lithology, vegetation cover, etc.) are reported elsewhere (Mosello *et al.*, 1993a and 1994a).

The structure of biological communities is simple (Pugnetti *et al.*, 1993). There are no fish, and phytoplanktonic species are few and small and typical of acidic lakes. The dominant taxa are Chrysophyceae and Peridineae, *Chromulina* sp. and *Mallomonas alveolata* dominate under the ice, and *Gymnodinium* spp. in summer. Nannoplanktonic flagellates dominate the plankton and their biomass is low. Copepods (*Cyclops abyssorum*) and rotifers dominate the zooplankton under the ice, whereas in summer *Daphnia longispina* is the most important species. The littoral macrozoobenthos is composed mainly of Chironomidae (*Zavrelimyia*, *Heterotrissocladius*, *Micropsectra* and *Paratanytarsus*) and Oligochaeta (Families Enchytraeidae and Lumbriculidae; Pugnetti *et al.*, 1993; Schnell *et al.*, 1994).

Materials and methods

Four sediment cores were collected between 1989 and 1991, using two types of gravity corers (a modified 4.5 cm diameter Kajak corer and a 6 cm diameter gravity corer). These cores were labelled as PS/89 (core recovery: 16 cm), PSUP1 (21 cm), PSUP2 (19 cm) and were extruded on site. For cores PSUP1 and PSUP2 an apparatus that allowed fine slicing (0.25 cm) was used (Glew, 1988). A fourth core, named PS/91 (35 cm), was collected in 1991, and cut longitudinally in the laboratory, dated, and used for additional analyses, such as, for example, stratigraphic descriptions (Fig. 3). Slicing at intervals of 1 cm was performed for this core and for core PS/89. These two cores were collected in a restricted area close to the deepest point of the lake and were analyzed in Italy, while cores PSUP1 and PSUP2 were collected in the southern part of the deepest area (Fig. 1) and were analyzed in England.

Wet densities were measured by filling a 2 cm^3 weighed brass vial with a subsample of homogenized sediment. Dry weights were determined by placing 1–

Table 1. Main geographic, morphometric and chemical (volume weighted mean concentrations in 1991 and 1992) characteristics of Lago Paione Superiore. Mean water temperature is also indicated (after Mosello *et al.*, 1993)

Location and morphometry		
Longitude	08°11′26″ E	
Latitude	46°10′39″ N	
Altitude	2269 m	
Max watershed altitude	2661 m	
Lake surface (a)	0.86 ha	
Watershed surface (b)	50 ha	
Ratio b/a	58.1	
Max depth	11.7m	
Mean depth	5.1 m	
Volume	0.04 $m^3 \times 10^6$	
Retention time	33 d	
Annual precipitation	1400 mm	
Water chemistry and temperature		
	Mean	Range
Dissolved oxygen (mg l^{-1})	9.8	8.2–11.4
Dissolved oxygen (% sat.)	88	76–108
pH	5.66	5.48–6.20
Conductivity (μs cm^{-1} 18°C)	9.2	8.0–9.8
Calcium (μeq l^{-1})	43	33–48
Magnesium (μeq l^{-1})	8	5–9
Sodium (μeq l^{-1})	9	6–12
Potassium (μeq l^{-1})	7	5–9
Ammonium (μeq l^{-1})	3	0–6
Σ cations	73	55–82
Alkalinity (μeq l^{-1})	0	(-2)–2
Sulphate (μeq l^{-1})	41	35–48
Nitrate (μeq l^{-1})	23	19–27
Chloride (μeq l^{-1})	4	3–5
Σ anions	70	64–74
Total Aluminium (μeq l^{-1})	42	23–43
Fluoride (μeq l^{-1})	7.3	7.0–7.7
Reactive Si (mg l^{-1})	0.43	0.77–0.87
Temperature (°C)	6.6	1.0–15.0

Reactive and total phosphorus was always below the detection limit of 3 μg P l^{-1}.

Table 2. List of diatom and scaled chrysophyte taxa found in the sediment core (PS/89) of Lago Paione Superiore. R = rare

Diatoms following Krammer & Lange-Bertalot (1986-91)	
Achnanthes curtissima Carter 1963	
Achnanthes didyma Hustedt 1933	
Achnanthes helvetica Lange-Bertalot & Krammer 1989	
Achnanthes helvetica fo *minor* Flower & Jones 1989	
Achnanthes helvetica var *alpina* Flower & Jones 1989	
Achnanthes marginulata Cleve & Grunow 1880	
Achnanthes marginulata fo *major* Flower & Jones 1989	
Achnanthes minutissima Kuetzing 1833	
Achnanthes scotica Flower & Jones 1989	
Anomoeoneis brachysira Grunow in Cleve 1895	
Anomoeoneis vitrea (Grunow) Ross 1966	
Aulacoseira alpigena Krammer 1990	
Aulacoseira distans (Ehrenberg) Simomsen 1979	
Aulacoseira distans var *nivalis* (W. Smith) Haworth 1988	
Aulacoseira lirata (Ehrenberg) Ross 1986	
Aulacoseira nygaardii Camburn & Kingston 1986	
Aulacoseira pfaffiana (Reinsch) Krammer 1990	
Aulacoseira valida (Grunow) Krammer 1990	
Caloneis bacillum (Grunow) Cleve 1894	
Cocconeis placentula Ehrenberg 1838	R
Cyclotella comensis Grunow in Van Heurck 1882	R
Cyclotella planctonica Brunnthaler 1901	R
Cymbella cuspidata Kuetzing 1844	R
Cymbella gaeumannii Meister 1934	
Cymbella gracilis (Ehrenberg 1843) Kuetzing 1844	
Cymbella hebridica (Grunow ex Cleve) Cleve 1894	R
Cymbella helvetica Kuetzing 1844	R
Cymbella silesiaca Bleisch in Rabenhorst 1864	
Denticula tenuis Kuetzing 1844	R
Diatoma hyemalis (Roth) Heiberg 1863	R
Diatoma mesodon (Ehrenberg) Kuetzing 1844	
Eunotia bilunaris (Ehrenberg) Mills 1934	
Eunotia exigua (Brebisson ex Kuetzing) Rabenhorst 1864	
Eunotia paludosa Grunow 1862	
Eunotia rhomboidea Hustedt 1950	R

2 g of wet sediment in a weighed crucible and drying to constant weight overnight at 105 °C. Loss-on-ignition (LOI) was measured after placing the crucible in a muffle furnace at 550 °C. Approximately 25 mg of dry sediment were used for biogenic silica ($BSiO_2$) analysis (Demaster, 1981). Total carbon and nitrogen were determined on dry sediment using a CHN analyzer (Carlo Erba). Inorganic and total phosphorus was extracted with sulfuric acid (1N) (Vogler, 1965; Marengo & Baudo, 1988) and then analyzed for reactive P, after Murphy & Riley (1962). Organic P was obtained by the difference between total P and inorganic P. Unfortunately, because of insufficient material in the topmost sample of core PS/89, P analyses were

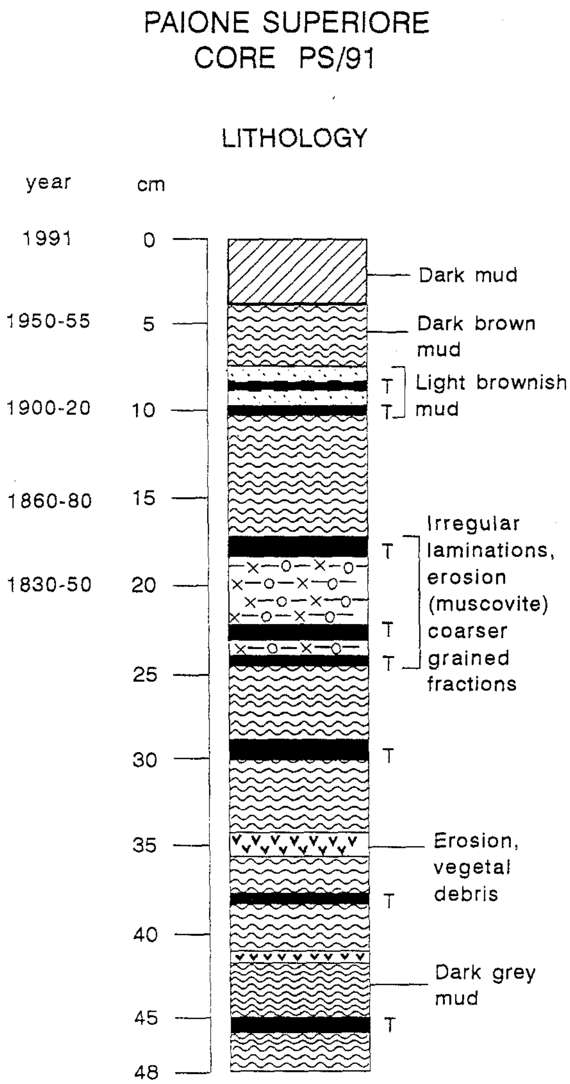

Fig. 3. Schematic reproduction of a sediment core of Lago Paione Superiore collected in 1991. T = turbidite.

not performed. Chlorophyll derivatives (CD) and total carotenoids (TC) were extracted with 90% acetone and expressed as in Guilizzoni *et al.* (1983) and Züllig (1982), respectively. Single algal pigments were determined by ion-pairing, reverse-phase HPLC (modified from Mantoura & Llewellyn, 1983; Lami *et al.*, 1994a and b), using a Beckman System Gold instrument.

Carbonaceous particles derived from fossil fuel combustion were analyzed following Rose (1990) and Renberg & Wik (1985).

Preparation and counting of diatoms and chrysophycean scales from sediment cores followed standard procedures (Battarbee, 1986; Marchetto & Lami, 1994). Cleaned diatoms were separately identified and counted by both the English Group in London and the Italian Group in Pallanza, under oil immersion at 1000 or 1200 × with phase contrast illumination. Chrysophycean scales were identified and enumerated at magnifications of 10 000 and 2400 ×, respectively, using a scanning electron microscope (Philips SEM E505). An average of 600 frustules and 400 scales was counted in each sediment section.

Chironomid head capsules were picked directly from fresh sediments mixed with water. No chemical treatment or sieving was applied (Schnell & Raddum, 1993).

Diatoms were used to reconstruct the pH history of the lake by weighted averaging with extra-regression (ter Braak, 1987) using the SWAP (Surface Water Acidification Programme) calibration data set developed from 178 lakes (Stevenson *et al.*, 1991) and a specific data set for the alpine region (31 high mountain lakes; Marchetto & Schmidt, 1993), here referred as the ALPS data set. Reconstruction of pH values used chrysophycean scales (Marchetto & Lami, 1994) and a new method based on algal pigment ratios (Guilizzoni *et al.*, 1992). Root mean square error of the prediction was obtained using the bootstraping technique described by Birks *et al.* (1990).

Using similar methods, radiometric analyses (Appleby *et al.*, 1986) were performed for ^{210}Pb, ^{137}Cs, ^{226}Ra and ^{241}Am at the University of Liverpool, and at the ENEL-CRTN laboratory in Milan, for cores PSUP1 and PS/91, respectively.

The dates reported in the lowest part of the cores were obtained extrapolating the oldest measured sedimentation rates.

Results

Dating

^{210}Pb chronologies were calculated using both the CRS and CIC models (Appleby & Oldfield, 1978). Dilutions of the atmospheric flux of ^{210}Pb activity violate the assumptions of the CIC model, and the ^{210}Pb dates have accordingly been based primarily on the CRS model. Significant differences between the two occur, however, only in sediments prior to 1960.

Down to a depth of *c.* 3 cm (dated to *c.* 1960), the results from two cores (PS/91 and PSUP1) agree relatively well, indicating a more or less constant sediment accumulation rate of 0.022–0.027 g cm^{-2} y^{-1} (0.120–0.043 cm y^{-1}). For the section of the cores from 3 cm

Table 2. Continued

Fragilaria capucina var *mesolepta* (Rabenhorst) Rabenhorst 1864	
Fragilaria capucina var *rumpens* (Kuetzing) Lange-Bertalot 1991	R
Fragilaria construens (Ehrenberg) Grunow 1862	R
Fragilaria construens fo *venter* (Ehrenberg) Hustedt 1957	R
Fragilaria pinnata Ehrenberg 1843	R
Frustulia rhomboides (Ehrenberg) De Toni 1891	
Gomphonema gracile Ehrenberg 1838	R
Gomphonema parvulum (Kuetzing) Kuetzing 1849	R
Navicula angusta Grunow 1860	R
Navicula cryptocephala Kuetzing 1844	
Navicula cuspidata (Kuetzing) Kuetzing 1844	R
Navicula digitulus Hustedt 1943	R
Navicula festiva Krasske 1925	R
Navicula gallica (W. Smith) Lagerstedt 1873 var *perpusilla* (Grunow) Lange-Bertalot 1985	
Navicula schmassmannii Hustedt 1943	R
Navicula seminulum Grunow 1860	
Navicula subminuscola Manguin 1941	
Navicula submolesta Hustedt 1949	R
Neidium affine (Ehrenberg) Pfitzer 1871	
Neidium alpinum Hustedt 1943	
Pinnularia interrupta W. Smith 1853	R
Pinnularia divergentissima (Grunow) Cleve 1895	R
Pinnularia microstauron (Ehrenberg) Cleve 1891	
Pinnularia viridis (Nitzsch) Ehrenberg 1843	
Stauroneis anceps Ehrenberg 1843	
Stauroneis legumen (Ehrenberg) Kuetzing 1844	
Stauroneis obtusa Lagerstedt 1873	
Stenopterobia curvula (W. Smith) Krammer 1987	R
Stenopterobia delicatissima (Lewis) Brebisson 1986	
Surirella linearis W. Smith 1853	
Surirella roba Leclercq 1983	
Tabellaria flocculosa (Roth) Kuetzing 1844	
Scaled chrysophytes following Asmund & Kristiansen (1985)	
Mallomonas actinoloma Takahashi 1969 var *maramuresensis* Peterfi and Momeu 1976	
Mallomonas alveolata Duerrschmidt 1983	
Mallomonas crassisquama (Asmund) Fott 1962	
Mallomonas flora Harris and Bradley 1960 var *palermii* Vigna 1981	

down to the deepest layers, the calculations suggest a significantly lower accumulation rate (0.016 ± 0.002 g cm^{-2} y^{-1}; 0.017–0.050 cm y^{-1}) in one core (PSUP1), compared to the other (0.05–0.07 g cm^{-2} y^{-1}, 0.100–0.140 cm y^{-1}, core PS/91; Guilizzoni *et al.*, 1992). The transition to higher sedimentation rates *c.* 1960 appears to be very abrupt, and as a consequence, CIC model dates beneath this level are significantly younger than those given by the CRS model. Accumulation rates prior to 1900 are difficult to assess, but appear to be typical of those for the period 1920–1960. These differences may only reflect differences in sampling. The cores were taken from somewhat different locations in the lakes, with different corers and, most importantly, were subsampled (sliced) with different techniques.

In spite of the different sedimentation rates obtained, integrated total activities were similar in the first seven slices of PSUP91 (25.8 pCi cm^{-3}) and PS/91 (26.3 pCi cm^{-3}). The ^{137}Cs record is dominated by very heavy fallout from the 1986 Chernobyl accident. The activity of this radionuclide in the near-surface sediments are two orders of magnitude higher than those from weapons test fallout. Because of this large disparity, the ^{134}Cs record (which reflects Chernobyl fallout alone) could not accurately partition ^{137}Cs into its Chernobyl and weapons test components. As a consequence, the depth recording the 1963 weapons fallout peak could not be determined. However, the ^{210}Pb chronology and the small peak in ^{241}Am activity (also a fallout product from nuclear weapons testing; Appleby *et al.*, 1991) observed at a depth of about 2 cm, in core PSUP1, suggest that the 1963 level should occur at this depth of the core.

Lithostratigraphy and geochemistry

All the cores consisted of dark (brownish) mud with mineral particles (some of muscovite, mostly <1 mm diameter) and irregular bands of lighter coloured mud (turbidites) (Fig. 3). When visible (e.g. in core PS/91) turbidites were not sampled to avoid contamination of undisturbed pelagic sediments with redeposited material. Towards the surface, the sequence graded into a darker sediment. Overall the cores have a high mineral content, reflected by high percentage dry weight values (25–64% w.w.) and variable LOI values (4–18% d.w.; Fig. 4). Wet density and percentage dry weight tend to decline towards the surface, reaching minima of 1.19 g cm^3 and 26%, respectively. Percentage LOI increases to a maximum of 13–15% at the sediment surface. A maximum value of 18% d.w. was found at the 5 cm level in core PS/91. The high mineral content of the sediments and spiky density and dry weight profiles of the cores (with reduced LOI values) indicate that a considerable proportion of the sediment material is derived from the lake catchment (see also the C:N ratio). Due to the very low calcium content of the minerogenic inwash of weathered rocks, the buffering capacity of the lake water does not increase.

From the base of the core PS/89 to 5–6 cm, the $BSiO_2$ profile is relatively stable at *c.* 1-5 mg g $d.w.^{-1}$ (Fig. 5). From 6 cm (mid 1940) to the surface (1989), there is a rapid and regular increase in biogenic silica concentration and accumulation rate (Fig. 5). This is consistent with a recent increase in diatom cell concentration (cf. Fig. 10) and in fucoxanthin (cf. Fig. 12), a carotenoid which is characteristic of all diatoms and chrysophytes. An increase in accumulation rates of $BSiO_2$ after 1930 is also evident from changes in the ratios $BSiO_2$:TP and $BSiO_2$:TN (Fig. 6). In sediments deposited after 1940 (above 6 cm), the $BSiO_2$:TP ratio ranged from 12 to 30, whereas in the sediments below 6 cm the ratio averaged 5.

The nutrient concentrations (i.e. carbon, nitrogen and phosphorus), show a decreasing trend from the base of the core up to 6 cm, then a slight increase, particularly in nitrogen (surface N concentration of 1% d.w.; Fig. 5). Total N is essentially organic N, since inorganic N was negligible.

The three species of phosphorus show similar profiles with higher values in the oldest layers of the core (max. values of TP *c.*1180 $\mu g\ g^{-1}$ d.w.; Fig. 5). A marked decrease in concentration is evident from the bottom of the core (1050 $\mu g\ g^{-1}$ d.w.) to about 6 cm (*c.* 680 $\mu g\ g^{-1}$ d.w.); then an increase towards the surface is observed (*c.* 900 $\mu g\ g^{-1}$ d.w. as TP). A large part of the total P is in the inorganic form (cf. Fig. 5).

In the lower part of the core (from 15 to 5 cm), the mass TN:TP ratios are rather constant and close to those found in oligotrophic lakes (2–3; Fukushima *et al.*, 1991). In the uppermost layers, the ratio increases to over 4 at the surface sediments (Fig. 6). However, with the exception of N in the upmost six sections of the core, which probably reflects recent atmospheric input of nitrogen compounds, the accumulation rates of nutrients show a steady decrease (0.07–0.02 mg TP $cm^{-2}\ y^{-1}$) from the mid 1800 A.D. to the present day.

Atomic nutrient ratios calculated for organic carbon, total nitrogen, total phosphorus and biogenic silica, also demonstrate consistent general patterns in the sediments (Fig. 6). Each ratio was relatively constant below 6–8 cm and then, except for C:N, increased markedly in the more recent sediments. The $BSiO_2$:TN and $BSiO_2$:TP increased especially after 1940, indicating that less N and P were stored relative to $BSiO_2$ than in other periods. The values of the C:N ratio suggest that the organic material is largely allochthonous, except for the top 0–1 cm (Fig. 6) (Meyers, 1994). A better grasp of nutrient inputs to the lake can be obtained from other sedimentary records, such as algal pigments and chironomid remains (see below).

Carbonaceous particles

High concentrations of carbonaceous particles (CP) do not occur before 1940–1950. In the case of the PSUP1

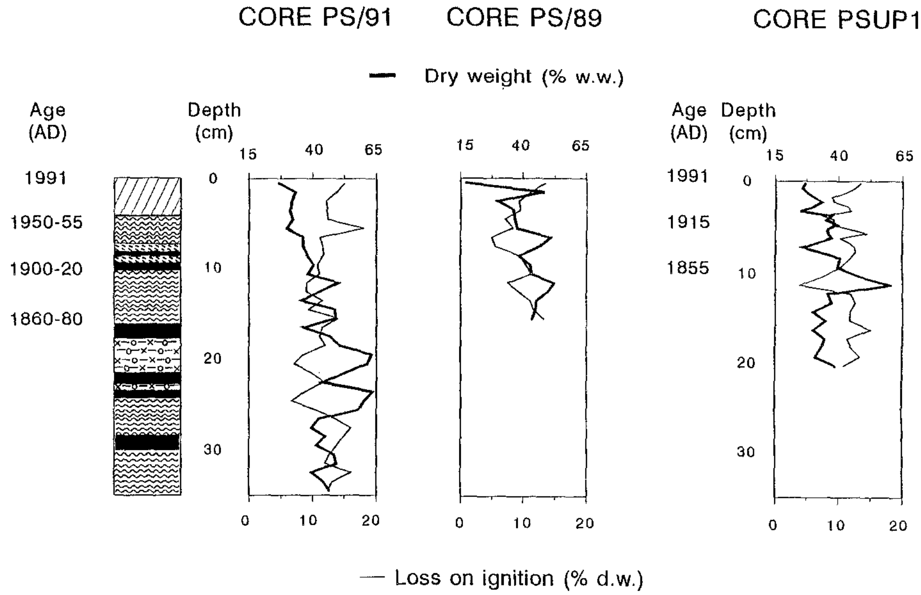

Fig. 4. Dry weight (DW) and organic matter (loss on ignition, LOI) of three sediment cores from Lago Paione Superiore (PS/89, PS/91 and PSUP1). A schematic reproduction of core PS/91 only, is also reported.

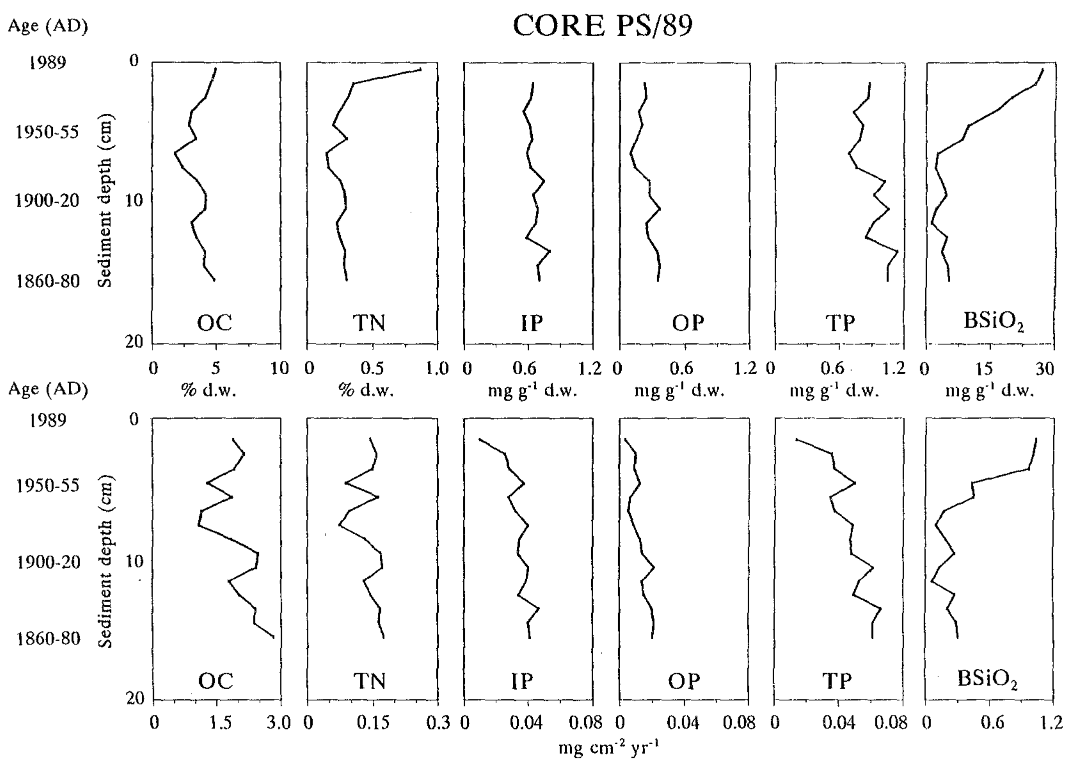

Fig. 5. Sediment sequence of nutrients concentrations (top) and accumulation rates (bottom) in Lago Paione Superiore (OC = organic carbon; ON = organic nitrogen; IP = inorganic phosphorus; OP = organic phosphorus; TP = total phosphorus; $BSiO_2$ = biogenic silica).

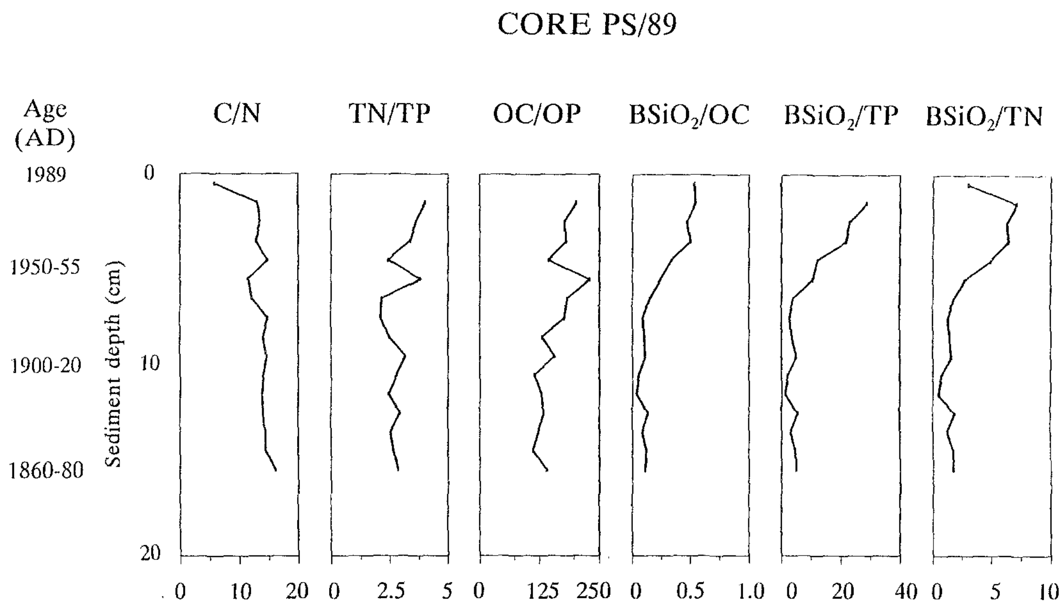

Fig. 6. Atomic nutrient ratios in sediment core PS/89 from Lago Paione Superiore.

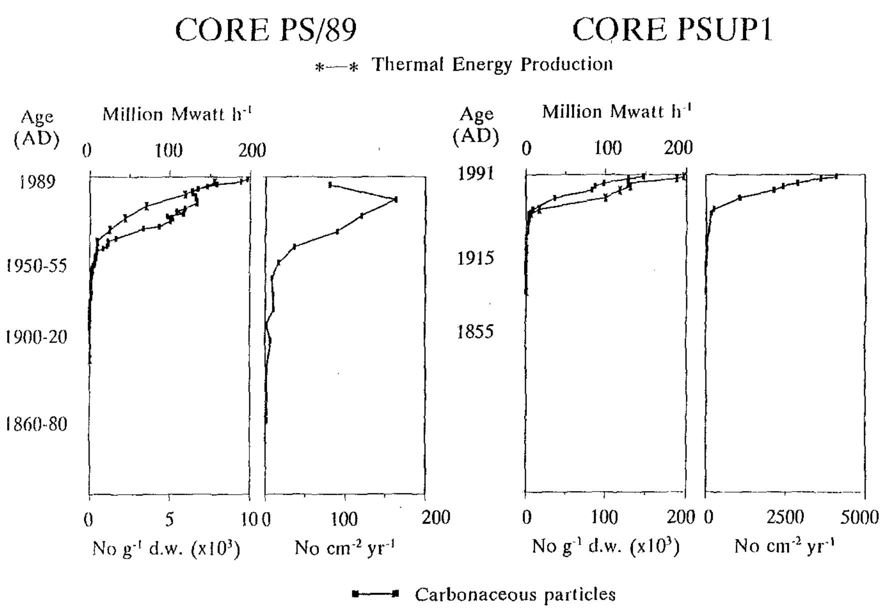

Fig. 7. Carbonaceous particle concentrations and accumulation rates in two sediment cores (PS/89 and PSUP1) from Lago Paione Superiore. Thermal energy production for Italy is also indicated.

core, CP appear around 1900 and increase in concentration throughout the core, although this increase is rapid only after 1950–60 (Fig. 7). The surface accumulation rate of *c.* 4000 CP cm^{-2} yr^{-1} found in PSUP1 is similar to the highest accumulation rates observed in the UK (Battarbee *et al.*, 1988). The surface concentrations are extremely variable, from *c.* 10000 g $d.w.^{-1}$ to 150000 g d.w.-1; however, the two cores, taken in 1989 and 1991, show similar trends (Fig. 7). There is no surface decline in either concentration or accumulation rate. The CP profile is very similar to the record of fossil-fuel combustion for Italy (United Nations energy statistics data 1991). The difference in absolute density of particles might be mainly explained by the lower

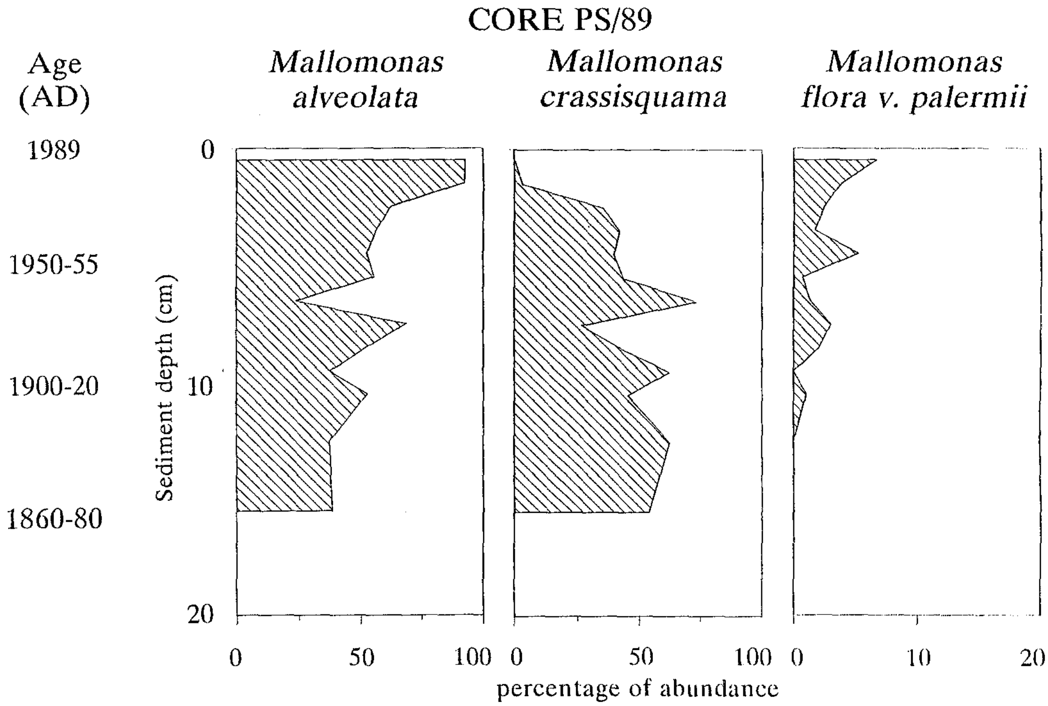

Fig. 8. Percentage of the dominant chrysophycean scales in a sediment core (PS/89) for Lago Paione Superiore (after Marchetto & Lami, 1994).

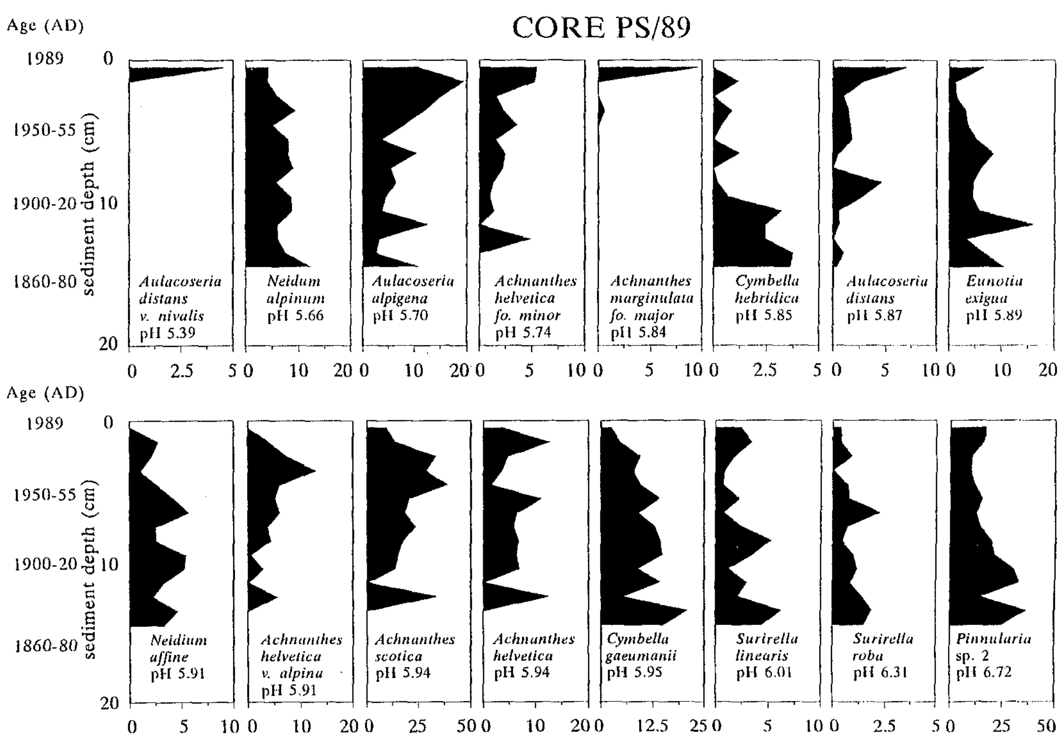

Fig. 9. Percentage of dominant diatom taxa (listed in increasing order of optimum of pH) in a sediment core (PS/89) for Lago Paione Superiore.

Table 3. The chironomid taxa found in a sediment core (PSUP 2) from Lago Paione Superiore

Depth in core (cm)	19.0–17.0	10.0–9.0	5.5–5.0	3.75–3.5	3.5–3.25	3.0–2.75	2.25–2.0	1.0–0.0
No. specimens	302	177	118	48	70	58	72	550
No. taxa	12	6	8	5	8	5	8	10
cm	2.00	1.00	0.50	0.25	0.25	0.25	0.25	1.00
Species cm^{-1}	151	177	236	196	280	232	288	550
Bryophaenocladius sp.	1	1	2	0	0	0	1	0
Chaetocladius sp.	1	1	0	0	0	0	0	0
Diamesa sp.	2	0	0	0	0	0	0	0
Heterotrissocladius marcidus (Walker)	15	4	3	4	2	1	5	65
Heterotrissocladius indet.	0	0	0	0	1	0	0	0
Limnophyes sp.	1	0	2	0	0	0	0	1
Micropsectraradialis Goetghebuer	261	161	95	31	42	37	36	180
Micropsectra indet.	3	0	0	0	0	0	1	3
Paratrichocladius sp.	1	0	1	0	0	0	1	0
Procladius sp.	13	9	5	4	7	5	2	17
Protanypus sp.	0	0	0	0	0	0	0	1
Pseudosmiffia sp.	2	0	4	2	2	1	1	2
Tanytarsus sp. A (norvegicus-group)	1	1	6	7	14	14	25	277
Zavrelimyia cf. *barbatipes* (Kieffer)	0	0	0	0	1	0	0	3
Orthocladiinae indet.	1	0	0	0	1	0	0	1

magnification used for counting the PS/89 that led to an underestimation of the smaller spherules (<10 μm), which were by far the most abundant particles in the samples.

Chrysophycean scales

In the acid Lago Paione Superiore, the most common chrysophycean scales belong to small forms, *Mallomonas alveolata* Dürrschmidt and the globally distributed species, *M. crassisquama* (Asmund) Fott. The latter are present at higher percentages in deeper sediment layers (Fig. 8). In other circumneutral lakes investigated (Marchetto & Lami, 1994), the dominant species was *Mallomonas crassisquama*, whereas *M. acaroides* var. *acaroides* and *M. alpina* dominated in alkaline lakes. A list of the taxa found in sediment core PS/89 is presented in Table 2.

Inferred pH values derived from weighted averaging with extra regression method (ter Braak, 1987) are lower in the upper four sections of the core, indicating some recent acidification (cf. Fig. 11; Guilizzoni *et al.*, 1993; Marchetto & Lami, 1994). The point-of-change of the pH profile was evaluated statistically using a maximum likelihood procedure (Esterby & Shaarawi,

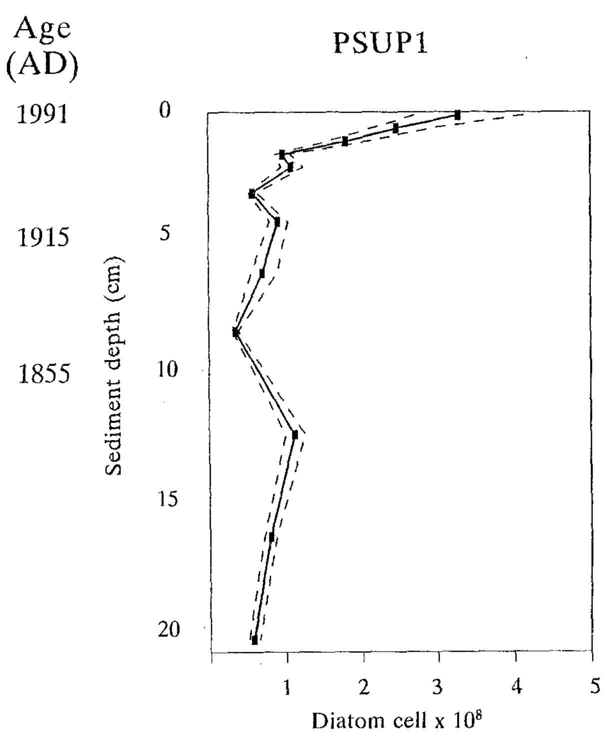

Fig. 10. Fossil diatom cell concentration with counting error in a core for Lago Paione Superiore (PSUP1).

1981). The inferred pH for the top section of the core slightly overestimates the pluriennal median pH (5.53: median value of data from 1991 to 1993; Fig. 11).

Diatoms

Diatom analysis was carried out on four cores, three were analyzed in Italy (Giorgis, 1993), and one in England. Because all cores gave very similar results, apart from the different sediment accumulation rate of core PSUP1, only one (core PS/89) is discussed.

Sixty-nine diatom taxa were found in the cores of Lake Paione Superiore (Table 2), 29 of which occurred at abundances of less than 1% of the total (shown as R = rare, in Table 2). The dominant species were benthic (Pugnetti *et al.*, 1993; Cameron *et al.*, 1994), acidophilous or acidobiontic. At the base of the cores, the diatom assemblages are dominated by the benthic *Pinnularia microstauron* (maximum 40%) and species of the genera *Achnanthes* and *Cymbella*. In the upper levels of the core (0–2 cm; Fig. 9), there is a sharp increase of the acidophilic species *Aulacoseira distans*, *Achnantes marginulata*, *Eunotia exigua*. Other taxa such as *Achnanthes helvetica* fo. *minor*, *A. marginulata* fo. *major*, *A. scotica*, *Aulacoseira distans*, *Neidium alpinum* and *Cymbella hebridica* were present in the 0–10 cm section at 5–10% frequency. Other acidophilous species (*Aulacoseira distans* var. *nivalis*, *A. lirata*, *A. valida* and *A. alpigena*) were much less frequent (<5%). *Stauroneis anceps*, *Surirella linearis*, *S. roba*, *Cymbella gracilis*, *Anomoeoneis brachysira* (= *Brachysira brebissonii*) and *Stenopterobia delicatissima* were present at very low frequencies along the whole core length (Fig. 9). At *c.* 10 cm, *Achnanthes didyma* and *A. minutissima* represented 10% of the diatoms. From 10 cm to the bottom (or to 35 cm in core PS/91, data not shown), *Pinnularia microstauron* and *Eunotia exigua* were still frequent, and *Cymbella gaeumannii*, *Achnanthes scotica*, *Neidium affine*, *N. alpinum* and *Navicula seminulum* increased. Finally, three small peaks of *Navicula gallica* var. *perpusilla* (<5%) were recorded at 18 cm, 26 cm and 30 cm.

From the base of the core to a depth of approximately 2 cm, cell concentration remains stable (Fig. 10). However, at 10 cm (8.5 cm in the core PSUP1) the cell concentration falls to a minimum, coincident with a peak in the abundance of *Pinnularia biceps* (only in core PSUP1) and in percentage of dry weight. This dilution of cell concentration supports the hypothesis that there is accelerated catchment erosion in this part of the sequence. From a depth of *c.* 1 cm to the top of the core, diatom cell concentration (but also $BSiO_2$, Fig. 5 and fucoxanthin, see below) increases sharply, reaching a maximum of over 4×10^8 cells g^{-1} d.w. (Fig. 10).

The pH history (Fig. 11) was inferred using the SWAP data set (Stevenson *et al.*, 1991) and the ALPS data set specific for the Alpine region (Marchetto & Schmidt, 1993). Both sets suggested similar patterns. The main differences are that the ALPS data set generated systematically higher pH values (by 0.3 units), whereas the values inferred by the SWAP data set underestimate measured median pluriennal pH (5.53; Fig. 11). However, SWAP data set is known to be biased toward acid values (ter Braak & Jaggins, 1993).

Algal pigments

Sedimentary pigments can be used as biochemical markers of algal development (Züllig, 1982; Lami *et al.*, 1994a and b). Total carotenoids, chlorophyll derivatives (CD) and β-carotene provide an estimate of total phytoplankton biomass, and a suite of other pigments indicate the presence and relative abundance of different algal species or genera. For example, the abundances of fucoxanthin and diadinoxanthin show that this community (Fig. 12) is dominated by diatoms and chrysophytes. The abundant concentration of lutein, which is a characteristic carotenoid of green algae and terrestrial plants, probably reflects allochthonous input, since no species of Chlorophyceae have been reported for the lake (Mosello *et al.*, 1993a; Pugnetti *et al.*, 1993). Despite the fact that Peridineae are also very abundant in the plankton community (Pugnetti *et al.*, 1993), their characteristic pigment peridinin is not the most abundant in the sediment (Mosello *et al.*, 1993a). Similar under-representations of dinoflagellate pigment have been recorded from other lakes (Züllig, 1982; Leavitt *et al.*, 1989; Hurley & Armstrong, 1990; Lami *et al.*, 1991) and is related to differences in susceptibility of the pigments to various degradative processes (Leavitt, 1993). With the exception of chlorophyll derivatives and fucoxanthin, whose recent profiles show a marked increase, there are no clear trends in single algal pigments (Fig. 12). Diatom abundance, indicated by fucoxanthin (a pigment also present in chrysophytes), is in good agreement with the diatom concentration and biogenic silica profiles. A slight, very recent increase in lake productivity is also indicated by fossil chironomid profiles (see below).

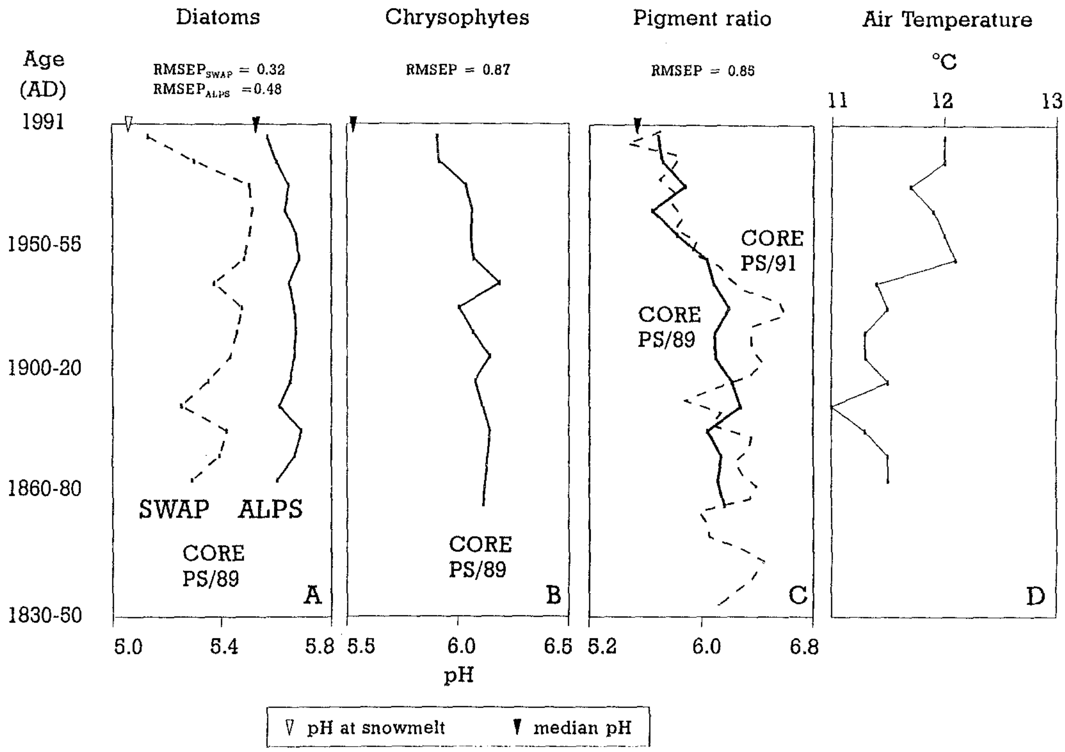

Fig. 11. Inferred pH from (A) diatoms (using two different calibration data sets, SWAP and ALPS), (B) chrysophycean scales, and (C) pigment ratios in two sediment cores (PS/89 and PS/91) for Lago Paione Superiore. (D) Mean annual air temperature recorded at Lugano, Switzerland since 1865, lake water pH and boot-strap root-mean-square-errors (RMSE) are also reported. The 15 temperature points represent the average of the annual mean temperature for the years corresponding to each sediment layer analyzed.

A red carotenoid astaxanthin is interpreted here as a biomarker for highly pigmented zooplankton populations (Pugnetti *et al.*, 1993; Guilizzoni *et. al.*, 1993; Lami *et al.*, 1994b), but no clear trend is evident in the profile (Fig. 12), and no relationship was noted with the increasing number of zooplankton (ephippia) remains (Schnell, unpublished data).

The significant decrease of the pigment ratios (430 nm:410 nm) (Guilizzoni *et al.*, 1992; Guilizzoni *et al.*, 1993) in the near surface layers of the cores is further evidence of progressive acidification. The pH history inferred by this index shows that the lake began to acidify between 1940 and 1950 A.D. (Fig. 11). In the present study, the inferred pH was calculated using a regression equation (not shown) different from the one published in Guilizzoni *et al.* (1992). The new regression equation (430 nm:410 nm = 0.133pH − 0.061) includes six extra lakes and resulted in a higher correlation coefficient ($r = 0.86$; $n = 28$; $P < 0.001$) than the one published in Guilizzoni *et al.* (1992).

Chironomids

Subfossil chironomid remains were analyzed in 11 samples from core PSUP2, which was collected very close to the ^{210}Pb dated PSUP1. Altogether, 15 taxa were found (Table 3), of these 11 were represented by only one or a few specimens. Other rare species (*Bryophaenocladius* sp., *Limnophyes* sp., *Pseudosmittia* sp., and *Chaetocladius* sp.) are most likely semi-terrestrial or terrestrial, whereas *Diamesa* sp., *Paratrichocladius* sp., and *Zavrelimyia* cf. *barbatipes* Kieffer are littoral dwellers, whose larval exuviae probably drifted into the deeper parts of the lake.

The four most important species (in order of abundance) were *Tanytarsus* species A *norvegicus*-group, *Micropsectra radialis* Goetghebuer (syn. *Lauterbornia coracina* Kieffer, syn. *Micropsectra coracina* Kieffer), *Heterotrissocladius marcidus* Walker, and *Procladius* sp., which together made up 93 to 99 percent of the chironomid remains in the samples.

The species identity of the larvae belonging to the *Tanytarsus norvegicus*-group cannot be stated with cer-

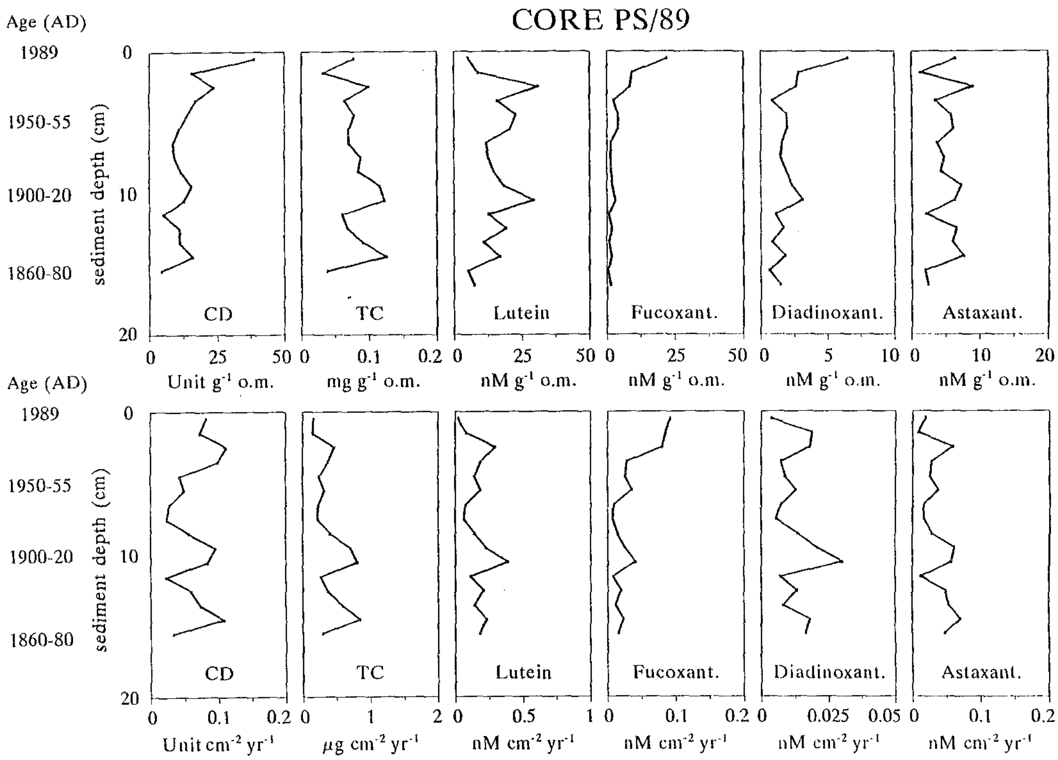

Fig. 12. Depth profiles of algal pigment concentrations and accumulation rates in a core (PS/89) for Lago Paione Superiore. Astaxanthin, a typical zooplankton carotenoid, is also indicated.

tainty; however, many adult males and pupal exuviae of *Tanytarsus niger* Søgaard-Andersen were found in water surface samples taken from the lake in July 1993. This taxon belongs to the *norvegicus* group, as defined by Reiss & Fittkau (1971), and there is a high probability that the *Tanytarsus* larvae (here called sp. A) in the core and also in the lake today are *T. niger*. Figure 13 illustrates the relationship between the populations of the two major chironomids in the lake. At approximately the turn of the century, *M. radialis* totally dominated the zoobenthos in the lake, for only single individuals of *Tanytarsus* sp. A were found. The population of *Tanytarsus* sp. A started to increase about 100 years ago, and has now displaced *Micropsectra radialis* as the dominant chironomid in the deepest parts of the lake. Bottom samples taken in 1992 showed a strong dominance of *Tanytarsus* sp. A and a relatively small population of *Micropsectra radialis*. The strong increase of *Tanytarsus* sp. A in Lago Paione Superiore during this century can be interpreted as a long-term, climatic trend.

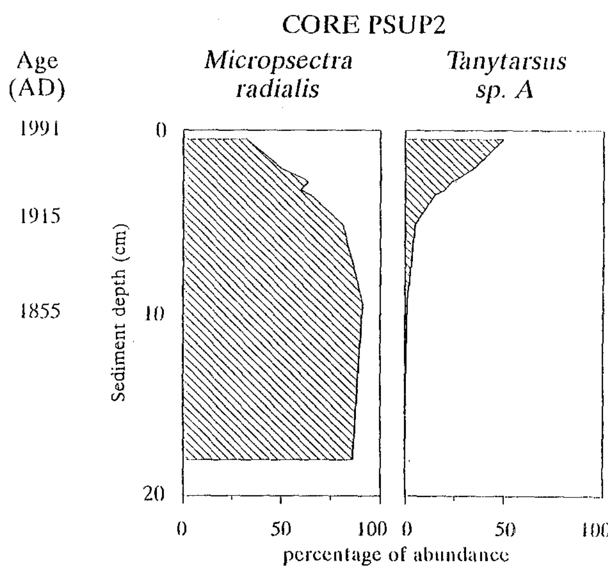

Fig. 13. Relative abundance of *Micropsectra radialis* Goetghebuer and *Tanytarsus* sp. A *norvegicus*-group in a sediment core (PSUP2) from Lago Paione Superiore.

Populations, especially of *Heterotrissocladius marcidus* but also of *Procladius* sp., seem to have increased during the last decade (Table 3). Both species are known to be very acid tolerant, and are, in addition to *Sergentia coracina* Zetterstedt, the dominant chironomids in chronically acidified Lake Lille Hovvatn in Norway (Schnell *et al.*, 1993, Schnell, paper in preparation). An increase of *H. marcidus* and *Procladius* sp. in the profundal zone suggests ongoing acidification in Lago Paione Superiore.

In addition to the changes in faunal composition, the abundance of chironomids in the lake seems to have increased; in fact, the number of specimens increases sharply in the uppermost samples (Table 3). This suggests eutrophication. Two additional grab bottom samples taken in 1992 indicated an abundance of more than 20 000 chironomid larvae per m^{-2} of lake bottom at 7 m depth.

Effect of temperature

It has already been suggested for other alpine lakes (Psenner & Schmidt, 1992; Marchetto *et al.*, 1993) that temperature had an important effect on pH values before the onset of atmospheric deposition of strong acids. At Lago Paione Superiore, the relationship between the diatom-inferred pH and mean annual air temperature measured at Lugano (Ambrosetti, 1991) is significant ($n = 13$; $r = 0.68$; $P < 0.01$) for the SWAP data set, when the data used are restricted to the period prior to recent atmospheric pollution (Fig. 11). Due to the restricted range of lakes included in the ALPS data set, the relation between temperature and pH from the ALPS data set is clearly evident only in some period before the recent atmospheric pollution, when warm years corresponded with local maxima of inferred pH, and cold periods were correlated with local minima.

No statistically significant correlation was found between temperature and pH, as inferred from chrysophyte assemblages or the pigment ratios.

Discussion

Lithostratigraphic analyses of cores revealed both smooth and spiked dry weight and LOI profiles. Smooth sections indicate catchment stability, whereas erratic profiles suggest accelerated catchment erosion (Fig. 4). Turbidites are clearly visible in the longitudinal section of core PS/91 (Fig. 3). These events of increased catchment erosion, rather evident in the past, may be directly related to local climatic variation, such as increased precipitation (annual mean rainfall of about 1800 mm yr^{-1}). Alternatively, they may reflect episodic collapse of surrounding slopes and inwash of material. The rates of sediment accumulation are variable between cores, one core less than 6 cm of sediment accumulated during the past 100 years, but at the other extreme over 10 cm of sediment accumulated in the same period (Fig. 4). Differences among the lithostratigrafic profiles of different cores taken close together in a lake basin are well documented (Engstrom & Swain, 1986; Anderson, 1990), and were also noted in sediments of two high mountain lakes, Milchsee (Italian Tyrol) and Etang d'Aube (French Alps), indicating consistently faster and slower accumulation rates in replicate cores (Cameron *et al.*, 1994). Problems with constructing a chronology were already found at such high altitude lakes, where lake sediments are often characterizated by low organic content, slow accumulation rates and, on occasions, for lakes located in granitic bedrock, high background ^{226}Ra rendering the determination of unsupported ^{210}Pb difficult (Jones *et al.*, 1993). Coring site (i.e, cores collected at different times and thus not from exactly the same area; cf. Fig. 1), subsampling (i.e. differences in core sectioning, 1 cm or 0.5 cm intervals) and subsample processing (i.e. cores extruded in the field or longitudinally opened and sub-sampled in the laboratory) would also contribute to the variability observed in the sedimentation rate profiles. The use of national fossil-fuel combustion statistics and meteorological data enable us to determine the possible regions of origin for the carbonaceous particles (Fig. 7). The carbonaceous particle profiles for Lago Paione Superiore shows the start of the particle record at the beginning of the century (1900–1920) and the rapid increase in concentration from about 1950–1960 (Fig. 7). The United Nations statistics for Italian electricity production, which is mostly thermal production from combustion of fossil-fuels, shows a very similar trend (Fig. 7). This suggests that the majority of carbonaceous particles deposited on Lago Paione Superiore could originate from Italy itself. The study site is close to the Swiss border, but it is unlikely that many of the particles are derived from Switzerland, which produces very little energy (2.2% of total in 1989) by fossil-fuel combustion (United Nations Statistics 1991). The study lake is also only about 70 km from Milan, and the prevailing wind direction during rainfall and snowfall events is mainly south to north, suggesting that the acid pollutants are derived from the Po Valley (Novo, 1987; Mosello *et al.*, 1992b).

Small forms of *Mallomonas alveolata*, and *M. actinoloma* var. *maramuresensis* were the most common species in acidic alpine lakes (Marchetto & Lami, 1994). The rapid decrease in recent years of *M. crassisquama* (Fig. 8), as well as the sharp increase of some acidophilic diatom species (e.g. *Aulacoseira distans*, *Achnanthes marginulata*, *Eunotia exigua*; Fig. 9), suggests that the acidification in Lago Paione Superiore has increased. Smol *et al.* (1984) and Hartmann & Steinberg (1986) have observed similar chrysophyte responses for acidification.

The accelerated inwash of inorganic sediment (turbidite) from the catchment in some periods (mainly in the middle part of the core) and weathering of rock, may have altered lake water chemistry (e.g. nutrient levels, but not the pH because of its very low calcium content) and may have introduced terrestrial diatoms to the lake (e.g. *Pinnularia interrupta*; Cameron *et al.*, 1994). More importantly, the changes in water pH may have caused changes in diatom community in the lake.

Three different types of fossil indicators (chrysophycean scales, diatom frustules and algal sedimentary pigments) have been used for pH reconstruction in Lago Paione Superiore (Fig. 11). These techniques have been compared statistically and the inferred pH values compared to contemporary lake water pH (Guilizzoni *et al.*, 1993). It was shown that the pH reconstructions based on pigment ratios have a higher rootmeansquare-standard error than that based on algal cell remains. In Lago Paione Superiore, the diatom assemblages are less affected by the interannual variability of pH because they are mostly benthic, and thus much less influenced by short-term fluctuations in pH (Guilizzoni *et al.*, 1993). On the other hand, studies carried out on alpine lakes (Marchetto & Lami, 1994) and in other geographical areas (Smol, 1990) showed that chrysophytes may be more sensitive early warning indicators of lake water pH change. Compared to the diatoms found in our alpine lake, chrysophytes are all planktonic and therefore not influenced by the buffering effect of bottom sediments or other substrates. In Lago Paione Superiore, chrysophytes mainly develop in spring (Mosello *et al.*, 1993a) when lake acidity is higher, and thus provide even a stronger acidification signal than diatoms. However, chrysophyte development in high mountain lakes does not always occur in spring; for example, in a small lake located near Lago Paione Superiore, a bloom of *Mallomonas crassisquama* was recorded in September (Garibaldi *et al.*, 1987).

A clear acidification signal was indicated by all three techniques (Fig. 11), although some discrepancies occurred between the measured pH and the pH reconstructed using different data sets. When pH values derived from the SWAP diatom data, which did not include sites from the Alps but covered a wider range of lakes and species, were compared with pH inferred from the ALPS data set, which was specifically developed for the Alps but represented a smaller number of lakes and species (Fig. 11), sample-to-sample differences in pH inferred from ALPS were lower. Discrepancies between the two data sets might be due to (1) differences in the ecology of the diatoms in separate geographical areas, (2) differences in the sampled lakes and in the pH gradient (smaller for the ALPS data set; Marchetto & Schmidt, 1993), or (3) a bias in the calibration technique (ter Braak & Juggins, 1993). Besides, the modern diatom/lakewater pH SWAP data-set used in the water analysis reconstructions lacked some taxa common in the cores, notably *Achnanthes helvetica* fo. *minor*. pH optima were therefore unavailable for these diatoms and they were omitted from the reconstruction. In any case, it is difficult to estimate 'average pH' accurately when only scattered water chemistry measurements are available. Lake water pH in Lago Paione Superiore varies (Fig. 2) up to almost 1.0 unit within the year (acid shock during snowmelt; pH = 5.06), and from year to year (Mosello *et al.*, 1993a and 1994b). To compare with the ALPS data set, we used the median of all available pH values (5.53; Fig. 11), but different values apply, for example, for the median summer pH (5.70) or for the late summer pH of surface water samples (5.90). The higher discrepancy found between the median water pH and the chrysophyte inferred pH in the topmost section, as compared with pH inferred from diatom or pigment ratio (Fig. 11), could be due to the relatively low number of available pH data in spring, when chrysophytes generally develop and the lake is ice-covered.

The analysis of chironomid head capsules also indicates recent lake acidification. Assuming that *Tanytarsus* sp. A is *Tanytarsus niger*, the replacement of *Micropsectra radialis* as the dominant chironomid by a species which probably can tolerate even harsher conditions is interesting (Fig. 13). The increase in the populations of *Heterotrissocladius marcidus* and *Procladius* sp. also suggests acidification (Table 3).

Little is known about the ecology of *Tanytarsus niger*. Søgaard-Andersen (1937) originally described it from specimens living in lakes on Greenland where it is an important member of the zoobenthos (Søgaard-Andersen, 1946). He also observed that larvae which are frozen in the sediments for about 8 months, showed no visible harm. The few other finds from the Southern parts of Europe are in high-altitude or oligotrophic lakes (Langton, 1992; Reiss, 1984; Verneaux & Vergon, 1974). We have no data on the effects of acidification on *Tanytarsus* sp. A *T. niger*.

Micropsectra radialis is regarded as a strong indicator of moderate to strong oligotrophy (Brundin, 1956; Sæther, 1979). It is found all over North and Central Europe, as far south as the Alps and the Pyrenees. In the lowlands between the Alps and the Pyrenees and Scandinavia, the species is found only in the profundal zones of deep oligotrophic lakes and is thought to be a glacial relict surviving only because of the low temperatures in these habitats. The species is known to be acid sensitive (Schnell & Raddum, 1993).

Evidence for the slight increase in lake productivity in the most recent horizons probably also reflects mild nutrient enrichment caused both by increasing atmospheric nitrogen loading (Arzet *et al.*, 1986) and increasing weathering of silicious rocks. Limnological studies carried out during the past 10 years confirm the sediment analyses described here in showing generally low productivity of Lago Paione Superiore, although there is a marked recent increase in total sedimentary nitrogen, biogenic silica, chlorophyll derivatives, fucoxanthin concentrations and the number of chironomid head capsules (Figs 5, 6, 12; Table 3). Also the increase in diatom concentrations in the upper 34 sections (0–1 cm) of the profile of Fig. 10 can be related to variations of lake trophy, although some *in situ* production by epipelic diatoms could explain the most recent peak. On the other hand, supposing the population of these benthic algae significantly sustain the whole lake productivity, there is no reason to believe that they were absent from the lake bottom in past periods (the lake was ultra-oligotrophic), and consequently the recent increase in their concentration may be a real phenomenon. Sediment core analysis of zooplankton ephippia remains showed the same recent increase, as well as rather elevated concentrations of chlorophyll *a* (*c.* 5 $\mu g\, l^{-1}$) were recorded in the water column (unpublished data).

N and P concentrations were higher in the bottom than in the middle of the core, but there is a recent (1940–1990) marked increase in the concentration of N (and consequently of the TN:TP ratio) (Figs 5 and 6). A slightly increasing trend in the N acccumulation rate was also noticed in the recent sediments. Because recent local human disturbance is minimal (with the exception of a few summer recreational activities such as mountain walking, and reduced grazing of goats), this change in the composition of the aquatic flora, nutrients, pigments and the high chironomid abundance could also be related to atmospheric pollution and nitrogen output in particular (Horvath & Meszaros, 1984; Henriksen & Brakke, 1988; Mosello *et al.*, 1993b). Studies carried out on snow core samples demonstrated that its watershed receives high loads of SO_4, NO_3 and NH_4 (Mosello & Tartari, 1987). This could be the cause of the slight eutrophication observed in the Lago Paione Superiore today. However, difficulties resulting from variable retention and post-depositional diagenesis make the interpretation of sedimentary N and P profiles problematic (Engstrom & Wright, 1985). One hypothesis (as outlined above) is that the decreases in nutrient accumulation rates could be associated with known disturbance of the catchment area in the past century and up to the beginning of this century, a period during which, for instance, the alpine regions were overgrazed (Landini, 1932; Schmidt & Psenner, 1992).

Lastly, a relationship was found between the instrumental record of temperature and the pH reconstructions based on diatom assemblages (Fig. 11). This correlation is similar to that described for diatom-based pH reconstructions and temperature in other alpine lakes (Psenner & Schmidt, 1992; Schmidt & Psenner, 1992; Marchetto *et al.*, 1993). Chemical surveys of mountain lakes of all the Alps (Marchetto *et al.*, 1995) have shown the importance of altitude (directly affecting temperature) and grass cover of the watersheds (indirectly related to temperature) in controlling rock weathering, and consequently summer lake acidity. Similar relations between altitude, temperature and weathering, affecting the acidity of lake water, were also found in alpine streams and lakes in Switzerland (Zobrist & Drever, 1990). However, at Lago Paione Superiore, the correlation between pigment- or chrysophyte-based pH reconstructions and instrumental temperature records were not significant. In spite of the fact that chrysophytes may be more sensitive indicators of chemical changes than diatoms in some lake systems (Dixit *et al.*, 1989), it is likely that the species-poor chrysophyte assemblage of Lago Paione Superiore is less suitable for detecting small changes in water chemistry than diatom assemblage. An alternate hypothesis to explain the different behaviour of inferred pH in relation with temperature is related to seasonal variability. Diatoms develop mainly in summer, when lake pH is largely controlled by weathering, and so are related to the temperature. In contrast, in Lago Paione Superiore the chrysophyte community develops mainly under ice (Pugnetti *et al.*, 1993), so it would not be influenced by the variability in summer pH caused by interannual variability in watershed weathering. Similarly, the pigment ratio may reflect the higher degradation rate of pigment during acidity pulses (i.e., snowmelt and high rainfall), rather than summer conditions.

Conclusions

A small alpine lake, Lago Paione Superiore (Central Alps), was investigated using multiple lines of palaeolimnological (nutrients, carbonaceous particles, diatoms, chrysophytes, pigments and chironomid head capsules), analyzed from different sediment cores. For some of these records (i.e. ^{210}Pb chronology, LOI, diatoms and chironomids), quality control of the data was made possible by an intercalibration exercise, as well as by exchanges among researchers.

Differences in sedimentation rates were noted in two cores.

This cooperative research established two diatom calibration data sets for inferring historical pH, one specific for the alpine region.

Most of the palaeolimnological parameters indicate clear changes in lake acidification (despite the relatively low atmospheric acid load) and a slight increase in lake trophy since the 1950's. High accumulation rates of nutrients (C, N, P), some pigments, and chironomid species in the 1800's were associated with more intensive use of alpine pastures in the past compared with some periods of this century.

Analyses of algal microfossils and of chironomids showed species replacements in diatoms, chrysophytes and chironomid communities.

Pigments increased around 1960, coincident with increased sediment loads of N and biogenic silica. The increase in sedimentary nitrogen could be related to the general increases in output of N in Europe. The lake was nitrogen (and phosphorus) limited (R. Mosello, pers. commun.), so the increase in nitrate and ammomium could have produced a slight eutrophication in the lake.

Finally, the findings that air temperature can influence the inferred pH, as shown in the alpine regions (Psenner & Schmidt, 1992; Marchetto *et al.*, 1993), was confirmed in the present study, although not all the biological records studied showed this effect.

Acknowledgments

We express our gratitude to Mr Gabriele Tartari and Dr Angela Boggero for assistance in the fieldwork and for the taxonomic study of chironomid larvae, respectively. Comments by R. Battarbee, R. Peters and two reviewers improved the quality of this paper. This study was partially supported by the CNR-ENEL Project – Interactions of Energy Systems with Human Health and Environment – Rome Italy, and by the EEC Environmental Research Programme (AL:PE, Contract No. EV-5VCT92-0205).

References

Ambrosetti, P., 1991. La ricerca sulle serie climatologiche secolari in Svizzera: risultati e prospettive. Mem. Soc. Geogr. Ital. 46: 227–239.

Anderson, N. J., 1990. Variability of diatom concentration and accumulation rates in sediments of a small lake basin. Limnol. Oceanogr. 35: 497–508.

Appleby, P. G., P. J. Nolan, D. W. Gifford, M. J. Godfrey, F. Oldfield, N. J. Anderson & R. W. Battarbee, 1986. ^{210}Pb dating by low background gamma counting. Hydrobiologia 141: 21–27.

Appleby, P. G. & F. Oldfield, 1978. The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. Catena 5: 1–8.

Appleby, P. G., N. Richardson & P. J. Nolan, 1991. ^{241}Am dating of lake sediments. Hydrobiologia 214: 35–42.

Arzet, K., K. Steinberg, R. Psenner & N. Schulz, 1986. Diatom distribution and diatom inferred pH in the sediment of four alpine lakes. Hydrobiologia 143: 247–254.

Battarbee, R. W., 1986. Diatom analysis. In B. E. Berglund (ed.), Handbook of Holocene Palaeoecology and Palaeohydrology. Wiley, Chichester: 527–570.

Battarbee, R. W., N. J. Anderson, P. G. Appleby, R. J. Flower, S. C. Fritz, E. Y. Haworth, S. Higgitt, V. J. Jones, A. Kreiser, M. A. R. Munro, J. Natkanski, F. Oldfield, S. T. Patrick, N. G. Richardson, B. Rippey & A. C. Stevenson, 1988. Lake acidification in the United Kingdom 1800–1986. Evidence from analysis of lake sediments. Ensis Publishing, London, 67 pp.

Battarbee, R. W. & D. F. Charles, 1986. Diatom-based pH reconstruction studies of acid lakes in Europe and North America: a synthesis. Wat. Air Soil Pollut. 30: 347–354.

Birks, H. J. B., J. M. Line, S. Juggins, A. C. Stevenson & C. J. ter Braak, 1990. Diatoms and pH reconstruction. Phil. Trans. r. Soc., Lond. B 327: 263–278.

Brundin, L., 1956. Die bodenfaunistischen Seetypen und ihre Anwendbarkeit auf die Südhalbkugel. Zugleich eine Theorie der produktionsbiologischen Bedeutung der glazialen Erosion. Report N. 37, Institute Freshwater Research, Drottningholm: 186–235.

Cameron, N. G., N. L. Rose, P. G. Appleby, R. W. Battarbee, S. T. Patrick, R. J. Flower & S. Juggins, 1994. In B. M. Wathne & S. T. Patrick (eds), AL:PE – Acidification of Mountain Lakes: Palaeolimnology and Ecology, AL: PE Report, Norwegian Institute for Water Research (NIVA), Oslo: 31–75.

Charles, D. F., R. W. Battarbee, I. Renberg, H. van Dam & J. P. Smol, 1989. Paleoecological analysis of lake acidification trends in

North America and Europe using diatoms and chrysophytes. In S. A. Norton, S. E. Lindberg & S. L. Page (eds), Acidic precipitation. 4. Soils, aquatic processes and lake acidification, Springer-Verlag, N.Y.: 207–275.

Charles, D. F., M. W. Binford, E. T. Furlong, R. A. Hites, M. J. Mitchell, S. A. Norton, F. Oldfield, M. J. Paterson, J. P. Smol, A. J. Uutala, J. R. White, D. R. Whitehead & R. J. Wise, 1990. Paleoecological investigation of recent lake acidification in the Adirondack Mountains, N.Y. J. Paleolimnol. 3: 195–241.

Demaster, D. J., 1981. The supply and accumulation of silica in the marine environment. Geochim. Cosmochimica Acta 45: 1715–1732.

Dixit, S. S., A. S. Dixit & J. P. Smol, 1989. Lake acidification recovery can be monitored using chrysophycean microfossils. Can. J. Fish. aquat. Sci. 46: 1309–1312.

Engstrom, D. R. & E. B. Swain, 1986. The chemistry of lake sediments in time and space. Hydrobiologia 143: 37–44.

Engstrom, D. R. & H. E. Wright Jr., 1985. Chemical stratigraphy of lake sediments as a record of environmental change. In J. W. G. Lund & E. Y. Haworth (eds), Lake sediments and environmental history. University of Leicester Press, Leicester: 11–67.

Esterby, S. R. & A. H. el-Shaarawi, 1981. Likelihood inference about the point of change in a regression regime. J. Hydrol. 53: 17–30.

Fott, J. (ed.), 1994. Limnology of Mountain Lakes. Developments in Hydrobiologia 93: 182 pp.

Fukushima, T., K. Amaro & K. Muraoka, 1991. Factors explaining sediment concentrations of 16 elements in 28 Japanese lakes. Wat. Sci. Technol. 23: 465–474.

Garibaldi, L., R. Mosello, B. Rossaro & F. Setti, 1987. Caratteristiche chimiche e biologiche di due laghi d'alta quota suscettibili ad acidificazione. In R. Mosello & B. De Margaritis (eds), Deposizioni acide: un problema per Acque e Foreste. Documenta dell'Istituto Italiano di Idrobiologia 14: 165–180.

Giorgis, A., 1993. Inquinamento atmosferico, pH delle acque e resti di diatomee nei sedimenti di due laghi alpini. Tesi di laurea, Università degli Studi di Milano, 103 pp.

Glew, J. R., 1988. A portable extruding device for close interval sectioning of unconsolidated core samples. J. Paleolimn. 1: 235–239.

Guilizzoni, P., G. Bonomi, G. Galanti & D. Ruggiu, 1983. Relationship between sedimentary pigments and primary production: evidence from core analyses of twelve Italian lakes. Hydrobiologia 103: 103–106.

Guilizzoni, P., A. Lami & A. Marchetto, 1992. Plant pigment ratios from lake sediments as indicators of recent acidification in alpine lakes. Limnol. Oceanogr. 37: 1565–1569.

Guilizzoni, P., A. Lami & A. Marchetto, 1993. The sediment core analyses in high altitude lakes of central Alps: comparison of three inferring pH techniques and effect of temperature on lake acidification. Mem. Ist. ital. Idrobiol. 52: 387–400.

Hartmann, H. & C. Steinberg, 1986. Mallomonadacean (Chrysophyceae) Scales: Early biotic paleoindicators of lake acidification. Hydrobiologia 143: 87–91.

Henriksen, A. & D. F. Brakke, 1988. Increasing contributions of nitrogen to the acidity of surface waters in Norway. Water Air Soil Pollut. 42: 183–201.

Horvath, L. & E. Meszaros, 1984. The composition and acidity of precipitation in Hungary. Atmospheric Environment 18: 1843–1847.

Hurley, J. P. & D. E. Armstrong, 1990. Fluxes and transformation of aquatic pigments in Lake Mendota, Wisconsin. Limnol. Oceanogr. 35: 384–398.

Jones, V. J., R. J. Flower, P. G. Appleby, J. Natkanski, N. Richardson, B. Rippey, A. C. Stevenson & R. W. Battarbee, 1993. Palaeolimnological evidence for the acidification and atmospheric contamination of lochs in the Cairngorm and Lochnagar areas of Scotland. J. Ecol. 81: 3–24.

Lami, A., P. Guilizzoni & J. Masaferro, 1991. Record of fossil pigments in an alpine lake (L. Tovel, N. Italy). Mem. Ist. ital. Idrobiol. 49: 117–126.

Lami, A., A. Marchetto, P. Guilizzoni, A. Giorgis & J. Masaferro, 1994a. Palaeolimnological study in alpine lakes: records of carotenoids and carbonaceous particles from the atmosphere. Hydrobiologia 274: 57–64.

Lami, A., F. Niessen, P. Guilizzoni, J. Masaferro & C. A. Belis, 1994b. Palaeolimnological study of the eutrophication of volcanic Lake Albano (Central Italy). J. Paleolimnol. 10: 181–197.

Landini, P., 1932. Lo spopolamento montanaro nelle Valli Ossolane. Bollettino Storico, Provincia Novara, 9 pp.

Langton, P. H., 1992. A key to pupal exuviae of west Palaearctic Chironomidae. Update 1. P.H. Langton, Huntingdon, Cambridgeshire, 386 pp.

Leavitt, P. R., S. R. Carpenter & J. F. Kitchell, 1989. Whole-lake experiments: the annual record of fossil pigments and zooplankton. Limnol. Oceanogr. 34: 700–717.

Leavitt, P. R., 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. J. Paleolimnol. 9: 109–127.

Mantoura, R. F. C. & C. A. Llewellyn, 1983. The rapid determination of algal chlorophyll and carotenoid pigments and their breackdown products in natural waters by reverse-phase high-performance liquid chromatography. Analyt. chim. Acta 151: 297–314.

Marchetto, A., P. Guilizzoni, A. Lami & A. Giorgis, 1993. Diatom based pH reconstruction in an alpine lake: the importance of temperature changes. In G. Giussani & C. Callieri (eds), Strategies for lake ecosystems beyond 2000. Proceedings of the 5th International Conference on the Conservation and Management of Lakes, 17–21 May, 1993, Stresa, Italy. Edizioni Istituto Italiano di Idrobiologia, Verbania Pallanza: 423–426.

Marchetto, A. & A. Lami, 1994. Reconstruction of pH by chrysophycean scales in some lakes of the Southern Alps. Hydrobiologia 274: 83–90.

Marchetto, A., R. Mosello, R. Psenner, G. Bendetta, A. Boggero, D. Tait & G. A. Tartari, 1995. Factors affecting water chemistry of alpine lakes. Aquatic Sciences (in press).

Marchetto, A. & R. Schmidt, 1993. A regional calibration data set to infer lake water pH from sediment diatom assemblage in alpine lakes. Mem. Ist. ital. Idrobiol. 51: 115–125.

Marengo, G. & R. Baudo, 1988. Forme di fosforo nei sedimenti lacustri. Acqua Aria 6: 717–721.

Meyers, P. A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chemical Geology 114: 289–302.

Mosello, R., 1984. Hydrochemistry of high altitude alpine lakes. Schweiz. Z. Hydrobiol. 46: 86–99.

Mosello, R., A. Boggero, M. Carmine, A. Marchetto, A. Sassi & G. A. Tartari, 1994a. Ricerche idrochimiche sui laghi alpini delle valli Ossola e Sesia, Alpi Pennine e Lepontine). Documenta dell'Istituto Italiano di Idrobiologia 46: 436 pp.

Mosello, R., M. Della Lucia, A. Marchetto & G. A. Tartari, 1993b. Trends in the chemistry of surface water in Northwerstern Italy. I. Atmospheric deposition. Mem. Ist. ital. Idrobiol. 51: 47–165.

Mosello, R., A. Lami, P. Guilizzoni, M. Manca & A. Nocentini, 1994b. Water chemistry. In B. M. Wathne & M. Johannessen (eds), Progress report 1993 – AL:PE Report 1/1994 ENVIRONMENT: 24–26.

Mosello, R., A. Lami, P. Guilizzoni, M. Manca, A. M. Nocentini, A. Pugnetti, A. Boggero, A. Marchetto, G. A. Tartari, R. Bettinetti, M. Bonardi & P. Cammarano, 1993a. Limnological studies on two acid sensitive lakes in the South Western Alps. (lakes Paione Superiore and Paione Inferiore, Italy). Mem. Ist. ital. Idrobiol. 51: 127–146.

Mosello, R., A. Marchetto & F. Decet, 1992b. Chemistry of atmospheric deposition and freshwater acidification: Research in Italy. In P. Guilizzoni, G. Tartari & G. Giussani (eds), Limnology in Italy. Mem. Ist. ital. Idrobiol. 50: 417–455.

Mosello, R. & G. A. Tartari, 1987. Chemistry of atmospheric depositions at L. Toggia (2160 m a.s.l.), with emphasis on the sampling procedure. 4th C.E.C. Symp. on Physico-chemical behaviuor of atmospheric pollutants. Stresa, Italy, 23–25 September 1986: 176–187.

Mosello, R., B. M. Whatne & G. Giussani (eds) 1992a. Limnology on groups of remote mountain lakes: ongoing and planned activities. Documenta dell'Istituto Italiano di Idrobiologia 32: 128 pp.

Murphy, J. & J. P. Riley, 1962. A modified single-solution method for determination of phosphate in natural waters. Analyt. Chim. Acta 23: 31–36.

Novo, A., 1987. Gruppo di studio delle caratteristiche chimiche delle precipitazioni atmosferiche dell'Italia Settentrionale. Rapporto finale anni 1983–1984. Quaderni Ingegneria Ambientale 6: 63 pp.

Psenner, R. & R. Schmidt, 1992. Climate-driven pH control of remote mountain lakes and effects on acid deposition. Nature 356: 781–783.

Pugnetti, A., M. Manca, A. M. Nocentini, A. Boggero, R. Bettinetti, M. Bonardi & P. Cammarano, 1993. Ecological aspects of two alpine lakes (lakes Paione, Italy). G. Giussani & C. Callieri (eds), Strategies for lake ecosystems beyond 2000. Proceedings of the 5th International Conference on the Conservation and management of lakes, 17–21 May 1993, Stresa, Italy. Edizioni Istituto Italiano di Idrobiologia, Verbania Pallanza: 440–443.

Reiss, F., 1984. Die Chironomidenfauna (Diptera, Insecta) des Osterseengebietes in Oberbayern. Ber. ANL 8: 186–194.

Reiss, F. & E. J. Fittkau, 1971. Taxonomie und Ökologie europäisch verbreiteter *Tanytarsus*-Arten (Chironomidae, Diptera). Arch. Hydrobiol. Suppl. 40: 75–200.

Renberg, I. & M. Wik, 1985. Soot particle counting in recent lake sediments. An indirect dating method. Ecological Bulletins 37: 53–57

Rose, N. L., 1990. A method for extraction of carbonaceous particles from lake sediment. J. Paleolimnol. 3: 45–53.

Sæther, O. A., 1979. Chironomid communities as water quality indicators. Holarct. Ecol. 2: 65–74.

Schnell, Ø. A., A. Fjellheim & G. G. Raddum, 1994. Invertebrates – past and present., AL:PE – Acidification of Mountain Lakes: Palaeolimnology and Ecology. In B. M. Wathne & S. T. Patrick (eds), AL:PE Report, Norwegian Institute for Water Research (NIVA), Oslo: 67–71.

Schnell, Ø. A. & G. G. Raddum, 1993. Past and present fauna of chironomids in remote mountain lakes. Preliminary results from the AL:PE-Project. In G. Giussani & C. Callieri (eds), Strategies for lake ecosystems beyond 2000. Proceedings of the 5^{th} International Conference on the Conservation and management of lakes, 17–21 May 1993, Stresa, Italy. Istituto Italiano di Idrobiologia, Verbania Pallanza: 444–447.

Schmidt, R. & R. Psenner, 1992. Climate changes and anthropogenic impacts as causes for pH fluctuations in remote high alpine lakes. Documenta dell'Istituto Italiano di Idrobiologia 32: 31–58.

Smol, J. P., 1990. Paleolimnology – recent advances and future challenges. Mem. Ist. ital. Idrobiol. 47: 253–276.

Smol, J. P., D. F. Charles & D. R. Whitehead, 1984. Mallomonadacean microfossil provide evidence of recent lake acidification. Nature 307: 628–630.

Søgaard-Andersen, F., 1937. Über die Metamorphose der Ceratopogoniden und Chironomiden Nordost-Grönlands. Medd. Grønland 116: 1–94.

Søgaard-Andersen, F., 1946. East Greenland lakes as habitats for chironomid larvae. Medd. Grønland 100: 1–65.

Stevenson, A. C., S. Juggins, H. J. B. Birks, D. S. Anderson, N. J. Anderson, R. W. Battarbee, F. Berge, R. B. Davies, R. J. Flower, E. Y. Haworth, V. J. Jones, J. C. Kingston, A. M. Kreiser, J. M. Line, M. A. R. Munro & I. Renberg, 1991. The Surface Waters Acidification Project Palaeolimnolgy Programme: Modern Diatom/Lake-Water Chemistry Data-Set. Ensis, London, 86 pp.

ter Braak, C. J. F., 1987. Calibration. Data analysis in community and landscape ecology. In R. H. G. Jongman, C. J. F. ter Braak & O. F. R. van Tongeren (eds) Pudoc, Wageningen, The Netherlands: 78–90.

ter Braak, C. J. F. & S. Juggins, 1993. Weighted averaging partial least square regression (WA-PLS): an improved methods for reconstructing environmental variables from species assemblages. Hydrobiologia 269/270: 485-502.

Tonolli, V., 1947. Gli alti laghi della Val Bognanco. Parte 1. Mem. Ist. ital. Idrobiol. 34: 185–269.

United Nations Department of International Economic and Social Affairs, 1991. 1989 Energy Statistics Yearbook. New York.

Verneaux, J. & J. P. Vergon, 1974. Faune dulcaquicole de Franche-Compté. Sixième partie: Les diptères chironomides. Annales scientifiques Université Besançon 3ème Série 11: 179–196.

Vogler, P., 1965. Phosphatanalytik in der Limnologie. II. Die Bestimmung des Gelössten – Phosphates. Fortsch. Wasserchemie und Ihrer Grenzgebiete 2: 109–119.

Wathne, B. M. & S. T. Patrick (eds), 1994. AL:PE – Acidification of Mountain Lakes: Palaeolimnology and Ecology. AL:PE 1 Report (April 1991–April 1993). Norwegian Institute for Water Research (NIVA), 318 pp.

Zobrist, J. & H. Drever, 1990. Weathering processes in alpine watersheds of mountain lakes. In M. Johannessen, R. Mosello & H. Barth (eds), Acdification processes in remote mountain lakes. CEC Air Pollution Research Report 20: 149–161.

Züllig, H., 1982. Untersuchungen über die Stratigraphie von Carotinoiden im geschichteten Sediment von 10 Schweizer Seen zur Erkundung früherer Phytoplankton-Entfaltungen. Schweiz. Z. Hydrobiol. 44: 1–98.