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ABSTRACT

A limnological study was performed during 1991 and 1992 on lakes Paione Superiore (LPS) and Paione Inferiore (LPI), located in the Ossola Valley, Central Alps. The two lakes are characterized by very low alkalinity values (LPI <30 μeq l^{-1}, LPS <3 μeq l^{-1}); notwithstanding the relatively low atmospheric acid load, diatom remains, carbonaceous particles and pigment profiles in the sediments all indicate that the two lakes have undergone acidification since the fifties. The biological communities (phyto-, zooplankton and macrobenthic fauna) are simplified, in consequence of the extreme physical and chemical conditions. The biological characteristics of the two lakes are discussed in relation to the water chemistry and the presence or absence of stocked fish.

Key words: mountain lakes, Alps, acidification, chemistry, phytoplankton, zooplankton, macrozoobenthos, sediment core

1. INTRODUCTION

Italian alpine lakes were studied, largely from a biological standpoint, during the 30s and 40s by researchers of the Istituto Italiano di Idrobiologia (Baldi 1939; Pirocchi 1949). Many studies were done on the lakes in the Bognanco Valley, particularly on lakes Paione Superiore and Inferiore (Tonolli 1947, 1949, 1954; Tonolli & Tonolli 1951); the net plankton community was examined in detail, whereas the chemical data (Tonolli 1947) are very poor and not really comparable with present measurements. No data on the macrobenthic fauna were collected.

During the eighties, in the framework of research on the acidification of

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freshwater, chemical studies were performed on the Paione lakes, which were found to be very poorly buffered due to the lithology of their watersheds (Mosello *et al.* 1985; Mosello 1986). For this reason they were chosen as 'representative lakes' for an ecological study as part of the EC STEP research on "Acidification of Mountain Lakes: Palaeolimnology and Ecology (AL:PE)" (Wathne 1992). The basic assumption of this research is that high altitude lakes are excellent indicators of air pollution and its effects, because they are not influenced by other forms of disturbance and because the geology, soils and relief of mountainous regions often give rise to surface water ecosystems sensitive to acid deposition.

This paper reports the results of a multidisciplinary study performed by the staff of the Istituto Italiano di Idrobiologia on the Paione lakes, in the framework of the AL:PE research. The main aims of this work were, on the one hand, to evaluate their recent evolution through sediment analysis and, on the other, to gather information on the present situation monitoring the seasonal variations in the chemical characteristics and in the planktonic and macrozoobenthic communities.

2. STUDY AREA

Lakes Paione Superiore (LPS) and Paione Inferiore (LPI) are located in the Bognanco Valley, a lateral of the Ossola Valley, in the Central Alps (Pennine) in Piedmont (Italy) (Fig. 1). The valley is crossed by the Simplon-Centovalli Fault and presents a heterogeneous lithology; for a description of the tectonics and geology of the area see Klein (1978) and Ferri (1982). The lithology of the watershed of the two lakes (Fig. 2) is characterized by clear banded orthogneisses and gray gneiss with potassium feldspar and epidote. Land cover, mainly hay meadows, is restricted to small areas (Fig. 2); bare rocks and debris characterize most of the watershed surface.

The main geographical and morphometric characteristics of the lakes are presented in table 1, and the bathymetric maps (Tonolli 1947) in figure 3.

3. SAMPLING AND METHODS

3.1. Air temperature and volume of precipitation

As there are no meteorological stations in the Bognanco Valley, temperature and precipitation were measured at six stations in the neighbouring valleys at altitudes between 1800 and 2600 m a.s.l., and at Lake Toggia (2160 m), about 30 km NNW of the Paione lakes (Fig. 1), where atmospheric deposition samples for chemical analysis are also collected weekly.

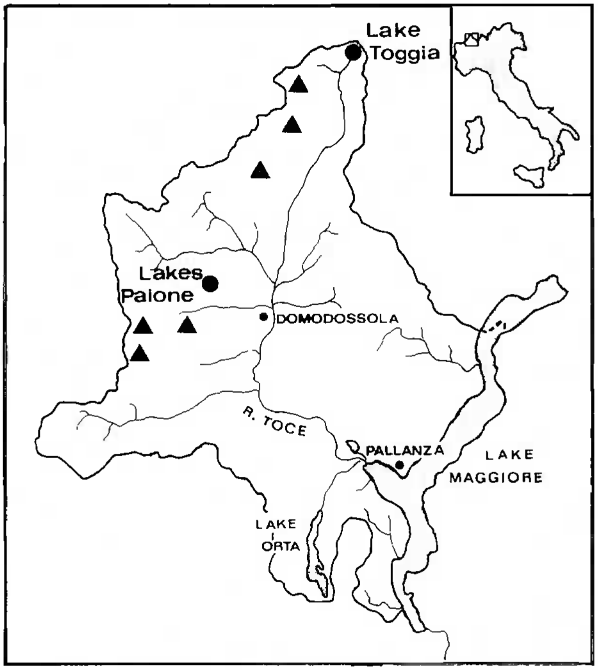

Fig. 1. Location of the Paione lakes, of the sampling site of atmospheric deposition for chemical analysis (Lake Toggia), and of the meteorological stations for measurement of temperature and amount of precipitation (triangles).

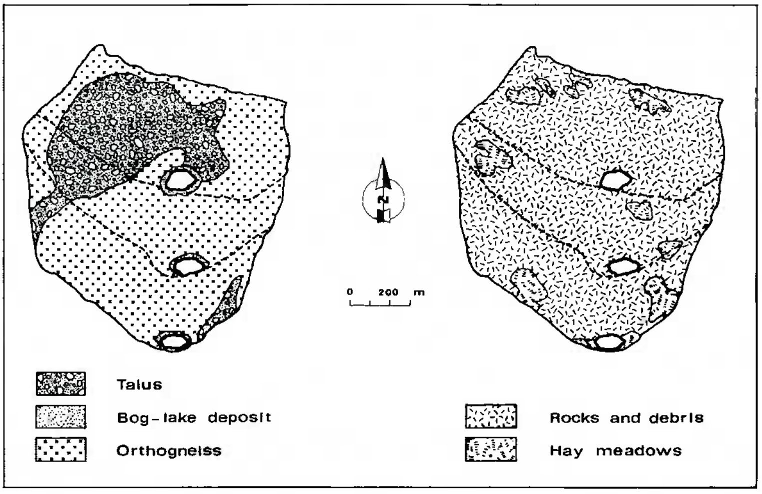

Fig. 2. Lithology and land cover of the watersheds of the studied lakes.

Tab. 1. Main geographic, morphometric and hydrological features of the Paione lakes.

		L. Paione Inferiore	L. Paione Superiore
Altitude	m a.s.l.	2002	2269
Longitude	East	8°11'23"	8°11'27"
Latitude	North	46°10'1"	46°10'26"
Lake surface area	km^2	0.014	0.014
Watershed area (lake included)	km^2	1.14	0.55
(Watershed+lake)/lake ratio		81	39
Maximum depth	m	13.5	11.7
Mean depth	m	7.35	5.12
Lake volume	10^6 m^3	103	69
Precipitation	mm y^{-1}	1450	1400
Mean residence time	days	23	33

3.2. Chemistry

Lake water samples for chemical analysis were collected at the maximum depth station at 0, 2.5, 5 and 8 m in LPS and at 0, 2.5, 5, 10 and 13 m in LPI. At the same depths temperature was measured with a reversing thermometer. Twelve and fourteen samplings were performed from October 1990 to September 1992 in LPS and LPI, respectively; in 1991 the samples were collected from July, and in 1992 from February.

The following variables were analyzed: pH (pHM 84, Radiometer) and conductivity (CDM 83, Radiometer), main ions (sulphate, nitrate, chloride, calcium, magnesium, sodium and potassium) by ion chromatography (Dionex 2010), ammonium (spectrophotometry, indophenol blue, Fresenius *et al.* 1988), alkalinity (acidimetric titration, end-points 4.5-4.2, Rodier 1984), reactive and total phosphorus (ammonium molibdate + ascorbic acid, Valderrama 1981), total aluminum (AAS, graphite furnace).

As no stable chemical stratification was detected during this study, the data in the text and tables are expressed as volume weighted means.

3.3. Phytoplankton

Integrated phytoplankton samples were taken at intervals of one meter from the surface to the bottom, simultaneously with those for chemical analysis, and immediately fixed with Lugol's solution. Countings were performed on 25 ml subsamples using the inverted microscope at a 400x magnification, on 100 randomly selected fields (Sandgren & Robinson 1984); the biomass was estimated from density data and mean cell volume (Smayda 1978). The chrysophycean *Mallomonas alveolata* was identified using the scanning electron microscope.

3.4. Zooplankton

Zooplankton samples were collected in 1992 in both lakes with a 126 µm mesh size plankton net, vertical hauls were made in the central zone of the lakes and under the ice cover. The samples were immediately fixed using alcohol 95% (Hall 1964) and then transferred into formalyn 10%. Most samples were counted entirely, under a compound microscope, using a 1 mm Hydro-Bios Kiel counting chamber. The different developmental stages were also taken into account.

3.5. Macrozoobenthos

Qualitative samples of macrobenthic fauna were collected at the same time as the chemical sampling in the two lakes along the shore-line to a maximum depth of 50 cm.

Five sampling sites (2 in LPS and 3 in LPI) (Fig. 3) were chosen, with differences of substrate and gradient. Sites 2 and 5 are fairly similar: they are level and consist of gravel and sand with a small amount of terrestrial plant remains; stations 1 and 4 are on steep slopes, the former with stony substrate consisting of landslip material and the latter with rocky substrate partly covered with sand. Station 3 is located along the outflow of LPI and consists of stony sediment with some coarse sand and sparse aquatic vegetation.

Samples were taken using a 225 µm hand collecting net, with the kick sampling method (Storey *et al.* 1991); they were fixed in 80% ethanol, sifted through a 225 µm net and sorted from the sediment in the laboratory.

In July 1992 three quantitative core samples (about 20 cm long, 5.6 cm internal diameter) were taken from the central zone of the lakes at the maximum depth.

3.6. Sediment core

A short core (about 20 cm) was collected in 1989 in LPS using a gravity corer. Algal pigments were extracted from *ca* 1.5 g of wet sediment with 90% acetone, and total carotenoids were quantified using the equation proposed by Züllig (1982). Data on absorbance at 430 and 410 nm were obtained from 90%

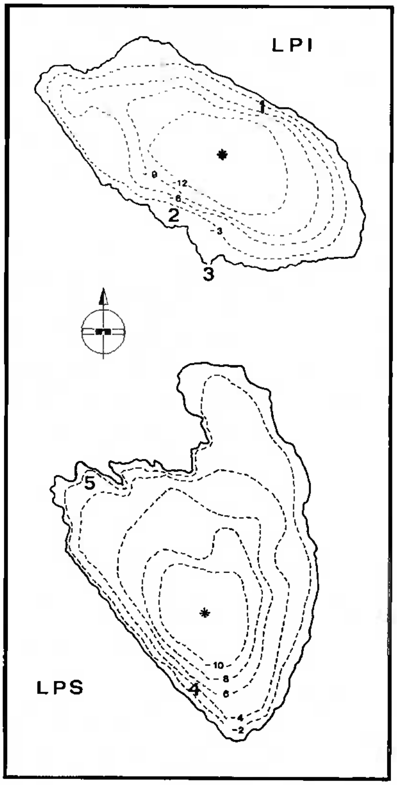

Fig. 3. Bathymetric maps of Lake Paione Inferiore (above) and Lake Paione Superiore (below) and sampling sites for temperature, water chemistry, plankton, sediment core (*) and macrobenthic fauna (numbers).

acetone extracts of sediments. Specific algal carotenoids were measured by TLC (Züllig 1982) and HPLC, mainly following the method of Mantoura & Llewellyn (1983) with some modification (Lami *et al.* 1993).

Pigment concentrations are used as indirect measures of the standing crop of planktonic communities. The ubiquitous ß-carotene represents an estimate of phytoplanktonic community development (Fig. 10). The specific carotenoids are descriptors of the following algal taxa (Züllig 1982): lutein for chlorophytes, fucoxanthin and diadinoxanthin for diatoms and chrysophytes, alloxanthin for cryptophytes, echinenone and zeaxanthin for cyanobacteria and dinoxanthin and peridinin for pyrrophytes. Astaxanthin is used here as an indicator of zooplankton community (Guilizzoni & Lami 1988).

Carbonaceous particles were analyzed following the method of Renberg & Wik (1985) and Rose (1990).

4. RESULTS AND DISCUSSION

4.1. Air temperature

The temperatures of the period January 1991-December 1992 were compared with those of the historical period 1951-91 on the basis of the monthly means of the daily values. In all the stations the summer values of the study period are 2-3 °C higher than the period 1951-1991; winter 1991-92 was warmer than the mean, while winter 1990-91 was not significantly different. Figure 4 shows the values for Lake Toggia, as representative of the six sampling stations.

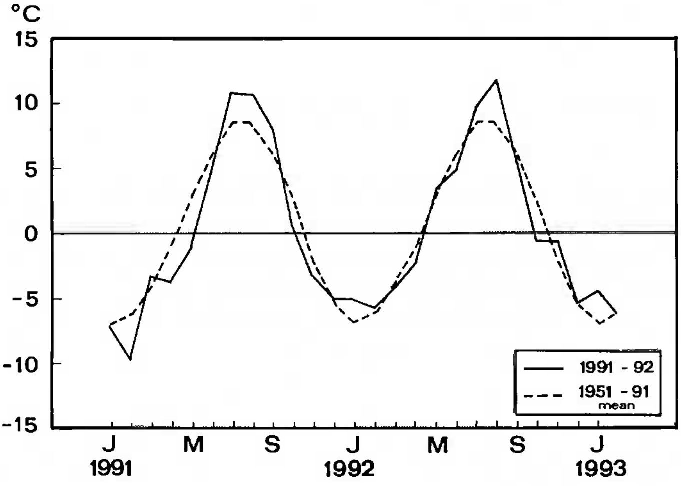

Fig. 4. Monthly averages of the daily mean temperature compared with the historical data (1951-91).

4.2. Atmospheric deposition

The amounts of precipitation during 1991 and 1992 at the station of Lake Toggia were 682 and 1153 mm, lower than the pluriannual average (1219 mm, reference period: 1951-91). Comparison of the monthly volume of precipitation with the historical means (Fig. 5) shows the lowest amount of precipitation in winter and spring 1991, while the highest value of 240 mm was measured in March 1992.

Comparison of the amounts of precipitation with the historical period at the other six meteorological stations surrounding the study area (Fig. 1), performed on an annual basis, shows differences comparable to those of Lake Toggia.

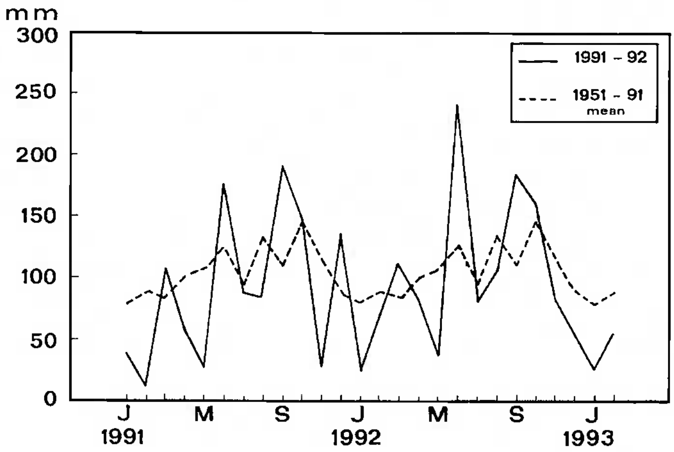

Fig. 5. Monthly volumes of precipitation compared with the historical (1951-91) means.

Volume weighted pH of atmospheric deposition at Lake Toggia for 1991 and 1992 (Tab. 2) was 5.21 and 5.60, respectively, with median values of 4.92 and 5.51. Sulphate and nitrate were the most important anions, while calcium and ammonium presented the highest concentrations among the cations.

Ionic fluxes (Tab. 2) in 1992 were about 50% higher than in 1991, because of the higher volume of precipitation.

Tab. 2. Volume weighted mean concentrations (A) and fluxes of ions (B) of atmospheric deposition at Lake Toggia. Conductivity µS cm^{-1} at 20°C, concentrations µeq l^{-1}, fluxes meq m^{-2} y^{-1}, pH recalculated from means [H^+].

	1991 A	1991 B	1992 A	1992 B
pH	5.2	-	5.6	-
Conductivity	9.7	-	9.6	-
Hydrogen ion	6	4	3	3
Ammonium	13	9	15	17
Calcium	24	16	16	19
Magnesium	3	2	3	4
Sodium	5	4	9	11
Potassium	2	1	3	4
Bicarbonate	6	4	9	10
Sulphate	24	16	20	23
Nitrate	15	10	14	16
Chloride	5	3	7	8
Sum cations	53	36	49	58
Sum anions	50	33	50	57

4.3. Lake temperature

Lake Paione Superiore was ice-free from August to September 1991 and from July to October 1992, while the ice-free periods for LPI were July-October 1991 and June-October 1992.

Temperature under the ice cover in March 1992 in LPS ranged from 0.8 (surface) to 4.1 °C (bottom). The lowest values of 0.6-1.2 °C were measured in the 0-7 m water layer in May 1992, during the snowmelt, while the temperature near the bottom was 3.1 °C. In July, a weak stratification occurred: the temperature was 12.8 at the surface and 8.2 °C at the bottom, while in August and September the values were homogeneous on the whole water column (14.5 and 8.2 °C, respectively).

In LPI the temperature ranged from 1.5 (surface) to 4.5 °C (bottom) under the ice cover in March 1992. The lake did not show a permanent thermal stratification during the summer. The highest temperature of 16 °C was measured in August 1992 in the 0-5 m layer.

4.4. Lake chemistry

Volume weighted mean concentrations of the main chemical variables and temperature are shown in table 3.

Tab. 3. Volume weighted mean concentrations in the lakes in 1991 and 1992.

		LPS Range	Mean	LPI Range	Mean
Temperature	(°C)	1.0-15.0	6.6	3.4-14.9	7.8
Diss. oxygen	(mg l^{-1})	8.2-11.4	9.8	9.1-11.4	10.2
Diss. oxygen	(% sat.)	76-108	88	79-119	94
pH		5.48-6.20	5.66	6.10-6.75	6.44
Conductivity	(at 18°C $\mu S\ cm^{-1}$)	8.0-9.8	9.2	10.7-13.2	12.2
Calcium	($\mu eq\ l^{-1}$)	33-48	43	66-87	77
Magnesium	($\mu eq\ l^{-1}$)	5-9	8	10-13	12
Sodium	($\mu eq\ l^{-1}$)	6-12	9	11-17	14
Potassium	($\mu eq\ l^{-1}$)	5-9	7	8-10	9
Ammonium	($\mu eq\ l^{-1}$)	0-6	3	0-2	1
Σ cations	($\mu eq\ l^{-1}$)	55-82	73	99-124	113
Alkalinity	($\mu eq\ l^{-1}$)	(-2)-2	0	15-34	27
Sulphate	($\mu eq\ l^{-1}$)	35-48	41	46-60	53
Nitrate	($\mu eq\ l^{-1}$)	19-27	23	22-34	27
Chloride	($\mu eq\ l^{-1}$)	3-5	4	3-6	4
Σ anions	($\mu eq\ l^{-1}$)	64-74	70	99-125	111
Total Al	($\mu g\ l^{-1}$)	23-63	42	7-35	17
Fluoride	($\mu g\ l^{-1}$)	7.0-7.7	7.3	10.6-15.7	12.3
Reactive Si	(mg l^{-1})	0.34-0.51	0.43	0.77-0.89	0.3

Oxygen concentration ranges between 8 and 11 mg l^{-1} in both lakes; as in the case of temperature and of the other chemical variables, no stratification was recorded.

The ion concentrations in LPS range between 120 and 160 μeq l^{-1} (conductivity values of 8.0-9.8 μS cm^{-1}); sulphate and nitrate are the main anions, in a ratio of 1.5 to 2.0.

In LPI the ion concentration is slightly higher (200-250 μeq l^{-1}) than in the upper lake, with corresponding conductivity values of 10.7-13.2 μS cm^{-1}. The main difference in the chemistry of the two lakes is in the alkalinity value, which is positive in all the samples in the case of LPI (range 15-34 μeq l^{-1}), while it is close to zero for LPS. The difference is due both to the higher watershed/lake surface ratio of LPI compared with LPS and to the presence of a small amount of calcareous schists in the watershed of LPI. As a consequence, pH is higher than 6 in the LPI samples, with a minimum of 6.1 during snowmelt. On the other hand the values are between 5.5 and 5.8 for the major part of the year in the case of LPS with a single value of 6.2 in September 1992. Alkalinity also explains the different aluminium concentrations, which range between 23-63 and 7-35 μg Al l^{-1} in LPS and LPI, respectively. Nitrate shows high concentrations (23 and 27 μeq l^{-1} in LPS and LPI, respectively) in comparison with values reported for remote lakes; in LPS ammonium also shows high levels, reaching a maximum value of 6 μeq l^{-1}. Reactive and total phosphorus is always below the detection limit of 3 μg P l^{-1}.

4.5. Phytoplankton

Two groups of algae are quantitatively important (Fig. 6), the Chrysophyceae and the Peridineae. In LPS three taxa make up the entire biomass: *Chromulina* sp., *Mallomonas alveolata* and *Gymnodinium* spp. These species are present throughout the year, but the Chrysophyceae are more important under the ice, and *Gymnodinium* in summer. In LPI the alternance between Chrysophyceae and Peridineae is more evident: some chrysophycean species (*Dinobryon sertularia*, *Uroglena* sp., *Chromulina* sp. and *Mallomonas alveolata*) coexist under the ice, while the biomass peak in summer (about 4 times higher than in LPS) is mainly caused by *Peridinium* cf *pusillum*.

The phytoplankton growing season in LPS occurs in the colder part of the year, with the highest biomass and density in winter under the ice-cover (Fig. 6); this well known phenomenon (Rodhe 1962; Wright 1964; Lecewicz *et al.* 1973; Maeda & Ichimura 1973; Nebaeus 1984) indicates a physiological adaptation of the phytoplankton community to a low energy regime. The biomass decline from March to May-June could be related to a more severe reduction in the underwater light, due to the deposition of a thick snow cover. The summer peak occurs just after the ice-melt and the algae tend to accumulate near the

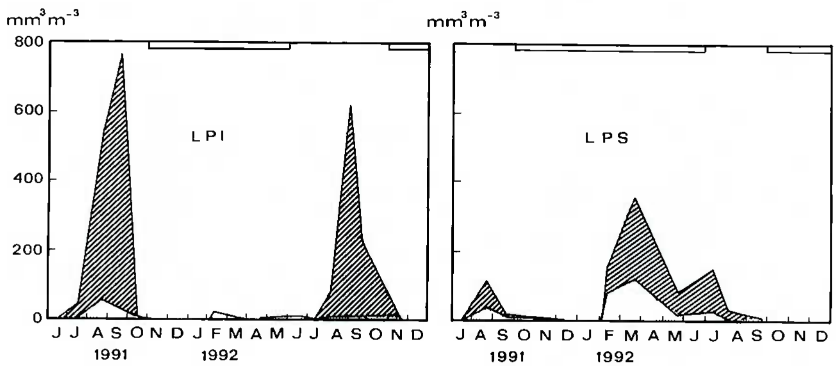

Fig. 6. Seasonal variations of phytoplankton biomass. Dotted area: Chrysophyceae. Dashed area: Dinophyceae.

bottom, where less light and lower temperature are found. The early decline of phytoplankton in summer corresponds to the beginning of the growing season of macro-filter-feeder zooplankton.

In LPI the highest phytoplankton biomass is observed in summer: the peak occurs one (1991) or two months (1992) later than in LPS, when the temperature reaches its highest values of the year; it is likely that the higher flushing rate of LPI limits phytoplankton growth during the early summer.

In both lakes the occurrence of the summer biomass peak is related to the earliness or lateness of the ice-melt: in 1992, when the ice melted one month earlier than in 1991, the biomass peak also occurred earlier (Fig. 6).

4.6. Zooplankton

In LPI two phases are observed, during which the total density of zooplankton is almost the same; the first when the lake is ice-covered, and the second in August (Fig. 7). Low density values are observed at the beginning of July, but we must take into account the fact that the late-July sampling was not performed, so that the data might be non-representative for the early summer phase. Under the ice cover only rotifers and copepods (mainly nauplii) are found; most copepods are cyclopoid nauplii, with very few copepodites or adults. Cladocera dominate in May, with *Bosmina longirostris* and *Daphnia longispina*. During August copepods represent more than 50% of the total population density, with *Cyclops abyssorum* and *Eucyclops serrulatus*. Among Cladocera, only Chydoridae Aloninae are present, with *Acroperus harpae* as dominant species.

In LPS zooplankton attain higher population density values (Fig. 7). Copepods dominate under the ice cover, reaching approximately the same den-

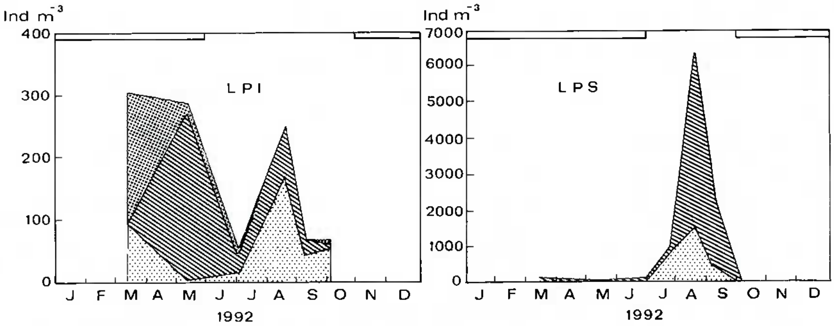

Fig. 7. Seasonal variations of zooplankton density in LPI and LPS. Light dotted area: copepods. Dashed area: cladocerans. Dark dotted area: rotifers.

sities as in LPI, but with copepodites much more abundant than nauplii and some adults also present. The July increase in density is due to copepods, mainly *Cyclops abyssorum*, and, to a lesser extent, to chydorid (*Chydorus sphaericus*, followed by *Acroperus harpae*). Copepods increase until August, when they attain their maximum density. Nauplii stages dominate with, in addition to *C. abyssorum*, *Eucyclops serrulatus* (whose adults are mainly found in the bottom sediments). The sharp August increase in population density is largely due to *Daphnia longispina*. Some chydorids are also present, mainly *Alona quadrangularis*, *Chydorus sphaericus* and *Acroperus harpae*. Rotifers are in general very scarce, with *Keratella quadrata* as dominant species.

The two lakes are quite different. In LPI rotifers and copepods dominate, whereas copepods and Cladocera are the most important groups in LPS. Species composition is also different: LPI is characterized by the considerable presence of *Bosmina longirostris* - not present in LPS - and by the relatively minor importance of *Daphnia longispina*. The summer growth phase is sustained in LPI by chydorids (with *Acroperus harpae* as a major species, followed by *Alona quadrangularis*), whereas in LPS *Daphnia* dominates.

Some important changes have occurred in the two lakes since the time of Tonolli's investigation (1947). *Arctodiaptomus bacillifer*, which was the dominant species together with *Daphnia longispina*, has apparently disappeared from both lakes. On the other hand, *Bosmina longirostris*, not found before, has become at least as abundant as *Daphnia longispina* during spring in LPI, where *Acroperus harpae* is also found.

The differences between the two lakes and between the past and present situations cannot be explained in terms of acidification. The lower pH cannot be responsible for the much higher population density of *Daphnia longispina* in LPS, nor can the development of *Bosmina* population in LPI be explained by the higher pH. It is more realistic to attribute both the differences in the structure of the zooplankton population of the two lakes and the differences with respect to the past to the presence of fish in LPI.

4.7. Macrozoobenthos

The littoral macrobenthic community of the two lakes is predominantly composed of Insecta, especially Diptera Chironomidae, followed by Oligochaeta. Acari and Turbellaria made up only a minor fraction of the community, while Mollusca Lamellibranchia of the genus *Pisidium* are present in small numbers in LPI only.

In LPS chironomids are mostly represented by *Heterotrissocladius* (Orthocladiinae), *Zavrelimyia* (Tanypodinae) and *Micropsectra* and *Paratanytarsus* (Tanytarsini), while in LPI *Psectrocladius* and *Corynoneura* among Orthocladiinae are also present in large amounts. Probably due to emergences, their numbers are relatively low at the snowmelt (Tab. 4), but increase considerably during summer and early autumn because of the presence of young individuals of the new generation. Other Insecta groups such as Diptera Culicidae and Limoniidae, Trichoptera Limnephilidae, Coleoptera Dytiscidae are well represented in LPS, but fairly scarce in LPI where Diptera Simulidae and Ceratopogonidae, Megaloptera Sialidae and Plecoptera Nemouridae can also be found. In both lakes the greatest proportion of Oligochaeta consisted of Enchytraeidae, but large numbers of Naididae together with a few individuals of Tubificidae and Lumbriculidae are also found in LPI.

Animals restricted to the deepest bottom are very scarce and are prevalently Diptera Chironomidae (*Procladius* and *Tanytarsus*), with Oligochaeta Tubificidae in LPI.

The extreme physico-chemical conditions (short ice-free period, low temperatures, low ionic concentration) and the oligotrophy of both lakes are the main cause of the qualitatively poor macrobenthic community. Nevertheless the possibility that the moderately acid water, associated with low alkalinity values, has a negative influence on the structure of the community, above all in LPS where lower values of pH were recorded, cannot be excluded (Okland & Okland 1986). In particular, the composition of the zoobenthos of both lakes seems to be strongly affected by minima of pH, usually reached at the snowmelt in a lake, especially along the shoreline (Merilainen & Hynynen 1990). Particularly significant from this point of view is the extreme scarcity in LPI, and the absence in LPS, of Mollusca, which are more sensitive to acidification (Okland & Okland 1986).

Moreover, the dominant groups present are those more tolerant of acidity: Chironomidae, Limnephilidae, Nemouridae, Sialidae and Dityscidae among Insecta (Hendrey & Wright 1975; Wiederholm & Eriksson 1977; Mossberg & Nyberg 1979; Raddum & Fjellheim 1984; Kenttamies *et al.* 1985), Enchytraeidae among Oligochaeta (Merilainen & Hynynen 1990).

Tab. 4. Percentages of abundance of some selected benthos taxa in LPI and LPS. Tri=Trichoptera; Col=Coleoptera; Cul=Culicidi; Lim=Limoniidae; Chi=Chronomidae; Ins=Other Insecta; Oli=Oligocheta; Tur=Turbellaria; Aca=Acari.

LPI

	Date	Chi	Ins	Oli	Tur	Aca	Mol	Tot. No
Station 1								
	16/07/91	76.3	17.6	0.0	0.0	6.1	0.0	114
	20/08/91	90.0	1.6	0.0	3.6	4.8	0.0	250
	17/09/91	97.9	0.1	0.1	1.2	0.7	0.0	2242
	16/06/92	78.5	8.4	5.3	0.0	7.6	0.2	584
Station 2								
	18/06/91	73.2	3.8	19.9	0.0	0.7	2.4	419
	16/07/91	51.5	5.5	36.6	0.5	5.7	0.2	440
	20/08/91	54.1	0.9	28.0	10.5	5.5	1.0	724
	17/09/91	91.2	1.0	3.3	2.3	1.5	0.7	1143
	18/05/92	18.4	2.2	76.9	0.0	2.5	0.0	489
	16/06/92	43.5	1.3	48.0	0.0	6.5	0.7	448
Station 3								
	16/07/91	73.7	13.8	5.0	3.7	3.8	0.0	80
	20/08/91	62.9	17.1	8.6	5.7	5.7	0.0	70
	17/09/91	85.0	3.3	5.8	4.2	1.7	0.0	120
	18/05/92	18.2	22.7	50.0	0.0	9.1	0.0	23
	16/06/92	62.4	17.8	19.2	0.0	0.6	0.0	338

LPS

	Date	Chi	Lim	Cul	Tri	Col	Oli	Tur	Aca	Tot. No
Station 4										
	16/07/91	36.4	0.0	27.3	9.1	18.2	9.1	0.0	0.0	11
	20/08/91	46.3	0.0	0.0	17.1	7.3	0.0	0.0	29.3	86
	17/09/91	81.7	0.0	0.0	0.8	2.3	0.8	4.6	9.9	131
	16/06/92	0.0	0.0	0.0	0.0	2.8	69.4	0.0	27.8	39
	07/07/92	66.7	0.0	0.0	7.9	3.2	1.6	0.0	20.6	69
	28/07/92	26.5	0.0	5.3	48.3	4.0	1.3	0.0	14.6	151
	14/09/92	3.8	31.7	0.0	12.2	0.0	49.3	0.0	3.0	370
Station 5										
	16/07/91	0.0	0.0	16.1	48.4	22.6	12.9	0.0	0.0	31
	20/08/91	12.4	0.0	21.2	17.7	17.7	6.2	0.0	24.8	118
	17/09/91	79.8	0.0	3.9	0.5	0.8	13.4	1.3	0.3	381
	07/07/92	2.9	0.0	14.3	28.6	17.1	17.1	0.0	20.0	38
	28/07/92	37.1	0.0	3.1	26.3	2.6	14.9	0.0	16.0	195
	14/09/92	19.5	53.9	0.0	12.0	3.0	8.2	0.0	3.4	267

4.8. Sediment core

We found that the 430:410 absorbance ratio is significantly correlated with lake water pH and that it can be considered as a new index for reconstructing pH history (Guilizzoni *et al.* 1992). The reduction of the 430:410 ratio at the top of the core (Fig. 8) shows the existence of an acidification process in LPS. PH curves inferred from this ratio show that LPS began to acidify at around 5-6 cm sediment depth, i.e., about 1950 A.D., as the mean sedimentation rate is 0.15 cm y^{-1}.

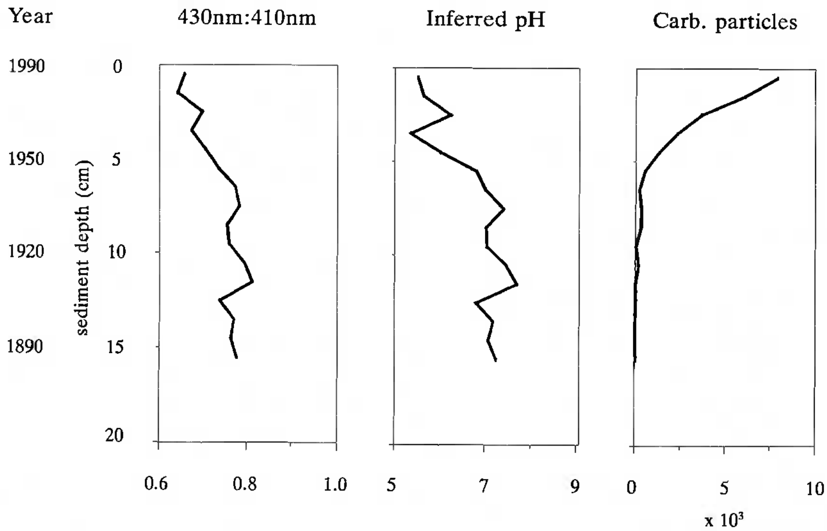

Fig. 8. Profile of the 430:410 nm absorbance ratio, inferred pH based on the absorbance ratio and carbonaceous particles (No g^{-1} d.w.) in a sediment core of LPS.

These changes in pH are related to the increase in carbonaceous particles deriving from fossil-fuel combustion (Lami *et al.* 1993). The reconstructed lake-water pH based on this ratio is in accordance with those based on chrysophyte and diatom remains (Guilizzoni *et al.* 1992; Marchetto & Lami 1993; Marchetto & Schimdt 1993).

According to hydrochemistry studies carried out during the 80s, absolute data on plant pigment concentrations (Fig. 9) confirm the oligotrophic condition of LPS, although wide variations in algal biomass have occurred over the sample time (130 years). The levels of lutein, fucoxanthin, and echinenone (with zeaxanthin) reflect the occurrence of organisms belonging to chlorophyceae, diatoms and cyanobacteria, respectively. As these algal groups are absent from the water column, the pigments indicate the presence of benthic forms.

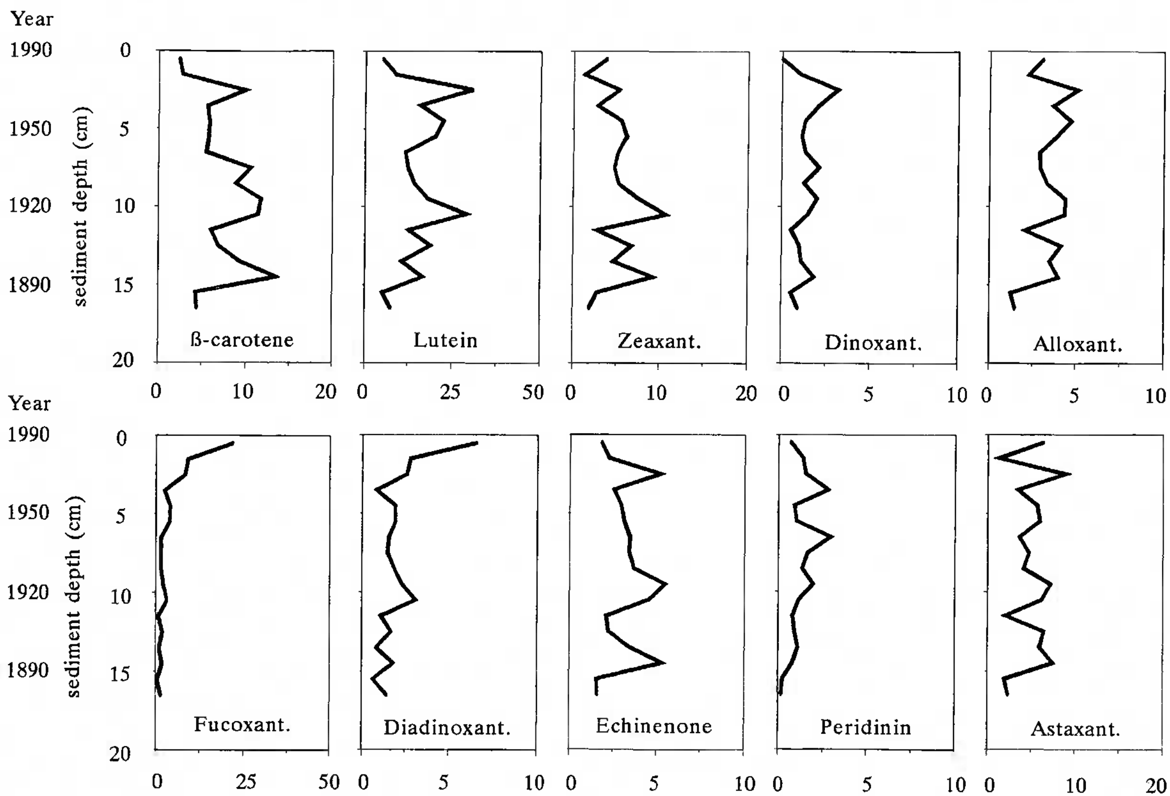

Fig. 9. Sedimentary profile of some carotenoids (nM g^{-1} o.m.) in a sediment core of LPS.

Unlike other pigments, fucoxanthin and diadinoxanthin concentrations increase sharply in the upper three sediment layers, in accordance with diatom counts (Cameron, pers. comm.) and biogenic silica profiles (data not shown).

Finally, the zooplankton community of LPS, as traced by astaxanthin, does not show any particular trend through time.

5. CONCLUSIONS

The Paione lakes are ultraoligotrophic, slightly acid lakes; small but persistent chemical differences between the two lakes have been found in all the samplings. Notwithstanding the relatively low atmospheric acid load, diatom remains, carbonaceous particle and pigment profiles in the sediments all indicate that the two lakes have undergone acidification since the fifties.

The biological communities are simplified, in consequence of the extreme physical and chemical conditions. The phytoplankton of the Paione lakes fits quite well with the general characteristics of the community in ultraoligotrophic high mountain lakes (Pechlaner 1971; Capblancq & Laville 1983), i.e., low number of species, dominance of nannoplanktonic flagellates and low biomass. The quantitative variations of phytoplankton and the differences between the two lakes would appear to be mainly determined by physical (hydrology, duration of ice-cover and underwater climate) and biological (zooplankton) factors. As for the effect of acidification on phytoplankton, the dominance of Chrysophyceae and Peridineae is quite typical of lakes with low pH (Bleiwas *et al.* 1984; Siegfried *et al.* 1987); however, the Peridineae seem to be the most acid-resistant group, increasing their biomass when pH decreases (Stokes 1986; Baker & Christensen 1990), while in the Paione lakes the reverse pattern is observed. The zooplankton differences between the two lakes can hardly be explained in terms of pH, because the most notable changes reported seem to occur at pH <5 (Locke 1991); moreover, *Bosmina*, one of the most acid-tolerant species (Keller & Yan 1991), is important in LPI but absent in the more acid LPS. The introduction of fish into LPI seems to be the factor most likely to explain the differences between the two lakes and some of the changes which have occurred. The littoral macrozoobenthos shows some indications of a pH effect, especially in LPS where the community is characterized by the absence of mussels, normally present in fair amounts in oligotrophic lakes but more sensitive to acidification (Raddum 1980), and by the presence of the more acid-tolerant groups among insects and oligochaetes.

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