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Palaeolimnological studies of the eutrophication of volcanic Lake Albano (Central Italy)

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Abstract

We use palaeolimnological techniques to reconstruct the eutrophication history of a volcanic lake (Lake Albano, central Italy) over the past three centuries. The presence of annual varves down to the bottom of the core (*c.* 1700 A.D.) indicated the lack of bioturbation and likely long-term meromixis. Sedimentation rates were estimated by varve counts (calcite/diatom couplets), indicating a mean rate of 0.15 cm yr^{-1}. The reconstruction of eutrophication was traced using past populations of algal and photosynthetic bacteria (through their fossil pigment), and geochemistry, as well as fossil remains of chironomids. Phaeophorbide *a* and the red carotenoid astaxanthin were used to detect past zooplankton development.

The first sign of trophic change related to human activities is dated *c.* 1870 A.D. From that period onward a sharp increase of authigenic $CaCO_3$, nitrogen, N:P ratio, and dinoxanthin, a characteristic carotenoid of Chrysophyceae and Dinophyceae, is observed.

Chironomid analyses showed the near absence of a deep water fauna throughout the core length. The populations of chironomid larvae are restricted to oxygenated littoral zones. In fact, the few fossil remains found are primarily of littoral origin, representing shallow water midges that were transported to profundal waters. The reduction of total chironomid in the uppermost layers of the core is to be related to human land uses.

Introduction and overview of Lake Albano

Palaeolimnological pilot studies (Masaferro, 1994) were carried out on Lake Albano and on an additional five volcanic lakes (Bolsena, Bracciano, Nemi, Mezzano, Martignano) to assess their potential for palaeolimnological investigations of Pleistocene/Holocene environmental changes. All lakes have their origin in Pleistocene volcanism (Niessen *et al.*, 1993). The northern Latium lakes are older than those in the south (e.g., L. Albano). The formation of the Albano crater lake is related to the last volcanic activity in this region, which had a strong explosive phreato-magmatic character. It is presently assumed that the Albano eruption took place about 40–50 kyr B.P. (Fornasieri, 1985), and the lake probably formed soon after. Seismic reflection profiles indicate an undisturbed sediment fill of at least 15 m thickness, which is mainly of a hemi-pelagic character (Niessen *et al.*, 1993). The maar Lake Albano (z_{max} = 175 m; mean depth = 77 m; surface area = 6 km^2; catchment area (lake excluded) = 3.68 km^2; τ w = 47 yr) is the deepest lake amongst those located in the volcanic lake district in Latium (Fig. 1). It receives water mainly from atmospheric precipitation and underwater springs. An outflow

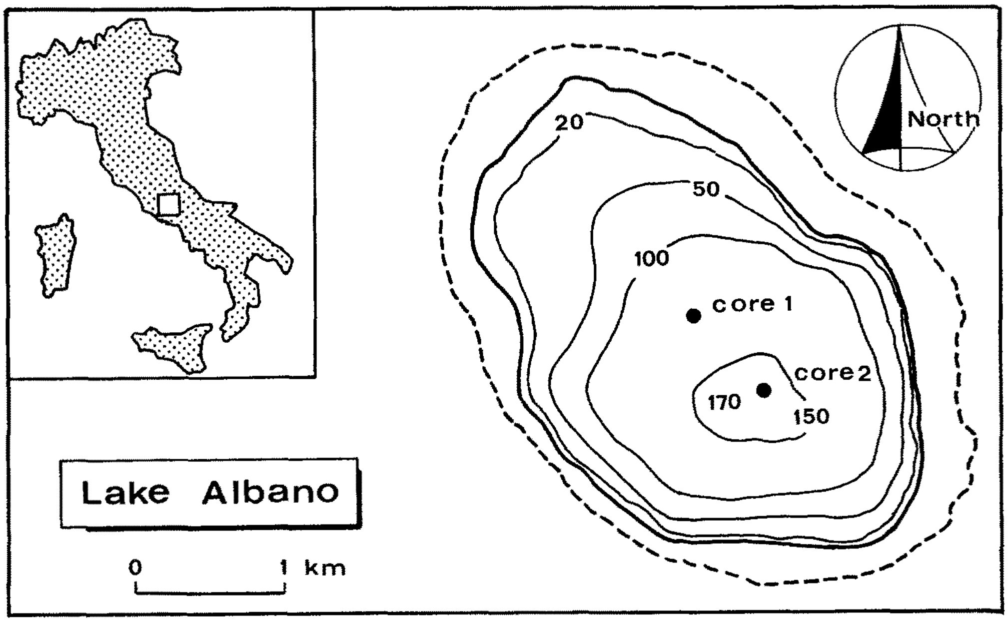

Fig. 1. Map of the Lake Albano showing the coring sites. The bathymetry and the watershed are also indicated.

canal was dug by the Romans in 398–397 B.C. (Stella & Socciarelli, 1949).

From the few literature data available it appears that below 60–100 m oxygen is absent all year round and as a consequence profundal macrobenthos is absent (Margaritora, 1992). The yearly temperature near the bottom ranged between 8.7 and 9.0. pH along the whole water column ranges from about 8.0 (surface) to 6.98 (bottom). Reactive phosphorus and N-NH_4 range from 0 in the epilimnion to about 170 $\mu g\ l^{-1}$ and 470 $\mu g\ l^{-1}$ in the hypolimnion, respectively (unpublished data). In contrast, N-NO_3 concentration is high (230 $\mu g\ l^{-1}$) in the epilimnion, approaching the values of eutrophic lakes (Bonacina *et al.*, 1992; Mosello, unpublished data), and zero in the hypolimnion. For most of its perimeter, Lake Albano has steep slopes (*c.* 10 °) particularly on the South-East side (Spinelli, 1983).

With the 1960 Olympic Games and the utilization of the area for tourism and recreational activities, the NW and NE lake shores were deeply modified by man (Margaritora, 1992). These modifications have significantly affected the density and community structure of the littoral benthos (Mastrantuono, 1988).

The phytoplankton is presently dominated by Cyanobacteria with high density and biomass of *Oscillatoria rubescens*, Chlorophyceae and diatoms (65%, 24% and 9% of biomass, respectively; Margaritora, 1992). *Ceratium hirundinella*, which was very abundant during the 1940s (Stella & Socciarelli, 1949), is now almost completely absent. Although this lake has suffered from anthropogenic eutrophication during the past 20–30 years, even in the 1940s there were reports of frequent algal blooms of *Aphanizomenon ovalisporum*, *Mougeotia elegantula* and *Oscillatoria rubescens* (Stella & Socciarelli, 1949; Cannicci, 1953). In addition, red blooms of *Botryococcus braunii* (Stella & Socciarelli, 1949), a cosmopolitan Chlorophyceae unusually rich in β-carotene, lutein and hydrocarbon oil content (Belker, 1968; Wake & Hillen, 1981; Züllig, 1985a), were common. *Botryococcus* colonies can not be associated with lake trophy because they are often present in waters rich in organic nutrients as well as in oligotrophic environments (Aaronson *et al.*, 1983).

Macrophytes include abundant rooted *Potamogeton*, *Ranunculus*, and *Ceratophyllum* populations along shallowest areas in the NW.

The zooplankton community of the pelagic zone is represented by 11 species of rotifers, 4 of cladocerans and 2 of copepods. In some periods, the metalimnetic development of *O. rubescens* leads to the crowding of *Daphnia hyalina* and other filter-feeding organisms in the surface waters (Margaritora, 1992).

The objectives of the pilot studies were twofold: (i) Short cores (50–100 cm) were collected to infer recent trophic changes in the lake and to assess the sensitivity of the Albano sediments for recording environmental changes. Long-term limnological data are available for very few lakes, historical information can thus be provided by a palaeolimnological approach. In particular, the long-term changes in the planktonic autotrophic populations can be inferred from the analysis of distinctive and group-specific carotenoids (Züllig, 1982, 1989). Moreover, the ecological range and sensitivity of chironomids often make it possible to interpret changes in aquatic environments (Hofmann, 1988; Walker, 1993). (ii) High resolution seismic reflection profiles provide information on the thickness and geometry of the basin fill and are particularly suitable for detection of long-term variation (kyr). These results are reported elsewhere (Niessen *et al.*, 1993).

Sedimentological investigation and data from physical, chemical and biological analyses (varves, authigenic carbonates, biogenic silica, nutrients, pigments and chironomid remains), which are particularly suitable for palaeoenvironmental reconstruction, are presented in this paper.

Materials and methods

Two *c.* 50 cm long sediment cores were collected in September 1990 from the centre of the lake (115 m water depth) and the deepest area (Fig. 1) using a gravity corer. For lateral core correlation the magnetic susceptibility was measured on both cores (whole core measurements) using a Bartington MS 2 meter and a 80 mm diameter core sensor. The method is explained in more detail by Thompson & Oldfield (1986).

In the laboratory, the cores were cut vertically and their lithology described. One half was used for sedimentological studies, the other half for geochemical analysis. Thin sections were made from freeze-dried sub-samples after resin preparation using Araldit by 158/Hy 2996 (Ciba Geigy Corp. Basle, Switzerland). Core ALB 90/2 was selected for additional analyses. For geochemical analysis, thirteen 2 cm thick slices were sampled throughout the core from intervals, which, from visual inspection, appeared to be dominated by autochthonous sediments (Fig. 2). Thick turbidites (>1 cm thickness) were not sampled to avoid contamination of undisturbed pelagic sediments with redeposited (turbidite) material. Minerals such as calcite and quartz were determined from dry sub-samples by the x-ray diffraction method (Tucker, 1988).

Approximately 25 mg of dry sediment was used for biogenic silica ($BSiO_2$) analysis (Demaster, 1981). Sediments were leached in 30 ml of 1.0% Na_2CO_3 at 85 °C for 5 h with a 0.5 ml sample being withdrawn at 1, 2, 3 and 5 h for analysis of soluble silica. For samples with high $BSiO_2$ concentrations no significant correlations were found with these time-course data. In these cases, a mean of the last three measurements was calculated.

Bulk density of the sediment layers was calculated using the equation proposed by Håkanson (1981).

Total carbon and nitrogen were determined on dry sediment using a CHN analyzer (Carlo Erba). The inorganic C was measured with the CHN analyzer on a subsample previously ignited at 550 °C. Total nitrogen was essentially organic N, since inorganic N was negligible ($\leq 5\%$). Phosphorus was obtained by the sulfuric acid (1 N) extraction (Vogler, 1965; Marengo & Baudo, 1988) and then analyzed for reactive phosphorus after Murphy & Riley (1962). Organic P was estimated as the difference between total and inorganic phosphorus. The organic matter and $CaCO_3$ were obtained by loss-on-ignition at 550 °C and 950 °C, respectively. Losses at 950 °C were calculated as $CaCO_3$ using a multiplying factor of 2.27 (Dean & Gorham, 1976).

Chlorophyll derivatives (CD) and total carotenoids (TC) were extracted with 90% acetone and expressed as in Züllig (1982) and Guilizzoni *et al.* (1983), respectively.

Algal and bacterial pigments were extracted (overnight, at 10 °C, in the dark and under nitrogen) from *c.* 1 g wet sediments using 90% acetone and then centrifugated at 3000 rpm for 10 min in 15 ml glass centrifuge tubes. Extractions were conducted with HPLC-grade solvents. No pigment degradation resulted from this procedure. Pigments were determined by ion pairing, reverse-phase HPLC (modified from Mauntoura & Llewellyn, 1983; Hurley, 1988). Data are expressed as nanomoles per gram of organic matter. The ion pairing (tetrabutyl ammonium phosphate 10^{-3} M) allows for greater resolution of the dephytolated acidic chloropigments (Chl *c*, chlorophyllide *a*, and phaeophorbide *a*). The equipment employed consisted of a gradient pumping system and dual channel variable wavelength UV-VIS detector (set at 460 nm and 656 nm for carotenoids and chloropigments, respectively) controlled by a computer (Beckman System Gold). An auto-injector equipped with a Rheodyne valve was connected through a precolumn to a reverse-phase C_{18} ODS column (5 μm particle size; 250 mm x 4.6 mm i.d.). After sample injection (300 μl of acetone extract not dried in a rotary evaporator), a gradient program that ramped from 85% mobile-phase A (80:20, by vol. methanol:aqueous solution of

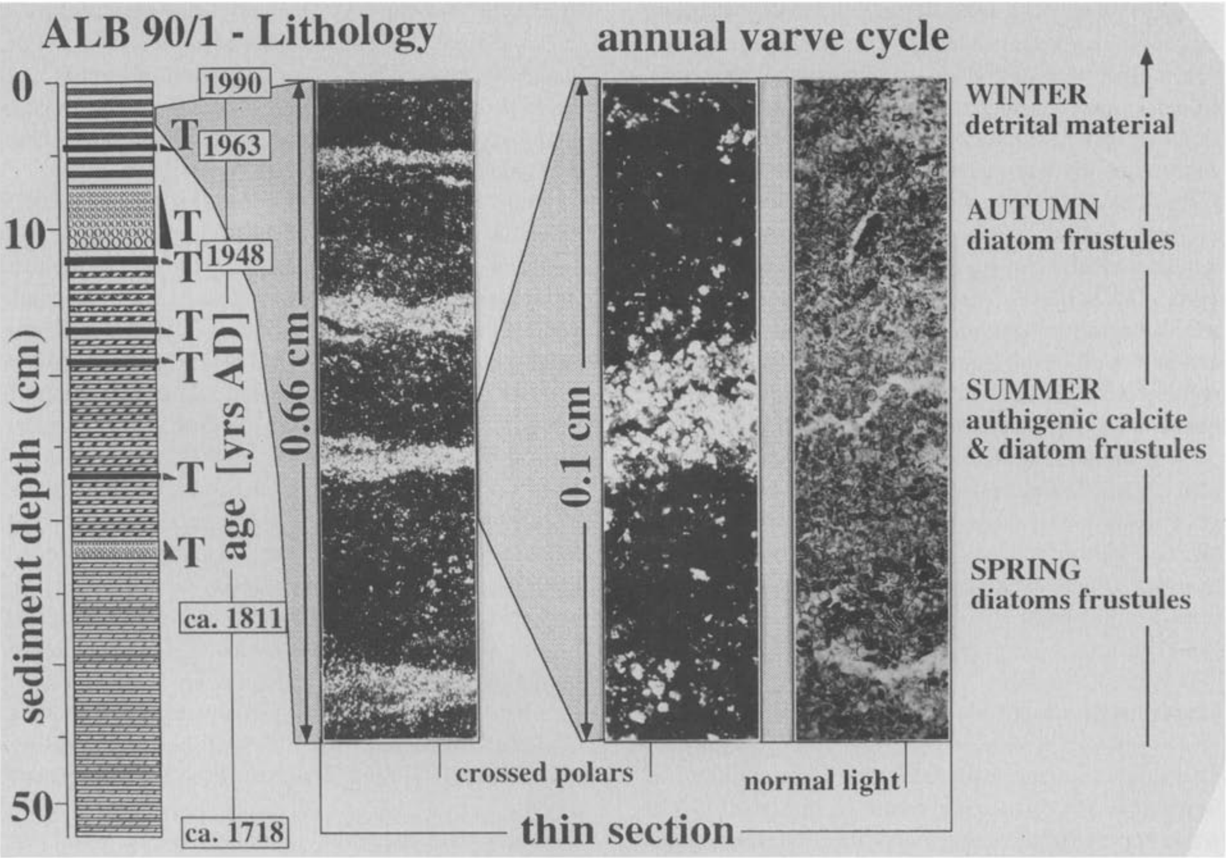

Fig. 2. Lithology of core ALB 90/1 (T = Turbidite).

0.001 M ion-pairing and 0.001 M propionic acid) to 100% mobile-phase B (60:40, acetone:methanol) in 30 min with a hold for 20 min provided sufficient resolution of all pigments of interest. Flow rate increased from 1 ml min^{-1} to 2 ml min^{-1}. The column was re-equilibrated between samples by linear ramping to 85% mobile- phase A for 5 min and maintenance for 10 min before sample injection. With this procedure, we were able to separate zeaxanthin from lutein and *beta*-carotene from phaeophytin *a* (Guilizzoni & Lami, 1992). Analysis of replicate sediment samples yielded a C.V. of 4.5%–11.5%, depending on pigments.

Identification of all pigments was confirmed by comparing the absorption spectral characteristics and chromatographic mobility of pigments isolated from sediments with those obtained from TLC analysis (Züllig, 1982; Guilizzoni *et al.*, 1986), commercial standards (Sigma Chemical Co.), standards kindly donated by Hoffmann-La Roche of Basle, water samples of known phytoplankton composition, and published values (Foppen, 1971; Davies, 1976; Züllig, 1982; Mantoura & Llewellyn, 1983). Standard of okenone was obtained from culture of *Chromatium okenii* kindly provided by Dr H. Züllig. Spectra were obtained with a Perkin-Elmer Lambda 6 spectrophotometer.

Pigment concentrations were determined, following Mantoura & Llewellyn (1983), on the basis of molar extinction coefficients at the detection wavelengths. The molar extinction coefficients $E^{1\%}_{460}$ and $E^{1\%}_{656}$ were derived from the $E^{1\%}_{max}$ reported in Davis (1976) and Mantoura & Llewellyn (1983).

Chironomid fossil analysis was performed following the methods of Hofmann (1983, 1986) and Warwick (1980), but slightly modified by us (Guilizzoni *et al.*, 1992a). Subsamples of about 5 g wet sediments were deflocculated with hot KOH 10% for about 45 min. Subsequently, the sediment matrix was removed by sieving (226 μ m and 50 μm) to reduce sample size. The sieved remains of each fraction were picked and mounted on glass slides. Taxonomic identifications were based on Hofmann (1971), Ferrarese & Rossaro (1981), Rossaro (1982), Ferrarese (1983), Wiederholm (1983), and Nocentini (1985).

The sedimentation rate of the lake was estimated by the varve counts. Our calculated average sedimentation rate of 0.15 cm yr^{-1} is in good agreement with those calculated in other volcanic lakes of the same district by the ^{137}Cs and ^{210}Pb methods (Simpson *et al.*, unpublished data).

Results and discussion

The sediment core comprises two lithostratigraphic elements: (i) regular alternation of laminae of authigenic calcite and diatom/organic matter, and (ii) graded mud turbidites (Fig. 2). The former dominate the sequence. As seen in thin sections, each couplet of the calcite/diatom laminae shows a characteristic cycle: there is organic rich mud dominated by diatom frustules at the base, overlain by a thin lamina of authigenic calcite best seen through polarized light (Fig. 2). Single calcite crystals show polyhedral morphometries and have grain sizes on the order of 5 μm. There is some increase of detrital material toward the top of the cycle. In freshly cut cores and under the microscope (polarized light), the couplets appear as regular alternations of white laminae (calcite) sandwiched by black organic/diatom-rich mud. The laminae-couplets are identical with varves (Fig. 2) typically observed in eutrophic or meromictic lakes with bottom water anoxia as described from many eutrophic lakes (Kelts & Hsü, 1978; Niessen & Sturm, 1987; Züllig, 1982) and thus assumed to have an annual repetition (varves).

One varve cycle can be best explained as the depositional product of seasonal changes of formation of lacustrine sediments and input of detrital matter from allochthonous and/or littoral sources: (i) Algal blooms (i.e., diatom blooms) occur in early spring due to warming up of the epilimnic water. (ii) Photosynthesis shifts the aquatic CO_2 system and the pH values increase. As a result, oversaturation with respect to $CaCO_3$ and subsequently precipitation of authigenic calcite occurs during late spring and summer. (iii) There are additional blooms of algae during autumn. Finally, between late autumn and early spring of the subsequent year, the detrital input from allochthonous sources and from shallow areas becomes more important.

The varves of Lake Albano are distinct in the upper part of the sequence (above *c.* 12 cm sediment depth, corresponding to an age of 1948 A.D.) becoming indistinct and thinner with depth mostly due to the occurrence of very thin calcite laminae. The latter results in some uncertainties as to the varve counting below this date. It is thus possible that a few calcite laminae were overlooked or were not present in places. In order to test the reproducibility of the varve counting for Lake Albano deposits, lamina couplets were counted in both cores ALB 90/1 and ALB 90/2 (Table 1). The countings are compared with lithological marker horizons, such as turbidites, distinctly observed in both cores as synchronous event deposits as well as with oscillations in magnetic susceptibility observed in both cores (Fig. 3). The latter are known to reflect lithological changes in the sediment sequence with high resolution (Thompson & Oldfield, 1986). Indeed, spikes of high susceptibility are in coincidence with turbidite occurrence for both Albano cores. This suggests that susceptibility oscillations are mainly controlled by fluctuations in allochthonous (volcanically derived) versus autochthonous material. Since the oscillations correlate from core to core, they are used as time-stratigraphic markers and were labelled from 1 to 10 (Fig. 3). This also implies that core ALB 90/1, which is analyzed in detail in this study, has the longer record and lower sedimentation rate because labels 8 to 10 were apparently not drilled in core ALB 90/2.

For both cores, varve counting consistently reveals 27 varves between the top of the cores and magnetic oscillation 1 (turbidite). This indicates a lake-wide occurrence of the regular lamination and supports the argument that the lamina couplets are annual deposits, which have no gaps. However, the varve-counting differences between the cores increase with sediment depth (Table 1). Presumably this is related to indistinct occurrences of white calcite laminae, as mentioned above. Therefore a dating error of ± 10% of the counts may be realistic in the lower part of the core (Table 1).

Turbidites can be distinguished in cores as products of redeposition from sediment-laden density currents by the following characteristics: fining upward of grain size, higher content of allochthonous detrital matter, and distinctly different (mostly reddish) colors. The turbidites are related to events, such as sub-aquatic slumps, due to slope instability (cf. Fig. 1) and/or major storms. Earthquake events, rather frequent in the region (Postpischi, 1985), could also be responsible for the occurrence of turbidites because they cause slope instabilities. Indeed, some of these occurred approximately at the same time also in the nearby Lake Nemi (Masaferro *et al.*, 1993). Seven larger turbidite events

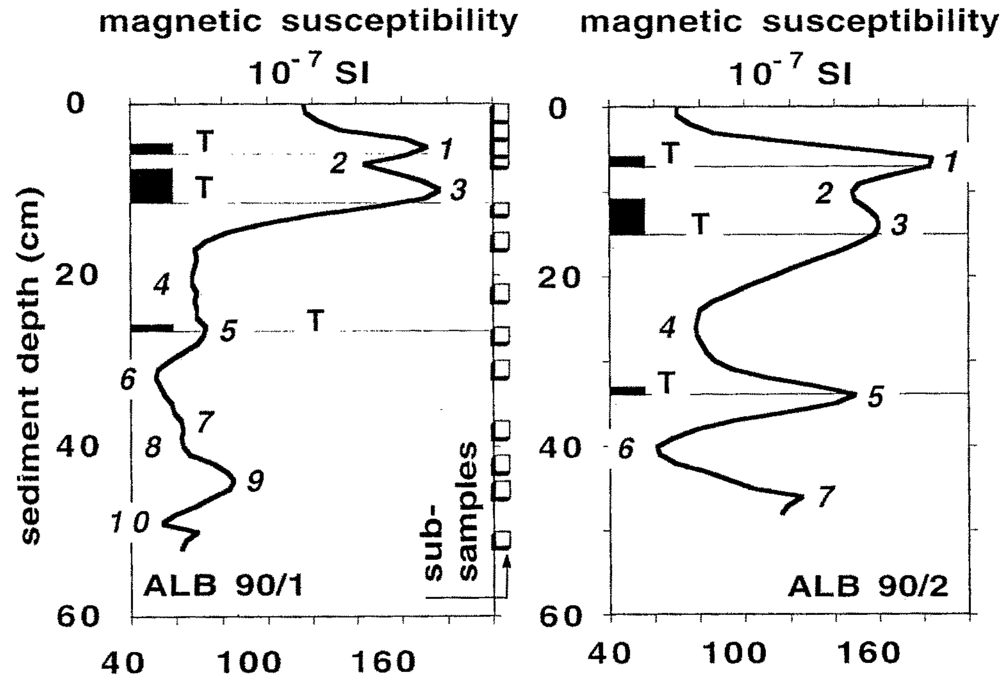

Fig. 3. Magnetic susceptibility of cores ALB 90/1 and ALB 90/2. Oscillations are labeled from top to bottom (1 to 10). T = Turbidite. Note positions of subsamples.

Table 1. Counting of lamina couplets (cumulative no. in parenthesis).

core ALB 90/1	counting difference	core ALB 90/2	reference layer
27	0	27	top of core (A.D. 1990)
12 (39)	1	11 (38)	magn. label 1 (turbidite)
91 (130)	8 (9)	83 (121)	magn. label 3 (turbidite)
22 (152)	11 (2)	33 (154)	magn. label 5 (turbidite)
			mag. label 6

are recorded throughout the core covering the last 270 years (Fig. 2).

The density of the sediment does not undergo any changes from 50 cm to 17 cm, but then starts to oscillate (Fig. 4). The dry weight parallels the density changes and increases from 20 cm to the surface. Loss-on-ignition, which approximates the organic matter content, undergoes marked changes, particularly from *c.* 25 cm onward. The O.M. curve is very similar to that of $BSiO_2$ (Fig. 4; correlation significant at $P \leq 0.01$, $r = 0.74$) and specular to calcite depth profile (negative correlation, $P \leq 0.01$, $r = -0.67$).

An indication of a change in trophic status in Lake Albano is also recorded in the geochemical results at the transition zone at *c.* 1870 A.D. From the profiles reported in Fig. 4 and from the nutrient ratios (Figs. 5 and 6), an abrupt change at the 25 cm horizon (*c.* 1870 A.D.) is observed. The sharp increases of $CaCO_3$ compared to relative constant contents of allochthonous quartz in the sediment sequence, as evidenced by x-ray diffraction results (not shown), indicate autochthonous production of calcite. Such marked changes in $CaCO_3$ of lake sediments are of interest with regard to primary production of lakes (Wetzel, 1970). As is the case for other Italian lakes (e.g., Varese, Adams *et al.*, 1978; Guilizzoni *et al.* 1986), it is possible that the increase in sedimentary $CaCO_3$ in the upper layers of Lake Albano can be related to precipitation of authigenic calcite induced by increased primary production

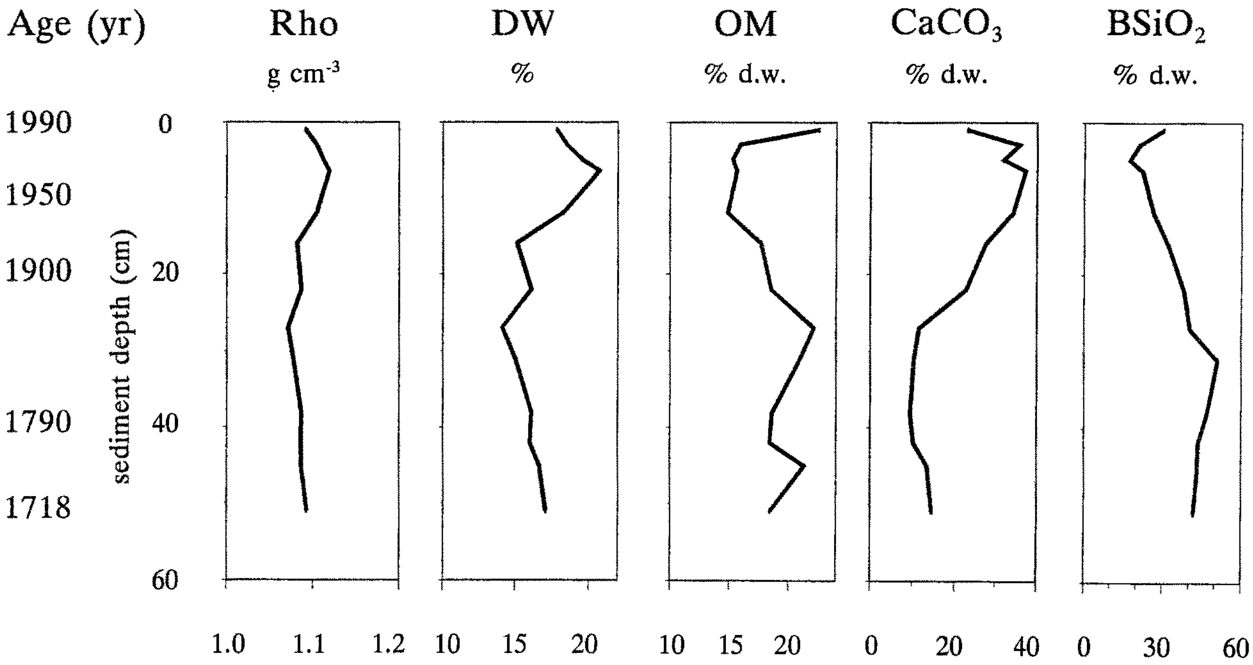

Fig. 4. Sediment sequence of bulk density (Rho), dry weight (DW), loss on ignition (OM), calcium carbonate and biogenic silica ($BSiO_2$) in Lake Albano sediment core.

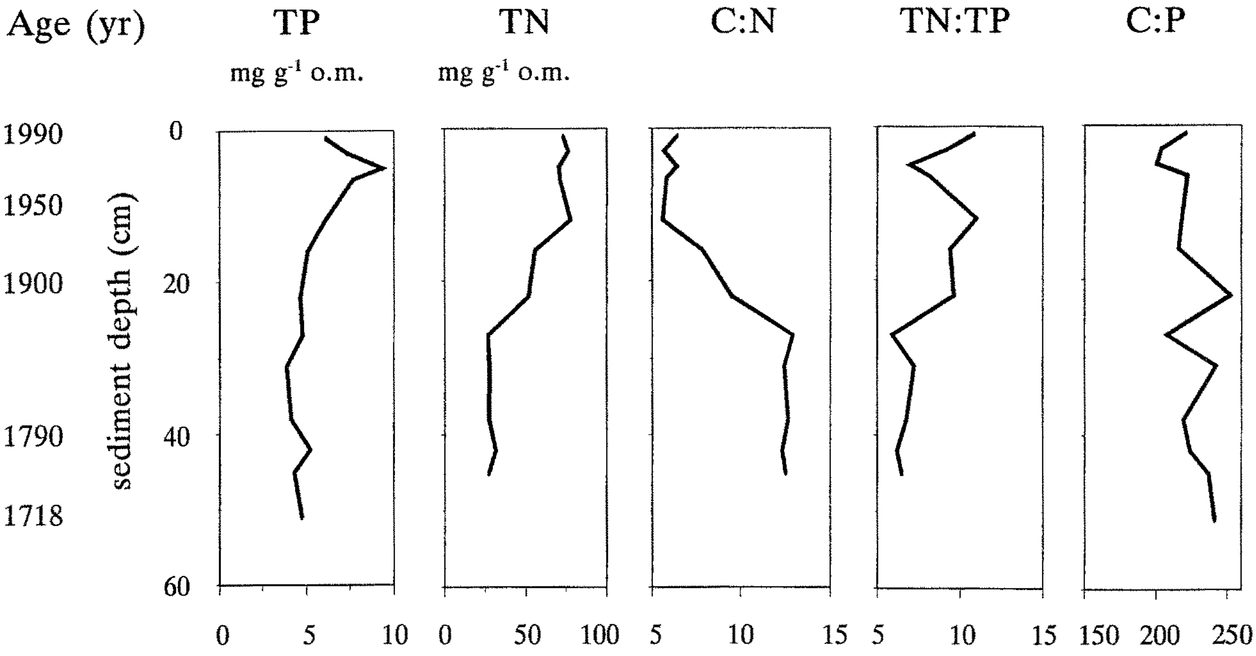

Fig. 5. Total phosphorus and total nitrogen expressed per unit organic matter in the sediment profile of Lake Albano. Atomic nutrient ratios are also indicated.

(Daley *et al.*, 1977; Guilizzoni *et al.*, 1982) and is not controlled by dissolution effects.

Concerning the problem of allochthonous or autochthonous contribution of the organic pool in sediments, the C:N ratios (Fig. 5) are a rough but generally

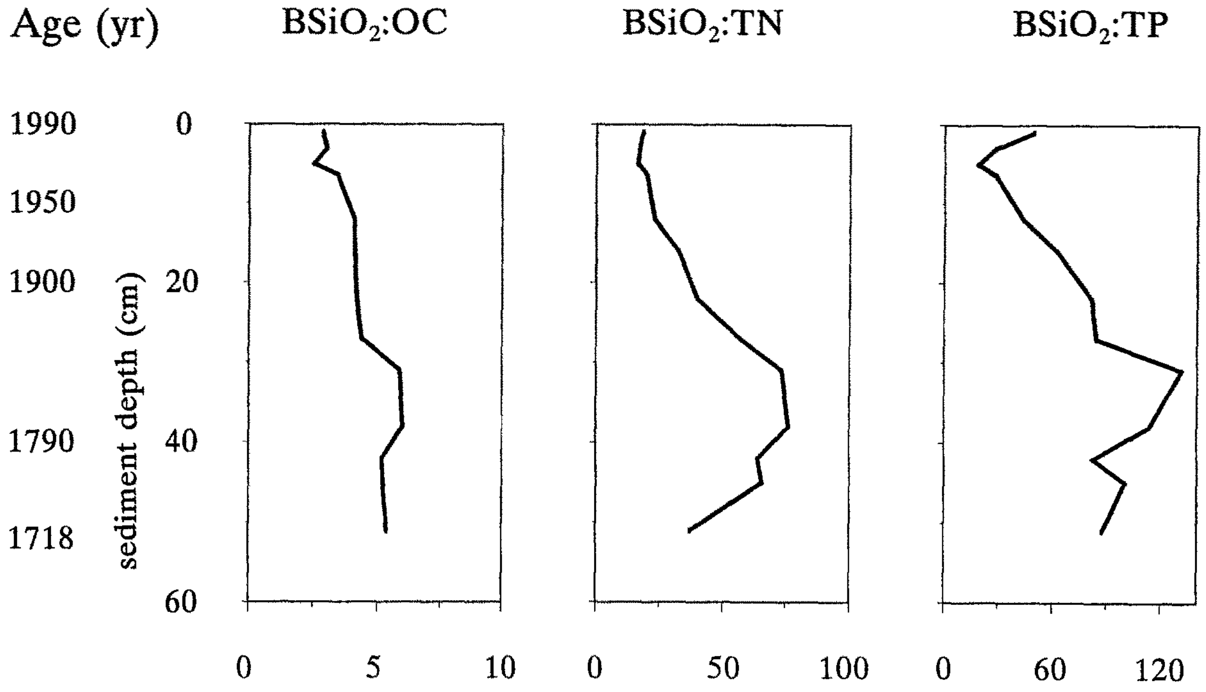

Fig. 6. Atomic nutrient ratios in the Lake Albano core. $BSiO_2$ = biogenic silica; OC = organic carbon; TN = total nitrogen; TP = total phosphorus.

reliable indicator (Wetzel, 1983; Meyers, 1993). The average composition of live planktonic materials is C_{106} N_{16} P, which gives a C:N ratio of about 6. Thus, in autochthonous organic matter the C:N usually varies between 6 and 12 (Wetzel, 1983). In contrast, most of the allochthonous organic matter supplied to lakes is relatively poor in N giving a high C:N ratio (C:N for humus in the range of 10–20, Hansen, 1961; colloidal and dissolved allochthonous matter C:N of 40–50, Wetzel, 1983). In Lake Albano, from *c.* 25 cm onward the sedimentary organic matter should be primarily considered of autochthonous origin (values well below 10; Kemp, 1971). However, sediment focussing, losses during deposition and diagenesis of organic matter are known to modify C:N ratios from their original values (Mitchel *et al.* 1990; Digerfeldt & Håkansson, 1993). According to recent marine studies, diagenesis is small and does not destroy its source information (Meyers, 1993 and papers cited therein).

The quantity of $BSiO_2$ stored in lake sediments is determined by the input of $BSiO_2$ to the sediments, as a function of siliceous algal production (as seen in thin sections, Fig. 2, mainly diatoms but also chrysophyte scales and sponge spicules), sediment focusing, and the fraction of $BSiO_2$ input that is dissolved during burial (Schelske *et al.*, 1985). The highest $BSiO_2$ concentration occurred at *c.* 30 cm, then a constant decrease is observed (Fig. 4). A dilution effect by $CaCO_3$ is not a major factor for such a decrease because the same $BSiO_2$ data expressed on $CaCO_3$-free dry weight reproduce a similar trend. However, the replacement of a diatom flora by other algal classes is not so evident from the analysis of characteristic carotenoids (see below).

In general, the sedimentary $BSiO_2$ concentration has been demonstrated to correlate well to absolute counts of diatom frustules in a number of lakes (Bradbury & Winter, 1976; Renberg, 1976; Schelske *et al.*, 1983; Engstrom *et al.*, 1985). Regression analyses of $BSiO_2$ and diatoms revealed that the concentration of $BSiO_2$ in the sediment was not a simple function of diatom numbers or biovolume but that factors such as the rate of dissolution and abundance of chrysophycean scales and cysts were also important (Newberry & Schelske, 1986). Also the very labile carotenoid fucoxanthin, was often correlated with fossil diatom counts in some Swiss and alpine lakes (Züllig, 1982; Guilizzoni *et al.*, in prep.). In Lake Albano, $BSiO_2$ and fucoxanthin concentrations throughout the core length are not correlated.

The $BSiO_2$:nutrient ratio profiles (Fig. 6) were similar among themselves and to the profile of $BSiO_2$.

This first signal of eutrophication, with a corresponding increase of biological productivity during the

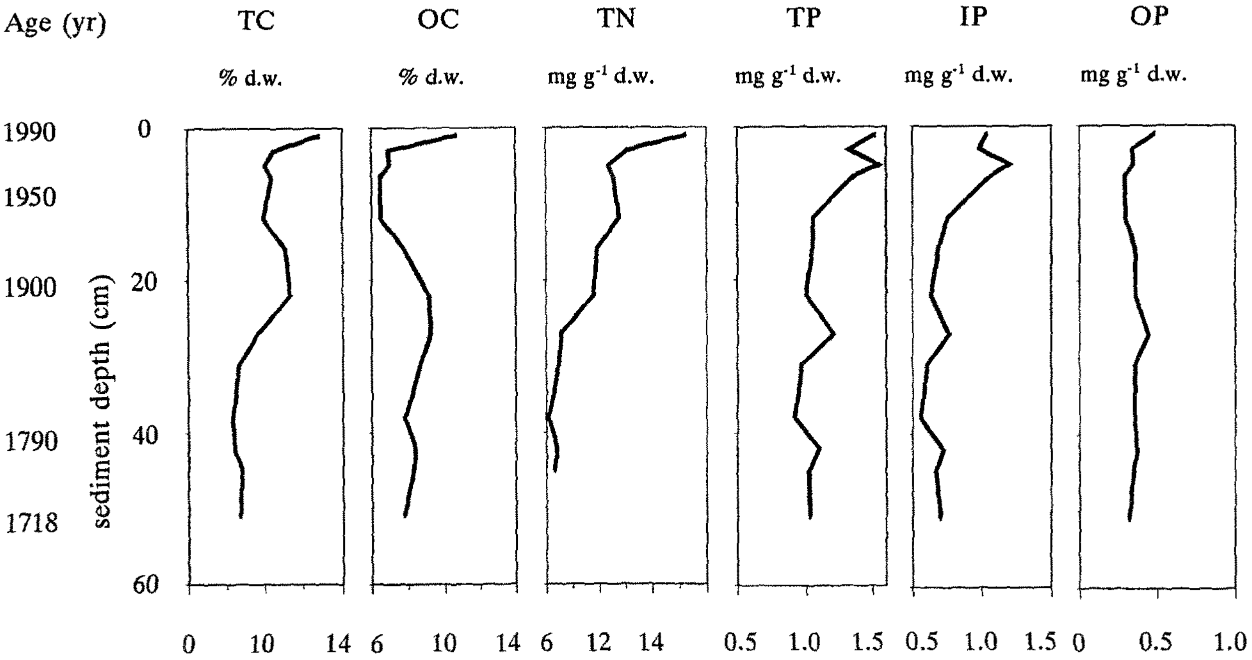

Fig. 7. Nutrient sediment stratigraphies in the Lake Albano sediment core. Total carbon (TC), organic carbon (OC), total nitrogen (TN), total phosphorus (TP), inorganic phosphorus (IP) and organic phosphorus (OP).

second half of the last century, is also supported by the increase of nutrients (N and P start to increase from about 1900–1920 A.D.; Fig. 7), and some algal pigments (see below). The concentrations of P and N, even when expressed per unit organic matter (Fig. 5), increase greatly from about 1870 A.D. Above the 30 cm level the Total N:Total P ratio increases from 6–7 to *c.* 10 (Fig. 5), reaching values similar to those for seston (Downing & McCauley, 1992). Then, wide fluctuations in the profile are observed during the past 40 years (upper 10 cm). In comparison with the nearby volcanic Lake Monterosi, the N:P values in Lake Albano are higher. This is because less P was stored in the anoxic deep hypolimnion of Lake Albano compared to the much shallower and well oxygenated Lake Monterosi (Hutchinson, 1970). It is hypothesized that, among the various combinations of factors that might affect the TN:TP ratio in lakes (e.g., sedimentation, fixation and biological transformation), mobilization from sediments is the most important process responsible for the reported nutrient trends (hydrochemical analysis has shown much higher concentrations of N and P in the bottom water layers compared with the surface ones; unpublished data). The organic matter N:P ratios (not shown) increase markedly from 30 cm upward, reaching maximum values (*c.* 40) in the upper sediment layers (also the C:P ratio begins to oscillate greatly at *c.* 30 cm). Rees *et al.* (1991) in a palaeolimnological study on a eutrophic, coastal marl lake in Wales, report values of organic matter N:P between 27 and 58 (range TN:TP of 20–30). However, this subject requires further consideration since, for example, Fukushima *et al.* (1991), in a study on 28 Japanese lakes, reported for oligotrophic, mesotrophic and eutrophic lakes, values of TN:TP in the sediments of 3.3, 6.3 and 2.5, respectively.

The presence of a record of annual varves down to the bottom of the core (*c.* 1700 A.D.) indicates a lack of bioturbation and suggests meromixis of this lake in this time period. This normally implies stable anoxic condition in the hypolimnetic waters. Indeed, past studies have revealed an oxygen depletion below 60–100 m all year round and the absence of a deep bottom fauna (Margaritora, 1992; Bonacina *et al.*, 1992).

Pigment preservation in meromictic lakes is high, mainly because their degradation under stable anoxic conditions is extremely slow (Sanger, 1988; Hurley, 1988; Leavitt 1988). In order to get an independent measure of pigment preservation, many authors have used the index proposed by Swain (1985), i.e. the proportion of sedimentary chlorophyll not degraded to phaeopigment as measured through acidification.

In Lake Albano (as was the case for other studied environments), some of the samples processed with the method showed negative values, so that this index has not been considered (the problem in estimating of phaeophytin in aquatic ecosystems is a well known phenomenon, Marker *et al.*, 1980; Bührer, 1991).

An indication of the pigment degradation (or preservation) can be obtained from the CD:TC ratio (Gorham *et al.* 1974; Swain, 1985; Sanger, 1988; Digerfeldt & Håkansson, 1993). It has been observed that under oxidizing conditions, carotenoids degrade slightly more rapidly than chlorophyll derivatives (Gorham & Sanger, 1967; Moss, 1968; Engstrom *et al.*, 1985), resulting in an increase of the CD:TC ratio. Allochthonous inputs of pigments are negligible in Lake Albano (cf. C:N ratio) because it receives water mainly from the atmosphere and underwater springs (Stella & Socciarelli, 1949). The observed decrease in the CD:TC ratio profile from about 18 cm onward (Fig. 8), after a long period of relatively stable conditions, could be the result of both enhanced pigment preservation conditions and/or a shift to greater production of carotenoid relative to chlorophylls (this period of low CD:TC ratio coincides with higher concentration of TC producing a low ratio). Besides, since cyanobacteria produce more carotenoids than do other taxa (Harris, 1978), the recorded recent increase of carotenoids could be at least in part produced by the increase of this algal group (see below).

Recently, another sedimentary index to pigment preservation has been established in studying Alpine lakes acidification (Guilizzoni *et al.*, 1992b). This index may be expected to bear some relation to the degree of conversion of chlorophyll to phaeopigments as expressed by the ratio of the optical density of an extract at 430 nm to that at 410 nm (Moss, 1967). In Lake Albano, the 430 nm:410 nm ratio is well correlated with the HPLC measured Chlorophyll *a*:phaeophytin *a* ratio ($r=0.72$; $P\leq 0.01$), and negatively correlated with the CD:TC ratio ($r=-0.96$; $P\leq 0.001$). Because values of 430 nm:410 nm ratio are high (0.84–1.03), close to those of an undegraded mixture of natural pigments, and fairly constant throughout the core (Fig. 8; a slight increase of this ratio is however observed in the two uppermost sediment layers), generally good conditions for pigment preservation in Lake Albano might be predicted. This pigment ratio, like all palaeoecological indicators, is fraught with hazard in interpretation (Sanger, 1988; Guilizzoni *et al.*, 1992b). For example, many carotenoids absorb strongly at 430 nm and thus may affect the ratio. However, Moss (1967) demonstrated a marked increase in the 430 nm:410 nm ratio only with high carotenoid content in extract of a cultured *Chlorella* sp.

As regards the degradation of a single pigment, it is now known that some carotenoids (e.g., peridinin, fucoxanthin) and chlorophylls (e.g., Chl. *b*) are very labile (Daley, 1973; Züllig, 1982; Hurley, 1988; Leavitt *et al.*, 1989; Hurley & Amstrong, 1990; Leavitt, 1993). Because of the poor conservation of these compounds, in the present study we could not detect any Chl. *b* and Chl. *c*, or the characteristic carotenoid of dinoflagellates (peridinin), in spite of the presence of the algae producing them.

The concentrations of chlorophyll derivatives (CD) and total carotenoids (TC) show a slight increase from 30 cm upward, and a more marked rise of TC in recent years (Fig. 8). These spectrophotometrical analyses of total pigments are well correlated with the total chlorophylls and carotenoids as measured by HPLC technique ($r=0.69$ and 0.83; $P\leq 0.01$ and 0.001, respectively).

Compared to the other taxa, Cyanobacteria (echinenone, myxoxantophyll, oscillaxanthin, zeaxanthin) and Chrysophyta (fucoxanthin, diadinoxanthin, dinoxanthin carotenoid concentrations), show a large increase during recent times (past 20–30 years; Fig. 9). From the oscillaxanthin curve it appears that *Oscillatoria* spp. was present in the algal flora during the past three centuries. In this period, the phytoplankton community is dominated by the Chlorophyta (lutein, also zeaxanthin) and Chrysophyta (fucoxanthin, diadinoxanthin and dinoxanthin). This latter carotenoid shows a large increase from 30 cm to the upper layers. The high values of lutein and phaeophorbides throughout the core may be the result of a better preservation of these pigments as compared to the others (Hurley & Armstrong, 1990) and/or of a contribution from *Botryococcus braunii* blooms and the littoral macrophyte community. A study on pigment decomposition from aquatic macrophytes has shown that lutein decays more slowly than all other carotenoids in emergent and submergent aquatic vegetation (Bianchi & Findlay, 1991). As reported above, the terrestrial contribution of pigments to sediments is thought to be unimportant in volcanic lakes such as Albano.

The absence of O_2 in deep waters during the past three centuries is also documented by the presence of two carotenoids (okenone and isorenieratene; Fig. 9). These pigments belong to strictly anaerobic photosynthetic sulfur bacteria (Züllig, 1985a, b). The ratio between the two carotenoids, which belong to Chroma-

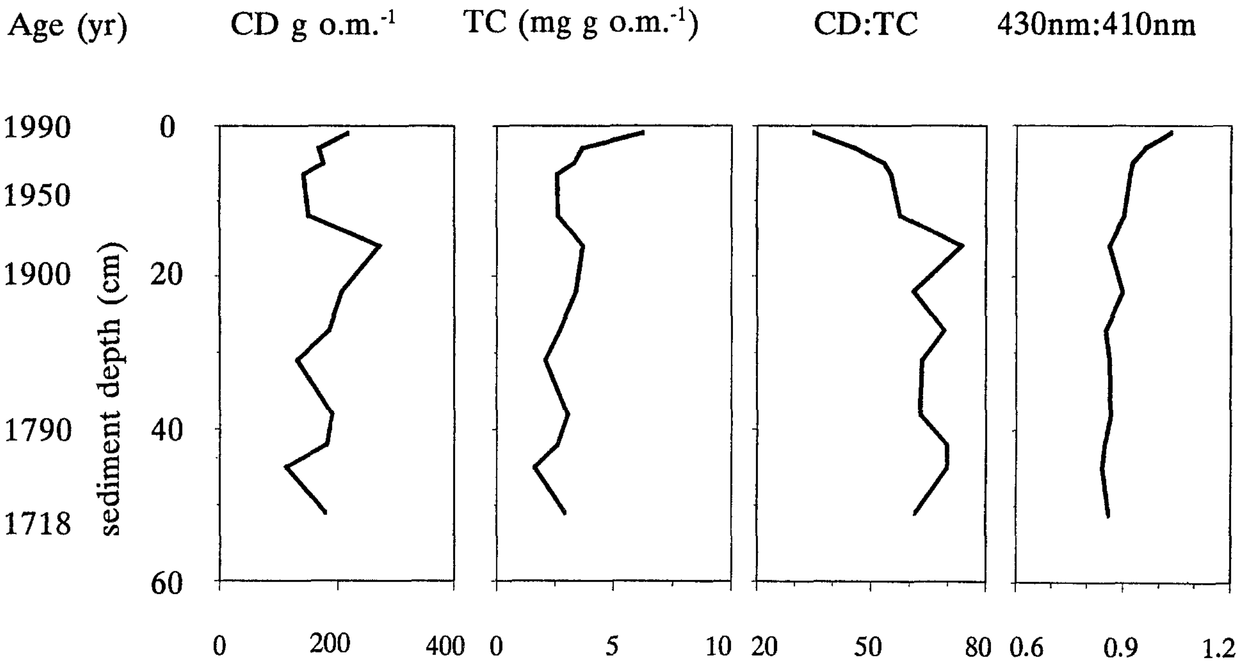

Fig. 8. Chlorophyll derivatives (CD; expressed in standard absorbance units) and total carotenoids (TC) in the Lake Albano sediment core. The 430 nm:410 nm ratio is also indicated.

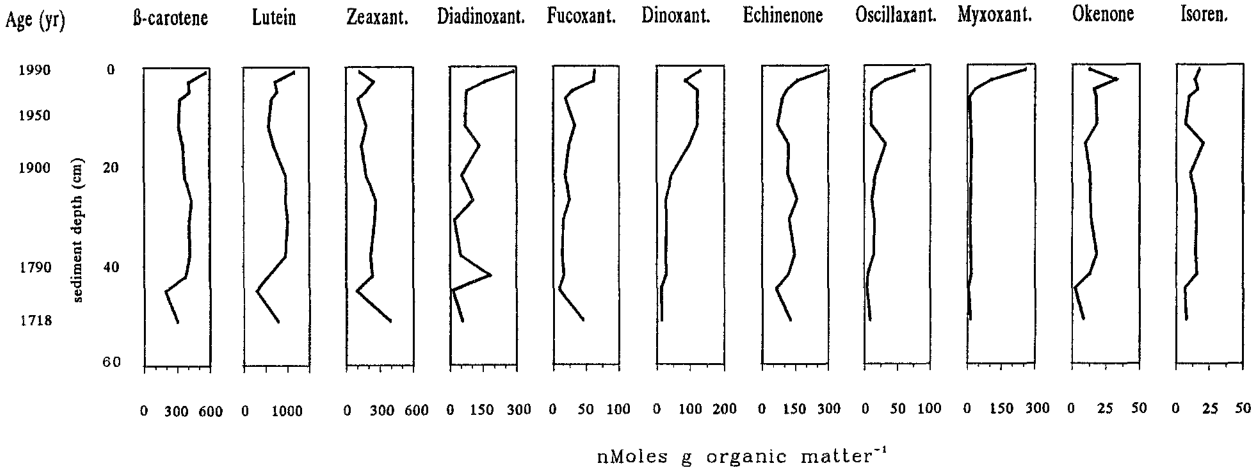

Fig. 9. Concentration of sedimentary fossil pigments in Lake Albano sediment core.

tiaceae and Chlorobiaceae respectively, is almost constant from 1700 A.D. to *c.* 1900 A.D. (Fig. 10). From then on, it becomes variable and increases during this century. Studies in Canada (Brown *et al.*, 1984) and Italy (Lami *et al.*, 1994), have related the okenone and isorenieratene levels to water transparency changes over time. Similarly, the relative increase of okenone compared to isorenieratene in the upper *c.* 10 cm of the core, is here interpreted as an increase in lake trophy and a decrease in water clarity. Isorenieratene is a characteristic pigment of the green sulfur bacteria, which typically form the deepest photosynthetic layer in lakes and can be drastically reduced by shading from overlying population (Brown *et al.*, 1984; Züllig, 1985a). A recent study in Lake Albano has shown an increased development of *Oscillatoria rubescens* in the metalimnetic zone (Margaritora, 1992) which could interfere with the development of bacteria population.

Astaxanthin is the main carotenoid of *Euglena heliorubescens* (Goodwin, 1976), *E. sanguinea*

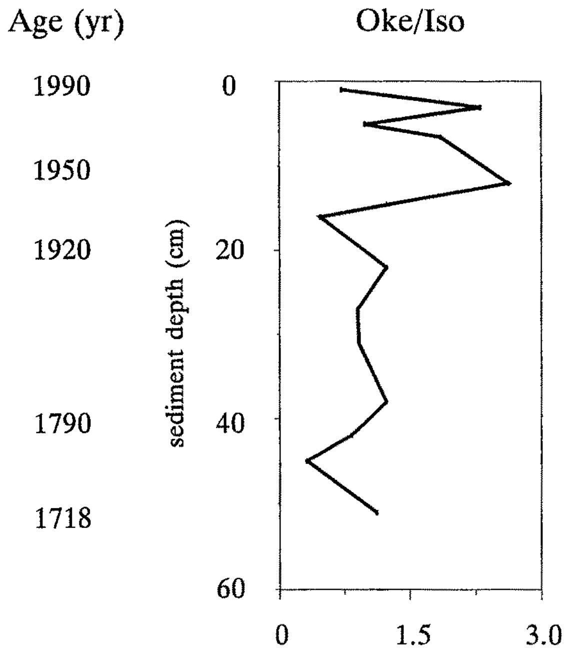

Fig. 10. Okenone:Isorenieratene ratios in Lake Albano sediment core.

(Barone & Naselli Flores, 1988) and *Glenodinium sanguineum* during blooms (Lami *et al.*, 1991). None of these species are present in the algal community of Lake Albano. Astaxanthin is also very abundant in Cladocera and Copepoda, and its stratigraphy along the core (Fig. 11) parallels that of phaeophorbide *a* ($r=0.88$; $P\leq 0.001$). These two curves are related to zooplankton development and grazing activity, respectively (Guilizzoni & Lami, 1988; Lami *et al.*, 1991; Leavitt *et al.*, 1989). A clear assignment of astaxanthin to a zooplankton source should, however, be carefully evaluated because this pigment can be synthesized in several algae that are nutrient-starved (Yentsch & Vaccaro, 1958; Manny, 1969; Watson & Osborne, 1979; Goodwin, 1976). The two curves have shown a slight change only very recently as is also noted by Margaritora *et al.* (1988) in a study on zooplankton population dynamics.

A low number of midge remains was found in the sediment core of Lake Albano; a total of only 547 chironomid head capsules representing 27 taxa were identified from the 13 sub-samples of the core. The total number of head capsules in the subsamples varied from 3 (section 6–8 cm) to 92 (section 11–13 cm), with an average of 2.6 head capsules g^{-1} d.w. The most important subgroups are Tanytarsinii (53% of total), Chironominii (20%), Tanypodinae (14%) and Orthocladinae (13%). The unidentified taxa represent 11% of the assemblage. Most of these organisms belong to the Orthocladinae, of primarily littoral origin. Their presence provides some insight into events and common processes affecting shorelines and the primary habitat of chironomid fauna (e.g., biological succession or cultural changes; Goulden, 1969; Brodin, 1986).

The abundance of chironomid remains in the core fluctuated considerably (Fig. 12). Comparing the four main subgroups, only the Tanytarsinii are well represented (50–60%) and relatively stable during the development history of the lake. Chironominii are important in the lower part of the core (about 40%), then decrease markedly up to 5 cm; in the very past, two high peaks of abundance stand out. The relative abundance of Tanypodinae shows a maximum at 18 cm coincident with a minimum of Chironominii and Orthocladinae (Fig. 12).

Figure 13 shows the temporal distribution of the most important taxa found in Lake Albano. *Cladotanytarusus* sp., a littoral taxon of Tanytarsinii, and *Procladius* sp. of Tanypodinae, appeared to be dominant in the middle and lower sections of the core; the relative abundance decreased from 15 cm to the top of the core. *Tanytarsus* spp. slowly increases its relative abundance from 35% to a maximum of 70% in the last 20 cm of the core.

The most important Chironominii were *Dicrotendipes* sp., *Polypedilum* sp. and *Chironomus* sp. (Fig. 13). The littoral species *Dicrotendipes* sp. and *Polypedilum* sp., appeared the dominant forms from this Tribe with their higher relative abundance in the upper part of the core (*c.* 18% and 10%, respectively). Conversely, *Chironomus* sp. was only important at 15 cm and in the lower sections of the core. The presence of *Xenochironomus* sp., a parasitic taxon on sponges and associated with aquatic plants, found also in the lower part of the core, reflects littoral inputs.

The *Tanytarsus sensu latu* group include littoral and profundal species (e.g., *Microspectra* sp.). Since from the fossil assemblages collected it was not possible to identify typical profundal organisms, we could not resolve the problem of the origin of this group. However, because surface sediment samples collected by grab at 90, 120 and 170 m depth were completely devoid of any macrobenthos (Bonacina *et al.*, 1992), it is reasonable to believe that the head capsules found are of littoral origin.

In conclusion, the continuous hypolimnetic oxygen depletion in Lake Albano seems to be the main controlling factor as regards chironomid distributions.

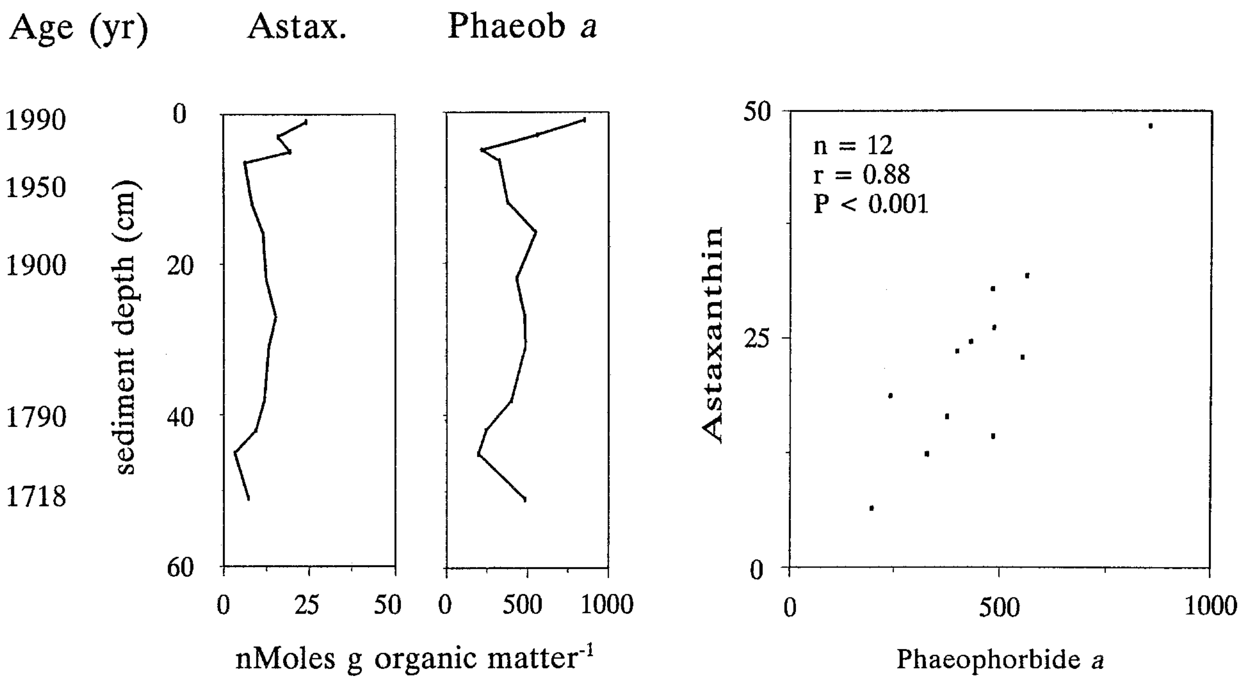

Fig. 11. Comparison between the profiles of the two pigments of zooplankton origin (astaxanthin and phaephorbide *a*) in the Lake Albano sediment core. Scatter diagram of the two pigments is also plotted.

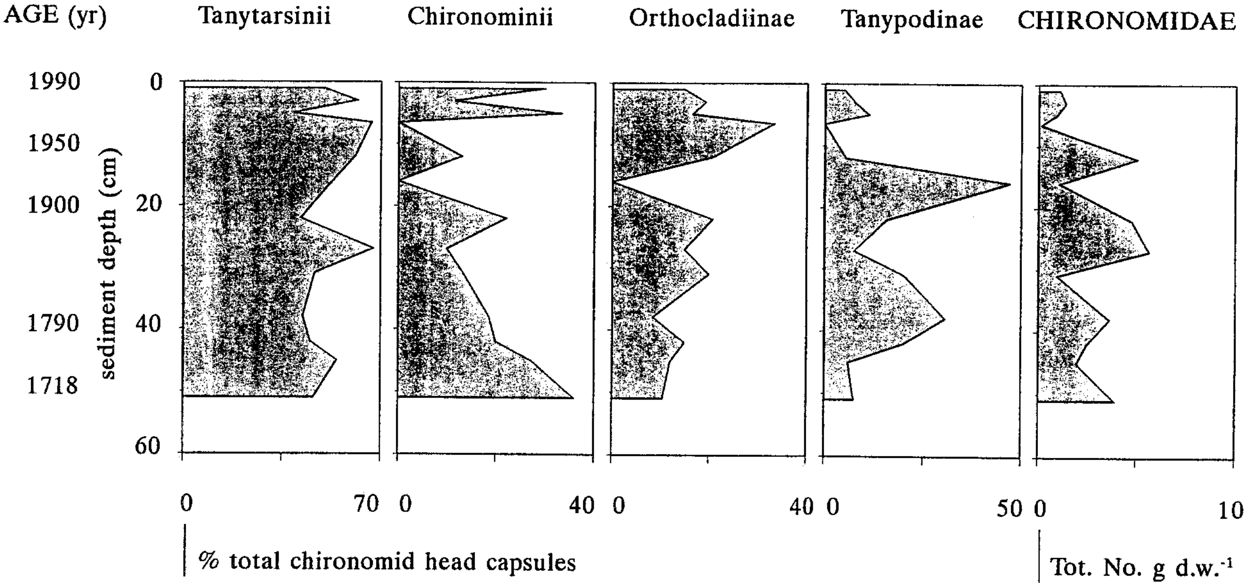

Fig. 12. The relative abundance (% of sum at each level) of the main chironomid subgroups in the Lake Albano sediment core. Total number of head capsules per g dry weight in each sample is also reported.

Though some of the taxa found have representatives in the profundal zone, among the fossil assemblages those of littoral origin are prevalent. This phenomenon was also described by Hutchinson (1970) in the nearby volcanic Lago di Monterosi. The presence of littoral taxa in our core is a result of a redeposition of shallow-water fauna on the deep-water bottoms. The fluctua-

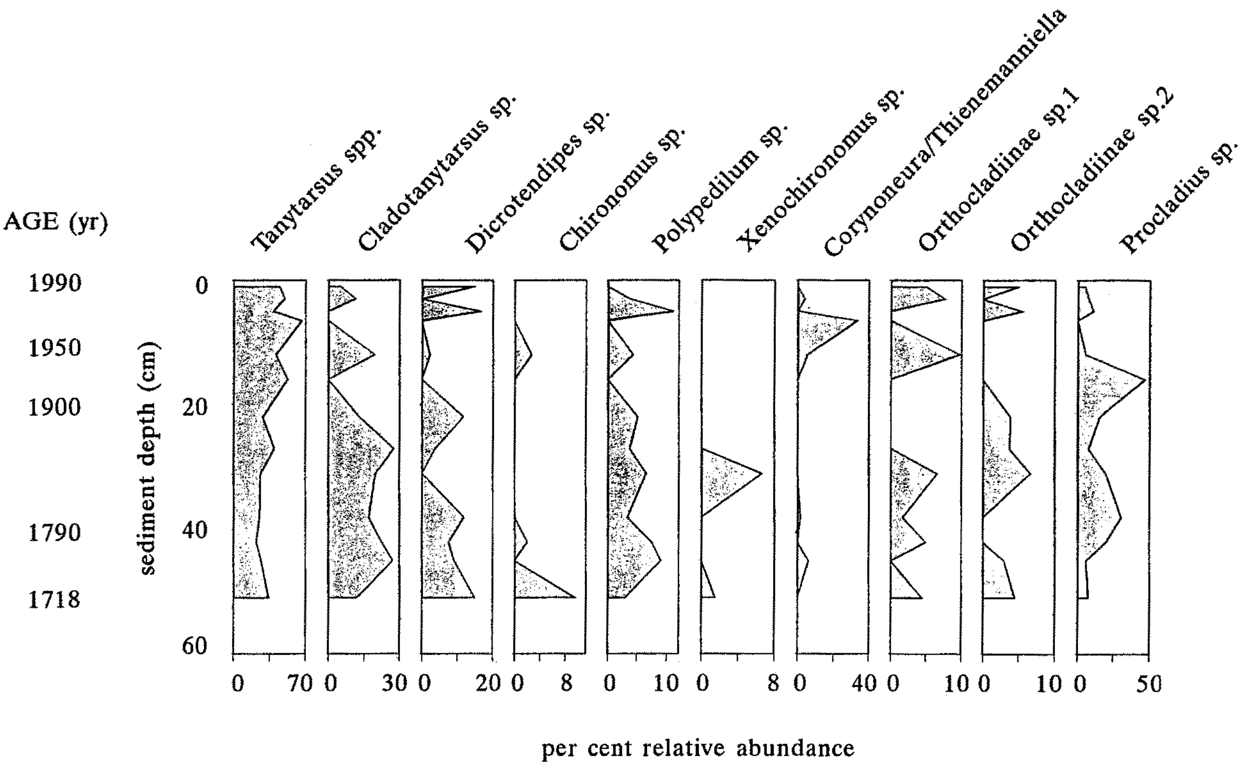

Fig. 13. The relative abundance (% of sum at each level) of the main taxa of fossil chironomids in the Lake Albano sediment core.

tions of Chironomidae are not correlated with changes in organic matter.

Our assertion here is therefore that the slight decrease of total remains in the uppermost 10 cm of the core (Fig. 12) is related to the recent human use of the lake: for example, during the 1960 Olympic games.

The ascertained slight increase in lake trophy during the past 30–40 years can be ascribed to anthropogenic disturbance (e.g., tourism, shore modification) on the lake (Margaritora, 1992), related to the increased pressure of urbanization in the watershed deriving from the nearby city of Rome (Spinelli, 1983). This process of eutrophication during the past 40–50 years has been well documented for other Italian lake systems (Guilizzoni *et al.*, 1983 and 1986; Guilizzoni & Lami, 1992). Algal blooms of Cyanobacteria (*Aphanizomenon ovalisporum, Mougeotia elegantula, Oscillatoria rubescens*) and chlorophyta (*Botryococcus braunii, Staurastrum* spp.) were quite frequent in Lake Albano from *c.* 1940 A.D. onward (Stella & Socciarelli, 1949; Cannicci, 1953).

So far we have no precise historical information about any anthropogenic impact on Lake Albano around *c.* 1870 A.D., which might explain the trophic changes observed at that time. However, a steady increase of the population of this area has been recorded since 1871 (Spinelli, 1983). Moreover, it is reasonable to suppose that there was a considerable human impact on the lake during that very important period in Italian history which saw, for example, the construction of a network of roads and a railway between the capital of the country, and the nearby Lake Albano.

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