

4. LONG TERM CHANGES IN WATER CHEMISTRY (Anna Hillbricht-Ilkowska, Irena Kufel)

Annual mean concentration of calcium in the surface and bottom layers found for the period February – October 1990–1993 ranged from 10.7 to 15.5 mg l⁻¹. These are clearly lower values than those reported for the years 1971–1973, i.e. directly after liming (1970), which varied from 13.5 to 19 mg l⁻¹ in successive years (Fig. 2). Nevertheless, the calcium level was still several times higher in the period 1990–1993 than before liming (2–4 mg l⁻¹). Calcium losses from the

Lake Flosek waters are still noticeable when compare mean values for 1993 with those for 1990, the former ones being by about 15% lower. The difference is statistically significant at $p = 0.02$. Assuming more or less steady rate of calcium losses from Lake Flosek between 1973 and 1993, yearly drop in calcium concentration would average 1–2%. This relates to both surface and bottom waters. The rate is fairly low considering hydrological regime of the lake (no surface outflow).

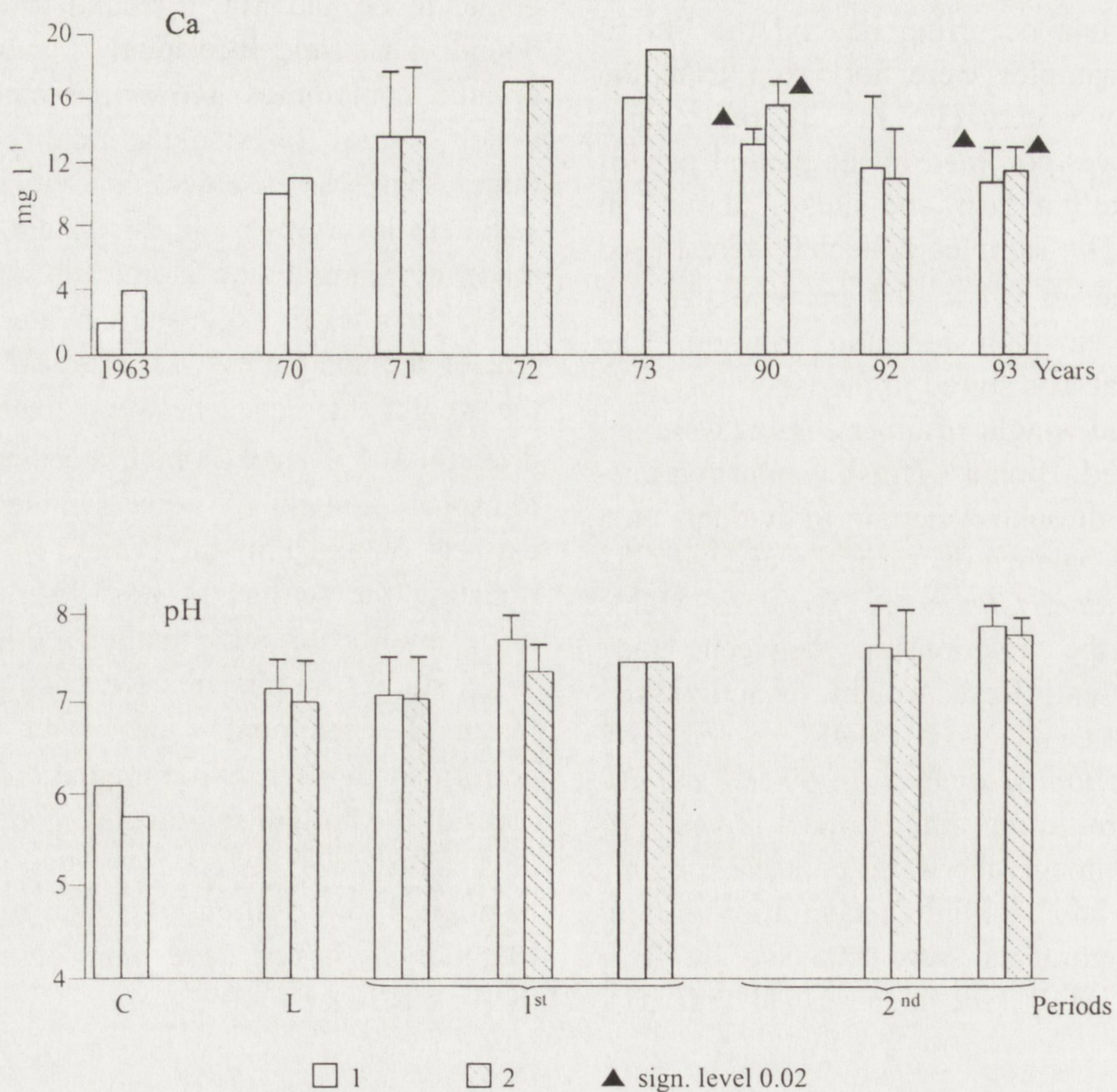


Fig. 2. Annual mean concentration of Ca (mg l⁻¹) and pH in control (C, 1963), liming (L, 1970) 1st post-liming (1970–1973) and 2nd post-liming period (1990–1993) in the surface (0.5 m) (1) and near bottom (5 m) (2) layers of Lake Flosek waters. Data for the liming year represent maximal values reported after the treatment. Vertical lines denote maximal values (from frequent samplings) from February to October. Data for 1963–1973 refer to Fig. 3 in Hillbricht-Ilkowska *et al.* (1977)

It also means that calcium level characteristic of pre-liming period may be expected to be reached in next 20–30 years.

It should be emphasised that maximum level of calcium in the water did not occurred in the treatment year (1970) (Fig. 3 in Hillbricht-Ilkowska *et al.* 1977), though it rose from 1 to 10–11 mg l⁻¹, but in the next year (1971) when it reached about 17–18 mg l⁻¹ (Fig. 2). This might be an effect of calcium dilution as Ca could be temporarily kept in the semi-liquid bottom sediments along with particles of limestone (cf.: Fig. 3 in Hillbricht-Ilkowska *et al.* 1977).

Seasonal dynamics in calcium concentrations in 1992 and 1993, i.e. 20 years after liming, has shown that lower values were characteristic for certain seasons, e.g. spring (March–May) 1992 and 1993, when lake production was intensive (Fig. 3). One possible reason of this might be biological decalcification of the

lake water. This suggests that the slow decline in calcium resources in the no-outflow lake consists in calcium re-deposition in bottom sediments owing to natural production processes. Calcium leaching from the lake (due to e.g. wash-out by snow-melt waters or rain-storms) should not be considered to be a principal factor, because the only surface outflow existing in the western part of the lake is almost permanently inactive. A likely reason is lowered ground water table in the region. No correlation has been found between monthly precipitation sums for 1990, 1992 and 1993 (data given by favour of dr. E. Bajkiewicz-Grabowska) and the corresponding changes in the calcium level.

Long term changes in pH of lake water began in the treatment year (1970) when the pH rose from 5.5 to 7.5 near the bottom, and from 6.2 to 7.5 near the surface (Fig. 2). Already in 1971, the pH stabilised at 7.0–8.0, and were slightly

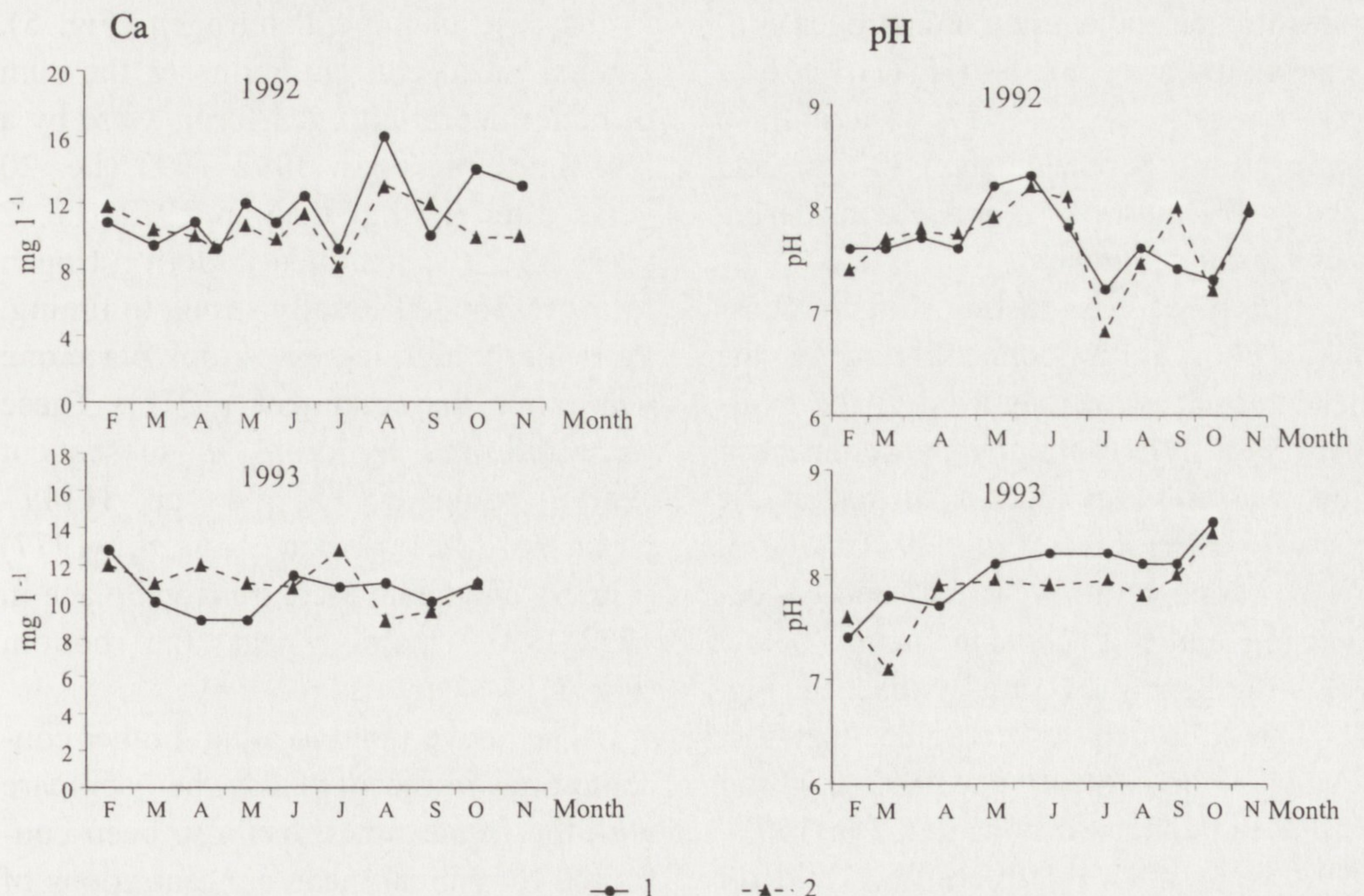


Fig. 3. Seasonal changes in Ca concentration and pH in 1992 and 1993 (22 and 23 years after liming) near surface (0.5 m) (1) and bottom (5 m) (2) in the Lake Flosek waters

higher in the bottom layers. Annual mean values of the pH in 1992 and 1993 tended to be slightly higher when compared with 70-ties. Alike tendency found for 1993 in comparison with 1992 was not statistically significant. The pH of about 8.0 was more frequently recorded in 1993 than 1992, and this seems to be responsible for high pH values in the period May–June (Fig. 3). A rapid drop in the pH observed in July 1992 (Fig. 3) may be attributed to doubled rainfall in that month (46 mm) in relation to the preceding one (22 mm). However, the shift was more likely related to a decline in filamentous algae that normally alkalise a site through their production processes (see: Chapter 7). In both years, higher pH values were noted when plant productivity peaked, i.e. in May–June, in comparison with the period preceding the peak (February–April) (Fig. 3).

At the time of liming and in a few subsequent years, (1st post-liming period) only the records of phosphate phosphorus, nitrate nitrogen and ammonium nitrogen concentrations were made (Hillbricht-Ilkowska *et al.* 1977). Therefore a comparison between the 70-ties and 1990–1993 period was made considering these forms of nutrients.

Sharp but short-lasting shifts in phosphate phosphorus concentration in the Lake Flosek water occurred in the treatment year. The annual mean concentration was however similar to that in the control year (Fig. 4). From 1971 to 1973, P-PO₄ concentration was steadily decreasing until a constant level below 0.010 mg l⁻¹ was eventually reached (Fig. 4). This is much lower value than that found for the control year (0.02–0.03 mg l⁻¹). Mean concentrations noted in 1991–1993 were also relatively low: clearly lower in 1990–1992 (< 0.01 mg l⁻¹), but slightly higher in 1993 (0.015–0.017

mg l⁻¹), especially when the maximal values are compared (Fig. 4). The difference in the mean values between 1992 and 1993 was statistically significant ($p = 0.05$). The sharp drop in that nutrient following liming could be explained by its utilisation in phytoplankton production (Hillbricht-Ilkowska *et al.* 1977). However, considering rapid development of fine detrito-bacterivore zooplankton and benthos, it seems that phosphorus might be utilised by heterotrophic bacteria (see: Chapters 8 and 9). The similar changes in P-PO₄ after liming, Bellemakers *et al.* (1994) has explained by P capturing by sediments. Low phosphate level in the Lake Flosek water had probably been maintained since liming until 1992–1993 when it substantially increased. The increase was particularly evident near the bottom where TP concentration was about 3 times higher than near the surface (Fig. 4).

Similar changes have been observed in the case of mineral nitrogen (Fig. 5). Annual mean concentrations of the sum of both mineral nitrogen forms were by a few times higher in 1992–1993 (i.e. 20 years after liming) than in 1972 (i.e. 2 years after the treatment). Both nitrogen forms responded equally strong to liming. Particularly high increases took place one year after the treatment (1971). These were followed by drops in subsequent years (compare Fig. 4 in Hillbricht-Ilkowska *et al.* 1977) (Fig. 5), and again increases took place in 1992–1993, mainly near the bottom (Fig. 5).

The above trend to attain higher concentrations in recent years when compared with the former ones, has also been confirmed for annual mean concentrations of total and dissolved phosphorus (Fig. 4) and the sum of organic and ammonium

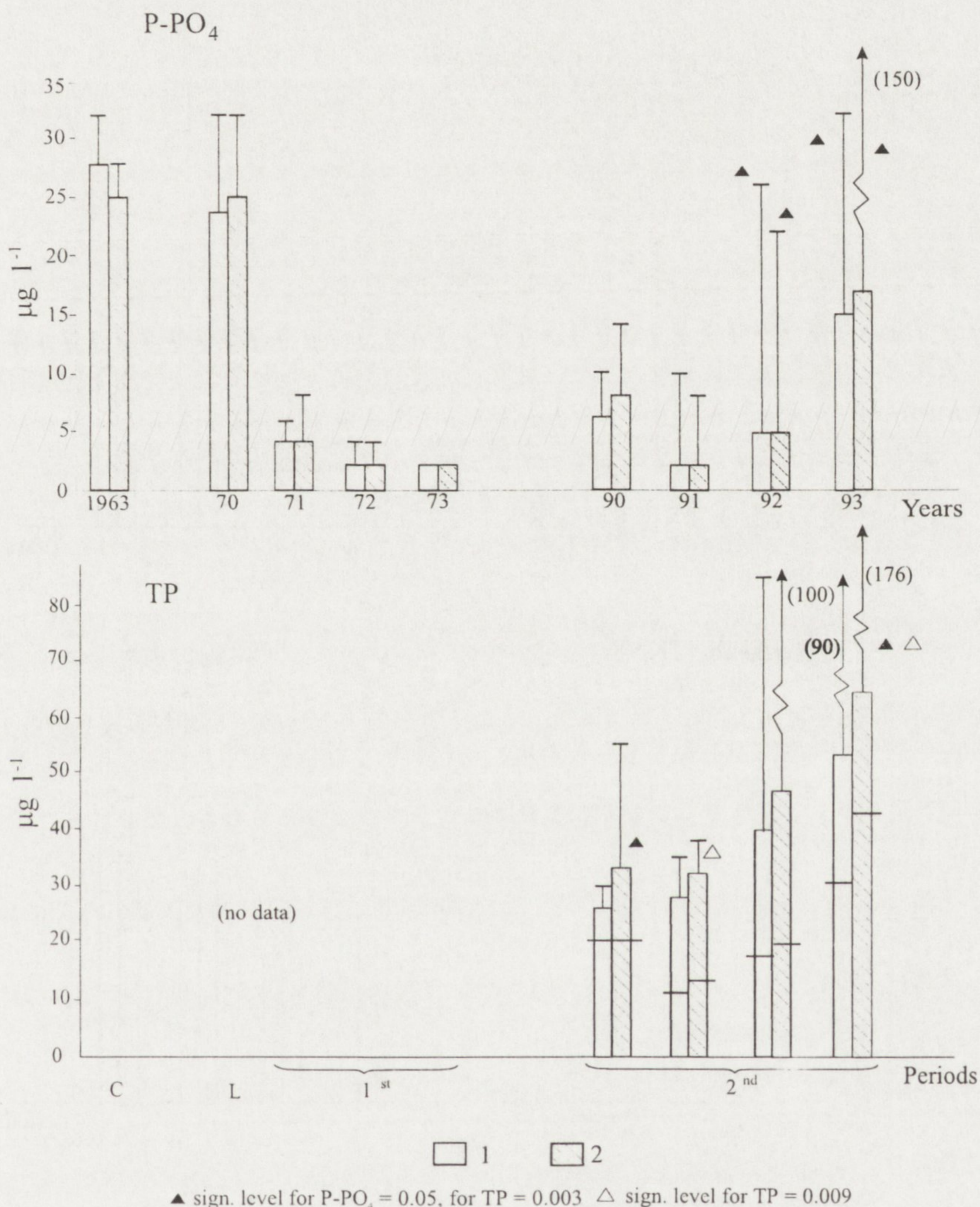


Fig. 4. Yearly mean (bars) and maximal (vertical lines) concentrations of P-PO₄ and TP near surface (0.5 m) (1) and bottom (5 m) (2) in Lake Flosek waters. Horizontal lines inside TP bars indicate DP content in TP. For other explanations see Fig. 2. Note different scales for P-PO₄ and TP!

nitrogen (so called Kjeldahl nitrogen) (Fig. 5); these compounds were measured in 1990–1993, but not in 70-ties. Mean contents of the total and dissolved fractions of the above nutrients in surface and/or bottom layers were significantly higher ($p \leq 0.1$) in 1992–1993 (or 1993 only) than 1990–1991. Maximal values were also higher in 1992 and 1993 than in the two preceding years (Figs 4, 5).

When compare long term changes in the nutrient contents, as well as pH and calcium concentration, the following hypothesis may be drawn. Except the secondary changes found in these parameters in the liming year, the annual mean values have presumably been maintained for almost 20 years at a fairly constant level similar to that found 3–4 years after the treatment (i.e. in 1972–1973). However, some changes noted in 1992–1993 indi-

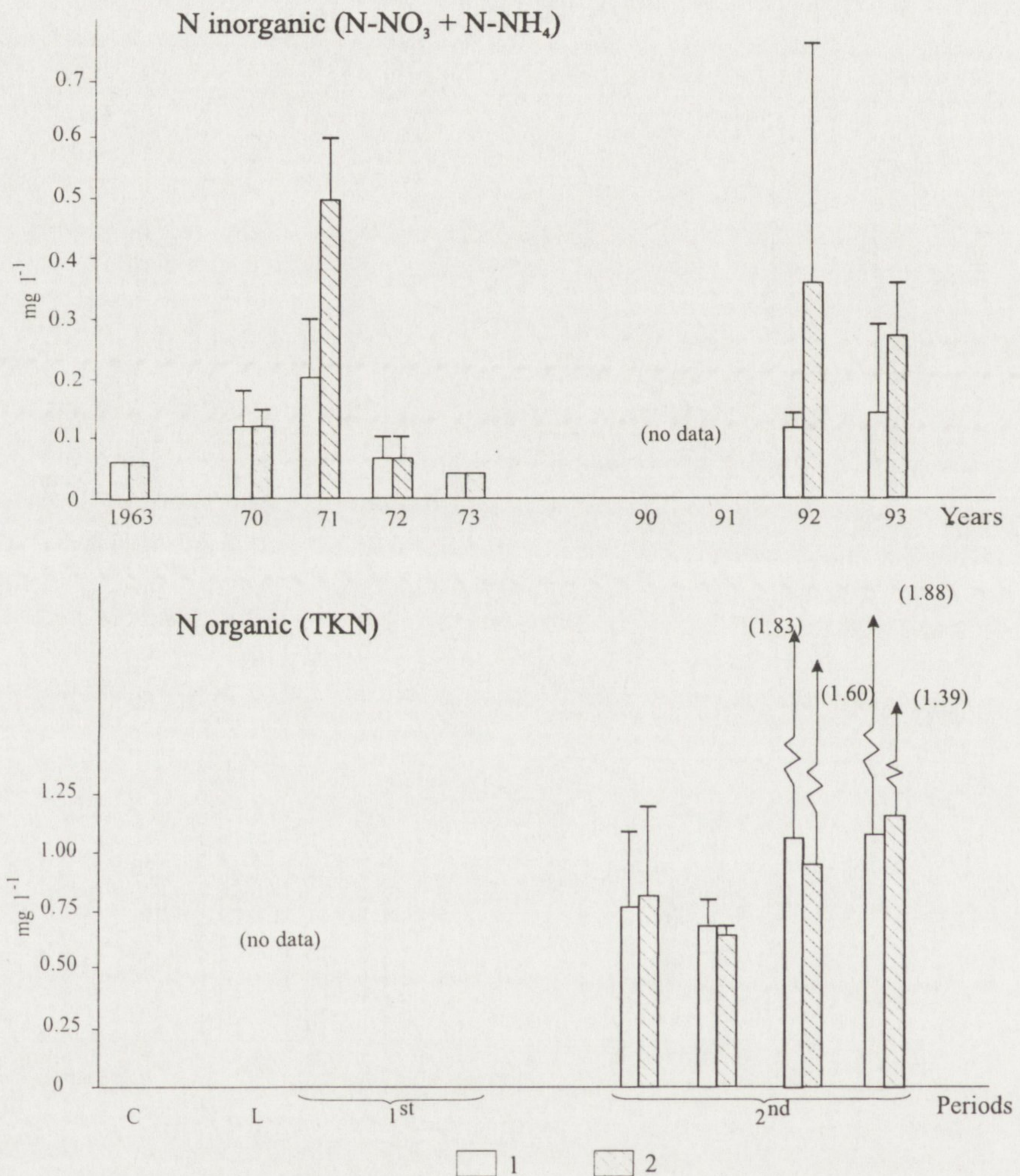


Fig. 5. Yearly mean (bars) and maximal (vertical lines) concentration of inorganic (N-NO₃ + N-NH₄) and organic N (total Kjeldahl nitrogen, TKN) near surface (0.5 m) (1) and bottom (5 m) (2) in Lake Flosek waters. See Fig. 2 for other explanations

cate an increase in nutrient concentrations in the lake waters, which are probably the symptoms of increased fertility and productivity of the lake.

Nevertheless, it should be stressed that concentrations of principal nutrients in Lake Flosek were generally low throughout the entire study period. This was decisive for low trophic status of the lake and characteristic of mesotrophic rather than eutrophic lakes. This is best

exemplified by total phosphorus concentration that was usually below 0.05 mg l⁻¹, and thus lower by one order of magnitude than that found for eutrophic lakes, i.e. 0.5 mg l⁻¹. According to Kajak's and Zdanowski's classification (in Hillbricht-Ilkowska 1989) based on TP summer concentrations, the values reached in Lake Flosek have never exceeded those characteristic of mesotrophic nor I purity class lakes (Kudelska

Table 2. Yearly mean and maximal (in brackets) concentrations (mg l^{-1}) of TOT-Fe in non-filtered water (and % in filtered water) in Lake Flosek in 1992 and 1993

Layer	1992		1993	
surface	0.08 (0.33)	46%	0.07 (0.10)	52%
over-bottom	0.12 (0.35)	57%	0.08 (0.12)	63%

et al. 1983). Nevertheless, the tendency for these nutrients to attain higher concentrations in 1992–1993 may indicate that the lake, after long period of being at equilibrium due to elevated calcium content, is becoming increasingly eutrophic and productive.

By contrast, iron concentrations (TOT-Fe), dissolved or bound to particulate matter, were not as high as in typical humic, low-productive lakes (Table 2). Iron concentrations were measured in 1992 and 1993 only. There are no data available from earlier periods including prelimiting period. Most frequently, the concentrations were about 0.01 mg l^{-1} in the surface and bottom (slightly higher values) water layers reaching occasionally 0.35 mg l^{-1} . Nearly half of the total Fe was bound to particulate matter. The above values are apparently lower than those reported by Zdanowski (1992) for other humic lakes, and similar to the values found for mesotrophic lakes.

In the years 1990–1993 the sharp vertical stratification of many parameters examined and frequent sudden changes in concentrations of various compounds were found. This was especially apparent in 1993, when water samples were taken at every 1 m from the surface down to the bottom (i.e. to 5 m) and in 1992, when the water samples were taken from the surface, and from 3 m and 5 m depths. This is exemplified by changes in Ca, TKN and P-PO_4 , the concentrations of which

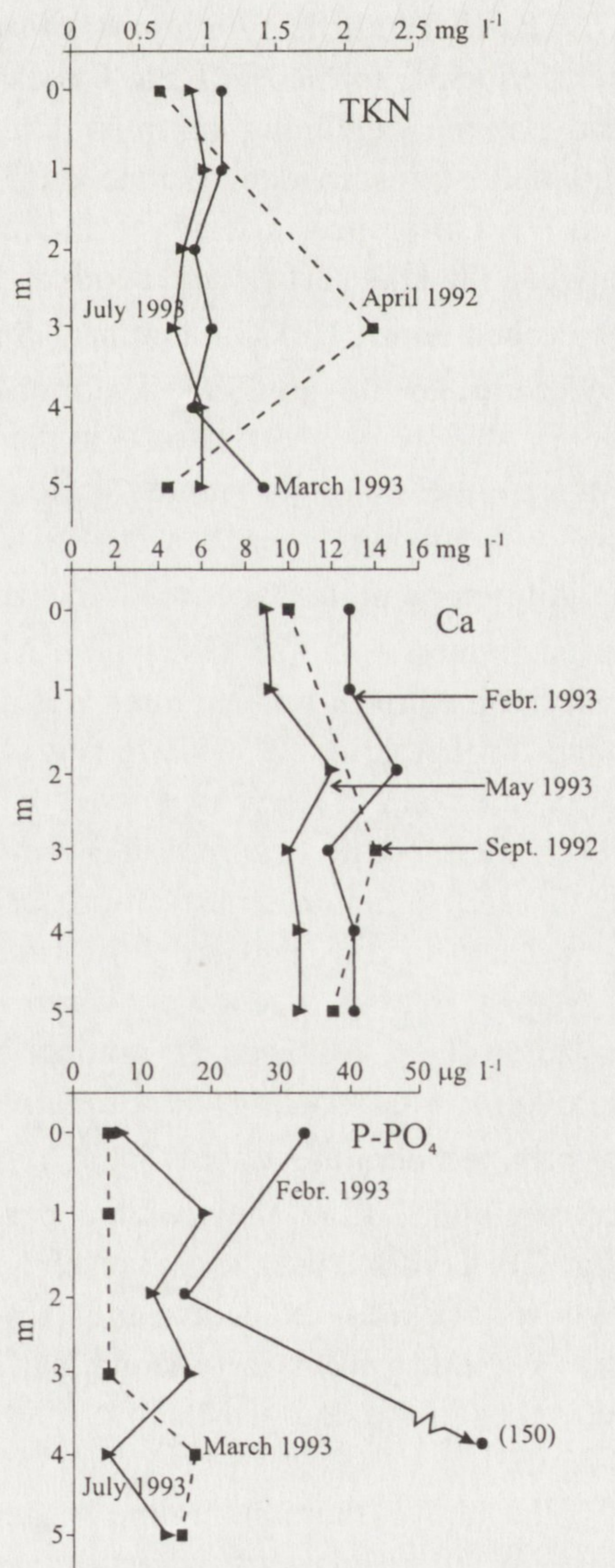


Fig. 6. Vertical distribution of concentration of selected compounds in Lake Flosek

were even several times higher at the depth of 3–4 m or 5 m than those in the deeper or shallower layers (Fig. 6). Such

a phenomenon took place usually in winter (February–March) when the lake was frozen.