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ANTHROPOGENIC INFLUENCE ON THE ^{14}C ACTIVITY AND OTHER CONSTITUENTS OF RECENT LAKE SEDIMENTS: A CASE STUDY[1]

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ABSTRACT. Anthropogenic activities that introduce an excess of nutrients and other pollutants into rivers and lakes are causing significant changes in their aquatic environment. Excessive nutrients greatly accelerate eutrophication, and lake marl formed during eutrophication differs from that formed in oligotrophic water.

We analyzed recent sediment cores from Prošće and Kozjak lakes located in Plitvice National Park, central Croatia. Analyses consisted of ^{14}C activity of calcareous lake marl, the ratio of stable isotopes ($\delta^{13}C$, $\delta^{18}O$), organic compounds in the sediment and the distribution of diatoms. Previous ^{14}C activity measurements helped to determine the sedimentation rate and thus the time period of increased input of nutrients into lakes. We determined the increased ^{14}C activity in lake sediments caused by nuclear bomb effect in recent depth profiles. We attributed the sudden increase in diatom species, *Cyclotella operculata unipuctata* and *Achnanthes clevei rostrata*, in the uppermost 5-cm layer, to eutrophication of the lake water.

We performed a molecular characterization of hydrocarbons isolated from the sediments, and applied computer-assisted high-resolution gas chromatography/mass spectrometry to estimate contributions of biogenic, fossil and pyrolytic hydrocarbons.

INTRODUCTION

The anthropogenic impact on lacustrine environments over the past 50–100 years is recorded in lake sediments in the form of significant changes in chemical and isotopic constituents (Schell & Barnes 1986; Giger, Schaffner & Wakeham 1980). In less affected environments, such as Plitvice National Park, located in a sparsely populated karst area of northwestern Dinarides, the concentration of major ionic species in freshwater, dissolved inorganic carbon (DIC) and sedimentation rates have not changed recently (Srdoč *et al.* 1985). Consequently, recent calcareous deposits in lake marl contain up to 95% of $CaCO_3$, undifferentiated from older sediments (Srdoč *et al.* 1986). However, trace elements, isotopes, organic compounds and diatom frustules reflect changes in the environment, mostly as a consequence of human activity.

We have investigated changes in the uppermost, ≈30-cm-thick layers of lake marl from karst lakes, Prošće and Kozjak, fed by springwater and interconnected by numerous cascades and falls formed by travertine barriers (Fig. 1). One of us (D.P.) retrieved several cores from each lake using a hand corer. Upper Lake Prošće has been exposed mostly to changes in global conditions, such as increased ^{14}C activity of atmospheric CO_2 due to thermonuclear bomb tests, whereas lower Lake Kozjak has, in addition, suffered increased local anthropogenic pollution. Lake Kozjak is situated in the middle of a busy tourist traffic center. The number of annual National Park visitors was recently estimated at one million.

Besides recent tourism, local farming and a primitive logging industry were recorded since 1800. Often interrupted by fire and two World Wars, logging and sawmills never developed into a mod-

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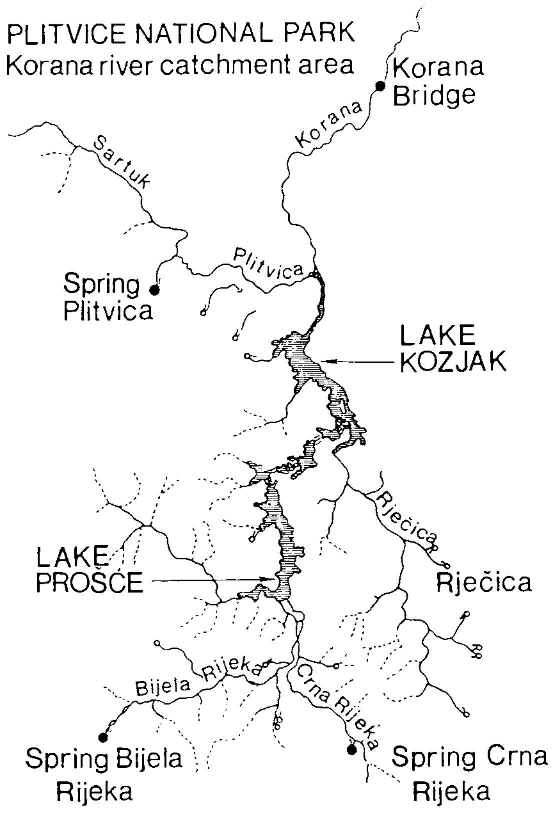

Fig. 1. Map of the central part of Plitvice National Park

ern, fossil-fuel-powered industry, and were phased out entirely by the early 1960s. However, thick deposits of partly degraded sawdust still cover the bottom of parts of Lake Kozjak.

EXPERIMENTAL

Ca. 50 g of sediment was dissolved in dilute HCl. The evolved CO_2 was flushed with nitrogen and trapped at liquid nitrogen temperature. Subsequent procedures including conversion of CO_2 to CH_4 and gas purification, as well as the counting procedure, are described elsewhere (Srdoč, Breyer & Sliepčević 1971).

We took samples for ^{14}C measurements from several ~30-cm-long cores from Lakes Kozjak and Prošće. The sediments were cored in 1989 and 1990 at several points and at different depths (21.5 m and 38 m in Lake Kozjak, and 20 m and 32 m in Lake Prošće). We used 5-cm-thick sections for ^{14}C activity measurements, except for the uppermost core section from Lake Kozjak, which was cut into 2-cm-thick slices for more precise determination of ^{14}C spatial distribution.

Milligram-sized samples of calcareous sediment were treated with diluted HCl to dissolve $CaCO_3$. Diatom frustules were subsequently cleaned with HNO_3 in oxidizing medium to remove organic detritus. Detailed microscopic analysis was carried out on a compound microscope at 600–1000 × magnifications (dry and oil immersion) using transmitted light and phase contrast illuminations.

Aliphatic and aromatic hydrocarbons have been extensively analyzed in various types of aquatic sediments (Blumer & Sass 1972; Youngblood & Blumer 1975; Laflamme & Hites 1978; Giger, Schaffner & Wakeham 1980; Wakeham, Schaffner & Giger 1980a, b). Giger and Schaffner (1978) described in detail the analytical methodology used in this study. Briefly, air-dried samples (3.5–

9 g) were Soxhlet-extracted with methylene chloride, fractionated into an aliphatic and aromatic fraction, and analyzed by high-resolution gas chromatography and gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

Isotope Measurements

^{14}C activity and stable isotope content (^{13}C and ^{18}O) of segments of long sediment cores retrieved in 1983 from both lakes (Srdoč *et al.* 1986), represent the reference points for comparison with recent changes in the uppermost sedimentary layer. It was assumed that the calcite sedimentation rate in both lakes has not changed recently, in spite of anthropogenic influence described in this paper. Recent morphologic measurements by Wong (1992) substantiate this assumption. Thus, on the basis of ^{14}C measurements of a 12-m-long sediment profile from Lake Prošće, we concluded that the sedimentation rate has been constant at 1.6 mm yr^{-1} over the past 8 ka. Lake Kozjak has had a more turbulent history, as demonstrated by stratigraphy, seismic, ^{14}C and diatom profiles of a 12-m-long core. However, the upper 2 m of sediment show a uniform stratigraphy and a constant diatom frequency, except in the uppermost 6 cm, which is affected by human influence. The sedimentation rate was determined by ^{14}C measurements at 0.8 mm yr^{-1} covering the past 2 ka (Srdoč *et al.* 1986). We have applied these sedimentation rates to estimate the age of short sediment cores.

The ^{14}C activity of the calcareous part of the lake sediment, expressed in percent modern carbon (pMC) *vs.* sediment depth, shows an interesting and peculiar shape, when compared to atmospheric CO_2 activity after the bomb-test period. Essentially, the ^{14}C activity of the lake marl increased due to the thermonuclear bomb tests in 1963. However, the peak ^{14}C activity in the lake sediment was less pronounced than the atmospheric ^{14}C peak (Fig. 2). While atmospheric ^{14}C activity doubled during the peak period in the northern hemisphere (Levin, Münnich & Weiss 1980), the highest ^{14}C activity of Lake Kozjak sediment reached ≈91 pMC, that is only ≈20% above the pre-bomb-test level (76 pMC, Krajcar Bronić *et al.* 1992). The explanation for such a damped response to the stepwise increase of atmospheric ^{14}C activity lies in the fact that most biogenic carbon in DIC is derived from biodegradation of topsoil detritus of terrestrial plants. This process is relatively slow in temperate zones (Scharpenseel & Becker-Heidmann 1989), averaging the ^{14}C activity in soil CO_2 over several decades. In addition, the bomb-produced ^{14}C activity penetrated deeply into sediment, reaching 8–10 cm below the injection level (Fig. 2). Assuming a constant sedimentation rate of 0.8 mm yr^{-1} in Lake Kozjak, this corresponds to 100–125 years, thus contaminating the entire uppermost layer deposited in this century. The process of sediment redeposition, caused very likely by bioturbation, also contributes to blurring the ^{14}C activity peak in sediments.

Although increased ^{14}C activity in lake sediments reflects a global change in the ^{14}C activity of atmospheric carbon, the two lakes differ in their responses to global ^{14}C increase. Lake Kozjak is fed by water from Lake Prošće (Fig. 1), cascading over dozens of cataracts and falls, which brings about an additional exchange with atmospheric CO_2, resulting in increased DIC ^{14}C activity of ≈4 pMC. This process is very fast, as opposed to the previously described biodegradation of organic detritus. We observed a pronounced ^{14}C peak in Lake Kozjak sediment after measuring 2-cm-thick sections, as opposed to 5-cm-thick core sections from Lake Prošće.

As expected, the carbon stable isotope content ($\delta^{13}C$) and that of oxygen ($\delta^{18}O$) in recent calcareous lake marl, consisting of calcite microcrystals, did not change with respect to older sediment. The $\delta^{13}C$ and $\delta^{18}O$ values remained constant for the past 8 ka, indicating steady climatic and hydrological conditions during the Holocene (Srdoč *et al.* 1986). In contrast to the inorganic sediment, the recent organic sediments, consisting mainly of degraded detritus of terrestrial and aquatic

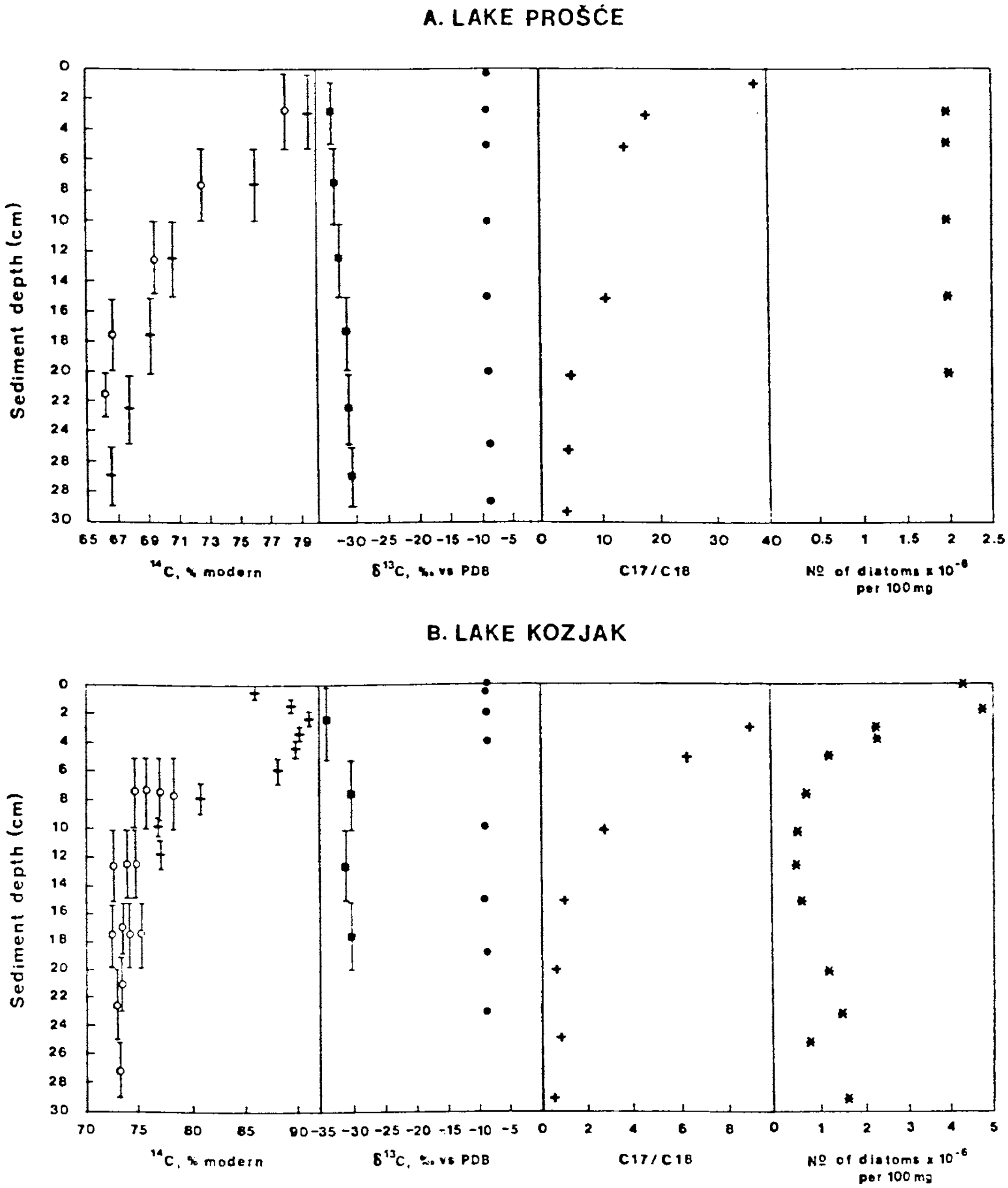

Fig. 2. Results of analyses of sediment cores from Lakes Prošće and Kozjak; ^{14}C activity: – and o = 2 cores, from A, Lake Prošće; B, Lake Kozjak; δ^{13}C: ▪ = organic residue; • = calcareous sediment; hydrocarbons: + = concentration ratio of n-heptadecane to n-octadecane; diatoms: * = number of diatom frustules/100 mg of dry sediment. See text for sediment profile age.

plants, showed a change toward more negative δ^{13}C values during the past 25–30 years, represented by the uppermost 3–4 cm of the sediment (Fig. 2). Along with noticeable eutrophication of the lake water, we observed more intensive growth of aquatic plants. Stands of *Miriophyllum verticillatum* cover parts of the bottom of both lakes, where only clean lake marl existed 20–30 years ago. In turn, expanded aquatic vegetation led to more detritus from aquatic plants in the uppermost 3–4 cm of sediment. Most of the aquatic plants growing in the lakes have very pronounced negative $\delta^{13}C$ values, down to –40‰ *vs.* PDB (Marčenko *et al.* 1989). This shift in $\delta^{13}C$ values for organic residue, from an average of –30.5‰ to –33.5‰ in the top layer, results from anthropogenically induced eutrophication in both lakes. The $\delta^{18}O$ value is not affected by human activity and remains constant throughout the sediment core.

Diatom Analysis

We recorded a substantial increase in diatom frustules in the upper 5 cm, and especially in the uppermost 2 cm of the sediment collected in 1989 in Lake Kozjak (Fig. 2), which is due to the sudden growth of diatoms, *Cyclotella operculata*, var. *unipunctata* associated with planktonic *Stephanodiscus minutulus* and *Achnanthes clevei* var. *rostrata. Cyclotella operculata* var. *unipunctata* is a tiny diatom that occurs facultatively in plankton, but may also be found in periphyton. *Achnanthes clevei* var. *rostrata* is a frequent member of diatom assemblages of alpine and Baltic lakes. In 1983 we found this species throughout the 12-m sediment core, but always below 1% of the total diatom population. We repeated the diatom analysis in sediments in 1990, using several short cores. We observed a decline in *Achnanthes* diatoms, which meant that their mass development may have been a temporary and/or local event. However, the samples collected in 1990 were dominated by another periphytic and facultative planktonic form, *Fragilaria construens.* Typical plankters, however, such as *Cyclotella plitvicensis, C. comta, Fragilaria crotonensis* and *Asterionella formosa*, decreased in frequency. Concurrent analyses of plankton indicate that the phytoplankton populations have also changed from dominance by diatoms to *Chrysophytes* and *Chlorophytes*, which, by itself, is a sign of accelerated eutrophication, probably due to an influx of waste waters. *Cyclotella operculata* and its var. *unipunctata* are gradually becoming dominant in Lake Prošće as well. However, the total number of diatoms g^{-1} of lake sediment in this lake did not change recently, as opposed to their substantial increase in Lake Kozjak (Fig. 2). Planktonic diatoms still dominate in this lake, although the cyanophyte, *Chroococcus turgidus f. quaternaria*, not present before, appears as an ominous sign of eutrophication.

Cyclotella operculata var. *unipunctata* remains dominant in both lakes. Once frequent planktonic forms, such as *Cyclotella plitvicensis, C. ocellata, Fragilaria crotonensis* and *Asterionella formosa*, which are still abundant in Lake Prošće, are depleted in Lake Kozjak. On the basis of diatom species and frequency analysis, Lake Prošće is less affected anthropogenically than Lake Kozjak. The occurrence of planktonic chrysophytes (*Dinobryon divergens*), chlorophytes (*Sphaerocystis planktonicus* and *Crucigenia irregularis*) and cyanophytes (*Microcystis*) in Lake Kozjak indicates a higher trophic level, compared to previous measurements in 1983.

Results of combined analyses of plankton and sediment raise concern about anthropogenic effects on the trophic level of these lakes.

Hydrocarbons in Sediments

Molecular characterization of sedimentary hydrocarbons is widely accepted as a valuable method of studying sources and transformations of organic matter in the aquatic environment. Such an approach proves to be particularly useful in investigations of aquatic sediments that contain historic record of the environmentally relevant events, such as climate, primary productivity, erosion and human activity.

We investigated recent sediments from Plitvice Lakes for their hydrocarbon composition in order to decouple various sources of organic matter, as well as to estimate the variability of particular inputs throughout the recent history of the lakes. Among the different classes of hydrocarbons, the highest concentrations were determined for n-alkanes, whereas the concentrations of polycyclic aromatic hydrocarbons (PAH) were much lower. Carbon preference indices (CPI) for all of the investigated samples varied in relatively narrow ranges of 5.97–9.49 and 6.92–8.40 for Lakes Kozjak and Prošće, respectively. Such high values of CPI clearly indicate that the major portion of the determined hydrocarbons was of terrestrial origin (Giger, Schaffner & Wakeham 1980). Figure 3 shows the sediment depth profiles for two dominant types of n-alkanes, n-heptadecane (n-C_{17}) and n-nonacosane (n-C_{29}). It is known that n-heptadecane represents a very good indicator of autochthonous planktonic input, particularly by diatoms (Giger, Schaffner & Wakeham 1980). Consequently, the increasing levels of this compound in the youngest sediments were attributed to an enhanced primary productivity of the lakes, *i.e.*, to eutrophication.

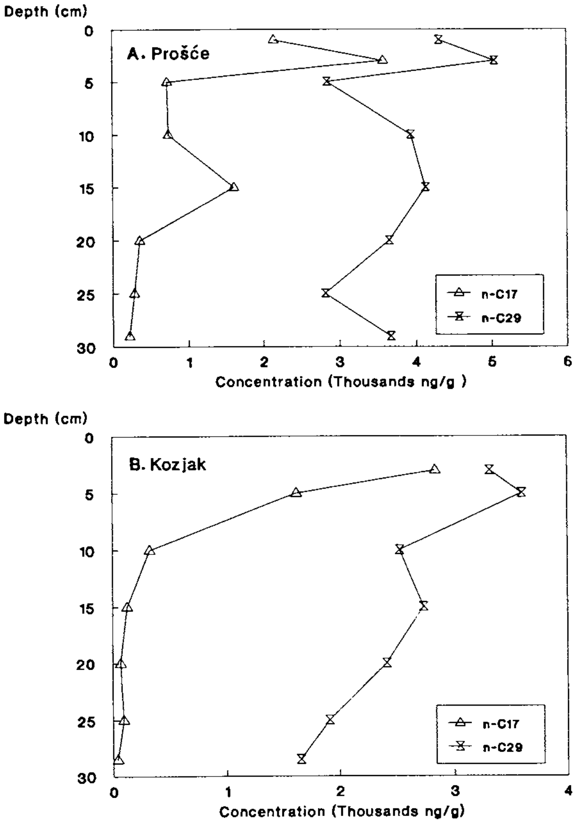

Fig. 3. Depth profiles of n-heptadecane (n-C_{17}) and n-nonacosane (n-C_{29}) in sediment cores from A, Lake Prošće and B, Lake Kozjak. See text for explanation of depth profiles.

A much clearer picture of the eutrophication trends can be obtained when concentration of heptadecane is normalized against the concentration of octadecane, a compound with a very similar chemical structure but of rather different origin (Giger, Schaffner & Wakeham 1980). The depth profile of n-C_{17}/n-C_{18} concentration ratio (Fig. 2) shows that the increase in eutrophication coincides with logging and sawmill activity around 1850, and that it significantly accelerated towards the youngest sediments in both lakes. In terms of absolute concentrations of n-heptadecane, the concentrations of that compound in the Plitvice Lakes are significantly lower than those found in highly eutrophic Greifensee (Giger, Schaffner & Wakeham 1980).

The concentrations of n-nonacosane are significantly higher than n-heptadecane in Lakes Prošće and Kozjak. This suggests that the dominant input of organic matter into the lakes derives from terrestrial plants (Giger, Schaffer & Wakeham 1980). A large part of that input can be considered of purely natural origin, since the lakes are surrounded by large forest areas. However, a portion of the input from this particular source is influenced by human activity, such as timber cutting and sawing, which could increase the input of higher plant debris, particularly sawdust, into the lakes.

We obtained very informative data about human activity around the Plitvice Lakes by analyzing PAH, which are predominantly of anthropogenic origin (Wakeham, Schaffner & Giger 1980a). Figure 4 shows the concentration profiles for three selected PAHs representing compounds with 4–6 rings. Apparently, the concentration profiles of individual PAH are very similar, suggesting that they might have had a common origin. As expected, the lowest anthropogenic PAH concentrations were determined in the deepest sections of the sediment cores. The maximum of the PAH contamination, found in sediment depths of 10–15 cm in Lake Prošće and 5–10 cm in Lake Kozjak, coincides with intensive timber cutting and sawmill activities around 1850. Recently, most of the industrial activity around the Plitvice Lakes ceased, and traffic was diverted farther from the lakes. Thus, the concentrations of the anthropogenic PAH sharply decreased to values similar to those found in sediment sections as old as 200–300 years.

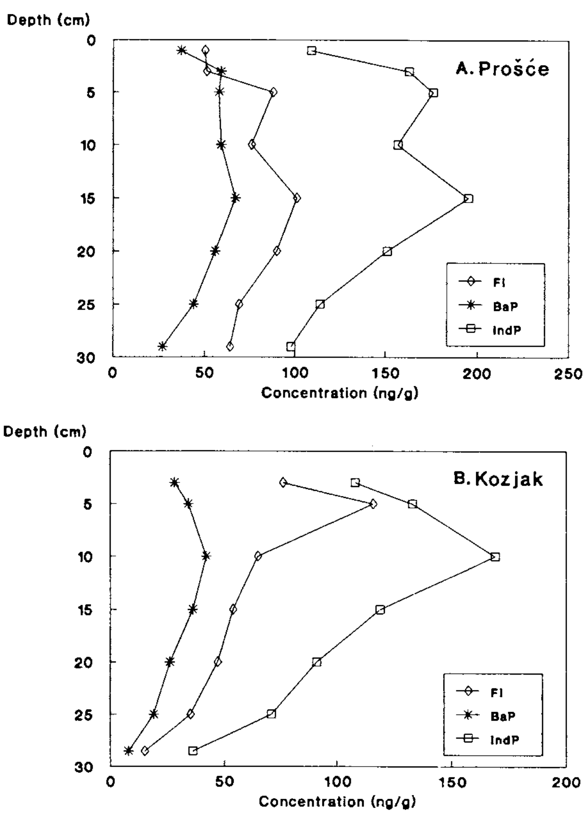

Fig. 4. Depth profiles of anthropogenic polycyclic aromatic hydrocarbons (PAH) in sediment cores from A, Lake Prošće and B, Lake Kozjak: Fl = fluoranthene; BaP = benzo(a) pyrene; IndP = indeno (1,2,3-cd) pyrene. See text for explanation of depth profiles.

Conclusions

Anthropogenic influence on ground and surface waters can be traced in recent lacustrine sediments. In many cases, the history of environmental pollution and future trends can be derived from sediment analyses. Both global and local impacts are recorded in lake sediments, very often featuring site-specific characteristics. In the Plitvice Lakes, contamination of lake sediment by bomb-produced ^{14}C has been pervasive, even though minor differences in ^{14}C activity of lake marl from two lakes are evident. We noticed a damped response to atmospheric ^{14}C contamination and, presently, a downward trend in the ^{14}C activity of the lake marl. The peak ^{14}C activity of the lake sediment reached 91 pMC, which is only 20% above the pre-bomb-test activity of the sediment.

Aliphatic and polycyclic aromatic hydrocarbons generated by natural processes or human activity usually spread over the entire drainage area. The hydrocarbon indicators in sediments also follow human activity in the region, peaking during the most intensive logging and sawmill activity. Whereas the concentration of n-alkanes (C_{17} and C_{29}) continues its upward trend in Lake Kozjak due to degradation of thick deposits of sawdust, it is interesting and encouraging to note that a recent tourist boom did not bring an increase to PAH concentration from fossil-fuel combustion. Under the environment-oriented National Park policy, traffic is diverted from the vicinity of the lakes. Unfortunately, local pollution of Lake Kozjak by waste waters persist, as is evident from diatom analysis.

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