

## RADIOCARBON DATING OF LAKE SEDIMENT FROM TWO KARST LAKES IN YUGOSLAVIA

DUŠAN SRDOČ, BOGOMIL OBELIĆ, NADA HORVATINČIĆ, INES  
KRAJCAR-BRONIĆ, ELENA MARČENKO

Rudjer Bošković Institute, P O B 1016, 41001 Zagreb, Yugoslavia

JOSEPH MERKT\*, HOW KIN WONG\*\*, and ADELA SLIEPČEVIĆ†

**ABSTRACT.** Samples of sediment cores from two lakes in the karst area of northwest Yugoslavia were analyzed. Both Lakes Kozjak and Prošće are in the Plitvice National Park, Central Croatia.  $^{14}\text{C}$  dating, sedimentologic, seismic, and isotopic studies, and distribution of diatoms are presented.

$^{14}\text{C}$  dating of lake marl revealed a uniform sedimentation rate in Lake Prošće as opposed to Lake Kozjak. Both lake sediments belong to the Holocene period.  $^{14}\text{C}$  dating of lake sediment is in agreement with seismic profiles, sedimentologic analysis, and diatom frequency measurements both in an undisturbed as well as in a disturbed lake sediment.

### INTRODUCTION

A comprehensive study of aquatic chemistry, hydrobiology, and hydrogeology of the Plitvice Lakes included coring of lake sediment and a subsequent systematic analysis of cores. Samples of cores taken every 5 to 50cm (depending on the type of analysis) were analyzed for pollen, diatom, and ostracode content, followed by sedimentologic, trace element, x-ray diffraction, stable isotope, and  $^{14}\text{C}$  analyses. The  $^{14}\text{C}$ , stable isotope, and diatom population analyses are presented here, along with a brief description of seismic and sedimentologic work.

Lake Kozjak core was retrieved from 24m water depth. Even though a surprisingly thick lake sediment prevented the extraction of all core material overlaying bedrock, the first 12m of sediment gave very useful and, to a certain extent, unexpected data. Radiocarbon ages of an acoustically well-stratified top section indicated a fairly constant sedimentation rate of 0.8mm/a for the last 1800 years.

Lake Prošće core was retrieved from 17.2m water depth and reached the clayey residual layer overlaying bedrock. Radiocarbon dating of lake sediment revealed a uniform sedimentation rate (1.4mm/a) as opposed to Lake Kozjak sediments. Both lake sediments belong to the Holocene.

The x-ray diffraction analyses showed that the sediments consist of calcite with traces of dolomite, indicating that the sediments were formed by decomposition of dissolved calcium bicarbonate without any significant contribution from detrital limestone or dolomite. This was substantiated by  $\delta^{13}\text{C}$  data, ranging between  $-8.5\text{‰}$  and  $-8.8\text{‰}$ , which is typical of sediments of biogenic origin.

### *Geologic Setting*

According to Polšak (1979) the Plitvice Lakes are surrounded by Triassic, Jurassic, and Cretaceous beds. The whole area is gently folded and intersected by numerous faults. Two most prominent faults run in a north-

\* Niedersächsisches Landesamt für Bodenforschung, D-3000 Hannover, FRG

\*\* Geologisch-Paläontologisches Institut der Universität, D-2000 Hamburg, FRG

† Faculty of Veterinary Sciences, University of Zagreb, YU-41000 Zagreb, Yugoslavia

west-southeast direction (so-called Dinaric direction). The Upper Triassic dolomites form impermeable beds which prevent sinking of water in the otherwise typical karst area.

#### *Stratigraphy*

The first 1.9m (Fig 1, A) of the Lake Kozjak core consists of fine-grained lake marl (Seekreide) intercalated with a few calcareous sand layers several mm thick. The next 3.1m (B) is a lake marl with a relatively low content of organic carbon consisting of very fine organic detritus. It is characterized by a large number of gas bubbles, which could be *in situ* but could have also evolved during sample extrusion. This is followed by 20cm (C) of calcareous turbidite with middle-sand grain sizes at its base and a conspicuously graded bedding towards the top. Underlying this turbidite are 1.8m (D) of lake marl with detrital clay. Few gas bubbles are present, organic detrital material in low concentration occurs in some sections and bioturbation is visible through these changes. The lowermost section cored (E, 5.35m) which is separated from the interval above by a gradational transition consists of lake marl, mostly very poor in clay. It is characterized by cyclic deposits typically 20 to 30cm thick. Both turbiditic origin and bioturbation become apparent by abrupt cyclic changes of sediment color and composition.

The sedimentary column of Lake Prošće is more monotonous; lake marl with rare oscillations of the contents of diatom silica, clay, and traces of dolomite. Almost no stratification or sedimentary pattern is visible. Near the base of the profile dolomite content increases; interspersed calcitic concretions (Schnegglisteine) and pieces of wood in the lake marl indicate the proximity of the shore.

#### *Seismic Profiles*

The seismic records close to the coring site in Lake Kozjak show typically an upper layer, S, ca 2m thick which is well-stratified and strongly acoustically reflecting (Fig 1). The next layer, T, is ca 3m thick. It may be divided into a strongly reflecting top section and a more-or-less acoustically transparent basal section. We correlate this layer with B and C of the Kozjak core attributing the high reflectivity of the upper part to the *in situ* occurrence of gas bubbles, possibly generated by bacterial degradation of organic material. The lower transparent section has an acoustic character typical of lake marl that is by and large homogenous. The inclusion of layer C in this correlation is based on sedimentologic grounds alone; this thin (20cm), sandy, turbidic unit constitutes the base of layer B, and its thickness is beyond the resolution ability of our equipment.

Below layer T is section U, some 2m thick, composed acoustically of hummocky to chaotic echoes. It appears to have undergone mass transport and redeposition. The mechanism responsible for slope failure that set the mass-wasting processes into motion can at best only be speculated upon. A comparison between the sediment structures in lakes Kozjak and Prošće suggests that regional causes, such as earthquake triggering, lake level fluctuations, or *in situ* changes in pore pressure of the lake deposits due to gas

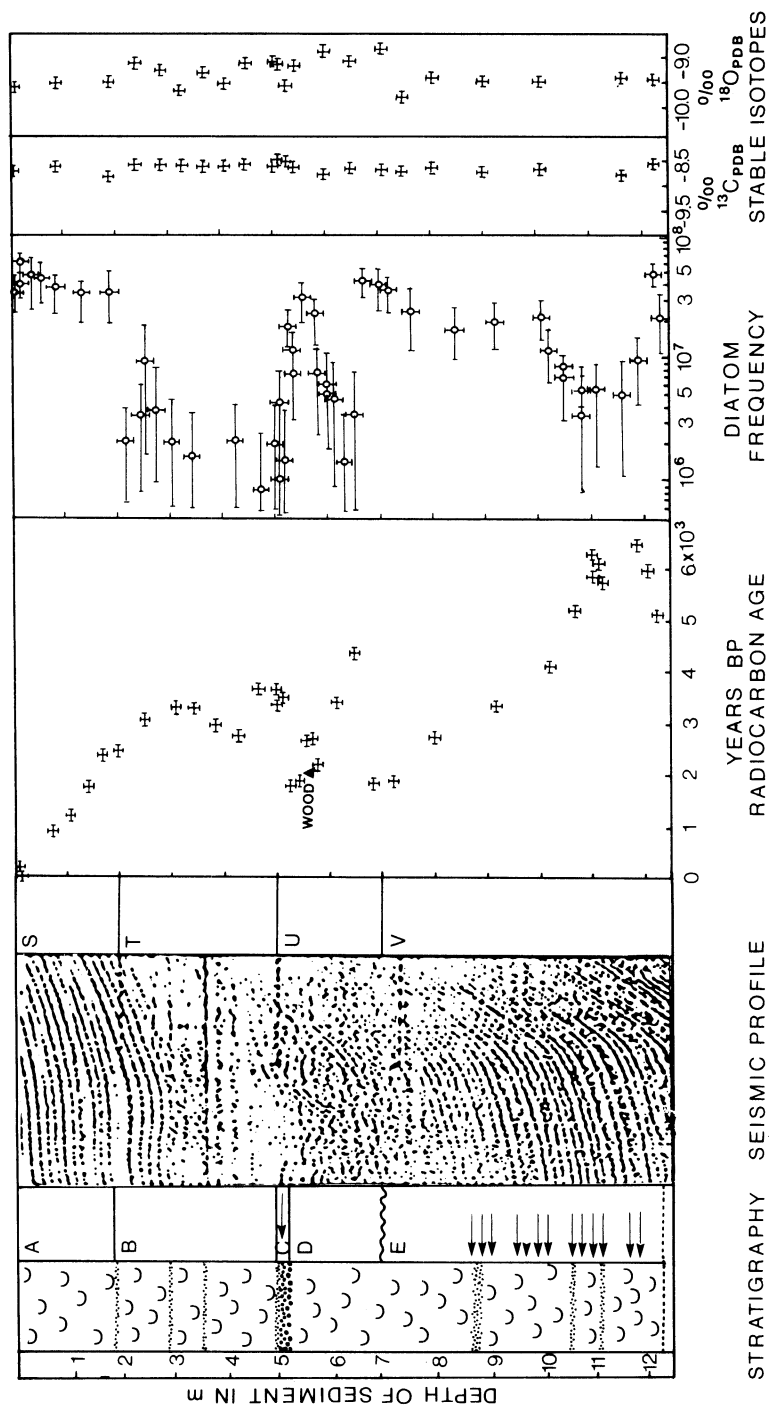


Fig 1. Lake Kozjak sediment profile. The stratigraphy, seismic record and description,  $^{14}\text{C}$  age, diatom frequency, and stable isotope data ( $^{13}\text{C}$  and  $^{18}\text{O}$ ) are shown vs core depth in m. The core sections labeled A-E and S-V are described in the text. Coarse calcite grain layers are indicated by dots; arrows show turbidite layers.

generation, cannot be considered causal for this catastrophic sedimentary event ca 1800 yr BP. Much more probable is the sudden collapse of tufa barriers which could have been weakened by hydrostatic overpressure, or triggered by neotectonic activities along the extension of the fault with a Dinaric strike sub-parallel to the eastern lakeshore. Such a collapse would be accompanied by failure of the adjacent oversteepened lacustrine slopes, leading to turbidite deposition. Remnants of tufa barriers on land as well as underwater attest to such an event.

The acousto-stratigraphic section, U, may be correlated to layer D of the Kozjak core. This layer consists of lake marl and detrital clay and is at least 90% turbiditic.

Section T + U, 5m thick, represents a geochronologic discontinuity in the core. Although it should be older than layer S which it underlies, the mass transport events caused age reversals and/or age repetitions.

Beneath the hummocky echoes is sequence V, 7.5m thick, which may be directly compared acoustically to the uppermost layer, S. Here, the reflectivity is high and stratification prominent. The correlation to the lowermost interval E (lake marl) of Kozjak core is highly probable.

Underlying the acoustic section, V, is a very strong and characteristic reflector, which is pervasive at this water depth in the central part of Lake Kozjak. Below this reflector is an acoustically turbid zone that is succeeded by an acoustically opaque horizon of considerable relief.

The seismic profiles from Lake Prošće are very monotonous. Over the core site, the presence of gas has limited penetration to a mere 3 to 4m. In the immediate vicinity, however, a homogeneous layer with a thickness varying between 10 to 12m is encountered. This constitutes the entire lacustrine deposition below which the pre-lacustrine base can be easily identified.

#### *Diatom Population*

The preserved vegetation in the sediment cores consists mostly of diatoms. It is represented by sinking planktonic forms (predominantly *Fragilaria crotonensis* and *Cyclotella plitvicensis*), several benthic forms and a few littoral forms. The density of diatom populations and the number of species increase from the bottom of the sediment core upwards. Deeper layers of sediments are devoid of planktonic forms and contain mostly various chain building *Fragilaria* forms. Several benthic species of *Amphora*, *Diploneis*, *Gyrosigma*, *Navicula*, *Achnanthes*, *Cymatopleura*, *Surirella*, *Campylodiscus*, *Stauroneis*, *Caloneis*, and *Cymbella* are present throughout the sediment depth in both lakes. Many of them are indicators of alkaline alpine waters.

The total number of diatoms per gram of sediment in Lake Prošće is fairly uniform throughout the core, ranging from  $1 \times 10^7$  to  $1 \times 10^8$  diatoms per gram, except at the lowest section of the core, where the population of diatoms rapidly decreases (Fig 2). In Lake Kozjak there is a more irregular pattern of diatom distribution, shown in Figure 1, which is in accordance with the findings of other investigations ( $^{14}\text{C}$  dating, acoustic measurements, and sedimentologic analyses). Diatom population varies

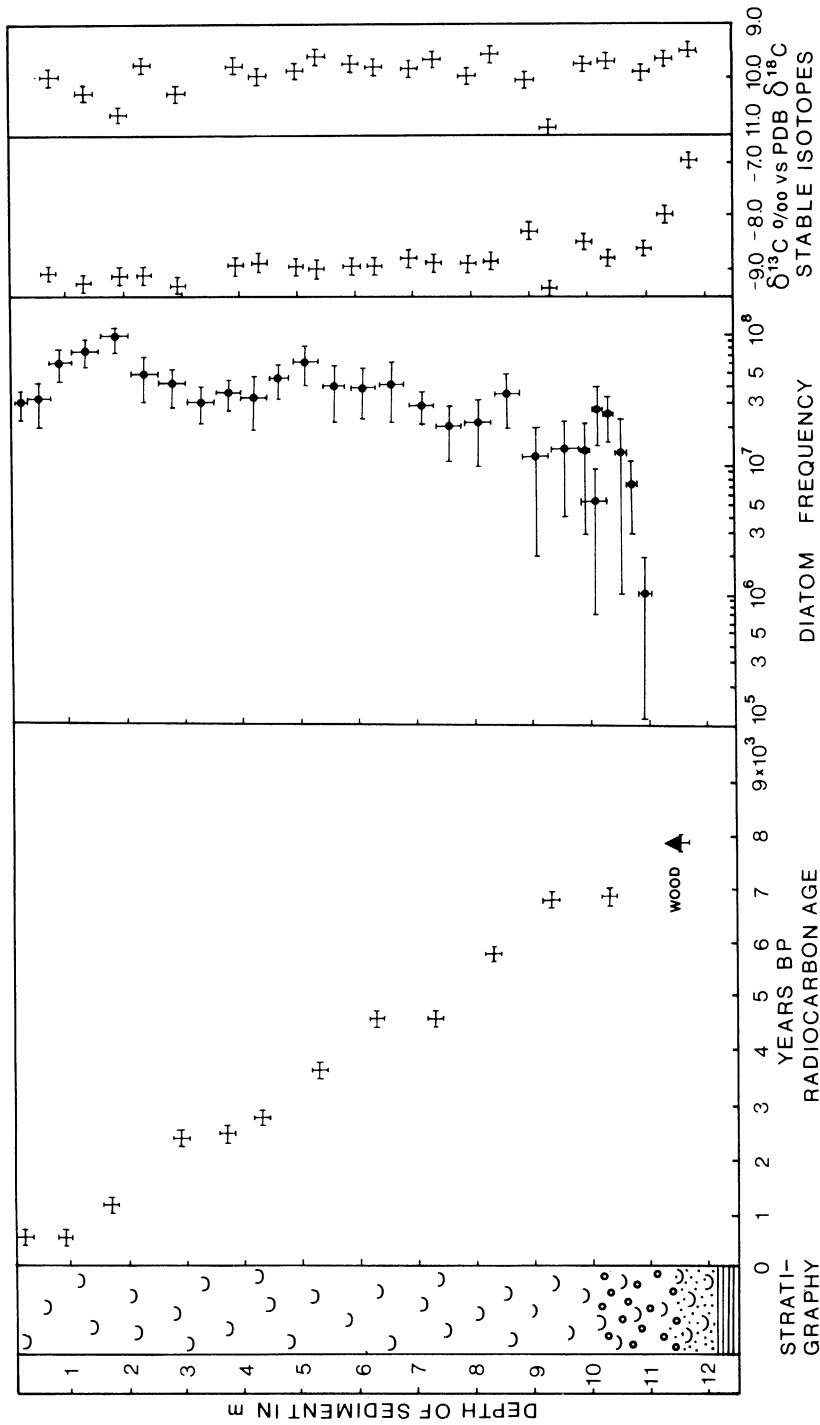


Fig. 2. Lake Prošće sediment profile. The stratigraphy,  $^{14}\text{C}$  age of sediment, diatom frequency, and stable isotope data ( $^{13}\text{C}$  and  $^{18}\text{O}$ ) are shown vs core depth. Coarse calcite grain layers are indicated by dots; open circles indicate calcite concretions.

between  $1 \times 10^6$  and  $7 \times 10^7$  per gram of sediment in the Lake Kozjak core.

#### *Stable Isotopes $^{13}\text{C}$ and $^{18}\text{O}$*

The results of stable isotope analyses for Lake Kozjak are shown in Figure 1 and for Lake Prošće in Figure 2. The  $\delta^{13}\text{C}$  values as well as those of  $\delta^{18}\text{O}$  are remarkably constant throughout the sediment profile.

The mean  $\delta^{13}\text{C}$  value for Kozjak is  $(-8.62 \pm 0.07) \text{‰}$  and for Prošće  $(-8.94 \pm 0.26) \text{‰}$  *vs* PDB standard which points to the biogenic origin of the sediment. The  $\delta^{13}\text{C}$  of the surrounding limestone and dolomite bedrock is close to  $0.0 \text{‰}$ . No significant contribution of detrital limestone or dolomite was found in the cores.

The mean  $\delta^{18}\text{O}$  value for Kozjak is  $(-9.32 \pm 0.25) \text{‰}$  and for Prošće  $(-9.93 \pm 0.34) \text{‰}$  *vs* PDB standard. The constancy of O-values for both stable isotopes indicates the fairly constant climatic conditions during the sedimentation process throughout the Holocene.

#### RADIOCARBON DATING OF LAKE SEDIMENT

##### *Experimental*

Ca 50g of sediment was dissolved in dilute HCl. The evolved  $\text{CO}_2$  was flushed with nitrogen and trapped at liquid nitrogen temperature. Subsequent procedures including reduction of  $\text{CO}_2$  to  $\text{CH}_4$  and gas purification, as well as the counting procedure are described elsewhere (Srdoč, Breyer & Sliepčević, 1971). The remaining liquid containing colloidal and dispersed organic substance has been stored for further processing.

##### *The Initial $^{14}\text{C}$ Activity of the Sediment*

An assessment or a measurement of the initial activity of the sediment is very important to avoid a systematic error in the calculation of the  $^{14}\text{C}$  age. Several approaches have been described to calculate the initial activity of ground water, which would help to calculate the initial activity of the carbonate precipitate. However, the calculated activities based on various models very often give unacceptable results for the area under investigation (Krajcar-Bronić *et al*, 1986). Therefore, the experimental method, if feasible, gives more reliable results.

Measurement of present activity of dissolved bicarbonates in the lake water cannot be used for the initial sediment activity ( $a_0$ ) calculation because of the contamination of surface waters with bomb-produced  $^{14}\text{C}$ . However, if pre-bomb-test sediments of known age from the investigated area are preserved, a precise measurement of  $a_0$  is possible. Due to continuous research activity in the National Park, we succeeded in finding tufa samples of known age. Since both tufa and lake sediment are precipitated from the same water and are chemically identical, the measured  $a_0$  of the tufa sample from year 1919 can be used for the sediment initial activity. We also measured the activity of submerged aquatic plants and found that their activity corresponds to the activity of lake water (Srdoč *et al*, 1980). The measurement of a sample of moss (*Cratoneurum commutatum*) from 1919

which was preserved in a dry form was in excellent agreement with the activity of contemporaneous tufa. Finally, pieces of wood were found in sediments in both Lakes Kozjak and Prošće and dated. Surrounding sediments were carefully collected and their activity was measured. The ratio of the sediment *vs* the wood activity gives the  $a_0$  (*cf* Table 1). When the  $a_0$  thus obtained was applied to calculate the age of all sediment samples in the particular profile, the upper linear part of the curve showing the  $^{14}\text{C}$  age *vs* sediment depth was shifted to zero age at the uppermost layer of the sediment covering the lake bottom. The measured  $a_0$  values for two investigated lake sediments are given in Table 1.

The experimentally obtained values are in accordance with the calculated values, based on the increase of  $^{14}\text{C}$  activity of bicarbonates in fresh water open to the atmosphere (Srdoč *et al*, 1986).

#### CONCLUSION

$^{14}\text{C}$  dating of lake sediment yielded concordant results with seismic profiles, sedimentologic analysis, and diatom frequency measurements both in an undisturbed and a disturbed lake sediment. Our  $^{14}\text{C}$  measurements showed that lake marl containing 96–98% of calcium carbonate of biogenic origin provides reliable ages, assuming that the so-called hard-water effect has been taken into account. The initial sediment activity  $a_0$  can be measured if the contemporaneous organic material is available. The  $a_0$  can be estimated from the shift of the sediment age *vs* depth line from zero at the lake bottom. This method could give reliable  $a_0$  values for a uniform sedimentation rate over the past several millennia.

#### ACKNOWLEDGMENTS

The following individuals and institutions are fully acknowledged for their help: Mebus A Geyh, Niedersächsisches Landesamt für Bodenfor-

TABLE 1  
Measured  $a_0$  values for Lakes Prošće and Kozjak  
Experimental errors range from 0.7 to 1.2%

Code	Sample description	Depth (m)	$^{14}\text{C}$ activity (% modern)	$a_0^*$
Lake Prošće				
Z-857	Moss ( <i>Cratoneurum commutatum</i> ) coll 1919	Surface	72.7	
Z-1307	Wood covered by tufa, coll 1919	Surface	97.3	
Z-1306	Tufa around wood, coll 1919	Surface	71.8	73.8
Z-1395	Wood ( <i>Abies</i> ) in sediment	11.60	38.5	
Z-1435	Sediment near the wood	11.65	27.8	72.2
Lake Kozjak				
Z-1168	Wood ( <i>Abies</i> ) in sediment	5.65	75.0	
Z-1173	Sediment near the wood	5.80	56.9	75.9

\* $a_0$  = % modern(calcareous deposit)/% modern(wood)

schung, for initiating and organizing the Plitvice Project Research; Helmut Müller, Bundesanstalt für Geowissenschaften and Rohstoffe, Hannover, for help and stimulating discussions; Jože Pezdič, Jožef Štefan Institute, Ljubljana, for stable isotope analyses; Stanko Popović, Rudjer Bošković Institute for x-ray diffraction analysis; Bundesministerium für Technologie and Wissenschaften of the Federal Republic of Germany, for partly financing the research, and Plitvice National Park Authorities, for partly financing and supporting the research.

## REFERENCES

- Krajcar-Bronić, I, Horvatinčić, N, Srdoč, D and Obelić, B, 1986, On the initial  $^{14}\text{C}$  activity in karst aquifers with short mean residence time, *in* Stuiver, M and Kra, R S, eds, Internatl  $^{14}\text{C}$  conf, 12th, Proc: Radiocarbon, this issue.
- Polšak, A, 1979, The Plitvice Lakes; 16th European micropalaeontological colloquium, Proc: Ljubljana, p 157–162.
- Srdoč, D, Breyer, B and Sliepčević, A, 1971, Rudjer Bošković Institute radiocarbon measurements I: Radiocarbon, v 13, p 135–140.
- Srdoč, D, Krajcar-Bronić, I, Horvatinčić, N and Obelić, B, 1986, The increase of  $^{14}\text{C}$  activity of dissolved inorganic carbon along a river course, *in* Stuiver, M and Kra, R S, eds, Internatl  $^{14}\text{C}$  conf, 12th, Proc: Radiocarbon, this issue.
- Srdoč, D, Obelić, B, Horvatinčić, N and Sliepčević, A, 1980, Radiocarbon dating of calcareous tufa; How reliable data can we expect? *in* Stuiver, M and Kra, R S, eds, Internatl  $^{14}\text{C}$  conf, 10th, Proc: Radiocarbon, v 22, no.3, p 858–862.