RADIOCARBON, Vol 50, Nr 2, 2008, p 233–253

TOWARDS A DEEPER UNDERSTANDING OF HOW CARBONATE ISOTOPES (^{14}C, ^{13}C, ^{18}O) REFLECT ENVIRONMENTAL CHANGES: A STUDY WITH RECENT ^{210}Pb-DATED SEDIMENTS OF THE PLITVICE LAKES, CROATIA

Nada Horvatinčić[1,2] • Jadranka Barešić[1] • Slavica Babinka[3] • Bogomil Obelić[1] • Ines Krajcar Bronić[1] • Polona Vreča[4] • Axel Suckow[3,5]

ABSTRACT. Five short cores (top 40–45 cm of sediment) from 4 lakes of the Plitvice Lakes system (Croatia) were measured for ^{210}Pb, ^{137}Cs, a^{14}C, δ^{13}C, and δ^{18}O in order to study the influence of environmental changes on the sediment system in small and large lakes. Sediment chronology based on the constant flux (CF) ^{210}Pb model was the most reliable. Lake sediments consisted mainly of autochthonous carbonates with higher sedimentation rates in small lakes. Sediments from 2 large lakes, Prošće and Kozjak, showed constant stable isotope profiles for the carbonate fraction and full agreement between the ^{137}Cs and ^{210}Pb chronologies. Sediments from 2 small lakes, Gradinsko and Kaluđerovac, showed synchronous increases in ^{14}C and δ^{13}C and disturbed ^{137}Cs records. All lakes showed an increase in a^{14}C in the carbonate sediments above the first occurrence of ^{137}Cs, which was interpreted as a damped (~10 pMC increase in a^{14}C) and decades-delayed consequence of the bomb-induced increase in a^{14}C in atmospheric CO$_2$. For the small lakes, increased δ^{13}C in the last 2 decades and part of the a^{14}C increase is probably due to an increase in primary productivity, which enhanced biologically induced calcite precipitation with concomitant changes in the carbon isotopic composition of carbonate sediments. δ^{13}C values of a near-shore sediment core close to the confluence of one of the tributaries of Lake Kozjak showed that the carbonates in this core are a mixture of autochthonous and eroded allochthonous mineral carbonate. This core had a higher fraction of organic material. The sedimentation rate at this core site was high, but rates could not be quantified by ^{210}Pb, ^{137}Cs, or ^{14}C.

INTRODUCTION

Recent lake sediment with its mineral, organic, and isotope composition, and trace element content, records environmental changes that occurred in the lake ecosystem and its watershed. It can also indicate whether these changes were natural or anthropogenic (Last and Smol 2001). This is important for understanding the mechanisms/processes of eutrophication that are often followed by extensive plant growth in lakes, estuaries, or slow streams. In karst districts, lake sediments are formed mainly by carbonate precipitation from dissolved inorganic carbon (DIC) in water. The carbon isotope exchange between the atmosphere and biosphere, including the carbon cycle of CO_2–HCO_3–$CaCO_3$, plays an important role in determining the final isotopic composition of the precipitated carbonates. The record of ^{14}C in recent carbonate sediments can be used to study the global contamination of atmospheric CO_2 with ^{14}C produced by nuclear bomb tests in the 1960s and environmental processes of carbon geochemistry, e.g. in speleothems (Genty et al. 1998; Genty and Massault 1999) and in lake sediments (Srdoč et al. 1992; McGeehin et al. 2004). Moreover, ^{14}C distribution in the sediment can be used to determine sedimentation rate (Srdoč et al. 1986a; Mayr et al. 2005). Stable isotope ratios of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ give additional information about past environmental conditions; they can reflect temperature variations, lake evaporation, bioactivity, and productivity, and indicate the origin of carbon in sediment and/or mechanisms of calcite precipitation (Chafetz and Lawrence 1994; Andrews et al. 1997; Horvatinčić et al. 2003; Andrews and Brasier 2005). Isotopic and geochemical analyses of organic and carbonate fractions of recent sediments (such as the changes in concentration of organic matter in sediments and of its C/N ratio) are also applied in studying processes related to eutrophication that occur during calcite precipitation, e.g. primary productivity and biologically

---

[1] Ruđer Bošković Institute, Bijenička 54, 10002 Zagreb, Croatia.
[2] Corresponding author. Email: nada.horvatincic@irb.hr.
[3] Leibniz Institute for Applied Geosciences, Stilleweg 2, 30655 Hannover, Germany.
[4] Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.
[5] Now at: International Atomic Energy Agency, Wagramerstrasse 5, A-1400 Vienna, Austria.

induced calcite precipitation (Schelske and Hodell 1991; Hodell et al. 1998; Brenner et al. 1999, 2001, 2006; Herczeg et al. 2001; Wan et al. 2003; Vreča 2003; Mayr et al. 2005; Vreča and Muri 2006).

Previous studies of the Plitvice Lakes focused on the processes of tufa/lake sediment precipitation using chemical and isotopic methods (Srdoč et al. 1985; Horvatinčić et al. 1989, 2003; Chafetz et al. 1994). Determination of the initial ^{14}C activity of DIC in water and tufa/lake sediments (Krajcar Bronić et al. 1986, 1992) as well as carbon isotope exchange processes in downstream flow (Srdoč et al. 1986b; Horvatinčić et al. 2003) were completed in connection with the ^{14}C dating of carbonate deposits. Results of ^{14}C dating of the 12-m-long lake sediments from the 2 biggest lakes, Prošće and Kozjak (Srdoč et al. 1986a), and of ^{14}C and ^{230}Th/^{234}U dating of tufa deposits from the Plitvice Lakes (Srdoč et al. 1985, 1994; Horvatinčić et al. 2000) were used to study paleoclimatic conditions in this area. An anthropogenic influence on ^{14}C activity and on the concentrations of some aliphatic and polycyclic aromatic hydrocarbons was observed in the sediments of 2 big lakes, Kozjak and Prošće (Srdoč et al. 1992).

Enhanced eutrophication was observed in the last decades, particularly in some lakes of the Plitvice Lakes National Park. This process is usually the consequence of the enrichment of lake water with nutrients/organic matter whose origin could be anthropogenic or natural. In this study, lake sediment cores in the Plitvice Lakes area were collected to investigate how the recent environmental changes of the lakes are reflected in the sediment geochemistry and carbonate isotopes. Besides the 2 biggest lakes, Kozjak and Prošće, which had been the target of several previous investigations, this study includes 2 small lakes, Gradinsko and Kaluđerovac, to see if the response of the lake sediment composition to recent environmental changes is dependent on lake size. Here, we present the results of ^{210}Pb and ^{137}Cs dating and of isotopic measurements (a^{14}C, δ^{13}C, δ^{18}O), mainly in the carbonate fraction in sediment cores from 4 lakes. In 1 core, we measured ^{14}C in the organic fraction of the lake sediments. The results are compared with published data on the mineral and organic composition of lake sediments (Obelić et al. 2005; Horvatinčić et al. 2006a,b).

SITE DESCRIPTION

The Plitvice Lakes, situated in the Dinaric karst in central Croatia, consist of 16 lakes of different sizes, connected by streams and waterfalls (Figure 1). The altitude of the area ranges between 636 and 505 m asl; the climate is continental; the 5-yr average air temperature is 8.7 °C; and the average annual precipitation is 1473 mm (Horvatinčić et al. 2003). The lakes receive water from 2 main springs (Bijela Rijeka and Crna Rijeka springs) and 2 tributaries (Rječica and Plitvica). The lakes are characterized by intense calcium carbonate precipitation from the water, forming tufa barriers and fine-grained lake sediments mainly composed of authigenic calcite (Srdoč et al. 1985, 1986a; Obelić et al. 2005). The surrounding area is covered largely with deciduous forests. The area is sparsely populated, is protected as a national park, and is included in the UNESCO World Heritage List. Consequently, human activities in the lake watersheds are relatively limited. However, numerous tourists visit this area every year.

Four lakes, the uppermost Lake Prošće (PR), Lake Gradinsko (GR), Lake Kozjak (K), and the lowermost Lake Kaluđerovac (KA), were selected for this study (Figure 1). The lakes have different characteristics (see Table 1). Lakes Kozjak and Prošće are the largest of the Plitvice Lakes and are hereafter referred to as "the big lakes," although on a global scale they are small lakes, with surface areas <1 km^2. "The small lakes," Gradinsko and Kaluđerovac, are shallower and about one-tenth the size. In Lake Kozjak, 2 sampling sites were selected, the first one (K1) in the lake center and the second (K2) at the shore, near the confluence of Rječica Brook. All sites differ in apparent trophic sta-

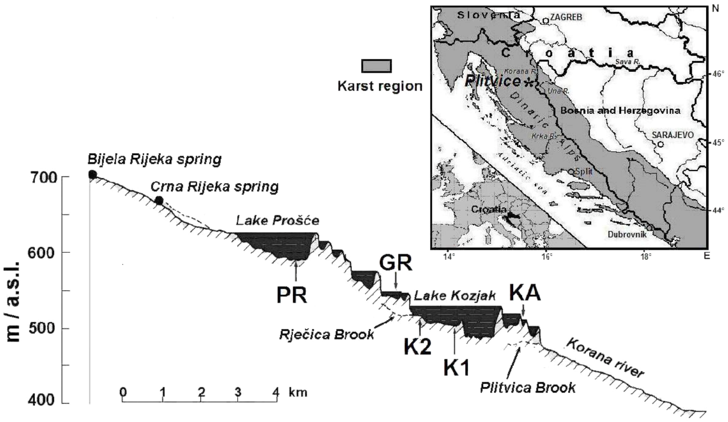

Figure 1 Sampling sites for lake sediments in the Plitvice Lakes: PR – Lake Prošće, GR – Lake Gradinsko, K2 – Lake Kozjak (at the mouth of the Rječica Brook), K1 – Lake Kozjak (in the middle of the lake), KA – Lake Kaluđerovac.

Table 1 Morphologic and sediment characteristics of the Plitvice Lakes (Horvatinčić et al. 2006a,b). Lakes are arranged in a downstream direction, except site Lake Kozjak K2, which is not in the main water stream.

	Lake Prošće PR	Lake Gradinsko GR	Lake Kozjak K1	Lake Kozjak K2	Lake Kaluđerovac KA
Lake area (km^2)	0.68	0.08	0.82	0.82	0.02
Max depth of lake (m)	37	10	46	46	13
Water depth (m) of sediment sampling	19	5	21	2	3
Sediment color	Dark gray	0–15 cm light yellow 15–45 cm light gray	Light gray	Black	Light gray
Calcite (%)	70–80	90–99	80–85	20–60	90–95
Organic matter (%)	7.5–10.5	1.1–5.6	3.9–7.4	11.4–36.6	1.9–3.4
C/N mass ratio	9.4–12.2	8.3–9.7	8.8–10.9	13.0–16.8	9.0–14.0

tus and plant growth, which is greater at sites GR and KA. The most intensive plant growth is observed at K2. Sites PR, GR, K1, and KA follow the downstream flow of water (Figure 1).

METHODS

Lake sediments were collected by scuba divers in November 2003 from 5 locations: PR, GR, K1, K2, and KA (Figure 1). Sediment cores were taken using plastic corers (50 cm length, 10 cm diameter) from different water depths (Table 1) and cores were immediately frozen. Four cores were collected at site K2 and 3 cores at other sites. In the laboratory, frozen cores were cut into 1- to 2-cm-thick layers and dried prior to analyses.

At each site, 3 sediment cores were retrieved, and the subsamples were used for various analyses. Stable isotope content and a^{14}C were determined for subsamples from the same core (usually core 3), gamma analyses were performed on a different core (usually core 1). To cross-check the results, several subsamples from other cores were taken for all analyses and showed agreement among cores.

Water content in the sediment samples was determined gravimetrically after drying at 105 °C. Dry bulk density (DBD, in g/cm^3) was computed from this water content w assuming a sediment grain density ρ of 2.4 g/cm^3 and the formula DBD = $(1-w) / (1-w+w\rho)$.

Activities of the anthropogenic (^{137}Cs, ^{134}Cs, ^{241}Am) and natural (^{210}Pb, ^{214}Pb, ^{214}Bi) radionuclides were determined on dry samples, closed air tight and after an ingrowth time of at least 4 weeks to establish secular equilibrium between ^{226}Ra and ^{214}Pb. Measurements were performed by gamma spectrometry using a low-background, well-type, high-purity germanium (HPGe) detector of 240 cm^3 active volume and 40 mm active well depth. The accuracy of ^{210}Pb activity measurements is mainly determined by differences in self-absorption of the 46.5-keV ray in the sample as compared to certified standards, and estimated to be in the range of 5–7% (Suckow and Gäbler 1997). Measurement precision for all nuclides is generally better than this value. The detection limit for ^{137}Cs depends on the counting time applied for the samples and is between 0.7 and 1 Bq/kg. ^{134}Cs and ^{241}Am were below the detection limit in all samples.

^{137}Cs (half-life 30.2 yr) is an anthropogenic isotope introduced into the atmosphere as a result of atmospheric nuclear weapons testing beginning in 1954 (Pennington et al. 1973). Sedimentation rates are obtained either by attributing 1954 to the deepest sample in the core containing ^{137}C, or attributing the peaks of the ^{137}Cs depth profile to the years 1963 (maximum bomb fallout) and 1986 (Chernobyl fallout). Since the magnitude of the Chernobyl fallout shows high variations from site to site and is unknown *a priori* for a specific site, interpretation of ^{137}Cs peaks can be ambiguous.

^{210}Pb (half-life 22.3 yr) occurs naturally as one of the radioisotopes in the ^{238}U decay series. Sediment dating with ^{210}Pb uses the fact that part of its progenitor ^{222}Rn, produced in local rocks and sediments, escapes to the atmosphere and decays there via short-lived isotopes to ^{210}Pb. ^{210}Pb is removed from the atmosphere by adsorption to aerosols and in precipitation or dry deposition, some of which falls on lake surface and is ultimately incorporated into the upper sediment layer (Appleby and Oldfield 1992). Since ^{210}Pb is also produced in the sediments *in situ*, total ^{210}Pb measured in the samples is the sum of "supported" ^{210}Pb (produced *in situ*) and "unsupported" or "excess" ^{210}Pb (^{210}Pb$_{\mathrm{exc}}$) originating from atmospheric fallout. Supported ^{210}Pb is estimated from the activity of ^{214}Bi and ^{214}Pb (from the gamma lines at 295 keV and 609 keV, respectively), total ^{210}Pb from the gamma line at 46.5 keV, and ^{210}Pb$_{\mathrm{exc}}$ calculated as the difference between these two.

^{210}Pb$_{\mathrm{exc}}$ is measured and reported as specific activity in Bq/kg on dry samples. Sedimentation rates are reported as accumulated dry mass per unit area per unit time [kg/(m^2 yr)] and account for sediment compaction. Age models used here report for "mass depth," describing the dry sediment mass (kg/m^2) above a certain depth in the core. For the calculation of sedimentation rates, the following models were used: CSR (constant sedimentation rate), CIC (constant initial concentration of ^{210}Pb$_{\mathrm{exc}}$), and CF (constant flux of ^{210}Pb$_{\mathrm{exc}}$) (Appleby and Oldfield 1992; the acronym CRS for "constant rate of supply," which also exists in the literature and is synonymous to CF, is not used here since it can be easily mixed up with the acronym CSR). The CIC and CF models allow age calculation with varying sedimentation rates, whereas the CSR model and dating using ^{137}Cs assume constant sedimentation rates. Models were computed using the LabData software package (Suckow and Dumke 2001; Suckow 2003).

^{14}C activity and stable isotopic composition of carbon and oxygen were determined in the carbonate fraction of the sediments. Only in core K2, which had high concentration of organic matter, was it possible to measure the ^{14}C activity of the organic fraction. For measuring ^{14}C activity, carbonate samples were dissolved in dilute HCl. The organic fraction (i.e. the remainder after dissolution by HCl) was combusted to CO$_2$. The CO$_2$ obtained either way was used for benzene synthesis (Horvatinčić et al. 2004). Measurement was performed using a liquid scintillation counter (Quantulus 1220). Oxalic acid II was used as the active standard, while anthracite and marble were used as background samples. The results were corrected for $\delta^{13}C$ and reported as $a^{14}C$ in percent of modern carbon (pMC) (Mook and van der Plicht 1999).

Carbon and oxygen isotopic composition were determined using a modified method of McCrea (1950). Subsamples weighing a few milligrams were placed into exetainers and flushed with helium. Concentrated H_3PO_4 (100%) was added and the isotopic composition of collected CO_2 was determined on a continuous-flow Europa 20-20 ANCA-TG stable isotope ratio mass spectrometer. Isotopic ratios are expressed in the standard delta notation ($\delta^{13}C$ and $\delta^{18}O$), as a per mil (‰) deviation from the VPDB standard. Samples were prepared in duplicates. The replicate error was less than ±0.1‰ for both variables. $\delta^{13}C$ of DIC in water was determined in the carbonate precipitated from water using $BaCl_2$.

Chemical analyses of sediments, mineralogical composition, organic matter analyses (C-H-N), and trace element analyses were also performed and described earlier (Obelić et al. 2005; Horvatinčić et al. 2006a,b). Some of these results are presented in Table 1. For organic fraction analyses, sediment samples were treated with 1N HCl. The carbonate free residues were then soaked with water, centrifuged, dried, and combusted in a PerkinElmer 2400 Series II CHNS analyzer. Organic matter concentrations were calculated on a whole-sediment basis after adjusting for the carbonate content removed by the acid treatment. Mass C/N ratios of the residue material were calculated from the measured carbon and nitrogen concentrations.

RESULTS

Composition of Sediments

With the exception of core GR from Lake Gradinsko, the sediment cores were homogenous in color, showing neither distinct layers nor any visual indication of bioturbation. Core GR showed a sharp transition from light yellow to light gray at 15 cm depth.

The water content of the sediments shows a general decline with depth (Figure 2). All cores from the same location show similar water content profiles, indicating sediments were not disturbed during sampling. Cores from site K1 had a high content of water (ice) in the top 10 cm, and were only 27 cm long. In most cores, water content was higher in the upper ~15 cm, thus showing little compaction in the topmost layers. Below 15 cm, the sediment cores were more compact and the water fraction remained relatively constant (PR 61%, GR 41%, K1 51%, K2 75%, and KA 35%). Therefore, the (linear) sedimentation rate obtained for deeper layers can be compared with the sedimentation rates obtained earlier from 12-m-long cores in lakes Kozjak and Prošće (Srdoč et al. 1986a).

Sediment cores from different sites are distinguished by color, from light gray (K1, KA, GR) to dark gray (PR) and black (K2), indicating different contents of organic matter (Table 1). The highest content of organic matter is in core K2 (11.4–36.6%) and the lowest in cores GR and KA (1.1–5.6% and 1.9–3.4%, respectively) (Horvatinčić et al. 2006a,b). The C/N ratio in the sediments is a good indicator of organic carbon sources; for example, fresh organic matter from lake algae has atomic C/N values that are commonly between 4 and 10, whereas land plants create organic matter that usually has C/N ratios of 20 and greater (Meyers 1994). The C/N mass ratios (C/N mass ratio = C/N atomic × 0.86) in our sediment cores points to algae as the main source of autochthonous organic matter in all sediments, except those from site K2 where sediments are mainly of terrestrial origin (Table 1). Mineralogical analyses showed that the dominant inorganic component was calcite, with

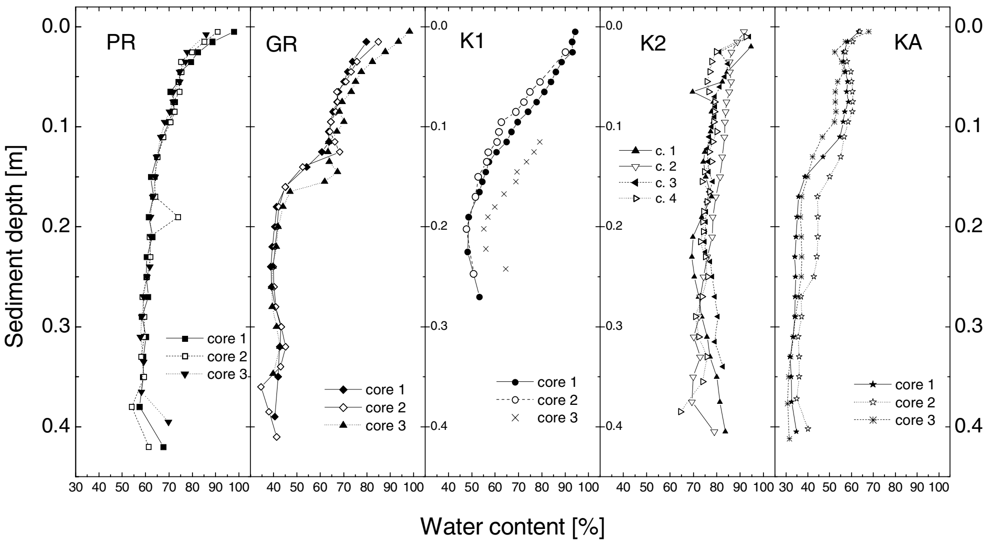

Figure 2 Water content of lake sediment cores

the exception of core K2 (Table 1). The rest was dolomite, quartz, and minor components such as aragonite, feldspars, and filosilicates (Horvatinčić et al. 2006a,b).

The concentration of dissolved oxygen (DO) in surface water at all sampling locations ranged between 5.8–16.0 mg/L (Horvatinčić et al. 2006a). The concentration of DO at the bottom of lakes Prošće (at 37 m water depth) and Kozjak (at 46 m water depth), measured in September 2004 during the period of stratification, was 3.7 mg/L and 6.7 mg/L, respectively. These concentrations of DO in the surface and deep water layers showed that water in the Plitvice Lakes is not anoxic. Lakes Kozjak and Prošće are oligotrophic and dimictic, with spring and autumn overturn, and the thermocline occurs in the summer at 10–15 m depth (Petrik 1958).

Isotopic Results

The results of ^{137}Cs, ^{214}Bi, ^{214}Pb, and ^{210}Pb in bulk sediments and δ^{13}C, δ^{18}O, and a^{14}C in the carbonate fraction of the sediments are presented in Figures 3–7. The cores from the lake centers are listed in a downstream direction (PR, GR, K1, KA), whereas Lake Kozjak core K2, taken at the lake boundary near the inflow of Rječica Brook, is discussed separately due to its different sedimentological situation. All 4 depth profile figures show the same structure and the same axis units in order to be directly comparable.

Lake Prošće - PR

Isotopic composition of the sediment from Lake Prošće (site PR) is shown in Figure 3. With more than 220 Bq/kg, ^{137}Cs in Lake Prošće sediment shows the highest values of all cores taken in the center of the lakes. Below 20 cm depth, all ^{137}Cs activities were at or below the detection limit. Supported ^{210}Pb is relatively constant throughout the core, and total ^{210}Pb shows a nearly exponential decrease. Results of sediment dating with ^{210}Pb and ^{137}Cs show remarkably good agreement with a mean value of 1.3 kg/(m^2 yr) for the CF model (Table 2). This ^{210}Pb model places 1986 at 8.5 cm depth (21.8 kg/m^2 mass depth) where the ^{137}Cs activity displays a well-resolved peak probably indicating fallout from the Chernobyl accident in May 1986. The ^{137}Cs activities below this depth are all

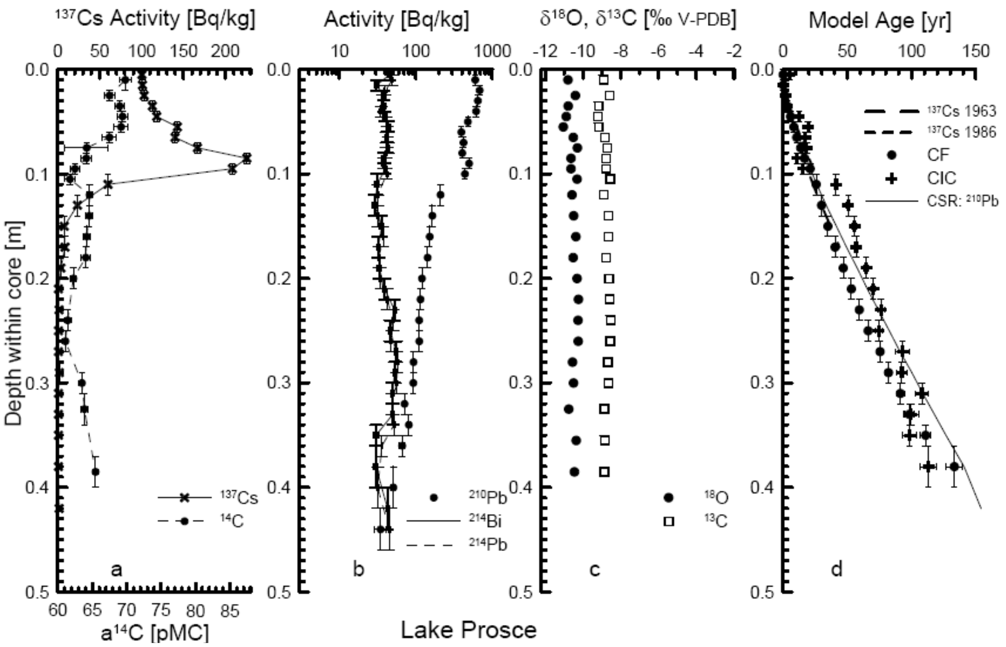

Figure 3 Isotopic composition of sediment in Lake Prošće, site PR. a) ^{137}Cs and ^{14}C profile, b) ^{214}Bi and ^{214}Pb (supported ^{210}Pb activity) and total ^{210}Pb profiles, c) δ^{18}O and δ^{13}C in carbonates, d) model ages derived assuming constant sedimentation rate (CSR) from ^{137}Cs (broken lines) and ^{210}Pb$_{\text{exc}}$ (solid line) and variable sedimentation rates from the CIC and CF models (crosses and circles, respectively).

measurable (around 8 Bq/kg) and can be attributed to bomb fallout. The onset of fallout in 1954 is within the numerical uncertainties of the CF model and in agreement with the deepest measured ^{137}Cs activity at 18–20 cm.

An increase in ^{14}C to higher than pre-bomb values occurs between 8 and 6 cm and is therefore approximately 12 cm shallower than the ^{137}Cs onset. With an increase from 65 pMC to nearly 70 pMC, the increase in a^{14}C is also much smaller than the roughly 2-fold increase observed in atmospheric ^{14}C (Levin and Kromer 1997). Vertical distribution of δ^{13}C shows slight fluctuations between –9.2 and –8.5‰; the mean δ^{13}C along the whole core is –8.8 ± 0.2‰. Fluctuations are somewhat more pronounced in the top 15 cm (±0.2‰) than in the lower layers (±0.1‰). δ^{18}O remains relatively constant throughout the profile (–10.5 ± 0.2‰), varying between –11.0 and –10.2‰.

Lake Gradinsko - GR

Isotopic composition of the sediment from Lake Gradinsko (site GR) is presented in Figure 4. The highest ^{137}Cs activity in this core is below 100 Bq/kg and thus much smaller than in Lake Prošće, but none of the samples measured from this core is below the detection limit for ^{137}Cs, the lowest activity being 2.1 Bq/kg. Both supported ^{210}Pb and ^{210}Pb$_{\text{exc}}$ show stronger variations with depth, which is reflected in a strong scatter of the resulting CIC ages. If the strong peak in ^{137}Cs at 6–7 cm depth and the smaller peak at 13–15 cm depth are interpreted as Chernobyl and bomb fallout, respectively, there is no agreement with the CF and CSR models for ^{210}Pb. The calculated mass accumulation rates are 1.2, 3.0, and 3.4 kg/(m^2 yr) for ^{137}Cs (Chernobyl, bomb fallout) and ^{210}Pb (CF), respectively (Table 2).

Table 2 Sedimentation rates determined by various radioactive isotopes, and mean δ^{13}C and δ^{18}O in sediment cores, compared with previous data, for the long sediment cores Prošće PR, Gradinsko GR, Kozjak K1, and Kaluđerovac KA. * : constant mass accumulation rate calculated from mass depth and Chernobyl fallout (May 1986, 17.5 yr before coring); ** : constant mass accumulation rate calculated from mass depth and deepest sample containing ^{137}Cs as start of ^{137}Cs fallout (1954). Row ^{210}Pb (CF) gives the mean value and standard deviation of computed sedimentation rates with the CF model.

	Prošće PR	Gradinsko GR	Kozjak K1	Kaluđerovac KA
Mass Accumulation Rates				
^{137}Cs [kg/(m^2 yr)]	1.3^{*} 1.4^{**}	1.2^{*} 3.0^{**}	0.9^{*}	1.8^{*} 5.9^{**}
^{210}Pb (CF) [kg/(m^2 yr)]	1.3 ± 0.4	3.4 ± 1.4	0.8 ± 0.1	2.6 ± 0.9
^{14}C long cores [kg/(m^2 yr)] (Srdoč et al. 1986a)	1.5		0.8 ± 1.0	
Mean Stable Isotopic Content				
δ^{13}C [‰ VPDB] present data	–8.8 ± 0.2	–6.7 ± 0.2 (0–15 cm) –8.6 ± 0.1 (15–40 cm)	–8.6 ± 0.2	–6.8 ± 0.2 (0–10 cm) –8.5 ± 0.2 (10–43 cm)
long cores (Srdoč et al. 1986a)	–8.9 ± 0.2		–8.6 ± 0.1	
top sediment (Srdoč et al. 1992)	–9.2 ± 0.2		–8.9 ± 0.1	
δ^{18}O (‰ VPDB) present data	–10.5 ± 0.2	–10.3 ± 0.2	–10.5 ± 0.2	–10.5 ± 0.2
long cores (Srdoč et al. 1986a)	–9.9 ± 0.3		–9.3 ± 0.2	

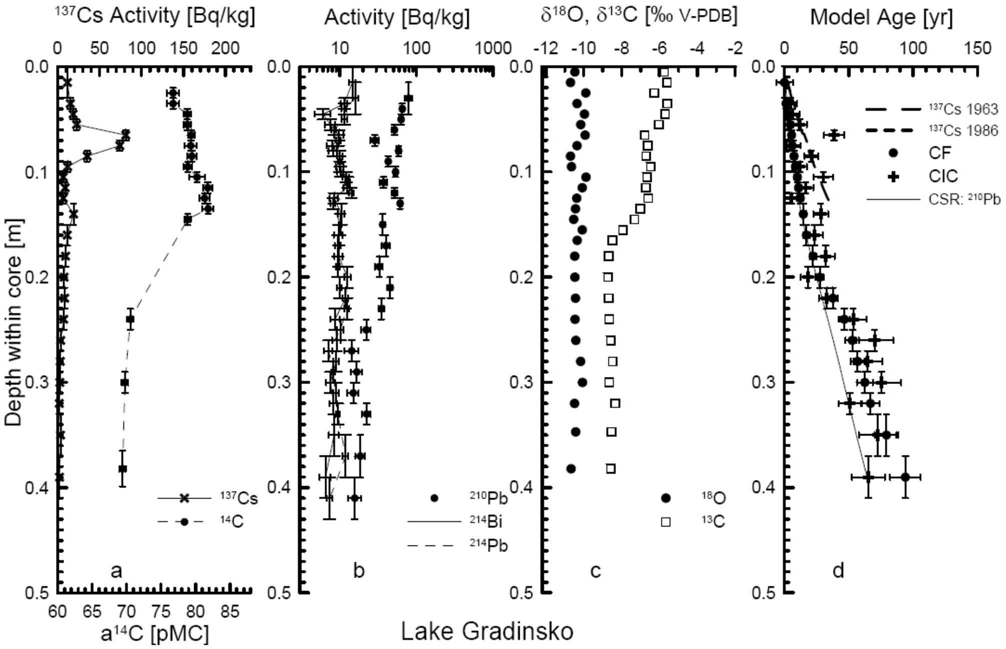

Figure 4 Isotopic composition of sediment in Lake Gradinsko, site GR. Explanation as in Figure 3.

δ^{13}C is relatively constant within the deeper layers (–8.6 ± 0.1‰, 16–40 cm). A sudden change occurs at 15 cm, and δ^{13}C increases and remains at about –6.6‰ between 12 and 6 cm. In the upper 6 cm, a change toward even more positive values of –5.6‰ occurs. δ^{18}O remains relatively constant throughout the profile with a mean value of –10.3 ± 0.2‰.

The change in $\delta^{13}C$ coincides with the change in $a^{14}C$ and with an increase in water content. A peak in ^{14}C activity of 81.8 pMC, which is ~15 pMC higher than the pre-bomb ^{14}C activity of the sediment, is observed between 11 and 14 cm.

Lake Kozjak - K1

Figure 5 shows the isotopic composition of sediment from Lake Kozjak, site K1. The top 10 cm of core 3 were combined as a single radiocarbon and stable isotope sample. Since the gamma spectrometric analysis requires less material, the profile was analyzed with higher resolution, but shows nearly constant activities for ^{137}Cs, supported ^{210}Pb, and total ^{210}Pb. No peaks are discernible in the ^{137}Cs depth profile, and similar to the findings in Lake Prošće, all samples from more than 15 cm depth are below the detection limit for ^{137}Cs. We therefore interpreted only the onset of ^{137}Cs at 15 cm depth as 1954. Due to the high water content, the 0–10 cm layer contained only 17.5 kg/m^2 dry mass (the other cores discussed below have 2–3 times higher values at this depth). Nevertheless, the plot of $^{210}Pb_{exc}$ against mass depth can be interpreted with the different age models and their agreement is remarkable. The shape of the curves in Figure 5d illustrates the effect of compaction and necessity to fit age versus mass depth and not depth. Mass accumulation rates are 0.9 kg/(m^2 yr) and 0.8 kg/(m^2 yr) for ^{137}Cs and ^{210}Pb, respectively (Table 2).

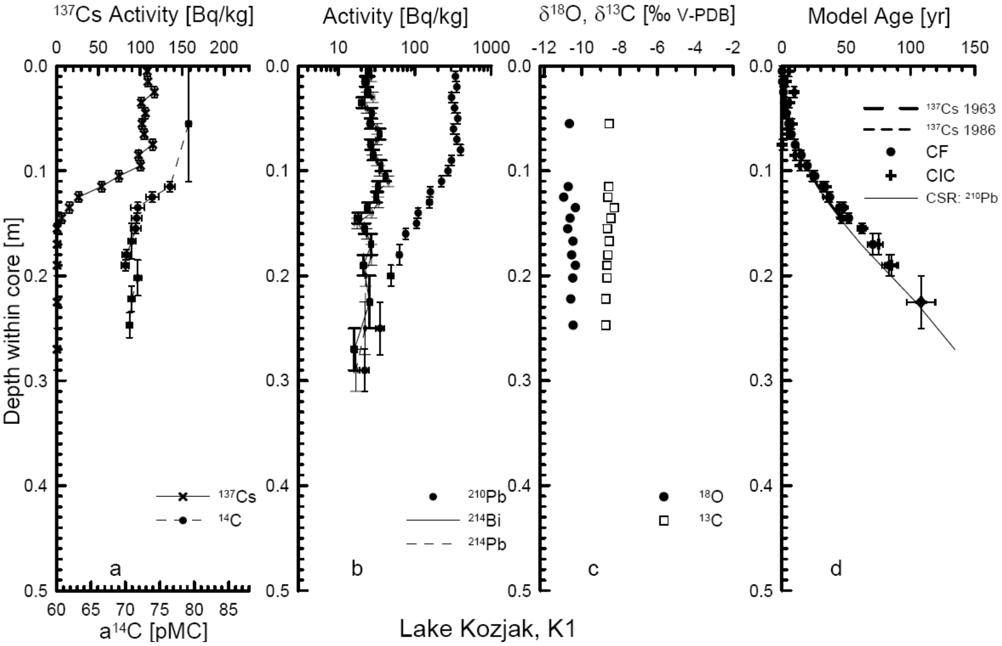

Figure 5 Isotopic composition of sediment in Lake Kozjak, site K1. Explanation as in Figure 3.

There is no significant change in $\delta^{13}C$ along the sediment profile. The mean $\delta^{13}C$ throughout the core is –8.6 ± 0.2‰. $\delta^{18}O$ remains constant throughout the depth profile, varying between –11.0 and –10.3‰ with a mean value –10.5 ± 0.2‰.

The ^{14}C activity of sediment cores from K1 increases at approximately the same depth interval where ^{137}Cs increases, from pre-bomb values around 71 pMC to nearly 80 pMC in the topmost sample.

Lake Kozjak - K2

In Figure 6, we present the isotopic composition of the sediment from Lake Kozjak, site K2, which is close to the Rječica Brook mouth and characterized by an extensive growth of macrophytes. ^{137}Cs shows very high values in this core over a very large depth range, reflected in the highest inventory of nearly 8 Bq/m^2. Activity never falls below the detection limit, with an 18 Bq/kg increase in the deepest sample as compared to the second deepest sample. The ^{210}Pb profile precludes dating with any model.

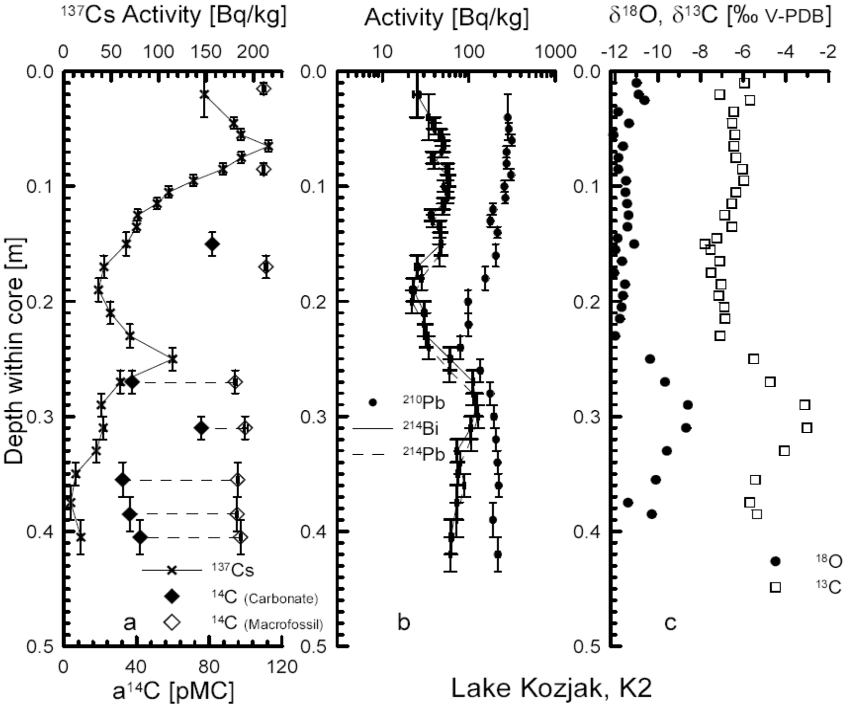

Figure 6 Isotopic composition of sediment in Lake Kozjak, site K2. a) ^{137}Cs profile and a^{14}C of both the carbonate and organic sediment fractions (full and open diamonds, respectively), b) ^{214}Bi and ^{214}Pb (the supported activity) and total ^{210}Pb profiles, c) δ^{18}O and δ^{13}C in carbonates.

δ^{13}C of the carbonate fraction at K2 is more positive than in all other lake sediments (mean –6.6‰ in the top 24 cm, with variations between –7.8 and –5.7‰). δ^{18}O shows much greater variations. In the upper layers, δ^{18}O is much lower (–11.6 ± 0.2‰) than in any other lake sediment. Especially interesting are simultaneous changes in both δ^{13}C and δ^{18}O between 25 cm and 40 cm depth that track changes in the supported ^{210}Pb depth profile. In these layers, the mean δ^{13}C is –4.5 ± 1.0‰ and the peak is –3.0‰.

The sediment from site K2 contains a high percentage of organic material (11–37%, Table 1), which is why we measured the ^{14}C activity in both organic and carbonate fractions. ^{14}C activity of the organic fraction in the top 20 cm is about 110 pMC, indicating sedimentation in the period after 1963. In the layers 25–40 cm, ^{14}C activity of organic material is about 95 pMC, indicating sediments older than AD 1950. However, a^{14}C of the carbonate fraction from 25–40 cm is between 30 and 40 pMC (and the single layer of core 2 gives 75 pMC).

Lake Kaluđerovac - KA

The isotopic composition of the sediment from Lake Kaluđerovac (site KA) is shown in Figure 7. Similar to Lake Gradinsko, this second small lake shows a ^{137}Cs peak around 100 Bq/kg, a second weaker peak around 25 Bq/kg, and detectable ^{137}Cs of 3.5 Bq/kg in samples as deep as 32–34 cm within the core. Only the 3 deepest samples have values near or at the detection limit. Both the supported and total ^{210}Pb profiles show some scatter, but the profile shows a radioactive decrease in ^{210}Pb$_{exc}$. Agreement between the different age models is reasonable when interpreting the shallow ^{137}Cs peak as Chernobyl fallout. The deepest measurable ^{137}Cs is in clear contradiction to the other age models since it occurs in a depth that ^{210}Pb dating attributes to well before 1954, which is the first possible occurrence of ^{137}C in sediments. The mass accumulation rates are 1.8, 5.9, and 2.6 kg/(m^2 yr) for ^{137}Cs (Chernobyl, bomb fallout) and ^{210}Pb, respectively.

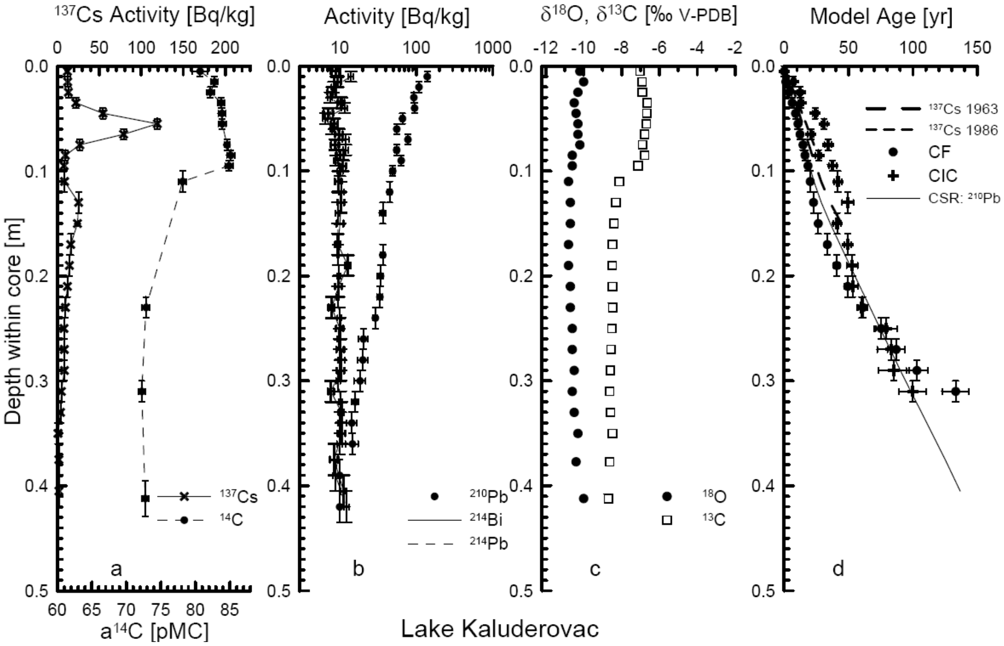

Figure 7 Isotopic composition of sediment in Lake Kaluđerovac, site KA. Explanation as in Figure 3.

As in Lake Gradinsko, δ^{13}C in small Lake Kaluđerovac is rather constant in the deeper layers, i.e. below 10 cm (–8.5 ± 0.2‰). A sudden change occurs at 10 cm, a depth that also shows an increase in ^{14}C and an increase in water content. In the upper 10 cm, δ^{13}C is relatively constant (mean –6.8 ± 0.2‰). δ^{18}O is also relatively constant throughout the depth profile (–10.5 ± 0.2‰). The highest a^{14}C value of 85.1 pMC (at 8–9 cm depth) is ~14 pMC higher than the pre-bomb a^{14}C of sediment.

DISCUSSION

Sediment Chronology

The 3 independent age-dating methods (^{210}Pb, ^{137}Cs, and ^{14}C) are not in complete agreement. Thus, there is a need to decide which method is most reliable. Some processes influence all age-dating methods in the same manner and are discussed first. Among the processes that can cause discrepancies between different methods, like event markers (^{137}Cs, ^{14}C) and integral or slope evaluating methods (^{210}Pb), the most prominent are loss of sediment during coring, sediment disturbance (profile smearing due to wall friction) during coring, and bioturbation.

Loss of sediment at the sediment-water interface would shift ages derived from identification of Chernobyl and bomb peaks relative to the age models of ^{210}Pb. In our case, these can be excluded due to the very careful and controlled coring by the scuba divers and because all frozen cores showed an undisturbed sediment-water interface.

A simple evaluation also excludes major sediment disturbances during the coring process. If the wall friction had shifted sediment particles to greater depth, young sediment would have been transported into layers originally containing only old sediments. All our cores had maximum ^{137}Cs activities of at least ~100 Bq/kg, some even >200 Bq/kg. On the other hand, the deepest layers of cores PR, K1, and KA had ^{137}Cs activities below the detection limit of 0.7 Bq/kg. In PR and K1, which were the cores obtained from the greatest water depth and therefore the most difficult to take, this analysis shows that during coring <1% of sediment was moved downward by more than 10 cm. Neither results for ^{210}Pb nor ^{14}C would have been influenced in a measurable way by such small sediment shifts since the sensitivity concerning young sediment material in old is much smaller for these methods than for ^{137}Cs.

Any downward movement of ^{137}Cs in the dissolved form seems highly improbable since typical activity concentrations of ^{137}Cs in water in similar systems are far below our detection limit (Harlacher and Voigt 1994). Besides, porewater flow in the sediments most probably is directed upward due to sediment compaction, not downward.

Bioturbation is more difficult to rule out. Even when strong, the ^{210}Pb curve may look like an undisturbed profile (Suckow et al. 2001), and the problem is only discernible in the sediment if different sediment colors are visibly intermixed. Bioturbation plays a minor role in our cores, in that sharp boundaries are preserved in the record, like the sharp color transition in Lake Gradinsko and the steep ^{137}Cs gradients in the vicinity of the peaks. We cannot, however, rule out that the ^{137}Cs activities measured in sediment of the small and shallow lakes GR and KA below 25 cm are caused by bioturbation. From the same arguments as above for the coring artifacts, we may conclude that even in case that small ^{137}Cs activities found at depths below 20 cm in lakes Gradinsko and Kaluđerovac are attributed to bioturbation, the effect on the ^{210}Pb and ^{14}C depth profiles would be below the measurement precision. ^{210}Pb dating would still be reliable because too little sediment mass is moved to influence these nuclides beyond measurement precision.

When evaluating the response of authigenic carbonate lake sediments to the anthropogenic ^{14}C bomb peak, one has to take into account the dilution of the atmospheric signal by geochemical processes in the groundwater that feeds the lake, and in the organic and dissolved inorganic carbon (DIC) pools. This dilution means that the expected magnitude of the signal is *a priori* unknown. Furthermore, the signal can be confounded by changes in the relative sizes of the different carbon pools or their exchange fluxes with time. This, even in the absence of an anthropogenic signal, can cause variations in the ^{14}C content of freshly precipitated sediments (Olsson 1979; Olsson and Vasari 1995). In the Plitvice Lakes area, such changes are expected due to possible eutrophication of the lakes, which was one of the motivations for the present study. Another problem is that most of the carbon in DIC is derived from the relatively slow process of biodegradation of topsoil detritus in spring recharge areas, and ^{14}C spends some time in the different reservoirs before it is precipitated as lake carbonate (Geyh et al. 1971). These processes can cause a considerable time lag of a decade or more. Although this time lag is negligible for most ^{14}C dating applications of lake sediments, in the present study, where the whole core history encompasses not much more than a century, it might be considerable. Therefore, ^{14}C is not used as an independent dating tool here, but rather as an indicator of geochemical changes and their timescales.

Whereas some authors report that ^{137}Cs is soluble and thus mobile in the water phase under certain geochemical conditions, especially under higher ionic strengths, no such mobility is known for ^{210}Pb, which is highly particle-reactive and tightly bound to sediment (Crusius and Anderson 1991). Together with the higher sensitivity of ^{137}Cs concerning sediment disturbance discussed above, these facts clearly argue for ^{210}Pb to derive the sediment chronology. Nevertheless, a ^{210}Pb model must be chosen. The constant initial concentration (CIC) model is based on the assumption that the initial concentration of $^{210}Pb_{exc}$ in the sediment was constant throughout the period when measurable $^{210}Pb_{exc}$ was deposited in the sediment record. This can only be true if the $^{210}Pb_{exc}$ decreases in a monotonic manner. Any downcore increases in $^{210}Pb_{exc}$ such as those observed in cores PR and KA argue against this model. The constant sedimentation rate (CSR) model assumes that both the initial concentration and the sedimentation rate measured as dry mass supply to a unit area per time remained constant (the latter being an implicit assumption in ^{137}Cs dating also). Thus, the CSR model can be excluded for the same reasons as the CIC, with the additional argument that constant sedimentation rates are not very probable in our lakes. The most reliable model is therefore the constant flux (CF) model, because it can accommodate changes in sediment accumulation rate. It assumes that the flux of $^{210}Pb_{exc}$ to the sediment remained constant with time and any deviations from the exponential decrease of $^{210}Pb_{exc}$ with mass depth are explained as variations in the "dilution" of this flux with ($^{210}Pb_{exc}$-free) sediment. The model can only be applied if the entire unsupported ^{210}Pb profile was collected, i.e. down to the supported/unsupported boundary, since the average flux of $^{210}Pb_{exc}$ is computed from the integral of $^{210}Pb_{exc}$ with depth. For cores PR and K1, all 3 models—CF, CSR (^{210}Pb), CSR (^{137}Cs)—agree within their uncertainty, and lead to the same interpretation.

Record of Anthropogenic Fallout Nuclides

The use of the CF ^{210}Pb age as the most reliable age leads to a history of "fallout nuclides" (^{137}Cs and ^{14}C) as depicted in Figure 8. To better demonstrate the detection limit (DL), the ^{137}Cs activities are plotted on a log scale in these figures. An increase in ^{14}C activity in all sediment profiles (PR, GR, K1, KA) is observed in a downstream direction corresponding to the earlier observed increase in a^{14}C of DIC (Srdoč et al. 1986b). This increase of ^{14}C along the water flow of the Plitvice Lakes system is a result of CO_2 degassing and carbon isotope exchange between atmospheric CO_2 and DIC in water, demonstrated also by the downstream increase of $\delta^{13}C_{DIC}$ (Figure 9).

The uppermost lake, Lake Prošće (PR), which is seated at the most upstream site within the National Park (Figure 1), shows a nearly undisturbed record of ^{137}Cs fallout (Figures 3 and 8). According to the CF-^{210}Pb dating, ^{137}Cs values are below or at the detection limit before 1955; the first intermediate maximum occurs 1963 as expected from bomb fallout; and the maximum activity is in the mid-1980s, coincident with the Chernobyl accident. There is a decrease in ^{137}Cs below the peak attributed to Chernobyl, but there is no zero activity recorded below that, although fallout was nearly zero between 1970 and 1986. This can be due to bioturbation of the layers with Chernobyl fallout, but can also be due to a residence time of some years for bomb ^{137}Cs in the watershed before final deposition in the sediment. No variations in the δ^{13}C in sediments of this lake indicate unaltered geochemical conditions of sedimentation. Therefore, we conclude that the increase in ^{14}C activity reflects the global contamination of atmospheric CO_2 by the thermonuclear bomb tests in the last century when the atmospheric ^{14}C activity almost doubled from 100 pMC to nearly 200 pMC in 1963 (Levin and Kromer 1997). In the sediments of Lake Prošće, this increase in a^{14}C corresponds to an increase of

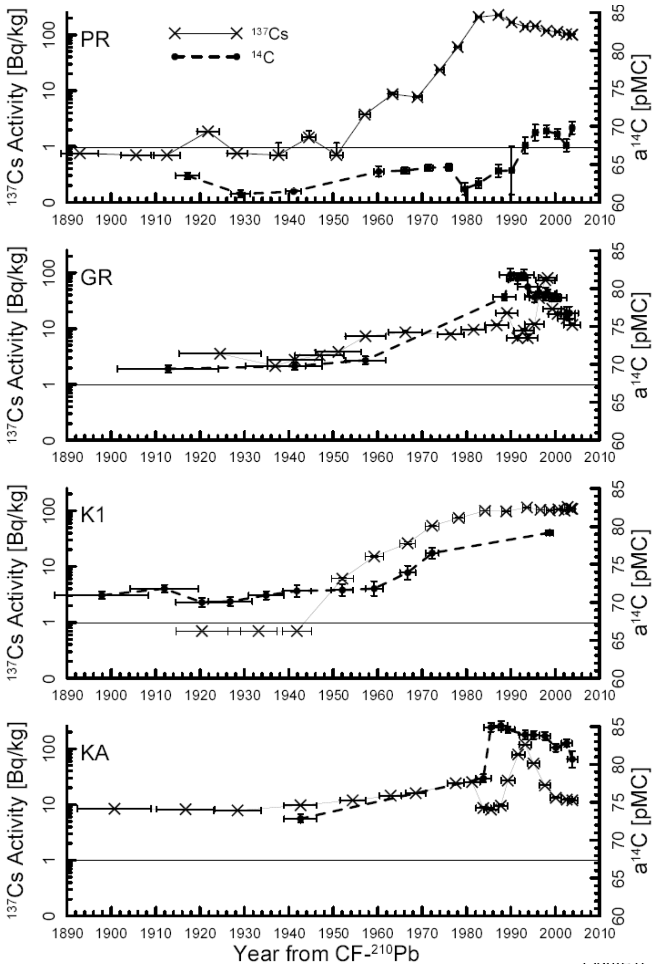

Figure 8 Chronology of the fallout nuclide ^{137}Cs and of a^{14}C in the cores from central lake positions. Cores are presented in a downstream direction.

<10 pMC compared to the pre-bomb a^{14}C in the sediment. This demonstrates how global atmospheric ^{14}C contamination is significantly damped because of various geochemical processes prior to sediment deposition (Genty et al. 2001; Krajcar Bronić et al. 1992). Furthermore, the increase in ^{14}C occurs several decades later than the increase in ^{137}Cs. A similar delayed and damped response of ^{14}C activity was observed in Lake Kozjak sediment (Srdoč et al. 1992) as well as in speleothems (Genty et al. 1998; Genty and Massault 1999). If the bomb-related ^{14}C increase is damped so drastically by the carbonate chemistry of lakes and watershed, this implies that other and weaker effects (e.g. the Suess effect) are simply not detectable in the record and therefore are not discussed here.

For the largest and deepest lake, Lake Kozjak (K1), interpretation of the sediment record is limited (Figures 5 and 8). It has the lowest sedimentation rate, 0.8–0.9 kg/(m^2 yr) (Table 2). In the topmost, cone-shaped surface layer, the depth resolution of both the ^{137}Cs and ^{14}C is poor and details cannot be interpreted. Nevertheless, the onset of ^{137}Cs corresponds to the expected year (1954). Again, ^{14}C increases nearly 2 decades later than ^{137}Cs, from 71 to 79 pMC. Since no variations in the δ^{13}C depth profile occur, we interpret this increase as a delayed atmospheric bomb signal.

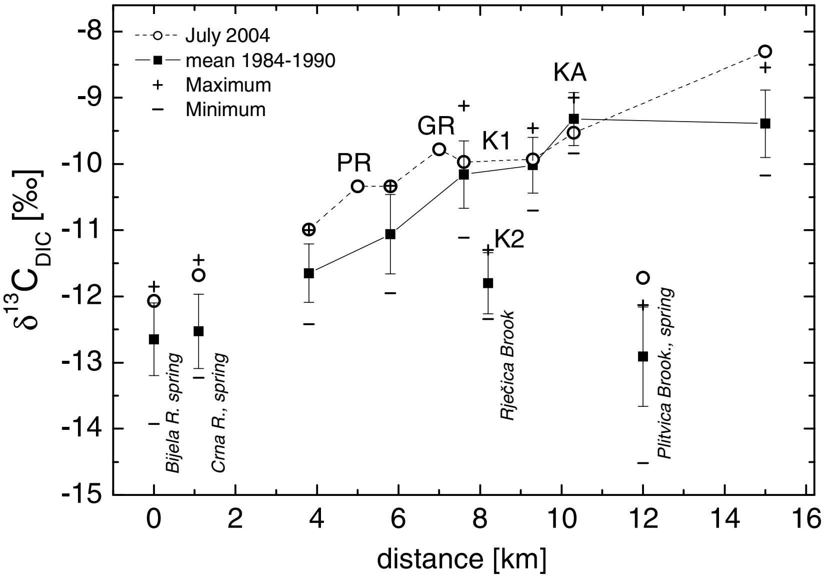

Figure 9 δ^{13}C of DIC along the water course of the Plitvice Lakes system. Comparison of the long-term data (mean values with ±1 σ, as well as the extreme values for the period 1984–1990) and data from sampling in July 2004. Karst springs and Rječica Brook are marked as well as the positions of the sediment sampling.

Interpretation of the fallout record in the small lakes is more difficult (Figures 4, 7, and 8 for GR and KA). These lakes are shallow and small enough that thermal stratification can be excluded throughout the year, whereas a well-defined thermocline was observed in lakes Prošće and Kozjak. The sedimentation rate is higher in the small lakes than in the big lakes (Table 2) and bioturbation might play a role here as discussed above. Topmost variations in ^{137}Cs show a very similar shape in both cores, and within the dating precision, they occur simultaneously in both lakes. The step-form change in ^{14}C and ^{13}C occurs approximately at the same time, together with sudden changes in water content, and in the case of Gradinsko also with sediment color. Taken together, the results suggest that the increase in a^{14}C by >12 pMC in these cores is not only related to the change in ^{14}C in atmospheric CO$_2$, but is in part due to a change in geochemical conditions of the organic and inorganic carbon pools in these lakes in the last 2 decades. The exact nature and origin of this change is unknown.

Stable Isotope Records

The chemical composition of sediments (see Table 1) differs among the lakes. In the small lakes Gradinsko (GR) and Kaluđerovac (KA), the concentration of calcite is higher (90–99%) than in the big lakes Prošće (PR) and Kozjak (K1) (70–85%), and vice versa concerning the content of organic matter. The C/N mass ratio (8.3–14.0) in sediments of the small lakes (Horvatinčić et al. 2006a) indicates phytoplankton as the main source of autochthonous organic matter in the sediment.

The stable carbon isotope composition of calcareous lake sediments is a mixture of authigenic carbonate precipitated from lake DIC and of terrigenous carbonates originating from catchment areas. We have an extensive record of δ^{13}C of DIC in waters of the Plitvice Lakes system, from the karst springs over the lakes downstream to the Korana River below the lakes for 1984–1990 (Srdoč et al. 1986b; Horvatinčić et al. 2003). In this period, DIC samples were taken at sampling points along the water course and in different seasons. However, seasonal fluctuations were not observed. Figure 9 summarizes our previous measurements (mean $\delta^{13}C_{DIC}$ values with 1-σ errors, as well as extreme values) and measurements in samples collected in July 2004. An increase in $\delta^{13}C_{DIC}$ along the water course ($\delta^{13}C_{DIC}$ = –10.5‰ in Prošće, –10.0‰ in Gradinsko, –9.8‰ in Kaluđerovac) is observed, which was interpreted earlier as the result of CO_2 degassing and carbon isotope exchange between atmospheric CO_2 and DIC in water and as the result of photosynthetic activity (Srdoč et al. 1986b; Horvatinčić et al. 2003). Although the values from 2004 fall within the range of earlier/long-term data, all of them are higher (more positive) than the mean long-term values.

We compared the $\delta^{13}C$ of lake sediment carbonate with that of DIC in water close to the sediment sampling site. For all sites (the whole profiles for PR and K1, and deeper layers below 15 cm for the smaller lakes GR and KA, except K2), the enrichment in $\delta^{13}C$ of lake sediment compared to that of DIC is between 1.1 and 1.6‰. We measured lake water variables monthly: pH of the lake waters in the area of carbonate sediment precipitation is between 8.2 and 8.5 and does not indicate a seasonal variation (Srdoč et al. 1985). Lake water temperature varies seasonally between 0 °C in winter and >20 °C in summer. The equilibrium fractionation ε between DIC and precipitated calcite is ~2‰, in the range of pH and temperature described above (Wigley et al. 1978, data from Deines et al. 1974). We may conclude that in the Plitvice Lakes, calcite precipitates under nearly equilibrium conditions. The $\delta^{13}C$ of the carbonate fraction of lake sediments also shows a slight downstream increase: $\delta^{13}C$ = –8.8‰ in PR, –8.6‰ in GR and K1, and –8.5‰ in KA, which was expected from the increase in $\delta^{13}C_{DIC}$ values.

The $\delta^{13}C$ values of the sediment carbonates are constant within analytical precision along the cores from the big lakes Prošće (–8.8 ± 0.2‰) and Kozjak (–8.6 ± 0.2‰) (Table 2). These values agree well with previous $\delta^{13}C$ measurements of 12-m-long sediment cores from the same lakes (Srdoč et al. 1986a), as well as with $\delta^{13}C$ of the top 30 cm of sediments collected in 1990 (Srdoč et al. 1992). In contrast, a significant change in $\delta^{13}C$ towards 1–3‰ more positive values in the upper sediment layers is observed in the small lakes Gradinsko (–6.7 ± 0.2‰, top 15 cm) and Kaluđerovac (–6.8 ± 0.2‰, top 10 cm). This change coincides with the increase in $a^{14}C$ and, according to ^{210}Pb dating, it occurred in the last 2 decades (Figure 8).

The increase in $\delta^{13}C$ in the surface layers could be the consequence of increased primary productivity in the lake waters. Primary productivity and calcite precipitation are tightly coupled because photosynthesis draws down dissolved CO_2 and increases calcite saturation. This process is referred to as "biologically induced" calcite precipitation (Hodell et al. 1998; Neumann et al. 2002). $\delta^{13}C$ of biologically induced calcite reflects the $^{13}C_{DIC}$ in the epilimnion. In turn, the carbon isotope composition of epilimnic DIC is controlled by primary productivity due to the preferential removal of $^{12}CO_2$ from the DIC pool (McKenzie 1985) and exchange of CO_2 between the lake and atmosphere (Lee et al. 1987; Schelske and Hodell 1991; Hammarlund et al. 1997). In previous investigations, it was shown that most of the carbonates precipitated in the Plitvice Lakes in the form of tufa and lake sediments are biologically induced calcite precipitation in the presence of diatoms and cyanobacteria (Kempe and Emeis 1985; Emeis et al. 1987; Chafetz et al. 1994).

An increase in water temperature could enhance primary productivity in the lake waters, increasing $\delta^{13}C_{DIC}$ and thus that of the carbonate sediment (Hodell et al. 1998 and references therein). We compared mean annual surface water temperatures in the Plitvice Lakes system for 1980–1985 (Srdoč et al. 1985) with those of the period 2002–2006, and found no change in mean temperatures observable in the karst springs (Crna Rijeka, Bijela Rijeka) and in the upper lakes including Lake Prošće. Downstream, however, recent mean annual temperatures of surface lake waters were 0.5 to 2 °C higher. This increase in lake water temperature reflects the increase in mean annual air temperature in the region—an increase of ~2 °C of mean annual air temperature in Zagreb has been observed between 1980 and 2000 (average slope 0.1 °C/yr) and 1 °C at Plitvice between 1986 and 2006 (average slope 0.05 °C/yr). This suggests that small, shallow lakes such as Gradinsko and Kaluđerovac, with maximum water depths of 10 m and 13 m, respectively, respond quickly to temperature rises that can increase the primary productivity. This in turn can cause enhanced biologically induced calcite precipitation, which is recorded in sediments as an increase in δ^{13}C and a^{14}C. This is also supported by higher $\delta^{13}C_{DIC}$ in lake waters in 2004 compared with values from the period 15–20 yr ago (1984–1990) (Figure 9).

These changes in primary productivity might also have occurred in the big lakes Prošće and Kozjak, with maximum water depths of 37 m and 46 m, respectively. They have a well-defined thermocline between 10–15 m depth (measured in September 2004), which inhibits mixing of water layers during summer. Variations in δ^{13}C of the carbonate sediment in lakes Prošće and Kozjak (K1) are not observable, suggesting that they either respond more slowly and/or with a much smaller signal to changes caused by primary productivity. However, a substantial increase was recorded in diatom frustules in the upper 5 cm of the sediment collected in 1989 in Lake Kozjak (Srdoč et al. 1992), which can also be indicator of an increase in primary productivity.

The relation between δ^{13}C and δ^{18}O in the carbonate fraction of all sediment cores is shown in Figure 10. Three groups can be distinguished: the first consists of sediments from large lakes Prošće and Kozjak (the whole profiles), and from the deeper layers (mostly 15–45 cm) of small lakes Gradinsko and Kaluđerovac. δ^{13}C ranges from –9.4 to –8.2‰ and δ^{18}O from –11.2 to –10.0‰. These values are in agreement with the previous measurements of the isotopic composition of lake sediments from the Plitvice Lakes (Table 2) (Srdoč et al. 1986a; Horvatinčić et al. 2003) and represent authigenic carbonate from DIC in water under equilibrium conditions. The second group is formed from the upper layers of lakes Gradinsko and Kaluđerovac, where δ^{13}C increased toward –5.5‰ and –6.5‰, respectively, while δ^{18}O remained constant. These values can be explained as the consequence of increased bioactivity in the lake water, i.e. of enhanced biologically induced calcite precipitation, resulting in higher sedimentation rates, more positive δ^{13}C values, and higher a^{14}C.

Stable isotope values of the carbonate fraction of core K2 are the most variable and form group 3 in Figure 10. Since site K2 is situated near the shore at the confluence of Rječica Brook to Lake Kozjak whereas all other cores were taken from the lake centers, K2 is not directly comparable with the other sampling sites. Sediments of K2 show a high concentration of organic material and higher C/N mass ratios (13.0–16.8), indicating mainly organic material of terrestrial origin (Table 1), and a very high sedimentation rate. δ^{18}O in the upper layers of K2 (3a in Figure 10) is much lower than δ^{18}O in any other lake. δ^{13}C values are comparable to δ^{13}C of upper layers in the 2 smaller lakes (group 2). The simultaneous changes in both δ^{13}C and δ^{18}O below 25 cm (3b in Figure 10) can be described by a linear correlation $\delta^{13}C = (1.2 \pm 0.1) \times \delta^{18}O + (7 \pm 1)$, $r = 0.98$, $n = 8$, $P < 0.0001$, which points to a mixing of 2 carbonate sources of different stable isotopic composition: authigenic carbonates precipitated *in situ* and eroded mineral carbonate of terrestrial origin. Since the δ^{13}C of DIC in Rječica Brook is on average –11.8‰ (Figure 9), the carbonate precipitated from Rječica DIC under equilibrium conditions would have a δ^{13}C value of –10.3‰. A simple mixing calculation with mineral carbonate (δ^{13}C of 0‰) would indicate 65% of carbonate in the sediment is authigenic. A similar mixing calculation using a^{14}C of DIC (70–75 pMC) and a^{14}C of eroded material (0 pMC) indicates ~55% of carbonate is authigenic, which is in reasonable agreement with the δ^{13}C results.

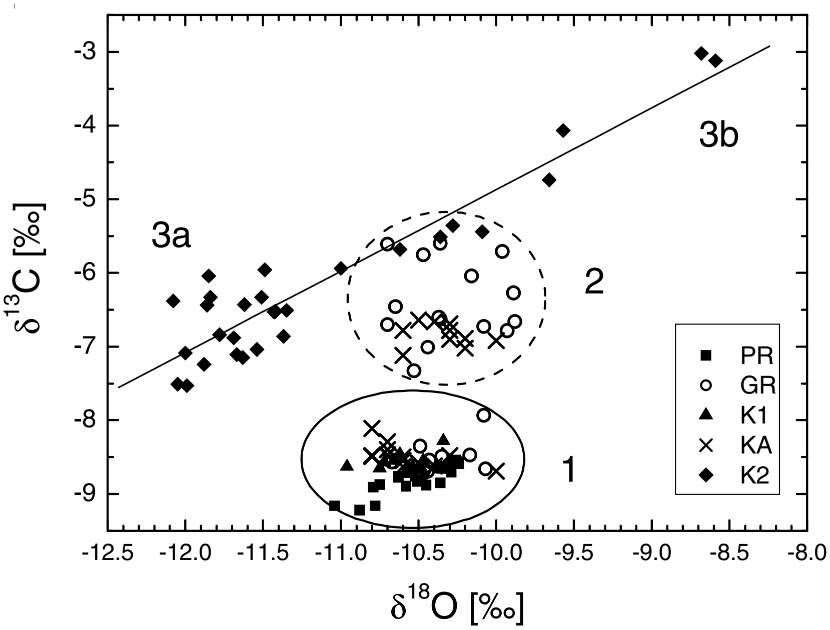

Figure 10 Relation between $\delta^{13}C$ and $\delta^{18}O$ in the carbonate fraction of sediment cores PR, GR, K1, KA, and K2. Group 1: PR + K1 all layers, GR + KA lower layers; Group 2: GR + KA upper layers; Group 3: K2, 3a – K2 upper layers, 3b – K2 lower layers.

CONCLUSIONS

We measured the isotopic composition of sediment from 5 cores, collected in 4 lakes of the Plitvice Lakes system in a karst area of Croatia, and dated them using ^{210}Pb and ^{137}Cs. The isotope values $\delta^{13}C$, $\delta^{18}O$, and $a^{14}C$ were determined in the carbonate fraction of all sediment cores. Additionally, $a^{14}C$ was measured in the organic fraction of the sediment from 1 near-shore site (K2). Sedimentation rates were higher in the small lakes than in the big lakes. Only the large lakes showed good agreement between the ^{210}Pb and ^{137}Cs dating methods.

In all cores, stratigraphic variations in ^{14}C activity were observed and interpreted as a delayed and damped response to bomb-produced ^{14}C in the atmosphere. For the small lakes, the increase of $\delta^{13}C$ in the last 2 decades and at least part of the increase of $a^{14}C$ is probably due to an increase in primary productivity, which enhanced biologically induced calcite precipitation with accompanying changes in the carbon isotopic composition of carbonate sediments. A steady downstream increase in both the ^{14}C activity and $\delta^{13}C$ of the carbonate fraction of the sediment was observed, corresponding to an increase in $a^{14}C_{DIC}$ and $\delta^{13}C_{DIC}$ in the water. This is explained as a result of CO_2 degassing and carbon isotope exchange between atmospheric CO_2 and DIC in water and photosynthetic activity.

One core from a different sedimentological situation at the shore of Lake Kozjak near the confluence of Rječica Brook (K2) showed a very high but unquantifiable sedimentation rate. According to mixing calculations using $\delta^{13}C$ and $\delta^{18}O$, this is the result of autochthonous carbonates and transported allochthonous carbonate minerals and organic material from Rječica Brook to the core site.

This comprehensive isotopic study of lake sediments formed in several karst lakes during the last ~100 yr revealed that the sediments reflect global changes with anthropogenic influence by an increase of atmospheric ^{14}C, ^{137}Cs fallout, and possible global warming. Some changes that are more expressed in the small lakes probably are the result of geochemical and biological processes in the Plitvice Lakes system, and are influenced by changes in the local environment. To completely understand the causes of these changes, further geochemical and biological investigations using different methods are necessary.

It has been shown that small lakes have a faster response to environmental change at the local scale, while global ^{14}C contamination has been reflected in the whole system.

ACKNOWLEDGMENTS

This work was funded by the Project 098-0982709-2741, Ministry of Science, Education and Sport of the Republic of Croatia and by the EU project ICA2-CT-2002-10009 ANTHROPOL.PROT.

REFERENCES

Andrews JE, Brasier AT. 2005. Seasonal records of climatic change in annually laminated tufas: short review and future prospects. *Journal of Quaternary Science* 20(5):411–21.

Andrews JE, Riding R, Dennis PF. 1997. The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. *Palaeogeography, Palaeoclimatology, Palaeoecology* 129(1–2):171–89.

Appleby PG, Oldfield F. 1992. Application of ^{210}Pb to sedimentation studies. In: Ivanovich M, Harmon RS, editors. *Uranium Series Disequilibrium. Applications to Earth, Marine and Environmental Sciences*. Oxford: Clarendon Press. p 731–78.

Brenner M, Whitmore TJ, Curtis JH, Hoddel DA, Schelske CL. 1999. Stable isotope (δ^{13}C and δ^{15}N) signatures of sedimented organic matter as indicators of historic lake trophic state. *Journal of Paleolimnology* 22(2):205–21.

Brenner M, Schelske CL, Keenan LW. 2001. Historical rates of sediment and nutrient accumulation in marshes of the Upper St. Johns River Basin, Florida, USA. *Journal of Paleolimnology* 26(3):241–57.

Brenner M, Hodell DA, Leyden BW, Curtis JH, Kenney WF, Gu B, Newman JM. 2006. Mechanisms for organic matter and phosphorus burial in sediments of a shallow, subtropical, macrophyte-dominated lake. *Journal of Paleolimnology* 35(1):129–48.

Chafetz HS, Lawrence JR. 1994. Stable isotopic variability within modern travertines. *Géographie Physique et Quaternaire* 48(3):257–73.

Chafetz HS, Srdoč D, Horvatinčić N. 1994. Early diagenesis of Plitvice Lakes waterfall and barrier travertine deposits. *Géographie Physique et Quaternaire* 48(3): 247–55.

Crusius J, Anderson RF. 1991. Immobility of ^{210}Pb in Black Sea sediments. *Geochimica et Cosmochimica Acta* 55(1):327–33.

Deines P, Langmuir D, Harmon RS. 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochimica et Cosmochimica Acta* 38(7):1147–64.

Emeis K-C, Richnow H-H, Kempe S. 1987. Travertine formation in Plitvice National Park, Yugoslavia: chemical versus biological control. *Sedimentology* 34(4):595–609.

Genty D, Massault M. 1999. Carbon transfer dynamics from bomb ^{14}C and δ^{13}C time series of a laminated stalagmite from SW France – modelling and comparison with other stalagmite records. *Geochimica et Cosmochimica Acta* 63(10):1537–48.

Genty D, Vokal B, Obelić B, Massault M. 1998. Bomb ^{14}C time history recorded in two modern stalagmites — importance for soil organic matter dynamics and bomb ^{14}C distribution over continents. *Earth and Planetary Science Letters* 160(3–4):795–809.

Genty D, Baker A, Massault M, Proctor C, Gilmour M, Pons-Branchu E, Hamelin B. 2001. Dead carbon in stalagmites: carbonate bedrock paleodissolution vs. ageing of soil organic matter. Implications for ^{13}C variations in speleothems. *Geochimica et Cosmochimica Acta* 65:3443–57.

Geyh MA, Merkt J, Müller H. 1971. Sediment-, Pollen- und Isotopenanalysen an jahreszeitlich geschichteten Ablagerungen im zentralen Teil des Schleinsees. *Archiv für Hydrobiologie* 69:366–99. In German.

Hammarlund D, Aravena R, Barnekow L, Buchardt B, Possnert G. 1997. Multi-component carbon isotope evidence of early Holocene environmental change and carbon-flow pathways from a hard-water lake in northern Sweden. *Journal of Paleolimnology* 18(3): 219–33.

Harlacher R, Voigt G. 1994. Distribution of radiocaesium activities in the waters of a Bavarian chain of lakes. *Radiation and Environmental Biophysics* 33(4):365–72.

Herczeg AL, Smith AK, Dighton JC. 2001. A 120 year record of changes in nitrogen and carbon cycling in Lake Alexandrina, south Australia: C:N, δ^{15}N and δ^{13}C in sediments. *Applied Geochemistry* 16(1):73–84.

Hodell DA, Schelske CL, Fahnestiel GL, Robbins LL. 1998. Biologically induced calcite and its isotopic composition in Lake Ontario. *Limnology and Ocean-*

ography 43(2):187–99.

Horvatinčić N, Srdoč D, Šilar J, Tvrdíková H. 1989. Comparison of the ^{14}C activity of groundwater and recent tufa from karst areas in Yugoslavia and Czechoslovakia. *Radiocarbon* 31(3):884–92.

Horvatinčić N, Čalić R, Geyh M. 2000. Interglacial growth of tufa in Croatia. *Quaternary Research* 53(2): 185–95.

Horvatinčić N, Krajcar Bronić I, Obelić B. 2003. Differences in the ^{14}C age, δ^{13}C and δ^{18}O of Holocene tufa and speleothem in the Dinaric karst. *Palaeogeography, Palaeoclimatology, Palaeoecology* 193(1):139–57.

Horvatinčić N, Barešić J, Krajcar Bronić I, Obelić B. 2004. Measurement of low ^{14}C activities in a liquid scintillation counter in the Zagreb Radiocarbon Laboratory. *Radiocarbon* 46(1):105–16.

Horvatinčić N, Briansó JL, Obelić B, Barešić J, Krajcar Bronić I. 2006a. Study of pollution of the Plitvice Lakes by water and sediment analyses. *Water, Air & Soil Pollution: Focus* 6(5–6):475–85.

Horvatinčić N, Barešić J, Obelić B, Krajcar Bronić I, Briansó JL. 2006b. Eutrophication process in the Plitvice Lakes, Croatia, as a consequence of anthropogenic pollution and/or natural processes. In: Onac BP, Tămas T, Constantin S, Persolu A, editors. *Archives of Climate Change in Karst*. Proceedings of the Symposium Climate Change: The Karst Record (IV). 26–29 May 2006, Băile Herculane, Romania. Leesburg, Virginia, USA: Karst Waters Institute. p 211–4.

Kempe S, Emeis K. 1985. Carbonate chemistry and the formation of Plitvice Lakes. *Mitteilungen des Geologisch-Paläontologischen Institutes der Universität Hamburg* 58:351–83.

Krajcar Bronić I, Horvatinčić N, Srdoč D, Obelić B. 1986. On the initial ^{14}C activity in karst aquifers with short mean residence time. *Radiocarbon* 28(2A):436–40.

Krajcar Bronić I, Horvatinčić N, Srdoč D, Obelić B. 1992. Experimental determination of the ^{14}C initial activity of calcareous deposits. *Radiocarbon* 34(3): 593–601.

Last WM, Smol JP, editors. 2001. *Tracking Environmental Changes Using Lake Sediments. Volume 2: Physical and Geochemical Methods.* Dordrecht: Kluwer Academic Publishers. 528 p.

Lee C, McKenzie JA, Sturm M. 1987. Carbon isotope fractionation and changes in the flux and composition of particulate matter resulting from biological activity during a sediment trap experiment in Lake Greifen, Switzerland. *Limnology and Oceanography* 32(1): 83–96.

Levin I, Kromer B. 1997. Twenty years of atmospheric $^{14}CO_2$ observations at Schauinsland station, Germany. *Radiocarbon* 39(2):205–18.

Mayr C, Fey M, Haberzettl T, Janssen S, Lücke A, Maidana NI, Ohlendorf C, Schäbitz F, Schleser GH, Struck U, Wille M, Zolitschka B. 2005. Palaeoenvironmental changes in southern Patagonia during the last millennium recorded in lake sediments from Laguna Azul (Argentina). *Palaeogeography, Palaeoclimatology, Palaeoecology* 228(3–4):203–27.

McCrea JM. 1950. On the stable isotopic chemistry of carbonates and a paleotemperature scale. *The Journal of Chemical Physics* 18:849–57.

McGeehin J, Burr GS, Hodgins G, Bennett SJ, Robbins JA, Morehead N, Markewich H. 2004. Stepped-combustion ^{14}C dating of bomb carbon in lake sediment. *Radiocarbon* 46(2):893–900.

McKenzie JA. 1985. Carbon isotopes and productivity in the lacustrine and marine environment. In: Stumm W, editor. *Chemical Processes in Lakes.* New York: John Wiley and Sons. p 99–118.

Meyers PA. 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology* 114(3–4):289–302.

Mook WG, van der Plicht J. 1999. Reporting ^{14}C activities and concentrations. *Radiocarbon* 41(3):227–39.

Neumann T, Stögbauer A, Walpersdorf E, Stüben D, Kunzendorf H. 2002. Stable isotopes in recent sediments of Lake Arendsee, NE Germany: response to eutrophication and remediation measures. *Palaeogeography, Palaeoclimatology, Palaeoecology* 178(1–2):75–90.

Obelić B, Horvatinčić N, Barešić J, Briansó JL, Babinka S, Suckow A. 2005. Anthropogenic pollution in karst lake sediments (Croatia). In: Özkul M, Yagiz S, Jones B, editors. *Proceedings of 1st International Symposium on Travertine*. Denizli: Kozan Ofset Matbaaçlk San. ve Tic. Ltd. Ankara 2005. p 188–96.

Olsson IU. 1979. The radiocarbon contents of various reservoirs. In: Berger R, Suess HE, editors. *Radiocarbon Dating*. Proceedings of the Ninth International Conference Los Angeles and La Jolla, 1976. Berkeley: University of California Press. p 613–8.

Olsson IU, Vasari Y. 1995. The long-term response of submerged plants in the hard-water lake, Säynäjälampi, to the bomb-radiocarbon injection. *PACT* 50:377–83.

Pennington W, Tutin TG, Cambray RS, Fisher EM. 1973. Observations on lake sediment using fallout ^{137}Cs as a tracer. *Nature* 242(5396):324–6.

Petrik M. 1958. Prinosi hidrologiji Plitvica (Contributions to the Hydrology of the Plitvice Lakes). In: Šafar J, editor. *Plitvička jezera, Nacionalni park.* Grafički zavod Hrvatske, Zagreb. p 49–172. In Croatian with English and German abstract.

Schelske CL, Hodell DA. 1991. Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnology and Oceanography* 36(5):961–75.

Srdoč D, Horvatinčić N, Obelić B, Krajcar I, Sliepčević A. 1985. Procesi taloženja kalcita u krškim vodama s posebnim osvrtom na Plitvička jezera (Calcite deposition processes in karstwaters with special emphasis on the Plitvice Lakes, Yugoslavia). *Carsus Iugoslaviae (Krš Jugoslavije)* 11(4–6):101–204. In Croatian with English abstract.

Srdoč D, Obelić B, Horvatinčić N, Krajcar Bronić I, Marčenko E, Merkt J, Wong HK, Sliepčević A. 1986a. Radiocarbon dating of lake sediments from two karst lakes in Yugoslavia. *Radiocarbon* 28(2A):495–502.

Srdoč D, Krajcar Bronić I, Horvatinčić N, Obelić B. 1986b. Increase of ^{14}C activity of dissolved inorganic carbon along the river course. *Radiocarbon* 28(2A): 515–21.

Srdoč D, Horvatinčić N, Ahel M, Giger W, Schaffner C, Krajcar Bronić I, Petricioli D, Pezdič J, Marčenko E, Plenković-Moraj A. 1992. Anthropogenic influence on the ^{14}C activity and other constituents of recent lake sediments: a case study. *Radiocarbon* 34(3):585–92.

Srdoč D, Osmond JK, Horvatinčić N, Dabous AA, Obelić B. 1994. Radiocarbon and uranium-series dating of the Plitvice Lakes travertines. *Radiocarbon* 36(2):203–19.

Suckow A. 2003. LabData: a database and laboratory management system for isotope hydrology, geochronology and geochemistry. In: *International Symposium on Isotope Hydrology and Integrated Water Resources Management, 19–23 May 2003*. IAEA-CN-104/P-81. Vienna: IAEA.

Suckow A, Gäbler HE. 1997. Radiometric dating and heavy metal content of a recent sediment core from Lake Trenntsee in northeastern Germany. *Isotopes in Environmental and Health Studies* 33(4):367–76.

Suckow A, Dumke I. 2001. A database system for geochemical, isotope hydrological, and geochronological laboratories. *Radiocarbon* 43(2A):325–37.

Suckow A, Treppke U, Wiedicke M, Weber M. 2001. Bioturbation coefficients of deep-sea sediments from the Peru Basin determined by gamma spectrometry of ^{210}Pb$_{exc}$. *Deep-Sea Research II* 48(17–18):3569–92.

Vreča P. 2003. Carbon cycling at the sediment-water interface in a eutrophic mountain lake (Jezero na Planini pri Jezeru, Slovenia). *Organic Geochemistry* 34(5): 671–80.

Vreča P, Muri G. 2006. Changes in accumulation of organic matter and stable carbon and nitrogen isotopes in sediments of two Slovenian mountain lakes (Lake Ledvica and Lake Planina) induced by eutrophication changes. *Limnology and Oceanography* 51(1/2): 781–90.

Wan GJ, Bai ZG, Qing H, Mather JD, Huang RG, Wang HR, Tang DG, Xiao BH. 2003. Geochemical records in recent sediments of Lake Erhai: implications for environmental changes in a low latitude-high altitude lake in southwest China. *Journal of Asian Earth Sciences* 21(5):489–502.

Wigley TML, Plummer LN, Pearson Jr FJ. 1978. Mass transfer and carbon isotope evolution in natural water systems. *Geochimica et Cosmochimica Acta* 42(8): 1117–39.