

# DISTRIBUTION OF AUTHIGENIC AND ALLOGENIC FRACTIONS IN RECENT LAKE SEDIMENT: ISOTOPIC AND CHEMICAL COMPOSITIONS

## PORAZDELITEV AVTIGENE IN ALOGENE FRAKCIJE V RECENTNIH JEZERSKIH SEDIMENTIH: IZOTOPSKA IN KEMIJSKA SESTAVA

Jadranka BAREŠIĆ<sup>1</sup>, Nada HORVATINČIĆ<sup>1\*</sup>, Polona VREČA<sup>2</sup> & Andreja SIRONIĆ<sup>1</sup>

### Abstract

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**Jadranka Barešić, Nada Horvatinić, Polona Vreča & Andreja Sironić: Distribution of authigenic and allogenic fractions in recent lake sediment: Isotopic and chemical compositions**

Recent sediments in Lake Kozjak, in the Plitvice Lakes National Park, Croatia, were used to study the impact of the material delivered to the lake sediment via Rječica Brook. Sediment cores, top 40 cm, were taken near the mouth of the Rječica Brook at three locations in the lake at different distances from the shore, water depth 2–9 m and analyzed using different isotopic and chemical methods. Sediment depth profiles of the following parameters were obtained: organic and carbonate fraction, C/N analyses of organic fraction,  $^{14}\text{C}$  activity ( $a^{14}\text{C}$ ) and  $\delta^{13}\text{C}$  values of carbonate ( $\delta^{13}\text{C}_{\text{carb}}$ ) and organic fraction ( $\delta^{13}\text{C}_{\text{org}}$ ) and  $\delta^{15}\text{N}$  of total nitrogen. The results were compared with sediment core collected in the middle of Lake Kozjak, water depth 21 m. Distribution of organic matter, C/N values,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  in sediment profiles showed strong influence of terrestrial organic and carbonate fraction run-off via Rječica Brook which decreased rapidly in the direction of the open lake. The sedimentation rate as well as the ratio of allogenic and authigenic fraction in sediments was estimated. Lower  $\delta^{13}\text{C}_{\text{org}}$  values in surface sediments might be a consequence of the increase in algal productivity but might also be a contribution of fossil fuel combustion. The anthropogenically induced  $^{14}\text{C}$  in the atmosphere in 1963/64 is visible though shadowed in sediments.

**Keywords:** Lake sediment, Authigenic and allogenic fraction, Radiocarbon, Stable isotopes of C and N, Organic matter, C and N analyses.

### Izvleček

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**Jadranka Barešić, Nada Horvatinić, Polona Vreča & Andreja Sironić: Porazdelitev avtogene in alogene frakcije v recentnih jezerskih sedimentih: izotopska in kemijska sestava**

V jezeru Kozjak na območju Nacionalnega parka Plitvička jezera smo v recentnih sedimentih raziskali vpliv snovi, ki dotekajo s potokom Rječica. Jedra sedimenta (zgornjih 40 cm) smo odvzeli na treh lokacijah v priobalnem območju jezera Kozjak na globinah od 2–9 m. V jedrih sedimenta smo določili delež organske in karbonatne frakcije, C/N razmerje v organski frakciji, aktivnost  $^{14}\text{C}$  ( $a^{14}\text{C}$ ),  $\delta^{13}\text{C}$  v karbonatni ( $\delta^{13}\text{C}_{\text{carb}}$ ) in organski ( $\delta^{13}\text{C}_{\text{org}}$ ) frakciji ter  $\delta^{15}\text{N}$  celotnega dušika. Rezultate naših analiz smo primerjali z rezultati iz osrednjega dela jezera, kjer je bil sediment odvzet na globini 21 m. Določili smo hitrost sedimentacije ter delež alogene in avtogene frakcije v sedimentih. Porazdelitve organske snovi, C/N vrednosti,  $\delta^{13}\text{C}_{\text{org}}$  in  $\delta^{13}\text{C}_{\text{carb}}$  v sedimentnih profilih kažejo na velik vpliv organske in karbonatne frakcije, ki sta s potokom Rječica prineseni s kopna. Vpliv potoka se z oddaljenostjo od sotočja z jezerom hitro zmanjšuje. Nižje vrednosti  $\delta^{13}\text{C}_{\text{org}}$  v površinskih sedimentih nakazujejo na vpliv rastoče primarne produkcije in vpliv izgorevanja fosilnih goriv. Ugotovili smo tudi vpliv atmosferskega antropogenega  $^{14}\text{C}$  iz let 1963/64.

**Ključne besede:** jezerski sedimenti, avtigena in alogena frakcija, radioaktivni ogljik, stabilni izotopi C in N, organska snov, C in N analize.

<sup>1</sup> Rudjer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia, e-mails: jadranka.baresic@irb.hr, nada.horvatincic@irb.hr, andreja.sironic@irb.hr

<sup>2</sup> Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, e-mail: polona.vreca@ijs.si

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## INTRODUCTION

Lake sediments may provide a continuous, high-resolution record of environmental changes within the lake ecosystem and regional catchment. Mineral, organic, and isotopic composition of lacustrine sediments can provide important information of palaeoenvironmental changes, human-induced impact and also help in predicting future trends in environmental evolution following the global and local/regional influence of these changes (Talbot & Laerdal 2000; Herczeg *et al.* 2001; Meyers 2003).

Lake sediments consist of organic and inorganic fraction that may be of varied origin. Organic matter in lake sediment has two sources: 1) It is produced in the lake by photosynthesis (autochthonous) and then buried as remains of organisms, 2) It is imported from the catchment via run-off rivers/streams (allochthonous), such as degraded remains of leaves, grass and soil organic matter (Meyers 2003). The inorganic fraction of the sediment consists of non-carbonate (mainly silicate) and carbonate minerals. The latter forms an important part of lake sediments in karst areas. The carbonate fraction can be authigenic precipitated from dissolved inorganic carbon (DIC) in water, or allogenic produced by eroded terrestrial material (Talbot 1990; Leng & Marshall 2004).

Both, isotopic and geochemical composition of land-derived and aquatic organic matter and carbonate fractions of the lake sediments may help to identify their sources. For example, the C and N isotopic compositions of organic matter in sediments trace past changes in productivity in lacustrine environments (Brenner *et al.* 1999) as well as C/N ratios (Talbot & Laerdal 2000; Herczeg *et al.* 2001). Likewise,  $\delta^{13}\text{C}$  and C/N values can be used to resolve changes in the lacustrine and terrestrial environment that have influenced estuarine evolution (Meyers 2003; Lamb *et al.* 2007). Stable isotope ratios of  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  give additional information about environmental conditions, e.g. origin of carbon in sediment in both organic and carbonate fraction, bioactivity and productivity can be studied by  $\delta^{13}\text{C}$  and temperature variations by  $\delta^{18}\text{O}$  (Talbot 1990; Hodell & Schelske 1998;

Lojen *et al.* 2004). Global contamination of atmospheric  $\text{CO}_2$  with  $^{14}\text{C}$  produced by nuclear bomb tests in the 1960s (Levine & Kromer 1997) can be seen in the  $^{14}\text{C}$  record of recent sediments and can be used to estimate sedimentation rate (Srdoč *et al.* 1986b; McGeehin *et al.* 2004).

Previous study of recent lake sediments from several Plitvice Lakes, Croatia, showed varied mineral and chemical composition (Horvatinčić *et al.* 2006). Isotope compositions reflect different sedimentation rates as well as different response to the environmental changes in small and big lakes e.g. increase in primary productivity in small lakes in the last two decades (Horvatinčić *et al.* 2008).

In this paper, we present further investigation of recent sediments in a particular area of Lake Kozjak in the Plitvice Lakes system, close to mouth of Rječica Brook, where enhanced eutrophication was observed in the last decades. The aim of this study was to investigate the influence of terrestrial material transported by the Rječica Brook into the Kozjak Lake and its contribution to the eutrophication processes. Additionally, any change in the environment in the last 50 to 100 years, when tourist activity increased rapidly in this area, could be reflected in the sediment composition in which case it would give insight into the vulnerability of the lake system to the human influence.

Isotopic and chemical analysis of recent lake sediments from the Lake Kozjak were used to get more information on the composition of sediments, distribution of organic and carbonate fractions and to determine the origin of both organic and carbonate fractions in sediments. Additional information was given from water analysis at the area. The ratio of allogenic and authigenic fractions in the sediments regarding the distance from the Rječica Brook mouth was determined by different isotopic and chemical parameters which were compared and discussed.

## STUDY SITE

Recent lake sediments were sampled from Lake Kozjak (altitude 540 m asl) which is part of the Plitvice Lakes system (Fig. 1). The Plitvice Lakes, situated in the Dinaric Karst in Central Croatia, consist of 16 lakes at different altitudes and are of different sizes. The lakes are interconnected by streams and waterfalls. The area is protected as

a national park and the surrounding area is covered with woods, mostly deciduous trees. The lakes are characterized by intense calcium carbonate precipitation in the form of tufa forming tufa barriers and fine-grained sediments composed of authigenic calcite (Chafetz *et al.* 1994; Horvatinčić *et al.* 2006). Lake Kozjak is the largest lake in

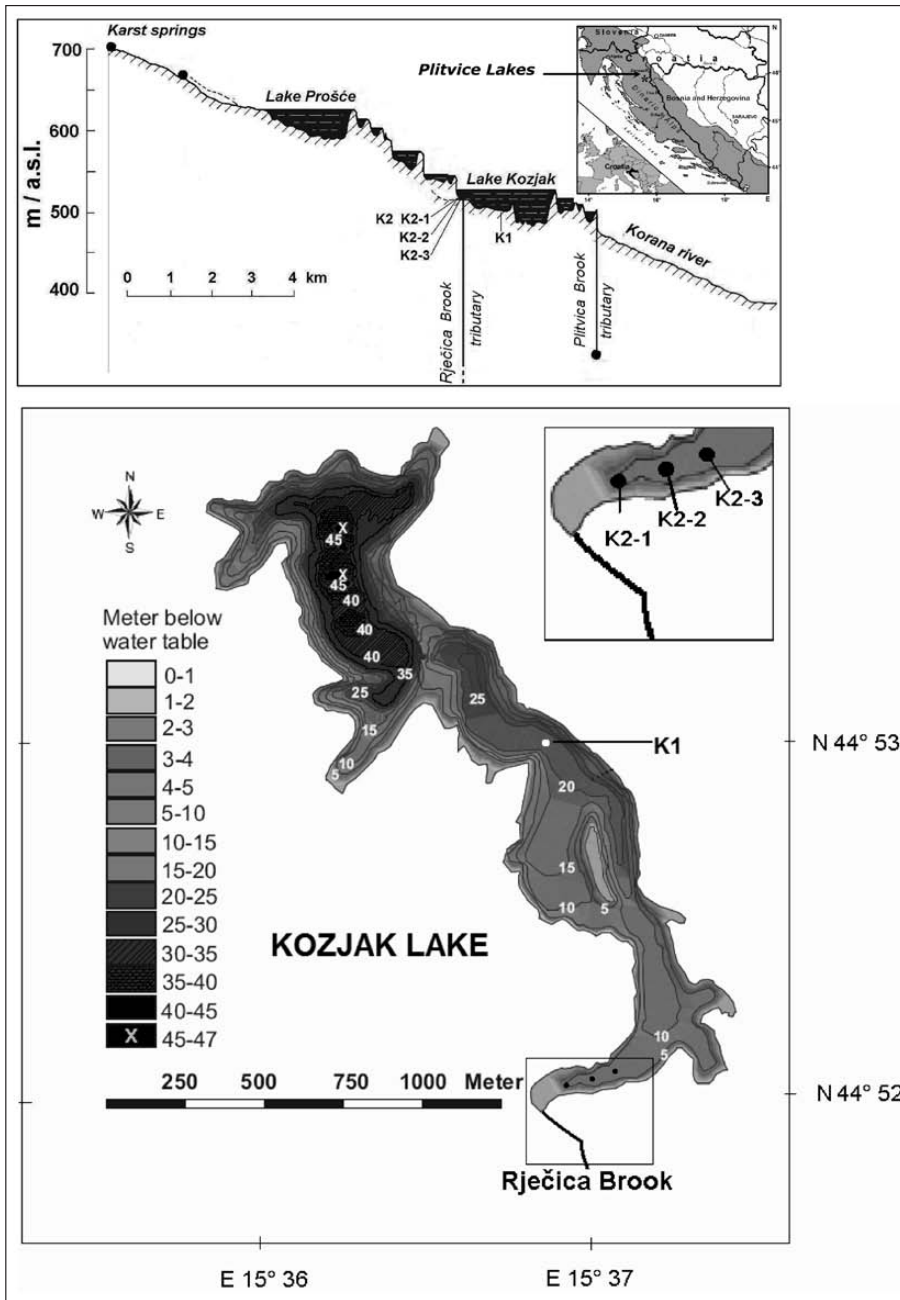


Fig. 1: Sampling sites for lake sediments in the Kozjak Lake presented in a cross section of the Plitvice Lakes system and in the map of Kozjak Lake. Sediment cores were taken in the lake center (K1) and in the area where the Rječica flows into the lake, at 3 different distances from the mouth of the stream. Kozjak Lake map after Petrik (1958) and Babinka (2007).

a submerged tufa barrier into two basins with maximum depth of 25 m (south basin) and 47 m (north basin). We investigated the inshore lake sediments close to the mouth of Rječica Brook, the most important tributary in the southern part of Lake Kozjak (Fig. 1, K2-1, K2-2 and K2-3 sites). This area is characterized by an extensive growth of macrophytes (reeds, grass, trees, etc.) inside the lake. The results of the sediment analyses from the Lake Kozjak close to the mouth of Rječica Brook (K2 sample sites) were compared with the composition of sediment collected in the centre of the Lake (K1), approximately 1000 m far from the mouth of Rječica Brook, where the influence

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## MATERIALS AND METHODS

### COLLECTION OF SAMPLES

Lake sediments were collected in the area where the stream flows into the lake (Fig. 1) at three points: (1) near to the mouth of the Rječica Brook (core K2-1), (2)

~50 m from the point 1 (core K2-2), and (3) ~100 m away from the point 1 (core K2-3). Sediment core K2-1 was taken very close to the lake area covered by aquatic plants, mainly reeds (water depth 2 m). Cores K2-2 and

K2-3 were taken from the open lake at 4 m and 9 m water depth, respectively. Lake sediments, top ~40 cm, were collected by scuba divers using plastic corers of 50 cm length, and 10 cm diameter. In addition, we also present here the results of sediment core collected in the centre of Lake Kozjak, K1, at a water depth of 21 m. The sediment cores were frozen and in the laboratory frozen sediments were cut into 1–2 cm thick layers and air dried (60 °C) prior to analyses.

METHODS

In the lake sediments we analyzed both organic and carbonate fractions. In the organic fraction, we analyzed <sup>14</sup>C activity (*a*<sup>14</sup>C<sub>org</sub>), isotopic composition of carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) and CHN composition. In the carbonate fraction, we analyzed <sup>14</sup>C activity (*a*<sup>14</sup>C<sub>carb</sub>), isotopic composition of carbon ( $\delta^{13}\text{C}_{\text{carb}}$ ), and oxygen ( $\delta^{18}\text{O}$ ). Isotopic composition of nitrogen ( $\delta^{15}\text{N}$ ) was analyzed in the bulk sediment samples.

For organic matter analyses, sediment samples were pre-treated with 1N HCl and the rest was analyzed by the Perkin Elmer 2400 Series II CHNS Analyser.

<sup>14</sup>C activity of both carbonate and organic fraction was measured on a liquid scintillation counter (Perkin Elmer, Quantulus 1220) using the benzene preparation

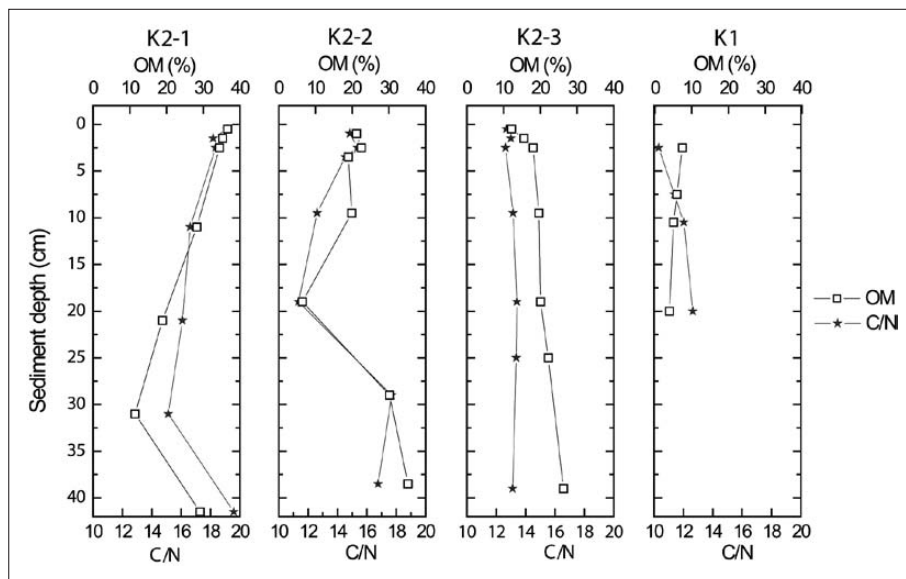
method (Horvatinčić *et al.* 2004). The results were corrected for  $\delta^{13}\text{C}$ , and reported as <sup>14</sup>C activity (*a*<sup>14</sup>C) in percent of modern carbon (pMC) (Mook & van der Plicht 1999), standard deviation 0.5 pMC.

$\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in the carbonate fraction was determined using a modified method by McCrea (1950). Samples were placed into exetainers and flushed with helium. Concentrated H<sub>3</sub>PO<sub>4</sub> was added and the isotopic composition of CO<sub>2</sub> was determined on a continuous-flow Europa 20–20 ANCA-TG stable isotope ratio mass spectrometer (Europa Scientific Ltd., Crewe, UK). Isotopic ratios are expressed in standard delta notation ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) as per mil (‰) deviation from the V-PDB standard. For  $\delta^{13}\text{C}$  analysis of the organic fraction, dry sediment samples were soaked in 1N HCl overnight to remove carbonates, and then filtered on quartz-fiber filters (Whatman GF/F), rinsed with de-ionized water, and re-dried. The stable isotopic composition of organic carbon was determined on a continuous-flow Europa 20–20 ANCA-SL isotope ratio mass spectrometer. The same spectrometer was used to measure the isotopic composition of total nitrogen in homogenized bulk samples. Nitrogen isotope ratios are reported as  $\delta^{15}\text{N}$  with respect to atmospheric N<sub>2</sub> (air).

RESULTS

Results of each parameter measured in sediment including organic matter (OM) and its C/N composition (Fig. 2), <sup>14</sup>C of organic and carbonate fraction (Fig. 3),

$\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of carbonate fraction (Fig. 4), and  $\delta^{13}\text{C}$  of organic fraction and  $\delta^{15}\text{N}$  of total nitrogen (Fig. 5) are presented in sediment profiles for four site locations following the direction from the mouth of Rječica Brook to the open Lake Kozjak, i.e. from K2-1, K2-2, K2-3 to K1 (Fig. 1). The minimum and maximum values and the average values of OM, C/N and the isotopic composition of all sediment profiles are compiled in Tab. 1. Physical



and its C/N ratio in all sediment profiles.

Fig. 2: Organic matter (OM) content and its C/N ratio in all sediment profiles.

Tab. 1: Summary of the results of organic matter (OM), C/N ratios and isotopic analyses for all sediment profiles. Results are presented as the range of minimum and maximum values and the average values for each sediment core.

	K2-1, Rječica Brook mouth		K2-2, 50 m from K2-1		K2-3, 100 m from K2-1		K1, Lake Kozjak centre	
	range	average	range	average	range	average	range	average
OM (%)	15.4 – 44.8	30.8	6.4 – 35.2	22.0	12.1 – 26.3	19.1	3.9 – 7.4	5.6
C/N	14.1 – 19.8	17.1	11.3 – 17.7	14.7	12.6 – 13.4	13.0	10.3 – 12.7	11.6
$a^{14}\text{C}_{\text{org}}$ (pMC)	94.4 – 111.3	101.8	97.5 – 108.5	102.2	92.5 – 106.7	96.4	85.0 – 91.0	88.7
$a^{14}\text{C}_{\text{carb}}$ (pMC)	32.3 – 75.7	51.7	32.6 – 83.7	65.6	54.0 – 64.6	58.6	70.0 – 79.2	72.4
$\delta^{13}\text{C}_{\text{org}}$ (‰)	-29.7 – (-28.2)	-29.0	-30.0 – (-28.8)	-29.5	-29.7 – (-27.9)	-28.7	-32.7 – (-30.9)	-31.7
$\delta^{13}\text{C}_{\text{carb}}$ (‰)	-7.5 – (-3.0)	-6.1	-7.8 – (-7.0)	-7.5	-8.3 – (-6.9)	-7.7	-8.7 – (-8.3)	-8.6
$\delta^{18}\text{O}_{\text{carb}}$ (‰)	-12.1 – (-8.6)	-11.1	-11.3 – (-10.4)	-10.6	-11.3 – (-10.2)	-10.8	-11 – (-10.3)	-10.6
$\delta^{15}\text{N}_{\text{tot}}$ (‰)	-1.7 – (-0.1)	-1.0	-1.7 – (-1.0)	-1.4	-0.2 – (+0.6)	0.2	+1.3 – (+2.4)	1.8

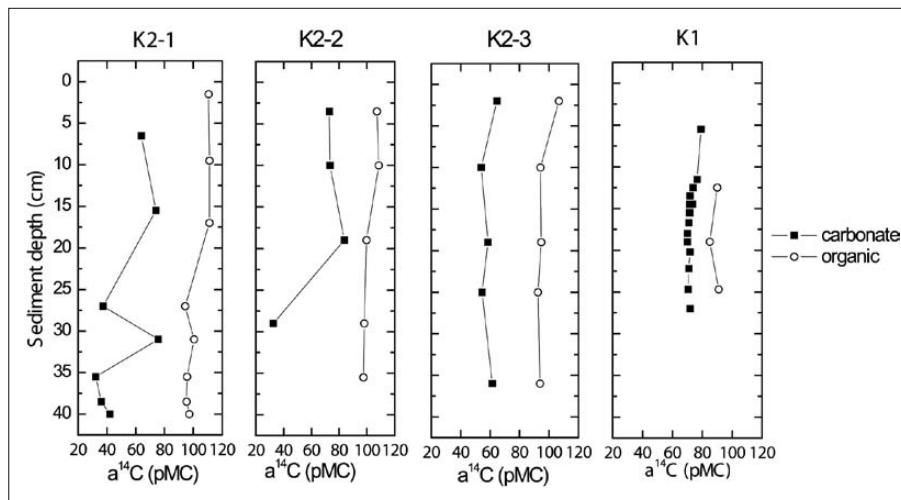


Fig. 3:  $^{14}\text{C}$  activity ( $a^{14}\text{C}$ ) of organic and carbonate fractions in all sediment profiles.

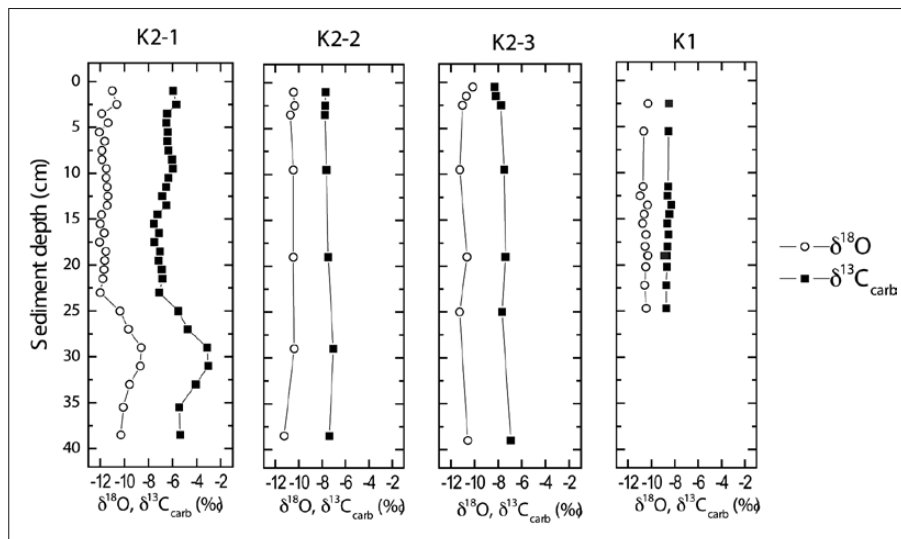


Fig. 4:  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonate fraction in all sediment profiles.

and chemical parameters and  $\delta^{13}\text{C}$  in dissolved inorganic carbonate ( $\delta^{13}\text{C}_{\text{DIC}}$ ) of surface waters at locations K1 and K2 are presented in Tab. 2.

#### ORGANIC MATTER AND C/N COMPOSITION OF SEDIMENT

The sediment cores from all locations are homogeneous in color without distinct layers. K2 sediment cores are black colored with visible leaves and other humus particles whereas the sediment at K1 site is light grey, homogeneous and fine-grained material. Concentrations of OM and C/N ratios of OM in all sediment profiles are presented in Fig. 2. OM decreases from the outflow of Rječica Brook towards the open lake (mean values): 31% at location K2-1, 22% at K2-2, 19% at K2-3, and 6% at K1 (Tab. 1).

The steady decrease of C/N is also observed in direction from the mouth of the Rječica Brook to the open lake. The mean values are: 17 at K2-1, 15 at K2-2 and 13 at K2-3 (Tab. 1). At the K1 site mean C/N value is 12. For K2-3 and K1 cores distribu-

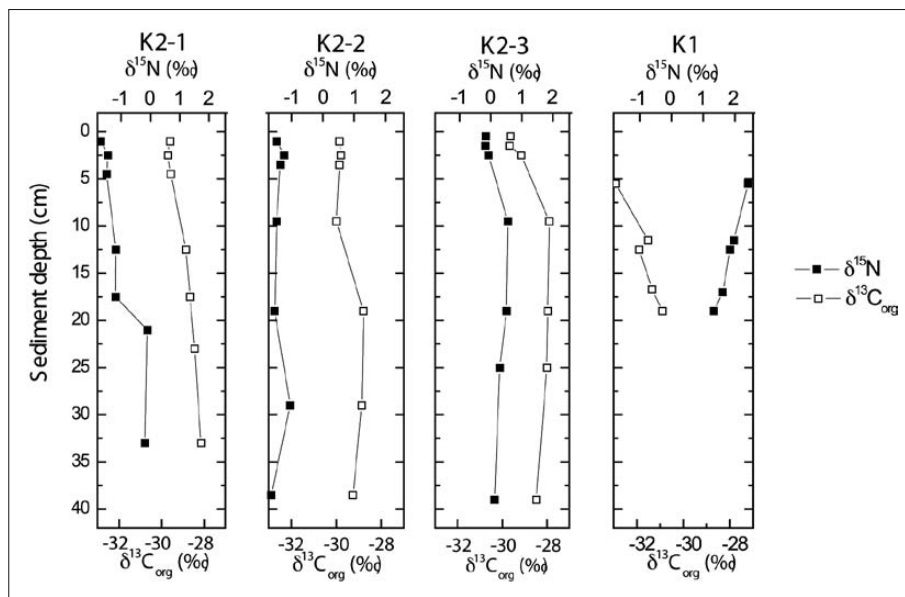


Fig. 5:  $\delta^{13}\text{C}_{\text{org}}$  values of organic fraction ( $\delta^{13}\text{C}_{\text{org}}$ ) and  $\delta^{15}\text{N}$  values in all sediment profiles.

tion of C/N values along the sediment profile is mostly uniform with slight variation, while for K2-1 and K2-2 the variations of C/N are significant. Good correlation between distribution of OM and C/N values along the sediment profiles was perceived.

#### ISOTOPIC COMPOSITION OF SEDIMENT

The  $^{14}\text{C}$  activity of organic ( $a^{14}\text{C}_{\text{org}}$ ) and carbonate ( $a^{14}\text{C}_{\text{carb}}$ ) fractions of the sediment profiles is shown in Figure 3. A significant difference in  $^{14}\text{C}$  activity between carbonate and organic fraction that is the result of the carbon origin in each is obvious for all the sediments. The  $a^{14}\text{C}_{\text{org}}$  of surface layers in all sediment cores at K2 locations are above 100 pMC and are on average about ~10 pMC higher than in the lower layers.

The mean values of  $a^{14}\text{C}_{\text{carb}}$  of K1 and K2 sediment profiles increase (exception is K2-3) from 52 pMC for K2-1 to 72 pMC for K1 (Tab. 1). The sediment cores closer to the Rječica Brook mouth have high  $a^{14}\text{C}_{\text{carb}}$  variations along the sediment profile, from 32 to 76 pMC and from 32 to 84 pMC for K2-1 and K2-2 site, respectively, while for K2-3 and K1 sediment cores the  $a^{14}\text{C}_{\text{carb}}$  values

are more uniform along the profile.

$\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonate fraction of the sediment profiles are shown in Fig. 4.  $\delta^{13}\text{C}_{\text{carb}}$  at K2-1 is more positive than in all other lake sediments (mean -6.1‰). Especially interesting are simultaneous changes in both  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  between 25 and 40 cm depth.  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  values in all other sediment profiles are rather constant with small variations in surface layers. The mean  $\delta^{13}\text{C}_{\text{carb}}$ , similar for K2-2 and K2-3, -7.5‰ and -7.7‰, respectively, and -8.6‰ for K1, show a decrease from the mouth to the open lake.

The  $\delta^{13}\text{C}$  values of organic fraction for all sediment profiles at K2 locations are in the range between -28‰ and -30‰ (Fig. 5 & Tab. 1) with similar mean  $\delta^{13}\text{C}_{\text{org}}$ : -29.0‰, -29.5‰ and -28.7‰ for K2-1, K2-2 and K2-3, respectively.  $\delta^{13}\text{C}_{\text{org}}$  of K1 sediment has a mean value of -31.7‰ covering the range from -30.9‰ to -32.7‰. It is observed that the  $\delta^{13}\text{C}_{\text{org}}$  values for all sediment profiles steadily decrease in the surface layers.

The  $\delta^{15}\text{N}$  values indicate the low content of  $^{15}\text{N}$  with slight variations in all sediment profiles (Fig. 5) and with steady increase of the mean  $\delta^{15}\text{N}$  from K2-1 (-1.0‰) to K1 (1.8‰). In all K2 sediments the change of  $\delta^{15}\text{N}_{\text{tot}}$  values along the sediment profile follows the change in  $\delta^{13}\text{C}_{\text{org}}$  with slight decrease in values in the surface sediments.

## DISCUSSION

Water analyses at both locations (Tab. 2) show the higher values for conductivity, bicarbonate, nitrate and dissolved organic carbon (DOC) concentrations at K2 site. That can be explained by water input of Rječica Brook flowing through the area covered by forest and so caring land-derived or soil based runoff. Also the low value of  $\delta^{13}\text{C}_{\text{DIC}}$

in Rječica Brook (mean value -11.9‰), compared with  $\delta^{13}\text{C}_{\text{DIC}}$  of center Kozjak Lake (mean value -10.4‰), suggests that the fraction of carbon in DIC originating from the  $\text{CO}_2$  plant respiration and/or soil/humus is higher at K2 than at K1 (Meyers 2003; Leng & Marshall 2004; Horvatinčić *et al.* 2008). Generally low concentration of

Tab. 2: Results of physical and chemical measurements of surface water presented as a mean values and the range of minimum and maximum values including all seasonal measurements.

Location	Temperature (°C)	pH	Conductivity ( $\mu\text{Scm}^{-1}$ )	O <sub>2</sub> (mgL <sup>-1</sup> )	HCO <sub>3</sub> (mmolL <sup>-1</sup> )	NH <sub>4</sub> /N (mgL <sup>-1</sup> )	NO <sub>3</sub> /N (mgL <sup>-1</sup> )	DOC (mgCL <sup>-1</sup> )	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)
Rječica mouth, K2	8.8 4.2–10.4	8.2 8.0–8.3	503 494–512	10.2 8.1–11.3	5.4 5.2–5.5	0.04 0.01–0.18	0.9 0.7–1.0	1.3 1.0–2.1	-11.9 -12.5–(-11.5)
Lake Kozjak, K1	12.6 3.6–21.6	8.3 8.1–8.4	390 377–404	10.1 8.1–12.5	3.8 3.5–4.2	0.03 0.01–0.05	0.6 0.4–0.9	1.1 0.7–2.0	-10.4 -11.7–(-9.7)

nutrients and DOC at both locations do not indicate anthropogenic pollution in waters.

#### RECORDS IN ORGANIC FRACTION OF SEDIMENT

Concentration of organic fraction in sediments (Fig. 2) close to the mouth of Rječica Brook (K2 locations) is much higher than in the centre of the Lake Kozjak at K1, which is approximately 1 km away from the Rječica mouth (Fig. 1). Also the sediment color is related to the content of organic matter, black colored at K2 and light grey at K1 location. Steady decrease of OM mean values in the sediment profiles towards the open lake is also followed by a decrease of C/N mean values in the same direction, from 17 at K2-1 to 12 at K1 (Tab. 1 & Fig. 2). The C/N ratio in the sediment is a good indicator of organic carbon sources; for example, organic matter from lake algae has C/N values between 4 and 10, and land plants have usually C/N ratio of 20 and more (Brenner *et al.* 1999; Herczeg *et al.* 2001; Meyers 2003). In our case the C/N values show that the OM in the sediments is the mixture of the allochthonous matter that decreases towards the open lake and autochthonous OM which dominates in the lake centre.

Additionally, the mean  $\delta^{13}\text{C}_{\text{org}}$  values of all K2 sediment profiles are similar (Fig. 5 & Tab. 1), while at K1 sediment the mean  $\delta^{13}\text{C}_{\text{org}}$  value is more negative. The relation between  $\delta^{13}\text{C}_{\text{org}}$  and C/N atomic ratios for all sediment profiles (Fig. 6) shows distinction between K1 and K2 sites due to diminishing of the Rječica Brook influence from K2 to K1. The K1 sediment shows characteristics of sedimentary organic matter produced in aquatic environment with lower C/N ratios and lower  $\delta^{13}\text{C}_{\text{org}}$ . It indicates that the main fraction of organic matter probably originates from in-lake processes, such as algal photosynthesis (Brenner *et al.* 1999; Meyers 2003). In contrast, K2 sediments cover a narrow range of  $\delta^{13}\text{C}_{\text{org}}$  values and are very similar to the  $\delta^{13}\text{C}$  values of terrestrial plants in the Plitvice Lakes area which varies between -28‰ and -29‰ (Marčenko *et al.* 1989). C/N values of K2 sediments decrease with increase in distance from the Rječica Brook inflow as discussed earlier. Results show that organic fraction of K2 sediments is a mixture of organic matter of different sources with a dominant

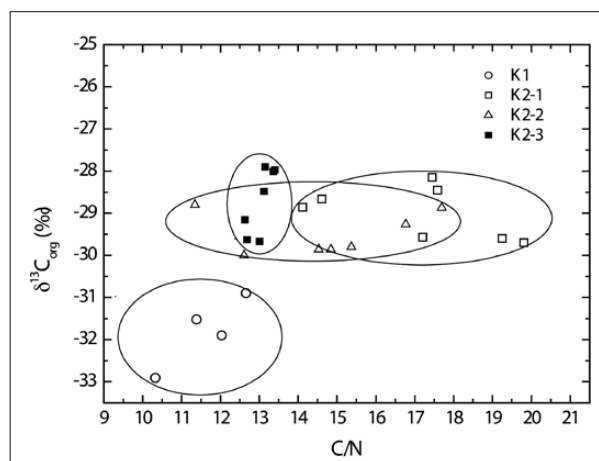


Fig. 6: Relation between  $\delta^{13}\text{C}$  and C/N ratio in organic fraction for all sediment profiles.

terrestrial organic fraction at K2-1 and increasing influence of aquatic organic fraction in off-shore direction as recorded at K2-3. It is also observed that the  $\delta^{13}\text{C}_{\text{org}}$  values for all sediment profiles steadily decrease in the surface layers that could be a consequence of the increase in algal productivity and <sup>13</sup>C depleted submerged plants (Marčenko *et al.* 1989) in the Lake Kozjak. Since the waters of Plitvice Lakes have low concentrations of nutrients (Horvatinčić *et al.* 2006), the possible reason of increase of productivity could be a slight increase of the surface water temperature of the Plitvice Lakes in the last three decades. Recent mean annual temperatures of the surface lake waters for period 2002–2006 were 0.5 to 2 °C higher than for period 1980–1985 (Horvatinčić *et al.* 2008). However, decreasing trend of  $\delta^{13}\text{C}_{\text{org}}$  values can be partly caused by the contribution of isotopically depleted CO<sub>2</sub> from fossil fuel combustion, i.e. the Suess effect. The influence of the Suess effect to  $\delta^{13}\text{C}$  values in recent lake sediments was also observed by Vreča & Muri (2006) and Verburg (2007) using model proposed by Schelske & Hodell (1995).

$\delta^{15}\text{N}$  values between 1.3‰ and 2.4‰ measured in K1 core (Fig. 5) are generally referred as the result of atmospheric nitrogen utilized by nitrogen-fixing cyanobacteria (Talbot & Laerdal 2000). Cyanobacteria and other microbial organisms play an important role in the

process of tufa/sediment precipitation in the waters of the Plitvice Lakes (Chafetz *et al.* 1994). The negative  $\delta^{15}\text{N}$  values measured in K2 sediments might have originated from soil nitrogen input (Pichlmayer *et al.* 1998; Kendall 1998; Talbot 2001; Sah & Brumme 2003; Kanduč *et al.* 2008) because soil run-off by the Rječica Brook is dominant. In all K2 sediments, the change of  $\delta^{15}\text{N}$  values along the sediment profile follows the change in  $\delta^{13}\text{C}_{\text{org}}$ , with slight decrease in values in the surface sediments. Changes of  $\delta^{15}\text{N}$  values in K2 cores could indicate organic matter degradation processes (Hodell & Schelske 1998; Brenner *et al.* 1999), and also varied sources of nitrogen in the sediment (Brenner *et al.* 1999; Herzeg *et al.* 2001; Vreča & Muri 2006). More positive  $\delta^{15}\text{N}$  values in K2-3 core (mean 0.2‰) follow the decreasing trend of terrestrial influence in off-shore direction. The slight increase of  $\delta^{15}\text{N}$  values, decrease of C/N and  $\delta^{13}\text{C}_{\text{org}}$  values in the K1 sediment surface is a probable indication of enhanced algal productivity but more detailed research is necessary to confirm this assumption. Similar indicators of enhanced algal productivity were described by Brenner *et al.* (1999), Teranes & Bernasconi (2000), and Herczeg *et al.* (2001).

The  $a^{14}\text{C}_{\text{org}}$  of sediment cores reflects the  $^{14}\text{C}$  activity of atmospheric  $\text{CO}_2$  and/or environmental vegetation including terrestrial and aquatic plants. In K2 sediments the  $a^{14}\text{C}_{\text{org}}$  is in the range 92–111 pMC (Tab. 1 & Fig. 3) and is significantly higher than in the K1 sediment (85–91 pMC). It is expected that in K1 sediment (centre of the Lake, Fig. 1) the organic matter is predominantly autochthonous one, formed by photosynthesis process of aquatic plants which use partly the  $\text{CO}_2$  from DIC in water, so called hard-water effect (Marčenko *et al.* 1989; Geyh *et al.* 1998). This is confirmed by the  $a^{14}\text{C}$  values of the Plitvice Lakes aquatic plants (range 81–92 pMC, Marčenko *et al.* 1989) and of the Kozjak Lake DIC (range 80–85 pMC, Srdoč *et al.* 1986a). The  $a^{14}\text{C}_{\text{org}}$  values higher at K2 than at K1 sites (Tab. 1) indicate the influence of terrestrial organic matter transported by Rječica Brook but also of the macrophytes remnants growing at K2. The  $a^{14}\text{C}$  of terrestrial plants at K2 (beech leaves and abies needles collected in 2005–2006, 105 pMC and 110 pMC, respectively) is in good correlation with  $a^{14}\text{C}_{\text{org}}$  of K2 sediments in the upper layers.

An increase in  $a^{14}\text{C}_{\text{org}}$  of ~10% from 95–97 pMC in the lower layers to the  $a^{14}\text{C}_{\text{org}}$  of 106–111 pMC in surface layers at K2 sediment cores (for K2-1 at 17–27 cm, for K2-2 at 10–20 cm, and for K2-3 at 5–10 cm from the surface, Tab. 1 & Fig. 3) could be attributed to the global contamination of atmospheric  $\text{CO}_2$  with  $^{14}\text{C}$  produced due to nuclear bomb tests in the last century. The atmospheric  $^{14}\text{C}$  activity, with almost 100% increase in 1963 (Levine & Kromer 1997), was also observed in

the tree rings collected in the Plitvice Lakes area (Krajar Bronić *et al.* 1998) and in the lake sediments from different Plitvice Lakes, in organic as well in carbonate fractions (Horvatinčić *et al.* 2008; Srdoč *et al.* 1992). The response to bomb-induced  $^{14}\text{C}$  in the atmospheric  $\text{CO}_2$  in the sediments, seen as a peak in  $a^{14}\text{C}$ , is damped and decades-delayed because of complex geochemical processes involved in sediment formation (Srdoč *et al.* 1992; Genty *et al.* 1998; Horvatinčić *et al.* 2008). In all K2 profiles the  $^{14}\text{C}$  activity peak was not observed probably because of relatively high sedimentation rates, but also because of possible physical mixing of sediments and transport of terrestrial organic matter by Rječica Brook. Assuming that the layers above 27 cm, 20 cm and 10 cm for K2-1, K2-2 and K2-3, respectively, belong to the period after 1963, the sedimentation rate for each site can be estimated as follows: 6.7 mm/yr for K2-1, 4.2 mm/yr for K2-2 and 2.5 mm/yr for K2-3. Previous investigation of Kozjak Lake sediment in the lake centre (close to K1 location) estimated the sedimentation rate of 0.8 mm/yr by  $^{14}\text{C}$  (Srdoč *et al.* 1986b) and by using  $^{210}\text{Pb}$  method the mass accumulation rate of 0.8 kg/m<sup>2</sup> yr (Horvatinčić *et al.* 2008). Although the sedimentation rates for K2 sites can be used only as estimated values, there is a consistent decrease of sedimentation rates towards the open lake which can be explained by strong influence of terrestrial material run-off by Rječica Brook.

#### RECORDS IN CARBONATE FRACTION OF SEDIMENT

Previous investigation of chemical composition of sediments (Horvatinčić *et al.* 2006) showed significant differences between K1 and K2 sediments. The mineral fraction of sediment K1 represents >90% and consists mainly of calcite (>80%), over quartz and dolomite while at the confluence of Rječica Brook (K2 sites, mineral fraction 60–85%) the concentration of calcite is <60% with the similar proportion of calcite, dolomite and quartz in the surface layer. The isotope analyses of carbonate fraction in all sediment cores are presented in Fig. 3 ( $a^{14}\text{C}_{\text{carb}}$ ) and Fig. 4 ( $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$ ). Carbon isotopes ( $a^{14}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$ ) of the Plitvice Lakes sediments mainly originate from the DIC in water (Srdoč *et al.* 1986a; Horvatinčić *et al.* 2003) as a result of geochemical processes in the groundwater that feeds the lakes (Krajar Bronić *et al.* 1992). Moreover, this is also the influence of carbon isotope exchange processes between DIC and atmospheric  $\text{CO}_2$  that were reflected in the steady downstream increase of  $a^{14}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  values in the Plitvice Lakes water (Srdoč *et al.* 1986a). The lower  $a^{14}\text{C}_{\text{carb}}$  mean values for K2 sediments with steady increase from Rječica Brook mouth (51.7 pMC at K2-1) to the open lake (72.4 pMC at K1) indicate the influence of the eroded carbonate frac-



tion originating from the catchment area of the Rječica Brook. Moreover, the highest  $\delta^{13}\text{C}_{\text{carb}}$  mean value of  $-6.1\text{‰}$  for K2-1 sediment core (Tab. 1 & Fig. 4) indicates the highest fraction of allogenic mineral carbonate, while in K1 sediment the mean  $\delta^{13}\text{C}_{\text{carb}}$  of  $-8.6\text{‰}$  is the typical value of lake sediment and/or tufa deposits precipitated from DIC in water of the Plitvice Lakes (Srdoč *et al.* 1986a; Horvatinčić *et al.* 2003). Also the lower  $\delta^{13}\text{C}_{\text{DIC}}$  values in water samples from Rječica Brook (mean value  $-11.9\text{‰}$ ), compared with center Kozjak Lake K1 (mean value  $-10.4\text{‰}$ ) (Tab. 2), suggest a higher fraction of DIC originating from the  $\text{CO}_2$  plant respiration from the soil/humus at K2 site (Meyers 2003; Leng & Marshall 2004; Horvatinčić *et al.* 2008).

Correlation of  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  values (Fig. 7) shows that sediments of K2-2 and K2-3 form groups with a similar range of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values, but more dispersed than K1 indicating possible mixing of carbonate sources of various origins, i.e. authigenic and

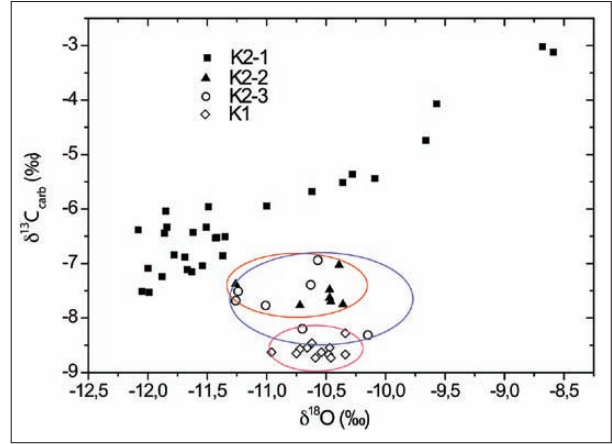


Fig. 7: Relation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in carbonate fraction of all sediment profiles.

allogenic fraction. The most dispersed values for K2-1 sediment show that in the sediment formation the mixing of authigenic and allogenic

fraction has an important role, which was also proved by variations of  $\delta^{14}\text{C}_{\text{carb}}$  in the same sediment profile.

Significant variations of  $\delta^{14}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}$  in the same layers of the K2-1 sediment core (25–35 cm, Figs. 3 & 4), indicate different fractions of eroded material in sediment layers transported by the Rječica Brook. In other sediment profiles the  $\delta^{14}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values are more uniform, but the slight increase of  $\delta^{14}\text{C}_{\text{carb}}$  is observed in the upper layers of all sediments. The change of  $\delta^{14}\text{C}_{\text{carb}}$  coincides with the increase of  $\delta^{14}\text{C}_{\text{org}}$  in the same layers (Fig. 3) what could be again a consequence

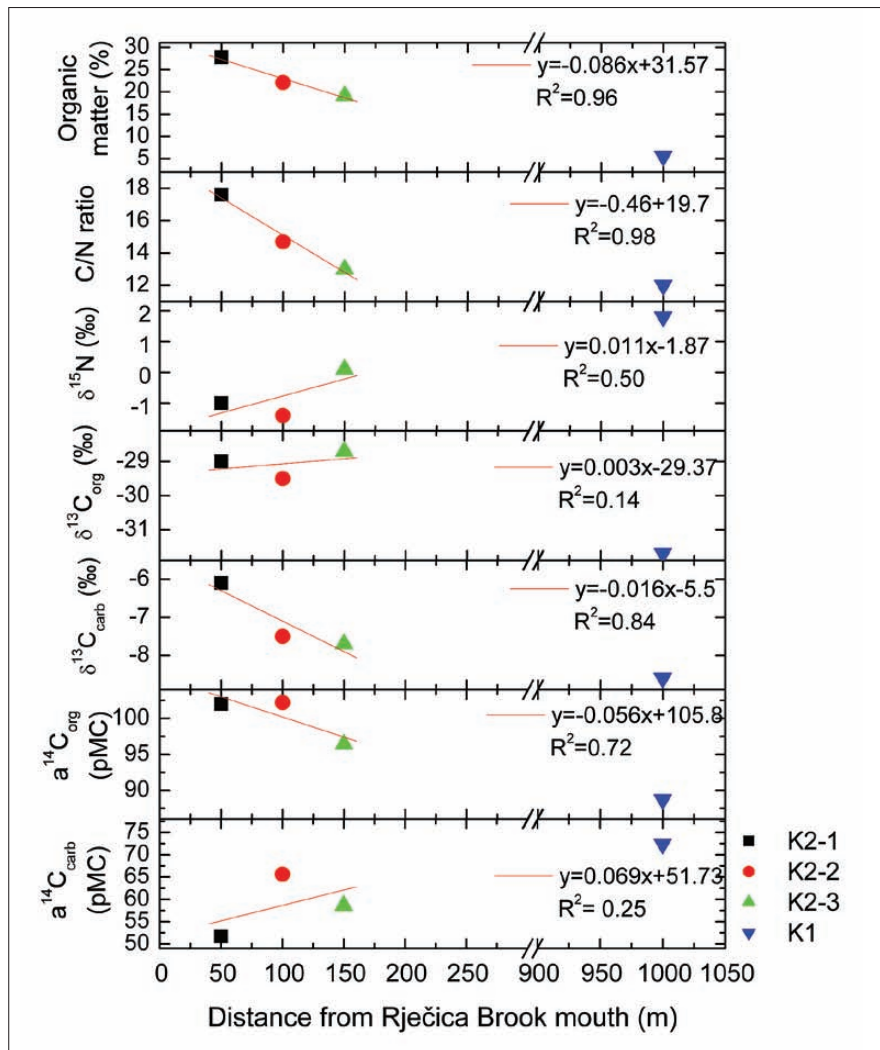


Fig. 8: Mean values of different chemical and isotopic parameters for all sediment profiles in correlation with distance from the mouth of Rječica Brook. The linear correlation and  $R^2$  values between measured parameters and distance from the Rječica Brook mouth at points K2-1, K2-2 and K2-3 are presented.

of the global  $^{14}\text{C}$  contamination of atmospheric  $\text{CO}_2$  by the thermonuclear weapon tests described earlier.

#### DISTRIBUTION OF ALLOGENIC AND AUTHIGENIC FRACTION

The summary of the results of different chemical and isotopic parameters used for study of contribution of the stream of Rječica Brook to the composition of the lake sediment is presented in Fig. 8. The results, mean values for each sediment profile, are presented in correlation with distance from the Rječica Brook mouth. The linear correlations between measured parameters and distance from the Rječica Brook mouth at K2-1, K2-2 and K2-3 sites are also presented.

Change of OM and C/N ratio shows good linear correlation ( $R^2 = 0.96$ ,  $p = 0.09$ ) for the sediments close to Rječica mouth, first ~150 m, and somewhat worse correlation for change of  $\delta^{13}\text{C}_{\text{carb}}$  ( $R^2 = 0.8$ ,  $p = 0.26$ ) and  $\text{a}^{14}\text{C}_{\text{org}}$  ( $R^2 = 0.7$ ,  $p = 0.35$ ). Changes of  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}_{\text{org}}$  and  $\text{a}^{14}\text{C}_{\text{carb}}$  values show weak correlation with distance. The values of all parameters are quite different for the sediment in the Lake centre, ~1000 m away from the Rječica Brook mouth. In this point the influence of Rječica Brook is not expected and these values confirm the authigenic origin of the sediment, i.e. precipitation of carbonate fraction mostly from DIC in water, and production of organic matter mainly by photosynthesis process.

Using the values which are characteristic for authigenic and allogenic fractions for carbonate and organic matter in the sediment we tried to approximate the distribution of authigenic and allogenic fractions regarding the distance from the Rječica Brook mouth. For this calculation we used the parameters which showed the best correlation (Fig. 8), i.e.  $\delta^{13}\text{C}_{\text{carb}}$  values for carbonate fraction and C/N values for organic fraction.

For carbonate fraction we used the mean values of  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  for the K2 and K1 sites, and assuming

equilibrium conditions for calcite precipitation, we calculate the approximate ratios of allogenic and authigenic fractions in sediment at each site. The equilibrium fractionation  $\epsilon$  between DIC and precipitated calcite is about 1.5‰ in the range of pH (8.2–8.3) and temperature (8.8–12.6 °C) typical for Kozjak Lake water at K1 and K2 sites (Tab. 2). Since  $\delta^{13}\text{C}$  of DIC is -11.9‰ and -10.4‰ on average in Rječica mouth K2, and Lake Kozjak K1, respectively, the carbonate precipitated from Rječica DIC and Kozjak DIC under equilibrium conditions would have  $\delta^{13}\text{C}$  value of -10.4‰ and -8.9‰, respectively. A simple mixing calculation with mineral carbonate ( $\delta^{13}\text{C}$  of 0‰) would indicate an approximate value of ~60% of authigenic carbonate in K2-1 sediment profile, ~70% in K2-2, ~75% in K2-3, and ~95% in K1 sediment profile. This calculation confirms that carbonate fraction of sediment in the centre of Lake Kozjak K1 precipitates almost completely from DIC in water, whereas in the Rječica Brook mouth carbonate fractions are composed of authigenic and allogenic fractions in different ratios. The allogenic fraction decreases with distance from the Rječica mouth.

For calculation of allogenic and authigenic fraction in organic matter of the sediment we used mean values of C/N for each sediment (Tab. 1) and assumed that C/N value of aquatic plant is 8 (Meyers 1994) and C/N of terrestrial plant (mixture of beech leaves and abies needles) is 30 (Meyers 1994; Rodin & Bazilevich 1967). A simple mixing calculation would indicate an approximate value of ~60% of authigenic OM in K2-1 sediment profile, ~70% in K2-2, ~75% in K2-3 and ~85% in K1. This calculation again confirms, such as in carbonate fraction of sediment, that authigenic fraction increases with the distance from the Rječica Brook mouth and in the centre of the Lake the OM is mostly of aquatic plant (photosynthesis) origin, i.e. authigenic.

## CONCLUSIONS

Chemical and isotopic analyses of lake sediments indicated that the Rječica Brook was the main supplier of terrestrial material in the inflow area to the Kozjak Lake. Decreasing trend of the fractions of terrestrial matter (both organic and carbonate) in lake sediment in off-shore direction is evident by values of OM content, C/N values and isotope values for  $\text{a}^{14}\text{C}_{\text{org}}$ ,  $\text{a}^{14}\text{C}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$ ,  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{15}\text{N}$ . All parameters showed the strong influence of allogenic fraction ~150 m away from the mouth of the Rječica Brook.

Authigenic and allogenic fractions of sediments were calculated using  $\delta^{13}\text{C}_{\text{carb}}$  and C/N values for carbonate and organic fraction of the sediment, respectively. The obtained values showed the significant increase of authigenic fraction from Rječica Brook mouth to the open Lake direction at the distance of ~150 m: from ~60% to 75% for carbonate fraction, and from ~60% to ~75% for organic fraction. In the Lake centre, ~1000 m away from the Rječica mouth the calculated values of authigenic fraction were ~95% and ~85% for carbonate

and organic fraction, respectively, confirming mostly the authigenic origin of the sediment and no influence of the Rječica Brook run-off.

The global anthropogenic  $^{14}\text{C}$  peak at 1963/64 in the biosphere is visible in the sediments as a slight increase of ~10% of  $a^{14}\text{C}_{\text{org}}$  in the surface layers. The steady decrease of the  $\delta^{13}\text{C}_{\text{org}}$  with decreasing depth in all sediment profiles might be a consequence of the increase in algal productivity in the last decades but might also be a contribution of fossil fuel combustion.

The estimated sedimentation rates in the Kozjak Lake with decreasing values from 6.7 mm/yr close to the mouth to 0.8 mm/yr at the Lake centre also showed

strong influence of terrestrial fraction run-off via Rječica Brook. As the consequence, the increase of allogenic fraction in the lake sediment, e.g. organic material originating from the catchment area enhances the growth of macrophytes and therefore accelerates the eutrophication process in this part of the lake.

The comprehensive chemical and isotopic study of the lake sediments in the Kozjak Lake does not indicate significant changes in last 100 years caused by anthropogenic activity, i.e. increased number of tourists in the area. The main nutrient supplier inside the Rječica Bay of the Lake Kozjak is stream of Rječica Brook causing increased growth of macrophytes in the lake.

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