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Spatial and seasonal variations in the stable C isotope composition of dissolved inorganic carbon and in physico-chemical water parameters in the Plitvice Lakes system

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Plitvice Lakes waters were collected at 14 sampling points, including springs, tributaries and lakes, for the period 2002–2007. The results of the physical and chemical conditions of calcite precipitation as well as the δ^{13}C values of dissolved inorganic carbon (DIC) were used to study the processes influencing calcite precipitation. Significant differences between spring, lake and stream waters as well as changes in the downstream direction were observed. The correlation between $\delta^{13}C_{DIC}$ values and physico-chemical conditions for calcite precipitation showed that calcite precipitates in lake waters which are oversaturated with respect to $CaCO_3$ (I_{sat} values 4–10) and with $\delta^{13}C_{DIC}$ values between −11.5 and −8.5 ‰. In spring waters, the $\delta^{13}C_{DIC}$ values were more negative, from −14 to −12 ‰, and I_{sat} values of 1–2 indicated that equilibrium conditions for calcite precipitation were not attained. The downstream increase in $\delta^{13}C_{DIC}$ correlated with the increase in the δ^{13}C values of calcite in the lake sediments, suggesting that the freshwater calcite was mainly of autochthonous origin and precipitated within the water column in isotopic equilibrium with DIC.

Keywords: calcite precipitation; ^{13}C; dissolved inorganic carbon; dissolved organic carbon; isotope geochemistry; Plitvice Lakes

1. Introduction

Precipitation of freshwater carbonates in the form of lake sediments or tufa depends on the physico-chemical conditions of the water. It is enhanced by the photosynthetic activity of aquatic primary producers (algae, bacteria and plants), indicating that the interaction between atmosphere and biosphere determines the CO_2–HCO_3^--$CaCO_3$ system [1,2].

Dissolved inorganic carbon (DIC) comprises CO_2, HCO_3^- and CO_3^{2-} species forming the largest pool of carbon in hard-water lakes and the main source of carbon for photosynthesis. In the karst region, DIC originates mainly from carbonate mineral (calcite and dolomite) dissolution by CO_2, generated by root respiration and decomposition of organic matter (OM) in the catchment area, producing HCO_3^- [3]. Another component of DIC is CO_2 from respiration and decomposition

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of OM in the aquifer and the water column as well as atmospheric CO_2. However, within a pH range of 6–10, the CO_2(aq) concentration is negligible and HCO_3^- is the main component of DIC [3]. The stable carbon isotope composition of DIC [$(^{13}C/^{12}C)_{DIC}$] depends on the mineral

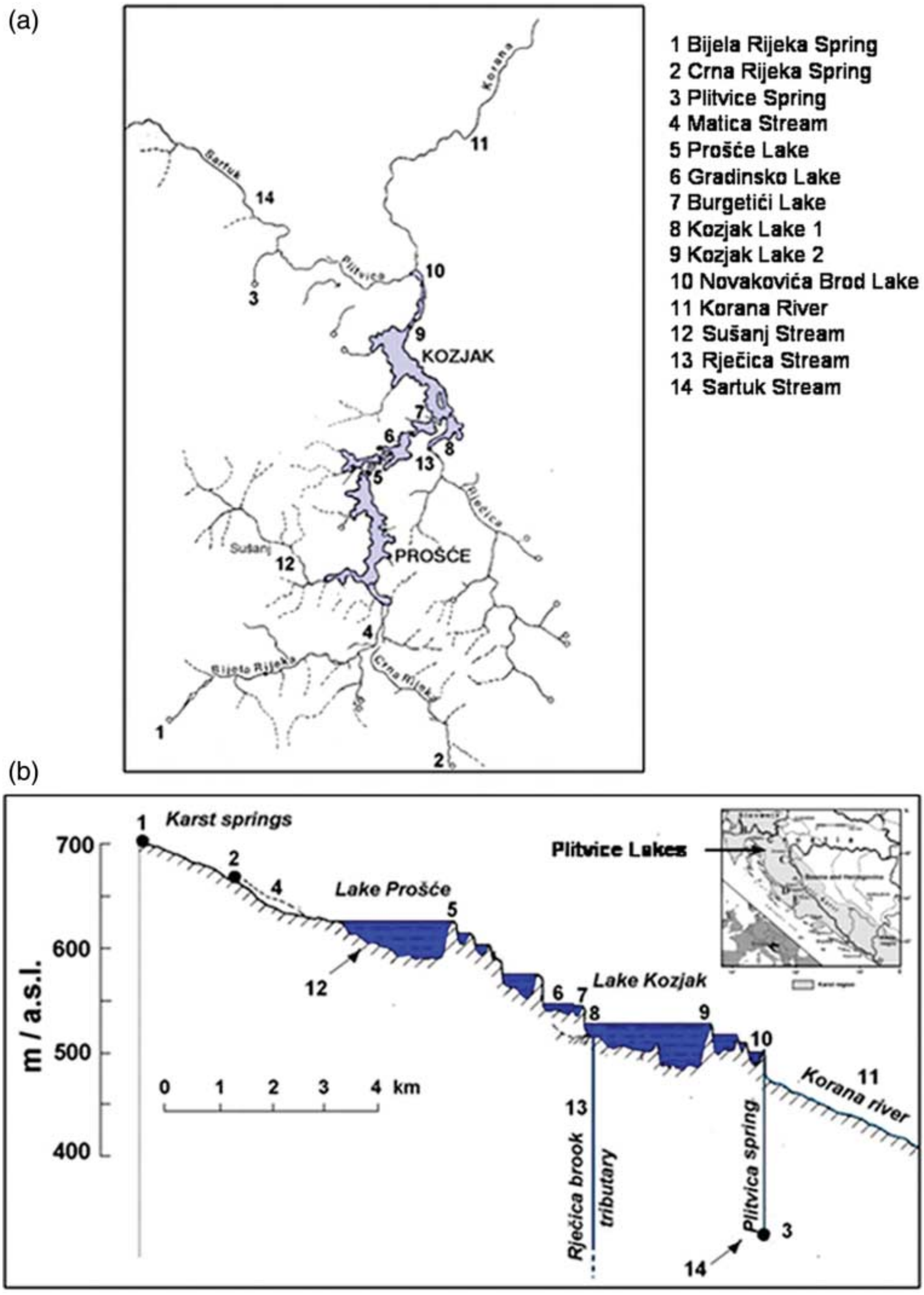

Figure 1. Sampling sites for waters in the Plitvice Lakes: (a) Map of the Plitvice Lakes including three main springs, five lakes, Korana River and three tributary streams. (b) Cross section of the Plitvice Lakes with sampling points. Total distance from springs to the Korana River is ~12 km.

dissolution by CO_2 of biogenic origin (formation of DIC) and photosynthesis (consumption of DIC) as well as isotope exchange of carbon between atmospheric CO_2 and DIC. $(^{13}C/^{12}C)_{DIC}$ is, therefore, a useful tracer for sources and processes of DIC (carbon cycle) in aquatic systems. Since calcite precipitates mainly from DIC, it is very important to understand the cycling of carbon, its sources and sinks. The isotopic composition of carbon species is a useful tool to understand the exchange processes between DIC and atmospheric CO_2, the equilibrium/non-equilibrium conditions of calcite precipitation and the influence of primary productivity and climate changes on the processes in the lakes [1, 4–6].

Another possible source of carbon in water is dissolved organic carbon (DOC), which can be of autochthonous origin, that is, produced by photosynthesis in water by phytoplankton (algae and bacteria, mainly cyanobacteria), and of allochthonous origin, that is, DOC introduced into the water system from soil leaching [7].

The aim of this work is to study the processes which influence the isotopic composition of DIC and calcite precipitation in waters of the Plitvice Lakes system including springs, lakes and tributary streams of the Plitvice Lakes. The downstream variation in $\delta^{13}C_{DIC}$ values were also studied, including a comparison of $\delta^{13}C_{DIC}$ values in the area where calcium carbonate precipitates strongly and where this process does not exist. For this study, we measured the temperature, pH values, alkalinity and DOC of the Plitvice Lakes waters seasonally at 14 sampling points in 2003–2007, as well as the $\delta^{13}C_{DIC}$ values in 2002–2007. The $\delta^{13}C_{DIC}$ values were compared with those published for 1984–1990 [8,9] to assess if any changes have occurred in the CO_2–HCO_3^-–$CaCO_3$ system at the Plitvice Lakes during the last two decades.

2. Site description

The Plitvice Lakes, situated in the Dinaric karst in Central Croatia, are surrounded by Triassic, Jurassic and Cretaceous beds [10]. The impermeable Upper Triassic and Lower Jurassic dolomites and marly limestones prevent vertical water circulation. Karst aquifers issuing at Crna Rijeka, Bijela Rijeka, Plitvica and Rječica springs represent the main sources feeding the Plitvice Lakes. The Plitvice Lakes feed the Korana River which issues from the lakes (Figure 1). In the valley of the Plitvice Lakes and their tributaries, the Mesozoic bedrock is overlain by layers of Quaternary tufa. The Plitvice Lakes consist of 16 lakes of different sizes, connected by streams and waterfalls. The altitude of the area ranges from 505 m to 636 m asl, the climate is mountain-continental, the average air temperature is 9.1°C and the average yearly precipitation is 1558 mm for the period 1986–2010 [Meteorological and Hydrological Service of Croatia, network of meteorological and climatological stations/data repository]. The total distance from the springs to the Korana River is approximately 12 km (Figure 1). The lakes and Korana River are characterised by intense calcium carbonate precipitation from the water, forming tufa barriers and fine-grained lake sediments, mainly composed of authigenic calcite [11,12]. The surrounding area is covered largely with deciduous forests. The area is protected as a National Park, and human activities in the lake watersheds are relatively limited, although numerous tourists visit the area every year.

3. Sampling and methods

Water samples were collected at 14 points including 3 springs, 5 lakes, 4 streams and Korana River. In Figure 1(a), all sampling points are numbered: springs: (1) Bijela Rijeka, (2) Crna Rijeka and (3) Plitvica; (4) Matica Stream, confluence of Crna and Bijela Rijeka; lakes: (5) Prošće, (6) Gradinsko, (7) Burgetić, (8) Kozjak 1 and (9) Kozjak 2, and (10) Novokovića Brod; (11) Korana

River, and tributary streams, (12) Sušanj, (13) Rječica and (14) Sartuk. The cross section of the Plitvice Lakes (Figure 1(b)) shows the sampling points from springs over the lakes to the Korana River in the downstream direction.

Surface water samples were collected several times a year in the period 2003–2007 including all seasons for physico-chemical measurement and less frequently during 2002–2007 for the determination of the $\delta^{13}C_{DIC}$. *In situ* measurements and sampling of water were performed ~0.5 m below the surface. Water samples were stored in 1–litre dark-glass bottles in the refrigerator until analyses. The concentration of HCO_3^- was determined by titration with 0.1 M HCl. The CO_2 concentration was derived from the temperature and the HCO_3^- and H^+ concentrations [3]. The saturation index of $CaCO_3$ was calculated as $I_{sat} = \text{IAP/K}$, where IAP is the ion activity product and K is the solubility product. Temperature and pH were measured *in situ* by a portable WTW LF 191. Waters for DOC analyses were collected in bottles washed with chromium sulphuric acid. DOC was measured by catalytic combustion with an IR detector (TOC-V (CSH/CSN analyzer), Shimadzu).

$\delta^{13}C$ values of DIC in water were determined in the carbonate precipitated from the water immediately after sampling. Carbonate was precipitated with $BaCl_2$ at pH>8, and $BaCO_3$ was filtrated, dried at 60°C and stored in plastic bags. Carbon isotope analysis was performed in the Stable Isotope Laboratory at Rijeka University using a modified method of McCrea [13]. For each sample, three different vials were filled with approximately 200 µg of water sample, then capped and flushed with helium gas. A few drops of anhydrous phosphoric acid were injected with a syringe into each vial. The reaction with the carbonate at 72°C produced carbon dioxide, which was analysed in continuous flow mode in a Gas Bench II/Delta Plus^{XP} mass spectrometer combination (Thermo Fisher Scientific, Bremen). In each run, three international standards (NBS-19, IAEA-CO-1 and IAEA-CO-9) were included for normalisation purposes. The resulting carbon isotope ratios were reported in the delta (δ) notation as per mil (‰) deviation relative to the Vienna Standard Pee Dee Belemnite (V-PDB): $\delta(‰) = [(R_{sample}/R_{standard}) - 1] \times 10^3$. The analytical precision was better than ±0.05 ‰.

4. Results and discussion

4.1. *Water chemistry*

Results of temperature, pH, HCO_3^- and CO_2 concentrations (Figure 2(a)–(d)), saturation index of $CaCO_3$ (I_{sat}) (Figure 3) and DOC (Figure 4) are given for a total distance of about 12 km in the downstream direction from the springs across the lakes to the Korana River. The sampling points which are not in the main stream direction (Figure 1), for example, Plitvica spring (3), and streams that form tributaries, Sušanj (12), Rječica (13) and Sartuk (14), are encircled separately in the figures. The results are presented for each sampling date in different months for the period 2003–2007. Additionally, the results are separated by dotted vertical lines to distinguish the spring, lake and stream waters. The numerical values of all the measured parameters are also presented in Table 1 as the range of minimum and maximum values and mean values for all 14 sampling points in downstream order.

The water temperatures of the three main springs (Figure 2(a)) were very uniform during the studied years. The lakes and Korana River showed typical seasonal variations in the water temperature with a big winter–summer difference of approximately 20°C, while in tributaries, the seasonal variations were not so significant.

The Plitvice Lakes waters had pH values in the range of 7.3–8.7. The low pH values (7.3–7.9) increased within several hundred meters from the karst springs due to rapid outgassing of CO_2 from spring waters (Figure 2(b) and (d)). In the lake area, the pH value slowly increased downstream due to a decrease in CO_2 level.

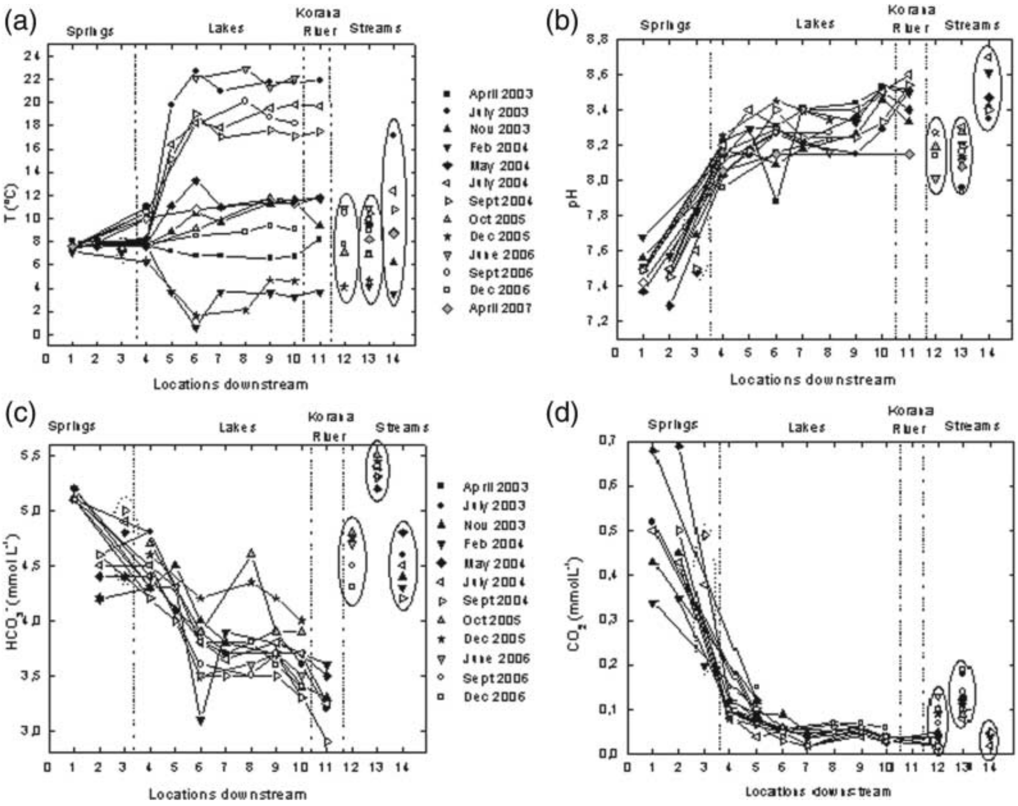

Figure 2. Monthly and downstream changes in (a) temperature, (b) pH, (c) HCO_3^- and (d) CO_2 concentration in the Plitvice Lakes system. Numbers represent sampling sites from Figure 1. Sites which are not in the main stream direction are encircled separately.

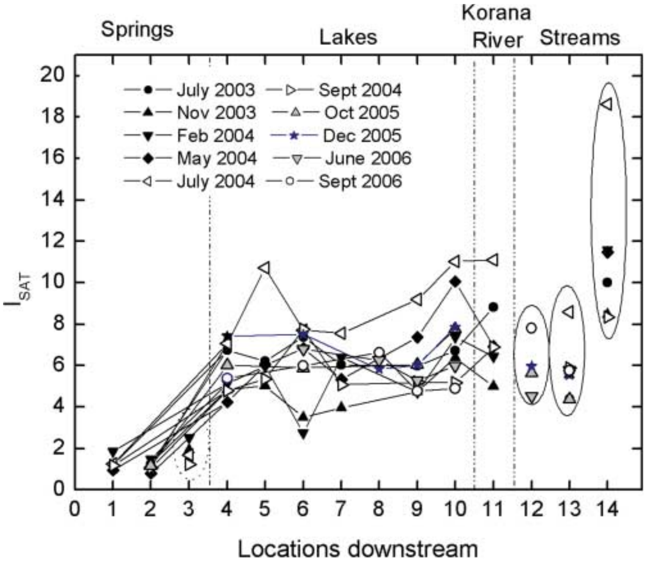

Figure 3. Monthly and downstream changes in the saturation index of $CaCO_3$ (I_{sat}) in the Plitvice Lakes system. Numbers represent sampling sites from Figure 1. Sites which are not in the main stream direction are encircled separately.

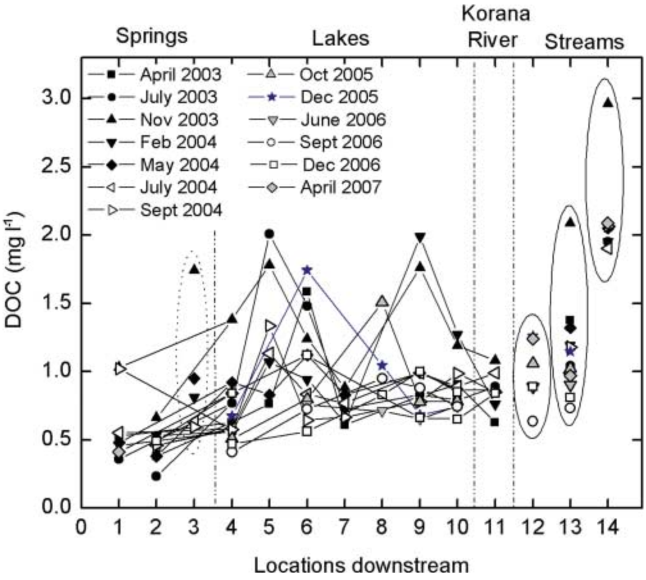

Figure 4. Monthly and downstream changes in DOC in the Plitvice Lakes system. Numbers represent sampling sites from Figure 1. Sites which are not in the main stream direction are encircled separately.

The main component of DIC in the pH range of the Plitvice Lakes waters is HCO_3^- [3]. The bicarbonate concentration decreased in the downstream direction from 4.2–5.2 mmol l^{-1} in the springs to 2.8 – 3.6 mmol l^{-1} in the Korana River (Table 1, Figure 2(c)).

The highest CO_2 concentrations were found in the springs (0.2–0.7 mmol l^{-1}) (Figure 2(d)) originating from OM degradation and root respiration in the soil of the groundwater-recharged area. Groundwater oversaturated with CO_2 dissolved mineral carbonates, mainly limestone, and became rich in bicarbonate. Thus, DIC originated from atmospheric/soil CO_2 and from carbonate dissolution. The CO_2 content decreased downstream and attained a value of 0.05 mmol l^{-1} in the open lake water. The downstream decrease in the CO_2 and HCO_3^- concentrations was the result of CO_2 degassing and decomposition of bicarbonate forming carbonates, as well as uptake of HCO_3^- by photosynthetic organisms (including freshwater algae, bacteria and aquatic green plants).

The result of these processes was reflected in the $CaCO_3$ saturation index I_{sat} (Figure 3). The lowest I_{sat} values, 1–2, were determined in spring waters, indicating equilibrium with respect to calcite; in this region, calcite did not precipitate. The significant increase in I_{sat} in the lake waters (3–10) and also in the Korana River indicated oversaturated waters with $CaCO_3$. In this region, the process of calcite precipitation in the form of tufa and lake sediments is very intense. In contrast, although the waters were highly oversaturated (I_{sat} values 4–18, similar to lake waters or even higher) in three tributary streams (12, 13 and 14), the calcite did not precipitate. All stream waters have flown through areas with forest soils rich in humic OM. Therefore, the input of dissolved humic substances could be significant. Higher DOC concentrations in stream waters, particularly in Sartuk brook (2–3 mg l^{-1}) (Figure 4), indicated this influence.

The DOC concentrations were generally low in lake waters, mostly 0.5–1 mg l^{-1}, but some higher values were observed in locations 5, 6 and 9. In these locations of Prošće Lake (5), Gradinsko Lake (6) and Kozjak Lake 2 (9), parts of the lakes in the near-shore area are covered with land vegetation and aquatic algae at lake bottom. In this case, enhanced primary production could increase the DOC concentration, but also DOC input from high productive areas in the watershed cannot be excluded [7].

Table 1. Range of minimum and maximum values and mean values of physical, chemical and isotopic results of waters in the Plitvice Lakes for 14 sampling points in downstream order.

		Temperature (°C)		pH		HCO_3^- (mmol l^{-1})		CO_2 (mmol l^{-1})	
Location no.	Location name	Range	Mean ± σ	Range	Mean ± σ	Range	Mean ± σ	Range	Mean ± σ
1	Bijela Rijeka Spring	7.1–8.1	7.6 ± 0.3	7.37–7.68	7.50 ± 0.09	5.1–5.2	5.13 ± 0.05	0.34–0.68	0.50 ± 0.11
2	Crna Rijeka Spring	7.6–8.0	7.8 ± 0.1	7.29–7.57	7.46 ± 0.09	4.2–4.6	4.42 ± 0.18	0.35–0.69	0.48 ± 0.11
3	Plitvica Spring	7.1–7.4	7.3 ± 0.1	7.48–7.83	7.62 ± 0.14	4.4–5.0	4.70 ± 0.28	0.20–0.49	0.37 ± 0.13
4	Matica Stream	6.3–11.0	8.8 ± 1.7	7.96–8.25	8.12 ± 0.09	4.2–4.8	4.47 ± 0.19	0.08–0.15	0.10 ± 0.02
5	Prošće Lake	3.7–19.8	11.7 ± 5.6	8.14–8.40	8.23 ± 0.10	4.0–4.5	4.25 ± 0.18	0.04–0.09	0.07 ± 0.02
6	Gradinsko Lake	0.6–22.7	12.4 ± 7.2	7.88–8.45	8.24 ± 0.15	3.1–4.2	3.74 ± 0.30	0.03–0.09	0.06 ± 0.02
7	Burgetići Lake	3.7–21.0	12.4 ± 6.3	8.18–8.41	8.29 ± 0.10	3.5–3.9	3.71 ± 0.14	0.02–0.05	0.03 ± 0.01
8	Kozjak Lake 1	2.1–22.9	13.5 ± 9.7	8.16–8.34	8.25 ± 0.08	3.5–4.6	3.97 ± 0.48	0.05–0.07	0.06 ± 0.01
9	Kozjak Lake 2	2.6–21.8	13.0 ± 6.2	8.08–8.44	8.28 ± 0.11	3.5–4.2	3.77 ± 0.18	0.04–0.07	0.06 ± 0.01
10	Novakovića Brod Lake	3.3–22.1	13.0 ± 6.3	8.18–8.53	8.38 ± 0.13	3.3–4.0	3.59 ± 0.23	0.03–0.06	0.04 ± 0.01
11	Korana River	3.7–21.9	13.0 ± 6.2	8.15–8.60	8.44 ± 0.15	2.9–3.6	3.29 ± 0.25	0.02–0.05	0.03 ± 0.01
12	Sušanj Stream	4.1–10.9	8.1 ± 2.8	8.01–8.27	8.18 ± 0.11	4.3–4.8	4.61 ± 0.21	0.07–0.13	0.10 ± 0.02
13	Rječica Stream	4.2–10.9	8.4 ± 2.3	7.93–8.30	8.14 ± 0.12	5.2–5.5	5.37 ± 0.10	0.08–0.19	0.13 ± 0.04
14	Sartuk Stream	3.7–17.1	9.8 ± 4.8	8.35–8.70	8.49 ± 0.14	4.2–4.8	4.47 ± 0.22	0.02–0.05	0.04 ± 0.01

		I_{sat}		DOC (mg l^{-1})		$\delta^{13}C_{DIC}$ (V-PDB ‰)	
Location no.	Location name	Range	Mean ± σ	Range	Mean ± σ	Range	Mean ± σ
1	Bijela Rijeka Spring	0.96–1.87	1.33 ± 0.31	0.36–1.03	0.60 ± 0.27	−12.88–(−12.07)	−12.48 ± 0.57
2	Crna Rijeka Spring	0.80–1.47	1.16 ± 0.21	0.23–0.66	0.45 ± 0.13	−13.43–(−11.68)	−12.56 ± 1.24
3	Plitvica Spring	1.23–2.51	1.84 ± 0.53	0.59–1.74	0.94 ± 0.47	−11.72–(−11.72)	−11.72
4	Matica Stream	4.23–7.43	5.74 ± 1.13	0.41–1.38	0.69 ± 0.26	−12.55–(−10.99)	−11.83 ± 0.63
5	Prošće Lake	5.03–10.72	6.55 ± 2.09	0.77–2.01	1.27 ± 0.47	−12.05–(−10.34)	−11.20 ± 1.21
6	Gradinsko Lake	2.74–7.74	6.21 ± 1.76	0.56–1.74	1.04 ± 0.38	−12.43–(−9.78)	−10.81 ± 0.92
7	Burgetići Lake	3.96–7.56	5.72 ± 1.23	0.61–0.88	0.73 ± 0.10	−10.61–(−9.97)	−10.29 ± 0.45
8	Kozjak Lake 1	5.83–6.63	6.24 ± 0.40	0.71–1.51	1.01 ± 0.31	−11.37–(−10.15)	−10.88 ± 0.64
9	Kozjak Lake 2	4.73–9.19	5.93 ± 1.41	0.65–1.99	0.99 ± 0.41	−11.69–(−9.93)	−10.86 ± 0.73
10	Novakovića Brod Lake	4.90–11.04	7.33 ± 1.98	0.65–1.27	0.88 ± 0.18	−11.08–(−9.53)	−10.34 ± 0.50
11	Korana River	4.50–11.11	7.53 ± 2.14	0.63–1.08	0.86 ± 0.14	−8.84–(−8.30)	−8.57 ± 0.38
12	Sušanj Stream	4.51–7.80	5.98 ± 1.37	0.64–1.26	0.99 ± 0.24	−12.95–(−11.73)	−12.37 ± 0.51
13	Rječica Stream	4.39–8.59	5.74 ± 1.15	0.73–2.09	1.14 ± 0.34	−12.55–(−11.54)	−11.95 ± 0.34
14	Sartuk Stream	8.34–18.62	11.41 ± 3.80	1.9–2.96	2.14 ± 0.37	−11.21–(−9.98)	−10.60 ± 0.87

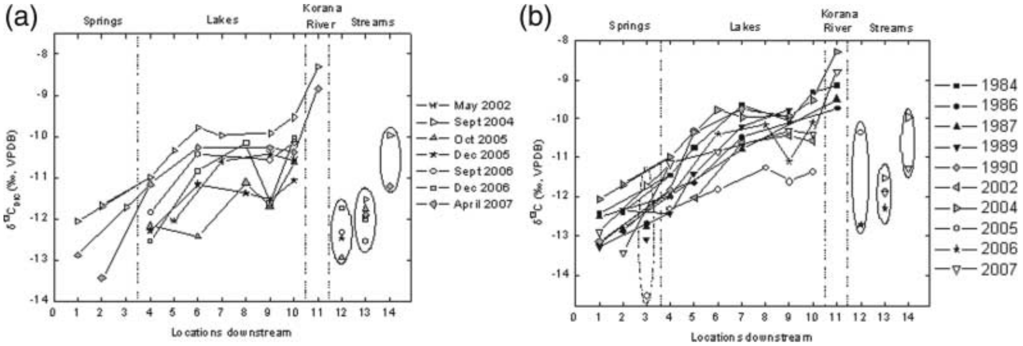

Figure 5. (a) Monthly and downstream changes in $\delta^{13}C_{DIC}$ in the Plitvice Lakes system for the period 2002–2007, (b) changes in mean yearly $\delta^{13}C_{DIC}$ in the downstream direction in the Plitvice Lakes system for the periods 1984–1990 and 2002–2007. Numbers present sampling sites from Figure 1. Sites which are not in the main stream direction are encircled separately.

4.2. *δ^{13}C values of DIC*

$\delta^{13}C_{DIC}$ values of the Plitvice Lakes waters collected in the period 2002–2007 are shown in Figure 5(a). The isotopic signature of DIC, which is the main source of carbon in the Plitvice Lakes water, is controlled by several biogeochemical processes, such as OM oxidation, dissolution of mineral carbonate, photosynthesis and respiration of phytoplankton, and exchange with the atmospheric CO_2. In the Plitvice Lakes, we distinguished springs, lakes and streams as three parts of the water flow system where different processes influence the isotope composition of DIC. The springs Bijela Rijeka, Crna Rijeka and Plitvica and the streams Sušanj and Rječica had more negative $\delta^{13}C_{DIC}$ values (between -13.5 and -11.5 ‰) than the lake waters and Korana River. The spring waters were supersaturated with CO_2 (Figure 2(d)), which originated from plant degradation and root respiration. The δ^{13}C values of these waters are generally between -33 and -22 ‰ [5,14,15]. Measurements of δ^{13}C values of soil humic material, leaves and twigs from the three spring areas at the Plitvice Lakes showed δ^{13}C values between -27.5 and -30.0 ‰ [16,17]. Dissolution processes of carbonate rocks (δ^{13}C around 0 ‰) with soil CO_2 (δ^{13}C around -28 ‰) in the recharge area of springs increased the concentration of HCO_3^- (Figure 2(c)). This mixing of biogenic and mineral DIC was also reflected in the $\delta^{13}C_{DIC}$ values between -13.5 and -11.5 ‰ at the Plitvice Lakes springs (Figure 5). The similar $\delta^{13}C_{DIC}$ values of the stream waters (locations 12 and 13) indicated similar processes involved in DIC formation. Both spring and stream waters are characterised by the absence of calcite precipitation in the water.

Degassing of CO_2 from the spring waters was very fast because of its high partial pressure in groundwater with respect to atmospheric CO_2 (Figure 2(d)); this led to increased $\delta^{13}C_{DIC}$ values. In the open lake area, the $\delta^{13}C_{DIC}$ values steadily increased in the downstream direction, with the highest values in the Korana River, -8.8 to -8.3 ‰ (Table 1, Figure 5). This downstream increase in $\delta^{13}C_{DIC}$ values was mainly due to the fractionation effect during both CO_2 degassing and calcite precipitation. Most submerged freshwater macrophites and algae obtained their carbon from the DIC. Thus, photosynthetic uptake of DIC species would contribute to ^{12}C depletion of the DIC of surrounding waters and cause further increase in $\delta^{13}C_{DIC}$ [18].

Using mean yearly $\delta^{13}C_{DIC}$ values for each location, Figure 5(b) compares $\delta^{13}C_{DIC}$ values measured in the period 2002–2007 with those of the period 1984–1990 [8,9]. The results showed no difference between the two periods; the ranges of $\delta^{13}C_{DIC}$ values in spring, lake and stream waters as well as the downstream increase in $\delta^{13}C_{DIC}$ were quite similar for both the periods. All $\delta^{13}C_{DIC}$ data were used for correlation with seasonal change (Figure 6). During the warm periods of the year, the photosynthetic activity of aquatic plants and the evaporation of water (both emphasised by temperature increase) resulted in more positive $\delta^{13}C_{DIC}$ values compared

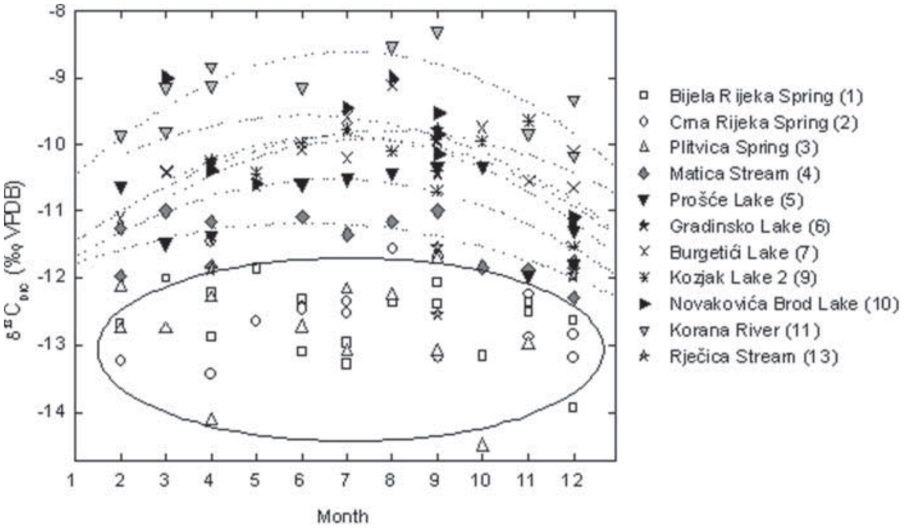

Figure 6. Seasonal variations in $\delta^{13}C_{DIC}$ values for spring, lake and stream waters. Encircled values without seasonal variations correspond to $\delta^{13}C_{DIC}$ of spring waters.

with winter. Such seasonal variations were more pronounced in the lake waters and in the Korana River where the seasonal temperature variation was significant (Figure 2(a)). The maximum difference between winter and summer $\delta^{13}C_{DIC}$ values was observed in the Korana River, 1.6 ‰, and in lake waters it was 1–1.5 ‰. Springs had a uniform temperature throughout the year and a seasonal variation in $\delta^{13}C_{DIC}$ values was not observed (Figure 6).

The linear correlation between the increasing DIC concentration and the decreasing $\delta^{13}C_{DIC}$ values in the waters of the Plitvice Lakes system (Figure 7, correlation coefficient $R = -0.65$) was also the result of the processes discussed above. In the spring waters, the dominant processes were oxidation of OM and dissolution of carbonate minerals. Therefore, the water was saturated with CO_2 and HCO_3^-, and the $\delta^{13}C_{DIC}$ values were more negative compared with those of the lake, river and stream waters. Under these conditions, I_{sat} of $CaCO_3$ was low and calcite did not

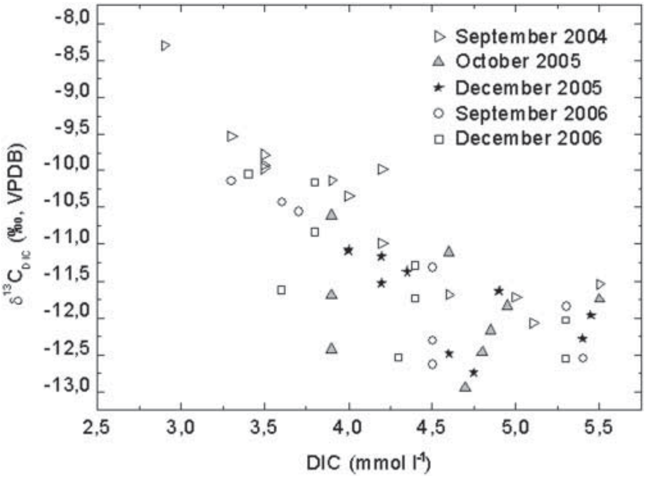

Figure 7. Relation between $\delta^{13}C_{DIC}$ values and DIC concentration in waters of the Plitvice Lakes system.

precipitate from the water. Downstream in the lake waters and in the Korana River, the processes of CO_2 outgassing, photosynthetic activity of aquatic plants and water evaporation occurred, resulting in an increase in I_{sat} and $\delta^{13}C_{DIC}$ values and a decrease in DIC concentration. In this area, the conditions for calcite precipitation were fulfilled and the formation of tufa deposits and lake sediments was very intense. A similar correlation of DIC and $\delta^{13}C_{DIC}$ ($R = -0.84$) was observed for Krka River by Lojen *et al.* [19] with a similar range of $\delta^{13}C_{DIC}$ values (-14.0 to -8.5 ‰) but with lower DIC concentrations (1.8 to 2.9 mmol l^{-1}).

4.3. *Correlation between DOC concentrations and $\delta^{13}C_{DIC}$*

The correlation between DOC concentrations and $\delta^{13}C_{DIC}$ values (Figure 8) gave additional information about the ecosystem of the Plitvice Lakes, particularly about the photosynthetic activity. Compared with other ecosystems [20,21], the DOC concentrations in the Plitvice Lakes were relatively low, within 0.4–3.0 mg l^{-1}, and the $\delta^{13}C_{DIC}$ values were in the range of -13.4 to -8.3 ‰ (Figure 8, Table 1). In St. Lawrence River [20], three types of ecosystems with respect to the carbon cycle can be differentiated: those dominated by (1) CO_2 exchange with the atmosphere ($\delta^{13}C_{DIC}$ -3 to $+3$ ‰, DOC concentration < 5 mg l^{-1}), (2) photosynthesis ($\delta^{13}C_{DIC}$ -12 to -1 ‰, DOC concentration 3–15 mg l^{-1}) and (3) respiration and decomposition of OM including baseflow ($\delta^{13}C$ -14 to -8 ‰ and high DOC concentrations). According to the ecosystems mentioned above, we can conclude that the dominating processes in the Plitvice Lakes were photosynthesis and CO_2 exchange with the atmosphere.

The springs Bijela Rijeka and Crna Rijeka and the streams Sušanj, Rječica and Matica (upper flow of the Plitvice Lakes, Figure 1) had the most negative $\delta^{13}C_{DIC}$ values (-13.5 to -11.5 ‰), indicating input of ^{13}C-depleted DIC from groundwater. Waters in the open lake area (Gradinsko, Kozjak and Novakovića Brod, Figure 1) and in the Korana River had less negative $\delta^{13}C_{DIC}$ values (-11.5 to -9.5 ‰) and low DOC concentrations, <1 mg l^{-1} (Figure 8, encircled values). In this area, the calcite precipitation in the form of tufa and lake sediments was very intense. Photosynthesis was more pronounced in open lake water; this was confirmed by higher summer $\delta^{13}C_{DIC}$ values (Figure 6). Low DOC concentrations showed the absence of allochthonous input,

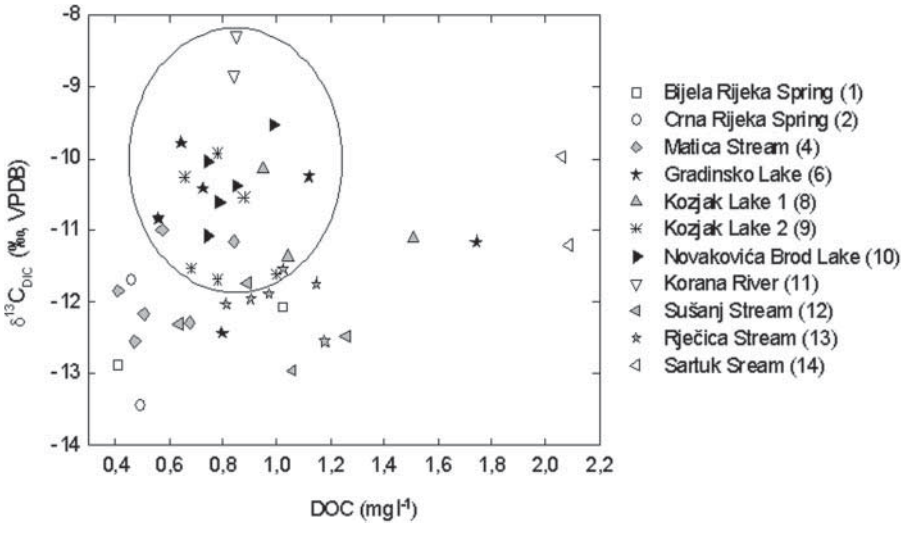

Figure 8. Relation between $\delta^{13}C_{DIC}$ values and DOC concentrations in waters of the Plitvice Lakes system. Encircled values correspond to the lake waters and the Korana River where calcite precipitation is very pronounced.

and $\delta^{13}C_{DIC}$ values indicated the balance between primary productivity and OM degradation. Water–atmosphere CO_2 exchange also contributed to the $\delta^{13}C_{DIC}$ increase in the downstream flow. The highest $\delta^{13}C_{DIC}$ has been measured in the Korana River (−8.5 ‰). This was the last sampling point in the Plitvice Lakes system (the lowest in the downstream flow) where photosynthesis and exchange of atmospheric CO_2 and DIC were most pronounced. The Sartuk stream was an exception, which had the highest DOC concentrations (>2 mg l^{-1}) and $\delta^{13}C_{DIC}$ −11 to −10 ‰, implying that this system was governed mainly by photosynthesis [20]. However, there was no calcite precipitation in the Sartuk stream, although the physico-chemical conditions were fulfilled ($I_{sat} > 8$, Figure 4). The reason could be that the presence of DOC was mainly allochthonous, and it could inhibit calcite precipitation [22].

4.4. *Correlation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{carb}$*

We correlated $\delta^{13}C$ of lake sediment carbonates ($\delta^{13}C_{carb}$) collected at four lakes in the Plitvice Lakes [9] with average $\delta^{13}C_{DIC}$ in waters close to the sediment sampling site (Figure 9). For $\delta^{13}C_{carb}$ values, we used mean values of vertical profiles of surface lake sediments from two big lakes, Prošće, first 40 cm (mean $\delta^{13}C_{carb} = -8.8 \pm 0.2$ ‰), and Kozjak, first 25 cm (mean $\delta^{13}C_{carb} = -8.6 \pm 0.2$ ‰). For two small lakes, Gradinsko and Kaluđerovac, two mean $\delta^{13}C_{carb}$ values for each 40 cm long profile were applied: the first 15 cm (Gradinsko 2 and Kaluđerovac 2) and deeper layers below 15 cm (Gradinsko 1 and Kaluđerovac 1). A good correlation between Prošće, Gradinsko 1, Kozjak and Kaluđerovac 1 was obtained, showing an increase in both $\delta^{13}C_{DIC}$ and $\delta^{13}C_{carb}$ values in the downstream direction (Prošće is the uppermost lake and Kaluđerovac is the lowermost lake, next to Novokovića Brod Lake) (Figure 1, site nos. 5 and 10). Differences between average $\delta^{13}C_{DIC}$ and $\delta^{13}C_{carb}$ of surface lake sediments were 2.1 ‰ in Prošće, 1.9 ‰ in Gradinsko 1, 1.8 ‰ in Kozjak and 1.7 ‰ in Kaluđerovac 1, showing enrichment of the solid carbonate phase (calcite) in ^{13}C relative to DIC in water. The equilibrium fractionation ε between DIC and precipitated calcite is ∼2 ‰ in the range of pH and temperature of the Plitvice Lakes

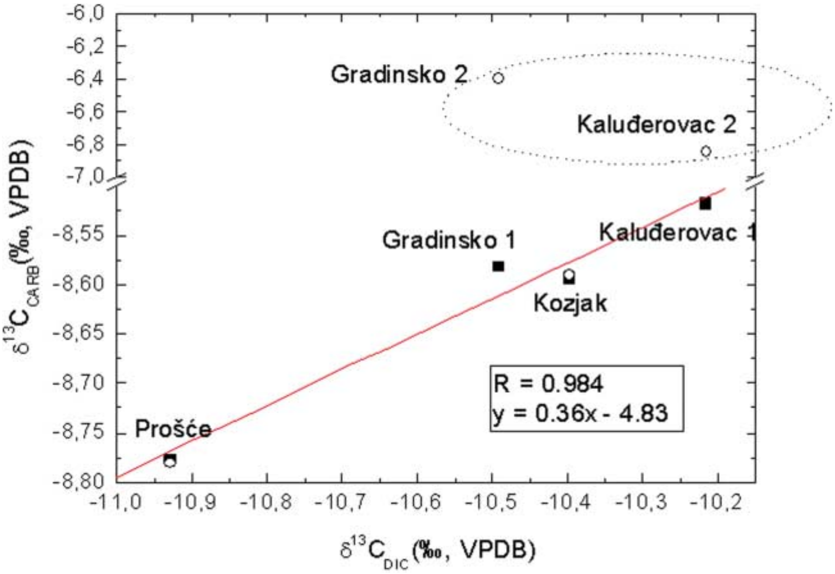

Figure 9. Relation between $\delta^{13}C_{DIC}$ and $\delta^{13}C_{carb}$ at four lake sediments in the Plitvice Lakes. Gradinsko 1 and Kaluđerovac 1 present mean $\delta^{13}C_{CARB}$ for the sediment layers below 15 cm, and Gradinsko 2 and Kaluđerovac 2 present mean $\delta^{13}C_{CARB}$ for the first 15 cm of the same sediment cores.

water (Figure 2(a) and (b)) [23,24]. According to the enrichment factors for the four lake sediments, we may conclude that the calcite precipitation in form of lake sediment occurred under near-equilibrium conditions. In contrast, the less negative values of $\delta^{13}C_{carb}$ for Gradinsko 2 (−6.4 ‰) and Kaluđerovac 2 (−6.8 ‰) indicated non-equilibrium conditions of precipitation. A possible reason for the increase in $\delta^{13}C_{carb}$ in the surface sediment layers (the first 10–15 cm) of the two small lakes Gradinsko and Kaluđerovac could be the increase in primary productivity in these two lakes where an increase in eutrophication has been observed in the last few decades. Primary productivity due to photosynthesis preferentially consumes $^{12}CO_2$ from DIC in water [18] and precipitated calcite thus is enriched by ^{13}C.

In previous investigations of tufa and lake sediments in the Plitvice Lakes, it was shown that the mean $\delta^{13}C$ values of lake sediments taken from 12 m long sediment cores [11], -8.9 ± 0.2 ‰ and -8.6 ± 0.1 ‰ for the Prošće Lake and the Kozjak Lake, respectively, were similar to the mean $\delta^{13}C$ for tufa from the Plitvice Lakes, -8.3 ± 1.0‰. However, sediments showed much smaller fluctuations [25]. The narrow range of lake sediment $\delta^{13}C$ indicated more stable and isotopic equilibrium conditions during calcite precipitation when compared with those which were associated with tufa precipitation. Calcite precipitation in form of tufa occurred very often on waterfall barriers covered with aquatic plants. Precipitation was accelerated by rapid outgassing of CO_2 from the water, a more intensive evaporation process, isotope exchange between atmospheric CO_2 and DIC in the water and photosynthesis. Under these environmental conditions, precipitation of tufa occurred in non-equilibrium conditions and $\delta^{13}C$ values varied between −6 and −9 ‰ [25]. Lojen *et al.* [19] investigated $\delta^{13}C$ and $\delta^{18}O$ variability in recent freshwater carbonates in the Krka River, Croatia, and showed that the $\delta^{13}C$ of tufa varied between −7.8 and −10.2 ‰ and the $\delta^{13}C$ of DIC varied between −8 and −14 ‰. Differences between average $\delta^{13}C_{DIC}$ and bulk tufa at four sites showed that precipitation occurred under non-equilibrium conditions and was probably influenced by vital effects and microenvironments around the nucleation sites.

5. Conclusions

The physical and chemical conditions of calcite precipitation in form of lake sediment/tufa in the waters of the Plitvice Lakes system, in correlation with $\delta^{13}C_{DIC}$, showed significant differences between spring, lake and stream waters, but also downstream at a distance of approximately 12 km.

In the area of the lakes where the process of calcite precipitation was very intense, the waters were oversaturated, and the I_{sat} of $CaCO_3$ varied from 4 to 10. The lake waters were characterised by a high seasonal temperature variation of ~20°C, pH values of 8.2–8.6 increasing downstream and a decreasing concentration of bicarbonates as the main components of DIC (from 4.5 to 3.5 mmol l^{-1}). Correlations between pH values and I_{sat} ($R = 0.87$) and $\delta^{13}C_{DIC}$ values ($R = -0.45$) were explained by CO_2 degassing and decomposition of bicarbonate/calcite precipitation.

In spring and tributary stream waters, calcite did not precipitate. Water analyses of the three main springs showed a very stable temperature during the year (7.1–8.1°C), low pH values of 7.3–7.8 with high concentrations of bicarbonate (4.2–5.2 mmol l^{-1}) and CO_2 (0.2–0.7 mmol l^{-1}), and equilibrium conditions with respect to calcite ($I_{sat} = 1$–2). In three tributaries, calcite was apparently not precipitated in spite of high oversaturation, most probably due to the input of allochthonous material (DOC) from the high productive areas in the watershed.

The $\delta^{13}C_{DIC}$ values showed a steady increase in the downstream direction, rising from the springs (mean $\delta^{13}C_{DIC}$ −12.7 ‰) to the lakes and Korana River (mean $\delta^{13}C_{DIC}$ −8.6 ‰). The negative HCO_3^-–$\delta^{13}C_{DIC}$ correlation ($R = -0.65$) may be explained by the processes of calcite precipitation and CO_2 degassing as well as biological activity of the aquatic algae and macrophites through photosynthesis. The downstream increase in $\delta^{13}C_{DIC}$ correlated with the increase in the $\delta^{13}C$ values of calcite in the lake sediments in the same direction, showing that calcite was mainly of autochthonous origin precipitated under equilibrium conditions. Non-equilibrium conditions for calcite precipitation were observed in the lake waters with enhanced eutrophication, that is, with an increased primary productivity. Seasonal variations in $\delta^{13}C_{DIC}$ were only observed in lake waters influenced by temperature variation and not in spring waters since their temperatures were stable during the year.

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