

# Origin and cycling of riverine inorganic carbon in the Sava River watershed (Slovenia) inferred from major solutes and stable carbon isotopes

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**Abstract** The Sava River and its tributaries in Slovenia represent waters strongly influenced by chemical weathering of limestone and dolomite. The carbon isotopic compositions of dissolved inorganic carbon (DIC) and suspended organic carbon (POC) fractions as well as major solute concentrations yielded insights into the origin and fluxes of carbon in the upper Sava River system. The major solute composition was dominated by carbonic acid dissolution of calcite and dolomite. Waters were generally supersaturated with respect to calcite, and dissolved CO<sub>2</sub> was about fivefold supersaturated relative to the atmosphere. The  $\delta^{13}\text{C}$  of DIC ranged from  $-13.5$  to  $-3.3\text{‰}$ . Mass balances for riverine inorganic carbon suggest that carbonate dissolution contributes up to 26%, degradation of organic matter  $\sim 17\%$  and exchange with atmospheric CO<sub>2</sub> up to 5%. The concentration and stable isotope diffusion models indicated that atmospheric exchange of CO<sub>2</sub> predominates in streams draining impermeable shales and clays while in the carbonate-dominated watersheds dissolution of the Mesozoic carbonates predominates.

**Keywords** Carbon cycling · Stable carbon isotopes · River ecosystem · Sava River

## Introduction

Rivers are the major pathways for the transport of carbon (C) from the continents to the oceans. Global river carbon fluxes are estimated to be 0.4 Pg C/year for total organic C (evenly divided between particulate and dissolved phases) and 0.4 Pg C/year for dissolved inorganic C (DIC). While these bulk fluxes are small components of the global C cycle, they are significant compared to the net oceanic uptake of anthropogenic CO<sub>2</sub> (Sarmiento and Sundquist 1992), and the inter-hemispheric transport of carbon in the oceans (Aumont et al. 2001). The global riverine flux of dissolved inorganic carbon to the ocean is about  $0.38 \times 10^{15}$  g/year (Meybeck 1993), similar in magnitude to the global riverine flux of organic carbon to the oceans, which is estimated to be  $0.4 \times 10^{15}$  g/year (Meybeck 1982; Ittekkot 1988). Investigations of riverine dissolved constituents and stable carbon isotope compositions of dissolved inorganic carbon (DIC) have been employed in several river systems for various purposes, such as to quantify rock weathering rates and carbon sources (e.g. Pawellek and Veizer 1994; Pawellek et al. 2002; Roy et al. 1999; Gaillardet et al. 1999a, b; Grosbois et al. 2000; Karim and Veizer 2000; Chen et al. 2002; Picouet et al. 2002), to identify carbon mass transport and

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cycling rates (e.g. Telmer and Veizer 1999; Barth et al. 2003; Raymond and Cole 2003; Wu et al. 2007), and to evaluate biogeochemical processes and anthropogenic inputs in rivers (e.g. Barth and Veizer 1999; Karim and Veizer 2000; Barth et al. 2003; Weiguang et al. 2003; Wachniew 2006).

Carbonate mineral dissolution commonly dominates solute inputs to rivers and also plays an important role in the transformation of terrestrial organic carbon in soils to inorganic carbon (Mayorga et al. 2005). Given the high reactivity and solubility of carbonates, the flux of DIC from sites of initial carbonate dissolution to ground and surface waters should increase with increasing water flux and soil zone  $p\text{CO}_2$  (e.g. Reardon et al. 1979; Van Breenan and Protz 1988). Studies of the carbonate system of major world rivers (e.g. the Amazon, Yangtze, and Rhine) show  $p\text{CO}_2$  in excess of 10 times atmospheric values, and thus these large rivers are a net source of  $\text{CO}_2$  to the atmosphere. Because a large fraction of the dissolved  $\text{CO}_2$  originates from terrestrial organic matter, this effectively transfers carbon from storage on the continents to rivers, with some fraction ultimately reaching the oceans (Stallard 1980; Kempe 1982; Gao and Kempe 1987; Barth et al. 2003).

Concentrations of DIC and its stable carbon isotope ratios ( $\delta^{13}\text{C}_{\text{DIC}}$ ) are governed by processes occurring in the river system, and these vary seasonally. Changes in DIC concentrations result from carbon addition or removal from the DIC pool, while changes of  $\delta^{13}\text{C}_{\text{DIC}}$  result from the fractionation accompanying transformation of carbon or from mixing of carbon from different sources (Atekwana and Krishnamurthy 1998). The major sources of carbon to riverine DIC loads are dissolution of carbonate minerals, soil  $\text{CO}_2$  derived from root respiration and from microbial decomposition of organic matter (often mainly of terrestrial origin but also including aquatic production), and exchange with atmospheric  $\text{CO}_2$ . The major processes removing riverine DIC are carbonate mineral precipitation,  $\text{CO}_2$  degassing, and aquatic photosynthesis.

Organic matter production (photosynthesis) and utilization (respiration) affect the riverine DIC pool and its  $^{13}\text{C}$  composition to a variable degree. Several parameters (e.g. dissolved oxygen, silica concentrations, pH, and saturation indexes of calcite) can be

used to help determine the relative balance of respiration and photosynthesis (Neal et al. 1998).

In general, direct addition of  $^{13}\text{C}$ —depleted biogenic  $\text{CO}_2$  by respiration would decrease the  $\delta^{13}\text{C}_{\text{DIC}}$  of the riverine DIC pool (Buhl et al. 1991; Pawellek and Veizer 1994; Taylor and Fox 1996; Yang et al. 1996), while photosynthetic uptake of DIC preferentially removes  $^{12}\text{C}$ , enriching the  $\delta^{13}\text{C}_{\text{DIC}}$  of the riverine DIC pool (Pawellek and Veizer 1994; Flintrop et al. 1996; Yang et al. 1996).  $\text{CO}_2$  exchange with the atmosphere, which has a  $\delta^{13}\text{C}$  value  $-7.8\text{‰}$  (Levin et al. 1987), would result in an isotopic enrichment with  $^{13}\text{C}$  in DIC (Buhl et al. 1991; Pawellek and Veizer 1994; Taylor and Fox 1996; Yang et al. 1996).

This study is the first comprehensive investigation of the chemical and isotopic composition of dissolved and suspended constituents of the Sava River watershed in Slovenia (Fig. 1). The Sava River represents an “ideal natural laboratory” for studying biogeochemical processes and tracing the riverine carbon cycle as a result of its geologically heterogeneous composition, relatively high specific discharge, and limited aquatic photosynthesis (Urbanc–Berčič 1999). The high flow rate and limited presence of aquatic autotrophs in the Sava River render carbon exchange though photosynthesis relatively unimportant, and hence this study focused on: (1) dissolution of carbonates, (2) degradation of organic matter, (3) equilibration with atmospheric  $\text{CO}_2$  regulating the inorganic carbon system.

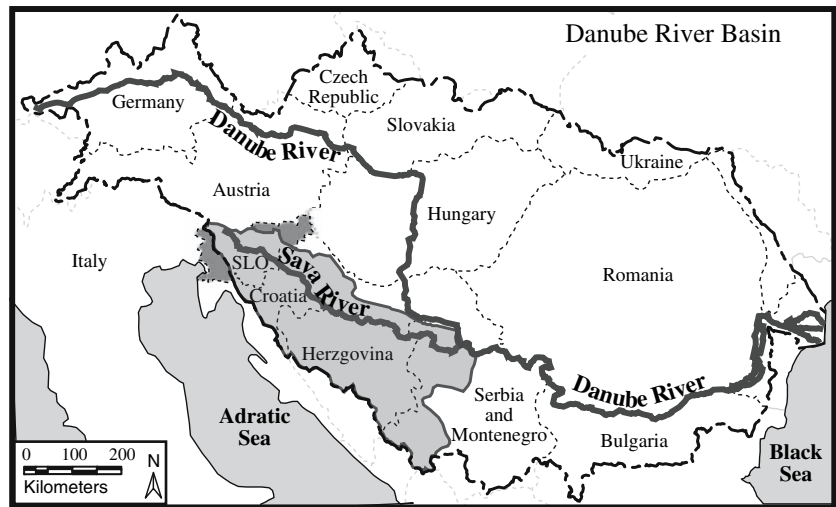
The main objectives of the current study were: (1) understand the major solute ( $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , Si and DOC) and stable carbon isotope dynamics ( $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{POC}}$ ) of the Sava River system through time and space, and (2) to evaluate and quantify riverine carbon sources, sinks and fluxes in the river. We employed thermodynamic modelling, total and  $^{13}\text{C}$  mass balance of dissolved inorganic carbon (DIC), and a diffusive evasion model to estimate the time needed for dissolved  $\text{CO}_2$  in river water to equilibrate with atmospheric  $\text{CO}_2$ .

## Materials and methods

### Characterization of the Sava River drainage basin

The characteristics of the Sava River watershed are summarized in Table 1 and a map of sampling

**Fig. 1** General map of the Danube River drainage basin indicating the location of Slovenia (SLO) and the Sava River study area



locations is presented in Fig. 2A. The Sava River, the largest river in Slovenia and a tributary of the Danube (the second largest river in Europe) (Fig. 1), contributes about 25% of the total discharge of the Danube, and comprises 15% of the total Danube River watershed (Haskoning 1994). Details on stream major and minor element geochemistry discharge and carbonate weathering fluxes for Slovenian watersheds including the Sava are presented elsewhere (Kanduč 2006; Szramek 2006; Szramek et al. 2007).

The Sava River originates in the Triassic carbonate hinterland at Zelenci (Fig. 2A, location 1) as the Sava Dolinka, and from the karst spring Savica (Fig. 2A, location 4) as the Sava Bohinjka. The confluence of these two sources is at Radovljica (Fig. 2A, location 6). Thereafter the river is named the Sava and finishes its course at Belgrade, merging with the Danube. The length of the Sava in Slovenia from the source of the Sava Dolinka to the national border with Croatia is 219 km.

Discharge regimes of the Sava River are controlled by precipitation and the configuration of the landscape. In the upper part of the Sava a snow–rain regime prevails and in the central and lower part a rain–snow regime prevails (Table 1; Hrvatin 1998). Annual discharge maxima are characteristic in spring and late summer, while discharge minima occur in the summer and winter months. The mean annual long-term discharge (from the years 1960–1991) for the gauging stations increases from 17 m<sup>3</sup>/s of the upper section of the Sava at Radovljica (location 6), to 182 m<sup>3</sup>/s of the central section at

Hrastnik (location 16) and to 290 m<sup>3</sup>/s in the lower section of the river at Čatež (location 22) (ARSO 2004–2005). Discharges are also controlled by hydrothermal outflows along the Sava River (locations 3, 10, 18). The discharge conditions for the Sava River and its tributaries during the study ranged from 2 m<sup>3</sup>/s to 344 m<sup>3</sup>/s during spring 2004 and from 1 m<sup>3</sup>/s to 144 m<sup>3</sup>/s during late summer 2004, and from 0.3 m<sup>3</sup>/s to 128 m<sup>3</sup>/s during winter 2004, respectively (Table 1). Discharge values, presented in Table 1, were available for sampling sites that are maintained and monitored by the Slovenian Environmental Agency (ARSO 2004–2005). Over the duration of the field study, riverine discharge underwent a typical annual cycle from highest discharges in the spring to the lowest discharge values in the winter (Table 1).

The watershed of the Sava extends in a NW–SE direction comprising almost half the surface area of Slovenia, and has a heterogeneous geological composition (Fig. 2B). Pleistocene fluvioglacial sediments form terraces at the confluence of the Sava Bohinjka and Sava Dolinka Rivers; downstream from the city of Ljubljana the watershed is mainly composed of Permo–Carbonian clastic sediments, which alternate with Triassic carbonates in the Zasavje region, an area of intensive mining, transitioning to Miocene sandstones, clays and gravels on the left bank of the river. In the Krško–Brežice area the watershed mainly consists of terraced Pleistocene sediments. The catchments of the Sava's tributaries are composed of Triassic and Jurassic carbonates,

**Table 1** Hydrological characteristics of the Sava River watershed

Location	Sampling point	Height above sea level (m)	Distance from the spring (km)	Catchment area A (km <sup>2</sup> )	Discharge regime (1961–1990) after Hrvatin (1998)	Spring 2004 Q (m <sup>3</sup> /s)	Late summer 2004 Q (m <sup>3</sup> /s)	Winter 2005 Q (m <sup>3</sup> /s)
1	Sava Dolinka spring	830	0.0		Alpine high mountain snow—rain regime			
2	Sava Dolinka Dovje <sup>a</sup>	704	18.0	257	Alpine high mountain snow—rain regime	13	11	7
3	Sava Dolinka Šobec <sup>a</sup>	459	39.8	505	Alpine high mountain snow—rain regime	42	29	15
4	River Savica <sup>a</sup>	700	42.6	667	Alpine high mountain snow—rain regime	8	n.d.	n.d.
5	Sava Bohinjka Nomenj <sup>a</sup>	509	42.6	355	Alpine high mountain snow—rain regime	49	11	3
6	Sava Otočce <sup>a</sup>	415	51.7	895	Alpine high mountain snow—rain regime	76	40	21
7	Tributary Tržiška Bistrica <sup>a</sup>	422	56.8	121	Alpine middle mountain snow—rain regime	10	2	3
8	Tributary Kokra <sup>a</sup>	407	65.7	220	Alpine middle mountain snow—rain regime	8	4	2
9	Sava Kranj <sup>a</sup>	350	65.7	1201	Alpine middle mountain snow—rain regime	100	32	10
10	Sava Smlednik <sup>a</sup>	336	76.3	2191	Alpine middle mountain snow—rain regime	138	67	92
11	Tributary Sora <sup>a</sup>	313	79.9	566	Dinaric rain—snow regime	21	4	7
12	Tributary Kaminška Bistrica <sup>a</sup>	260	100.4	208	Alpine high mountain snow—rain regime	10	0.7	0.3
13	Tributary regime	89	7	18	Ljubljana <sup>a</sup>	267	100.6	1763
Dinaric alpine rain—snow								
14	Tributary Jevnica	240	108.9		Alpine rain—snow regime			
15	Sava Litija <sup>a</sup>	230	123.5	4821	Alpine rain—snow regime	208	105	55
16	Sava Hrastnik <sup>a</sup>	210	148.4	5176	Alpine rain—snow regime	282	92	62
17	Tributary Savinja <sup>a</sup>	200	156.4	1842	Alpine rain—snow regime	39	25	12
18	Sava Radeče	193	159.1		Alpine rain—snow regime			
19	Tributary Mirna <sup>a</sup>	191	173.3	270	Dinaric alpine rain snow regime	4	2	1
20	Sava Brežice	145	202.9		Alpine rain—snow regime			
21	Tributary Krka <sup>a</sup>	140	203.7	2238	Dinaric alpine rain snow regime	53	27	12
22	Sava Mostec <sup>a</sup>	140	205.9	10186	Dinaric alpine rain snow regime	290	120	96

**Table 1** continued

Location	Sampling point	Height above sea level (m)	Distance from the spring (km)	Catchment area A (km <sup>2</sup> )	Discharge regime (1961–1990) after Hrvatin (1998)	Spring 2004 Q (m <sup>3</sup> /s)	Late summer 2004 Q (m <sup>3</sup> /s)	Winter 2005 Q (m <sup>3</sup> /s)
23	Tributary Sotla <sup>a</sup>	140	212.6	558	Panonian rain snow regime	6	2	2
24	Sava Bregana <sup>a</sup>	135	213.2	10881	Alpine rain—snow regime	344	144	128

n.d.—Not determined

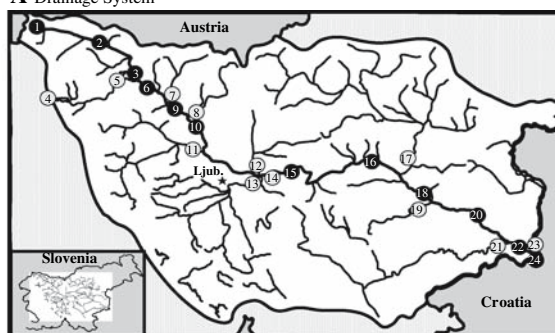
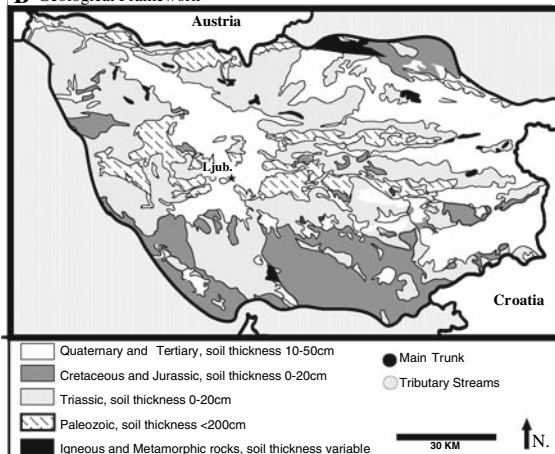
<sup>a</sup> Gauging station

Permo-Carbonian, Oligocene, Miocene clastic rocks and Pleistocene sediments (Buser 1987).

### Sampling protocols and field measurements

Sampling locations of the Sava watershed are presented in Fig. 2A. Surface water sampling locations were selected based on their relationship to confluences of the major and minor streams, typically sampled before and after the confluence. Sampling was performed at 24 locations (Table 1, Fig. 2A) in different seasons (spring = April, 2004, late summer = September 2004 and winter = January 2005), according to the discharge regimes of the Sava (12 sampling locations) and its tributaries (12 sampling locations). In this paper, location 24 is termed the Sava River “mouth” which is located at the border with Croatia. Temperature, conductivity, dissolved oxygen (DO), and pH measurements were performed in the field. The precision of dissolved oxygen saturation and conductivity measurements was  $\pm 5\%$ . Because pH is sensitive to CO<sub>2</sub> degassing and warming, water samples were collected in a large volume, air-tight container and pH was measured at least twice to verify electrode stability. The field pH was determined on the NBS scale using two buffer calibrations with a reproducibility of  $\pm 0.02$  pH unit.

Sample aliquots collected for chemical analysis were passed through a 0.45  $\mu\text{m}$  nylon filter into bottles and kept refrigerated until analyzed. Samples for cation (pre-treated with HNO<sub>3</sub>), anion and alkalinity analyses were collected in HDPE bottles. Samples for dissolved inorganic carbon (pre-treated with CuCl<sub>2</sub>) and  $\delta^{13}\text{C}_{\text{DIC}}$  analyses were stored in glass serum bottles filled with no headspace and sealed with septa.

**A** Drainage System**B** Geological Framework

**Fig. 2** (A) Detailed location map of the numbered sampling sites in the Sava River watershed. Sample sites are described in Table 1. (B) Geological framework of the Sava River watershed in Slovenia with information of soil thickness for different lithological units (after Buser 1987)

Samples for stable carbon isotope analysis of particulate organic carbon ( $\delta^{13}\text{C}_{\text{POC}}$ ) in spring and late summer 2004 were collected in LDPE bottles. The samples for stable isotope composition of particulate inorganic carbon ( $\delta^{13}\text{C}_{\text{PIC}}$ ) were taken only in late summer 2004. In addition, carbonate



rocks ( $n = 10$ ) of Mesozoic age which form the landscape of the Sava watershed were sampled from outcrops, as were gravels in the river channel for stable carbon analyses ( $\delta^{13}\text{C}_{\text{ca}}$ ). Also, representative terrestrial plants were collected during the growing season for stable carbon isotope analysis ( $\delta^{13}\text{C}_{\text{plant}}$ ).

### Laboratory analyses

Total alkalinity was measured within 24 h of sample collection by Gran titration (Gieskes 1974) with a precision of  $\pm 1\%$ . DIC concentrations were measured only in the samples collected in late summer 2004. Regression between alkalinity and DIC concentrations was 96% when both were measured.

Concentrations of dissolved Ca and Mg were determined using a Jobin Yvon Horiba ICP-OES with a precision of  $\pm 2\%$ . Concentrations of DIC were determined on a UIC Coulometrics  $\text{CO}_2$  coulometer with a precision of  $\pm 2\%$ . Dissolved organic carbon (DOC) concentrations were measured using by high-temperature platinum-catalyzed combustion followed by infrared detection of  $\text{CO}_2$  (Shimadzu TOC-5000A) with a precision of  $\pm 2\%$ .

The stable isotope composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) was determined with a Europa Scientific 20-20 continuous flow IRMS ANCA-TG preparation module. Phosphoric acid (100%) was added (100–200  $\mu\text{l}$ ) to a septum-sealed vial which was then purged with pure He. The water sample (6 ml) was injected into the septum tube and headspace  $\text{CO}_2$  was measured (modified after Miyajima et al. 1995; Spötl 2005). In order to determine the optimal extraction procedure for surface water samples, a standard solution of  $\text{Na}_2\text{CO}_3$  (Carlo Erba) with a known  $\delta^{13}\text{C}_{\text{DIC}}$  of  $-10.8 \pm 0.2\text{‰}$  was prepared with a concentration of either 4.8 meq/l (for samples with an alkalinity above 2 meq/l) or of 2.4 meq/l (for samples with alkalinity below 2 meq/l).

The carbon stable isotope composition of particulate organic carbon ( $\delta^{13}\text{C}_{\text{POC}}$ ) and plant material ( $\delta^{13}\text{C}_{\text{plant}}$ ) were determined with a Europa Scientific 20-20 continuous flow IRMS ANCA-SL preparation module. For POC, 1 l of the water sample was filtered through a Whatman GF/F glass fibre (0.7  $\mu\text{m}$ ). Filters were treated with 1 M HCl to remove carbonate material and then dried at  $60^\circ\text{C}$  and stored until analyses. Approximately 1 mg of particulate matter

was scraped from the filter for analysis. Plant material (0.5 mg) was analyzed with no acid pretreatment. NBS 22 (oil) and IAEA-CH 7 were used as reference materials to relate results to VPDB standards.

Particulate inorganic carbon ( $\delta^{13}\text{C}_{\text{PIC}}$ ) collected on filters was measured by placing the filters into ampoules, which were capped, flushed with helium, and then reacted with anhydrous  $\text{H}_3\text{PO}_4$  for 1 day at  $25^\circ\text{C}$ . The released  $\text{CO}_2$  was then measured with a Europa Scientific 20-20 continuous flow IRMS ANCA-TG preparation module. Carbonate rocks ( $n = 10$ ) were first ground to powder in an agate mortar and then 2 mg of sample was transformed to  $\text{CO}_2$  by the same acid treatment. NBS 18 and NBS 19 were used as reference materials. All stable isotope results for carbon are expressed in the conventional delta ( $\delta$ ) notation, defined as per mil (‰) deviation from the reference standard VPDB. Precision was  $\pm 0.2\text{‰}$  for  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{POC}}$ ,  $\delta^{13}\text{C}_{\text{plant}}$ ,  $\delta^{13}\text{C}_{\text{PIC}}$  and  $\delta^{13}\text{C}_{\text{ca}}$ .

Thermodynamic modelling was used to evaluate  $\text{pCO}_2$  and the saturation state of calcite ( $\text{SI}_{\text{calcite}}$ ) using pH, alkalinity, and temperature as inputs to the PHREEQC speciation program (Parkhurst and Appelo 1999).

## Results

### Major solute chemistry

The major solute composition of the Sava River and its tributaries was dominated by  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Concentrations varied seasonally according to discharge (Table 1), with higher concentrations observed in late summer at lower discharge and lower concentrations during spring snow melt and the rainy season due to dilution. Dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are largely supplied by the weathering of carbonates with smaller contributions from silicate weathering, as indicated by the relatively high  $\text{HCO}_3^-$  and low Si concentrations (Tables 2–4).

Oxygen saturation and silica concentrations during the spring and late summer seasons are presented in Fig. 3. The pH,  $\text{pCO}_2$  and  $\text{SI}_{\text{calcite}}$  are presented in Tables 2–4 and Fig. 5A–F. Dissolved oxygen saturation (DO) varied seasonally from 60 to 130%. DO ranged from 66.7 to 127.8% in spring 2004, and from 62.2 to 118% in late summer 2004 (Fig. 3A, B).

Silica concentrations ranged from 5.08  $\mu\text{M}$  to 158  $\mu\text{M}$  in spring 2004 and from 7.12  $\mu\text{M}$  to 194  $\mu\text{M}$  in late summer 2004 (Fig. 3C, D). The lower silica concentration observed in the spring sampling season is due to dilution in the watershed, while the higher concentrations of silica observed in the central and lower parts of the Sava River are probably due to weathering of clastic rocks.

Seasonal variations of carbonate alkalinity are shown in Fig. 4A–C. Speciation calculations identified  $\text{HCO}_3^-$  as the most abundant dissolved carbonate species, contributing about 90% of the DIC. The alkalinity concentrations in the main channel sampling sites varied seasonally from 2.60 meq/l to 3.75 meq/l in spring, from 2.63 meq/l to 4.79 meq/l in late summer 2004, and from 2.67 meq/l to 4.17 meq/l during winter. The upper alpine

headwater catchments of the Sava River (Sava Dolinka and Sava Bohinjka, locations 1–6) have thin soils developed on carbonate bedrock. These headwater catchments tend to have lower and more constant alkalinity values compared to sites further downstream where soils are deeper. In the central and lower part of the Sava River watershed, tributary streams have more variable alkalinity concentrations, ranging from about 0.39 up to 6.02 meq/l.

Dissolved organic carbon (DOC) concentrations were typically less than 0.4 mM during the spring and winter sampling seasons and showed little variability with downstream distance (Fig. 4D–F). During the late summer sampling DOC concentrations ranged from 0.28 mM to 1.15 mM (Tables 2–4), which is typical for unpolluted rivers (Tao 1998). The higher DOC in the river and its tributaries for the late

**Table 2** Chemical and isotopic data for the Sava River watershed, spring 2004

Sampling point	DO (%)	T (°C)	Conductivity ( $\mu\text{S/cm}$ )	pH	Total alkalinity (meq/l)	DIC (mM)	DOC (mM)	$\text{Ca}^{2+}$ (mM)	$\text{Mg}^{2+}$ (mM)	Si ( $\mu\text{M}$ )	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{13}\text{C}_{\text{POC}}$ (‰)
1	88.0	8.6	276	7.83	2.98	2.98	0.32	1.01	0.53	25.63	−10.7	−27.5
2	96.0	9.7	251	8.14	2.62	2.54	0.34	0.99	0.53	25.78	−8.6	−26.9
3	98.6	9.7	283	8.48	3.19	2.81	0.23	1.12	0.43	24.78	−9.6	n.a.
4	102.5	6.2	172.3	8.32	2.00	1.65	0.25	0.75	0.18	5.08	−5.8	n.a.
5	96.0	9.5	203	8.43	2.30	2.24	0.12	1.00	0.20	13.27	−9.1	n.a.
6	102.6	10.3	254	8.57	2.91	2.47	0.18	1.09	0.33	19.63	−9.0	n.a.
7	111.4	11.0	277	8.95	2.60	n.a.	0.18	1.21	0.45	28.70	−6.8	−25.2
8	100.5	12.1	264	8.10	2.64	2.45	0.12	1.07	0.44	16.00	−7.0	−26.1
9	108.8	10.5	246	8.59	2.89	2.60	0.28	1.14	0.36	22.05	−9.5	−28.0
10	86.5	10.6	305	8.42	2.79	2.73	0.25	1.18	0.38	24.04	−10.2	−24.0
11	94.7	10.2	260	8.37	2.48	2.43	0.09	0.93	0.44	46.57	−11.2	−26.5
12	107.0	11.2	381	8.17	3.90	n.a.	0.17	1.41	0.47	36.76	−12.4	−25.0
13	97.0	10.9	391	8.10	4.01	3.65	0.19	1.46	0.51	25.01	−13.5	−27.5
14	99.4	13.0	62.3	7.79	0.39	0.44	0.32	0.14	0.08	158.4	−8.1	n.a.
15	114.0	12.1	323	8.27	3.28	n.a.	0.20	1.33	0.46	26.51	−12.3	−25.7
16	84.6	10.8	349	8.08	3.38	2.95	n.a.	1.32	0.47	23.64	−11.5	−27.1
17	127.8	14.4	375	8.98	3.04	2.74	0.54	1.29	0.44	31.58	−8.5	−27.0
18	66.7	11.6	375	8.10	3.66	3.27	n.a.	1.34	0.47	26.27	−11.1	−25.8
19	95.6	12.9	443	8.48	4.57	4.27	n.a.	1.65	0.83	66.70	−11.5	−27.2
20	90.2	14.2	396	8.04	3.39	3.25	n.a.	1.41	0.53	32.07	−11.9	−28.5
21	105.5	13.5	423	8.32	4.33	3.75	n.a.	1.66	0.51	36.30	−12.9	−27.4
22	98.0	13.4	412	8.28	3.52	3.53	n.a.	1.51	0.51	32.89	−11.1	−26.7
23	91.5	14.0	570	8.15	5.22	5.09	0.32	2.33	0.69	86.36	−11.8	−28.5
24	106.3	13.8	398	8.23	3.75	3.47	n.a.	1.48	0.51	32.05	−11.1	−27.4

n. a.—Not analyzed

Locations are plotted on Fig. 1

**Table 3** Chemical and isotopic data for the Sava River watershed, late summer 2004

Sampling point	DO (%)	T (°C)	Conductivity (μS/cm)	pH	Total alkalinity (meq/l)	DOC (mM)	Ca <sup>2+</sup> (mM)	Mg <sup>2+</sup> (mM)	Si (μM)	δ <sup>13</sup> C <sub>DIC</sub> (‰)	δ <sup>13</sup> C <sub>POC</sub> (‰)	δ <sup>13</sup> C <sub>PIC</sub> (‰)	δ <sup>13</sup> C <sub>Ca</sub> (‰)
1	110.0	5.6	279	7.54	2.63	0.76	0.91	0.47	21.9	-7.8	-25.7	2.1	2.5
2	103.0	8.5	286	7.56	2.67	0.59	1.00	0.51	25.2	-7.3	-27.4	n.a.	2.7
3	118.0	10.7	311	8.31	3.06	0.89	1.12	0.51	26.2	-7.3	-26.0	1.1	1.5
4	116.0	6.0	190	8.08	2.19	1.14	0.75	0.23	7.12	-3.3	n.a.	n.a.	n.a.
5	118.0	12.0	247	8.11	2.69	0.43	1.08	0.24	17.0	-7.2	-23.6	n.a.	n.a.
6	112.0	12.2	305	8.26	3.24	0.58	1.18	0.47	28.6	-7.3	-26.8	1.6	-1.4
7	107.0	11.3	378	8.44	2.81	0.40	1.38	0.60	51.7	-6.4	-25.6	1.7	n.a.
8	109.0	10.7	333	8.20	3.22	0.80	1.23	0.54	45.7	-7.5	-27.0	1.1	n.a.
9	107.0	14.7	632	7.57	3.22	0.54	1.38	0.52	43.4	-8.8	-27.0	n.a.	2.2
10	109.0	12.8	307	8.17	4.76	0.80	1.22	0.42	30.6	-8.1	n.a.	n.a.	2.5
11	104.0	12.5	379	7.48	4.51	0.45	1.38	0.63	72.3	-10.5	-27.6	n.a.	n.a.
12	99.0	13.8	554	7.74	4.60	0.52	1.72	0.58	67.0	-9.3	-26.5	n.a.	n.a.
13	96.0	15.7	500	7.93	4.79	1.15	1.72	0.74	36.3	-11.8	-27.0	n.a.	n.a.
14	100.0	11.9	118.5	7.24	0.84	n.a.	0.30	0.14	194.2	-9.0	n.a.	n.a.	n.a.
15	100.0	12.1	393	7.81	3.48	n.a.	1.48	0.49	n.a.	-10.9	-26.7	n.a.	1.4
16	100.0	13.5	376	8.52	3.45	0.53	1.32	0.51	54.5	-10.2	-27.0	n.a.	-0.6
17		14.3	473	8.82	3.42	n.a.	1.62	0.56	100.8	-10.2	-25.8	n.a.	n.a.
18		14.4	397	8.54	3.36	0.30	1.46	0.53	57.8	-9.9	-27.2	n.a.	1.4
19		14.4	511	8.99	5.49	0.24	1.73	1.15	92.4	-11.2	-27.7	n.a.	n.a.
20		14.4	428	7.86	3.29	0.40	1.57	0.56	65.4	-10.8	-26.9	1.4	1.9
21		14.5	459	8.77	4.65	0.28	n.a.	n.a.	n.a.	-11.1	-28.8	n.a.	n.a.
22		14.7	412	8.20	3.74	0.37	1.49	0.54	63.8	-11.5	-27.5	1.4	n.a.
23		12.4	630	8.61	6.02	0.63	2.38	0.84	160.7	-12.2	-26.3	n.a.	n.a.
24	88.0	14.0	424	7.93	3.51	0.51	1.52	0.55	59.4	-10.8	-27.3	0.5	n.a.

n. a.—Not analyzed

Locations are plotted on Fig. 1

summer is probably related to higher organic matter production and consequent decomposition in the terrestrial environment, which increases DOC leached from soils (Fig. 4D–F). The DOC concentrations in the downstream reaches of the main Sava River decreased by about 0.2 mM from the upstream reaches during the late summer sampling season. Higher concentrations of DOC may be attributed to input from soil waters and wetlands, especially at the Sava Dolinka source (location 1). DOC may be photochemically degraded downstream towards the mouth, where lower DOC concentrations are observed.

Calculated CO<sub>2</sub> partial pressures (pCO<sub>2</sub>) varied from near atmospheric (400 ppmv) to over 30-fold supersaturated (9000 ppmv) (Fig. 5A–C). In late summer all sampling locations in the Sava River

watershed are above equilibrium with atmospheric CO<sub>2</sub>. These higher partial pressures in late summer are probably due to higher degradation of organic matter in the river at the end of the summer season (Dever et al. 1983). In the winter season soil leaching processes as well as degradation of organic matter are limited, so most probably higher pCO<sub>2</sub> pressures should be attributed to the greater solubility of CO<sub>2</sub> at low temperatures (Atkins 1994).

The calcite saturation index (SI<sub>calcite</sub> = log ([Ca<sup>2+</sup>] [CO<sub>3</sub><sup>2-</sup>])/K<sub>calcite</sub>; where K<sub>calcite</sub> is the solubility product of calcite was generally well above equilibrium (SI<sub>calcite</sub> = 0) (Fig. 5D–F), indicating that calcite was supersaturated and precipitation was thermodynamically favoured along most of the course of the Sava River. River water in the spring and late summer sampling seasons was more supersaturated with



**Table 4** Chemical and isotopic data for the Sava River watershed, winter 2005

Sampling site	T (°C)	Conductivity (μS/cm)	pH	Total alkalinity (meq/l)	DOC (mM)	Ca <sup>2+</sup> (mM)	Mg <sup>2+</sup> (mM)	Si (μM)	δ <sup>13</sup> C <sub>DIC</sub> (‰)
1	5.3	257	8.06	2.73		0.98	0.48	9.07	−9.3
2	5.1	288	8.25	2.67	0.90	1.09	0.53	12.0	−7.5
3	3.3	327	8.43	3.14	0.06	1.29	0.58	17.2	−6.3
4	3.0	187	8.51	1.81	n.a.	n.a.	n.a.	n.a.	−4.2
5	3.2	260	8.75	2.73	n.a.	1.20	0.28	8.84	−7.3
6	3.1	391	8.21	3.42	0.09	1.41	0.56	17.6	−8.9
7	3.0	385	8.42	2.48	0.08	n.a.	n.a.	32.0	−5.8
8	2.4	337	8.51	3.18	0.26	n.a.	n.a.	21.3	−6.4
9	4.2	440	8.02	3.64	0.02	1.55	0.59	21.7	−9.4
10	4.4	373	8.10	3.51	0.04	n.a.	n.a.	19.0	−8.7
11	3.6	334	8.22	3.11	0.06	1.30	0.59	36.8	−9.7
12	7.7	565	7.76	4.89	0.14	1.98	0.68	33.0	−10.9
13	5.5	401	8.14	3.95	0.07	n.a.	n.a.	20.6	−11.9
14	1.6		7.85	0.44	0.12	0.17	0.08	82.7	n.a.
15	4.3	441	8.31	4.00	0.14	n.a.	n.a.	23.2	−9.7
16	3.9	421	7.97	4.17	0.03	n.a.	n.a.	15.7	−9.5
17	1.3	481	8.54	3.80	n.a.	1.80	0.60	36.1	−8.8
18	3.4	444	8.14	3.88	0.04	1.50	0.58	21.6	−10.5
19				5.10	n.a.	n.a.	n.a.	n.a.	−10.0
20	6.2	467	8.08	3.96	0.03	n.a.	n.a.	27.1	−10.6
21	2.8	469	8.44	4.33	n.a.	n.a.	n.a.	n.a.	−10.3
22	5.4	445	8.27	3.54	0.05	n.a.	n.a.	22.5	−10.4
23	0.4	606	8.22	5.91	0.07	2.42	0.91	45.6	−10.9
24	4.9	445	8.29	3.49	0.04	n.a.	n.a.	22.0	−9.8

n.a.—Not analyzed

Locations are plotted on Fig. 1

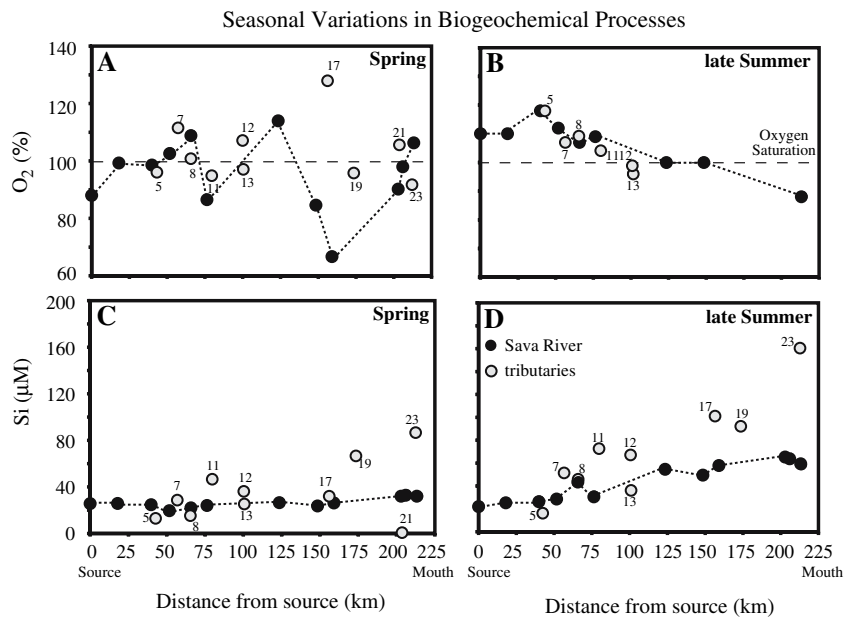
respect to calcite than in the winter sampling season. Only one tributary of the Sava River was undersaturated with respect to calcite (location 14, Tables 2–4); its watershed lacks carbonate rocks and contains Permo–Carbonian shales.

#### DIC carbon isotope ratios: equilibration with atmospheric and soil CO<sub>2</sub> reservoirs

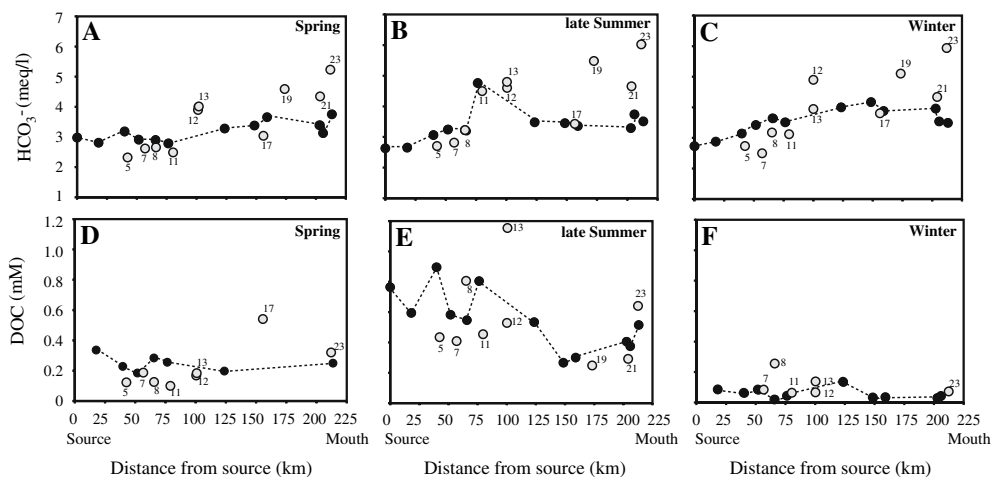
The δ<sup>13</sup>C<sub>DIC</sub> can elucidate the contributions of organic matter decomposition, carbonate mineral dissolution, and equilibration with atmospheric CO<sub>2</sub> to DIC in the Sava River watershed. The δ<sup>13</sup>C<sub>DIC</sub> varied seasonally from −12.7 to −8.6‰ in spring 2004, from −11.8 to −7.3‰ in late summer 2004, and from −10.6 to −6.3‰ in winter 2005 (Fig. 5G–I). The

Sava River tributaries had δ<sup>13</sup>C<sub>DIC</sub> values that varied from −13.5 to −5.8‰ in spring 2004, from −12.8 to −3.3‰ in late summer 2004, and from −11.9 to −4.2‰ in winter 2005. δ<sup>13</sup>C<sub>DIC</sub> was lower during the spring at higher discharge (Fig. 5G–I). The δ<sup>13</sup>C<sub>DIC</sub> of the Sava is also controlled by bedrock lithology within the watershed. The upstream watersheds of the Sava Bohinjka and Sava Dolinka (locations 1–5) are mainly influenced by carbonate mineral dissolution and/or atmospheric equilibration of CO<sub>2</sub>, whereas the downstream sections of the Sava River are also influenced by weathering of carbonate and clastic rocks with higher contents of organic material, which is reflected in the lower δ<sup>13</sup>C<sub>DIC</sub> values. The lower part of the Sava River watershed is surrounded with shallow hill slope soil rich in organics (especially those developed over mudstones), representing a

**Fig. 3** Biogeochemical variables in Sava River waters. Silica concentrations (A, B) and dissolved oxygen saturation (C, D) in different sampling seasons versus distance along course of Sava River



Seasonal Variations in Organic- Inorganic Carbon Contents



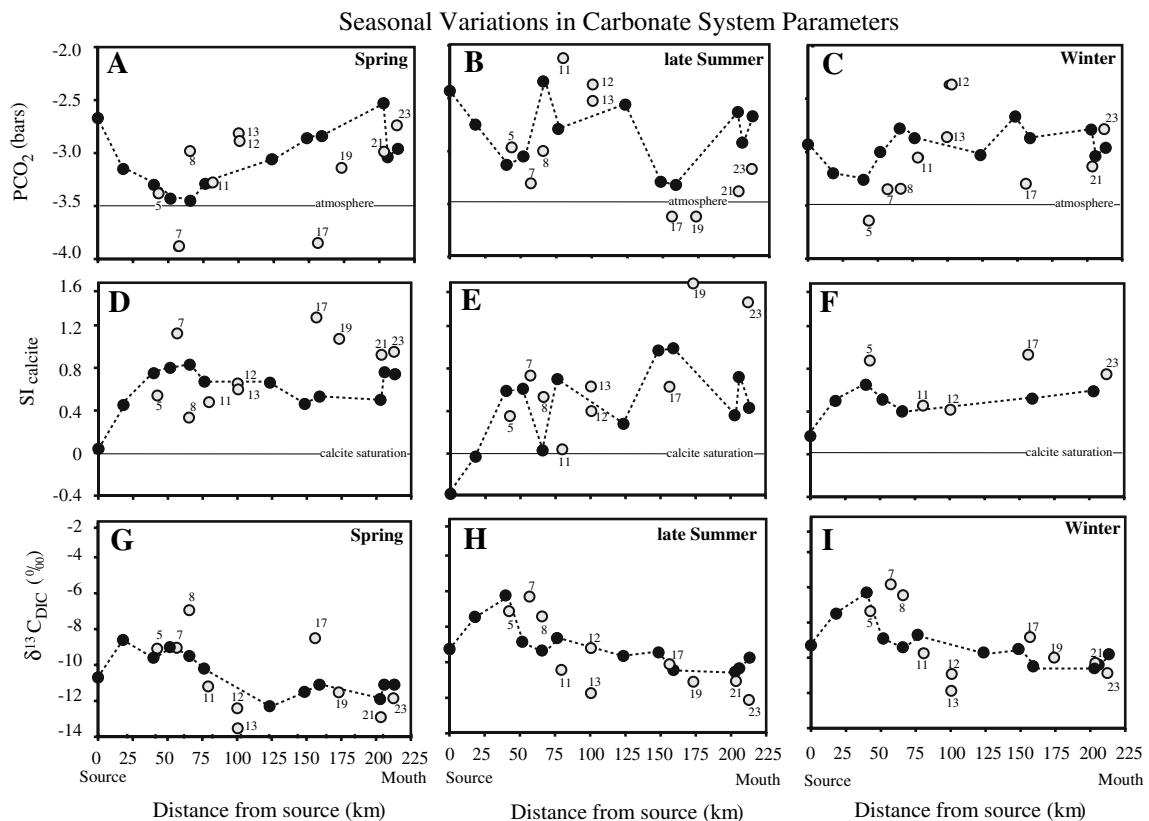
**Fig. 4** Carbon geochemical parameters. Alkalinity concentrations in different sampling seasons (early spring, late summer and winter: A, B, and C, respectively) and dissolved organic

matter (DOC) concentrations (early spring, late summer and winter: D, E, and F, respectively)

source of isotopically light biogenic carbon and a source of mineralization. Storm runoff events flush not only <sup>13</sup>C-depleted DIC but also POC and DOC that can be subsequently mineralized in the stream. Therefore, it is unclear how much mineralization occurs in the terrestrial ecosystem versus in the streams.

The  $\delta^{13}\text{C}$  of Mesozoic carbonate rocks ( $\delta^{13}\text{C}_{\text{ca}}$ ) from the Sava River watershed ranged from  $-1.4$  to

$2.7\text{‰}$  (Table 3), with an average of  $1.4 \pm 1.3\text{‰}$  ( $n = 10$ ). The  $\delta^{13}\text{C}$  of particulate inorganic carbon ( $\delta^{13}\text{C}_{\text{PIC}}$ ) in the river waters varied from  $0.5$  to  $2.1\text{‰}$  (Table 3) with an average of  $1.3 \pm 0.5\text{‰}$  ( $n = 9$ ).  $\delta^{13}\text{C}_{\text{PIC}}$  of the Sava River was therefore only slightly depleted relative to the  $\delta^{13}\text{C}$  of Mesozoic carbonate rocks. This indicates a predominantly detrital sedimentary source, with a small contribution of modern river/soil authigenic carbonates. Modern authigenic



**Fig. 5** Seasonal variation in  $p\text{CO}_2$  (A, B, C) calcite saturation index (D, E, F), and  $\delta^{13}\text{C}_{\text{DIC}}$  (G, H, I) in the main channel and tributaries of the Sava River (spring 2004, late summer 2004 and winter 2005)

carbonate, accumulating in soil would have  $\delta^{13}\text{C}$  values around  $-12\text{‰}$  (Aucour et al. 1999), while  $\delta^{13}\text{C}_{\text{PIC}}$  from the Sava River watershed suggests a detrital carbonate source.

The plants growing on the banks of the Sava River are  $\text{C}_3$  plants, except maize (*Zea mays*), which is a  $\text{C}_4$  plant. The most abundant vegetation is woody vegetation like *Salix* sp. and the herbaceous plant *Impatiens glandulifera* (Mrak personal communication). The stable isotope composition of plant litter ( $\delta^{13}\text{C}_{\text{plant}}$ ) varied from  $-34.8$  to  $-29.2\text{‰}$  (Kanduč 2006), with an average of  $-31.6 \pm 1.5\text{‰}$  ( $n = 22$ ). *Zea mays* had a  $\delta^{13}\text{C}$  value of  $-13.6\text{‰}$ . Soil organic matter  $\delta^{13}\text{C}$  was  $-26.2\text{‰}$  ( $n = 4$ ). The  $\delta^{13}\text{C}$  of particulate organic carbon ( $\delta^{13}\text{C}_{\text{POC}}$ ) in the Sava River system varied in the Spring season from  $-26.5$  to  $-23.8\text{‰}$ , with an average of  $-26.7 \pm 1.2\text{‰}$  (Table 2), and in the late summer season from  $-28.8$  to  $-23.0\text{‰}$ , with an average of  $-26.7 \pm 1.0\text{‰}$  (Table 3). Therefore, suspended organic matter in the

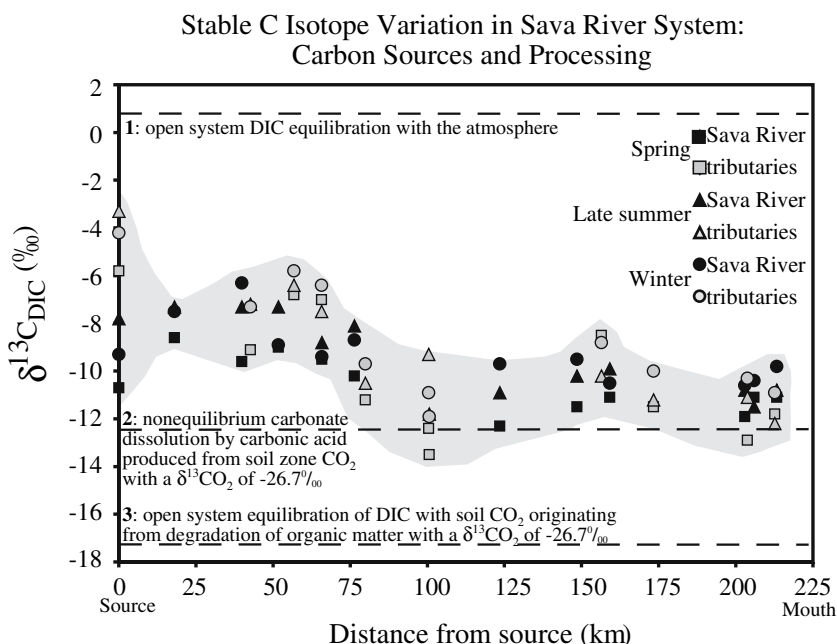
river was mostly derived from soil and plant material (Ittekkot 1988; Hedges 1992). Phytoplankton evidently did not make a major contribution to the suspended organic matter within the Sava River system; based on the  $\delta^{13}\text{C}_{\text{DIC}}$  and a typical algal fractionation factor, the  $\delta^{13}\text{C}$  of phytoplankton would range between  $-34.0\text{‰}$  and  $-28.0\text{‰}$  (Hedges et al. 1986; Hellings et al. 1999, Kendall et al. 2001).

## Discussion

### Carbon sources and controls on $\delta^{13}\text{C}_{\text{DIC}}$

Figure 6 shows  $\delta^{13}\text{C}_{\text{DIC}}$  versus distance from the source for river water samples in different sampling seasons. Changes over the course of the rivers indicate processes affecting  $\delta^{13}\text{C}_{\text{DIC}}$ , e.g. respiration of organic matter, carbonate mineral dissolution, and equilibration with atmospheric  $\text{CO}_2$  (Barth et al.

**Fig. 6** Variation in the Sava River  $\delta^{13}\text{C}_{\text{DIC}}$  versus distance from the source, with lines indicating processes occurring in the Sava River watershed. These include values calculated for: (1) open system DIC in equilibration with the atmosphere, (2) nonequilibrium carbonate dissolution by carbonic acid produced from soil zone  $\text{CO}_2$ , and (3) open system equilibration of DIC with soil  $\text{CO}_2$  originating from degradation of organic matter with  $\delta^{13}\text{C} = -26.7\text{‰}$



2003). An average  $\delta^{13}\text{C}_{\text{POC}}$  of  $-26.7\text{‰}$  was assumed to calculate the isotopic composition of DIC derived from in-stream respiration. Open system equilibration of DIC with  $\text{CO}_2$  enriches DIC in  $^{13}\text{C}$  by about 9‰ (Mook et al. 1974), thus yielding the estimate of  $-17.7\text{‰}$  shown in Fig. 6 (line 3). This open system equilibration assumes an unlimited reservoir of  $\text{CO}_2$  that imprints its isotopic composition and the associated isotope shifts on the DIC species present. These are  $-1.1\text{‰}$ ,  $+9\text{‰}$  and  $+11\text{‰}$  for  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , respectively, at an average water temperature of  $12^\circ\text{C}$  (Mook et al. 1974). Nonequilibrium dissolution of carbonates with one part of DIC originating from soil  $\text{CO}_2$  ( $-26.7\text{‰}$ ), and the other from carbonates with an average  $\delta^{13}\text{C}_{\text{Ca}}$  of  $1.4\text{‰}$ , produces an intermediate  $\delta^{13}\text{C}_{\text{DIC}}$  value of  $-12.7\text{‰}$  (line 2 in Fig. 6). Given the isotopic composition of atmospheric  $\text{CO}_2$  ( $-7.8\text{‰}$ ; Levin et al. 1987) and the equilibrium fractionation with DIC of  $+9\text{‰}$ , DIC in equilibrium with the atmosphere should have a  $\delta^{13}\text{C}_{\text{DIC}}$  of about  $1\text{‰}$  (line 1 in Fig. 6).

The  $\delta^{13}\text{C}_{\text{DIC}}$  values from the Sava River watershed (Fig. 6) indicate nonequilibrium carbonate dissolution predominates in the central part of the Sava River system, where the watershed is composed of carbonate and clastic rocks, approaching the  $\delta^{13}\text{C}_{\text{DIC}}$  of  $-12.7\text{‰}$ . In the upper part of the Sava River dissolution of carbonate minerals prevails, which

leads to higher  $\delta^{13}\text{C}_{\text{DIC}}$ . The downstream locations of the Sava River water are characterized by lower  $\delta^{13}\text{C}_{\text{DIC}}$ . Mineralization of organic matter appears to be the dominant source for  $\delta^{13}\text{C}_{\text{DIC}}$  at downstream locations where the greater soil thickness enables accumulation of soil  $\text{CO}_2$  due to the greater degrees of silicate rock weathering (Fig. 2B), which leads to more negative  $\delta^{13}\text{C}_{\text{DIC}}$  (Figs. 5G–I, 6).

#### $\text{CO}_2$ fluxes based on a diffusion model

The evasion of  $\text{CO}_2$  from the Sava River to the atmosphere  $[\text{DIC}]_{\text{ex}}$  can be estimated based on the thin-film diffusive gas exchange model (Broecker 1974):

$$[\text{DIC}]_{\text{ex}} = \frac{D}{Z}([\text{CO}_2] - [\text{CO}_2]_{\text{eq}}) \quad (1)$$

where  $D$  is the  $\text{CO}_2$  diffusion coefficient in water of  $1.26 \times 10^{-5} \text{ cm}^2/\text{s}$  at a temperature of  $10^\circ\text{C}$  and  $1.67 \times 10^{-5} \text{ cm}^2/\text{s}$  at a temperature of  $20^\circ\text{C}$  (Jähne et al. 1987),  $z$  is the empirical thickness of the liquid layer [cm],  $[\text{CO}_2]_{\text{eq}}$  and  $[\text{CO}_2]$  are the dissolved  $\text{CO}_2$  concentrations at equilibrium with the atmosphere and with the studied water [ $\text{mol}\cdot\text{cm}^{-3}$ ], respectively. The thickness of the boundary layer  $z$ , a thin film existing at the air–water interface, depends largely on wind velocity (Broecker et al. 1978) and water

turbulence (Holley 1977).  $D/z$ , therefore, is the gas exchange rate, which gives the height of the water column which will equilibrate with the atmosphere per unit time. Using a mean wind speed of 4 m/s in all sampling seasons in the Sava watershed (ARSO 2004–2005),  $D/z$  was estimated to be 8 cm/h at low turbulence conditions, 28 cm/h at moderate turbulence conditions and 115 cm/h at high turbulence conditions.

The theoretical  $\text{CO}_2$  diffusive evasion rates at the Sava River mouth, according to Eq. 1, ranged between  $2.6 \times 10^{-7}$  and  $9.0 \times 10^{-7} \text{ mol/cm}^2 \cdot \text{h}$  in spring 2004, from  $6.0 \times 10^{-7}$  to  $20 \times 10^{-7} \text{ mol/cm}^2 \cdot \text{h}$  in late summer 2004, and from  $2.7 \times 10^{-7}$  to  $9.4 \times 10^{-7} \text{ mol/cm}^2 \cdot \text{h}$  in winter 2005. Taking into consideration the river surface area of  $9.3 \text{ km}^2$  (a mean width of 44 m and length of 219 km), then the estimated total diffusive loss of inorganic carbon in the spring ranged from a minimum of  $6.0 \times 10^5 \text{ mol/day}$  during periods of low wind speeds to a maximum of  $2.0 \times 10^6 \text{ mol/day}$  during storm events (at high turbulence conditions). The estimated total diffusive loss of inorganic carbon in the late summer ranged from  $1.0 \times 10^6$  to  $5.0 \times 10^6 \text{ mol/day}$  and from  $6.0 \times 10^5$  to  $2.1 \times 10^6 \text{ mol/day}$  in winter. The Sava River in Slovenia showed seasonal patterns of  $\text{CO}_2$  diffusive evasion that are similar to other large rivers, like the Rhine, where the annual net flux of  $\text{CO}_2$  into the atmosphere was estimated to be  $2.5 \times 10^7 \text{ mol/day}$  (Kempe 1982). High  $\text{pCO}_2$  values and an increase in  $\text{pCO}_2$  downstream were also reported for the Changjiang (Gao and Kempe 1987), but a lower  $\text{pCO}_2$  value was observed in the St. Lawrence river (Yang et al. 1996), where the long residence time in the Great Lakes upriver enables equilibration of  $\text{CO}_2$  across the water–atmosphere interface.

The temporal evolution of stream  $\text{pCO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$  was calculated using available diffusion models (e.g. Broecker 1974; Richey et al. 1990; Aucour et al. 1999). These calculations yield the amount of time needed for  $\text{CO}_2$  evasion and for stream–atmosphere isotopic exchange relative to the transit time of stream waters. The calculations were conducted for two contrasting tributaries, a carbonate watershed (location 4) and a silicate watershed draining Permo–Carbonian shales (location 14) in late summer 2004 (Fig. 2, Tables 2–4). These locations are characterized by  $\text{pCO}_2$  values near atmospheric equilibrium and by relatively high

$\delta^{13}\text{C}_{\text{DIC}}$ . Equilibration of  $\text{CO}_2$  in the spring sampling is favoured due to the higher discharge conditions, which increases turbulence ( $D/z$ ). The estimated rate of change of DIC concentration due to  $\text{CO}_2$  evasion can be calculated by:

$$\frac{d[\text{DIC}]}{dt} = \frac{D}{zh} \cdot ([\text{CO}_2]_{\text{eq}} - [\text{CO}_2]) \quad (2)$$

and the DIC concentration in water can be expressed as a function of time by:

$$[\text{DIC}] = [\text{CO}_2]_{\text{eq}} - ([\text{CO}_2]_{\text{eq}} - [\text{CO}_2]_0) \cdot e^{-\frac{D}{zh}t} \quad (3)$$

where  $h$  is the mean depth of the river [cm] and  $t$  is the time needed for equilibration [min], all other parameters being previously determined in Eq. 1. The calculations assume an upper limit of 115 cm/h for  $D/z$  (very turbulent water) for location 4 and 28 cm/h for  $D/z$  at location (14) (Mook 1970) and  $h$  values of 10 and 50 cm. The results according to Eq. 3 show that equilibrium between atmospheric  $\text{CO}_2$  and dissolved riverine  $\text{CO}_2$  would be approached between 29.4 and 148.8 min at location 4 and between 2.1 h and 10.4 h at location 14.

Additionally, the rate of change of  $\delta^{13}\text{C}_{\text{DIC}}$  due to  $\text{CO}_2$  exchange between the river and the atmosphere was also estimated by the equation (Aucour et al. 1999):

$$\frac{d\delta^{13}\text{C}_{\text{DIC}}}{dt} = \frac{D[\text{CO}_2]_{\text{eq}}}{zh[\text{DIC}]} \cdot (\delta^{13}\text{C}_a - \delta^{13}\text{C}_{\text{DIC}} + \varepsilon) \quad (4)$$

and again the DIC concentration ( $[\text{DIC}]$ ) can be expressed as a function of time ( $t$ ) by:

$$\delta^{13}\text{C}_{\text{DIC}} = (\delta^{13}\text{C}_a - \varepsilon) - (\delta^{13}\text{C}_a - \varepsilon - \delta^{13}\text{C}_{\text{DIC},0}) \cdot e^{-\frac{D[\text{CO}_2]_{\text{eq}}}{zh[\text{DIC}]}t} \quad (5)$$

In Eqs. 4 and 5  $\delta^{13}\text{C}_a$  and  $\delta^{13}\text{C}_{\text{DIC}}$  are the  $\delta^{13}\text{C}$  values of atmospheric  $\text{CO}_2$  (−7.8‰; Levin et al. 1987) and DIC, respectively,  $\delta^{13}\text{C}_0$  is the initial  $\delta^{13}\text{C}$  value of DIC and  $\varepsilon$  is the equilibrium fractionation factor between  $\text{CO}_2$  and  $\text{HCO}_3^-$  (Zhang et al. 1995).

Starting with the  $\delta^{13}\text{C}_{\text{DIC}}$  value of −12.5‰ (Aucour et al. 1999) and an  $h$  value of 10 cm, 8 h

would be required to reach the equilibrium value for location (4) and 3.9 h for location 14. This time interval for location 4 is greater than the expected transit time of 24.4 min suggesting that stream–atmosphere isotopic exchange alone cannot explain the  $^{13}\text{C}$  enrichment of DIC in this carbonate catchment. However, 3.9 h (location 14) would also be comparable to the 2.9 h calculated from Eq. 3, indicating possible equilibration with atmospheric  $\text{CO}_2$  in the relatively impermeable silicate watershed. The enrichment in  $^{13}\text{C}$  in DIC at location 4 probably results from carbonate dissolution in the carbonate watershed, while in impermeable silicate drainages the longer residence time of water could enhance the equilibration with atmospheric  $\text{CO}_2$ .

#### Mass balances of dissolved inorganic carbon at the mouth of the Sava River in Slovenia

A simple isotopic mass balance calculation was performed in order to quantify different sources of DIC at the Sava River mouth (location 24), encompassing the sum of tributary inputs and in-stream biogeochemical processes throughout the river system in Slovenia. The major inputs to the DIC flux ( $\text{DIC}_{\text{out}}$ ) and  $\delta^{13}\text{C}_{\text{DIC}}$  originate from tributaries ( $\text{DIC}_{\text{tri}}$ ), degradation of organic matter ( $\text{DIC}_{\text{org}}$ ), exchange with the atmosphere ( $\text{DIC}_{\text{ex}}$ ), and dissolution of carbonates ( $\text{DIC}_{\text{ca}}$ ):

$$\text{DIC}_{\text{out}} = \text{DIC}_{\text{tri}} - \text{DIC}_{\text{ex}} + \text{DIC}_{\text{org}} + \text{DIC}_{\text{ca}} \quad (6)$$

$$\text{DIC}_{\text{out}} \cdot \delta^{13}\text{C}_{\text{out}} = \text{DIC}_{\text{tri}} \cdot \delta^{13}\text{C}_{\text{tri}} - \text{DIC}_{\text{ex}} \cdot \delta^{13}\text{C}_{\text{ex}} + \text{DIC}_{\text{org}} \cdot \delta^{13}\text{C}_{\text{POC}} + \text{DIC}_{\text{ca}} \cdot \delta^{13}\text{C}_{\text{Ca}} \quad (7)$$

The process of photosynthesis was considered insignificant and therefore excluded from the mass balance calculations. Dissolved oxygen saturation reached a maximum of only 118% in the late summer sampling and the  $\delta^{13}\text{C}_{\text{POC}}$ , with an average value of  $-26.7\text{‰}$ , indicates that organic matter derived from aquatic photosynthesis is relatively insignificant in the Sava River system. It has been observed that phytoplankton take up  $\text{H}_2\text{CO}_3$  and impose a  $^{13}\text{C}$

fractionation of  $\sim -20\text{‰}$ , leading to biomass  $\delta^{13}\text{C}$  values of  $-34$  to  $-28\text{‰}$  in mixed and lowland rivers (Hedges et al. 1986; Devol and Hedges 2001). In the Sava River watershed all measured biogeochemical parameters (pH, DO,  $\text{pCO}_2$ , dissolved silica and  $\text{SI}_{\text{calcite}}$ ) were relatively constant during all sampling seasons and no correlation was observed between these parameters. On the contrary, in the River Thames (Neal et al. 1998) lower pH, lower  $\text{SI}_{\text{calcite}}$ , and higher silica concentrations and  $\text{pCO}_2$  were observed during the period of higher biological productivity. Also, in-stream carbonate precipitation/dissolution was excluded in this study since the isotope composition of particulate inorganic carbon ( $\delta^{13}\text{C}_{\text{PIC}}$ ) was similar to that of the bedrock carbonate ( $\delta^{13}\text{C}_{\text{Ca}}$ ) forming the Sava River watershed. The contribution of rainwater to riverine DIC is considered to be minimal as it contains only a small amount of DIC (Yang et al. 1996).

$\text{DIC}_{\text{out}}$  and  $\text{DIC}_{\text{tri}}$  were calculated from the concentrations of alkalinity (Tables 2–4) and water discharge (Table 1), with the corresponding measured  $\delta^{13}\text{C}$  values for  $\delta^{13}\text{C}_{\text{out}}$ ,  $\delta^{13}\text{C}_{\text{tri}}$ ,  $\delta^{13}\text{C}_{\text{POC}}$ , and  $\delta^{13}\text{C}_{\text{Ca}}$ . The average diffusive flux of  $\text{CO}_2$  from the river to the atmosphere,  $\text{DIC}_{\text{ex}}$ , estimated from Eq. 1, was taken into account. In Eqs. 6 and 7 the minus sign indicates outgassing of  $\text{CO}_2$ , which is observed in all sampling seasons at location 24. The  $\delta^{13}\text{C}_{\text{ex}}$  value was calculated according to the equation for equilibrium isotope fractionation between atmospheric  $\text{CO}_2$  and carbonic acid in water (Zhang et al. 1995), where a  $\delta^{13}\text{C}$  value of  $-7.8\text{‰}$  for

atmospheric  $\text{CO}_2$  was used (Levin et al. 1987). The isotopic composition of the contribution of equilibration between atmospheric  $\text{CO}_2$  and DIC ( $\delta^{13}\text{C}_{\text{ex}}$ ) would then be  $1.4\text{‰}$ ,  $1.2\text{‰}$  and  $1.2\text{‰}$  in spring 2004, late summer 2004 and winter 2005, respectively, considering atmospheric  $\text{CO}_2$  as the ultimate source of  $\text{CO}_2$  in the Sava drainage system in Slovenia. For  $\delta^{13}\text{C}_{\text{POC}}$  and  $\delta^{13}\text{C}_{\text{Ca}}$  average values of  $-26.7\text{‰}$  and  $1.4\text{‰}$ , respectively, were used in the mass balance equations.



**Table 5** Calculated dissolved inorganic carbon fluxes of different contributions at the Sava River mouth: tributaries ( $\text{DIC}_{\text{tri}}$ ), degradation of organic matter ( $\text{DIC}_{\text{org}}$ ),  $\text{CO}_2$  flux to atmosphere ( $\text{DIC}_{\text{ex}}$ ) and dissolution of carbonates ( $\text{DIC}_{\text{ca}}$ )

Sampling season	$\text{DIC}_{\text{tri}}$ (mol/day)	$\text{DIC}_{\text{org}}$ (mol/day)	$\text{DIC}_{\text{ex}}$ (mol/day)	$\text{DIC}_{\text{ca}}$ (mol/day)	$\text{DIC}_{\text{out}}$ (mol/day)
Spring 2004	$7.8 \times 10^7$	$1.3 \times 10^7$	$-9.4 \times 10^5$	$2.2 \times 10^7$	$1.1 \times 10^8$
Late summer 2004	$2.7 \times 10^7$	$7.3 \times 10^6$	$-2.2 \times 10^6$	$1.1 \times 10^7$	$4.4 \times 10^7$
Winter 2005	$1.9 \times 10^7$	$3.0 \times 10^6$	$-9.8 \times 10^5$	$6.2 \times 10^6$	$2.8 \times 10^7$

The  $\text{DIC}_{\text{org}}$  and  $\text{DIC}_{\text{ca}}$  values were determined by solving the mass balance equations. The calculated fluxes for different sampling seasons are presented in Table 5. The calculated contributions to the average DIC budget from  $\text{DIC}_{\text{tri}}:\text{DIC}_{\text{ex}}:\text{DIC}_{\text{org}}:\text{DIC}_{\text{ca}}$  at the Sava River mouth were 70: -1: 11: 19% in spring 2004, 63: -7: 17: 26 in the late summer 2004, and 71: -5: 11: 23% in winter 2005, respectively. It was observed that the next most important contribution to DIC is the dissolution of carbonates (up to 26%), resulting in higher  $\delta^{13}\text{C}_{\text{DIC}}$  values. The relative contribution of DIC fluxes from organic matter sources and the degassing of  $\text{CO}_2$  are more pronounced in late summer, of up to 17% and -7%, respectively. The data gathered in this study do not permit identification of the proportion of organic degradation occurring in the terrestrial versus the aquatic (riverine) environment. Mass balance calculations suggest that downstream depletion in  $^{13}\text{C}$  is mainly caused by the inflow of water from tributaries and that among the biogeochemical processes, dissolution of carbonates prevails over degradation of organic matter as a source of DIC in all sampling seasons. Degradation of organic matter and dissolution of carbonates are more intensive in the late summer season due to higher temperatures, which coincide with higher soil  $\text{pCO}_2$  values in the watershed. A less significant process is equilibration with atmospheric  $\text{CO}_2$ . Dissolution of carbonates contributes a higher proportion in all sampling seasons, which moves  $\delta^{13}\text{C}_{\text{DIC}}$  to more positive values.

#### Comparison with other temperate rivers

The DIC concentrations in the Sava River system ( $\sim 3$  mM) far exceed the average world river concentration of 0.9 mM (Livingstone 1963) and also lie well above the average concentration in European rivers of 1.5 mM (Kempe et al. 1991). The average annual DIC flux based on long term alkalinity data

(EIONET 2005) of DIC, assuming  $\text{HCO}_3^-$  is the most abundant species at the pH of these waters, is estimated to be  $4.1 \times 10^{11}$  g C/year at the Sava River mouth (location 24). This yields an area-normalized average DIC flux of  $4 \times 10^7$  g C/(km<sup>2</sup> year). Thus, these area-normalized DIC fluxes for the Sava river watershed above the border with Croatia are about four times higher than those of the upper Danube (Pawellek et al. 2002), 10 times higher than the Mississippi River, and 13 times higher than world average rivers (Amiotte Suchet and Probst 1993). In addition, we estimate that downriver at Belgrade the annual DIC flux of the Sava River would be  $1.02 \times 10^{13}$  g C/year, based on an alkalinity of 4 meq/l (Pawellek and Veizer 1994) and the average discharge at Belgrade (6500 m<sup>3</sup>/s). Therefore, the Sava River in Slovenia contributes approximately 4% of the Danube annual dissolved inorganic carbon flux. The annual DOC flux at the Sava River mouth (location 24) is much lower compared to the DIC flux and was estimated to be  $2.8 \times 10^6$  g C/(year km<sup>2</sup>).

The isotopic composition of DIC has been studied in several temperate European and North American river systems, including the Danube (Pawellek and Veizer 1994; Pawellek et al. 2002), the Rhine (Buhl et al. 1991), the Rhône (Aucour et al. 1999), small rivers in the Netherlands (Mook 1970), the Lagan (Barth et al. 2003), the River Scheldt (Hellings et al. 1999), the Vistula (Wachniew 2006) and the St. Lawrence system (Yang et al. 1996; Telmer and Veizer 1999; Hélie et al. 2002). The Rhine, the Danube and the Rhône show significant spatial and temporal variation in  $\delta^{13}\text{C}_{\text{DIC}}$  caused by their headwaters and major tributaries. Similar variation was also observed in the Sava River. All the rivers in the Sava River system have higher  $\delta^{13}\text{C}_{\text{DIC}}$  due to the strong influence of carbonate weathering in their Alpine headwater catchments. On the other hand, the Vistula River has relatively stable  $\delta^{13}\text{C}_{\text{DIC}}$  values between -12‰ and -11‰ because of the small contribution of carbonate-free areas and smaller

climatic variability in the catchment (Wachniew 2006). It should be mentioned that in all of these river systems the isotopic composition of DIC is more strongly affected by photosynthetic  $\text{CO}_2$  uptake compared to the Slovenian reaches of the Sava River system. Therefore, the Sava River presents an opportunity to examine the carbon cycling without the complication of aquatic photosynthetic activity.

## Conclusions

The major solute composition of Sava River water is dominated by  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Seasonal (spring 2004, late summer 2004 and winter 2005) concentrations of  $\text{HCO}_3^-$  ranged from 2.63 to 4.79 meq/l, while its tributaries had concentrations of  $\text{HCO}_3^-$  ranging from 0.39 to 6.02 meq/l. The majority of the Sava River system was supersaturated or near equilibrium (in the upper range of the river flow) with respect to calcite in all sampling seasons. However, back-precipitation via authigenic carbonate formation appears to be of limited significance because  $\delta^{13}\text{C}_{\text{PIC}}$  values reflect local carbonate rock sources rather than stream DIC values. According to the calculated  $\text{pCO}_2$  pressures, the Sava represents a source of  $\text{CO}_2$  (on average five times supersaturated) to the atmosphere during all sampling seasons. Seasonal variations of major chemical constituents and stable isotope composition are due to differences in discharge conditions; lower ion concentrations ( $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , Si),  $\text{pCO}_2$ , and  $\delta^{13}\text{C}_{\text{DIC}}$  were observed in spring, while higher ion concentrations,  $\text{pCO}_2$ , and  $\delta^{13}\text{C}_{\text{DIC}}$  were observed in late summer. The observed differences in  $\text{pCO}_2$ , alkalinity and  $\delta^{13}\text{C}_{\text{DIC}}$  between the carbonate rock drainages versus mixed lithology watersheds (carbonate and clastic rocks) at downstream locations are the consequence of the soil thickness since carbonate rocks are more resistant to mechanical weathering processes. The partial pressure is lower in the carbonate part of the watershed and higher at downstream locations. Lower alkalinities and higher  $\delta^{13}\text{C}_{\text{DIC}}$  values are observed in the upper carbonate part of the watershed, while higher alkalinities and lower  $\delta^{13}\text{C}_{\text{DIC}}$  values are observed in the central and lower part of the Sava River system.

The biogeochemical processes affecting DIC concentrations and  $\delta^{13}\text{C}_{\text{DIC}}$  were quantified by total C and  $^{13}\text{C}$  mass balance calculations, showing that the

most important biogeochemical processes at the Sava River mouth in order of significance in different sampling seasons are: (1) carbonate mineral dissolution comprising 19.4% in spring to 25.9% in late summer, (2) degradation of organic matter comprising 10.8% in winter to 16.7% in late summer, and (3) atmospheric exchange comprising 0.8% in spring to 4.9% in late summer. Dissolution of carbonates, degradation of organic matter and evasion of  $\text{CO}_2$  from the river system are most significant in the late summer season. Exchange between atmospheric and dissolved  $\text{CO}_2$  is most significant only in the impermeable silicate drainages. DIC inputs of Sava River tributaries comprised up to 71% from mass balance calculations and showed similar seasonal patterns, but with much wider ranges of measured chemical and stable isotopic compositions compared to the mainstream Sava River, indicating that these control both the chemical composition as well as the  $\delta^{13}\text{C}_{\text{DIC}}$  values.

The Sava River in Slovenia has high specific discharge and low in-stream photosynthetic activity, and represents a river system where among the biogeochemical processes geological factors prevail (carbonate dissolution). Construction of hydroelectric power plants in the central and lower Sava flow in the next 5 years will affect the carbon cycle, e.g., via enhanced aquatic primary production, degradation of organic matter, and degassing of  $\text{CO}_2$  from the river. This investigation will also help to evaluate the biogeochemical state of the river after dam construction.

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