GEOLOGIJA *60/1*, 9-26, Ljubljana 2017 © Author(s) 2017. CC Atribution 4.0 License

https://doi.org/10.5474/geologija.2017.001

Biogeochemistry of some selected Slovenian rivers (Kamniška Bistrica, Idrijca and Sava in Slovenia): insights into river water geochemistry, stable carbon isotopes and weathering material flows

Biogeokemija izbranih slovenskih rek (Kamniška Bistrica, Idrijca in Sava v Sloveniji): vpogled v rečno vodno geokemijo, stabilne izotope ogljika in snovne tokove preperevanja

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Prejeto / Received 19. 10. 2016; Sprejeto / Accepted 23. 5. 2017; Objavljeno na spletu / Published online 9.6.2017

Dedicated to Professor Jože Pezdič on the occasion of his 70th birthday

Key words: water geochemistry, biogeochemistry, carbon stable isotopes, weathering fluxes, rivers
Ključne besede: vodna geokemija, biogeokemija, stabilni izotopi ogljika, snovni tokovi, reke

Abstract

Review of biogeochemical processes studied in three Slovenian rivers (River Kamniška Bistrica, River Sava in Slovenia and River Idrijca), which represent an ideal natural laboratory for studying biogeochemical processes and anthropogenic impacts in catchments with high weathering capacity is presented. The River Kamniška Bistrica, the River Sava in Slovenia and the River Idrijca water chemistry is dominated by HCO_3^-, Ca^{2+} and Mg^{2+}, and Ca^{2+}/Mg^{2+} molar ratios indicate that calcite/dolomite weathering is the major source of ions to the river system. The Kamniška Bistrica River, the River Sava and River Idrijca and its tributaries are oversaturated with respect to calcite and dolomite. pCO_2 concentrations were on average up to 25 times over atmospheric values for River Kamniška Bistrica, 20 times for River Sava and 13 times over atmospheric values for River Idrijca. $\delta^{13}C_{DIC}$ values ranged from -12.7 to -2.7 ‰ in River Kamniška Bistrica, from -12.7 to -6.3 ‰ in River Sava in Slovenia, from -10.8 to -6.6 ‰ in River Idrijca, respectively. In all investigated rivers we found out that carbonate dissolution is the most important biogeochemical process affecting carbon isotopes in the upstream portions of the catchment, while carbonate dissolution and organic matter degradation control carbon isotope signatures downstream, except for River Idrijca where both processes contribute equally from source to outflow to River Soča.

Izvleček

Predstavljen je pregled biogeokemisjkih procesov, ki smo jih preučevali v treh slovenskih rekah (Kamniška Bistrica, Sava v Sloveniji in Idrijci) in predstavljajo idealen naravni laboratorij za študij biogeokemisjkih procesov in antropogenih vplivov v porečjih z visoko intenzivnostjo preperevanja. Vodna geokemija Kamniške Bistrice, Save v Sloveniji in Idrijce je dominirana s HCO_3^-, Ca^{2+} in Mg^{2+} ter Ca^{2+}/Mg^{2+} molarnim razmerjem in kaže da je kalcitno/dolomitno preperevanje glavni vir ionov v rečnem sistemu. Kamniška Bistrica, reka Sava v Sloveniji in Idrijca ter njeni pritoki so prenasičeni glede na kalcit in dolomit. Koncentracije pCO_2 so v povprečju 25 krat nad atmosferskimi vrednostmi v Kamniški Bistrici, 20 krat nad atmosferskim v reki Savi v Sloveniji ter 13 krat v reki Idrijci. $\delta^{13}C_{DIC}$ vrednosti se v Kamniški Bistrici spreminjajo od -12,7 do -2,7 ‰, od -12,7 do -6,3 ‰ v reki Savi v Sloveniji in od 10,8 do -6,6 ‰ v reki Idrijci. V vseh raziskanih rekah je raztapljanje karbonatov najpomembnejši biogeokemijski proces, ki vpliva na izotopsko sestavo ogljika v zgornjem delu porečja, medtem ko raztapljanje karbonatov in razgradnja organske snovi kontrolirata izotopsko sestavo ogljika v spodnjem delu porečja, razen v reki Idrijci, kjer oba procesa vplivata enako od izvira do izliva v reko Sočo.

Introduction

Systematic studies of river water geochemistry provide important information on chemical weathering of bedrock/soil and natural and anthropogenic processes that may control the dissolved chemical loads (Schulte et al., 2011; Gibbs, 1972; Reeder et al., 1972; Huh et al., 1998; Négrel & Lachassagne, 2000). Since carbonate weathering largely dominates the water chemistry of river waters, characterization of rivers draining carbonate-dominated terrain is crucial to precisely identify the various contributions of the different sources of water solutes, and to estimate the weathering fluxes of the continental crust and associated CO_2 consumption (Liu & Zhao, 2000).

Freshwaters cover small fraction of the Earth's surface area, inland freshwater ecosystems (particularly lakes, rivers and reservoirs) have rarely been considered as potentially important quantitative components of the carbon cycle at either global or regional scales (Cole et al., 2007). Rivers are the major pathways for the transport of carbon (C) from the continents top the oceans. Global river carbon fluxes are estimated to be 0.4 Pg C/year of organic C (evenly divided between particulate and dissolved phases) and 0.4 Pg C/year for dissolved inorganic carbon (DIC). Bulk fluxes are small components of the global C cycle but are significant compared to net oceanic uptake of anthropogenic CO_2 (Sarmiento & Sundquist, 1992).

Concentrations of DIC and its isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) are governed by processes occurring in the river system and vary seasonally. Changes of DIC concentrations result from carbon addition or removal from the DIC pool, while changes of its isotopic composition result from the fractionation accompanying transformation of carbon or mixing of carbon from different sources (Atekwana & Krishnamurthy, 1998). The major sources of carbon to riverine DIC loads are dissolution of carbonate minerals, soil CO_2 derived from root respiration and from microbial decomposition of organic matter and exchange with atmospheric CO_2. The major processes removing riverine DIC are carbonate mineral precipitation, CO_2 degassing, and aquatic photosynthesis (Atekwana & Krishnamurthy, 1998). Rivers in Slovenia 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 (Germ et al., 1999).

The relative contributions of C3 and C4 vegetation to an ecosystem can be reconstructed using the isotopic composition of particulate organic carbon (POC, e.g. $\delta^{13}C_{POC}$), because of their different isotopic composition, which ranges from -32.0 to -20.0 ‰ for C3 plants and from -15.0 to -9.0 ‰ for C4 plants (Deines, 1980). Vegetation of the River Sava watershed in Slovenia is described in detail in Kanduč et al. (2007) and references therein. Detail evaluation of some selected sites of River Sava watershed was described with aquatic moss *Fontinalis antipyretica* (Mechora & Kanduč, 2016). Hydrogeochemical and isotopic characterization of River Pesnica, Slovenia was described in detail in Kanduč et al. (2016).

Application of stable isotopes and biogeochemical processes in environmental studies is presented in Pezdič (1999). In this study we represent summary (review) of biogeochemical research with application of stable isotope analysis of river systems; three rivers were subject of investigation during years 2004–2011 in different time related to national research projects and program founding P1-0143 in Slovenia: River Kamniška Bistrica (Kanduč et al., 2013), River Sava in Slovenia (Kanduč et al., 2007) and River Idrijca (Kanduč et al., 2008) presented in the Figures 1 and 2.

Study area

Catchment and hydrological characteristics of gravel bed rivers

River Kamniška Bistrica is the left tributary of the River Sava, which is the largest river in Slovenia (Figs. 1 and 2). Kamniška Bistrica emerges at the southern foothills of Kamnik-Savinja Alps at 630 m a.s.l. elevation. The river is 32.8 km long and drains an area of 380 km^2, with an average discharge of 15.4 m^3/s at its confluence with River Sava. The average discharge at the mouth of the River Kamniška Bistrica measured during this study was 0.7-12.1 m^3/s. According to discharge regimes of all rivers and streams in Slovenia, River Kamniška Bistrica has an alpine high mountain snow-rain regime (Hrvatin, 1998). The maximum discharge occurs in autumn (November) and spring (May) and minimum occurs in summer (August) and winter (February). Major

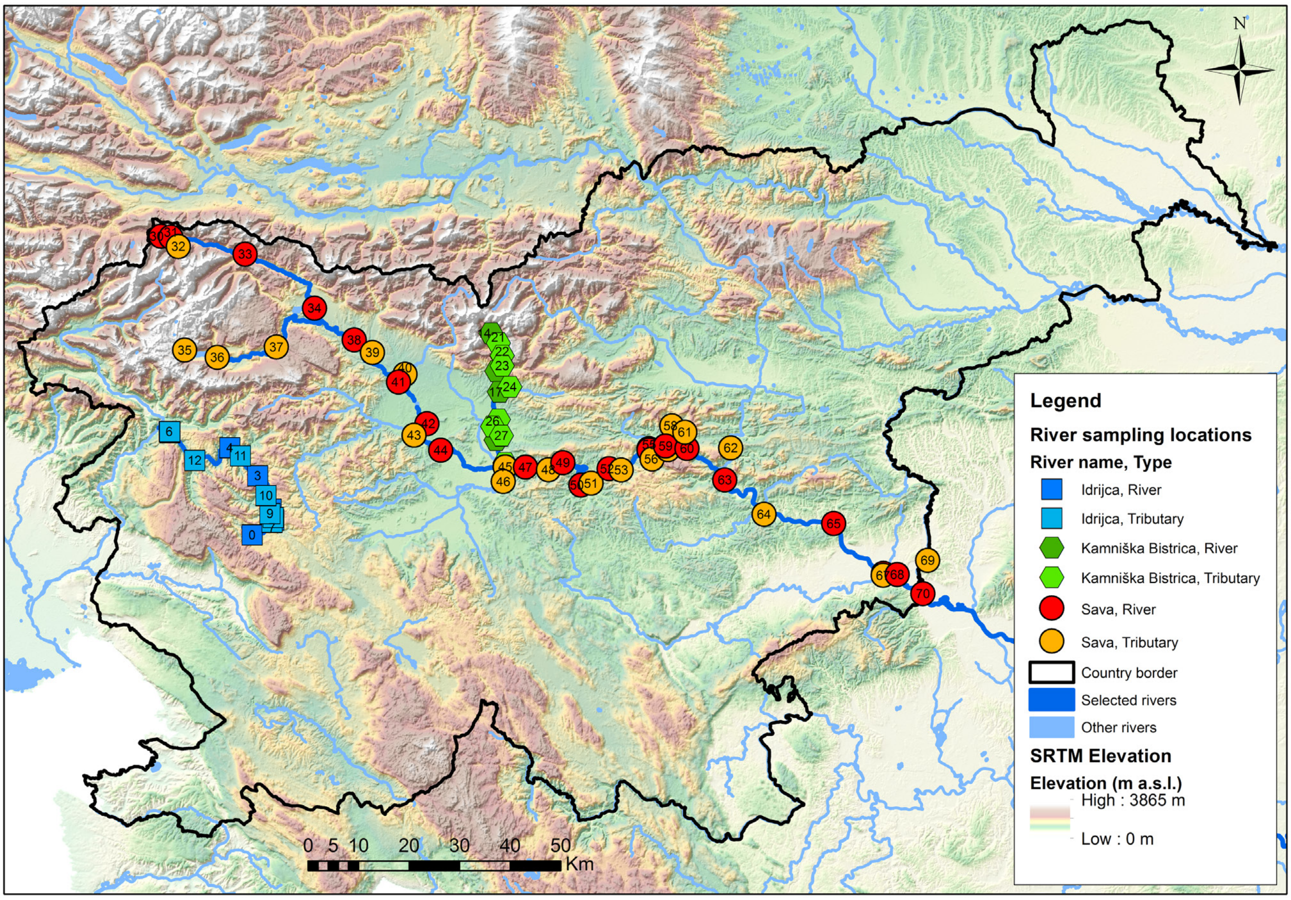

Fig. 1. General topographic map of the major river network in Slovenia, with a detailed location map of the numbered sampling sites for the rivers Kamniška Bistrica, Sava (Slovenian part) and Idrijca. Digital elevation model (DEM) was obtained from the Shuttle Radar Topography Mission (SRTM) dataset (Internet 1). Numbers correspond to the sampling points IDs (see Tables 1 and 2).

tributaries of the River Kamniška Bistrica are the Črna and Nevljica rivers on the left and River Pšata on the right. In the upper reaches, from the headwater spring to Stahovica (at the confluence with River Črna), River Kamniška Bistrica changes over a short distance (6.8 km downstream) from a clean alpine river to industrially and agriculturally affected river at the confluence with the tributary River Črna, which carries sediments and waste waters from the abandoned Črna kaolin mine (Radinja et al., 1987).

Discharge regimes of the River Sava are controlled by precipitation and the configuration of the landscape. In the upper part of the River Sava a snow-rain regime prevails and in the central and lower part a rain-snow regime (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^3/s of the upper section of the River Sava at Radovljica (location 35, Table 1, Fig. 1) to 182 m^3/s of the central section at Hrastnik (location 60, Table 1, Fig. 1) and to 290 m^3/s in the lower section of the river at Čatež (location 68, Table 1, Fig. 1) (Internet 2). Discharges are also controlled by hydropower outflows along the Sava River. The discharge conditions for the River Sava and its tributaries during the study ranged from 2 to 344 m^3/s during spring 2004, from 1 to 144 m^3/s during late summer 2004, and from 0.3 to 128 m^3/s during winter, respectively. The River Idrijca joins the River Soča in the middle stretch at the village of Most na Soči. Both rivers have torrential characteristics. Detail description of the Idrijca catchment is described in Kanduč et al. (2008). High peaks and steep mountain slopes prevent air circulation in the valley and induce severe erosion. Characteristic long-term discharge data (from the years 1949 to 2015) according to the Slovenian Environment Agency for the gauging station on the Idrijca at Hotešk, which is located above the confluence with the River Soča, are as follows: low long-term discharge varies from 3.4 to 8.5 m^3/s, mean long-term discharge varies from 14.3 to 39 m^3/s, and high long-term discharge varies from 113 to 644 m^3/s (Internet 2).

General geological setting of selected river watersheds

This chapter summarizes the general geological setting of the river watershed areas, as the geological composition of each river basin is very complex (Fig. 1). Therefore, the prevailing geological units are described below. Detailed general description of geological setting of investigated Slovenian rivers is described in detail in Kanduč et al. (2007, 2008 and 2013).

River Kamniška Bistrica. The upper part of the River Kamniška Bistrica is underlain by massive and stratified limestone and dolomite of middle and upper Triassic age (Fig. 2), and carbonates generally prevail in the watershed. The middle part of the river is underlain by marlstone and limestone of Miocene age (Buser, 1987). The lower reaches of the River Kamniška Bistrica, along the right bank and before the confluence with the River Sava, is underlain by Pleistocene and Holocene age gravels, while the left bank is underlain by Permo-Carboniferous shales with a cover of Quaternary gravel. The River Kamniška Bistrica is also one of the Slovenian watersheds identified as having a high weathering capacity, due to the predominance of carbonate bedrock and high relief and precipitation (Kanduč et al., 2013).

River Sava in Slovenia. The valley of the Sava River extends in a NW-SE direction comprising almost half the surface area of Slovenia and has a very heterogeneous geological composition. Both branches of the Sava River (Sava Bohinjka and Sava Dolinka rivers) emerge in the Julian Alps, composed mostly of Triassic limestones and dolomites. Leaving the Alps approximately at the confluence of the Sava Bohinjka and Sava Dolinka rivers, river then flows on the Holocene and Pleistocene fluvioglacial sediments (terraces) (Žlebnik, 1971). Eastwards from the city of Ljubljana, the watershed in Sava folds is mainly composed of Permo-Carbonian clastic sediments, which alternate with some Triassic carbonates, with Miocene sandstones, clays and gravels in some of the valleys. Leaving the Sava folds, the watershed in the Krško-Brežice area mainly consists of terraced Holocene and Pleistocene sediments - sands and gravels. The catchments of the River Sava's tributaries are composed of Triassic and Jurassic carbonates, Permo-Carbonian sandstones and siltstones, Oligocene clay and volcanic rocks, Miocene clastic rocks and Pleistocene sediments (Buser, 1987).

River Idrijca. The beds in the upper part of the River Idrijca are composed of various sedimentary and volcanic rocks, predominantly massive and stratified Triassic limestones and dolomites. Along Idrijca, Middle Permian mica quartz sandstone and red sandstone with conglomerate are exposed as the oldest rocks. In the lower part of the flow, before the confluence with the River Soča, stratified and massive Upper Triassic dolomites and Cretaceous limestones with marls appear (Buser, 1987). In general, the Idrija region has a very complex tectonic structure (Mlakar & Čar 2009; Čar, 2010) with several major faults dissecting the area and tectonic nappes overlying several units.

Materials and methods

Sampling and used methods

Surface water sampling locations (Fig. 1, Tables 1 and 2) were selected based on their relationship to confluence of the major and minor streams, typically sampled before and after the confluence. Sampling of river water and tributaries was performed at different sampling seasons according to discharge regimes (Hrvatin, 1998; Fratar, 2005). Temperature, conductivity, dissolved oxygen (DO), and pH measurements were performed in the field. The precision of dissolved oxygen saturation and conductivity measurements was ±5 %. The field pH was determined on the NBS scale using two buffer calibrations with reproducibility of ±0.02 pH unit. Total alkalinity was measured within 24h of sample collection by Gran titration (Gieskes, 1974) with a precision of ±1%. Carbonate rocks from hinterland of river watershed were ground to powder in an agate mortar and then approximately 2 mg of sample was first flushed with He and then transformed to CO_2 by H_3PO_4 acid treatment. NBS 18 and NBS 19 were used as reference materials. The isotopic composition of carbonate ($\delta^{13}C_{CaCO3}$) was measured with a Europa Scientific 20-20 continuous flow IRMS ANCA-TG preparation module. All methods are described in detail in Kanduč et al. (2007, 2008 and 2013).

All stable isotope results for carbon are expressed in the conventional delta (δ) notation, defined as per mil (‰) deviation from the reference standards VPDB. Precision was ±0.2 ‰ for $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$ and $\delta^{13}C_{CaCO3}$.

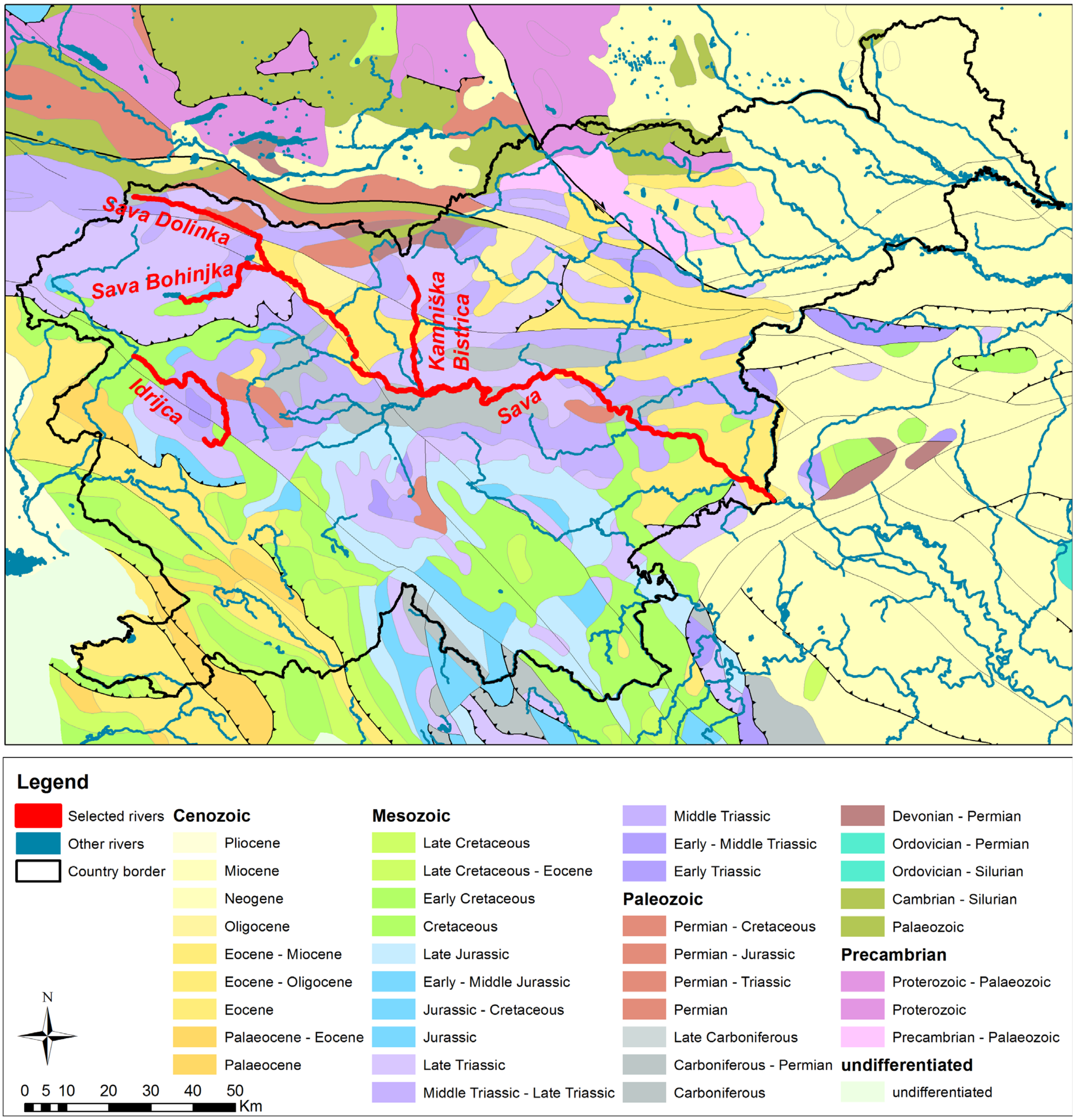

Fig. 2. General geological map of Slovenia with selected three rivers: Kamniška Bistrica, Sava in Slovenia and Idrijca. Geological data were obtained from the 1: 5 Million International Geological Map of Europe and Adjacent Areas (IGME 5000) dataset (Internet 3).

Major and minor cation chemistry was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) technique. The precision of the method was ±2% for major (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and ±5% for minor elements (Sr and Si). The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined with a Europa Scientific 20-20 continuous flow IRMS ANCA-TG preparation module. Phosphoric acid (H_3PO_4, 100 %) was added (100-200 µl) to a septum-sealed vial which was then purged with pure He. The water sample (6 mL) was injected into a septum tube and headspace 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 Na_2CO_3 (Carlo Erba) with a known $\delta^{13}C_{DIC}$ of -10.8 ‰ ± 0.2 ‰ was prepared with a concentration of either 4.8 mol/L (for samples with alkalinity above 2 mmol/L) or of 2.4 mmol/L (for samples with alkalinity below 2 mmol/L). The carbon stable isotope composition of particulate organic carbon ($\delta^{13}C_{POC}$) was determined with a

Table 1. Sampling locations and geochemical data for spring sampling season (sampling years: Idrijca: 2006-2007, Kamniška Bistrica: 2010-2011, Sava: 2004-2005). ID numbers correspond to the locations in Figure 1.

ID	Name	River	Type	LAT (°)	LON (°)	Z (m)	T (°C)	pH (-)	Alkal. mmol/L	EC (µS/cm)	Ca^{2+} mmol/L	Mg^{2+} mmol/L	Na^{+} mmol/L	K^{+} mmol/L	Si mmol/L	SO_4^{2-} mmol/L	Cl^{-} mmol/L	NO_3^{-} mmol/L	pCO_2 (bar)	$SI_{calcite}$ (-)	$SI_{dolomite}$ (-)	$\delta^{13}C_{DIC}$ (‰)
0	Idrijca	Confluence Idrijca/Belca	River	45.963396	13.981281	389	9.00	8.43	4.12	333.0	0.82	0.74	0.05	0.00	0.00	0.04	0.03	0.06	-3.14	0.66	1.17	-9.4
1	Idrijca	Podroteja	River	45.990652	14.035864	325	7.30	7.92	4.20	353.0	0.93	0.75	0.07	0.00	0.00	0.05	0.07	0.09	-2.62	0.20	0.16	-10.6
2	Idrijca	Kolektor	River	46.009519	14.028858	316	10.8	8.43	4.33	367.0	1.15	0.87	0.11	0.05	0.02	0.11	0.10	0.05	-3.12	0.84	1.48	-10.1
3	Idrijca	Travnik	River	46.068869	13.993716	267	11.4	8.44	4.43	485.0	1.00	1.22	0.10	0.02	0.02	0.72	0.10	0.05	-3.12	0.80	1.62	-9.2
4	Idrijca	Kozarska grapa	River	46.117877	13.921682	227	11.7	8.29	4.26	416.0	1.01	0.89	0.11	0.02	0.03	0.36	0.11	0.04	-2.97	0.66	1.21	-9.3
5	Idrijca	Before Bača	River	46.143312	13.767604	153	13.0	8.82	4.27	383.0	1.16	0.85	0.10	0.05	0.00	0.00	0.00	0.47	-3.53	1.22	2.27	-8.4
6	Idrijca	After Bača	River	46.144954	13.765608	152	12.7	8.77	4.20	356.0	1.15	0.84	0.11	0.05	0.02	0.00	0.00	0.05	-3.48	1.16	2.15	-8.3
7	Idrijca	Zala	Tributary	45.986561	14.031768	328	10.6	8.09	4.87	420.0	1.27	0.98	0.17	0.04	0.03	0.07	0.15	0.06	-2.72	0.60	1.00	-9.7
8	Idrijca	Ljubevšča	Tributary	45.995142	14.034411	325	10.2	8.54	5.04	444.0	1.32	1.05	0.30	0.05	0.07	0.10	0.29	0.05	-3.17	1.04	1.90	-9.6
9	Idrijca	Nikova	Tributary	46.00197	14.026078	325	10.1	8.67	4.81	418.0	1.31	0.91	0.20	0.06	0.04	0.10	0.13	0.04	-3.33	1.14	2.03	-9.4
10	Idrijca	Kanomljica	Tributary	46.033902	14.015139	302	10.8	8.29	4.33	368.0	1.23	0.87	0.08	0.05	0.04	0.15	0.00	0.04	-2.93	0.78	1.32	-9.4
11	Idrijca	Cerknica	Tributary	46.103916	13.948576	245	11.8	8.35	3.52	349.0	1.25	0.47	0.19	0.06	0.10	0.19	0.12	0.02	-3.12	0.75	1.00	-7.6
12	Idrijca	Trebuščica	Tributary	46.094549	13.832344	188	11.6	8.37	4.01	181.0	1.00	0.85	0.06	0.04	0.02	0.05	0.03	0.05	-3.08	0.71	1.29	-8.0
13	Idrijca	Bača	Tributary	46.144888	13.767263	154	12.2	8.37	3.15	282.0	1.18	0.32	0.08	0.05	0.07	0.08	0.00	0.05	-3.21	0.74	0.86	-6.9
14	Kamniška Bistrica	Spring	River	46.3257344	14.58846446	623	5.70	8.29	1.55	188.5	0.70	0.18	0.04	0.00	0.00	0.01	0.00	0.03	-3.42	0.04	-0.68	-2.7
15	Kamniška Bistrica	before Stahovica	River	46.28567753	14.61692482	530	7.10	8.40	2.33	194.0	0.80	0.24	0.03	0.00	0.01	0.02	0.01	0.04	-3.36	0.39	0.10	-5.0
16	Kamniška Bistrica	after Stahovica	River	46.25867675	14.60364769	450	7.70	8.63	2.38	198.6	0.90	0.27	0.05	0.00	0.01	0.03	0.03	0.04	-3.60	0.64	0.62	-5.6
17	Kamniška Bistrica	Kamnik	River	46.2215134	14.61034338	378	10.6	8.61	2.86	238.4	1.04	0.33	0.11	0.01	0.02	0.03	0.06	0.04	-3.54	0.80	0.97	-7.4
18	Kamniška Bistrica	Vir	River	46.14710269	14.60453603	310	14.6	8.73	2.82	239.3	1.04	0.32	0.09	0.01	0.02	0.01	0.03	0.02	-3.59	0.98	1.45	-6.9
19	Kamniška Bistrica	Domžale	River	46.13584974	14.60277837	300	9.50	8.54	3.35	282.7	1.20	0.42	0.21	0.02	0.03	0.06	0.16	0.04	-3.34	0.85	1.15	-7.3
20	Kamniška Bistrica	Videm	River	46.08835696	14.62594168	260	12.5	8.34	4.39	368.3	1.50	0.50	0.38	0.05	0.05	0.04	0.16	0.11	-3.01	0.91	1.36	-9.6
21	Kamniška Bistrica	Dolski Graben	Tributary	46.30851523	14.60699003	570	7.80	8.15	2.92	239.7	1.21	0.18	0.05	0.00	0.35	0.03	0.02	0.05	-3.00	0.41	-0.13	-9.8
22	Kamniška Bistrica	Bistričica	Tributary	46.28606501	14.61710383	470	9.90	8.49	3.79	317.1	1.17	0.66	0.13	0.02	0.06	0.08	0.06	0.05	-3.25	0.85	1.36	-8.7
23	Kamniška Bistrica	Črna	Tributary	46.26802869	14.61710383	470	8.70	8.47	2.72	291.0	1.12	0.50	0.24	0.02	0.06	0.08	0.22	0.05	-3.36	0.66	0.86	-8.7
24	Kamniška Bistrica	Nevljica	Tributary	46.23068024	14.63750483	460	10.4	8.42	4.53	358.4	1.72	0.43	0.18	0.02	0.07	0.11	0.11	0.05	-3.07	0.99	1.28	-11.0
25	Kamniška Bistrica	Radomeljska Mlinščica	Tributary	46.17251455	14.60803291	340	8.90	8.54	2.91	234.0	1.05	0.32	0.11	0.01	0.02	0.04	0.07	0.04	-3.40	0.74	0.85	-7.10
26	Kamniška Bistrica	Pšata	Tributary	46.16032599	14.59330627	338	16.1	8.34	4.25	409.4	1.20	0.35	0.24	0.04	0.04	0.09	0.23	0.22	-2.96	0.82	1.11	-10.5
27	Kamniška Bistrica	Rača	Tributary	46.14401047	14.61606564	310	13.5	8.38	4.33	390.3	0.60	0.38	0.21	0.02	0.03	0.09	0.41	0.05	-3.04	0.59	0.96	-10.7
28	Kamniška Bistrica	Homška Mlinščica	Tributary	46.09543708	14.62563539	290	10.5	8.61	3.09	243.9	1.05	0.33	0.19	0.01	0.02	0.05	0.17	0.05	-3.43	0.85	1.12	-6.9
29	Kamniška Bistrica	Pšata channel	Tributary	46.08835696	14.62594168	280	9.80	8.38	3.58	327.1	1.40	0.41	0.22	0.04	0.08	0.08	0.16	0.09	-3.15	0.80	0.96	-10.9
30	Sava	Sava Dolinka, spring	River	46.49238108	13.73738958	830	8.60	7.83	2.98	276.0	1.02	0.52	0.05	0.00	0.03	0.06	0.00	0.03	-2.67	0.04	-0.34	-10.7
31	Sava	Sava Dolinka, Podkoren	River	46.4910896	13.76249572	829	8.90	8.14	2.62	244.0	0.00	0.00				0.10	0.15	0.02	-3.80			-10.3
32	Sava	Pišnica at Kranjska gora	Tributary	46.47464479	13.78197234	819	7.60	8.36	2.37	216.0	0.82	0.44	0.07	0.00	0.01	0.07	0.00	0.04	-3.31	0.36	0.31	-7.9
33	Sava	Sava Dolinka, Dovje	River	46.46265059	13.95393196	704	9.70	8.28	2.81	251.0	1.00	0.53	0.07	0.00	0.03	0.13	0.00	0.03	-3.15	0.45	0.54	-8.6
34	Sava	Sava Dolinka, Šobec	River	46.36797849	14.13464505	459	9.70	8.48	3.19	283.0	1.12	0.43	0.09	0.00	0.02	0.15	0.00	0.04	-3.30	0.75	0.98	-9.6

ID	Name	River	Type	LAT (°)	LON (°)	Z (m)	T (°C)	pH (-)	Alkal. mmol/L	EC (µS/cm)	Ca^{2+} mmol/L	Mg^{2+} mmol/L	Na^+ mmol/L	K^+ mmol/L	Si mmol/L	SO_4^{2-} mmol/L	Cl^- mmol/L	NO_3^- mmol/L	pCO_2 (bar)	$SI_{calcite}$ (-)	$SI_{dolomite}$ (-)	$\delta^{13}C_{DIC}$ (‰)
35	Sava	River Savica	Tributary	46.29039117	13.80250167	700	6.20	8.32	2.00	172.3	0.76	0.18	0.01	0.00	0.01	0.03	0.00	0.04	-3.34	0.21	-0.37	-5.8
36	Sava	Lake Bohinj, outlet	Tributary	46.278398	13.8863417	557	12.3	8.26	2.35	201.0	0.90	0.20	0.05	0.00	0.01	0.04	0.00	0.04	-3.19	0.38	0.06	-8.3
37	Sava	Sava Bohinjka, Nomenj	Tributary	46.29801526	14.03757249	509	9.50	8.43	2.30	203.0	1.01	0.19	0.03	0.00	0.01	0.04	0.03	0.04	-3.39	0.54	0.26	-9.1
38	Sava	Sava Otoček	River	46.31216997	14.23744784	415	10.3	8.57	2.91	254.0	1.10	0.33	0.07	0.00	0.02	0.09	0.00	0.04	-3.43	0.80	0.99	-9.0
39	Sava	Tržiška Bistrica, Bistrica	Tributary	46.29011458	14.28442503	422	11.0	8.95	2.60	277.0	1.22	0.44	0.09	0.00	0.03	0.36	0.00	0.04	-3.89	1.12	1.73	-6.8
40	Sava	Kokra, Kranj	Tributary	46.25204699	14.36869104	407	12.1	8.10	2.64	264.0	1.08	0.43	0.07	0.00	0.02	0.19	0.00	0.04	-2.98	0.33	0.20	-7.0
41	Sava	Sava, Kranj	River	46.23782813	14.35202318	350	10.5	8.59	2.89	246.0	1.15	0.35	0.08	0.01	0.02	0.12	0.08	0.05	-3.45	0.83	1.07	-9.5
42	Sava	Sava, Smlednik	River	46.16419816	14.42555633	336	10.6	8.42	2.79	305.0	1.18	0.38	0.13	0.03	0.02	0.14	0.00	0.06	-3.29	0.67	0.76	-10.2
43	Sava	Sora, Ladja	Tributary	46.14358732	14.39285266	313	10.2	8.37	2.48	260.0	0.93	0.43	0.12	0.01	0.05	0.12	0.00	0.09	-3.29	0.48	0.52	-11.2
44	Sava	Sava, Tacen	River	46.11722401	14.46118304	280	10.4	8.43	3.16	302.0	1.15	0.39	0.10	0.00	0.03	0.14	0.00	0.07	-3.25	0.72	0.88	-10.7
45	Sava	Kamniška Bistrica, Beričevo	Tributary	46.08842291	14.62648002	260	11.2	8.17	3.90	381.0	1.42	0.46	0.35	0.03	0.04	0.17	0.00	0.21	-2.89	0.64	0.72	-12.4
46	Sava	Ljubljanica, Zalog	Tributary	46.06220617	14.62169268	267	10.9	8.10	4.01	391.0	1.47	0.50	0.17	0.00	0.03				-2.81	0.60	0.67	-13.5
47	Sava	Sava, Dolsko	River	46.08799496	14.67835027	265	10.9	8.23	3.27	338.0	1.36	0.45	0.17	0.00	0.03	0.15	0.00	0.10	-3.03	0.61	0.66	-12.7
48	Sava	Jevnica, Jevnica	Tributary	46.08360965	14.73719533	240	13.0	7.79	0.39	62.3	0.15	0.08	0.13	0.03	0.16	0.07	0.07	0.03	-3.47	-1.56	-3.46	-8.1
49	Sava	Sava, Kresnice	River	46.09632929	14.77395623	235	11.1	8.20	3.60	324.0	1.33	0.45	0.17	0.01	0.03	0.14	0.00	0.09	-2.56	0.61	0.68	-12.5
50	Sava	Sava, Litija	River	46.05646171	14.82051447	230	12.1	8.27	3.28	323.0	1.34	0.45	0.16	0.00	0.03	0.15	0.00	0.12	-3.06	0.66	0.79	-12.3
51	Sava	Reka pri Bregu, Litija	Tributary	46.05962086	14.84614684	245	13.4	8.18	2.59	272.0	0.80	0.62	0.17	0.03	0.11	0.14	0.00	0.08	-3.05	0.29	0.43	-13.2
52	Sava	Sava, Log	River	46.08563083	14.89206999	230	11.2	8.18	3.00	344.0	1.26	0.45	0.15	0.01	0.03	0.14	0.16	0.09	-3.01	0.50	0.98	-12.0
53	Sava	Polšnik, Sava	Tributary	46.08337901	14.92308091	260	8.40	8.17	1.87	208.0	0.57	0.45	0.15	0.03	0.14	0.15	0.09	0.03	-3.21	-0.06	-0.36	-11.6
54	Sava	Medija, Zagorje	Tributary	46.12125638	14.99434953	240	8.70	8.16	4.15	491.0	1.64	0.76	0.29	0.05	0.10	0.38	0.00	0.12	-2.87	0.66	0.87	-13.0
55	Sava	Sava, Zagorje	River	46.11889003	14.99455671	225	10.4	8.10	3.32	380.0	1.34	0.48	0.17	0.00	0.03	0.16	0.17	0.10	-2.89	0.48	0.41	-11.0
56	Sava	Šklendrovec, Zagorje	Tributary	46.10301833	15.00215046	350	8.70	8.34	4.26	424.0	1.48	0.91	0.15	0.01	0.05	0.25	0.16	0.05	-3.04	0.80	1.28	-12.4
57	Sava	Mitovšica, Trbovlje	Tributary	46.11971806	15.04299911	350	8.40	8.19	3.34	318.0	1.57	0.34	0.03	0.00	0.03	0.17	0.05	0.08	-2.99	0.60	0.41	-12.6
58	Sava	Trboveljščica, Trbovlje	Tributary	46.16192117	15.05268008	230	10.1	8.31	3.56	389.0	0.91	0.76	0.39	0.04	0.12	0.28	0.01	0.11	-3.08	0.53	0.89	-10.5
59	Sava	Sava, Trbovlje	River	46.12621671	15.03632723	220	10.7	8.08	3.57	395.0	1.37	0.49	0.20	0.01	0.03	0.21	0.18	0.10	-2.84	0.50	0.46	-11.5
60	Sava	Sava, Hrastnik	River	46.12155113	15.0916258	210	10.8	8.08	3.38	349.0	1.32	0.47	0.18	0.01	0.02	0.16	0.17	0.10	-2.86	0.46	0.39	-11.5
61	Sava	Boben, Hrastnik	Tributary	46.15057264	15.08592694	220	11.0	8.10	4.48	573.0						1.13	0.21	0.15	-2.74			-9.5
62	Sava	Savinja, Rimske Toplice	Tributary	46.12262895	15.20328147	200	14.4	8.98	3.04	375.0	1.30	0.43	0.32	0.03	0.03	0.30	0.00	0.12	-3.85	1.27	2.06	-8.5
63	Sava	Sava, Radeče	River	46.06552039	15.18817906	193	11.6	8.10	3.66	375.0	1.34	0.47	0.20	0.02	0.03	0.19	0.00	0.10	-2.84	0.53	0.54	-11.1
64	Sava	Mirna, Dol Bostanj	Tributary	46.0042524	15.28807396	191	12.9	8.48	4.57	443.0	1.66	0.82	0.11	0.00	0.07	0.19	0.00	0.05	-3.14	1.07	1.80	-11.5
65	Sava	Sava, Brestanica	River	45.98708882	15.46596947	150	13.4	8.42	3.17	383.0	1.38	0.48	0.19	0.01	0.03	0.18	0.16	0.10	-3.23	0.82	1.14	-10.0
66	Sava	Sava, Brežice	River	45.89794945	15.59147525	145	14.2	8.04	3.39	396.0	1.42	0.52	0.21	0.02	0.03	0.22	0.00	0.10	-2.53	0.50	0.54	-11.9
67	Sava	Krka, Čatež	Tributary	45.89436142	15.59106334	140	13.5	8.32	4.33	423.0	1.67	0.50	0.11	0.00	0.04	0.10	0.00	0.09	-2.99	0.92	1.30	-12.9
68	Sava	Sava, Mostec	River	45.89565401	15.62699197	140	13.4	8.28	3.52	412.0	1.52	0.50	0.16	0.00	0.03	0.16	0.16	0.10	-3.04	0.76	1.02	-11.1
69	Sava	Sotla, Rakovec	Tributary	45.92058244	15.70479521	140	14.0	8.15	5.22	570.0	2.33	0.68	0.37	0.05	0.09	0.41	0.29	0.11	-2.74	0.95	1.35	-11.8
70	Sava	Sava, Bregana	River	45.86110493	15.69178091	135	13.8	8.23	3.75	398.0	1.48	0.50	0.17	0.01	0.03	0.19	0.00	0.09	-2.96	0.74	0.98	-11.1

Table 2. Sampling locations and geochemical data for autumn sampling season (sampling years: Idrijca: 2006-2007, Kamniška Bistrica: 2010-2011, Sava: 2004-2005). ID numbers correspond to the locations in Figure 1.

GIS_ ID	Name	River	Type	LAT (°)	LON (°)	Z (m)	T (°C)	pH	Alkal. mmol/L	EC µS/cm	Ca^{2+} mmol/L	Mg^{2+} mmol/L	Na^{+} mmol/L	K^{+} mmol/L	Si mmol/L	SO_4^{2-} mmol/L	Cl^{-} mmol/L	NO_3^{-} mmol/L	pCO_2 bar	SI_{cal}	SI_{dol}	$\delta^{13}C_{DIC}$ (‰)
0	Idrijca	Confluence Idrijca/Belca	River	45.963396	13.981281	389	8.8	8.17	4.35	338.0	1.05	0.76	0.06	0.02	0.03	0.07	0.04		-2.77	0.61	0.96	-10.1
1	Idrijca	Podroteja	River	45.990652	14.035864	325	8.0	7.96	3.88	327.0	1.23	0.68	0.06	0.01	0.02	0.06	0.07		-2.61	0.42	0.44	-9.3
2	Idrijca	Kolektor	River	46.009519	14.028858	316	6.5	7.73	3.93	364.0	1.16	0.78	0.07	0.01	0.02	0.08	0.07		-2.38	0.14	-0.05	-10.8
3	Idrijca	Travnik	River	46.068869	13.993716	267	8.5	8.34	4.01	375.0	1.18	0.94	0.08	0.02	0.02	0.14	0.08		-2.98	0.78	1.33	-10.1
4	Idrijca	Kozarska grapa	River	46.117877	13.921682	227	9.0	8.06	3.99	409.0	1.26	0.97	0.12	0.06	0.02	0.35	0.11		-2.70	0.54	0.86	-9.4
5	Idrijca	Before Bača	River	46.143312	13.767604	153	9.5	8.82	4.21	410.0	1.26	1.03	0.09	0.01	0.02	0.37	0.08		-2.92	0.80	1.41	-9.2
6	Idrijca	After Bača	River	46.144954	13.765608	152	9.6	8.26	4.66	412.0	1.26	1.00	0.11	0.03	0.02	0.38	0.10		-2.83	0.80	1.40	-9.0
7	Idrijca	Zala	Tributary	45.986561	14.031768	328																
8	Idrijca	Ljubevšča	Tributary	45.995142	14.034411	325	8.3	8.29	5.10	465.0	1.37	1.09	0.33	0.04	0.05	0.17	0.31		-2.83	0.87	1.53	-10.4
9	Idrijca	Nikova	Tributary	46.00197	14.026078	325	8.4	8.23	4.70	434.0	1.38	0.89	0.23	0.04	0.04	0.14	0.19		-2.80	0.80	1.28	-9.9
10	Idrijca	Kanomljica	Tributary	46.033902	14.015139	302	8.2	8.34	4.08	378.0	1.26	0.90	0.07	0.02	0.03	0.21	0.06		-2.98	0.81	1.34	-8.7
11	Idrijca	Cerknica	Tributary	46.103916	13.948576	245	9.5	8.19	3.63	378.0	1.35	0.51	0.37	0.05	0.09	0.09	0.78		-2.86	0.65	0.80	-6.9
12	Idrijca	Trebuščica	Tributary	46.094549	13.832344	188	8.6	7.77	3.89	348.0	1.01	0.86	0.05	0.01	0.02	0.07	29.76		-2.41	0.16	0.12	-8.2
13	Idrijca	Bača	Tributary	46.144888	13.767263	154	9.2	8.27	3.09	282.0	1.17	0.34	0.08	0.02	0.06	0.10	0.04		-3.01	0.63	0.62	-6.6
14	Kamniška Bistrica	Spring	River	46.3257344	14.58846446	623	5.9	7.35	1.93	160.7	0.73	0.18	0.05	0.00	0.01	0.01	0.01	0.03	-2.37	-0.77	-2.34	-3.6
15	Kamniška Bistrica	before Stahovica	River	46.28567753	14.61692482	530	6.5	8.02	2.74	211.0	0.96	0.29	0.07	0.01	0.01	0.02	0.02	0.04	-2.89	0.15	-0.39	-6.7
16	Kamniška Bistrica	after Stahovica	River	46.25867675	14.60364769	450	6.8	8.10	3.00	225.5	1.00	0.32	0.07	0.01	0.03	0.03	0.03	0.04	-2.90	0.28	-2.95	-7.3
17	Kamniška Bistrica	Kamnik	River	46.2215134	14.61034338	378	7.7	8.15	3.48	269.3	1.21	0.35	0.11	0.02	0.05	0.06	0.06	0.06	-2.91	0.48	0.28	-9.2
18	Kamniška Bistrica	Vir	River	46.14710269	14.60453603	310	9.3	8.23	3.51	277.9	1.29	0.35	0.12	0.02	0.06	0.06	0.07	0.06	-2.98	0.61	0.54	-9.7
19	Kamnišk Bistrica	Domžale	River	46.13584974	14.60277837	300	9.1	8.18	3.72	259.7	1.30	0.39	0.17	0.02	0.07	0.07	0.12	0.07	-2.91	0.61	0.59	-10.1
20	Kamniška Bistrica	Videm	River	46.08835696	14.62594168	260	9.7	7.92	4.19	334.8	1.43	0.45	0.25	0.03	0.07	0.08	0.20	0.11	-2.59	0.42	0.24	-10.7
21	Kamniška Bistrica	Dolski Graben	Tributary	46.30851523	14.60699003	570	7.0	7.82	3.61	259.7	1.34	0.19	0.10	0.01	0.02	0.03	0.02	0.05	-2.57	0.20	-0.60	-10.8
22	Kamniška Bistrica	Bistričica	Tributary	46.28606501	14.61710383	470	7.3	8.12	4.31	267.0	1.27	0.66	0.11	0.02	0.07	0.07	0.04	0.06	-2.79	0.54	0.64	-10.0
23	Kamniška Bistrica	Črna	Tributary	46.26802869	14.61710383	470	6.8	8.26	3.25	272.6	1.07	0.41	0.17	0.02	0.07	0.07	0.12	0.09	-3.06	0.49	0.41	-9.9
24	Kamniška Bistrica	Nevljica	Tributary	46.23068024	14.63750483	460	8.3	8.04	4.58	355.6	1.93	0.22	0.12	0.01	0.06	0.09	0.06	0.10	-2.68	0.67	0.28	-12.6
25	Kamniška Bistrica	Radomeljska Mlinščica	Tributary	46.17251455	14.60803291	340	8.3	8.21	3.55	274.5	1.24	0.35	0.11	0.02	0.05	0.06	0.06	0.06	-2.96	0.56	0.45	-9.2
26	Kamniška Bistrica	Pšata	Tributary	46.16032599	14.59330627	338	8.4	8.07	3.90	309.1	1.46	0.33	0.16	0.03	0.10	0.08	0.11	0.10	-2.78	0.53	0.29	-12.1
27	Kamniška Bistrica	Rača	Tributary	46.14401047	14.61606564	310	9.0	8.03	3.92	329.1	1.29	0.52	0.30	0.04	0.09	0.10	0.25	0.09	-2.73	0.45	0.39	-12.7
28	Kamniška Bistrica	Homška Mlinščica	Tributary	46.09543708	14.62563539	290	8.8	8.25	3.45	276.4	1.21	0.35	0.15	0.02	0.00	0.07	0.09	0.07	-3.01	0.59	0.52	-8.8
29	Kamniška Bistrica	Pšata channel	Tributary	46.08835696	14.62594168	280	9.5	7.93	4.12	338.0	1.51	0.42	0.17	0.03	0.09	0.09	0.13	0.11	-2.61	0.44	0.23	-12.6
30	Sava	Sava Dolinka, spring	River	46.49238108	13.73738958	830	5.6	7.54	2.63	279.0	0.91	0.47	0.07	0.01	0.02	0.05	0.07	0.03	-2.44	-0.39	-1.25	-7.8
31	Sava	Sava Dolinka, Podkoren	River	46.4910896	13.76249572	829	7.1	7.56	2.67	380.0	0.93	0.47	0.13	0.00	0.05	0.10	0.30	0.03	-2.45	-0.34	-1.12	-8.6
32	Sava	Pišnica at Kranjska gora	Tributary	46.47464479	13.78197234	819	7.6	7.82	3.36	239.0	0.86	0.44	0.05	0.02	0.01	0.05	0.04	0.03	-2.61	-0.01	-0.44	-5.4
33	Sava	Sava Dolinka, Dovje	River	46.46265059	13.95393196	704	8.5	7.86	2.65	286.0	1.00	0.51	0.07	0.02	0.03	0.40	0.06	0.06	-2.76	-0.04	-0.50	-7.3
34	Sava	Sava Dolinka, Šobec	River	46.36797849	14.13464505	459	10.7	8.31	3.06	311.0	1.12	0.51	0.10	0.01	0.03	0.19	0.12	0.06	-3.14	-0.58	0.73	-7.3

GIS_ ID	Name	River	Type	LAT (°)	LON (°)	Z (m)	T (°C)	pH	Alkal. mmol/L	EC µS/cm	Ca^{2+} mmol/L	Mg^{2+} mmol/L	Na^{+} mmol/L	K^{+} mmol/L	Si mmol/L	SO_4^{2-} mmol/L	Cl^{-} mmol/L	NO_3^{-} mmol/L	pCO_2 bar	SI_{cal}	SI_{dol}	$\delta^{13}C_{DIC}$ (‰)
35	Sava	River Savica	Tributary	46.29039117	13.80250167	700	6.0	8.08	2.19	190.0	0.75	0.23	0.01	0.00	0.01	0.03	0.01	0.03	-3.06	0.01	-0.68	-3.3
36	Sava	Lake Bohinj, outlet	Tributary	46.278398	13.8863417	557	9.5	7.85	4.11	369.0	2.33	0.51	0.28	0.02	0.04	0.06	0.24	0.09	-2.56	0.52	0.28	-12.8
37	Sava	Sava Bohinjka, Nomenj	Tributary	46.29801526	14.03757249	509	12.0	8.11	2.69	247.0	1.08	0.24	0.04	0.01	0.02	0.08	0.08	0.05	-2.98	0.35	-0.01	-7.2
38	Sava	Sava Otočec	River	46.31216997	14.23744784	415	12.2	8.26	3.24	305.0	1.18	0.47	0.11	0.03	0.03	0.15	0.10	0.05	-3.06	0.60	0.74	-7.3
39	Sava	Tržiška Bistrica, Bistrica	Tributary	46.29011458	14.28442503	422	11.3	8.44	2.81	378.0	1.38	0.60	0.11	0.01	0.05	0.58	0.06	0.04	-3.31	0.73	1.04	-6.4
40	Sava	Kokra, Kranj	Tributary	46.25204699	14.36869104	407	10.7	8.20	3.22	333.0	1.23	0.54	0.09	0.01	0.05	0.21	0.06	0.05	-3.01	0.53	0.61	-7.5
41	Sava	Sava, Kranj	River	46.23782813	14.35202318	350	14.7	7.57	3.22	632.0	1.38	0.52	0.17	0.01	0.04	0.18	0.19	0.10	-2.35	0.02	-0.41	-8.8
42	Sava	Sava, Smlednik	River	46.16419816	14.42555633	336	12.8	8.17	4.76	307.0	1.22	0.42	0.11	0.02	0.03	0.13	0.10	0.06	-2.80	0.69	0.87	-8.1
43	Sava	Sora, Ladja	Tributary	46.14358732	14.39285266	313	12.5	7.48	4.51	379.0	1.38	0.63	0.19	0.05	0.07	0.15	0.19	0.15	-2.13	0.03	-0.33	-10.5
44	Sava	Sava, Tacen	River	46.11722401	14.46118304	280	13.2	7.32	2.99	379.0	0.00	0.00				0.13	0.11	0.07	-2.11			-8.6
45	Sava	Kamniška Bistrica, Beričevo	Tributary	46.08842291	14.62648002	260	13.8	7.74	4.60	554.0	1.72	0.58	0.74	0.17	0.07	0.18	0.51	0.69	-2.38	0.39	0.29	-9.3
46	Sava	Ljubljanica, Zalog	Tributary	46.06220617	14.62169268	267	15.7	7.93	4.79	500.0	1.72	0.74	0.52	0.06	0.04	0.14	0.46	0.10	-2.54	0.62	0.88	-11.8
47	Sava	Sava, Dolsko	River	46.08799496	14.67835027	265	14.0	8.08	3.44	366.0	1.34	0.50	0.23	0.04	0.04	0.15	0.19	0.12	-2.84	0.52	0.59	-9.9
48	Sava	Jevnica,Jevnica	Tributary	46.08360965	14.73719533	240	11.9	7.24	0.84	118.5	0.30	0.14	0.16	0.03	0.19	0.08	0.09	0.03	-2.60	-1.51	-3.42	-9.0
49	Sava	Sava, Kresnice	River	46.09632929	14.77395623	235	11.5	7.29	3.58	387.0	1.45	0.49	0.18	0.04	0.05	0.15	0.14	0.10	-2.04	-0.25	-1.03	-11.8
50	Sava	Sava, Litija	River	46.05646171	14.82051447	230	12.1	7.81	3.48	393.0	1.48	0.49	0.23	0.05	0.05	0.15	0.18	0.12	-2.57	0.27	0.01	-10.9
51	Sava	Reka pri Bregu, Litija	Tributary	46.05962086	14.84614684	245	13.6	7.89	3.93	416.0	0.00	0.00				0.15	0.30	0.11	-2.57			-11.6
52	Sava	Sava, Log	River	46.08563083	14.89206999	230	13.6	8.32	3.81	378.0	1.44	0.49	0.17	0.03	0.05	0.14	0.14	0.10	-3.05	0.81	1.13	-10.2
53	Sava	Polšnik, Sava	Tributary	46.08337901	14.92308091	260	12.7	8.34	2.59	316.0	0.00	0.00				0.18	0.09	0.03	-3.20		1.13	-10.4
54	Sava	Medija, Zagorje	Tributary	46.12125638	14.99434953	240	18.5	8.64	4.89	574.0	1.69	1.00	0.41	0.09	0.11	0.31	0.26	0.12	-3.27	1.31		-11.0
55	Sava	Sava, Zagorje	River	46.11889003	14.99455671	225	13.7	8.35	3.63	403.0	1.49	0.52	0.18	0.02	0.06	0.15	0.16	0.10	-3.01	0.92	2.44	-9.8
56	Sava	Šklendrovec, Zagorje	Tributary	46.10301833	15.00215046	350	14.7	8.74	5.15	487.0	1.52	0.00	0.12	0.00	0.06	0.24	0.11	0.05	-3.37	1.33	1.35	-10.1
57	Sava	Mitovšica, Trbovlje	Tributary	46.11971806	15.04299911	350	15.0	8.72	4.03	414.0	1.54	0.55	0.06	0.03	0.04	0.23	0.07	0.07	-3.44	1.24	2.53	-10.9
58	Sava	Trboveljščica, Trbovlje	Tributary	46.16192117	15.05268008	230	12.5	8.04	4.22	512.0	1.41	1.00	0.71	0.10	0.15	0.13	0.10	0.06	-2.72	0.55	2.04	-11.4
59	Sava	Sava, Trbovlje	River	46.12621671	15.03632723	220	17.2	8.48	3.54	403.0	1.48	0.52	0.22	0.04	0.05	0.18	0.16	0.11	-3.23	0.99	0.90	-10.9
60	Sava	Sava, Hrastnik	River	46.12155113	15.0916258	210	13.5	8.52	3.45	376.0	1.43	0.51	0.19	0.04	0.05	0.15	0.15	0.17	-3.30	0.96	1.56	-10.2
61	Sava	Boben, Hrastnik	Tributary	46.15057264	15.08592694	220	17.3	8.34	3.42	575.0	1.67	1.01	0.77	0.12	0.13	0.44	0.41	0.10	-3.11	0.87	1.44	-11.6
62	Sava	Savinja, Rimske Toplice	Tributary	46.12262895	15.20328147	200	14.3	8.82	3.42	473.0	1.62	0.56	0.68	0.08	0.10	0.51	0.34	0.12	-3.63	1.25		-10.2
63	Sava	Sava, Radeče	River	46.06552039	15.18817906	193	14.4	8.54	3.36	397.0	1.46	0.53	0.32	0.04	0.06	0.24	0.21	0.10	-3.33	0.98	1.55	-9.9
64	Sava	Mirna, Dol Bostanj	Tributary	46.0042524	15.28807396	191	14.4	8.99	5.49	511.0	1.73	1.15	0.23	0.09	0.09	0.18	0.14	0.05	-3.63	1.59	2.04	-11.2
65	Sava	Sava, Brestanica	River	45.98708882	15.46596947	150	14.6	8.63	3.60	453.0	0.00	0.00				0.25	0.23	0.12	-3.35		1.51	-10.4
66	Sava	Sava, Brežice	River	45.89794945	15.59147525	145	14.4	7.86	3.29	428.0	1.57	0.56	0.37	0.06	0.07	0.28	0.24	0.11	-2.64	0.35	3.01	-10.8
67	Sava	Krka, Čatež	Tributary	45.89436142	15.59106334	140	14.5	8.77	4.65	459.0	0.00	0.00				0.10	0.16	0.12	-3.09			-11.1
68	Sava	Sava, Mostec	River	45.89565401	15.62699197	140	14.7	8.20	3.74	412.0	1.49	0.54	0.34	0.05	0.06	0.27	0.23	0.10	-2.93	0.71	0.97	-11.5
69	Sava	Sotla, Rakovec	Tributary	45.92058244	15.70479521	140	12.4	8.61	6.02	630.0	2.38	0.84	0.67	0.17	0.16	0.39	0.39	0.13	-3.18	1.41	2.33	-12.2
70	Sava	Sava, Bregana	River	45.86110493	15.69178091	135	14.0	7.93	3.51	424.0	1.52	0.55	0.30	0.05	0.06	0.22	0.06	0.04	-2.68	0.42	0.37	-10.8

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 fiber filter (0.7 μm). Filters and soil were treated with 1 M HCl to remove carbonate.

Thermodynamic geochemical modeling was used to evaluate CO_2 partial pressures (pCO_2) and the saturation state of calcite and dolomite ($SI_{calcite}$ and $SI_{dolomite}$) using pH, alkalinity, and temperature as inputs to the PHREEQC speciation program (Parkhurst & Appelo, 1999).

Results and discussion

Aquatic geochemistry of selected gravel bed rivers in Slovenia

The temperature of surface water in River Kamniška Bistrica, pH and conductivity ranged from 1.7 to 26.6 °C, 7.1 to 8.8, and 160.7 to 497.4 μS/cm. DO saturation varied seasonally from 59.6 to 76.8 % in the winter and from 68 to 140 % (Kanduč et al., 2013). In River Idrijca water temperature was 7.3 to 13.0 °C, conductivity ranged from 181 to 465 μS/cm, pH ranged from 7.77 to 8.82 (Kanduč et al., 2008). Temperature in River Sava water ranged from 0.4 to 15.7 °C, conductivity ranged from 62.3 to 632 μS/cm and pH ranged from 7.24 to 8.99, respectively (Kanduč, 2006; Kanduč et al., 2007). All results are described in detail in Kanduč et al. (2007, 2008 and 2013).

The major solute composition of selected gravel-bed rivers was dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Concentrations varied seasonally according to discharge, with higher concentrations observed in autumn at lower discharge and lower concentrations during the spring sampling season. Dissolved Ca^{2+} and Mg^{2+} are largely supplied by the weathering of carbonates (Fig. 3), which are the most dominant rocks in the watersheds, and prone to chemical dissolution, with smaller contributions from silicate weathering, as indicated by the relatively high HCO_3^- and low Si concentrations (Kanduč, 2006; Kanduč et al., 2007, 2008 and 2013).

Figure 3 presents $Ca^{2+} + Mg^{2+}$ versus alkalinity for all three selected gravel bed rivers in Slovenia. Most of the samples have a 2:1 mole ratio of HCO_3^- to $Ca^{2+} + Mg^{2+}$ following the reactions (Gaillardet et al., 1999):

Calcite: $CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$ (1)

Dolomite:

$$Ca_{0.5}Mg_{0.5}(CO_3) + CO_2 + H_2O \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \quad (2)$$

Some samples deviate from 2:1 line due to weathering of other minerals in river watershed, like albite and anorthite:

$$\underset{\text{Anorthite}}{CaAl_2Si_2O_8} + 3H_2O + 2CO_2 \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + Ca^{2+} + 2HCO_3^- \quad (3)$$

$$\underset{\text{Albite}}{NaAlSi_3O_8} + CO_2 + {}^{11}/_2\, H_2O \rightarrow Na^+ + ½\, \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2H_4SiO_4 + HCO_3^- \quad (4)$$

The pH, temperature and pCO_2 of a watershed determine the carbonate speciation, controlling the HCO_3^- carrying capacity. In Slovenian watersheds, total alkalinity comprises carbonate alkalinity (Kanduč, 2006; Kanduč et al., 2007), and therefore the total alkalinity is assumed as HCO_3^-, which is also the main DIC species at the pH of 7.0 to 9.0 measured in all investigated watersheds. Concentrations of HCO_3^- in main channel of River Kamniška Bistrica (Fig. 3A) vary seasonally from 1.93 to 4.19 mM in autumn 2010, from 1.88 to 4.99 mM in winter 2011, from 1.55 to 4.39 mM in spring 2011 and from 1.70 to 5.57 mM in summer 2011, respectively. Concentrations of HCO_3^- (alkalinity) in tributaries vary seasonally and range from 3.25 to 4.58 mM in autumn 2010 (Fig. 3A). The alkalinity concentrations in the main channel sampling sites varied seasonally in River Sava (Fig. 3B) in the main channel from 2.60 to 3.75 mM in spring, from 2.63 to 4.79 mM in late summer 2004, and from 2.67 to 4.17 mM during winter. The upper alpine headwater catchments of the River Sava have thin soils developed on carbonate bedrock. In the central and lower part of the River Sava watershed, tributary streams have more variable alkalinity concentrations, ranging from about 0.39 to 6.02 mM (Kanduč et al., 2007). River Idrijca (Fig. 3C) had alkalinities in range from 3.88 to 4.66 mM in autumn 2006 and from 4.12 to 4.43 mM in spring 2007, while in tributaries alkalinities range from 3.09 to 5.10 mM in autumn 2006 and in spring 2007 from 3.15 to 5.04 mM (Kanduč et al., 2008).

Differences in alkalinities in carbonate-bearing watersheds are related to the geological composition of the watershed (Fig. 2), the relief (Fig. 1), the mean annual temperature, the depth of the weathering zone, the soil thickness and the water residence time in the system. Weathering rates increase in thicker soils like shales due to the higher residence time of shallow groundwater in contact with minerals in comparison to watersheds composed of carbonate minerals.

Mg^{2+} versus Ca^{2+} relations indicate the relative contribution of calcite/dolomite to carbonate weathering intensity in gravel bed rivers (Fig. 4). Most of the samples indicate that weathering of calcite is dominant over the entire River Kamniška Bistrica, especially in the upper and central reaches (Fig. 4A). A Mg^{2+}/Ca^{2+} ratio around 0.33 is typical for weathering of calcite for the entire length of the River Kamniška Bistrica as well as for rivers comprising Danube watershed (Kanduč et al., 2013). In contrast, rivers comprising St. Lawrence watershed (North America) have ratios Mg^{2+}/Ca^{2+} greater than 0.33 (Szramek et al., 2007). Most of the samples in River Sava (Fig. 4B) fall below 0.22 line, indicating weathering of calcite, only some samples in River Sava tributaries fall above 0.5 Mg^{2+}/Ca^{2+} line indicating weathering of dolomite. From Figure 4C it can be observed that most of the samples indicate that weathering of dolomite is dominant over the entire River Idrijca,

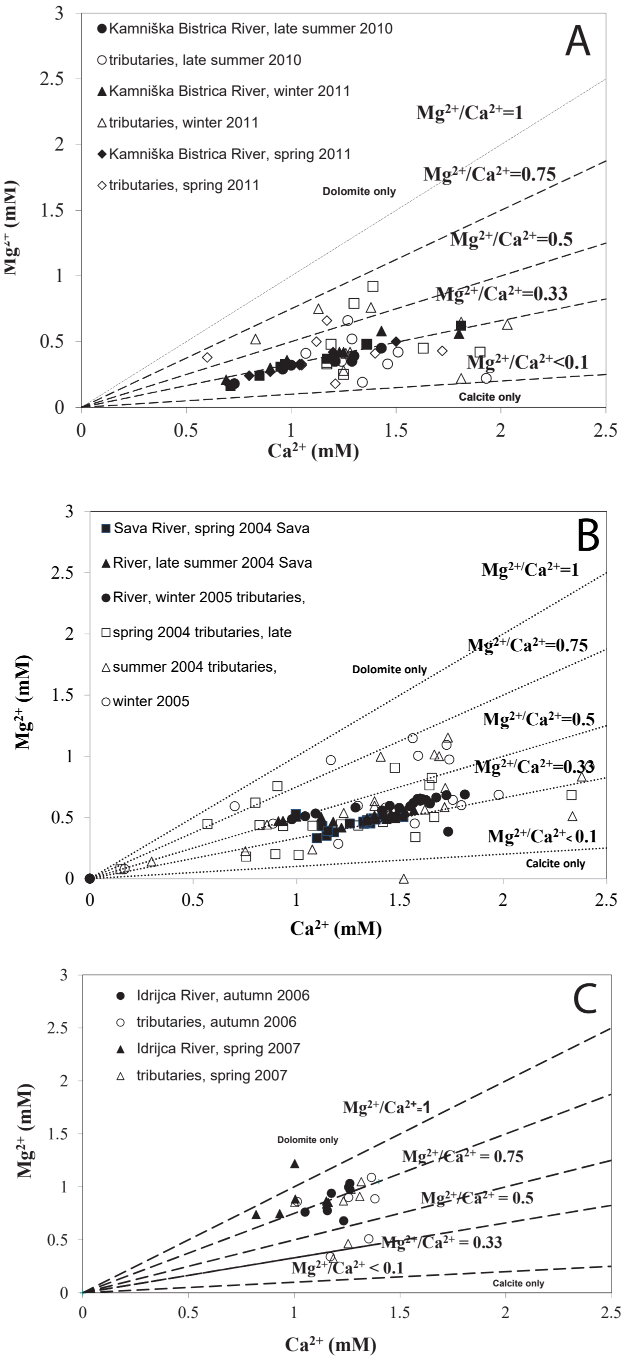

Fig. 4. Mg^{2+} versus Ca^{2+} indicating weathering of calcite and dolomite in watershed (rivers: A: Kamniška Bistrica, B: Sava in Slovenia, C: Idrijca).

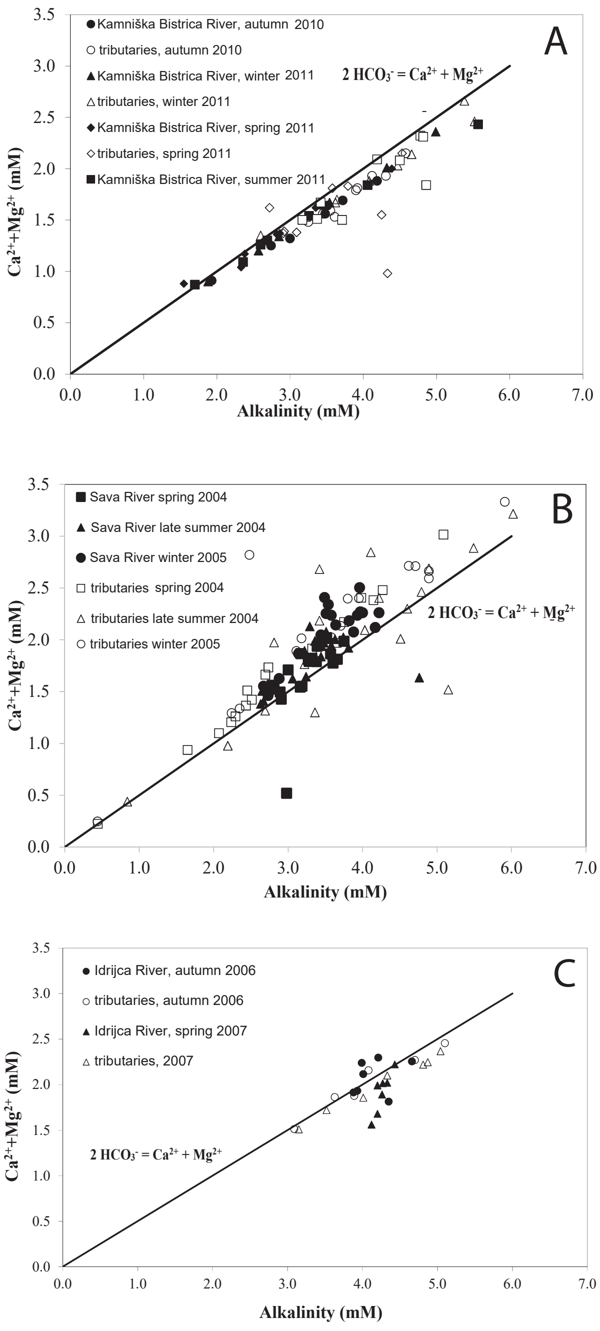

Fig. 3. $Ca^{2+}+Mg^{2+}$ ratio versus alkalinity with line 1: 2 indicating weathering of carbonates in the watershed (rivers: A: Kamniška Bistrica, B: Sava in Slovenia, C: Idrijca).

especially in the upper and central flow of the river. A Mg^{2+}/Ca^{2+} ratio around 0.33 is characteristic only in the lowland tributaries of the River Idrijca composed mainly of limestone.

The major control on carbonate weathering intensity is runoff (Amiotte Suchet & Probst, 1993). Carbonate weathering intensity normalized to drainage area, quantifies HCO_3^- produced from mineral weathering. Figure 5 compares carbonate weathering intensities as a function of specific runoff for the River Idrijca watershed, combining new data from this study with published official data for the River Sava, River Kamniška Bistrica and data from Berner & Berner (1996) for world rivers and the River Danube. Global theoretical models of CO_2 consumption in carbonate watersheds show an alkalinity value around 3 mmol/L determined from a best-fit line (Amiotte Suchet & Probst, 1993). The climate and topographic relief in Slovenian watersheds importantly influence the carbonate weathering intensity and specific runoff. Roy et al. (1999) noted that linked factors such as lithology, residence time of water, mechanical erosion, etc., have more influence together than they do separately. The watershed of the River Idrijca is typically an environment where enhanced mechanical weathering increases chemical weathering (Fairchild et al., 1999; Anderson et al., 2000; Jacobson et al., 2000) and causes a high carbonate weathering intensity, since the river is a steep mountain river with torrential character, e.g. River Idrijca with 80 mmol/l·km²·s (Fig. 5) and Kamniška Bistrica with the highest weathering intensity of 150 mmol/l·km²·s (Fig. 5).

The world average value for carbonate weathering intensity is 7 mmol/l km² s (Berner & Berner, 1996). For the River Sava and its tributaries, the mean long term weathering intensity is from 37 to 140 mmol/l km² s.

Also carbonate weathering intensity (HCO_3^- in mmol/l km² s) of some other world rivers (Mississippi, World, Danube) is presented on Figure 5. From Figure 5 it can be observed that Slovenian gravel bed rivers have higher HCO_3^- weathering intensity in comparison to world rivers.

Thermodynamic modeling and isotope geochemistry with emphasize on carbon cycle

Thermodynamical modeling software PHREEQC for Windows was used to calculate pCO_2 and saturation indices for calcite and dolomite ($SI_{calcite}$ and $SI_{dolomite}$) along the main water channel and tributaries. In all investigated bed rivers a high value of pCO_2 was observed during all sampling seasons, meaning that rivers represent sources of CO_2 into air.

Calculated pCO_2 varied from 977 to 4,169 ppm in autumn and from 295 to 2,398 ppm in the spring sampling season. Normal atmospheric pressure is around 316 ppm according to Clark & Fritz (1997). Calculated pCO_2 varied from near atmospheric up to 25-fold supersaturated at River Kamniška Bistrica at Videm in summer season in year 2010 to 2011. Partial pressure in River Sava and its tributaries ranges from 128.8 to 2,951 ppm in April 2004, in September 2004

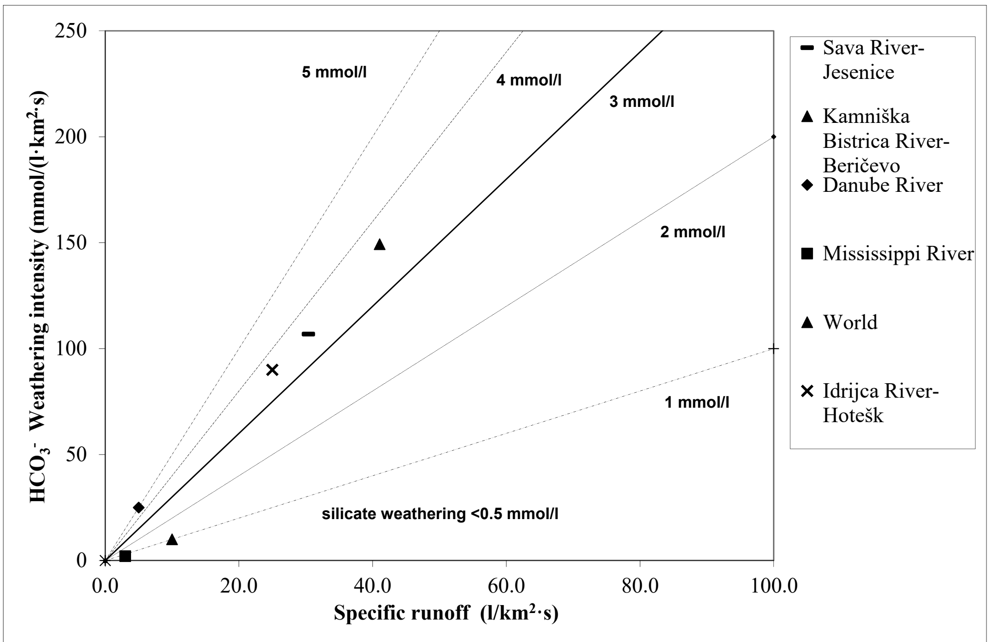

Fig. 5. Carbonate weathering intensity (HCO_3^- in mmol/l km² s) versus specific runoff (1/km²s) indicating high carbonate weathering intensity in selected rivers in Slovenia (River Kamniška Bistrica, River Sava in Slovenia, River Idrijca) and in the world. Data include mean long-term data of discharge and alkalinity from the Slovenian Environment Agency (2004-2011) for the Slovenian rivers, and Berner & Berner (1996) for world rivers, River Danube and Mississipi River.

from 234.4 to 9,120 ppm in April and from 223.9 to 4,074 ppm in January 2005 (Kanduč, 2006). In autumn all sampling locations on the River Idrijca watershed are above equilibrium with atmospheric CO_2. These higher partial pressures in autumn are probably due to higher degradation of organic matter in the river and due to lower discharge (Dever et al., 1983). Lower pCO_2 (below normal atmospheric pressure at locations 5 and 6, Table 1, Fig.1) in the spring are observed due to the higher pH of the water, which lowers the evasion of CO_2 from water.

The calcite saturation index ($SI_{calcite}$=log([-Ca^{2+}]*[CO_3^{2-}])/$K_{calcite}$; where $K_{calcite}$ is the solubility product of calcite and was generally well above equilibrium ($SI_{calcite}$=0)), indicates that calcite was supersaturated and precipitation was thermodynamically favoured along most of the course of all selected gravel bed rivers in Slovenia (Fig. 6). Calcite and dolomite were supersaturated and carbonate precipitation was thermodynamically favoured along most of the course of River Kamniška Bistrica (Fig. 6A). $SI_{calcite}$ and $SI_{dolomite}$ seasonally change in River Sava and their tributaries and reach oversaturation in central and lower flow of the river, while in upper part of the river rarely reach saturation (Fig. 6B). Low $SI_{calcite}$ and $SI_{dolomite}$ are observed at tributary location of River Sava (Fig. 6B). In most of the samples of River Idrijca and its tributaries calcite and dolomite are oversaturated, only one sample in River Idrijca is undersaturated with respect to dolomite (Fig. 6C).

Mass balance calculation with evaluation of biogeochemical processes in selected gravel bed rivers in Slovenia

Mass balance calculations were performed in previous studies (Kanduč et al., 2007, 2008 and 2013).

The $\delta^{13}C_{DIC}$ value can determine the contributions of organic matter decomposition, carbonate mineral dissolution, and exchange with atmospheric CO_2 to DIC in selected gravel bed rivers in Slovenia. The $\delta^{13}C_{DIC}$ values of the main channel of the river varied seasonally (year 2010–2011) from -10.9 ‰ (River Kamniška Bistrica, location 20, Table 1, Fig. 1) to -2.7 ‰ (River Kamniška Bistrica Spring, location 14, Table 1, Fig. 1) while $\delta^{13}C_{DIC}$ in tributaries ranged from -12.7 ‰ (Rača, location 27, Table 1, Fig.1) to -6.9 ‰ (Kamniška Bistrica Spring, location 14, Table 1, Fig.1) (Kanduč et al., 2013). The $\delta^{13}C_{DIC}$ in River Sava 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. The River Sava tributaries had $\delta^{13}C_{DIC}$ values that varied from -13.5 to -5.8 ‰ in spring 2004, from -12.8 to 3.3 ‰

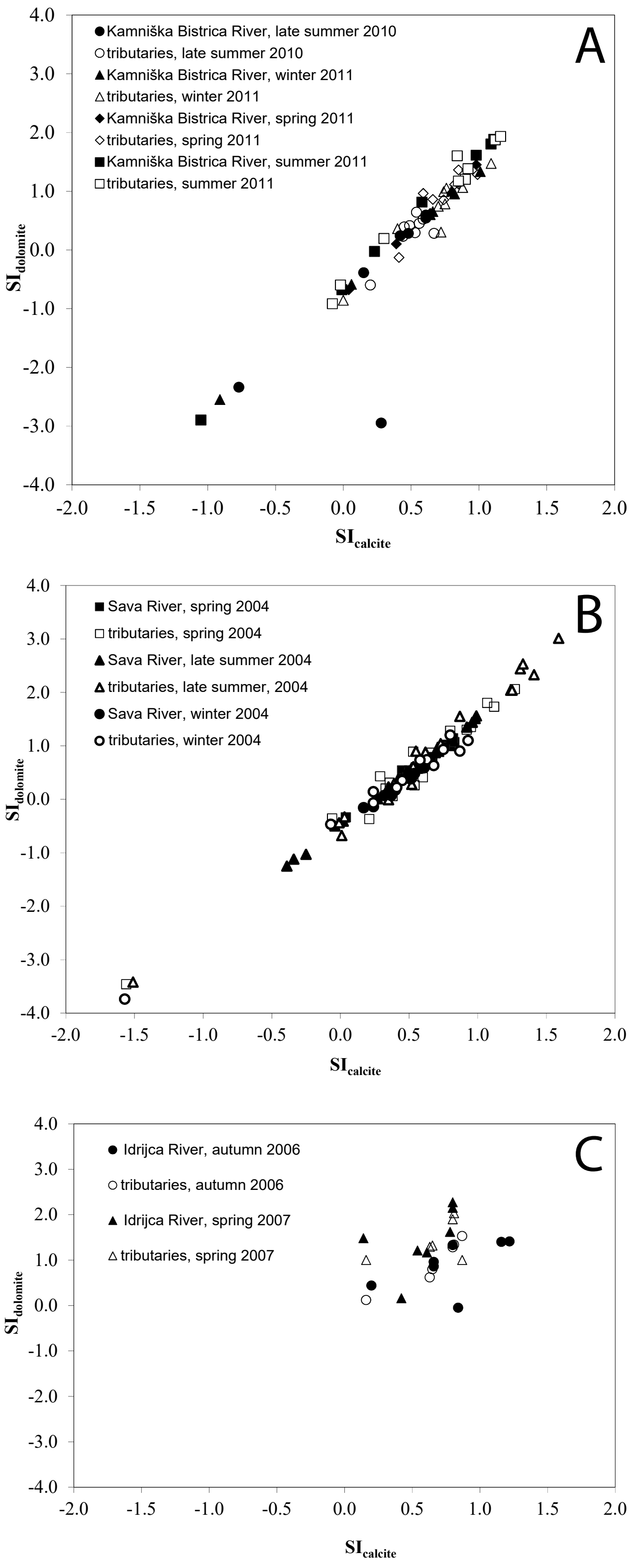

Fig. 6. $SI_{calcite}$ versus $SI_{dolomite}$ in different sampling seasons in different periods for the selected rivers (A: Kamniška Bistrica, B: Sava in Slovenia, C: Idrijca).

in late summer 2004, and from -11.9 to -4.2 ‰ in winter 2005 (KANDUČ et al., 2007). $\delta^{13}C_{DIC}$ varied seasonally in River Idrijca watershed from -10.8 to -9.0 ‰ in autumn 2006 and from -10.6 to -8.3 ‰ in spring 2007. The $\delta^{13}C_{DIC}$ value of the river water is controlled by the geological composition of the watershed. Along the River Idrijca flow the dissolution of carbonates is the major contributor to $\delta^{13}C_{DIC}$ values, but some parts of the watershed also drain shales, mudstones, and sandstones (KANDUČ et al., 2008). Thus, in those parts $\delta^{13}C_{DIC}$ is much lower (central part of the River Idrijca, lower reaches of River Kamniška Bistrica and central and lower flow of River Sava in Slovenia) since the thickness of soil is on this bedrock much higher and soil CO_2 contributes much more to DIC than on carbonate bedrocks. $\delta^{13}C_{DIC}$ was also generally lower during spring season at higher discharge (Fig. 7). The average $\delta^{13}C$ value of Mesozoic carbonate rocks ($\delta^{13}C_{CaCO3}$) in the hinterland of River Kamniška Bistrica is +2.4 ‰ (KANDUČ et al., 2013). The $\delta^{13}C$ of Mesozoic carbonate rocks ($\delta^{13}C_{CaCO3}$) from the River Sava watershed ranged from -1.4 to +2.7 ‰, with an average of +1.4±1.3 ‰ (N=12) (KANDUČ et al., 2007). The $\delta^{13}C$ value of Mesozoic carbonate rocks ($\delta^{13}C_{CaCO3}$), which forms the slopes in the watershed of the River Idrijca is on average +2.0±0.7 ‰ (N = 8) (KANDUČ et al., 2008).

Figure 7 shows a plot of $\delta^{13}C_{DIC}$ versus alkalinity in different sampling seasons for selected gravel bed rivers in Slovenia. Changes over the course of the rivers indicate processes affecting $\delta^{13}C_{DIC}$, e. g. degradation of organic matter (line 3), carbonate mineral dissolution (line 2), and equilibration with atmospheric CO_2 (line 1) (BARTH et al., 2003).

At River Kamniška Bistrica source carbonate dissolution prevails, while in central and lower part of the river degradation of organic matter and dissolution of carbonates prevails (Fig. 7A). The $\delta^{13}C_{DIC}$ values from the River Idrijca watershed (Fig. 7C) indicate that nonequilibrium carbonate dissolution predominates along the flow of river, since the watersheds are mainly composed of carbonate rocks with inclusions of clastic rocks, approaching a $\delta^{13}C_{DIC}$ value of -12.3 ‰. In tributaries of the River Idrijca watershed (Fig. 7C), River Kamniška Bistrica (Fig. 7A) and River Sava in Slovenia (Fig. 7B) dissolution of carbonate minerals prevails, which leads to higher $\delta^{13}C_{DIC}$ values. Mineralization of organic matter appears to be the dominant source of $\delta^{13}C_{DIC}$ along

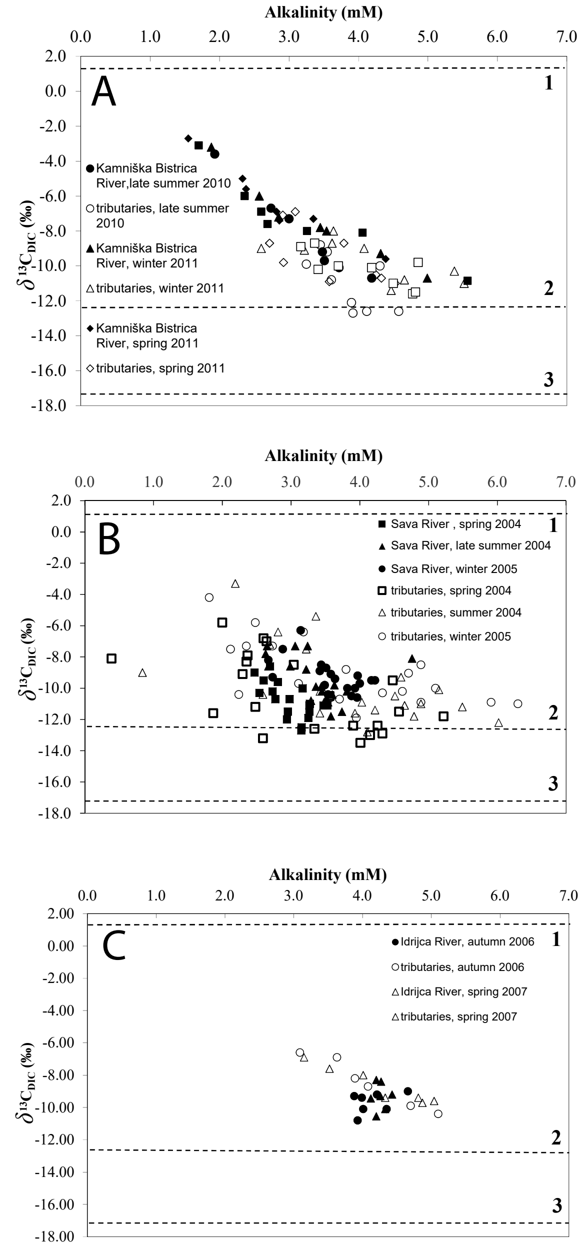

Fig. 7. $\delta^{13}C_{DIC}$ versus alkalinity of selected gravel bed rivers in Slovenia (rivers: A: Kamniška Bistrica, B: Sava in Slovenia, C: Idrijca).

the Idrijca flows (Fig. 7C), where the greater soil thickness enables accumulation of soil CO_2 due to the greater degree of silicate rock weathering, which leads to more a negative $\delta^{13}C_{DIC}$.

The evasion of CO_2 from the River Kamniška Bistrica, River Sava in Slovenia and River Idrijca can be calculated (equation 5) based on the thin-film diffusive gas exchange model (BROECKER, 1974; RAYMOND et al., 2012):

$$[DIC]_{ex} = D/z * ([CO_2]_{eq} - [CO_2]) \quad (5)$$

where D is the CO_2 diffusion coefficient in water of 1.26 $*10^{-5}$ cm^2/s at a temperature of 10 °C and 1.67 $*10^{-5}$ cm^2/s at a temperature of 20 °C (Jähne et al., 1987), and z is the empirical thickness of the liquid layer [cm].

A simple isotopic mass balance calculation was performed in order to quantify different sources of DIC in all three selected gravel bed rivers: at River Kamniška Bistrica mouth (location 20, Table 1, Fig.1), at the River Idrijca mouth (location 6, Table 1, Fig. 1), at River Sava in Slovenia mouth (location 70, Table 1, Fig.1) considering the sum of tributary inputs and biogeochemical processes in the watershed. The major inputs to the DIC flux (DIC_{RI}) and $\delta^{13}C_{DIC}$ originate from tributaries (DIC_{tri}), degradation of organic matter (DIC_{org}), exchange with the atmosphere (DIC_{ex}), and dissolution of carbonates (DIC_{ca}) can be estimated by Eqs. (6 and 7):

$$DIC_{RI} = DIC_{tri} - DIC_{ex} + DIC_{org} + DIC_{ca} \quad (6)$$

$$DIC_{RI}*\delta^{13}C_{RI} = DIC_{tri}*\delta^{13}C_{tri} - DIC_{ex}*\delta^{13}C_{ex} + DIC_{org}*\delta^{13}C_{POC} + DIC_{ca}*\delta^{13}C_{CaCO3} \quad (7)$$

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).

DIC_{RI} and DIC_{tri} were calculated from the concentrations of alkalinity and water discharge, with the corresponding measured $\delta^{13}C$ values for $\delta^{13}C_{RI}$ and $\delta^{13}C_{tri.}$ The average diffusive flux of CO_2 from the river to the atmosphere, DIC_{ex}, estimated from Eq. (5), was taken into account. In Eqs. (5 and 6) the minus sign indicates outgassing of CO_2, which is observed in autumn, but not in the spring season. The $\delta^{13}C_{ex}$ value was calculated according to the equation for equilibrium isotope fractionation between atmospheric CO_2 and carbonic acid in water (Zhang et al., 1995), where a $\delta^{13}C$ value of -7.8 ‰ for atmospheric CO_2 was used (Levin et al., 1987). The isotopic composition of the contribution of equilibration between atmospheric CO_2 and DIC ($\delta^{13}C_{ex}$) would then be +1.4 ‰ in the autumn and +1.8 ‰ in the spring sampling season, considering atmospheric CO_2 as the ultimate source of CO_2 in the River Sava in Slovenia, River Idrijca and River Kamniška Bistrica drainage system. For $\delta^{13}C_{POC}$ and $\delta^{13}C_{CaCO3}$ average values of -26.6 ‰ and +2.0 ‰ were used in the mass balance equations.

Contributions of DIC from various biogeochemical processes were determined using steady state equations for different sampling seasons at the mouth of the River Kamniška Bistrica; results indicate that: (1) 1.9-2.2 % of DIC came from exchange with atmospheric CO_2, (2) 0-27.5 % of DIC came from degradation of organic matter, (3) 25.4–41.5 % of DIC came from dissolution of carbonates and (4) 33.0–85.0 % of DIC came from tributaries (Kanduč et al., 2013). In both sampling seasons the most important biogeochemical process is weathering of carbonates, while degradation of organic matter is more expressed in the spring sampling season. A less significant process in both sampling seasons is exchange with atmospheric CO_2 and is not marked in the spring sampling season due to the pCO_2 value (at location 28, Table 1, Fig.1), which is near equilibrium with atmospheric CO_2 pressure. In River Sava mouth among biogeochemical processes dissolution of carbonates contributes the highest proportion in both sampling seasons, which moves $\delta^{13}C_{DIC}$ to more positive values. Mass balances for riverine inorganic carbon suggest that carbonate dissolution contributes up to 26 %, degradation of organic matter ~17 % and exchange with atmospheric CO_2 up to 5 %. The concentration and stable isotope diffusion models indicated that atmospheric exchange of CO_2 predominates in streams draining impermeable shales and clays while in the carbonate-dominated watersheds dissolution of the Mesozoic carbonate predominates (Kanduč et al., 2007). The calculated contributions to the average DIC budget from DIC_{tri}:DIC_{ex}:DIC_{org}:DIC_{ca} at the River Idrijca mouth were 61:-11:19:31 % in autumn 2006 and 35:0:26:39 % in spring 2007 (Kanduč et al., 2008).

Conclusions

The major solute composition of the River Kamniška Bistrica is dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Concentrations of HCO_3^- ranged from 1.6 mM to 5.6 mM in main channel and from 2.6 to 5.5 mM in tributaries. The majority of River Kamniška Bistrica system was supersaturated or near equilibrium with respect to calcite/dolomite in all sampling seasons. According to the calculated pCO_2 values, the river is source of CO_2 to the atmosphere during all sampling seasons, higher pCO_2 is observed during summer season. Lower alkalinities and higher $\delta^{13}C_{DIC}$ values of -2.7 ‰ were observed in the upper carbonate part of the watershed, while higher alkalinities and more negative $\delta^{13}C_{DIC}$ values of -12.7 ‰ were observed in the central and lower part of the Kamniška Bistrica system.

The major chemical composition of River Sava water is HCO_3^-, Ca^{2+} and Mg^{2+}. Seasonal (spring 2004, late summer 2004 and winter 2005) concentrations of HCO_3^- range from 2.63 to 4.79 mM, while its tributaries have concentrations of HCO_3^- ranging from 0.39 to 6.02 mM. The majority of the River Sava system is supersaturated or at equilibrium (in the upper part of the river flow) with respect to calcite in all sampling seasons. $\delta^{13}C_{DIC}$ values range from -12.7 to -6.3 ‰ and were observed in late summer. The observed differences in pCO_2, alkalinities and $\delta^{13}C_{DIC}$ 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 $\delta^{13}C_{DIC}$ values are observed in the upper carbonate part of the watershed, while higher alkalinities and lower $\delta^{13}C_{DIC}$ values are observed in the central and lower part of the River Sava watershed.

The biogeochemical processes affecting DIC and $\delta^{13}C_{DIC}$ values were quantified by concentration and isotope mass calculations and it can be concluded that the most important biogeochemical processes at the River Sava mouth in order of significance in different sampling seasons are: (1) carbonate 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, while (3) atmospheric exchange comprises 0.8 % in spring to 4.9 % in late summer.

The River Sava in Slovenia has high discharge, low 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 five years will affect the carbon cycle, e.g accelerated primary production, degradation of organic matter, degassing of CO_2 from the river. This investigation will also help to evaluate the biogeochemical state of the river after dam constructions.

The major solute composition of River Idrijca water is dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Seasonal alkalinity concentrations ranged from 3.88 to 4.66 mM, while its tributaries had concentrations of HCO_3^- ranging from 3.09 to 5.10 mM. The majority of the River Idrijca system was supersaturated or near equilibrium with respect to calcite. The biogeochemical processes affecting DIC concentrations and $\delta^{13}C_{DIC}$ (in the range from -10.8 to -6.6 ‰) calculated by mass balance equations showed that the most important biogeochemical processes at the River Idrijca mouth are: carbonate mineral dissolution, degradation of organic matter and atmospheric exchange. The River Idrijca is a river with torrential character, has a high specific discharge and therefore high weathering intensity.

In all three investigated rivers carbonate dissolution and degradation of organic matter are the most important biogeochemical processes in river system, while exchange with atmosphere could be negligible according to mass balance equations.

Acknowledgements

The authors are thankful to Research Agency of Republic of Slovenia, program research groups P1-0143 and P1-0195. The authors are also thankful to previous research projects funded by Research Agency of Republic of Slovenia and ongoing research project L2–6778 (2014–2017). Finally, our sincere thanks go to prof. dr. Jožef Pezdič for introducing us to stable isotopic geochemistry and hydrogeochemistry and for his guidance in the research and pedagogical work.

References

Amiotte Suchet, P. & Probst, J.L. 1993: Modelling of atmospheric CO_2 consumption by chemical weathering of rocks: Application to the Garonne, Congo and Amazon basins. Chem. Geol., 107/3-4: 205-210, doi:10.1016/0009-2541(93)90174-H.

Anderson, S.P., Drever, J.I., Frost, C.D. & Holden, P. 2000: Chemical weathering in the foreland of a retreating glacier. Geochim. Cosmochim. Acta, 64/7: 1173-1189, doi:10.1016/S0016-7037(99)00358-0.

Atekwana, E.A. & Krishnamurthy, R.V. 1998: Seasonal variations of dissolved inorganic carbon and $\delta^{13}C$ of surface waters: Application of a modified gas evaluation technique. Hydrology Journal, 205/3-4: 265-278, doi:10.1016/s0022-1694(98)00080-8.

Barth, J.A.C., Cronin, A.A, Dunlop, J. & Kalin, R.M. 2003: Influence of carbonates on the riverine carbon cycle in an anthropgenically dominated catchment basin: evidence from major elements and stable carbon isotopes in the Lagan River (N. Ireland). Chem. Geol., 200/3-4: 203-216, doi:10.1016/S0009-2541(03)00193-1.

Berner, E.K. & Berner, R.A. 1996: Global environment, water, air, and geochemical cycles. Prentice Hall, Upper Saddle River.

Broecker, W.S. 1974: Chemical oceanography. Harcourt Brace Jovanovich, New York.

Buser, S. 1987: Geological map of Slovenia. In: Vogler D. (ed.): Encyclopedia of Slovenia No. 8, Mladinska knjiga, Ljubljana (in Slovene): 4-416.

Clark, I. & Fritz, P. 1997. Environmental Isotopes in Hydrogeology. New York: Lewis Publishers.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J. Striegl, R.G., Duarte, C.M. Kortelainen, P., Downing, J.A., Middelburg, J.J. & Melack, J. 2007. Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget. Ecosystems, 10: 171-184, doi:10.1007/s10021-006-9013-8.

Čar, J. 2010: Explanatory book to the map: geological structure of the Idrija - Cerkno hills. Geological Survey of Slovenia, Ljubljana: 125 p.

Deines, P. 1980: The isotopic composition of reduced organic carbon. In: Fritz P. & Fontes J.C. (eds.): Hanbook of Environmental Isotopic Geochemistry, 1: 329-406, Elsevier, Amsterdam.

Dever, L., Durand, R., Fontes, J. C.H. & Vaicher, P. 1983: Etude pédogénétique et isotopique des néoformations de calcite dans un sol sur craie. Caractéristiques et origins. Geochimica Cosmochimica Acta, 47: 2079-2090.

Fairchild, I.J., Killawee, J.A., Hubbard, B. & Dreybodt, W. 1999: Interactions of calcareous suspended sediment with glacial meltwater: a field test of dissolution behaviour. Chem. Geol., 155: 243-263, doi:10.1016/s0009-2541(98)00170-3.

Fratar, P. 2005: River Flow Regimes of Slovene Rivers and their fluctuations = Pretočni režimi slovenskih rek in njihova spremenljivost. Ujma, 19: 145-153.

Gaillardet, J., Dupré, B., Louvat, P. & Allègre, C.J. 1999: Global silicate weathering and CO_2 consumption rates deduced from the chemistry of large rivers. Chem. Geol., 159: 3-30.

Germ, M., Gaberščček A. & Urbanc-Berčič, O. 1999: Aquatic macrophytes in the River Sava, Kolpa and Krka. Ichtyos, 16: 23-34.

Gibbs, R.J. 1972. Water chemistry of the Amazon River. Geochim. Cosmochim. Acta, 36: 1061-1066.

Gieskes, J.M. 1974. The alkalinity-total carbon dioxide system in seawater. In: Goldberg, E.D. (ed.): Marine chemistry of the sea, 5: 123-151.

Hrvatin, M. 1998. Discharge regimes in Slovenia. Geografski zbornik, XXXVIII: 60-87.

Huh, Y., Tsoi M.Y., Zaitsev A. & Edmond, J.M. 1998: The fluvial geochemistry of the rivers of Eastern Siberia: I. Tributaries of the Lena River draining the sedimentary platform of the Siberian Craton. Geochim. Cosmochim. Acta, 62:1657–1676.

Jacobson, A.D., Blum, J.D. & Walter, L.M. 2003: Reconciling the elemental and Sr isotope composition of Himalayan weathering fluxes: insights from the carbonate geochemistry of streams. Geochim. Cosmochim. Acta, 66/19: 3417-3429, http://dx.doi.org/10.1016/S0016-7037(02)00951-1

Jähne, B., Heinz, G. & Dietrich, W. 1987: Measurements of the Diffusion Coefficients of sparingly soluble gases in water. J Geophys Res Oceans, 92: 10767-10776.

Kanduč, T. 2006. Hydrogeochemical characteristics and carbon cycling in the Sava River watershed in Slovenia. PhD Dissertation. University of Ljubljana, Ljubljana: 141 p.

Kanduč, T., Szramek, K., Ogrinc, N. & Walter, L.M. 2007: Origin and cycling of riverine inorganic carbon in the Sava River watershed (Slovenia) inferred from major solutes and stable carbon isotopes. Biogeochemistry, 86: 137-154, doi:10.1007/s10533-007-9149-4

Kanduč, T., Kocman, D. & Ogrinc, N. 2008: Hydrogeochemical and stable isotope characteristics of the river Idrijca (Slovenia), the boundary watershed between the Adriatic and Black seas. Aquatic geochemistry, 14: 239-262, doi:10.1007/s10498-008-9035-2.

Kanduč T., Šturm, MB. & McIntosh, J. 2013. Chemical dynamics and evaluation of biogeochemical processes in alpine River Kamniška Bistrica, North Slovenia. Aquatic Geochemistry, 19:323-346, doi:10.1007/s10498-013-9197-4.

Kanduč, T., Samardžija, Z., Mori, N., Jerebic, A., Levačić, J., Kračun, M., Robinson, J.A., Žigon, S., Blažeka, Ž., Kocman, D. 2016: Hydrogeochemical and isotopic characterization of Pesnica River, Slovenia. Geologija, 59/2: 179-192, doi:10.5474/geologija.2016.010.

Levin, I., Kromer, B., Wagenback D. & Münnich, K.O. 1987: Carbon isotope measurements of atmospheric CO_2 at a coastal station in Antartctica. Tellus, 39B: 89-95.

Liu, Z. & Zhao, J. 2000: Contribution of carbonate rock weathering to the atmospheric CO_2 sink. Environmental Geology, 39:1053–1058, doi: 10.1007/s002549900072.

Mechora, Š. & Kanduč, T. 2016: Environmental assessment of freshwater ecosystems of the River Sava watershed and Cerkniško Lake, Slovenia, using the bioindicator species Fontinalis antipyretica: insights from stable isotopes and selected elements. Isotopes Environ. Isotopes in Environmental and Health Studies, 52/3:239-57, doi:10.1080/10256016.2016.1114933

Miyajima, T., Yamada, Y. & Hanba, Y.T. 1995: Determining the stable isotope ration of total dissolved inorganic carbon in lake water by GC/C/IRMS. Limnology Oceanography, 40:994-1000.

Mlakar, I. & Čar, J. 2009: Geological map of the Idrija - Cerkno hills between Stopnik and Rovte 1:25.000. Geological Survey of Slovenia.

Négrel, P. & Lachassagne, P. 2000: Geochemistry of the Maroni River (French Guiana) during the low water stage: implications for water--rock interactions and groundwater characteristics. Journal of Hydrology, 237:212–233, doi: 10.1016/S0022-1694(00)00308-5.

Parkhurst, D.L. & Appelo, C.A.J. 1999: User's guide to PHREEQC (version 2)-a computer program for speciation, batch –reaction, ne-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report, 99-4259.

Pezdič, J. 1999: Izotopi in geokemijski procesi (In Slovene). Univerza v Ljubljani, Naravoslovnotehniška fakulteta, Oddelek za geologijo. Univerzitetni učbenik, Ljubljana: 269 p.

Radinja, D., Grbović, J., Povž, M., Zupan, M. & Skoberne, P. 1987: Kamniška Bistrica. In: Javornik, M. (ed.): Encyclopedia Slovenia 4. Mladinska knjiga, Ljubljana, pp 382 (in Slovene).

Raymond, P.A., Zappa, C.J., Butman, D., Bott, T.L., Potter, J., Mulholland, P., Lauersen, A.E., McDowell, W.H. & Newbold, D. 2012: Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. Limnology Oceanography Fluids Environment, 2: 41-53, doi:10.1215/21573689-1597669.

Reeder, S.W., Hitchon, B. & Levinson, A.A. 1972: Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada: 1. Factors controlling inorganic composition. Geochim. Cosmochim. Acta, 36:181–192.

Roy, S., Gaillardet, J. & Allegre, C.J. 1999: Geochemistry of dissolved and suspended loads of the Seine River, France: anthropogenic impact, carbonate and silicate weathering. Geochimica Cosmochimica Acta, 63: 1277-1292, doi:10.1016/S0016-7037(99)00099-X.

Sarmiento, J.L. & Sundquist, E.T. 1992: Revised budget for the oceanic uptake of anthropogenic carbon –dioxide. Nature, 356/6370: 589-593.

Schulte, P., Van Geldern, R., Freitag, H., Karim, A., Négrel, P., Petelet-Giraud, E., Probst, A., Telmer, K., Veizer, J. & Barth, J.A.C. 2011: Applications of stable water and carbon isotopes in watershed research: weathering, carbon cycling, and water balances. Earth Science Review, 109: 20-31, doi:10.1016/j.earscirev.2011.07.003.

Spötl, C. 2005: A robust and fast method of sampling and analysis of $\delta^{13}C$ of dissolved inorganic carbon in ground waters. Isotopes Environ Health Stud, 41: 217-221.

Szramek, K., McIntosh, J.C., Williams, E.L., Kanduč, T., Ogrinc, N. & Walter, L.M. 2007: Relative weathering intensity of calcite versus dolomite in carbonate-bearing temperature zone watersheds: carbonate geochemistry and fluxes from catchments within the St. Lawrence and Danube river basin. Geochem Geophys, 8: 1-26, doi:10.1029/2006gc001337.

Zhang, J., Huang, W.W., Létole, R. & Jusserand, C. 1995: Major element chemistry of the Huange (Yellow River), China-weathering processes and chemical fluxes. J Hydrol., 168/1–4: 173-203, doi:10.1016/0022-1694(94)02635-O.

Žlebnik, L. 1971. Pleistocen Kranjskega, Sorškega in Ljubljanskega polja (In Slovene). Geologija, 14: 5–51.

Yang, C., Telmer, K. & Veizer, J. 1996: Chemical dynamics of the "St. Lawrence" riverine system: δD_{H2O}, $\delta^{18}O_{H2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{sulfate}$ and dissolved $^{87}Sr/^{86}Sr$. Geochim. Cosmochim. Acta, 60: 851-866, doi:10.1016/0016-7037(95)00445-9.

Internet resources:

Internet 1: http://srtm.csi.cgiar.org/ (18.10.2016)

Internet 2: http://www.arso.gov.si/en/ (18.10.2016)

Internet 3: http://www.bgr.de/karten/igme5000/igme.htm (18.10.2016)