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# Hydrogeochemical characteristics of the River Idrijca (Slovenia)

## Hidrogeokemijske značilnosti reke Idrijce

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*Key words*: River Idrijca, chemical composition, stable isotopes, carbon, oxygen, Slovenia
*Kjučne besede*: Idrijca, kemijska sestava, stabilni izotopi, ogljik, kisik, Slovenija

### Abstract

The hydrogeochemical and isotope characteristics of the River Idrijca, Slovenia, where the world's second largest mercury (Hg) mine is located, were investigated. The River Idrijca, a typical steep mountain river has an $HCO_3^-$ - $Ca^{2+}$ - $Mg^{2+}$ chemical composition. Its $Ca^{2+}/Mg^{2+}$ molar ratio indicates that dolomite weathering prevails in the watershed. The River Idrijca and its tributaries are oversaturated with respect to calcite and dolomite. The $pCO_2$ pressure is up to 13 times over atmospheric pressure and represents a source of $CO_2$ to the atmosphere. $\delta^{18}O$ values in river water indicate primary control from precipitation and enrichment of the heavy oxygen isotope of infiltrating water recharging the River Idrijca from its slopes. The $\delta^{13}C_{DIC}$ values range from –10.8 to –6.6 ‰ and are controlled by biogeochemical processes in terrestrial environments and in the stream: 1) exchange with atmospheric $CO_2$, 2) degradation of organic matter, 3) dissolution of carbonates, and 4) tributaries. The contributions of these inputs were calculated according to steady state equations and are estimated to be -11 %: 19 %: 31 %: 61 % in the autumn and 0 %: 6 %: 9 %: 35 % in the spring sampling seasons.

### Izvleček

Hidrogeokemijske in izotopske raziskave so bile izvedene v porečju reke Idrijce, kjer se nahaja drugi največji rudnik živega srebra na svetu. Reka Idrijca je hudourniška reka, ki ima kemijsko sestavo $HCO_3^-$ - $Ca^{2+}$ - $Mg^{2+}$. Njeno molarno razmerje $Ca^{2+}/Mg^{2+}$ kaže, da dolomitno preperevanje v porečju prevladuje. Idrijca in njeni pritoki so prenasičeni s kalcitom in dolomitom. Parcialni tlak ($pCO_2$) je do 13 krat višji v primerjavi z atmosferskim in predstavlja vir $CO_2$ v ozračje. Vrednosti $\delta^{18}O$ v rečni vodi kažejo, da na njeno $\delta^{18}O$ vplivajo padavine in infiltrirajoča voda, ki je obogatena s težjim kisikovim izotopom. $\delta^{13}C$ vrednosti v vodi se spreminjajo od -10.8 ‰ do 6.6 ‰ in odražajo biogeokemijske procese v kopenskem okolju in tudi v sami reki. Ti procesi so: 1) izmenjava z atmosferskim $CO_2$, 2) razgradnja organske snovi, 3) raztapljanje karbonatov in 4) pritoki. Prispevki posameznih procesov so bili izračunani upoštevajoč masno bilančni izračun in ocenjeni kot sledi: -11 %: 19 %: 31 %: 61 % v jesenskem času in 0 %: 26 %: 39 %: 35 % v spomladanski vzorčni sezoni.

### Introduction

The geochemical study of river water allows important information to be obtained on chemical weathering of rocks/soil and to determine different natural processes that provide chemical elements to the dissolved load (Gibbs 1972; Reeder et al., 1972; Hu et al., 1982; Stallard & Edmond, 1983; Goldstein & Jacobsen, 1987; Elderfield et al., 1990; Zhang et al., 1995; Huh et al., 1998; Négrel & Lachassagne, 2000). With regard to small catchments, the application of geochemical tools may provide important constraints on runoff (Ben Othmann et al., 1997) and on the different end-members, e.g natural and anthropogenic (Petelet et al., 1998).

Rivers also reflect the biogeochemical processes occurring in their catchment areas and help to quantify material transport from land to ocean (Palmer et al., 2001). Within this context, understanding of the carbon cycle is particularly important because it helps to evaluate the health of the river and its catchment basin (Telmer & Veizer, 1999). Carbonate mineral dissolution and precipitation reactions generally dominate solute inputs to rivers and also play an important role in the transformation of terrestrial organic carbon in soils to inorganic carbon. Investigations of major elements and stable carbon isotopes of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) are useful for such studies (Karim & Veizer, 2000; Barth et al., 2003).

Stable isotopes of carbon and nitrogen give information on biogeochemical processes occurring in the river, while stable isotopes in water give insight of recharge conditions in the watershed since it is known that rivers represent a part of hydrological cycle and a linkage between

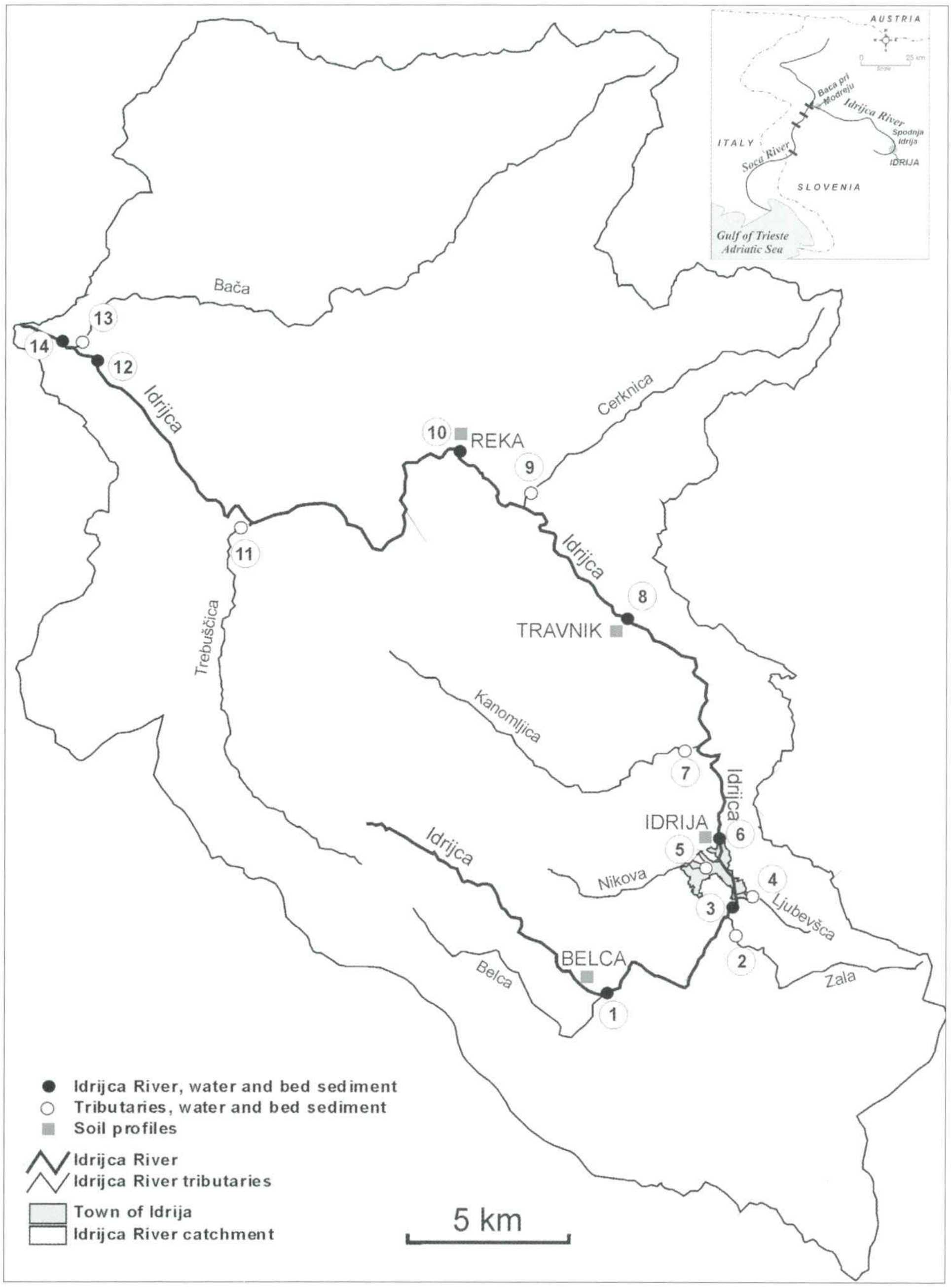


Figure 1. General map of the River Soča drainage basin indicating the location of Slovenia (SLO) and the River Idrijca study area, with a detailed location map of the numbered sampling sites in the River Idrijca watershed. Sample sites are described in Tables 1 and 2

precipitation and groundwater. Stable isotopes of oxygen and hydrogen are used to trace processes of evaporation, condensation, snow melting, mixing of waters of different origin in the studied watersheds (GAT, 1996; CLARK & FRITZ, 1997). Hydrogeochemical characteristics and carbon cycling of River Sava are presented elsewhere (KANDUČ et al., 2007, KANDUČ & OGRINC, 2007) and represent the basis for calculation the fluxes and mass balance in riverine ecosystem.

The present work concerns the small – sized catchment of the River Idrijca in Slovenia, which flows into the River Soča and further to the Gulf of Trieste. The main objectives of the current study were: 1) understand the major solute ($HCO_3$, $Ca^{2+}$, $Mg^{2+}$ and DOC) and stable carbon isotope dynamics ($\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$) of the River Idrijca system through time and space; and 2) to evaluate and quantify riverine carbon sources, sinks and fluxes in the river. We employed thermodynamic modelling, and the total and $^{13}C$ mass balance of dissolved inorganic carbon (DIC) to estimate the most important biogeochemical processes in the River Idrijca.

## Catchment characteristics of the River Idrijca Drainage Basin

The River Idrijca is 48 km long with a drainage area of 624 km$^2$ and it originates on the Vojskarska plateau (924 m. a. s. l.). Along the valley the River Idrijca flows through the town of Idrija and merges with the River Soča (Isonzo in Italy) about 40 km downstream from Idrija (Figure 1). The River Idrijca joins the River Soča in the middle stretch at the village of Most na Soči. Both rivers have torrential characteristics. As the mountains (Julian Alps) block air circulation from the northern Adriatic Sea to the north, annual precipitation is very high and ranges between 2400 and 5200 mm/year. The average winter temperature (ARSO, 2006-2007) is –5.4 °C, average summer temperature 10.4 °C and average yearly temperature in the valley 2.7 °C. High peaks and steep mountains slopes prevent air circulation in the valley and induce severe erosion. Due to abundant annual precipitation in the watershed, its average long-term discharge before the confluence with the River Soča is 33.6 m$^3$/s. The watershed also has many karst springs (Divje jezero, Podroteja) and several tributaries (right Belca, Zala, Cerknica and Bača, left Nikova, Kanomljica and Trebuša). Its discharge regime is a karst variant of a rain-snow discharge regime; the first maximum being in November, the second in April; with the lowest in summer and an above average winter discharge (Radinja, 1990).

Characteristic long term discharge data (from the years 1949 to 2004) according to the Agency of the Republic of Slovenia for the Environment (ARSO, 2006-2007) 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.

The upper part of the River Idrijca is composed of massive and bedded Triassic limestone and dolomite, which alternates with massive dolomite and conglomerates, which are composed of dolomite. The central part of the Idrijca is composed of Permian green grey conglomerate sandstone, mica quarz sandstone, and red sandstone with conglomerate on the right bank of the river. The left bank of the River Idrijca in its central flow is composed of Triassic dolomite, which alternates with sandstones, mudstones and marl. The lower part, before the confluence with the River Soča, is composed of Triassic stratus and massive dolomite and Cretaceous limestone breccia with marls (Buser et al., 1970; Buser et al., 1973; Buser et al., 1976; Buser et al., 1986). The surroundings of Idrijca have a complicated tectonic structure with a typical fold structure rupture, with faults in different directions. The greatest is the Idrijca fault, which ruptures the whole area of Slovenia and is also one of the largest in Europe (Radinja, 1990).

## Sampling Protocols and Field Measurements

Sampling locations in the Idrijca watershed for water samples and soils are presented in Figure 1. Surface water sampling locations were selected based on their relationship to confluences of major and minor streams, typically sampled before and after the confluence. Sampling was performed at 14 locations (Figure 1) in different seasons (autumn = November 2006 and spring = May 2007), according to the discharge regimes of the Idrijca (7 sampling locations) and its tributaries (7 sampling locations). Considering the long-term discharge regime of the River Idrijca, it should be mentioned that sampling was performed in low (autumn, 2006) and mean (spring, 2007) discharges. Temperature, conductivity, dissolved oxygen (DO), and pH measurements were performed in the field. The precision of dissolved oxygen saturation and conductivity measurements was ± 5 %. Because pH is sensitive to $CO_2$ 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 ± 0.02 pH unit.

Sample aliquots collected for chemical analysis were passed through a 0.45 µm nylon filter into polythene/glass bottles and kept refrigerated until analysed. Samples for cation (pre-treated with $HNO_3$), anion and alkalinity analyses were collected in HDPE bottles. Samples for dissolved inorganic carbon (pre-treated with $CuCl_2$) and $\delta^{13}C_{DIC}$ analyses were stored in glass serum bottles filled with no headspace and sealed with septa.

Sampling of water samples for $\delta^{18}O$ analyses was performed in plastic bottles of volume 50 ml filled to the top. Rainwater from the Idrijca location was sampled only at that location in autumn 2006 and spring 2007 during river water sampling.

Samples for stable carbon isotope analysis of particulate organic carbon ($\delta^{13}C_{POC}$) in autumn 2006 and spring 2007 were collected in LDPE bottles. In addition, carbonate rocks (n = 8) of Mesozoic age which form the landscape of the Idrijca watershed were sampled from outcrops for stable carbon analyses ($\delta^{13}C_{ca}$).

## Laboratory Analyses

Total alkalinity was measured within 24 h of sample collection by Gran titration (Gieskes 1974) with a precision of ± 1 %.

Major and minor cation chemistry was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Jobin Yvon Horiba instrument. The precision of the method was ± 2 % for major (Ca, Mg, Na and K) and ± 5 % for minor elements (Sr and Si). Anions were analyzed on a Dionex ICS-2500 IC apparatus with an analytical precision of ±2 %. Dissolved organic carbon (DOC) concentrations were measured using high-temperature platinum-catalyzed combustion followed by infrared detection of $CO_2$ (Shimadzu TOC-5000A) with a precision of ± 2 %.

Samples for determination of the isotopic composition of oxygen in water ($\delta^{18}O$) were first equilibrated with $CO_2$ according to the method of Epstein & Mayeda (1953) and then determined with a Varian Mat 250 mass spectrometer. NIST reference materials RM 8535 and RM 8537 with values 0±0 ‰ and -55.5±0 ‰ were used to relate results to VSMOW values (Craig, 1961; Coplen, 1988).

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined with a Europa Scientific 20-20 continuous flow IRMS (isotope ratio mass spectrometer) with ANCA -

Table 1. Chemical and isotopic data for the River Idrijca watershed, autumn 2006. Locations are plotted on Figure 1

Table 2. Chemical and isotopic data for the River Idrijca watershed, spring 2007. Locations are plotted on Figure 1

Table 1

| Location on the map | River Idrijca | A (km$^2$) | Q (m$^3$/s) | Distance from the town of Idrija (km) | Date of sampling | T (°C) | Conductivity (μS/cm) | pH | DO (%) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | Sr (mM) | Si (mM) | SO$_4$ (mM) | Cl (mM) | DOC (mM) | pCO$_2$ (bars) | SI$_{calcite}$ | SI$_{dolomite}$ | δ$^{13}$C$_{DIC}$ (‰) | δ$^{13}$C$_{POC}$ (‰) | δ$^{18}$O (‰) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Confluence Idrijca/Belca | | | -7,70 | 17.11.2006 | 8,8 | 338 | 8,17 | 107,4 | 4,35 | 1,05 | 0,76 | 0,06 | 0, 02 | 0,00 | 0,03 | 0,07 | 0,04 | 0,52 | -2,77 | 0,6 | 1,0 | -10,1 | -26,7 | -8,4 |
| 3 | Podroteja | 112,84 | 3,48 | -1,20 | 17.11.2006 | 8,0 | 327 | 7,96 | 92,4 | 3,88 | 1,23 | 0,68 | 0,06 | 0,01 | 0,00 | 0,02 | 0,06 | 0,07 | 0,66 | -2,61 | 0,4 | 0,4 | -9,3 | -25,7 | -8,4 |
| 6 | Kolektor | | | 0,50 | 17.11.2006 | 6,5 | 364 | 7,73 | 97,1 | 3,93 | 1,16 | 0,78 | 0,07 | 0,01 | 0,00 | 0,02 | 0,08 | 0,07 | 0,00 | -2,38 | 0,1 | -0,1 | -10,8 | | -8,6 |
| 8 | Idrijca Travnik | | | 9,85 | 17.11.2006 | 8,5 | 375 | 8,34 | 86,4 | 4,01 | 1,18 | 0,94 | 0,08 | 0,02 | 0,00 | 0,02 | 0,14 | 0,08 | 0,09 | -2,98 | 0,8 | 1,3 | -10,1 | -27,9 | -8,6 |
| 10 | Idrijca (Kozarska grapa) | | | 19,40 | 17.11.2006 | 9,0 | 409 | 8,06 | 82,7 | 3,99 | 1,26 | 0,97 | 0,12 | 0,06 | 0,00 | 0,02 | 0,35 | 0,11 | 0,00 | -2,70 | 0,5 | 0,9 | -9,4 | -27,8 | -8,5 |
| 12 | Idrijca pred Bačo | | | 37,50 | 17.11.2006 | 9,5 | 410 | 8,82 | 99,9 | 4,21 | 1,26 | 1,03 | 0,09 | 0,01 | 0,00 | 0,02 | 0,37 | 0,08 | 0,17 | -2,92 | 0,8 | 1,4 | -9,2 | | -8,4 |
| 14 | Idrijca po Bači | 442,83 | 4,37 | 37,70 | 17.11.2006 | 9,6 | 412 | 8,26 | 106,2 | 4,66 | 1,26 | 1,00 | 0,11 | 0,03 | 0,00 | 0,02 | 0,38 | 0,10 | 0,49 | -2,83 | 0,8 | 1,4 | -9,0 | | -8,2 |
| **Location on the map** | **River Idrijca tributaries** | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | Zala | | | -2,10 | 17.11.2006 | | | | | | | | | | | | | | | | | | | | |
| 4 | Ljubevšča | | | -0,50 | 17.11.2006 | 8,3 | 465 | 8,29 | 102,0 | 5,10 | 1,37 | 1,09 | 0,33 | 0,04 | 0,00 | 0,05 | 0,17 | 0,31 | 0,23 | -2,83 | 0,9 | 1,5 | -10,4 | | -8,3 |
| 5 | Nikova | | | 0,00 | 17.11.2006 | 8,4 | 434 | 8,23 | 88,1 | 4,70 | 1,38 | 0,89 | 0,23 | 0,04 | 0,01 | 0,04 | 0,14 | 0,19 | 0,00 | -2,80 | 0,8 | 1,3 | -9,9 | | -8,0 |
| 7 | Kanomljica | | | 4,45 | 17.11.2006 | 8,2 | 378 | 8,34 | 99,0 | 4,08 | 1,26 | 0,90 | 0,07 | 0,02 | 0,01 | 0,03 | 0,21 | 0,06 | 1,57 | -2,98 | 0,8 | 1,3 | -8,7 | | -8,6 |
| 9 | Cerknica | 40,3 | 0,342 | 15,85 | 17.11.2006 | 9,5 | 378 | 8,19 | 94,6 | 3,63 | 1,35 | 0,51 | 0,38 | 0,05 | 0,00 | 0,09 | 0,09 | 0,78 | 0,37 | -2,86 | 0,7 | 0,8 | -6,9 | | -8,5 |
| 11 | Trebušica | 54,7 | 0,548 | 28,87 | 17.11.2006 | 8,6 | 348 | 7,77 | 88,6 | 3,89 | 1,01 | 0,86 | 0,05 | 0,01 | 0,00 | 0,02 | 0,07 | 0,03 | 0,53 | -2,41 | 0,2 | 0,1 | -8,2 | | -8,5 |
| 13 | Bača | 142,31 | 2,92 | 37,60 | 17.11.2006 | 9,2 | 282 | 8,27 | 95,1 | 3,09 | 1,17 | 0,34 | 0,08 | 0,02 | 0,00 | 0,06 | 0,10 | 0,04 | 1,13 | -3,01 | 0,6 | 0,6 | -6,6 | | -8,1 |

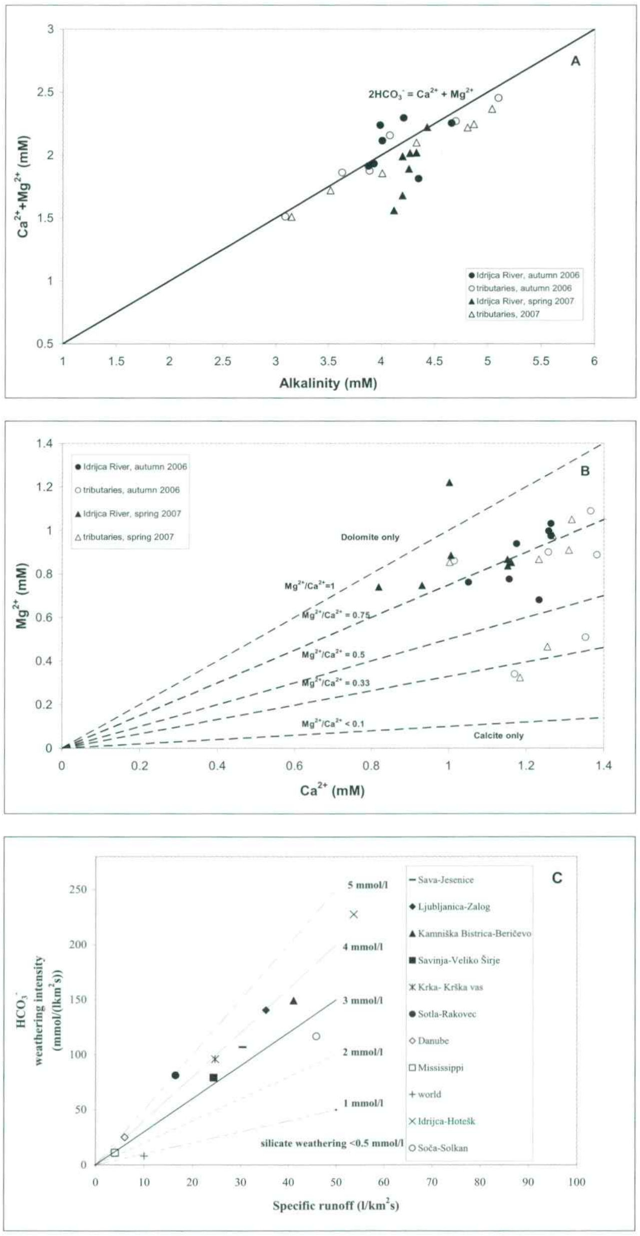
Table 2

| Location on the map | River Idrijca | A (km$^2$) | Q (m$^3$/s) | Date of sampling | T (°C) | Conductivity (μS/cm) | pH | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | Sr (mM) | Si (mM) | NO$_3$ (mM) | SO$_4$ (mM) | Cl (mM) | DOC (mM) | pCO$_2$ (bars) | SI$_{calcite}$ | SI$_{dolomite}$ | δ$^{13}$C$_{carb}$ (‰) | δ$^{13}$C$_{DIC}$ (‰) | *δ$^{13}$C$_{o+i}$ (‰) | δ$^{13}$C$_{POC}$ (‰) | δ$^{18}$O (‰) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Confluence Idrijca/Belca | | | 18.5.2007 | 9,0 | 333 | 8,43 | 4,12 | 0,82 | 0,74 | 0,05 | 0,00 | 0,00 | 0,00 | 0,06 | 0,04 | 0,03 | 0,40 | -3,14 | 0,7 | 1,2 | 0,8 | -9,4 | -22,7 | -27,8 | -8,5 |
| 3 | Podroteja | 112,84 | 8,99 | 18.5.2007 | 7,3 | 353 | 7,92 | 4,20 | 0,93 | 0,75 | 0,07 | 0,00 | 0,00 | 0,00 | 0,09 | 0,05 | 0,07 | 1,83 | -2,62 | 0,2 | 0,2 | 1,8 | -10,6 | -29,3 | -28,0 | -8,7 |
| 6 | Kolektor | | | 18.5.2007 | 10,8 | 367 | 8,43 | 4,33 | 1,15 | 0,87 | 0,11 | 0,05 | 0,00 | 0,02 | 0,05 | 0,11 | 0,10 | 0,33 | -3,12 | 0,8 | 1,5 | 2,0 | -10,1 | -15,9 | -26,9 | -8,6 |
| 8 | Idrijca Travnik | | | 18.5.2007 | 11,4 | 485 | 8,44 | 4,43 | 1,00 | 1,22 | 0,10 | 0,02 | 0,00 | 0,02 | 0,05 | 0,72 | 0,10 | 1,10 | -3,12 | 0,8 | 1,6 | 1,7 | -9,2 | -26,3 | -28,1 | -8,7 |
| 10 | Idrijca (Kozarska grapa) | | | 18.5.2007 | 11,7 | 416 | 8,29 | 4,26 | 1,01 | 0,89 | 0,11 | 0,02 | 0,00 | 0,03 | 0,04 | 0,36 | 0,11 | 1,29 | -2,97 | 0,7 | 1,2 | 1,9 | -9,3 | -25,4 | -27,1 | -8,7 |
| 12 | Idrijca pred Bačo | | | 18.5.2007 | 13,0 | 383 | 8,82 | 4,27 | 1,16 | 0,85 | 0,10 | 0,05 | 0,00 | 0,00 | 0,47 | 0,00 | 0,00 | 1,50 | -3,53 | 1,2 | 2,3 | | -8,4 | -24 | -27,3 | -8,6 |
| 14 | Idrijca po Bači | 442,83 | 23,77 | 18.5.2007 | 12,7 | 356 | 8,77 | 4,20 | 1,15 | 0,84 | 0,11 | 0,05 | 0,00 | 0,02 | 0,05 | 0,00 | 0,00 | 0,42 | -3,48 | 1,2 | 2,2 | 3,1 | -8,3 | -22,5 | -28,1 | -8,5 |
| **Location on the map** | **River Idrijca tributaries** | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | Zala | | | 18.5.2007 | 10,6 | 420 | 8,09 | 4,87 | 1,27 | 0,98 | 0,17 | 0,04 | 0,00 | 0,03 | 0,06 | 0,07 | 0,15 | 0,24 | -2,72 | 0,6 | 1,0 | | -9,7 | -31,6 | -31,3 | -8,5 |
| 4 | Ljubev‘ča | | | 18.5.2007 | 10,2 | 444 | 8,54 | 5,04 | 1,32 | 1,05 | 0,30 | 0,05 | 0,00 | 0,07 | 0,05 | 0,10 | 0,29 | 0,70 | -3,17 | 1,0 | 1,9 | | -9,6 | -25,8 | -27,6 | -8,5 |
| 5 | Nikova | | | 18.5.2007 | 10,1 | 418 | 8,67 | 4,81 | 1,31 | 0,91 | 0,20 | 0,06 | 0,01 | 0,04 | 0,04 | 0,10 | 0,13 | 0,35 | -3,33 | 1,1 | 2,0 | | -9,4 | -26,8 | -27,5 | -8,5 |
| 7 | Kanomljica | | | 18.5.2007 | 10,8 | 368 | 8,29 | 4,33 | 1,23 | 0,87 | 0,08 | 0,05 | 0,00 | 0,04 | 0,04 | 0,15 | 0,00 | 0,26 | -2,93 | 0,8 | 1,3 | | -9,4 | -24,2 | -26,7 | -8,7 |
| 9 | Cerknica | 40,3 | 1,84 | 18.5.2007 | 11,8 | 349 | 8,35 | 3,52 | 1,25 | 0,47 | 0,19 | 0,06 | 0,00 | 0,10 | 0,02 | 0,19 | 0,12 | 0,20 | -3,12 | 0,8 | 1,0 | | -7,6 | -24,5 | -26,6 | -8,7 |
| 11 | Trebu‘ica | 54,7 | 2,83 | 18.5.2007 | 11,6 | 181 | 8,37 | 4,01 | 1,00 | 0,85 | 0,06 | 0,04 | 0,00 | 0,02 | 0,05 | 0,05 | 0,03 | 0,13 | -3,08 | 0,7 | 1,3 | 2,9 | -8,0 | -26,2 | -27,3 | -8,6 |
| 13 | Bača | 142,31 | 6,94 | 18.5.2007 | 12,2 | 282 | 8,40 | 3,15 | 1,18 | 0,32 | 0,08 | 0,05 | 0,00 | 0,07 | 0,05 | 0,08 | 0,00 | 0,53 | -3,21 | 0,7 | 0,9 | 2,1 | -6,9 | -23,9 | -26,8 | -8,3 |

*δ13Co+i - isotopic composition of organic and inorganic carbon on filters

TG preparation module. Phosphoric acid (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 the 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 mM (for samples with an alkalinity above 2 mM) or of 2.4 mM (for samples with an alkalinity below 2 mM).

The carbon stable isotope composition of particulate organic carbon ($\delta^{13}C_{POC}$) was 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 filter (0.7 μm). Filters and soil were treated with 1M HCl to remove carbonate material and then dried at 60 °C and stored until analyses. Approximately 1 mg of particulate matter was scraped from the filter for analysis. Also, the isotopic composition of carbon of bulk particulate matter (organic and inorganic) with no acid pre-treatment was measured. IAEA CH-7 and IAEA N1 (ammonium sulphate) were used. Carbonate rocks (n = 8) were ground to powder in an agate mortar and then 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 ($\delta^{13}C_{ca}$) was measured with a Europa Scientific 20-20 continuous flow IRMS ANCA - TG preparation module.



All stable isotope results for carbon and oxygen are expressed in the conventional delta (σ) notation, defined as per mil (‰) deviation from the reference standards VPDB, AIR and VSMOW. Precision was ± 0.2 ‰ for $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$, $\delta^{13}C_{soil}$ and $\delta^{13}C_{ca.}$ and 0.1 ‰ for $\delta^{18}O$.

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

## Results and discussion

### Chemical composition and carbonate weathering intensity

The major solute composition of the River Idrijca and its tributaries was dominated by $HCO_3^-$, $Ca^{2+}$ and $Mg^{2+}$. Concentrations varied seasonally according to discharge (Tables 1 - 2), 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, with smaller contributions from silicate weathering, as indicated by the relatively high $HCO_3^-$ and low Si concentrations (Tables 1-2).

Figure 2A presents $Ca^{2+}$ + $Mg^{2+}$ versus alkalinity. Most of the samples have a 2:1 mole ratio of $HCO_3^-$ to $Ca^{2+}$ + $Mg^{2+}$ following the reactions of carbonate and dolomite dissolution (Barth et al., 2003).

Differences in $HCO_3^-$ concentrations in carbonate-bearing watersheds are related to the geological composition of the watershed, relief, mean annual temperature, the depth of the weathering zone, the soil thickness and residence time in the system. Weathering rates increase in thicker soils like shales due to the

Figure 2. Geochemical parameters:

**A.** $Ca^{2+}$ + $Mg^{2+}$ ratio versus alkalinity with line 1:2 indicating weathering of carbonates in the watershed in both sampling seasons

**B.** $Mg^{2+}$ versus $Ca^{2+}$ with lines indicating the dominance of dolomite or calcite weathering in the watershed

**C.** Carbonate weathering intensity ($HCO_3^-$ mmol/(km$^2$·l)) versus specific runoff indicating high carbonate weathering intensity in the Idrijca watershed in comparison to other rivers in Slovenia and in the world

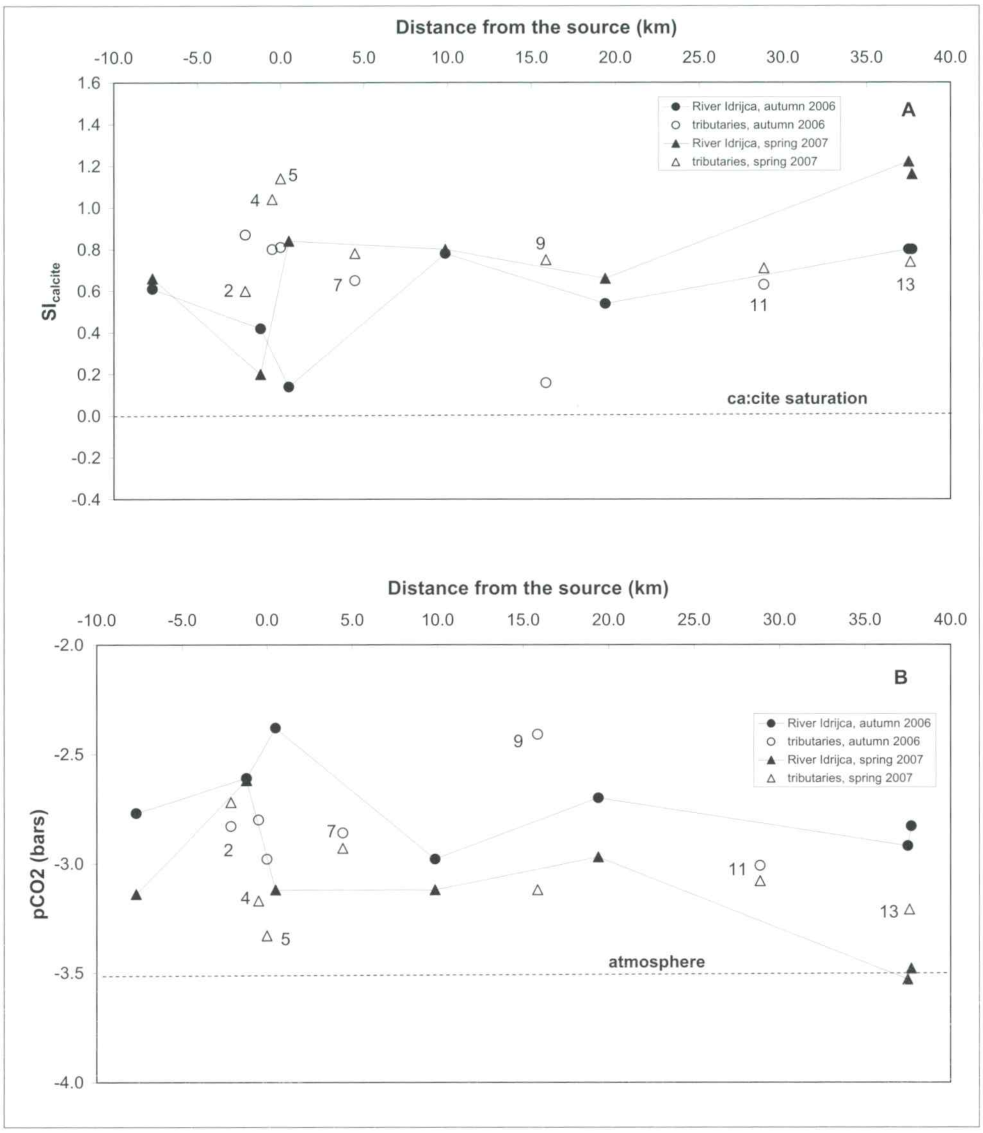


Figure 3. Thermodynamic modelling of the River Idrijca and its tributaries:

**A.** $pCO_2$ versus distance to the source,

**B.** $SI_{calcite}$ versus distance to the source in both sampling seasons (autumn 2006 and spring 2007)

higher residence time of shallow groundwaters in contact with minerals in comparison to watersheds composed of carbonate minerals. The results for $Ca^{2+}$ + $Mg^{2+}$ ranging from 1.5 to 2.5 and alkalinity concentrations ranging from 3.1 to 5.1 mM (Tables 1-2) in the Idrijca watershed indicate that dissolution of carbonates alone has the significant role in the upper part of the River Idrijca (location 1), and also in the lower part at location 13 (Bača tributary), which coincides with the geological composition of the watershed. It has been found that the $Ca^{2+}$ + $Mg^{2+}$ ratio ranges from 0.6 to 1.6 mM and $HCO_3^-$ between 1.2 to 3.2 mM in watersheds composed mostly from carbonates in the River Sava watershed in Slovenia (Szramek et al., 2007). Deviations are probably due to weathering of other minerals like anorthite and albite which also contribute to alkalinity in the watershed.

Figure 2 B represents $Mg^{2+}$ versus $Ca^{2+}$ and therefore determines the relative contribution of dolomite to carbonate weathering intensity in the Idrijca watershed. It was previously found that Slovenian streams have a wide range of $Mg^{2+}/Ca^{2+}$ ratios, indicating variations in the relative contribution of calcite and dolomite in different tributaries, ranging from 0.2 to nearly 0.8 (Szramek et al., 2007). Similar trends were observed in the River Idrijca, but it has to be emphasized that most of the samples indicate that weathering of dolomite is dominant over the entire River Idrijca, especially in the upper and central flow of the river, where weathering of dolomite prevails. A $Mg^{2+}/Ca^{2+}$ ratio around 0.33, which is typical for weathering of calcite with magnesium, is characteristic only in the lowland tributaries of the River Idrijca composed mainly of calcite (Cerknica – location 12 and Bača - location 14).

The major control on carbonate weathering intensity is runoff, (e.g., Holland, 1978; Amiotte Suchet & Probst, 1993). Carbonate weathering intensity normalized to drainage area quantifies $HCO_3^-$ produced from mineral weathering. 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 et. al., 2007), and therefore total alkalinity is assumed as $HCO_3^-$, which is

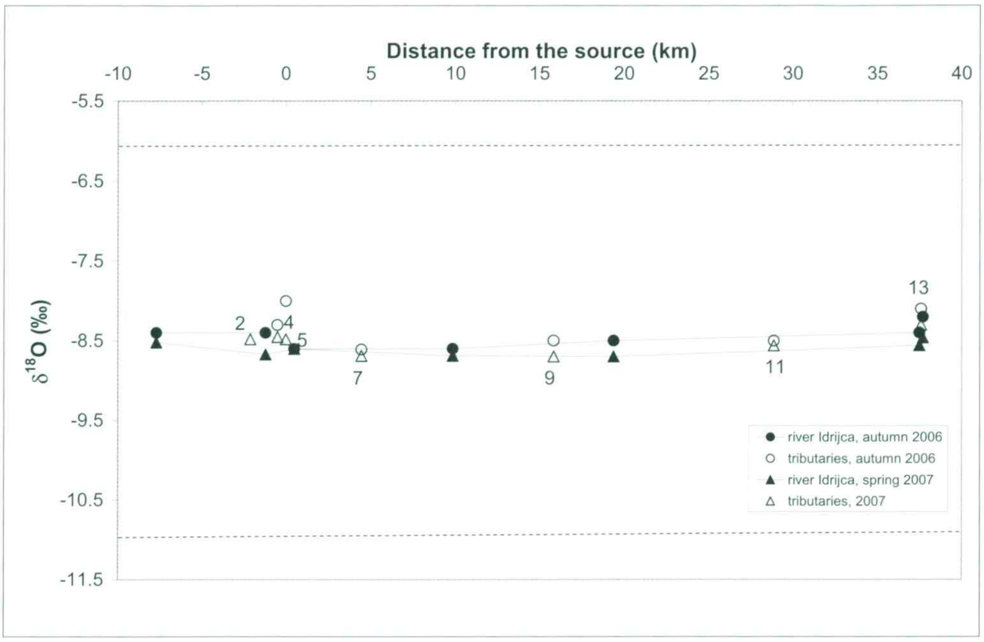


Figure 4: $\delta^{18}O$ in the River Idrijca and its tributaries versus distance to the source in both sampling seasons (autumn 2006 and spring 2007). Dashed lines indicate $\delta^{18}O$ values of precipitation, which range from –11.1 to –5.9 ‰ during sampling

the main DIC species at the pH of 7.73 to 8.82 measured in the Idrijca watershed. Figure 2 C compares carbonate weathering intensities as a function of specific runoff for the Idrijca watershed, combining new data from this study with published official data for the river Sava (largest river in Slovenia) (EIONET, 2005) and data from BERNER AND BERNER, 1996 for world rivers and the Danube. Global theoretical models of $CO_2$ consumption in carbonate watersheds show an alkalinity value around 3 mmol/1 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 & BLUM, 2003) and causes a high carbonate weathering intensity, since the river is a steep mountain river with torrential character.

The world average value for carbonate weathering intensity is 7 mmol/(l·km$^2$·s). For the River Sava and its tributaries the mean long term weathering intensity is from 37 to 140 mmol/(l·km$^2$·s). It was estimated from available data (mean long term discharge, alkalinity, drainage area, ARSO 2006 - 2007) that the River Idrijca at the Hotešk location (14) has a much higher carbonate weathering intensity of around 227 mmol//(l·km$^2$·s).

Seasonal variations of carbonate alkalinity are shown in Tables 1 - 2. The alkalinity concentrations in main channel sampling sites varied seasonally from 3.93 to 4.66 mM in autumn and from 4.12 to 4.43 mM in spring 2007. Alkalinity in tributaries varies from 3.09 to 5.10 mM in autumn 2006 and from 3.15 to 5.04 mM in spring 2007. The high alkalinities (around 5 mM) observed in tributaries could also be a consequence of uncontrolled industrial sewage and municipal wastes.

Calculated $CO_2$ partial pressures ($pCO_2$) varied from 977 to 4169 ppm in autumn and from 295 to 2398 ppm in the spring sampling season (Figure 3 A). Normal atmospheric pressure is around 316 ppm according to CLARK & FRITZ 1997. 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 12 and 14) in the spring are observed due to the higher pH of the water, which lowers evasion of $CO_2$ from water.

The calcite saturation index ($SI_{calcite}$ = log $([Ca^{2+}]\cdot[CO_3^{2-}])/K_{calcite}$; where $K_{calcite}$ is the solubility product of calcite was generally well above equilibrium ($SI_{calcite} = 0$) (Figure 3 B), indicating that calcite) was supersaturated and precipitation was thermodynamically favoured along most of the course of the River Idrijca in spring and autumn sampling seasons.

## Isotopic composition of oxygen in the Idrijca watershed

$\delta^{18}O$ values in the River Idrijca watershed at the sampling locations (Tables 1-2) dependent on several factors: precipitation, evaporation, evapotranspiration, infiltration and equilibration with run-off (YEE et al., 1990). The $\delta^{18}O$ value in the River Idrijca seasonally ranged from –8.6 to –8.2 ‰ in autumn 2006, and from –8.7 to –8.5 ‰ in spring 2007. Values of $\delta^{18}O$ of Idrijca tributaries varied from –8.6 to –8.0 ‰ in autumn 2006, and from –8.7 to –8.3 ‰ in spring 2007 (Tables 1-2, Figure 4). $\delta^{18}O$ of precipitation in Idrija ranged

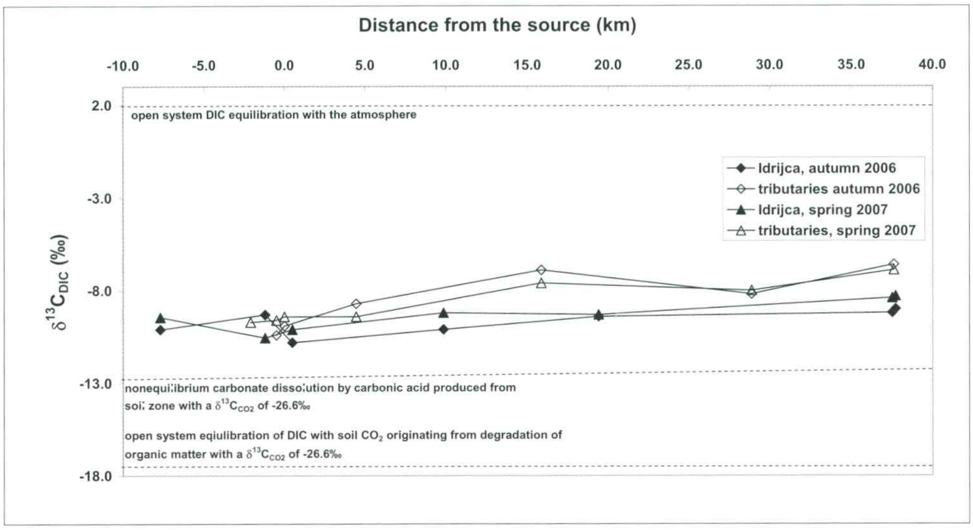


Figure 5. Variation in the $\delta^{13}C_{DIC}$ versus distance from the source in the River Idrijca, with lines indicating processes occurring in the River Idrijca watershed. These include values calculated for: 1) open system DIC in equilibration with the atmosphere, 2) nonequilibrium carbonate dissolution by carbonic acid produced from soil zone $CO_2$, and 3) open system equilibration of DIC with soil $CO_2$ originating from degradation of organic matter with $\delta^{13}C_{soil}$ = -26.6 ‰

from –11.1 ‰ to –5.9 ‰, which is over a larger range than river water. Differences in precipitation in Slovenia result from different water masses from continental, Alpine and Mediterranean sources, as is fully described in Vreča et al. 2004. Thus, seasonal variation of $\delta^{18}O$ values in the Idrijca watershed results from the different origin of precipitation and isotopic enrichment of soil water from slopes recharging the watershed. The height of the recharge area of the River Idrijca is below 1000 m a. s. l along the whole watershed. Kinetic effects during evaporation also affect the $\delta^{18}O$ value and therefore should not be neglected. These effects may be attributed to surface water temperature, wind velocity (shear at the surface water) and, most importantly, the relative humidity of the air (molecular diffusion between water-atmosphere) (Gonfiantini, 1986).

## Sources of dissolved inorganic carbon (DIC) in the River Idrijca inferred from the isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and mass balances of dissolved inorganic carbon.

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 the River Idrijca watershed. $\delta^{13}C_{DIC}$ varied seasonally from –10.8 to –9.0 ‰ in autumn 2006 and from –10.6 to –8.3 ‰ in spring 2007 (Figure 5). The River Idrijca tributaries had $\delta^{13}C_{DIC}$ values that varied from –10.4 to –6.6 ‰ in autumn 2006 and from –9.7 to –6.9 ‰ in spring 2007. $\delta^{13}C_{DIC}$ was lower during the spring at higher discharge (Figure 5). The $\delta^{13}C_{DIC}$ value of the Idrijca is also controlled by the geological composition of the watershed. Along the 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. Thus, in those parts $\delta^{13}C_{DIC}$ is much lower (central part of the River Idrijca) since the thickness of soil is on this bedrock much higher and soil $CO_2$ contributes much more to DIC than on carbonate bedrocks.

The $\delta^{13}C$ value of Mesozoic carbonate rocks ($\delta^{13}C_{ca}$), which forms the slopes in the watershed of the River Idrijca, ranged from 0.8 to 3.1 ‰ (Table 2), with an average of 2.0 ± 0.7 ‰ (n = 8).

A simple isotopic mass balance calculation was performed in order to quantify different sources of DIC at the River Idrijca mouth (location 14), 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:

$$DIC_{RI} = DIC_{tri} - DIC_{ex} + DIC_{org} + DIC_{ca} \qquad (1)$$

$$DIC_{RI}\cdot\delta^{13}C_{RI} = DIC_{tri}\cdot\delta^{13}C_{tri} - DIC_{ex}\cdot\delta^{13}C_{ex} + DIC_{org}\cdot\delta^{13}C_{POC} + DIC_{ca}\cdot\delta^{13}C_{Ca} \qquad (2)$$

In Eq. (1) and (2) the minus sign indicates outgassing of $CO_2$, which is observed in autumn, but not in the spring season. 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 (Tables 1-2) and water discharge (Tables 1-2), 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. (3), was taken into account as follows (Broecker, 1974; Broecker et al., 1978):

$$[DIC]_{ex} = \frac{D}{z}\cdot([CO_2]_{eq} - [CO_2]) \qquad (3)$$

where $D$ is the $CO_2$ diffusion coefficient in water of 1.26 x $10^{-5}$ $cm^2/s$ at a temperature of 10 °C and 1.67 x $10^{-5}$ $cm^2/s$ at a temperature of 20 °C (Jähne et al., 1987), $z$ is the empirical thickness of the liquid layer [cm], $[CO_2]_{eq}$ and $[CO_2]$ are the dissolved $CO_2$ concentrations at equilibrium with the atmosphere and with the studied water [mol · $cm^{-3}$], 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.

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 Idrijca drainage system. For $\delta^{13}C_{POC}$ and $\delta^{13}C_{Ca}$ average values of –26.6 ‰ and 2.0 ‰ were used in the mass balance equations.

The $DIC_{org}$ and $DIC_{Ca}$ values were determined by solving the mass balance equations. The calculated fluxes for both sampling seasons are presented in Table 4. 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. 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 14), which is near equilibrium with atmospheric $CO_2$ pressure. Among biogeochemical processes dissolution of carbonates contributes the highest proportion in both sampling seasons, which moves $\delta^{13}C_{DIC}$ to more positive values.

## Conclusions

The major solute composition of River Idrijca water is dominated by $HCO_3^-$, $Ca^{2+}$ and $Mg^{2+}$. Seasonal (autumn 2006, spring 2007) 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 in both sampling seasons. According to the calculated $pCO_2$ pressures, the Idrijca represents a source of $CO_2$ (on average 4 times supersaturated) to the atmosphere during autumn and spring sampling seasons, except at the Idrijca River mouth. Seasonal variations of major chemical constituents and of stable isotope composition are due to differences in discharge conditions (low long term discharge in autumn, mean long term discharge in spring); lower ion concentrations ($HCO_3^-$, $Ca^{2+}$ and $Mg^{2+}$, Si), $pCO_2$, and $\delta^{13}C_{DIC}$ were observed in spring, while higher ion concentrations, $pCO_2$, and $\delta^{13}C_{DIC}$ were observed in autumn. $\delta^{13}C_{POC}$ values indicated that suspended matter is composed of degraded organic material from C3 plants. $\delta^{18}O$ values in the River Idrijca are controlled by precipitation and evapotranspiration processes in soil.

The biogeochemical processes affecting DIC concentrations and $\delta^{13}C_{DIC}$ were quantified by carbon component mass balance calculations, showing that the most important biogeochemical processes at the River Idrijca mouth in order of significance in different sampling seasons are: (1) carbonate mineral dissolution comprising 30.5 % in autumn to 38.6 % in spring, (2) degradation of organic matter comprising 19.6 % in autumn to 26.1 % in spring, and (3) atmospheric exchange comprising 0 % in spring to 11 % in autumn. Dissolution of carbonates (carbonate weathering) and degradation of organic matter are the most significant in the spring sampling season.

The River Idrijca is a river with torrential character, has a high specific discharge and therefore high weathering intensity. Among the biogeochemical processes geological factors prevail (carbonate dissolution).

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