Hydrogeochemical characteristics of the River Idrijca (Slovenia)

Tjaša KANDUČ
Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana

Key words: River Idrijca, chemical composition, stable isotopes, carbon, oxygen, Slovenia

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. δ$^{18}$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 δ$^{13}$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 %: 8 %: 9 %: 35 % in the spring sampling seasons.

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; NÉGRE & LACHASSAGNE, 2000). With regard to small catchments, the application of geochemical tools may provide important constraints on runoff (BEN OTTMANN 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 (δ$^{13}$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
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 (HCO₃, Ca²⁺, Mg²⁺ and DOC) and stable carbon isotope dynamics (δ¹³CDOC, δ¹³CPOC) 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 δ¹³C 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 km² 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 m³/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 (Radina, 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 Hotešek, which is located above the confluence with the River Soča, are as follows: low long term discharge varies from 3.4 to 8.3 m³/s, mean long term discharge varies from 14.3 to 39 m³/s and high long term discharge varies from 113 to 644 m³/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 quartz 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 (Busser et al., 1970; Busser et al., 1973; Busser et al., 1976; Busser 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 greatest is the Idrijca fault, which ruptures the whole area of Slovenia and is also one of the

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 CO₂ (Shimadzu TOC-5000A) with a precision of ±2 %.

Samples for determination of the isotopic composition of oxygen in water (δ¹⁸O) were first equilibrated with CO₂ 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 (δ¹³C) was determined with a Europa Scientific 20-20 continuous flow IRMS (isotope ratio mass spectrometer) with ANCA -
Table 1

<table>
<thead>
<tr>
<th>Location on the map</th>
<th>River Idrijca</th>
<th>Distance from the town of Idrija (km)</th>
<th>Date of sampling</th>
<th>T (°C)</th>
<th>Conductivity (μS/cm)</th>
<th>pH</th>
<th>DIC (‰)</th>
<th>Alkalinity (mM)</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
<th>Na (mM)</th>
<th>K (mM)</th>
<th>Sr (mM)</th>
<th>Cl (mM)</th>
<th>SO₄ (mM)</th>
<th>CO₂ (mM)</th>
<th>DOC (%)</th>
<th>δ¹³C (‰)</th>
<th>δ¹⁸O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Confluence Idrija/Bela</td>
<td>139.0</td>
<td>0.0</td>
<td>18.5.2007</td>
<td>7.0</td>
<td>0.43</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-2.02</td>
<td>0.6</td>
<td>1.5</td>
<td>-20.4</td>
</tr>
<tr>
<td>Podreberje</td>
<td>122.64</td>
<td>0.99</td>
<td>18.5.2007</td>
<td>7.3</td>
<td>0.43</td>
<td>0.75</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-2.64</td>
<td>0.6</td>
<td>1.5</td>
<td>-20.6</td>
</tr>
<tr>
<td>Košičko</td>
<td>112.07</td>
<td>0.83</td>
<td>18.5.2007</td>
<td>7.4</td>
<td>0.43</td>
<td>0.75</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-2.85</td>
<td>0.6</td>
<td>1.5</td>
<td>-20.5</td>
</tr>
<tr>
<td>Idrija Travnik</td>
<td>106.64</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>7.6</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.04</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.2</td>
</tr>
<tr>
<td>Idrija (Koritnica gora)</td>
<td>106.6</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>7.8</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.13</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.0</td>
</tr>
<tr>
<td>Idrija (Dolavec)</td>
<td>101.44</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>8.0</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.21</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.3</td>
</tr>
<tr>
<td>Idrija (Boljevci)</td>
<td>98.23</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>8.2</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.13</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.2</td>
</tr>
<tr>
<td>Idrija (Preddolavec)</td>
<td>95.06</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>8.4</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.22</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.5</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Location on the map</th>
<th>River Idrijca</th>
<th>Distance from the town of Idrija (km)</th>
<th>Date of sampling</th>
<th>T (°C)</th>
<th>Conductivity (μS/cm)</th>
<th>pH</th>
<th>DIC (‰)</th>
<th>Alkalinity (mM)</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
<th>Na (mM)</th>
<th>K (mM)</th>
<th>Sr (mM)</th>
<th>Cl (mM)</th>
<th>SO₄ (mM)</th>
<th>CO₂ (mM)</th>
<th>DOC (%)</th>
<th>δ¹³C (‰)</th>
<th>δ¹⁸O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Confluence Idrija/Bela</td>
<td>139.0</td>
<td>0.0</td>
<td>18.5.2007</td>
<td>7.0</td>
<td>0.43</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-2.02</td>
<td>0.6</td>
<td>1.5</td>
<td>-20.4</td>
</tr>
<tr>
<td>Podreberje</td>
<td>122.64</td>
<td>0.99</td>
<td>18.5.2007</td>
<td>7.3</td>
<td>0.43</td>
<td>0.75</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-2.64</td>
<td>0.6</td>
<td>1.5</td>
<td>-20.6</td>
</tr>
<tr>
<td>Košičko</td>
<td>112.07</td>
<td>0.83</td>
<td>18.5.2007</td>
<td>7.4</td>
<td>0.43</td>
<td>0.75</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-2.85</td>
<td>0.6</td>
<td>1.5</td>
<td>-20.5</td>
</tr>
<tr>
<td>Idrija Travnik</td>
<td>106.64</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>7.6</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.04</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.2</td>
</tr>
<tr>
<td>Idrija (Koritnica gora)</td>
<td>106.6</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>7.8</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.13</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.0</td>
</tr>
<tr>
<td>Idrija (Dolavec)</td>
<td>101.44</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>8.0</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.21</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.3</td>
</tr>
<tr>
<td>Idrija (Boljevci)</td>
<td>98.23</td>
<td>1.00</td>
<td>18.5.2007</td>
<td>8.2</td>
<td>0.45</td>
<td>0.74</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-3.13</td>
<td>0.6</td>
<td>1.5</td>
<td>-21.2</td>
</tr>
</tbody>
</table>
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 CO₂ 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 Na₂CO₃ (Carlo Erba) with a known δ¹³C_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 (δ¹³C_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.

Thermodynamic modelling was used to evaluate pCO₂ 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 HCO₃⁻, Ca²⁺ and Mg²⁺. 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 Ca²⁺ and Mg²⁺ are largely supplied by the weathering of carbonates, with smaller contributions from silicate weathering, as indicated by the relatively high HCO₃⁻ and low Si concentrations (Tables 1-2).

Figure 2A presents Ca²⁺ + Mg²⁺ versus alkalinity. Most of the samples have a 2:1 mole ratio of HCO₃⁻ to Ca²⁺ + Mg²⁺ following the reactions of carbonate and dolomite dissolution (BARTH et al., 2003).

Differences in HCO₃⁻ 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
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
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\textsubscript{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\textsuperscript{2})-s. For the River Sava and its tributaries the mean long term weathering intensity is from 37 to 140 mmol/(l-km\textsuperscript{2})-s. It was estimated from available data (mean long term discharge, alkalinity, drainage area, ARSO 2006 - 2007) that the River Idrijca at the Hotešek location (14) has a much higher carbonate weathering intensity of around 227 mmol/(l-km\textsuperscript{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 alkalinitities (around 5 mM) observed in tributaries could also be a consequence of uncontrolled industrial sewage and municipal wastes.

Calculated CO\textsubscript{2} partial pressures (pCO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} from water.

The calcite saturation index (SI\textsubscript{calcite} = log ([Ca\textsuperscript{2+}][CO\textsubscript{3}\textsuperscript{2-}])/K\textsubscript{calcite}; where K\textsubscript{calcite} is the solubility product of calcite) was generally well above equilibrium (SI\textsubscript{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

δ\textsuperscript{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 δ\textsuperscript{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 δ\textsuperscript{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). δ\textsuperscript{18}O of precipitation in Idrija ranged

![Figure 4: δ\textsuperscript{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 δ\textsuperscript{18}O values of precipitation, which range from −11.1 to −5.9 ‰ during sampling](image-url)
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 Vreća 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 \((\delta^{13}C_{\text{DIC}})\) and mass balances of dissolved inorganic carbon.**

The \(\delta^{13}C_{\text{DIC}}\) 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. \(\delta^{13}C_{\text{DIC}}\) 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 \(\delta^{13}C_{\text{DIC}}\) values that varied from \(-10.4\) to \(-6.6\%\) in autumn 2006 and from \(-9.7\) to \(-6.9\%\) in spring 2007. \(\delta^{13}C_{\text{DIC}}\) was lower during the spring at higher discharge (Figure 5). The \(\delta^{13}C_{\text{DIC}}\) 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 \(\delta^{13}C_{\text{DIC}}\) values, but some parts of the watershed also drain shales, mudstones, and sandstones. Thus, in those parts \(\delta^{13}C_{\text{DIC}}\) 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 \((\delta^{13}C_{\text{car}})\), 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 \(\pm\) 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$_{\text{RI}}$) and \(\delta^{13}C_{\text{DIC}}\) originate from tributaries (DIC$_{\text{tri}}$), degradation of organic matter (DIC$_{\text{org}}$), exchange with the atmosphere (DIC$_{\text{at}}$), and dissolution of carbonates (DIC$_{\text{car}}$) can be estimated by:

\[
\text{DIC}_{\text{RI}} = \text{DIC}_{\text{tri}} - \text{DIC}_{\text{ex}} + \text{DIC}_{\text{org}} + \text{DIC}_{\text{at}} \tag{1}
\]

\[
\text{DIC}_{\text{RI}}\delta^{13}C_{\text{RI}} = \text{DIC}_{\text{tri}}\delta^{13}C_{\text{tri}} - \text{DIC}_{\text{ex}}\delta^{13}C_{\text{ex}} + \text{DIC}_{\text{org}}\delta^{13}C_{\text{org}} + \text{DIC}_{\text{at}}\delta^{13}C_{\text{at}} \tag{2}
\]

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$_{\text{RI}}$ and DIC$_{\text{at}}$ 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_{\text{RI}}$ and \(\delta^{13}C_{\text{at}}$. The average diffusive flux of CO$_2$ from the river to the atmosphere, DIC$_{\text{at}}$ estimated from Eq. (3), was taken into account as follows (Broecker, 1974; Broecker et al., 1978):

\[
[DIC]_{\text{at}} = \frac{D}{2} \cdot [\text{CO}_2]_{eq} - [\text{CO}_2] \tag{3}
\]

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 (Jahn 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

---

**Figure 5.** Variation in the \(\delta^{13}C_{\text{DIC}}\) 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 \(\delta^{13}C_{\text{car}} = -26.6\%\).
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 $\delta^{13}C_{\text{org}}$ 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 equilibrium between atmospheric CO$_2$ and DIC ($\delta^{13}C_{\text{DIC}}$) 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 $\delta^{13}C_{\text{POC}}$ and $\delta^{13}C_{\text{Ca}}$, average values of $-26.6$ % and $2.0$ % were used in the mass balance equations.

The DIC$_{\text{org}}$ and DIC$_{\text{Ca}}$ 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$_{\text{org}}$:DIC$_{\text{Ca}}$:DIC$_{\text{Ca}}$:DIC$_{\text{Ca}}$ 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 $\delta^{13}C_{\text{DIC}}$ 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 $\delta^{13}C_{\text{DIC}}$ were observed in spring, while higher ion concentrations, pCO$_2$, and $\delta^{13}C_{\text{DIC}}$ were observed in autumn. $\delta^{13}C_{\text{POC}}$ 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 $\delta^{13}C_{\text{DIC}}$ 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).

Acknowledgements

The author is grateful to Mr. Stojan Čigon, Mrs. Leonida Mehle and Corey Lambert for technical support. The authors acknowledge financial support from the state budget by the Slovenian Research Agency and programme research group “Cycling of nutrients and contaminants in the environment, mass balances and modelling environmental processes and risk analysis” (P1-0143). Special thanks are given to Anthony Byrne for linguistic corrections.

References


The fluvial geochemistry of the rivers


Hydrogeochemical characteristics of the River Idrijca (Slovenia)


SPOTL, C. 2005: A robust and fast method of sampling and analysis of δ¹³C of dissolved inorganic carbon in ground waters. Isotopes in Environmental and Health Studies, 41: 217-221.


