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Tracing biogeochemical processes and pollution sources with stable isotopes in river systems: Kamniška Bistrica, North Slovenia

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Abstract

Biogeochemical processes were investigated in the Kamniška Bistrica River (Slovenia), which represents an ideal natural laboratory for studying pollution sources in catchments with high weathering capacity. The Kamniška Bistrica River water chemistry is dominated by HCO_3^-, Ca^{2+}, and Mg^{2+} and Ca^{2+}/Mg^{2+} molar ratios indicate that calcite weathering is the major source of solutes to the river system. The Kamniška Bistrica River and its tributaries are oversaturated with respect to calcite and dolomite. pCO$_2$ concentrations were on average up to 25 times over atmospheric values. δ^{18}O values in river water ranged from −10.4 to −7.7 ‰ and plotted near the local meteoric water line, $\delta^{13}C_{DIC}$ values ranged from −12.7 to −2.7 ‰, controlled by biogeochemical processes in the catchment and within the stream; carbon dissolution is the most important biogeochemical process affecting carbon isotopes in the upstream portions of the catchment, while carbon dissolution and organic matter degradation control carbon isotope signatures downstream. Contributions of DIC from various biogeochemical processes were determined using steady state equations for different sampling seasons at the mouth of the Kamniška Bistrica River; results indicate that: (1) 1.9 to 2.2 % of DIC came from exchange with atmospheric CO$_2$, (2) 0 to 27.5 % of DIC came from degradation of organic matter, (3) 25.4 to 41.5 % of DIC came from dissolution of carbonates, and (4) 33 to 85 % of DIC came from tributaries. δ^{15}N values of nitrate ranged from −5.2 ‰ at the headwater spring to 9.8 ‰ in the lower reaches. Higher δ^{15}N values in the lower reaches of the river suggest anthropogenic pollution from agricultural activity.

1 Introduction

Systematic studies of river water geochemistry provides important information on chemical weathering of bedrocks/soil and natural and anthropogenic processes that may control the dissolved chemical load (Gibbs, 1972; Reeder et al., 1972; Hu et al., 1982; Elderfield, 1990; Zhang et al., 1995; Huh, et al., 1998; Négrel and Lachassagne, 2000; Schulte et al., 2011 and the references therein). Since carbonate weathering largely dominates the water chemistry of river waters, characterization of the water chemistry of rivers draining carbonate-dominated terrain is crucial to precisely identify the various contributions of the different sources of water solutes, and to estimate weathering rates of the continental crust and associated CO_2 consumption (Gaillardet et al., 1999a,b; Liu and Zhao, 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-member solute sources, e.g. natural and anthropogenic (Petelet et al., 1998).

Rivers also reflect the biogeochemical processes occurring in their catchment areas, riparian zones and in-stream, and help to quantify material transport from the land to oceans (Palmer et al., 2001). The global riverine flux of dissolved inorganic carbon to the ocean is about 0.38×10^{15} g yr^{-1} (Meybeck, 1993), similar in magnitude to the global riverine flux of organic carbon to the oceans, which is estimated to be 0.4×10^{15} g yr^{-1} (Meybeck, 1982; Ittekot, 1988). Riverine C represents a significant part of the global C budget since the total annual anthropogenic C input from fossil fuels is $5–6 \times 10^{15}$ g yr^{-1} (Berner and Berner, 1996).

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 and Veizer, 1999). Carbon in rivers may occur as: dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), inorganic particulate carbon (PIC) and particulate organic carbon (POC) (Cartwright, 2010). 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 and Veizer, 2000; Barth et al., 2003, Hagedorn and Cartwright, 2010; Cartwright, 2010). Suspended organic matter in rivers is mostly derived from soil and plant material, and therefore the isotopic composition of suspended organic matter ($\delta^{13}C_{POC}$) in rivers has been used to ascertain the contribution of terrestrial vegetation and soil matter in the river ecosystem (Ittekot, 1988; Hedges, 1992). Most soil organic matter (SOM) is plant-derived; only a small fraction of the yearly litter and root input becomes part of the stable organic matter pool, most of it after repeated processing by soil microorganisms (Six et al., 2004). The natural abundance of the ^{13}C and ^{15}N content in SOM is usually higher than that of the plant and fresh litter input (Amundson et al., 2003).

Stable isotopes of carbon and nitrogen provide insight into biogeochemical processes occurring in the river. Stable isotopes of oxygen and hydrogen are frequently used to trace processes of evaporation, condensation, snow melt discharge, and mixing of waters of different origins in watersheds (Gat, 1996; Clark and Fritz, 1997).

Nitrogen is a biologically active element and participates in a multitude of reactions that are important for life, and that affect water quality. At concentrations above $10\,mg\,l^{-1}$ N-NO_3^- it causes methemoglobinemia (Clark and Fritz, 1997). Ammonium tends to be oxidized to nitrate in a two-step process: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ by aerobic chemoautotrophic bacteria. This nitrification process can even occur if levels of dissolved oxygen decline to a value as low as $1.0\,mg\,O_2\,l^{-1}$ (Stumm and Morgan, 1996; Wetzel, 2001). Macrophytes, algae and bacteria can assimilate NH_4^+, NO_2^- and NO_3^- and remove them from water (Smith, 2003). Furthermore, denitrification can take place in anoxic water resulting in formation of N_2O and N_2 (Pearl et al., 2002). Anthropogenic inputs of particulate nitrogen and organic nitrogen to the environment can also result in inorganic nitrogen pollution (National Research Council, 2000). Previous studies have attempted to identify sources of nitrate in water systems using stable isotopic ratios (e.g. Harrington et al., 1998; Hebert and Wassenaar, 2001; Mayer et al., 2002; Kellman and Hillaire-Marcel, 2003; Voss et al., 2006). If nitrate sources (atmospheric deposition, fertilizer, soil, and manure) have distinct isotopic signatures, stable isotopes of nitrate may be used to distinguish contamination sources in the environment. In the mineralization of soil organic matter N, the $\delta^{15}N$ of the resulting NO_3^- will be the same as that of the original organic N (+4 to +9 ‰ range; Heaton, 1986). The distinct differences in

$\delta^{15}N$ of NO_3^- values originating from animal waste (generally > 10‰) versus mineral N fertilizers (typically close to or < 0‰) means that NO_3^- in waters originating from a combination of these sources should lie within the range of these samples if NO_3^- behaves conservatively during transport (Heaton, 1986). A complicating factor in source identification is bacterial denitrification, which could occur in stream transport during low flow periods and causes fractionation that results in the progressive enrichment of the remaining NO_3^- in ^{15}N (Kendall, 1998; Kellman and Hillaire-Marcel, 2003).

In this study we use multiple tracers to better constrain biogeochemical processes and pollution sources in the Kamniška Bistrica River, a small size catchment (535 km^2) in Slovenia, which changes from a relatively pristine Alpine River at its headwaters to a polluted river downstream. The Kamniška Bistrica River is also an important recharge source to the northeastern part of the Ljubljana aquifer in Slovenia, which is a major groundwater resource in the region.

The main objectives of the current study were to: (1) understand the spatial and temporal dynamics of dissolved (Ca^{2+}, Mg^{2+}, HCO_3^-, $NO_3^-\delta^{13}C_{DIC}$, $\delta^{18}O$, $\delta^{15}N_{NO_3^-}$) and suspended species ($\delta^{13}C_{POC}$, $\delta^{15}N_{PN}$) of carbon and nitrogen; (2) evaluate and quantify riverine carbon and nitrogen sources, sinks and fluxes; and (3) determine most important biogeochemical processes and pollution sources in river system using geochemical and isotopic approaches. This study also represents the first systematic hydrogeochemical study of Alpine Rivers in Slovenia. Previous studies of river systems in Slovenia were conducted on Dinaric Rivers and rivers with high/flashy discharges draining to the Black and Adriatic Seas; these studies were mainly focused on investigation of weathering fluxes in carbonate watersheds and on sources of carbon to rivers (Kanduč et al., 2007; Szramek et al., 2007; Ogrinc et al., 2008; Kanduč et al., 2008).

2 Catchment characteristics

Kamniška Bistrica River is the left tributary of the River Sava, which is the major river in Slovenia (Fig. 1a). It emerges on the south foothills of Kamniško-Savinjske Alps at 630 m elevation (Table 1). The river drains an area of 380 km^2, is 32.8 km in length, and has an average discharge of 15.4 $m^3 s^{-1}$ at its confluence with the River Sava. The average discharge measured during this study was 0.7 to 12.1 $m^3 s^{-1}$. According to discharge regimes of all rivers and streams in Slovenia, 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 tributaries of the Kamniška Bistrica are the Črna and Nevljica at the left and Pšata as the major tributary from the right. In the upper reaches, from the headwater spring to Stahovica (Fig. 1a), the Kamniška Bistrica River is a typical Alpine River in an incised alpine valley. Kamniška Bistrica River changes over a short distance (6.8 km downstream) from a clean Alpine River to a polluted river at the confluence with the tributary Črna, which carries sediments and waste waters from the kaolin mine (Radinja et al., 1987). In the lower reaches, the river is strongly polluted due to animal waste from pig farms (Ihan) and industrial waste waters (chemical industry of explosives at Kamnik, pulp and paper industry at Količevo and pitch, paintwork industry at Domžale) (Fig. 1a). The upper part of the Kamniška Bistrica watershed is composed of broad-leaf, coniferous, and mixed forest and grasslands land cover, while in central and lower part of the watershed urban industrial and agricultural (pig farms) land use is dominant (Fig. 1b). Tributaries of the River Kamniška Bistrica collect water mainly from forested areas with C3 type plants (Kanduč, 2006). The prevailing forest communities in the River Kamniška Bistrica watershed are different types of European beech (*Fagus sylvatica* L.) forests depending on climatic and edaphic conditions, altitude and relief. In higher altitudes (900 to 1500 m), European beech is associated with Norway spruce (*Picea abies* L.) Karst, silver fir (*Abies alba* P. Mill.) and European larch (*Larix decidua* P. Mill.) (Marinček and Čarni, 2002). Riparian vegetation is comprised of a thin belt of herbaceous plants and willow (*Salix* spp.) communities that grade into communities with alder (*Alnus* sp.). Denser stands of hydrophytes (*Callitriche* spp., *Potamogeton nodosus* Poir., *Ranunculus* subg. *Batrachium* (DC.) A. Gray, mosses and macroscopic algae can be found only in lowland slow-flowing watercourses, where silt and fine-grained substratum are deposited (Jogan et al., 2004). The isotopic values of C3 plants in the River Sava watershed are fully described in Kanduč et al. (2007).

The upper part of the Kamniška Bistrica River is underlain by massive and stratified limestone and dolomite of middle and upper Triassic age (Fig. 1c; simplified geologic map). The middle reaches of the river is underlain by marlstone and limestone of Miocene age (Buser, 1987). The lower reaches of the Kamniška Bistrica River, 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 and Quaternary gravel. The Kamniška Bistrica River 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., 2008). The quality of the river water is also important due to its recharge of the northeastern part of the Ljubljana field ($\sim 800\,\mathrm{mm\,yr^{-1}}$; Jamnik et al., 2001), which is the largest aquifer in Slovenia for domestic water supply, and is highly vulnerable to contamination (Vižintin et al., 2009).

3 Sampling protocols and field measurements

Surface water sampling locations were selected based on their relationship to confluences of the major and minor streams, typically sampled before and after the confluence (Fig. 2b, c). Sampling was performed at 16 locations (Tables 1–4, Figs. 2b, c) in different seasons (November 2010 = autumn, February 2011 = winter, May 2011 = spring, August 2011 = summer), according to the discharge regimes (Hrvatin, 1998) of the Kamniška Bistrica (7 sampling locations) and its tributaries (9 sampling locations). Temperature, conductivity, dissolved oxygen (DO), and pH were measured 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 a reproducibility of ±0.02 pH unit.

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

Samples for stable carbon isotope analysis of particulate organic carbon ($\delta^{13}C_{POC}$), particulate nitrogen ($\delta^{15}N$), and suspended matter were collected in LDPE bottles (Schuster and Reddy, 2001). In addition, carbonate rocks ($n = 12$) of Triassic age forming the landscape of the Kamniška Bistrica watershed were sampled from outcrops, as were gravels in the river channel for stable carbon analyses ($\delta^{13}C_{ca}$). Four liters of water was collected in plastic bottles at the source of the river and one liter of water at the mouth of the river for $\delta^{15}N_{NO_3^-}$ analysis.

4 Laboratory analyses

Total alkalinity was measured by Gran titration (Gieskes, 1974) with a precision of ±1 % within 24 h of sample collection. Major ion chemistry was analyzed in the Hydrology and Water Resources Department at the University of Arizona (UA). Major cations (Ca, Mg, Na, K, Sr, Si) were analysed (precision ±2 %) with a Perkin-Elmer Optima 5100DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), and major anions (Cl, SO_4^{2-} and NO_3^-) were analysed (precision ±2 %) with a Dionex Ion Chromatograph (IC) Model 3000, using an AS23 analytical column. The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined with an Isoprime GV mass spectrometer. Phosphoric acid (100 %) was added (100–200 µl) to a septum tube and then purged with pure He. The water sample (1 ml) was then injected into the septum tube and CO_2 was directly measured from the headspace after extraction (modified after Kanduč et al., 2007). A standard solution of Na_2CO_3 (Carlo Erba) with a known $\delta^{13}C_{DIC}$ value of $-10.8‰\pm0.2‰$ was used to control $\delta^{13}C_{DIC}$ measurements (Kanduč et al., 2007).

Analysis of ^{18}O and D/H isotope ratios in liquid water samples were measured simultaneously using a Laser Water Isotope Analyzer V2 (Los Gatos Research, Inc., Mountain View, CA, USA). Sample isotope ratios are standardized using a range of working standards that have been calibrated against IAEA standard reference materials (VSMOW, GISP, and SLAP). Precision for water samples at natural abundance is typically $\leq 0.3‰$ for ^{18}O and $\leq 0.8‰$ for D/H. Final $^{18}O/^{16}O$ and D/H values are reported relative to VSMOW.

To determine mass of suspended matter a 0.7 µm pore size (GF/F) filters were used, which comprises CPOM (coarse particulate organic material, > 63 µm) and FPOM (fine particulate organic material, 63–0.1 µm) (Devol and Hedges, 2001). Filters were ignited before sampling at 480 °C with the aim of eliminating impurities, and then dried and weighed after filtering of suspended matter. 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. After sampling, one liter of the water sample was filtered through a Whatman GF/F glass fibre (0.7 µm). Filters were treated with 1 M HCl to remove carbonate material and then they were dried at 60 °C and stored until analyses. Approximately 1 mg of POM was scraped from the filter into a tin capsule. Approximately 10 mg of POM was scrapped from the filter (with no acid pre-treatment) for nitrogen analysis. The isotopic composition of nitrogen and carbon was determined after combustion of the capsules in a hot furnace (temperature 1000 °C). Generated products were reduced in a Cu tube (600 °C), where excess O_2 was absorbed. H_2O was trapped on a drying column composed of $MgClO_4$. Gases were separated on a chromatographic column and ionized. NBS 22 (oil) and IAEA N-1 (ammonium sulphate) reference materials were used to relate the analytical results to the VPDB and AIR standards.

Carbonate rocks ($n = 12$) were first ground to a powder in an agate mortar and then 2 mg of sample was acidified with H_3PO_4 and then transformed to CO_2. The released CO_2 was then measured with a Europa Scientific 20-20 continuous flow IRMS ANCA-TG preparation module. NBS 18 and NBS 19 were used as reference materials. All stable isotope results for carbon are expressed in the conventional delta (δ) notation, defined as per mil (‰) deviation from reference standard VPDB. Overall analytical error was ±0.2 ‰ for $\delta^{13}C_{DIC}$, $\delta^{13}C_{POC}$ and $\delta^{13}C_{ca}$.

Thermodynamic computations were used to evaluate chemical speciation with the carbonate system (e.g. partial pressures of CO_2 (pCO_2), saturation states of calcite and dolomite ($SI_{calcite}$, $SI_{dolomite}$) using pH, alkalinity, and temperature as inputs to the PHREEQC speciation program (Parkhurst and Appelo, 1999).

For the determination of the isotopic composition of nitrate, $\delta^{15}N_{NO_3^-}$, filtered samples (0.45 µm) were prepared according to a method of Silva et al. (2000) and modified by Fukada et al. (2003). First samples were passed through the cation exchange resin (BIO-RAD AG 50W-X8, Hydrogen Form, USA) in order to remove dissolved organic material. Afterwards, nitrate was isolated from the sample by passing the sample through the anion exchange resin (BIO-RAD AG2-X8, Chloride Form, USA). The sample was then eluted from the anion exchange columns with 30 ml of 3 M HCl. The acid eluant was neutralized with Ag_2O, filtered and dried to obtain solid $AgNO_3$. Dried samples were put into silver capsules together with brown sugar (1 : 2.5 ratio) and measured on a Europa Scientific 20-20 continuous flow IRMS ANCA-SL preparation module. Results are expressed in the conventional delta (δ) notation, defined as per mil (‰) deviation from reference standard N_{air} with an estimated analytical error of ±0.3 ‰.

Principal component analysis (PCA) based on a covariance matrix was used to examine the variation in measured geochemical parameters (pH, conductivity, alkalinity, Ca, Mg, Na, K, Si, SO_4, Cl, NO_3, $\delta^{13}C_{DIC}$) for Kamniška Bistrica River as well as tributaries collected in four different seasons (autumn 2010, winter 2011, spring 2011 and summer 2011). The CANOCO software package (ter Braak and Šmilauer, 2002) was used for the PCA analysis.

5 Results

5.1 Geochemistry of Kamniška Bistrica River

The major chemical composition of the Kamniška Bistrica River and its tributaries was dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Concentrations varied seasonally according to discharge (Tables S1–S4, Supplement), with higher concentrations observed in late summer at lower discharge and lower concentrations during spring snow melt and the rainy season due to dilution. The temperature (T) of surface water, pH and conductivity ranged from 1.7 to 26.6 °C, 7.1 to 8.8 and 160.7 to 497.4 µS cm^{-1}, respectively (Tables S1–S4, Supplement). Dissolved oxygen saturation (DO) varied seasonally from 59.6 to 76.8 % in the winter and 68 to 140 % in the spring (Tables S1–S4, Supplement). Calculation of speciation of carbon species performed by program PHREEQC for Windows in water at certain pH, T and alkalinity as input data identified HCO_3^- as the most abundant dissolved carbonate species in river water, contributing about 90 % of the DIC. The upper alpine headwater catchments of the Kamniška Bistrica River have thin soils developed on carbonate bedrock (Fig. 1c). These headwater catchments tend to have lower and more constant alkalinity values compared to sites further downstream where soils are deeper (Fig. 1c). Alkalinity concentrations ranged from 1.6 to 5.6 mM in main channel and from 2.6 to 5.5 mM in tributaries (Table 1–4). The overall variation of TDS (total dissolved solids) along Kamniška Bistrica River was similar in all sampling campaigns and varied from 0.1 to 23.8 mg l^{-1} in main channel and from 1.0 to 84.4 mg l^{-1} in tributaries (Tables S1–S4, Supplement).

Calculated CO_2 partial pressures (pCO_2) varied from near atmospheric (360 ppmv) up to 25 fold supersaturated (Tables S1–S4, Supplement). In late summer all sampling locations in the Sava River watershed were above equilibrium with atmospheric

CO_2, likely due to the higher degradation of organic matter in the river at the end of the summer season (Drever et al., 1983). In the winter season soil leaching processes as well as degradation of organic matter are limited, so most probably higher $p\mathrm{CO}_2$ pressures should be attributed to the greater solubility of CO_2 at low temperatures (Atkins, 1994). The calcite saturation index ($\mathrm{SI}_{\mathrm{calcite}} = \log([\mathrm{Ca}^{2+}]\cdot[\mathrm{CO}_3^{2-}])/K_{\mathrm{calcite}}$), where K_{calcite} is the solubility product of calcite and dolomite, was generally well above equilibrium ($\mathrm{SI}_{\mathrm{calcite}} = 0$, $\mathrm{SI}_{\mathrm{dolomite}} = 0$), indicating that calcite and dolomite was supersaturated and precipitation was thermodynamically favoured along most of the course of the Kamniška Bistrica River (Tables S1–S4, Supplement).

5.2 Suspended matter

The mass of total suspended matter in the Kamniška Bistrica watershed varied from 0.1 to 23.8 $\mathrm{mg\,l^{-1}}$ in the main channel. According to Meybeck (1981), the river falls into the lower classes of rivers worldwide in terms of sediment loads (first class: 0 to 15 $\mathrm{mg\,l^{-1}}$; second class: 15 to 50 $\mathrm{mg\,l^{-1}}$; Tables S1–S4, Supplement). The mass of suspended matter is related to slope denudation processes and rises during the rainy season (Summerfield, 1991) in areas with less vegetation, higher soil thickness and steeper slopes in the watershed composed of clastic rocks (lower reaches of the Kamniška Bistrica River).

5.3 Carbon isotopes

Carbon isotope values of dissolved inorganic carbon (DIC) can elucidate the contributions of organic matter decomposition carbonate mineral dissolution and exchange with atmospheric CO_2 since rivers are regarded as open systems (Clark and Fritz, 1997). The $\delta^{13}C_{\mathrm{DIC}}$ value of the main channel of the river varied seasonally from −10.7 to −3.6 ‰ in autumn 2010, −10.7 to −3.2 ‰ in winter 2011, −9.6 to −2.7 ‰ in spring 2011, and −10.9 to −3.1 ‰ in summer 2011. $\delta^{13}C_{\mathrm{DIC}}$ values of the tributaries ranged from −12.7 to −8.8 ‰ in autumn 2010, −11.4 to −8.0 ‰ in winter 2011, −11.0 to

−6.9 ‰ in spring 2011, and −11.6 to −8.7 ‰ in summer 2011. More negative $\delta^{13}C_{DIC}$ values are attributed to high flow periods and dilution due to precipitation. More negative $\delta^{13}C_{DIC}$ values are observed in the upper reaches of the Kamniška Bistrica River (location 1–5), while higher values are observed in central and lower reaches of the Kamniška Bistrica River (locations 5–16) (Tables S1–S4, Supplement). The average $\delta^{13}C$ value of Mesozoic carbonate rocks ($\delta^{13}C_{CaCO3}$) in the hinterland is 2.4 ‰.

The $\delta^{13}C$ value of particulate organic carbon ($\delta^{13}C_{POC}$) in the main channel of the Kamniška Bistrica River varies from −28.6 to −25.4 ‰, and from −29.9 to −25.2 ‰ in the tributaries of the Kamniška Bistrica. Suspended organic matter was mostly derived from soil and plant material coming from the recharge area and drained through fissures, channels and pores to the spring (Ittekot, 1988).

5.4 Oxygen/hydrogen and nitrogen isotopes in river water

$\delta^{18}O$ values of the main channel ranged from −10.7 to −8.8 ‰, and from −9.8 to −8.0 ‰ in tributaries of the Kamniška Bistrica River. δD values were measured only for the main locations and tributaries in the watershed (Tables S1–S4, Supplement).

Nitrogen isotopes of nitrate were measured at locations selected from land cover/use map to obtain the widest range of variability in $\delta^{15}N_{NO_3}$ values. $\delta^{15}N_{NO_3}$ values of surface water ranged from −1.9 to +8.0 ‰ in autumn 2010, −5.2 to 4.5 ‰ in winter 2011, and −0.9 to 9.8 ‰ in spring 2011, indicating different sources of nitrate (Tables S1–S4, Supplement). $\delta^{15}N$ values of particulate nitrogen ranged from 0.9 to 5.9 ‰, within the range of soil N (Kanduč et al., 2008).

6 Discussion

6.1 Chemical composition of surface water

The major solute composition of the River Kamniška Bistrica and its tributaries was dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Concentrations varied seasonally according to discharge (Tables S1–S4, Supplement), with higher concentrations observed in summer and winter at lower discharge and lower concentrations during the spring and autumn high discharge periods. 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 S1–S4, Supplement). Most of the water samples have a 2 : 1 mole ratio of HCO_3^- to $Ca^{2+} + Mg^{2+}$ (Fig. 2a) following the reactions:

$$\text{Calcite:} \qquad CaCO_3 + CO_{2(g)} + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

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

Differences in HCO_3^- concentrations in watersheds composed mostly of carbonates are typically 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 (Kanduč et al., 2008). Weathering rates increase in thicker soils (e.g. lower part of the Kamniška Bistrica watershed, underlain by clastics rocks) due to the higher weathering capacity of clastics rocks in comparison to carbonate rocks (Kanduč et al., 2007). The DIC concentrations in the Kamniška River system (> 1 mM) exceed the average world river concentration of 0.9 mM (Livingstone, 1963) and also lie above concentration in European rivers of 1.5 mM (Kempe et al., 1991).

$Ca^{2+} + Mg^{2+}$ and alkalinity concentrations ranging from 0.87 to 2.66 mM, and 1.6 to 5.6 mM, respectively (Fig. 2a) in the Kamniška Bistrica watershed indicate that dissolution of carbonates alone dominants the solute budget in the upper reaches of the River Kamniška Bistrica (location 1), which coincides with the bedrock lithology of the watershed (Fig. 1c). Deviations from the 2 : 1 $Ca^{2+} + Mg^{2+} : HCO_3^-$ relationship is probably due to weathering of other minerals like anorthite and albite, which also contribute to alkalinity in the watershed.

Mg^{2+} versus Ca^{2+} relations indicates the relative contribution of calcite to carbonate weathering intensity in the Kamniška Bistrica watershed. Most of the samples indicate that weathering of calcite is dominant over the entire Kamniška Bistrica River, especially in the upper and central reaches (Fig. 2b). A Mg^{2+}/Ca^{2+} ratio around 0.33, which is typical for weathering of calcite with magnesium, is characteristic along entire length of the river. These Mg^{2+}/Ca^{2+} ratio of 0.33 is also characteristic for rivers comprising Danube watershed e.g. Sava river, Tisa River, Ilz River, Inn River (Kanduč et al., 2007; Szramek et al., 2007). In contrast, rivers comprising St. Lawrence watershed have ratio $Mg^{2+}/Ca^{2+} > 0.33$ (Szramek et al., 2007).

Most of the researched rivers in Slovenia (Szramek et al., 2007; Kanduč et al., 2007, 2008) have $Ca^{2+} + Mg^{2+} : HCO_3^-$ ratio 2 : 1 indicating that geological composition (carbonates prevail) controls geochemical composition of river waters. Due to high relief HCO_3^- weathering capacity of Kamniška Bistrica River is estimated to be 150 meq km^{-2} s^{-1} (Kanduč et al., 2008), higher in Alpine rivers (up to 320 meq km^{-2} s^{-1}) in comparison to Dinaric karst rivers, which comprise Danube River watershed (Szramek et al., 2007). On contrast, rivers of St. Lawrence watershed also located in carbonate-bearing temperate zone have much lower HCO_3^- weathering capacity (up to 100 meq km^{-2} s^{-1}). The lowest weathering capacity is in river watersheds composed of silicates up to 20 meq km^{-2} s^{-1} (Szramek et al., 2007).

6.2 Characterization of suspended matter and fluxes of suspended and dissolved carbon species in the Kamniška Bistrica River System

The highest calculated $p\text{CO}_2$ (up to 8912 ppm) values were observed during the summer season, with the lowest values (up to 177.8 ppm) in the spring (Fig. 3a). $p\text{CO}_2$ concentrations in river systems mainly depend on thermodynamic conditions (e.g. temperature, pH and alkalinity) and do not include mixing conditions (turbulent flow). Most of the samples in the watershed were supersaturated with respect to calcite/dolomite according to thermodynamic conditions (Fig. 3b), except for upstream locations (locations 1, 2, 4 and 5).

The evasion of CO_2 from the Kamniška Bistrica River to the atmosphere $[\mathrm{DIC}]_{\mathrm{ex}}$ can be estimated based on the thin-film diffusive gas exchange model (Broecker, 1974):

$$[\mathrm{DIC}]_{\mathrm{ex}} = \frac{D}{z} \cdot ([\mathrm{CO}_2]_{\mathrm{eq}} - [\mathrm{CO}_2]) \qquad (1)$$

where D is the CO_2 diffusion coefficient in water of $1.26 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at a temperature of 10 °C and $1.67 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at a temperature of 20 °C (Jähne et al., 1987), z is the empirical thickness of the liquid layer (cm), $[\mathrm{CO}_2]_{\mathrm{eq}}$ and $[\mathrm{CO}_2]$ are the dissolved CO_2 concentrations at equilibrium with the atmosphere and with the studied water ($\mathrm{mol\,cm^{-3}}$), 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. Using a mean wind speed of $4\,\mathrm{m\,s^{-1}}$ in both sampling seasons in the Kamniška Bistrica watershed (ARSO 2010–2011), D/z was estimated to be $8\,\mathrm{cm\,h^{-1}}$ at low turbulence conditions, $28\,\mathrm{cm\,h^{-1}}$ at moderate turbulence conditions and $115\,\mathrm{cm\,h^{-1}}$ at high turbulence conditions.

The theoretical CO_2 diffusive evasion rates at the mouth of the Kamniška Bistrica River, according to Eq. (1), ranged between 3.0×10^{-7} to $1.1 \times 10^{-6}\,\mathrm{mol\,cm^{-2}\,h^{-1}}$ in autumn 2010, 1.8×10^{-7} to $6.2 \times 10^{-7}\,\mathrm{mol\,cm^{-2}\,h^{-1}}$ in winter 2011, 4.5×10^{-8} to $1.6 \times 10^{-7}\,\mathrm{mol\,cm^{-2}\,h^{-1}}$ in spring 2011, and 4.2×10^{-8} to $2.2 \times 10^{-7}\,\mathrm{mol\,cm^{-2}\,h^{-1}}$ in summer 2011, respectively. Taking into consideration the river surface area of $0.8\,\mathrm{km^2}$ (a mean width of 20 m and length of a 40 km), then the average estimated total diffusive loss of inorganic carbon in different sampling seasons would range from $7.4 \times 10^4\,\mathrm{mol\,day^{-1}}$ in autumn 2010, 4.4×10^4 in winter 2011, $1.1 \times 10^4\,\mathrm{mol\,day^{-1}}$ in spring 2011, and 8.6×10^4 mol day^{-1} in summer 2011. The Kamniška Bistrica River showed seasonal patterns of CO_2 diffusive evasion that are similar to the Sava and Idrijca Rivers in Slovenia (Kanduč et al., 2007).

In accordance with mean long term discharges reported by Slovenian Environment Agency (ARSO), the DIC, DOC, POC and evasion CO_2 fluxes were calculated. Seasonal concentrations of DOC in Kamniška Bistrica (location 16) ranged from 1.66 to 2.1 mg l^{-1} and POC from 5 to 25 % (Kanduč, 2006). The DIC fluxes ranged from 5.8×10^8 mol yr^{-1} in autumn to 3.2×10^9 mol yr^{-1} in spring, with an average DIC flux of 1.89×10^9 mol yr^{-1}. The DOC fluxes ranged from 2.38×10^7 in autumn to 1.29×10^8 mol yr^{-1} in spring, while the average DOC flux was 7.65×10^7 mol , yr^{-1}. According to the POC concentration in the Sava River (Kanduč et al., 2007) of 8.39 % and concentrations of total suspended solids (m_{TSS}) from ARSO (2006–2007) data, which vary from 3.14 mg l^{-1} in autumn to 60.7 mg l^{-1} in spring, the calculated POC flux was 3.63×10^7 in autumn and 3.82×10^9 in spring, with an average POC flux of 1.93×10^9 mol yr^{-1}. The evasion CO_2 flux, calculated according to Eq. (2), ranged from 7.04×10^7 mol yr^{-1} in autumn and only 9.17×10^4 mol yr^{-1} in spring, with an average CO_2 evasion flux of 3.52×10^7 mol yr^{-1}. Thus, in the Kamniška Bistrica watershed the ratios of the percentage of DIC : DOC : POC : pCO_2 flux is 73 % : 9.4 % : 15.4 % : 2.2 %.

Our estimates of carbon fluxes indicated the dominance of DIC in river system and is typical, the estimated proportions of DIC : DOC : POC fluxes (not considering pCO_2 flux) were estimated for River Sava 89 % : 9 % : 2 % (Ogrinc et al., 2008), which is comparable Yangtze River (DIC : DOC : POC = 71 % : 4 % : 11 %, Wu et al., 2007) and the Rhone River (DIC : DOC : POC = 82 % : 6 % : 8 %; Sempere et al., 2000), but are distinct from the mean proportions for world rivers draining to the oceans (DIC : DOC : POC = 45 % : 37 % : 18 %; Meybeck, 1993).

6.3 Sources of dissolved inorganic carbon (DIC) in surface water inferred from isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and mass balances calculation

$\delta^{13}C_{DIC}$ values can help to decipher the contributions of organic matter decomposition, carbonate mineral dissolution, equilibration with atmospheric CO_2 to DIC, and in-stream biological processes in the Kamniška Bistrica watershed. Fig. 4 shows $\delta^{13}C_{DIC}$ versus distance from the source for the river water samples in different sampling seasons. More negative $\delta^{13}C_{DIC}$ values were observed during autumn sampling season, probably due to more intense degradation of organic matter in stream and leaching from terrestrial into river system, while more positive $\delta^{13}C_{DIC}$ values are obtained during winter sampling season due to limited leaching and erosion from terrestrial system and consequently dissolution of carbonates (Fig. 4). An average $\delta^{13}C_{POC}$ value of −26.6 ‰ (Kanduč et al., 2007) was assumed to represent the isotopic composition of DIC derived from in-stream respiration. Open system equilibration of DIC with CO_2 enriches DIC in ^{13}C by about 9 ‰ (Mook et al., 1974), which corresponds to the value of −17.6 ‰ shown in Fig. 4. Nonequilibrium dissolution of carbonates with one part of DIC originating from soil CO_2 (−26.6 ‰), and the other from carbonates with an average $\delta^{13}C_{Ca}$ of +2.6 ‰ produces an intermediate $\delta^{13}C_{DIC}$ value of −12.0 ‰ (Fig. 4). Given the isotopic composition of atmospheric CO_2 (−7.8 ‰, Levin et al., 1987) and the equilibration fractionation with DIC of +9 ‰, DIC in equilibrium with the atmosphere should have a $\delta^{13}C_{DIC}$ of about +1 ‰ (Fig. 4). $\delta^{13}C$ values in the Kamniška Bistrica watershed indicate that in upper reaches of the river dissolution of carbonates dominant (from sampling location 1–6), while in the central reaches values approach open system equilibration with soil CO_2 and dissolution of carbonates, and in lower reaches values approach the open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with a $\delta^{13}C_{CO2}$ value of −26.6 ‰. Mineralization of organic matter is the dominant source for $\delta^{13}C_{DIC}$ in downstream locations where the greater soil thickness enables accumulation of soil CO_2 due to the greater influence of weathering of clastic rocks, which results in more negative $\delta^{13}C_{DIC}$ values (Fig. 4). $\delta^{13}C_{DIC}$ was investigated in several temperate European, North American river systems and Australian (Yang et al., 1996; Aucour et al., 1999; Hélie et al., 2002; Pawellek et al., 2002; Barth et al., 2003; Wachniew, 2006; Cartwright, 2010). $\delta^{13}C_{DIC}$ is mostly controlled by geological composition of headwaters, more positive $\delta^{13}C_{DIC}$ value is observed in carbonate bearing catchments, while exchange with atmospheric CO_2 (also cause enrichment with ^{13}C) is more pronounced in catchments composed of impermeable rocks (Kanduč et al., 2007).

A simple isotopic mass balance calculation was performed in order to quantify different sources of DIC at the Kamniška Bistrica River mouth (location 16), 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:

$$DIC_{RI} = DIC_{tri} - DIC_{ex} + DIC_{org} + DIC_{ca} \quad (2)$$

$$DIC_{RI} \cdot \delta^{13}C_{RI} = DIC_{tri} \cdot \delta^{13}C_{tri} - DIC_{ex} \cdot \delta^{13}C_{ex} + DIC_{org} \cdot \delta^{13}C_{POC} + DIC_{ca} \cdot \delta^{13}C_{Ca} \quad (3)$$

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 (Supplement) and water discharge (Supplement), 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. (1), was taken into account. In Eqs. (2) and (3) the minus sign indicates outgassing of CO_2. 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 +1.9 ‰ in the autumn

2010, +2.5 ‰ in summer 2011, +1.5 ‰ in spring 2011 and +0.41 ‰ in the summer 2011, considering atmospheric CO_2 as the ultimate source of CO_2 in the Kamniška Bistrica drainage system. For $\delta^{13}C_{POC}$ and $\delta^{13}C_{Ca}$ average values of −26.6 ‰ and +2.6 ‰ 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 1. The calculated contributions to the average DIC budget from $DIC_{tri} : DIC_{ex} : DIC_{org} : DIC_{ca}$ at the River Kamniška Bistrica mouth were 33 : −1.9 : 27.5 : 41.5 % in autumn 2010, 67.2 : −4.1 : 11.5 : 25.4 % in winter 2011, 69.6 : −2.3 : 1.4 : 31.2 % in spring 2011 and 84.9 : −22.2 : −0.6 : 37.8 % in summer 2011. In all sampling seasons, the most important biogeochemical process affecting stream water carbon budgets is weathering of carbonates (reflected in the more positive $\delta^{13}C_{DIC}$ values), while degradation of organic matter is more important in autumn. Exchange with atmospheric CO_2 was minimal (around 0 %) during all sampling seasons, except in the summer, when degassing reached 22.2 %. Mass balances for riverine inorganic carbon in River Sava in Slovenia suggest that carbonate dissolution contributes up to 26 %, degradation of organic matter ~17 % and exchange with atmospheric CO_2 up to 5 % (Kanduč et al., 2007) , which is comparable to Kamniška Bistrica River.

Major factor controlling water chemistry of Kamniška Bistrica surface water is geological composition since 59.8 % of variance is explained on first axes and 9.9 % on second axes (Fig. 5). The parameters that explain 59.8 % of variance on first axes are alkalinity, conductivity, Ca^{2+}, Na^+, K^+, SO_4^{2-} and Cl^- and are controlled by geological composition of the watershed. According to parameters (Ca^{2+}, Mg^{2+}, Na^+, K^+, Si, SO_4^{2-}, Cl^-, NO_3^-, $\delta^{13}C_{DIC}$), which were used as input data for PCA statistical analyses (Fig. 5) locations could be separated to upstream – non-polluted locations with lower alkalinity, conductivity (sampling locations from 1–7) and higher $\delta^{13}C_{DIC}$ and downstream locations with higher alkalinity, conductivity, and lower $\delta^{13}C_{DIC}$ (sampling locations from 8–16), the gradient is most obvious in the main channel of the river, while the gradient is less obvious at tributaries (Fig. 5).

6.4 Isotopic composition of oxygen/hydrogen in the Kamniška Bistrica watershed

δ^{18}O values in the Kamniška Bistrica River watershed at the sampling locations (Supplement) dependent on several factors: precipitation, evaporation, evapotranspiration, infiltration and equilibration with run-off (Yee et al., 1990). The δ^{18}O values of the river varied seasonally from −10.3 to −8.8 ‰ in autumn 2010, −10.4 to −8.8 ‰ in winter 2011, −10.7 to −9.3 ‰ in spring 2011, and −10.0 to −9.1 ‰ in summer 2011. More positive δ^{18}O values (−9.8 to −8.0 ‰) were observed in the tributaries compared to the main channel; the Kamniška Bistrica River originates from a spring in the Kamniško-Savinjske Alps, recharged at an altitude of approximately 1606 m a.s.l. (Kanduč et al., 2012). More negative δ^{18}O values in all sampling seasons (Fig. 6a) are due to snow melt inputs from the high mountains. All river water samples have δD and $\delta^{18}O_{H_2O}$ values that fall between the local meteoric water line (LMWL) and the global meteoric water line (GMWL) (Fig. 6b), indicating a meteoric water origin with little indication of evaporation or water-rock reaction. Similar all river samples of Garonne River originating in Pyrenees Mountains plot close to the global and local meteoric-water lines, indicating only minor impact of evaporation (Schulte et al., 2011).

δ^{18}O of precipitation at Kamniška Bistrica spring (location 1) for different seasons (June 2010, August 2010 and November 2010) were calculated according to multiple regression model (Kanduč et al., 2012) and ranged from −9.2 to −10.2 ‰ similar to measured values in Kamniška Bistrica river water (Fig. 6b). Seasonal variation in δ^{18}O values in the Kamniška Bistrica watershed results from different origin of precipitation and isotopic enrichment of soil water from hillslopes contributing water to the stream. The altitude of the recharge area of the River Kamniška Bistrica from sampling point 6 (Fig. 1b) is below 1000 m a.s.l. along the central and lower reaches of the river (Radinja et al., 1987).

Kinetic effects during evaporation from soils recharging the watershed and in-stream also affect the δ^{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).

6.5 Origin of nitrogen in the Kamniška Bistrica watershed

The Kamniška Bistrica River is likely not subjected to denitrification since the water is oxic (DO from 59.6 to 140 %; Supplement). Most common reactive forms of dissolved inorganic nitrogen in aquatic ecosystems are ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-). These nitrogen species can come from atmospheric deposition, surface and groundwater runoff, dissolution of nitrogen-rich geological deposits, N_2 fixation by certain prokaryotes and biological degradation of organic matter or can be present in aquatic system anthropogenically (Camargo and Alonso, 2006 and the references therein). In the lower reaches of the Kamniška Bistrica River, surface runoff from animal manure and use of fertilizers (e.g. $NaNO_3$, KNO_3, NH_4) in agricultural areas (Fig. 1b) contributes nitrogen to the stream. Animal waste ammonium is mobilized in the subsurface by nitrification where conditions are oxidizing in stream water (Tables S1–S4, Supplement). Nitrate has low affinity for anion exchange sites in soils and aquifer matrices (Burt and Trudgill, 1993). Long-term monitoring performed on the Sava River by the Environmental Agency of Republic of Slovenia reports that NO_3^- comprises ~ 90 % of dissolved nitrogen (ammonium – NH_4^+, NO_3^-, NO_2^-), making it the most important nitrogen species in Slovenian rivers (EIONET, 2005). The highest concentration of NO_3^- (0.69 mmol l^{-1}; 42.8 mg l^{-1}) was measured in the Kamniška Bistrica watershed (sampling location 16) in autumn 2005 (Kanduč, 2006); such high concentrations were not observed during this study (0.28 mmol l^{-1}; 17.4 mg l^{-1} maximum; Fig. 7a). The threshold nitrate value for tap water, established by the World Health Organization (WHO) and the Environmental Protection Agency (EPA) is 10 mg l^{-1} N-NO_3^- (45.7 mg l^{-1}) (Beller et al., 2004).

Higher NO_3^- values (up to 42.8 mg l^{-1}) correspond to higher δ^{15}N values (up to 16.7 ‰), indicating a fertilizer source of nitrogen (organic fertilizers) at the mouth of Kamniška Bistrica River, consistent with Kanduč (2006).

Figure 7a shows concentration of nitrate versus distance from the source for the river water in different sampling seasons. Changes in concentrations of nitrate over the course of the river are due to change in land use/cover (Fig. 1b). From the source of the river (sampling point 1 to sampling point 8) to the central reaches, the watershed is dominated by forest and pastures and nitrate concentrations are relatively low (0.01–0.07 mM). The highest concentrations of nitrate (0.11–0.28 mM) were observed at tributaries in the central and lower reaches of the river (sampling locations 10 and 15). These tributaries also contribute higher concentration of nitrate in the lower reaches of the river (from location 11 to 16). Concentrations of nitrate in the main channel and tributaries change according to discharge and are higher during winter/summer seasons at low discharge conditions at locations 10 and 16 (Fig. 7a). The Kamniška Bistrica spring (location 1) is recharged from precipitation according to $\delta^{15}N_{NO_3^-}$ values, which autumn in the range of atmospheric nitrate (Fig. 7a; Freyer, 1991). The values of $\delta^{15}N_{NO_3^-}$ at location 8 (central reach of the river) are in the range of average values of most soils (Kendall, 1998) and plant materials in the Sava River watershed (Kanduč et al., 2007). The lower reaches of the river (location 16) and tributaries (location 15) have average $\delta^{15}N_{NO_3^-}$ values of organic fertilizers frequently used in Slovenia (Šturm and Lojen 2011) and indicate an anthropogenic (agricultural) influence (Fig. 7b). More positive $\delta^{15}N_{NO_3^-}$ (> 10 ‰) seem to be typical for the contribution of soil-manure nitrate, as has been documented in the Mississippi River Basin (Chang et al., 2002). The combination of high nitrate value and high δ^{15}N is consistent with production of nitrate by nitrification following ammonification and ammonia volatilization. This does imply that organic fertilizer is the main nitrate source. Other material rich in organic nitrogen are possible sources such as domestic wastewater and animal wastes.

7 Conclusions

The major solute composition of the Kamniška Bistrica River 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 Kamniška Bistrica system was supersaturated or near equilibrium (in the upper reaches of the river) with respect to calcite/dolomite in all sampling seasons. According to the calculated $p\mathrm{CO}_2$ values (from near atmospheric to 25 times supersaturated), the river is a source of CO_2 to the atmosphere during all sampling seasons. Seasonal variations of major chemical constituents and stable isotope composition are due to differences in discharge conditions: lower ion concentrations and $\delta^{13}C_{DIC}$ values were observed in autumn/spring, while higher ion concentrations and $\delta^{13}C_{DIC}$ values were observed in winter/summer. The observed differences in $p\mathrm{CO}_2$, alkalinity and $\delta^{13}C_{DIC}$ between the carbonate rock drainages versus mixed lithology watersheds (carbonate and clastic rocks) at central and lower flow of the and are the consequence of higher soil thickness. 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.

Average carbon fluxes of DIC, POC, DOC, and $p\mathrm{CO}_2$ in the Kamniška Bistrica watershed were estimated to be 1.89×10^9 mol yr^{-1}, 1.93×10^9 mol yr^{-1}, 7.7×10^7 mol yr^{-1}, and 3.52×10^7 mol yr^{-1}, respectively. $\delta^{13}C_{DIC}$ values change seasonally from −12.7 ‰ to −3.1 ‰ and reflect relations between terrestrial, riverine and atmospheric inputs and the following processes: (1) contributions from tributaries, (2) dissolution of carbonates, (3) degradation of organic material, and (4) equilibration with atmospheric CO_2. According to DIC and $\delta^{13}C$ mass calculations, it was calculated that the most important processes influencing DIC at the mouth of the river is dissolution of carbonate (up to 41.5 %), degradation of organic matter, (up to 27.5 %) and exchange with atmospheric CO_2 (up to 22.2 %). Equilibration of stream waters with atmospheric CO_2 is more pronounced during the summer season, probably due to lower solubility of gases under warmer conditions. DIC inputs of Kamniška Bistrica tributaries comprised up to 85 % from mass balance calculations and showed similar seasonal patterns, but with much wider ranges of measured chemical and isotopic compositions compared to the mainstream Kamniška Bistrica River, indicating that geochemistry of the main channel is controlled with tributaries. Kamniška Bistrica has high specific discharge and represents a river system where geological factors (i.e. carbonate dissolution) dominant stream biogeochemical processes.

Oxygen isotope values ranged from −10.7 ‰ to −8.8 ‰ in the main channel, with more positive δ values (−9.8 ‰ to −8.0 ‰) in the tributaries. Lower $\delta^{18}O_{H_2O}$ values were observed in spring months due to snow melt inputs, while in the winter months $\delta^{18}O_{H_2O}$ values were comparable to the late summer months.

It was shown in this study that $\delta^{15}N_{NO_3^-}$ is a useful tracer to identify nitrogen sources in Kamniška Bistrica watershed since this river is not oxygen limited and denitrification does not alter the nitrate-N source signatures. $\delta^{15}N$ values are related to land cover and use; the highest concentrations of nitrate (up to 0.17 mM), and most positive $\delta^{15}N$ values (9.8 ‰) were found at the mouth of the Kamniška Bistrica River in the spring and summer due to ferilizer inputs. Low nitrate concentrations (0.01 to 0.03 mM) with $\delta^{15}N$ values ranging from −5.2 to −0.9 ‰ were observed in the upper reaches of the watershed, characteristic of precipitation and soil-N inputs. Both measured parameters $\delta^{13}C_{DIC}$ and $\delta^{15}N$ of nitrate could be used as pollution tracers since more positive $\delta^{15}N$ values are well correlated with more negative $\delta^{13}C_{DIC}$ values at lower reaches of the river flow (sampling points 10, 15 and 16) indicating fertilizer inputs and more expressed degradation of organic matter.

Major ion chemistry and stable isotopes were shown to be useful tracers of biogeochemical processes and pollution sources in the Kamniška Bistrica watershed, providing a tool for management of water resources.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/9/9711/2012/ bgd-9-9711-2012-supplement.pdf.

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Table 1. Calculated dissolved inorganic carbon fluxes of different contributions of the River Kamniška Bistrica mouth: tributaries (DIC_{tri}), degradation of organic matter (DIC_{org}), CO_2 flux to atmosphere (DIC_{ex}), and dissolution of carbonates (DIC_{Ca}).

Sampling season	DIC_{ex} (mol day^{-1})	DIC_{org} (mol day^{-1})	DIC_{Ca} (mol day^{-1})	DIC_{trib} (mol day^{-1})	DIC_{RI} (mol day^{-1})
Autumn 2010	-7.43×10^4	1.07×10^6	1.61×10^6	1.28×10^6	3.89×10^6
Winter 2011	-4.41×10^4	1.24×10^5	2.75×10^5	7.27×10^5	1.08×10^6
Spring 2011	-1.12×10^4	7.05×10^3	1.54×10^5	3.43×10^5	4.92×10^5
Summer 2011	-5.44×10^4	-1.49×10^3	9.29×10^4	2.09×10^5	2.46×10^5

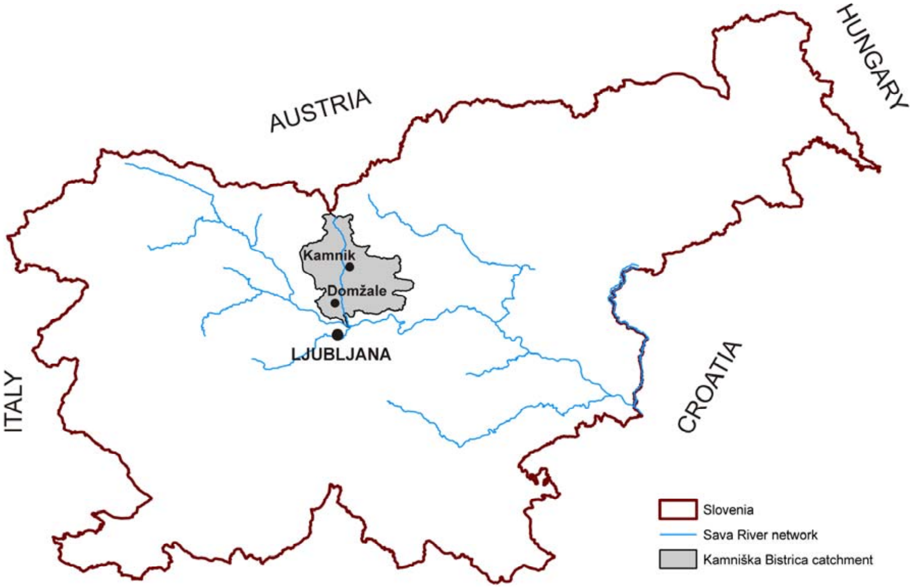

Fig. 1a. General map of the Kamniška River drainage basin indicating the location of Slovenia (SLO) and the Kamniška Bistrica study area, with a detailed location map of the numbered sampling sites in the Kamniška Bistrica watershed. Sampling sites are described in the Supplement.

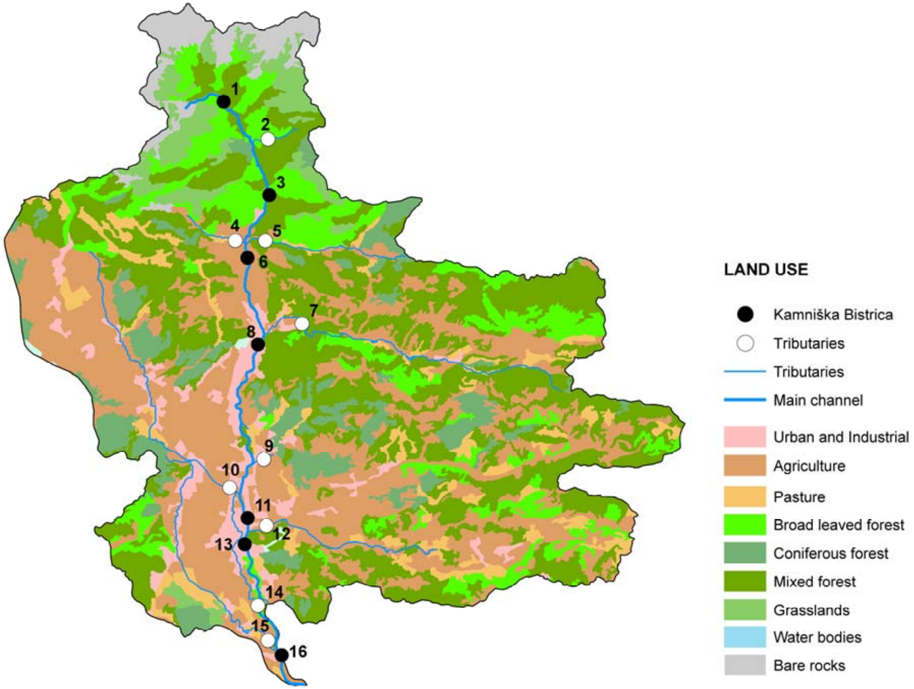

Fig. 1b. Land cover and land use of Kamniška Bistrica River watershed.

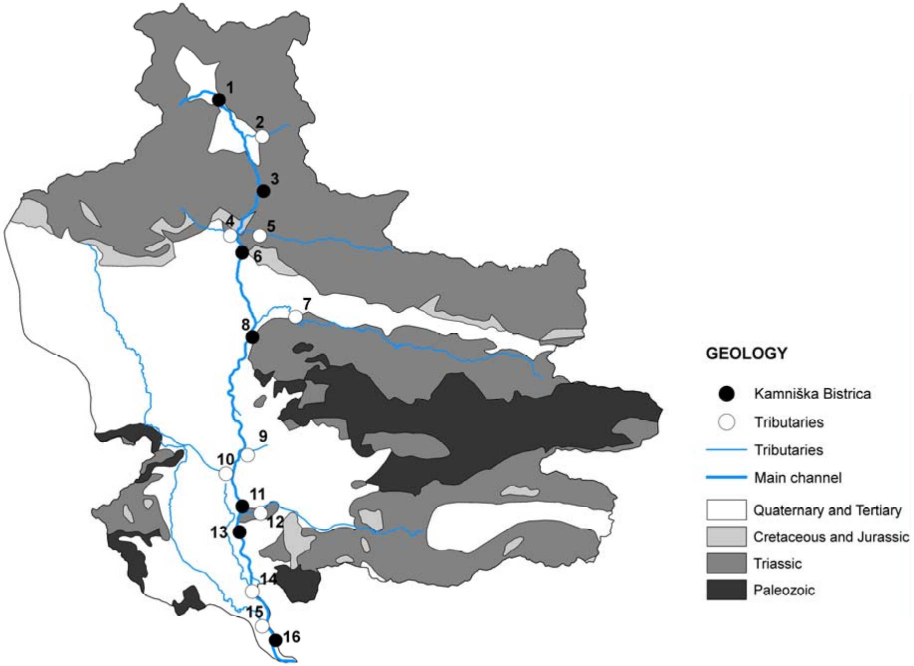

Fig. 1c. Geological composition of Kamniška Bistrica watershed (modified after Buser, 1987).

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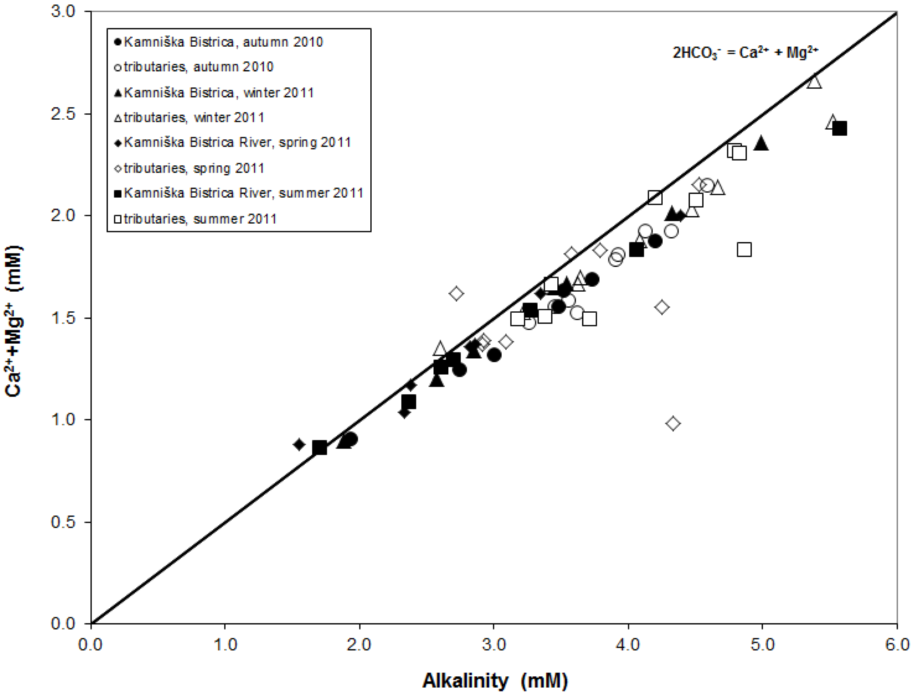

Fig. 2a. $Ca^{2+} + Mg^{2+}$ ratio versus alkalinity with line 1 : 2 indicting weathering of carbonates in the watershed in different sampling seasons (autumn 2010, winter 2011, spring 2011 and summer 2011).

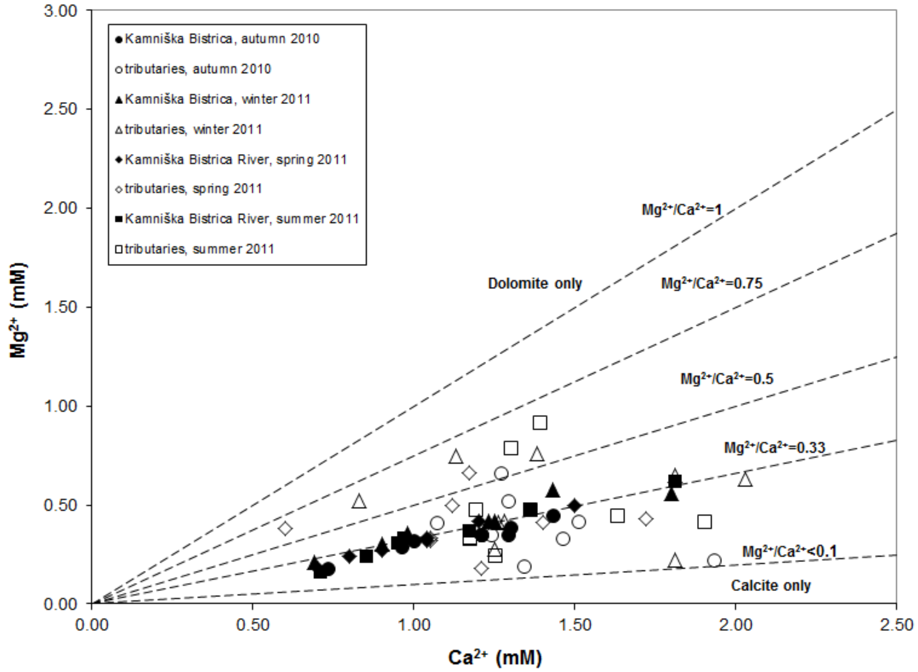

Fig. 2b. Mg^{2+} versus Ca^{2+} in Kamniška Bistrica River watershed, indicating the dominance of calcite in the watershed.

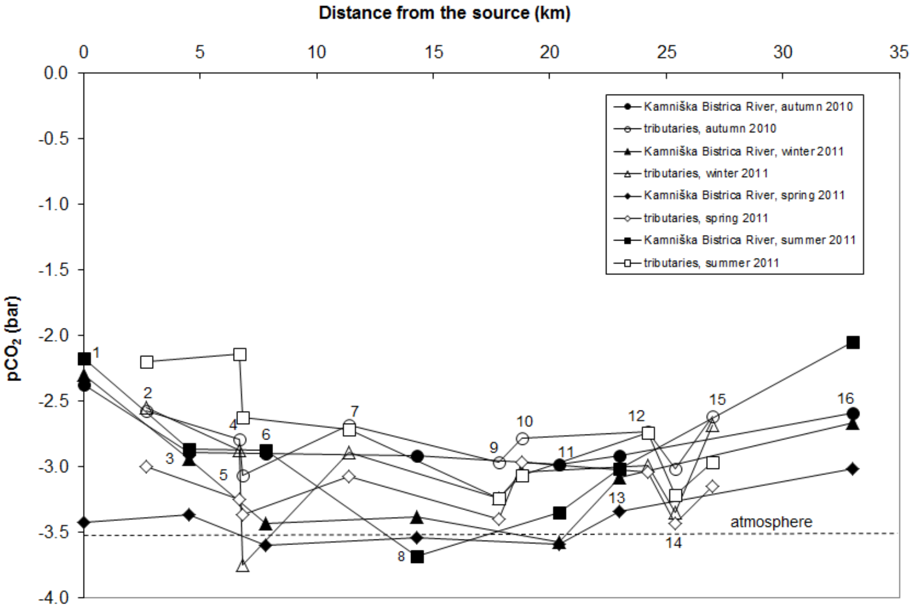

Fig. 3a. $p\mathrm{CO}_2$ versus distance from the source in Kamniška Bistrica River and its tributaries in different seasons (autumn 2010, winter 2011, spring 2011 and summer 2011).

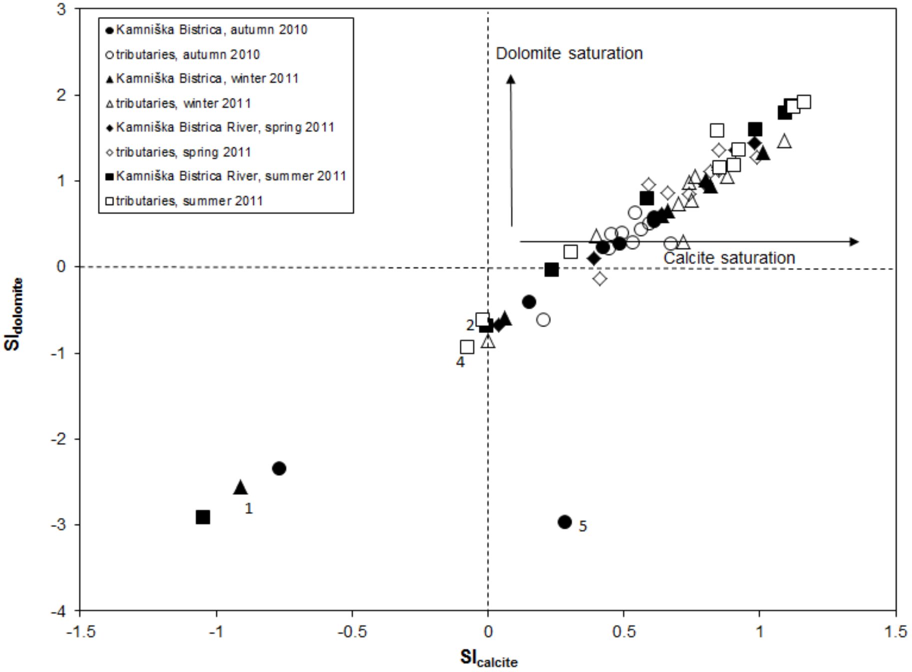

Fig. 3b. SI$_{calcite}$ versus SI$_{dolomite}$ in Kamniška Bistrica River and its tributaries in different seasons (autumn 2010, winter 2011, spring 2011 and summer 2011).

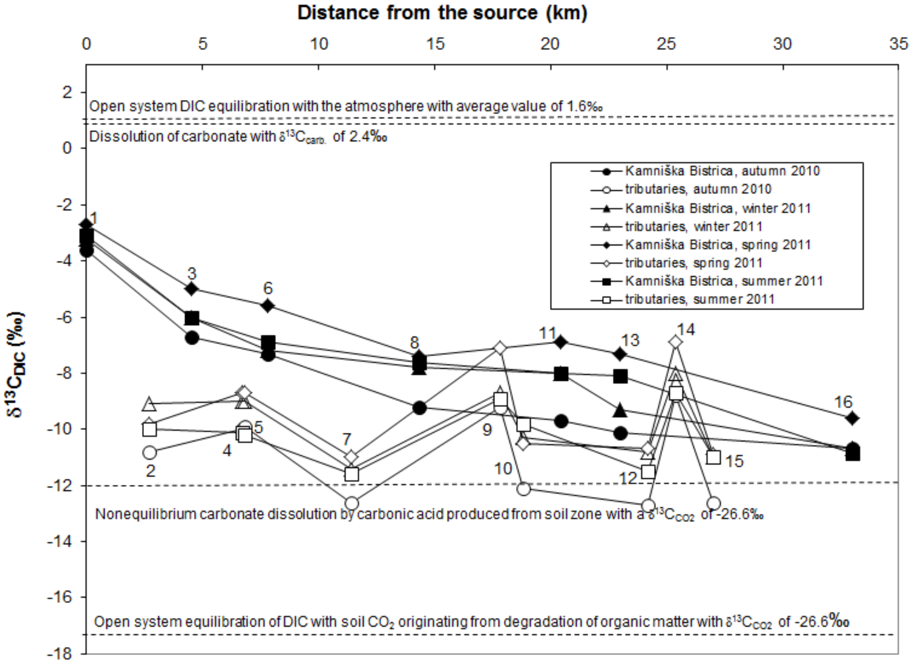

Fig. 4. Seasonally variation in the δC_{DIC} versus distance from the source in the Kamniška Bistrica River, with lines indicating biogeochemical processes occurring in the Kamniška Bistrica River and its tributaries.

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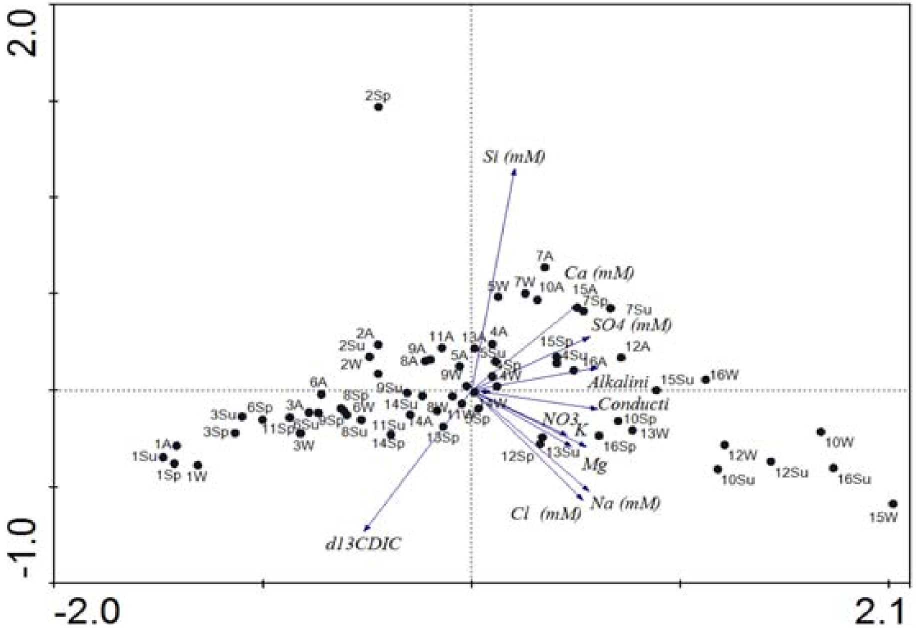

Fig. 5. PCA ordination diagram of geochemical parameters (arrows) and sampling locations (points) as well as seasons (A – autumn, Sp – spring, Su – summer, W – winter). The gradient is observed from upstream locations (sampling locations from 1 to 6 – non polluted locations to downstream sampling locations 6–16).

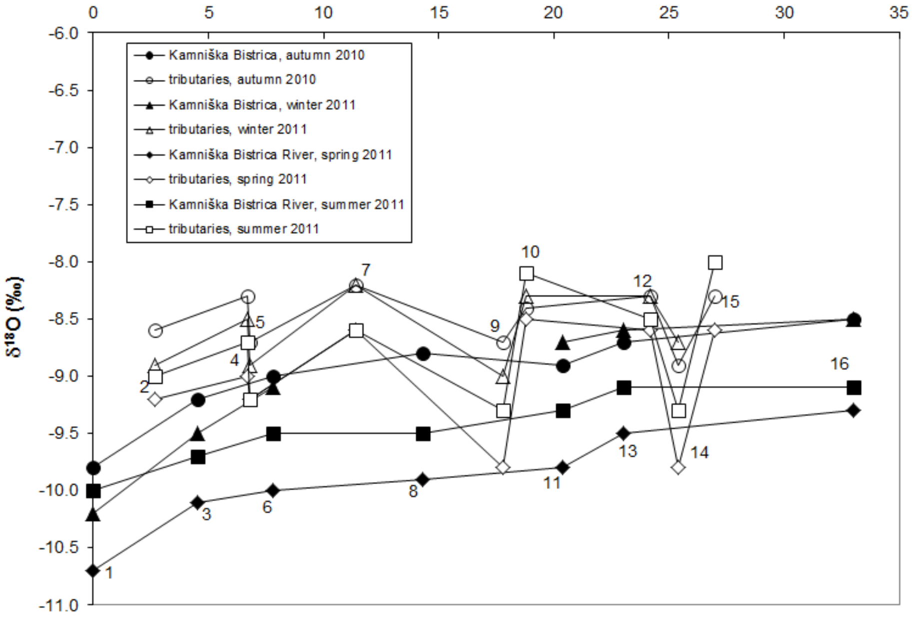

Fig. 6a. Seasonally (autumn 2010, winter 2011, spring 2011 and summer 2011) δ^{18}O variations versus distance from the source of Kamniška Bistrica River and its tributaries.

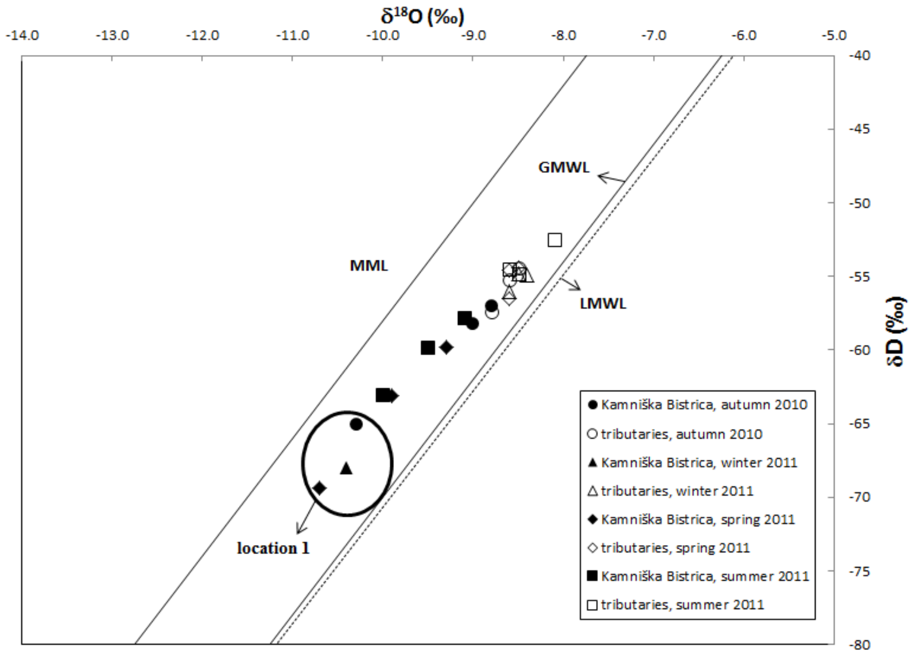

Fig. 6b. δD versus δ^{18}O values together with Global Meteoric Water Line (GMWL: $\delta D = 8 \times \delta^{18}O + 10$) (Craig, 1961), Mediterranean Meteorological Line (MML: $\delta D = 8 \times \delta^{18}O + 22$) and Local Meteorological Water Line (LMWL: $\delta D = 8 \times \delta^{18}O + 8.3$). More negative δ^{18}O values belong to locations in upper river reaches.

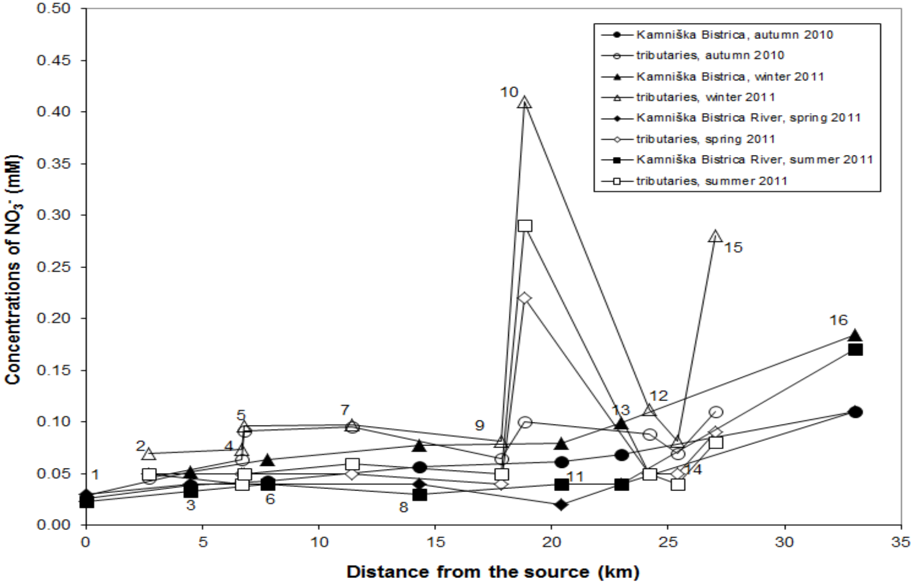

Fig. 7a. Seasonally variation of $\delta^{15}N_{NO_3^-}$ versus distance from the source of the Kamniška Bistrica River and its tributaries.

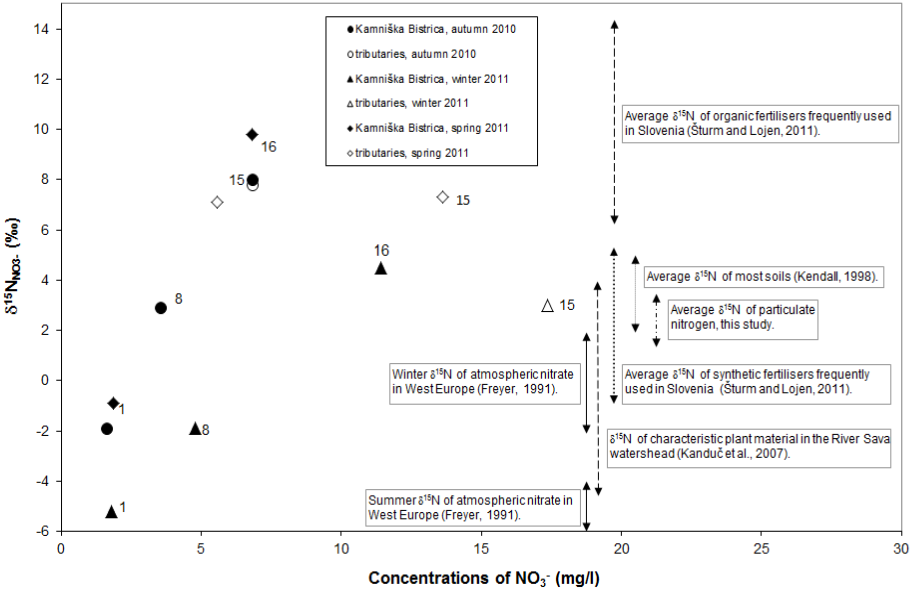

Fig. 7b. $\delta^{15}N_{NO_3^-}$ versus NO_3^- concentrations indicating different sources of nitrate in Kamniška Bistrica River watershed.