

Accepted Manuscript

Hydrogeochemistry of Alpine springs from North Slovenia: Insights from stable isotopes

Tjaša Kanduč, Nataša Mori, David Kocman, Vekoslava Stibilj, Fausto Grassa

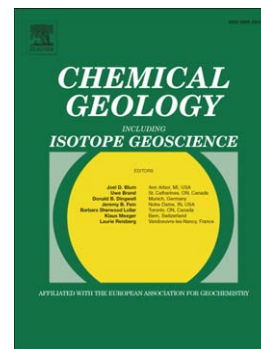
PII: S0009-2541(12)00030-7
DOI: doi: [10.1016/j.chemgeo.2012.01.012](https://doi.org/10.1016/j.chemgeo.2012.01.012)
Reference: CHEMGE 16420

To appear in: *Chemical Geology*

Received date: 28 February 2011
Revised date: 13 January 2012
Accepted date: 18 January 2012

Please cite this article as: Kanduč, Tjaša, Mori, Nataša, Kocman, David, Stibilj, Vekoslava, Grassa, Fausto, Hydrogeochemistry of Alpine springs from North Slovenia: Insights from stable isotopes, *Chemical Geology* (2012), doi: [10.1016/j.chemgeo.2012.01.012](https://doi.org/10.1016/j.chemgeo.2012.01.012)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Hydrogeochemistry of Alpine springs from North Slovenia: insights from stable isotopes

Tjaša Kanduč^{a,*}, Nataša Mori^b, David Kocman^a, Vekoslava Stibilj^a, Fausto Grassa^c

^a*Department of Environmental Science, Jožef Stefan Institute, Jamova cesta 39, Ljubljana 1000, Slovenia*

^b*National Institute of Biology, Department of freshwater and terrestrial ecosystems research, Večna pot 111, 1000 Ljubljana, Slovenia*

^c*Istituto Nazionale di Geofisica e Vulcanologia. Sezione di Palermo, Via Ugo La Malfa, 153, 90144, Palermo, Italy*

***Corresponding author**

Current address:

Dr. Tjaša Kanduč

Tel: +386 1 5885 238

Fax: +386 1 5885 346

E-mail: tjasa.kanduc@gmail.com

January 2012

Abstract

Spring water chemistry and carbon cycling in our study mainly depend on geological composition of the aquifer. The investigated Alpine springs in Slovenia represent waters strongly influenced by chemical weathering of Mesozoic limestone and dolomite, only one spring was located in Permo-Carboniferous shales. The carbon isotopic composition of dissolved inorganic carbon (DIC) and suspended organic carbon (POC) as well as major solute concentrations yielded insights into the origin of carbon in Alpine spring waters. The major solute composition was dominated by carbonic acid dissolution of calcite. Waters were generally close to saturation with respect to calcite, and dissolved CO₂ was up to fortyfold supersaturated relative to the atmosphere. $\delta^{13}\text{C}$ of DIC indicates the portion of soil CO₂ contributed in water and is related with soil thickness of infiltrating water in aquifer and could be therefore used as a tool for vulnerability assessment. The $\delta^{13}\text{C}$ of DIC ranged from -15.8‰ to -1.5‰ and indicated less and more vulnerable aquifers. Mass balances of carbon for spring waters draining carbonate rocks suggest that carbonate dissolution contributes from approximately 49% to 86% and degradation of organic matter from 13.7% to 51.4%, depending on spring and its relation with rock type, soil environment, and geomorphic position. Stable oxygen isotope composition of water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$), and tritium values range from -12.2 to -9.3‰ and from 6.4 to 9.8 TU, respectively and indicate recharge from modern precipitation. According to active decay of tritium and tritium in modern precipitation the age of spring waters are estimated to be about 2.6 years for springs located in Julian Alps, about 5 years for springs located in Karavanke and about 5 years for springs located in Kamniško-Savinjske Alps.

Keywords: Hydrogeochemistry; Stable isotopes; Carbon; Oxygen; Springs; Tritium

1. Introduction

Approximately 25% of the world's drinking water comes from karst groundwater systems (Drew and Hötzl, 1999). In Slovenia, approximately half of the population is supplied by karst waters. In Slovenia, karst is developed where Devonian to Miocene age carbonate rocks are present at or near the land surface. Slovenian karst systems are divided into three units, based on geological, hydrological and morphological conditions: Alpine karst, Dinaric karst and Dinaric-alpine intermediary and isolated karst (Habič, 1969). Alpine karst is present in mountainous regions of the northwestern and northern parts of Slovenia. Although a significant portion of groundwater is discharged from alpine karst, capacities of the alpine springs are not yet fully known (Petrič, 2004). As the degree of pollution in sparsely inhabited mountainous areas is still relatively low and amount of stored groundwater is large, alpine aquifers are invaluable reservoirs of drinking water and an important potential water source also for the future. At the same time, as highly heterogeneous and anisotropic environments they are particularly vulnerable to pollution. Due to fast infiltration and groundwater flow, which can transport pollutants rapidly in karst conduits over large distances, the rate of their self-cleaning capacity is low (Petrič, 2004). To adequately protect them, better understanding of their characteristics and dynamics is necessary (Petrič, 2004). Karst aquifers in Slovenia are also known for their heterogeneity and irregular complex flow patterns which make them more difficult to model and demand specific modeling approaches (Janža, 2010). Slovenian alpine karst springs also significantly contribute to the discharge of major alpine rivers, which drain to the Sava River. Alluvial aquifers associated with the Sava River are a major groundwater resource for the country.

Hydrochemistry and stable isotope compositions of karst spring waters provide critical information regarding sources of groundwater recharge, timing of recharge, water-rock interaction along flow paths, and mixing of distinct groundwater bodies. Ionic and isotopic concentrations can be easily changed or fractionated in aquifers through processes such as plant activity (O'Leary, 1988), isotopic exchange with surrounding materials, mineral or gas dissolution (Deines et al., 1974; Lesniak and Sakai, 1989), or redox reactions such as denitrification (Bottcher et al., 1990), sulfate reduction (Sakai, 1968; Machel et al., 1995), sulfide oxidation (Fry et al., 1988), or methanogenesis (Klass, 1984) along the flow path. Carbon isotopes are used to assess the origin of dissolved inorganic carbon (DIC), which is the main species in waters draining carbonate watersheds, and particulate organic carbon

(POC), which is also an important parameter in food web studies of biota within watersheds. Concentrations of DIC and its stable carbon isotope ratios ($\delta^{13}\text{C}_{\text{DIC}}$) are governed by processes occurring in the soil - aquifer system, and these vary seasonally. Changes in DIC concentrations result from carbon addition or removal from the DIC pool, whereas changes of $\delta^{13}\text{C}_{\text{DIC}}$ result from the fractionation accompanying transformation of carbon or from mixing of carbon from different sources. The major sources of carbon to aquifer DIC loads are dissolution of carbonate minerals, soil CO_2 derived from root respiration and from microbial decomposition of organic matter (often mainly of terrestrial origin but also including aquatic production). The major processes removing DIC in aquifer systems is carbonate mineral precipitation (Atekwana and Krishnamurthy, 1998). Water isotopic composition ($\delta^{18}\text{O}$ or δD) behaves conservatively in low - temperature aquifer environments (Kendall et al., 1995). As a result, researchers have often used stable isotope composition of water as tracers for determining the water provenance (Epstein and Mayeda, 1953; Kennedy et al., 1986; Mayo and Loucks, 1995; Taylor et al., 1992; Katz et al., 1997; Cartwright et al., 2000; Larsen et al., 2001).

In this study, we used hydrochemical ($\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios) and isotope (carbon, oxygen, hydrogen and tritium) tracers to characterize: 1) water-rock interactions, 2) origin of carbon and biogeochemical processes, and 3) recharge area and flow paths of some of the most important Alpine aquifers in northern Slovenia. A thorough knowledge of hydrogeochemical characteristics of Alpine springs is important for interpretation of the sources of waters and origins of solutes, which could be used as an additional tool in vulnerability estimation, risk assessment analysis and groundwater management practice.

2. Hydro-geological and meteorological characteristics

In aquifer studies, the uncertainty about recharges sources and processes along flowpaths is the major consideration. In this study, spatially distributed data on meteorology, hydrogeology and land use were used for the characterization of the springs, using the advantages of Geographical Information System (GIS) technology. This makes characterization of springs easier and more objective, though constrained by the quality of the input data. For each of the springs, characteristics presented in Table 1 and Figure 1 were extracted from corresponding GIS maps prepared by the Environmental Agency of the

Republic of Slovenia (EARS) and the Geological Survey of Slovenia, respectively, using the ArcGIS 9.3 software (ESRI).

Investigated springs are located within valleys of high mountainous areas composed of carbonate rocks, predominantly Triassic age limestone with some dolomite and dolomitized limestone. Rocks are well karstified and different surface and underground karst features are developed. The dominant hydrogeological units are highly permeable karst-fissured aquifers with fissured porosity. In some areas, where dolomite is more prevalent, fissured aquifers are slightly less permeable (Buser, 1987). More detailed hydro-geological descriptions of springs are presented in Table 1.

The climate of the region is alpine, with a mean annual temperature of 4 to 9 °C and annual precipitation from 1721 to 2335 mm (Ogrin, 1998). The majority of springs are situated along deep, narrow Alpine valleys at altitudes from 645 to 941 m. Three of them emerge higher on the slopes with altitudes of 1107 – 1236 m (Table 1). Precipitation and infiltration data for all springs are presented in Table 1. The vegetation of springs is composed of C3 plants (mixed forest, grasslands and coniferous forest) and is described in detail for the Sava River watershed elsewhere (Kanduč et al., 2007a). All the springs are part of the larger Sava River watershed (Figure 1). Locations of Alpine karst springs as well as their hydrogeological characteristics are presented on Figure 1 and Table 1.

Groundwater resources are divided into three subgroups: intergranular aquifers, karstic aquifers and fissured aquifers according to EU Water Framework Directive. Intergranular aquifers are a geological medium where porosity is a consequence of contact between grains in sediment and rock, while karstic aquifers are a geological medium where channel porosity prevails and fissured aquifers are a geological medium where the porosity of fissures and joints are predominant, although intergranular and channel porosity may also be present (Brenčič et al., 2009). In our study all types of aquifers were investigated (Table 1).

3. Sampling Protocols and Field Measurements

Sampling was performed during 3 different seasons (spring = June, summer = August/September and autumn = October/November) in years 2009 and 2010. Samples for stable isotope and tritium analyses were taken only in year 2010. Temperature, dissolved oxygen (DO) and conductivity of the spring waters were measured under the water surface in spring. Temperature and conductivity were measured using a WTW Multiline P4, TetraCon

325, respectively. Dissolved oxygen (DO) was measured with WTW Multiline P4, Cellox 325 and pH was measured using a WTW pH 540 GLP, with a SenTix 81. Discharge was measured using an OTT ADC flow meter at each spring and during each sample collection. Data of estimated discharges were calculated according to flow velocity and surface area of the springs (Table 1).

Sample aliquots collected for cation (pre-treated with HNO_3), anion and alkalinity analyses were passed through a $0.45 \mu\text{m}$ nylon filter into HDPE bottles and kept refrigerated until analyzed. Samples for $\delta^{13}\text{C}_{\text{DIC}}$ 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 ($\delta^{13}\text{C}_{\text{POC}}$) in all 2010 sampling seasons were collected in LDPE bottles (5 liters from each location). In addition, carbonate rocks of Mesozoic age from all locations (except of Perkova pušča (location 9), which is located in Permo-Carboniferous clastics rocks), were sampled from outcrops for stable carbon analyses ($\delta^{13}\text{C}_{\text{CaCO}_3}$).

For $\delta^{18}\text{O}$ and δD analyses samples were collected in 30 ml HDPE bottles with no filtering. For tritium analyses 1 l of sample was collected per location.

4. Laboratory analyses

Alkalinity was measured using Gran titrations (Clesceri et al., 1998). For waters investigated in Sava River watershed it was found out that regression between alkalinity and DIC concentrations was 96% when both were measured (Kanduč et al., 2007b). Cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (SO_4^{2-} , NO_3^- , Cl^-) were measured by ion chromatography (Metrohm, 761 Compact IC) with a precision of $\pm 2\%$. Analytical uncertainty is estimated between 10-20%. Detection limits for Ca^{2+} , Mg^{2+} , Na^+ and K^+ are 0.035 mg/l. Detection limits for NO_3^- , SO_4^{2-} and Cl^- are 0.01 mg/l.

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) was determined with a Europa Scientific 20-20 continuous flow IRMS (isotope ratio mass spectrometer) with an ANCA - TG preparation module. Phosphoric acid (100%) was added (100-200 μl) to a septum-sealed vial which was then purged with pure He. The water sample (6 ml) was injected into the septum tube and headspace CO_2 was measured (modified after Miyajima et al., 1995; Spötl, 2005). In order to determine the optimal extraction procedure for surface water samples, a standard solution of Na_2CO_3 (Carlo Erba) with a known $\delta^{13}\text{C}_{\text{DIC}}$ of –

10.8 ±0.2‰ was prepared with a concentration of 4.8 mM (for samples with an alkalinity from 1 to 4 mM).

The carbon stable isotope composition of particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$) was determined with a Europa Scientific 20-20 continuous flow IRMS ANCA - SL preparation module. For POC, 5 l of the water sample was filtered through a Whatman GF/F glass fiber filter (0.7 μm). Filters 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. $\delta^{13}\text{C}_{\text{POC}}$ was determined after combustion of the capsules in a hot furnace (1000°C). Generated products were reduced in Cu tube (600°C). Gases were separated on a chromatographic column and ionized. NBS 22 (oil) and IAEA N-1 (ammounium sulphate) reference materials were used.

Carbonate rocks from each location ($n = 4$) were ground to a powder in an agate mortar and then 2 mg of sample was first flushed with He and then transformed to CO_2 by H_3PO_4 acid treatment. CO-1 and NBS 19 were used as reference materials. The carbon isotope composition of carbonate ($\delta^{13}\text{C}_{\text{ca}}$) was measured with a Europa Scientific 20-20 continuous flow IRMS ANCA - TG preparation module.

All stable isotope results for carbon are expressed in the conventional delta (δ) notation, defined as per mil (‰) deviation from the reference standard VPDB. Precision of working standards or/and reference materials was ± 0.2‰ for $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{POC}}$, and $\delta^{13}\text{C}_{\text{ca}}$, respectively.

Oxygen isotope ratios were measured using $\text{CO}_2\text{-H}_2\text{O}$ equilibration (Epstein and Mayeda, 1953). Stable hydrogen isotope ratios were determined by $\text{H}_2\text{-H}_2\text{O}$ equilibration (Coplen et al., 1991). Oxygen and hydrogen isotopic results are reported in per mill (‰) relative to VSMOW (Vienna Standard Mean Ocean Water) and normalized (Coplen, 1994) on scales such that the oxygen and hydrogen isotopic values of SLAP (Standard Light Antartic Precipitation) are -55.5 and -428‰, respectively. Precision is estimated at ±0.2 and ±2.0 ‰ for $\delta^{18}\text{O}$ and δD , respectively.

Concentrations of tritium were performed with electrolytic enrichment method (Gröning and Rozanski, 2003; Villa and Mannjón, 2004; Plastino et al., 2007). Precision of determination of ^3H (samples determined 6 times) is ±0.5 TU and measurement uncertainty of results is ≥ 10%. Detection limit for tritium measurement is 3 TU.

Thermodynamic modeling was used to evaluate $p\text{CO}_2$ and the saturation state of calcite (SI_{calcite}) and dolomite (SI_{dolomite}) using pH, alkalinity, and temperature as inputs to the PHREEQC speciation program (Parkhurst and Appelo, 1999).

Principal component analysis (PCA) based on a covariance matrix was used to examine the variation in measured geochemical parameters from 12 springs collected on three occasions during the year 2010 (June, August, October). The CANOCO software package (ter Braak & Šmilauer, 2002) was used for the PCA analysis.

5. Results

Results of the chemical composition of Alpine karst springs are presented in Table 2 for year 2009 and Table 3 for year 2010. Temperature measured in springs is relatively constant in all sampling seasons (spring, summer and autumn during sampling campaign 2009-2010; Tables 2-3), suggesting that water is constantly recharging from slopes. The spring with the lowest temperature (4.8 to 5.0°C) is Javorniški potok (location 6), and the spring with the highest temperature (7.6 to 8.1°C) is Rogovilec (location 11). Discharge values range from 0.2 to 360 l/s. The lowest discharge is observed in spring Perkova pušča (location 9), whereas the highest discharge is observed at Kamniška Bistrica (location 12). According to water balance calculations (Van Abs et al., 2000):

$$P = Q + ET + dS \quad (1)$$

Where ET is water lost to evapotranspiration, P represents precipitation, Q is direct surface runoff and dS is change in groundwater storage

Based on the data of precipitation, surface runoff, evapotranspiration and infiltration (Frantar, 2007) and with the application of ArcGIS 9.3 software (ESRI) for each spring location the % of infiltration was calculated according to known parameters in water balance equation. The infiltration varies from 35.2% to 55.9% with the rest belonging to surface runoff and evapotranspiration. The highest conductivity (176 to 315 $\mu\text{S}/\text{cm}$) is observed in spring Črna rečica (location 4), whereas the lowest conductivity (64 to 99 $\mu\text{S}/\text{cm}$) is in spring Perkova pušča (location 9) (Tables 2-3). Lower conductivity is observed during higher discharge (Table 1). Oxygen saturation in spring waters ranged from 75 to 152% in spring, 74 to 125% in summer and from 79 to 120% in autumn during years 2009 to 2010; therefore reduction

processes (e.g. sulphate reduction and methanogenesis) are likely not important in the investigated springs.

The major solute composition of karst Alpine springs was dominated by HCO_3^- , Ca^{2+} and Mg^{2+} (Figure 2) and is comparable to the Sava River in Slovenia (Kanduč et al., 2007b) where all these springs drain via tributaries (Figure 1). Concentrations varied seasonally according to precipitation and flow velocity/discharge, with similar concentrations of solutes in all sampling seasons (Tables 2 and 3). In general lower concentrations are observed in summer due to longer melting of snow from spring till summer. Ca^{2+} ranges from 0.29 to 1.51 mM in spring, from 0.32 to 1.74 mM in summer and from 0.35 mM to 1.83 mM in autumn. Mg^{2+} ranges from 0.11 to 0.51 mM in spring, from 0.14 to 0.50 mM in summer and 0.15 to 0.52 mM in autumn. Concentrations of DIC range from 0.83 to 3.11 mM in spring, from 0.94 to 2.94 mM in summer and from 0.90 to 3.42 mM in autumn during the 2009 and 2010 sample periods. Only one sample (location 9) indicated low HCO_3^- concentrations due to weathering of Permo-Carboniferous shales (Tables 1, 2 and 3). Sample Mošenik, location 7 has a higher SO_4^{2-} concentration (ranging from 0.11 to 0.16 mM during investigated period 2009-2010) and is related with oxidation of pyrite in carbonate rocks (Buser, 1987) (Tables 2 and 3). NO_3^- concentrations in observed springs are low, ranging from 0.02 to 0.05 mM (corresponding to 1.24 to 3.1 mg/l) during all sampling campaigns.

Calculated CO_2 partial pressures (p_{CO_2}) varied from near atmospheric (316 ppmv) to over 40-fold supersaturated (10000 ppmv). The highest p_{CO_2} was observed in a spring located in Permo-Carboniferous shales, where low pH values (ranging from 6.50 to 7.55) were also observed during all sampling seasons. The calcite saturation index ($\text{SI}_{\text{calcite}} = \log([\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] / K_{\text{calcite}}$; where K_{calcite} is the solubility product of calcite) ranged from -2.15 to 0.55 during sampling campaign (Tables 2 and 3).

The $\delta^{13}\text{C}_{\text{DIC}}$ can elucidate the contributions of organic matter decomposition and carbonate mineral dissolution since springs are treated as closed systems in comparison to rivers, which are regarded as open systems (Clark and Fritz, 1997). $\delta^{13}\text{C}_{\text{DIC}}$ values varied seasonally from -15.3 to -1.5‰ in spring 2010, from -15.8 to -2.2‰ in summer 2010 and from -15.4 to -2.4‰ in autumn 2010. More negative $\delta^{13}\text{C}_{\text{DIC}}$ values are attributed to higher flow velocity/discharge and dilution due to precipitation. More negative $\delta^{13}\text{C}_{\text{DIC}}$ values are observed at spring Perkova pušča (location 9), whereas more positive values are observed at spring Kamniška Bistrica (location 12) (Table 3).

The $\delta^{13}\text{C}$ values of particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$) in investigated springs varied from -28.3 to -25.9‰ in spring 2010, from -28.5 to -22.5‰ in summer 2010 and -29.1 to -25.6‰ in autumn 2010. Suspended organic matter in springs was mostly derived from soil and plant material in recharge areas and drained through fissures, channels and pores to the spring (Ittekkot, 1988). The $\delta^{13}\text{C}$ values of Mesozoic carbonate rocks ($\delta^{13}\text{C}_{\text{CaCO}_3}$) composing slopes from investigated springs ranged from 1.8 to 5.0‰ (Table 3). $\delta^{13}\text{C}_{\text{CaCO}_3}$ was not measured at Perkova pušča (location 9) since the recharge area is composed of Permo-Carboniferous shales.

$\delta^{18}\text{O}$ and δD values range from -12.2 to -9.8‰ and -79 to -64‰ in spring 2010, from -11.5 to -9.1‰ and -76 to -48‰ in summer 2010, and from -11.1 to -9.6‰ and -77 to -61‰ in autumn 2010, respectively. Concentrations of tritium, which were only measured during the autumn sampling season, ranged from 6.5 TU to 9.9 TU (Table 3).

6. Discussion

6.1 Chemical composition in spring waters

Dissolved Ca^{2+} and Mg^{2+} are largely supplied by the weathering of carbonates as indicated by the relatively high HCO_3^- (Figure 2A). Major chemical data of investigated Alpine karst springs indicate that the major cation species are Ca^{2+} and Mg^{2+} and the major anion species is HCO_3^- . Weathering of rocks contributes a significant part of HCO_3^- in most water systems and therefore plays an important role in carbon cycle (Barth et al., 2003). HCO_3^- is the main inorganic carbon species in water at pH between 6.4 and 10.3 (Clark and Fritz, 1997) and also the main species in water of investigated karst Alpine springs. Na^+ and K^+ are found in springs in lower concentrations and are originated mostly from feldspars (albite, anorthite) and weathering products of carbonates such as clay minerals (Buser, 1987). Only one sample (Perkova pušča, location 9) indicates a different origin of water; its water chemistry is related to a different geological composition of the aquifer (clastic rocks) in comparison to other investigated springs, which are from typical carbonate karst regions (Table 1).

The major cation (Ca^{2+} , Mg^{2+}) and anion (HCO_3^-) species are formed through weathering reactions of carbonates present within aquifers (Drever, 1988):

Calcite/Aragonite:

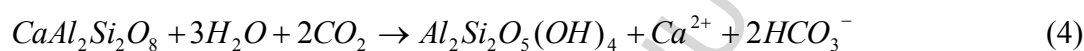


Dolomite:



The cation (Ca^{2+} and Na^+) and anion (HCO_3^-) species could also be formed through weathering reactions of feldspars:

Anorthite:



Albite:

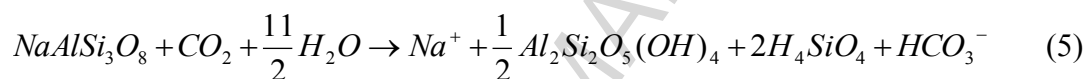


Figure 2B presents $Ca^{2+} + Mg^{2+}$ versus alkalinity. All the samples from our study are in excess of carbonate dissolution line 2:1 mole ratio of HCO_3^- to $Ca^{2+} + Mg^{2+}$, meaning that cations are not solely leached from carbonates (equations 1, 2, 3 and 4). It has been found that the $Ca^{2+} + Mg^{2+}$ ranges from 0.6 mM to 1.6 mM and HCO_3^- between 1.2 and 3.2 mM in watersheds composed mostly of carbonates in the River Sava watershed in Slovenia (Szramek et al., 2007). $Ca^{2+} + Mg^{2+}$ ranges from 0.9 to 2.2 mM in karst Alpine springs (the location 9 falls out of this range and is not treated as carbonate spring) recharging River Sava. Observed HCO_3^- values range from 1.43 to 1.67 mM (Kamniška Bistrica, location 12) and from 2.72 to 3.42 mM (Črna rečica, location 4), and fall in the same range as samples of the Sava River watershed and its tributaries (Kanduč et al., 2007a). The lowest alkalinity is observed at location 9 (Perkova pušča) located in Permo-Carboniferous shales. Deviations from carbonate dissolution line 2:1 are probably due to weathering of other minerals such as anorthite and albite, which also contribute alkalinity (equations 4 to 5).

Figure 2C shows Mg^{2+} versus Ca^{2+} values to determine the relative contribution of dolomite versus calcite to carbonate weathering intensity in springs. It can be observed that calcite dominates the water chemistry of Alpine springs. In only one sample, Perkova pušča (location 9) not shown on the plot, the cations are the result of feldspar weathering; this spring is located in Permo-Carboniferous shales. It was previously found that Slovenian streams have a wide range of Mg^{2+}/Ca^{2+} ratios, indicating variations in the relative contributions of

calcite and dolomite in different tributaries, ranging from 0.2 to nearly 0.8 (Szramek et al., 2007). The Mg^{2+}/Ca^{2+} ratio observed in Alpine karst springs from our study is in the range of 0.07 to 0.37 during 2009 to 2010, indicating lower Mg^{2+} contribution to headwaters recharging the Sava River.

All of the springs are oversaturated with CO_2 relative to the atmosphere (Figure 3A). Saturation of springs is pH dependent; lower pH results in higher p_{CO_2} . Higher p_{CO_2} , which ranges from $10^{-2.17}$ to $10^{-2.00}$, is observed in the spring from the Permo-Carboniferous shales (location 9) with the lowest pH. Saturation with CO_2 in springs draining carbonate aquifer, where p_{CO_2} ranges from $10^{-3.36}$ to $10^{-2.18}$, indicate as much as 10 times of saturation of atmospheric CO_2 .

Most of the spring waters are close to saturation or are slightly supersaturated with respect to calcite. Only spring Perkova pušča (location 9) is undersaturated with respect to calcite since it is located in area with different geological composition (Permo-Carboniferous shales, location 9). Slovenian streams in the Sava River watershed are also supersaturated with respect to calcite (Szramek et al., 2007). Increase in calcite saturation results from degassing and can lead to possible Ca-carbonate precipitation in streams. Ca-carbonate precipitation typically occurs in waters that are 5-10 times saturated for calcite (Herman and Lorah, 1987). Based on the isotopic composition of suspended carbon matter in Sava River watershed, precipitation of carbonate is unlikely (Kanduč et al., 2007b). Suspended matter composition reveals detrital carbonate with no evidence of precipitated carbonate in the water system. All of the springs investigated from our study are undersaturated with respect to dolomite (Figure 3B). Undersaturation of dolomite is expected since water chemistry of springs is controlled by calcite dissolution (Figure 2C).

6.2 Sources of Dissolved Inorganic Carbon (DIC) in spring waters inferred from the Isotopic Composition of Dissolved Inorganic Carbon ($\delta^{13}C_{DIC}$)

$\delta^{13}C_{DIC}$ value can determine contributions of organic matter decomposition and carbonate mineral dissolution in springs. $\delta^{13}C_{DIC}$ in spring waters is also controlled by the geological composition of the recharge area. Figure 4 shows different contributions of two carbon sources in the $\delta^{13}C_{DIC}$ value of spring waters in different sampling seasons: (1) organic matter degradation, and (2) carbonate dissolution. Figure 4 shows that springs can be grouped

based on $\delta^{13}\text{C}_{\text{DIC}}$ values into four clusters: 1) carbonate aquifer (location 12) with $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from -2.4 to -1.5‰ and alkalinity ranging from 1.48 to 2.81 mM, 2) aquifer with soil CO_2 contribution without carbonate contribution (location 1) with $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from -15.8 to -15.3‰ and alkalinity ranging from 0.92 to 1.03 mM, 3) aquifers with more soil CO_2 contribution (locations 1, 3, 9, 10 and 5) with $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from -11.3 to -7.3‰ and alkalinity 2.8 to 3.1 mM, and 4) aquifers with less soil CO_2 contribution with $\delta^{13}\text{C}_{\text{DIC}}$ values ranging from -8.7 to -4.8 ‰ (locations 2, 5, 6, 7 and 8) and alkalinity ranging from 2.2 to 2.5 mM. Springs with numbers from 1 to 8 and from 10 to 12 are all regarded as Alpine karst springs with more or less carbonate dissolution (Figure 4).

A simple mass balance calculation in spring waters is presented (equations 6 and 7), considering the following processes: organic matter degradation (DIC_{org}) and carbonate dissolution (DIC_{ca}) as springs are considered as systems without atmospheric exchange:

$$1 = \text{DIC}_{\text{org}} + \text{DIC}_{\text{ca}} \quad (6)$$

$$\text{DIC}_{\text{spring}} \cdot \delta^{13}\text{C}_{\text{DIC}} = \text{DIC}_{\text{org}} \cdot \delta^{13}\text{C}_{\text{org}} + \text{DIC}_{\text{ca}} \cdot \delta^{13}\text{C}_{\text{Ca}} \quad (7)$$

$\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{13}\text{C}_{\text{Ca}}$ measured values (Tables 2-3) were taken into account in the mass balance equations for each sampling season for year 2010. The contribution of rainwater in mass balance of $\text{DIC}_{\text{spring}}$ is considered to be minimal as it contains only a small amount of DIC (Yang et al., 1996). Anyway during the flow path from recharge to emerge probably microbial reactions or vital effects could take place, but those processes were neglected. Springs in our study are saturated with oxygen in all sampling seasons (Tables 2-3), therefore redox reactions e.g. denitrification, sulphate reduction and methanogenesis are not likely to happen during the flow path from recharge to emerge. The DIC_{org} and DIC_{Ca} values were determined by solving the mass balance equations. The calculated contribution of dissolution of carbonates (DIC_{Ca}) varies from 49% (location 4, Črna rečica) to 86% (location 12, Kamniška Bistrica) through all sampling seasons. Mass balance was not performed at location Perkova pušča (location 9), where carbon is mostly sourced from soil CO_2 (Figure 4). An average $\delta^{13}\text{C}_{\text{POC}}$ value of -27.2‰ was assumed to calculate lines 1-3 on Figure 4. Open system equilibration of DIC with soil CO_2 enriches DIC in ^{13}C by about 9‰ (Mook et al., 1974), thus yielding the estimate of -18.2‰ shown in Figure 4. Nonequilibrium dissolution of carbonates with one part of DIC originating from soil CO_2 with -27.2‰ and other from

carbonate dissolution with an average $\delta^{13}\text{C}_{\text{Ca}}$ of 2.2‰ produces an intermediate $\delta^{13}\text{C}_{\text{DIC}}$ value of -12.5‰ (Figure 4). Considering average isotopic composition of carbonates ($\delta^{13}\text{C}_{\text{Ca}}$) comprising in the recharge area and isotopic fractionation due to dissolution of carbonates, which is 1.0‰±0.2‰ enrichment with ^{12}C (Romanek et al., 1992) the $\delta^{13}\text{C}_{\text{DIC}}$ would be 1.2‰±0.2‰.

PCA explained 60.4 % of the variance in the data by the first two ordination axes (Figure 5). The first axis is primarily explaining gradients in pH, Ca^{2+} concentrations, alkalinity (negative), and Na^+ and K^+ concentrations (positive), whereas the second axis explains primarily gradients in Cl^- and $\delta^{13}\text{C}_{\text{DIC}}$. The geologic composition of the aquifers seems to be the major factor in controlling water chemistry of spring waters. According to analysed parameters (pH, conductivity, DO, alkalinity, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-} , NO_3^- and $\delta^{13}\text{C}_{\text{DIC}}$) and data processing with PCA analyses, four groups of springs (1 – carbonate aquifer, 2 – aquifer with soil CO_2 contribution without carbonate contribution, 3- aquifers with more soil CO_2 contribution and 4 – aquifer with less soil CO_2 contribution) are indicated on Figure 5. The results of PCA analyses are also in good agreement with Figure 4, where 4 groups of springs were also identified.

It was already discovered (Kanduč et al., 2007a) that the vulnerability of Slovenian water systems could be related to the soil thickness. Lower $\delta^{13}\text{C}_{\text{DIC}}$ values in spring waters measured in this study are related to the presence of thicker soils (more soil CO_2 contribution) in recharge areas. The thicker the soil profile is the more isotopically depleted CO_2 is contributed to aquifer and the longer the infiltration rate is, which leads to higher filtration capacities of soils prior to waters reaching aquifers. Therefore, we can say that the most vulnerable aquifers are ones with low soil CO_2 contributions (more than 50% of carbonate contribution calculated from equations 5 and 6 and high $\delta^{13}\text{C}_{\text{DIC}}$ values (>-1.4‰; e.g. aquifers: 1, 2, 5, 6, 7, 8 and 12). Less vulnerable aquifers are ones with more soil CO_2 contributions and lower $\delta^{13}\text{C}_{\text{DIC}}$ values (<-15.3‰; e.g. locations: 3, 4, 9, 10 and 11).

6.3 Origin and age of spring waters based on Oxygen, Hydrogen and Tritium isotopes

$\delta^{18}\text{O}$ and δD values of springs are similar to river waters and depend on several factors: precipitation, evapotranspiration, runoff and infiltration (Yee et al., 1990) and physical parameters, such as temperature and humidity (Clark and Fritz, 1997). All samples

investigated in our study fall between GMWL (Global Meteoric Water Line)/LMW (Local Meteorological Water Line) and MML (Mediterranean Meteorological Line), suggesting that springs originated from local Alpine and Mediterranean precipitation (Figure 6). Differences in $\delta^{18}\text{O}$ and δD values between springs from different Alpine massives (Julijan Alps, Karavanke and Kamniško – Savinjske Alps) mostly result from difference in the origin of precipitation, which may be sourced from Continental, Alpine and Mediterranean sources, as described in Vreča et al., 2004; Vreča et al., 2006. Precipitation in the study area is comparable to precipitation in Ljubljana (within the Sava River watershed). Precipitation in Ljubljana had $\delta^{18}\text{O}$ values from -11.8‰ to -7.8‰ in the autumn sampling season in years 2004-2005 (Kanduč, 2007a). The $\delta^{18}\text{O}$ values of springs sampled as part of this study are similar to previous samples of the Sava River, which ranged from -11.0 to -8.8‰ (Kanduč, 2007b). Alpine springs from our study have more negative $\delta^{18}\text{O}$ values in the spring sampling season, while during the summer sampling season more positive $\delta^{18}\text{O}$ values are observed due to heavier precipitation and enrichment in ^{18}O from evapotranspiration and groundwater flow through aquifer channels and fissures during summer growth season (Figure 6). This effect was then used to estimate the altitude of the groundwater recharge area for the individual spring. Assuming precipitation is the most important source of water for these springs, altitude of the recharge area was calculated using a simple multiple regression model of $\delta^{18}\text{O}$ in precipitation as described by Ogrinc et al., 2010. In that model, combined dependence of latitude and elevation on spatial distribution of $\delta^{18}\text{O}$ in precipitation over Slovenia is considered. Adopting this model and based on the measured average $\delta^{18}\text{O}$ in springs (Table 2-3) the height of recharge area (H) was calculated according to following equation (8):

$$H = (0.011 \cdot \text{LAT}^2 - 1.1579 \cdot \text{LAT} + 22.054 - \delta^{18}\text{O}) / (0.002) \quad (8)$$

Where LAT is the latitude of springs locations and $\delta^{18}\text{O}$ is isotopic composition of springs. It should be noted that this regression model is limited by the available data, and thus oversimplifies complexity of the $\delta^{18}\text{O}$ signal in precipitation. However this model was tested with average measured $\delta^{18}\text{O}$ values in springs and revealed good agreement ($r = 0.88$) between measured and calculated $\delta^{18}\text{O}$ values, confirming that average $\delta^{18}\text{O}$ value in springs mainly depends on $\delta^{18}\text{O}$ in precipitation. The calculated height of recharge area is presented in Table 1.

Tritium is a radioactive isotope used to detect waters that are less than 50 years old (Clark and Fritz, 1997). Concentrations of tritium in surface waters of the Sava River watershed ranged from 9.9 to 25.1 TU. Higher concentrations of tritium up to 25.1 TU are detected in surface waters around Krško nuclear power plant (Kanduč and Ogrinc, 2007c). Precipitation, which was sampled in Ljubljana during the same sampling period (autumn season) as springs for tritium analysis, had an average value of 6.4 TU (Glavič-Cindro, 2011). From the research of Sava River watershed it was found that concentrations of tritium indicate recharge with precipitation and shallow groundwater, which was retained in slopes of the Sava River watershed. According to radioactive decay of tritium and a 6.4 TU value for modern precipitation the following equation was used to calculate the age of spring waters:

$$t = 17.88 \cdot \ln \left(\frac{{}^3\text{H}_{\text{sample}}}{{}^3\text{H}_{\text{precipitation}}} \right) \quad (9)$$

From equation (9) the age of spring waters was calculated to be ~2.6 years in Julijske Alps, ~5 years in Karavanke and ~5.1 years in Kamniško-Savinjske Alps (Table 3). For Sava River watershed (main channel and tributaries) the estimated age of surface waters was from 4 to 14 years (Ogrinc et al., 2008). Estimated residence time for springs in Mošenik and Završnica located in Karavanke was estimated between 3.2 to 4.1 years (Brenčič and Polting, 2008), which is comparable with our results. The differences in estimated age of springs depend on several factors such as tritium concentration in precipitation, elevation of recharge area, flow path distance from the recharge area to where springs emerge, and mixing with older waters. For better estimation of the age of spring waters long-term monitoring of springs and precipitation would need to be conducted.

7. Conclusion

Spring water solute chemistry is dominated by HCO_3^- , Ca^{2+} and Mg^{2+} . Seasonal (spring, summer and autumn) concentrations of HCO_3^- ranged from 0.83 to 3.42 mM. Most springs were near equilibrium with respect to calcite in all sampling seasons, except Perkova pušča spring, which is located in a clastic rock aquifer. According to the calculated pCO_2 values, springs represent a source of CO_2 to the atmosphere. Alkalinity and $\delta^{13}\text{C}_{\text{DIC}}$ values were used to trace carbon cycling in spring waters. Seasonal $\delta^{13}\text{C}_{\text{DIC}}$ values (spring, summer and autumn) ranged from -15.8 to -1.5‰. The observed differences in pCO_2 , alkalinity and

$\delta^{13}\text{C}_{\text{DIC}}$ values between the carbonate rock aquifers versus aquitards composed of clastics rocks are the consequence of the soil thickness. Lower alkalinities and more positive $\delta^{13}\text{C}_{\text{DIC}}$ values are observed in karst aquifer Kamniška Bistrica, while higher alkalinities and more negative $\delta^{13}\text{C}_{\text{DIC}}$ values are observed in aquitard Perkova pušča. Since vulnerability of groundwater in Slovenia is highly related with soil profiles (i.e. thicker soils lead to longer infiltration times, which reduces vulnerability to surface contaminants) we can also conclude that $\delta^{13}\text{C}_{\text{DIC}}$ values can be used to assess vulnerability of springs. Those aquifers with less soil CO_2 contribution (more positive $\delta^{13}\text{C}_{\text{DIC}}$ values) and did not pass through a significant thickness of soil zone are likely more vulnerable to potential pollution. According to $\delta^{13}\text{C}_{\text{DIC}}$ values we can conclude that spring Kamniška Bistrica (location 12) is located within an aquifer with the greatest vulnerability.

The biogeochemical processes affecting DIC concentrations and $\delta^{13}\text{C}_{\text{DIC}}$ values were quantified by mass balance calculation, showing that the most important process in all investigated springs is carbonate mineral dissolution with DIC contribution ranging from 48.6% (Črna rečica, location 4) to 86.3% (Kamniška Bistrica, location 12). Only one spring is regarded as an aquitard with no carbonate dissolution (Perkova pušča, location 9). Based on PCA analysis, including geochemical parameters (pH, conductivity, DO, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , alkalinity, SO_4^{2-} , NO_3^- and Cl^-) and $\delta^{13}\text{C}_{\text{DIC}}$, the springs can be separated into 4 groups: 1) springs located in carbonate aquifers, 2) springs located in carbonate aquifers with less soil CO_2 contribution, 3) springs located in aquifers with more CO_2 contribution, and 4) springs located in non carbonate aquifers (only 1 sampled as part of this study). It can be concluded that geological composition of the aquifer primarily controls the water chemistry of springs.

$\delta^{18}\text{O}$ and δD values, ranging from -12.2‰ to -9.3‰ and -79‰ to -48‰ during sampling seasons indicate that springs are mostly recharged directly from precipitation, which was also confirmed with the use of multiple regression models for precipitation. ^3H concentrations in spring waters indicate short residence times ranging from 2.6 to 5.1 years.

Since recharge of the aquifers studied depends greatly on the amount of precipitation in the area (shallow basin aquifer) and the residence times are short due to highly permeable rocks with fissured porosity, it is highly probable that spring discharge will respond quickly to changes in precipitation amounts in the future. The elevation of aquifer recharge areas is important to limit protection zones of drinking water and for integrated management of water sources according to the Water Framework Directive. This study presents a complementary approach to the Water Framework Directive, and shows that stable isotopes and tritium are

useful tracers to determine the origin of water and its solutes. Therefore, stable isotopes and tritium could be additional and relatively inexpensive tool in solving problems in groundwater and surface water protections zones to prevent future pollution and estimate aquifer vulnerabilities for risk assessment studies.

8. Acknowledgments

The authors are grateful to Mr. Stojan Žigon, Andreja Jerebic and Barbara Svetek for technical support and Irena Bertoncej and Basak Oz for the help in the field. The authors would also like to thank Dr. Mihael Brenčič for his introduction to the investigated area and for helping with spring selection for the study. The authors acknowledge financial support from the state budget by the Slovenian Research Agency (Z1—2213) and programme research group "Cycling of nutrients and contaminants in the environment, mass balances and modeling environmental processes and risk analysis" (P1-0143). The study is partly funded by the EU project Alp-Water-Scarce (Alpine Space programme, 2008-2011). Special thanks are given to Dr. Jennifer McIntosh for linguistic corrections.

9. References

- Atekwana, E.A., Krishnamurthy, R.V., 1998. Seasonal variations of dissolved inorganic carbon and $\delta^{13}\text{C}$ of surface waters: application of a modified gas evaluation technique. *J. Hydrol.* 205, 260–278.
- Barth, J.A.C., Cronin, A.A., Dunlop, J., Kalin, R.M., 2003. Influence of carbonates on the riverine carbon cycle in an anthropogenically dominated catchment basin: evidence from major elements and stable carbon isotopes in the Lagan River (N. Ireland). *Chem. Geol.* 200, 203-216.
- Bottcher, J., Strebel, O., Voerkelius, S., Schmidt, H.L., 1990. Using isotope fractionation of nitrate nitrogen and nitrate oxygen for evaluation of denitrification in a sandy aquifer. *Hydrogeol. J.*, 114, 413-424.

Brenčič, M., Poltnig, W., 2008. Podzemne vode Karavank : skrito bogastvo = Grundwasser der Karawanken Versteckter Schatz, Geološki zavod Slovenije, Ljubljana, Joanneum Research Forschungsgesellschaft, Gratz (in Slovene, in German).

Brenčič, M., Prestor, J., Kompare, B., Matoz, H., Kranjc, S., 2009. Integrated approach to delineation of drinking water protection zones. *Geologija*, 52 (2), 175-182.

Buser, S., 1987. Geological map of Slovenia. In: Encyclopedia of Slovenia No. 8. Mladinska knjiga, Ljubljana (in Slovene).

Cartwright, I., Weaver, T., Tweed, S., Ahearne, D., Cooper, M., Czapnik, C., Tranter, J., 2000. O, H, C isotope geochemistry of carbonated mineral springs in central Victoria, Australia: sources of gas and water-rock interactions during basaltic volcanism. *J. Geochem. Explor.* 69-70, 257-261.

Clark, I., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, Boca Raton, New York.

Clesceri, L.S., Greenberg, A.E., Eaton, A.D., 1998. Standard methods for the examination of water and wastewater. 20th edition. APHA, AWWA, WEF, Baltimore.

Coplen, T. B., Wildman, J. D., Chen, J., 1991. Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis. *Analytical Chem.* 63, 910-912.

Coplen, T. B., 1994. Reporting and stable hydrogen, carbon, and oxygen isotopic abundances. *Pure and Applied Chem.* 66, 273-276.

Craig, H., 1961. Isotopic variation in meteoric waters. *Science* 133, 1702-1703.

Deines, P., Langmuir, D., Harmon, R. S., 1974. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate groundwaters. *Geochim. Cosmochim. Acta* 38, 1147-1164.

Drever, J. I., 1988. The geochemistry of Natural Waters. New Jersey: Englewood Cliffs, Prentice-Hall, pp. 473.

Drew, D., Hoetzi, H., 1999. Karst hydrogeology and human activities. Impacts, consequences and implications. IAH-International contributions to hydrogeology, A.A. Balkema, p. 322, Rotterdam, Brookfield.

Epstein, S., Mayeda, T., 1953. Variations of ^{18}O contents of water from natural sources. Geochim. Cosmochim. Acta 4, 213-224.

Frantar, P. 2007. Geographical overview of water balance of Slovenia 1971-2000 by main river basins. Acta Geographica Slovenica 47, 25-45.

Fry, B., Ruf, W., Gest, H., Hayes, J. M., 1988. Sulphur isotope effects associated with oxidation of sulphide by O_2 in aqueous solution. Chem. Geol. (Isotope Geoscience Section) 73, 205- 210.

Glavič-Cindro, D., 2011. Yearly report on gamma- and beta ray emitters activity measurements. No 8/21, Jožef Stefan Institute (working report), 25 pp.

Gröning, M., Rozanski, K., 2003. Uncertainty assessment of environmental tritium measurements in water, Accreditation and Quality Assurance, 8: 359-366.

Habič, P., 1969: Hidogeografska rajonizacija krasa v Sloveniji. Krš Jugoslavije, 6, pp. 79-97, Zagreb (in Slovene).

Herman, J.S., Lorah, M.M., 1987. CO_2 outgassing and calcite precipitation in Falling Spring Creek, Virginia, U. S. A., Chem. Geol. 62, 251-262.

Ittekkot, V., 1988. Global trends in the nature of organic matter in the river suspensions. Nature 332, 436-438.

Janža, M., 2010. Hydrological modeling in the karst area, Rižana spring catchment, Slovenia, Environmental Earth Science 61, 909-920.

Kanduč, T., Ogrinc, N., Mrak, T. 2007a. Characteristics of suspended matter in the River Sava watershed, Slovenia. *Isotopes in Environ. Health Stud.* 43, 369-385.

Kanduč, T., Szramek, K., Ogrinc, N., Walter, L. M., 2007b. Origin and cycling of riverine inorganic carbon in the Sava River watershed (Slovenia) inferred from major solutes and stable carbon isotopes. *Biogeochemistry* 86, 137-154.

Kanduč, T., Ogrinc, N., 2007c. Hydrogeochemical characteristics of the river Sava watershed in Slovenia. *Geologija* 50, 157-177.

Katz, B.G., Coplen, T.B., Bullen, T.D., Davis, J. H., 1997. Use of chemical and isotopic Tracers to characterize the interactions between ground water and surface water in mantled karst. *Ground Water* 36 (6), 1014-1028.

Kendall, C., Sklash, M. G., Bullen, T. D., 1995. Isotope tracers of water and solute sources in catchments. In: Trudgill, S. T. (Ed.), *Solute, Modelling in Catchment System*. Wiley, Somerset, NJ, pp. 261-303.

Kennedy, V.C., Kendall, C., Zellweger, G.W., Wyerman T.A., Avanzino R. J., 1986. Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River Basin, California. *J Hydrol.* 84, 107-140.

Klass, D. L., 1984. Methane from anaerobic fermentation. *Science* 223, 1021-1028.

Larsen, D., Swihart, G. H., Xiao, Y., 2001. Hydrochemistry and isotope composition of springs in the Tecopa basin, southeastern California, USA, *Chem. Geol.* 179, 17-35.

Lesniak, P. M., Sakai, H., 1989. Carbon isotope fractionation between dissolved carbonate (CO_3^{2-}) and CO_2 (g) at 25° and 40 ° C. *Earth Planet. Sci. Lett.* 95, 297-301.

Machel, H. G., Krouse H. R., Sassen R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulphate reduction. *Appl. Geochem.* 10, 373-389.

Mayo, A. L., Loucks, M. D. 1995. Solute and isotopic geochemistry and groundwater flow in the central Wasatch Range, Utah. *J. Hydrol.* 172, 31-59.

Miyajima, T., Yamada, Y., Hanba, Y.T. 1995. Determining the stable isotope ratio of total dissolved inorganic carbon in lake water by GC/C/IRMS. *Limnol. Oceanogr.* 40(5), 994-1000.

Mook, W.G., Bommerson, J.C., Staverman, W.H. 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett.* 22, 169-176.

O'Leary, M. H., 1988. Carbon isotopes in photosynthesis. *Bioscience* 38, 328.

Ogrin, D., 1998. Podnebje = Climate. (ur.= Ed.) Fridl, J., Kladnik, D., Adamič, M., Perko, D. V=In: Geografski atlas, Ljubljana, DZS:110-111 pp. (in Slovene).

Ogrinc, N., Kanduč, T., Stichler, W., Vreča, P., 2008. Spatial and seasonal variations in $\delta^{18}\text{O}$ and δD values in the river Sava in Slovenia. *J. Hydrol.* 359, 303-312.

Ogrinc, N., Kocman, D., Vreča, P., Kanduč, T., Žigon, S., 2010. Isotope investigation of the river Sava in Slovenia: long-term isotopic monitoring of surface water and precipitation at selected sites, (IJS working report, 10628).

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

Petrič, M., 2004. Alpine karst waters in Slovenia, *Acta Carsologica* 33, 11-24.

Plastino, W., Chereji, I., Cuna, S., Kaihola, L., Felice, P., Lupsa, N., Balas, G., Mirel, V., Berdea, P., Baciu, C. 2007. Tritium in water electrolytic enrichment and liquid scintillation counting. *Radiation Measurements* 42, 68-73.

Romanek, C.S., Grossman, E.L., Morse, J.W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: effects temperature and precipitation rate: *Geochim. Cosmochim. Acta* 46, 419 – 430.

Sakai, H., 1968. Isotopic properties of sulphur compounds in hydrothermal processes. *Geochem. J.* 2, 29-49.

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

Szramek, K., McIntosh, J.C., Williams, E.L., Kanduč, T., Ogrinc, N., Walter, L.M., 2007. Relative weathering intensity of calcite versus dolomite in carbonate-bearing temperate zone watersheds: Carbonate geochemistry and fluxes from catchments within the St. Lawrence and Danube river basins. *Geochem. Geophys. Geosystems (G3)* 8, 1-26.

Taylor, C.B., Brown, L.J., Cunliffe, J.J., Davidson, P.W., 1992. Environmental tritium and ^{18}O in a hydrological study of the Wairau Plain and its contributing mountain catchments, Marlborough, New Zealand, *J. Hydrol.* 138, 269-319.

Ter Braak, C. J. F., Šmilauer P., 2002. CANOCO, version 4.5 2002.

Van Abs, D.J., Stanuikynas, T.J. 2000: Water Budget in the Raritan River Basin. A Technical Report for the Raritan Basin Watershed Management Project New Jersey Water Supply Authority. Internet:

<http://www.raritanbasin.org/Reports/WaterBudgetReport.pdf> (23.1.2006).

Villa, M., Mannjón, G. 2004. Low-level measurements of tritium in water. *Appl. Rad. Isotopes* 61, 319-323.

Vreča, P., Kanduč, T., Žigon, S., Trkov, Z. 2004. Isotopic composition of precipitation in Slovenia. In: *Isotopic composition of precipitation in the Mediterranean basin in relation to air circulation pattern and climate: final report of a coordinated research project 2000-2004*, (IARA-TECDOC, 1453), Vienna, IAEA, 157-172.

Vreča, P., Krajcar Bronić, I., Horvatinčić, N., Barešić, J. 2006. Isotopic characteristics of precipitation in Slovenia and Croatia: comparison of continental and maritime stations. *J. Hydrol.* 330, 457-469.

Yang, C., Telmer, K., Veizer, J., 1996. Chemical dynamics of the 'St. Lawrence' riverine system: δD_{H_2O} , $\delta^{18}O_{H_2O}$, $\delta^{13}C_{DIC}$, $\delta^{34}S_{sulfate}$, and dissolved $^{87}Sr/^{86}Sr$. *Geochim. Cosmochim. Acta* 60, 851-866.

Yee, P., Edgett, R., Eberhardt, A., 1990. Great lakes – St. Lawrence River regulation; what it means and how it works. Joint publication of Environment Canada Ontario Region, and the U. S. Army Corps of Engineers.

List of tables

Table 1: Names, locations, estimated discharge, and hydrogeological characteristics of Alpine springs sampled in the Sava River watershed.

Table 2: Chemical data for Alpine springs from North Slovenia for year 2009.

Table 3: Chemical and isotopic data for Alpine springs from North Slovenia for year 2010.

Figure captions

Figure 1: General map of the Sava River drainage basin indicating the location of Slovenia and numbered sampling locations of Alpine springs. Sample sites are described in Table 1. Quaternary and Tertiary rocks are composed of carbonate and clastics rocks, Cretaceous and Jurassic rocks are composed of carbonates and clastics rocks, Triassic carbonates are composed of carbonates, Paleozoic rocks are composed of carbonates and clastics rocks.

Figure 2: (A) Ternary plot for basic hydrogeochemistry species for cations (Ca^{2+} - Mg^{2+} - $Na^{+}+K^{+}$) and anions (HCO_3^{-} - NO_3^{-} - $SO_4^{2-}+Cl^{-}$), average concentrations are presented during period 2009-2010 (B) $Ca^{2+} + Mg^{2+}$ ratio versus alkalinity with lines: 1:2 indicating weathering

of carbonates and 1:1 indicating weathering of albite in investigated period during 2009 and 2010 in different sampling seasons (spring, summer and autumn) (C) Mg^{2+} versus Ca^{2+} indicating the dominance of dolomite or calcite in the watershed in years 2009 and 2010 for different sampling seasons (spring, summer and autumn).

Figure 3: A) p_{CO_2} versus pH of Alpine karst springs in different sampling seasons (spring, summer and autumn) in years 2009 and 2010. All samples have p_{CO_2} values greater than atmospheric ($10^{-3.5}$) causing increase in calcite saturation. B) Saturation index of calcite ($SI_{calcite}$) versus dolomite ($SI_{dolomite}$) in Alpine karst springs in different sampling seasons (spring, summer and autumn) in years 2009 and 2010. Saturation for calcite/dolomite is defined as $\log IAP/K = 0$.

Figure 4: Seasonal variation in the $\delta^{13}C_{DIC}$ values in Alpine karst springs, with lines indicating processes occurring in springs. These include: (1) dissolution of carbonates according to the average $\delta^{13}C_{CaCO_3}$ (2.2‰) value of all measured samples composing the recharge area of springs (except Perkova pušča, location 9), causing $1‰ \pm 0.2‰$ enrichment in ^{12}C in DIC (Romanek et al., 1992); (2) nonequilibrium carbonate dissolution by carbonic acid produced from soil zone CO_2 ; and (3) open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{soil} = -27.2‰$.

Figure 5: PCA ordination diagram of geochemical parameters (arrows) and sampling locations (points). Springs are grouped according to geological composition of recharged area showing that geological composition is the main factor controlling water chemistry and $\delta^{13}C_{DIC}$ of spring waters.

Figure 6: δD versus $\delta^{18}O$ 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: $\delta D = 7.9 \times \delta^{18}O + 8.3$). All samples fall within the GMWL and LMWL.

Table 1

| Number of location | Spring name | Lat., deg N | Long., deg W | Altitude (m) | Height of recharge area according to equation (7) | Average discharge (l/s) | Precipitation (mm) | Infiltration (mm) | Land use | Type of aquifer | General characteristics and geological composition |
|--------------------|---|-------------|--------------|--------------|---|-------------------------|--------------------|-------------------|-------------------|-----------------|--|
| 1 | spring near Peričnik waterfall, Julian Alps | 41.61 | 14.49 | 733 | 1860 | 3.5 | 2065 | 818 | Mixed forest | Karst-fissured | Discharges as permanent rheochrene spring in the Vrata valley under the steep walls of Kukova Špica and Sleme, flows as small brook for 30 m and then as a stream Bistrica flows to Sava Dolinka. The aquifer is composed of massive and stratified limestone of Triassic age. |
| 2 | Zmrzlek, Julian Alps | 42.45 | 13.91 | 698 | 1679 | 10 | 2008 | 945 | Mixed forest | Karst-fissured | Discharges from steep NE slopes of Pokljuka as linear spring. It drains most of the north-eastern part of Pokljuka and Mežakla plateau and then as a stream flows to the River Radovna and further to Sava Dolinka. The aquifer is composed of massive limestone and coarse-grained dolomite of Triassic age. |
| 3 | Lipnik, Julian Alps | 42.56 | 13.83 | 692 | 1500 | 15 | 1969 | 1100 | Mixed forest | Karst-fissured | Discharges from steep NE slopes of Pokljuka. Discharges as linear spring under carbonate rock faces. It drains most of the north-eastern part of Pokljuka and Mežakla plateau and then as a stream flows to the River Radovna and further to Sava Dolinka. The aquifer is composed of massive limestone and coarse-grained dolomite of Triassic age. |
| 4 | Črna rečica, Julian Alps | 42.83 | 13.97 | 653 | 1103 | 22 | 1902 | 948 | Coniferous forest | Karst-fissured | Discharges as intermittent rheochrene spring (a spring, which literally flows directly out of the ground, the water being often forced out under pressure; it directly forms a stream) from the steep slopes of NE Mežaklja, after 20 m flows in the stream Rečica which further flows to Sava Dolinka. The aquifer is composed of alternation of marls, miltstones, stratified limestone, massive dolomite, limestone breccia, ignimbrite volcanic rocks of Triassic age. |
| 5 | Presušnik, Karavanke | 42.29 | 14.83 | 1203 | 1729 | 1.8 | 2087 | 1016 | Mixed forest | Karst-fissured | Discharges as small rheochrene spring by side of stream Presušnik. The aquifer is composed of massive and stratified dolomite and limestone of Triassic age. |
| 6 | Javorniški potok, Karavanke | 43.20 | 14.67 | 1107 | 1964 | 32 | 2335 | 1089 | Mixed forest | Karst-fissured | Discharges as several rheochrene springs in the steep slopes under Stol that after 30 m flow as Javorniški potok which flows into Sava Dolinka near Jesenice. The aquifer is composed of massive and stratified dolomite and limestone of Triassic age. |
| 7 | Završnica, Karavanke | 43.86 | 14.17 | 941 | 1548 | 22 | 2158 | 1077 | Mixed forest | Karst-fissured | Several (28) rheochrene springs are discharging in the length of 1300 m and width of 300 m in the beginning of Završnica valley. The aquifer is composed of stratified limestone with lateral gradation to massive dolomite of Triassic age. |
| 8 | Mošenik, Karavanke | 44.42 | 14.16 | 797 | 1446 | 28 | 2051 | 1029 | Coniferous forest | Karst-fissured | Several rheochrene springs emerge from the side and from the channel of stream Mošenik near village Lajba. Sampling was conducted in springs across from former restaurant. The aquifer is composed of stratified limestone with lateral alternation to massive dolomite of Triassic age. |
| 9 | Perkova pušča, Karavanke | 46.96 | 14.19 | 1236 | 1451 | 0.9 | 2026 | 907 | Coniferous forest | Aquitard | Small rheochrene spring discharging at the end of steep meadow near Pavičevo sedlo, continues as 1 m width stream which flows into Savinja. The aquitard is composed of alternation of sandstones, claystones and conglomerate of Permo-Carboniferous age. |
| 10 | Črna, Kamniško-Savinjske Alps | 47.23 | 14.06 | 744 | 1318 | 9.9 | 1966 | 927 | Mixed forest | Karst-fissured | Slow flowing rheochrene spring emerging from a large rock in the beginning of Logarska Dolina (left side), a spring brook flows for a few 100 m until it discharges into the Savinja River. The aquifer is composed of stratified limestone with lateral gradation to massive dolomite of Triassic age. |
| 11 | Rogovilc, Kamniško-Savinjske Alps | 47.78 | 13.94 | 645 | 1038 | 1.3 | 1721 | 606 | Pastures | Karst-fissured | A group of few rheochrene springs emerging 20 m from the River Savinja near Robanov Kot. The aquifer is composed of gradation of stratified limestone and massive dolomite of Triassic age. |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 46.89 | 13.16 | 596 | 1606 | 216 | 2260 | 1168 | Mixed forest | Karst | Discharges from many locations under carbonate rock faces (only the results of saturated zone are presented in this paper). The spring recharges stream with the same name Kamniška Bistrica, which outflows into to River Sava. The aquifer is composed of limestone of upper Triassic age. |

Table 2

| Spring | | | | | | | | | | | | | | | | | |
|---------------------|--|-----------------|--------|------|----------------------|--------|-----------------|---------|---------|---------|--------|----------------------|----------------------|---------|-------------------------|-----------------------|------------------------|
| Location on the map | Location | Discharge (l/s) | T (°C) | pH | Conductivity (µS/cm) | DO (%) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | SO ₄ (mM) | NO ₃ (mM) | Cl (mM) | pCO ₂ (bars) | SI _{calcite} | SI _{dolomite} |
| 1 | sping near Peričnik waterfall, Julian Alps | 2.6 | 5.8 | 8.15 | 195 | 90 | 1.95 | 0.90 | 0.28 | 0.01 | 0.00 | 0.02 | 0.03 | 0.01 | -3.18 | 0.10 | -0.50 |
| 2 | Zmrzlek, Julian Alps | 5.4 | 5.9 | 8.17 | 215 | 96 | 2.17 | 1.16 | 0.17 | 0.02 | 0.00 | 0.02 | 0.03 | 0.02 | -3.16 | 0.27 | -0.46 |
| 3 | Lipnik, Julian Alps | 29 | 6.5 | 7.81 | 248 | 114 | 2.41 | 1.39 | 0.12 | 0.06 | 0.00 | 0.02 | 0.03 | 0.07 | -2.66 | 0.12 | -0.99 |
| 4 | Črna rečica, Julian Alps | 19 | 7.7 | 7.70 | 313 | 152 | 3.11 | 1.46 | 0.51 | 0.02 | 0.00 | 0.04 | 0.05 | 0.02 | -2.71 | 0.02 | -0.56 |
| 5 | Presušnik, Karavanke | 2.4 | 9.1 | 8.00 | 238 | 86 | 2.37 | 1.23 | 0.23 | 0.01 | 0.00 | 0.04 | 0.04 | 0.01 | -2.94 | 0.21 | -0.42 |
| 6 | Javorniški potok, Karavanke | 34 | 4.9 | 7.95 | 190 | 105 | 1.89 | 0.92 | 0.24 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -3.00 | -0.11 | -1.01 |
| 7 | Završnica, Karavanke | 29 | 5.6 | 7.88 | 203 | 140 | 1.96 | 1.06 | 0.18 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.91 | -0.10 | -1.16 |
| 8 | Mošenik, Karavanke | 26 | 6.9 | 7.93 | 227 | 150 | 2.00 | 1.02 | 0.33 | 0.03 | 0.00 | 0.12 | 0.04 | 0.03 | -2.95 | -0.04 | -0.73 |
| 9 | Perkova pušča, Karavanke | 1.2 | 7.2 | 6.79 | 87 | 82 | 0.83 | | | 0.08 | 0.02 | 0.03 | 0.03 | 0.02 | -2.17 | -2.04 | -4.54 |
| 10 | Črna, Kamniško-Savinjske Alps | 8.3 | 7.0 | 7.91 | 271 | 102 | 2.90 | 1.24 | 0.45 | 0.01 | 0.00 | 0.04 | 0.03 | 0.01 | -2.77 | 0.16 | -0.27 |
| 11 | Rogovilc, Kamniško-Savinjske Alps | 1.6 | 7.9 | 8.00 | 285 | 97 | 2.74 | 1.48 | 0.25 | 0.03 | 0.00 | 0.08 | 0.04 | 0.02 | -2.88 | 0.32 | -0.26 |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 230 | 5.6 | 7.9 | | | 1.48 | 0.79 | 0.12 | 0.02 | 0.00 | 0.01 | 0.03 | 0.01 | -3.36 | -0.01 | -1.02 |
| Summer | | | | | | | | | | | | | | | | | |
| Location on the map | Location | Discharge (l/s) | T (°C) | pH | Conductivity (µS/cm) | DO (%) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | SO ₄ (mM) | NO ₃ (mM) | Cl (mM) | pCO ₂ (bars) | SI _{calcite} | SI _{dolomite} |
| 1 | sping near Peričnik waterfall, Julian Alps | 3.4 | 6.00 | 7.88 | 191 | 103 | 1.83 | 0.87 | 0.26 | 0.01 | 0.00 | 0.02 | 0.03 | 0.01 | -2.94 | -0.20 | -1.09 |
| 2 | Zmrzlek, Julian Alps | | | | | | | | | | | | | | | | |
| 3 | Lipnik, Julian Alps | 10 | 6.80 | 7.66 | 305 | 103 | 2.85 | 1.74 | 0.18 | 0.06 | 0.01 | 0.03 | 0.04 | 0.09 | -2.53 | 0.05 | -1.04 |
| 4 | Črna rečica, Julian Alps | | | | | | | | | | | | | | | | |
| 5 | Presušnik, Karavanke | | | | | | | | | | | | | | | | |
| 6 | Javorniški potok, Karavanke | 26 | 4.80 | 7.89 | 199 | 125 | 1.88 | 0.89 | 0.25 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.93 | -0.20 | -1.16 |
| 7 | Završnica, Karavanke | 17 | 5.80 | 7.82 | 203 | 99.9 | 1.99 | 1.01 | 0.20 | 0.01 | 0.01 | 0.03 | 0.04 | 0.01 | -2.84 | -0.17 | -1.23 |
| 8 | Mošenik, Karavanke | 22 | 7.20 | 7.74 | 243 | 90 | 2.06 | 1.04 | 0.36 | 0.04 | 0.00 | 0.16 | 0.04 | 0.03 | -2.74 | -0.20 | -1.02 |
| 9 | Perkova pušča, Karavanke | 1.2 | 7.60 | 6.67 | 98 | 77.3 | 0.94 | | | 0.08 | 0.01 | 0.03 | 0.03 | 0.03 | -2.00 | -2.06 | -4.56 |
| 10 | Črna, Kamniško-Savinjske Alps | 6.7 | 7.80 | 7.75 | 279 | 84.8 | 2.75 | 1.21 | 0.43 | 0.02 | 0.00 | 0.04 | 0.03 | 0.01 | -2.63 | -0.01 | -0.61 |
| 11 | Rogovilc, Kamniško-Savinjske Alps | 1.9 | 8.10 | 7.91 | 303 | 94.9 | 2.87 | 1.28 | 0.50 | 0.03 | 0.01 | 0.11 | 0.04 | 0.02 | -2.77 | 0.19 | -0.16 |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 96 | 5.40 | 7.89 | 162 | 94 | 1.54 | 0.79 | 0.16 | 0.01 | | 0.01 | 0.03 | 0.01 | -3.02 | -0.31 | -1.48 |
| Autumn | | | | | | | | | | | | | | | | | |
| Location on the map | Location | Discharge (l/s) | T (°C) | pH | Conductivity (µS/cm) | DO (%) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | SO ₄ (mM) | NO ₃ (mM) | Cl (mM) | pCO ₂ (bars) | SI _{calcite} | SI _{dolomite} |
| 1 | sping near Peričnik waterfall, Julian Alps | 4.0 | 6.0 | 8.10 | 191 | 95.3 | 1.91 | 0.87 | 0.28 | 0.01 | 0.00 | 0.02 | 0.03 | 0.01 | -3.14 | 0.03 | -0.61 |
| 2 | Zmrzlek, Julian Alps | 14 | 6.0 | 7.90 | 260 | 95.3 | 2.55 | 1.35 | 0.20 | 0.02 | 0.00 | 0.02 | 0.03 | 0.03 | -2.82 | 0.13 | -0.74 |
| 3 | Lipnik, Julian Alps | 14 | 6.9 | 7.89 | 294 | 93.2 | 2.80 | 1.59 | 0.15 | 0.05 | 0.01 | 0.03 | 0.04 | 0.07 | -2.77 | 0.24 | -0.70 |
| 4 | Črna rečica, Julian Alps | 27 | 7.5 | 7.94 | 315 | 100.1 | 3.17 | 1.56 | 0.45 | 0.02 | 0.00 | 0.04 | 0.04 | 0.02 | -2.76 | 0.33 | -0.03 |
| 5 | Presušnik, Karavanke | | | | | | | | | | | | | | | | |
| 6 | Javorniški potok, Karavanke | 21 | 4.9 | 8.07 | 202 | 108 | 2.14 | 0.88 | 0.26 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -3.07 | 0.04 | -0.65 |
| 7 | Završnica, Karavanke | 22 | 5.8 | 7.96 | 209 | 99.2 | 2.06 | 1.02 | 0.19 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.97 | -0.01 | -0.93 |
| 8 | Mošenik, Karavanke | 33 | 7.1 | 7.98 | 243 | 96.4 | 2.10 | 1.02 | 0.37 | 0.04 | 0.00 | 0.14 | 0.03 | 0.03 | -2.98 | 0.03 | -0.54 |
| 9 | Perkova pušča, Karavanke | 0.6 | 7.5 | 6.79 | 95 | 80.6 | 0.90 | | | 0.08 | 0.02 | 0.03 | 0.02 | 0.02 | -2.14 | -1.91 | -4.13 |
| 10 | Črna, Kamniško-Savinjske Alps | 12 | 7.4 | 7.89 | 280 | 89.2 | 2.81 | 1.23 | 0.46 | 0.02 | 0.00 | 0.04 | 0.03 | 0.01 | -2.76 | 0.14 | -0.30 |
| 11 | Rogovilc, Kamniško-Savinjske Alps | 0.2 | 7.7 | 8.04 | 290 | 99.5 | 2.82 | 1.37 | 0.37 | 0.03 | 0.01 | 0.10 | 0.04 | 0.02 | -2.91 | 0.34 | -0.04 |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 360 | 5.6 | 7.94 | 166 | 101 | 2.81 | 1.23 | 0.46 | 0.02 | 0.00 | 0.04 | 0.03 | 0.01 | -2.76 | 0.14 | -0.30 |

Table 3

| Spring | | | | | | | | | | | | | | | | | | | | | | | | |
|---------------------|---|-----------------|--------|------|----------------------|--------------|-----------------|---------|---------|---------|--------|----------------------|----------------------|---------|-------------------------|-----------------------|----------------------|--------------------------------------|--------------------------------------|-----------------------|--------|--|---------------------|-------------|
| Location on the map | | Discharge (l/s) | T (°C) | pH | Conductivity (µS/cm) | D. O. (%) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | SO ₄ (mM) | NO ₃ (mM) | Cl (mM) | pCO ₂ (bars) | SI _{calcite} | SI _{gypsum} | δ ¹³ C _{DIC} (‰) | δ ¹³ C _{POC} (‰) | δ ¹⁸ O (‰) | δD (‰) | δ ¹³ C _{CaCO3} (‰) | | |
| 1 | spring near Peričnik waterfall, Julian Alps | 3.6 | 5.9 | 8.06 | 117 | 93.0 | 2.02 | 0.91 | 0.29 | 0.01 | 0.00 | 0.02 | 0.03 | 0.01 | -2.99 | 0.11 | -0.46 | -5.1 | -27.2 | -10.8 | -71 | 3.4 | | |
| 2 | Zmrzlek, Julian Alps | 4.4 | 6.0 | 7.99 | 136 | 101.0 | 2.25 | 1.22 | 0.15 | 0.02 | 0.00 | 0.01 | 0.03 | 0.02 | -2.88 | 0.21 | -0.66 | -8.7 | -27.2 | -10.8 | -71 | 3.4 | | |
| 3 | Lipnik, Julian Alps | 14.0 | 6.6 | 7.95 | 164 | 88.0 | 2.57 | 1.51 | 0.11 | 1.35 | 0.00 | 0.02 | 0.03 | 0.08 | -2.78 | 0.32 | -0.65 | -10.9 | -27.7 | -10.9 | -71 | 3.3 | | |
| 4 | Črna rečica, Julian Alps | 24 | 7.6 | 8.00 | 176 | 102.0 | 2.72 | 1.39 | 0.27 | 0.01 | 0.00 | 0.02 | 0.04 | 0.01 | -2.8 | 0.37 | -0.11 | -11.3 | -25.9 | -10.0 | -65 | 3.6 | | |
| 5 | Presušnik, Karavanke | 1.6 | 7.6 | 8.13 | 159 | 89.0 | 2.51 | 1.26 | 0.28 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.97 | 0.42 | 0.05 | -7.3 | -26.4 | -11.7 | -75 | 3.5 | | |
| 6 | Javorniški potok, Karavanke | 34 | 5.0 | 7.99 | 120 | 107.0 | 1.95 | 1.00 | 0.26 | 0.01 | 0.00 | 0.02 | 0.04 | 0.01 | -2.94 | 0.06 | -0.67 | -5.1 | -28.3 | -11.5 | -76 | 3.1 | | |
| 7 | Završnica, Karavanke | 29 | 5.9 | 7.97 | 128 | 94.0 | 2.04 | 1.09 | 0.18 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.9 | 0.1 | -0.75 | -5.7 | -27.9 | -11.3 | -72 | 2.8 | | |
| 8 | Mošenik, Karavanke | 26 | 8.0 | 8.04 | 151 | 75.0 | 2.11 | 1.02 | 0.36 | 0.05 | 0.00 | 0.11 | 0.04 | 0.05 | -2.95 | 0.19 | -0.22 | -4.8 | -27.1 | -11.2 | -71 | 2.9 | | |
| 9 | Perkova pušča, Karavanke | 1.2 | 7.3 | 6.50 | 95 | 81.0 | 0.92 | | | | 0.08 | 0.00 | 0.02 | 0.02 | -1.75 | -2.15 | -4.75 | -15.3 | -27.1 | -11.2 | -72 | | | |
| 10 | Črna, Kamniško-Savinjske Alps | 8.3 | 6.8 | 7.82 | 279 | 102.0 | 2.71 | 1.20 | 0.43 | 0.02 | 0.00 | 0.04 | 0.03 | 0.02 | -2.62 | 0.11 | -0.38 | -8.9 | -26.7 | -10.6 | -68 | 5.0 | | |
| 11 | Rogovlec, Kamniško-Savinjske Alps | 1.6 | 7.9 | 8.00 | 282 | 93.0 | 2.53 | 1.38 | 0.28 | 0.03 | 0.00 | 0.08 | 0.05 | 0.01 | -2.83 | 0.34 | -0.14 | -9.8 | -26.9 | -9.8 | -64 | 1.8 | | |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 230 | 5.1 | 8.21 | 148 | 101.0 | 1.43 | 0.77 | 0.12 | 0.10 | 0.00 | 0.00 | 0.02 | 0.00 | -3.29 | 0.05 | -0.92 | -1.5 | -26.0 | -12.2 | -79 | 2.4 | | |
| Summer | | | | | | | | | | | | | | | | | | | | | | | | |
| Location on the map | | Discharge (l/s) | T (°C) | pH | Conductivity (µS/cm) | D. O. (mg/l) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | SO ₄ (mM) | NO ₃ (mM) | Cl (mM) | pCO ₂ (bars) | SI _{calcite} | SI _{gypsum} | δ ¹³ C _{DIC} (‰) | δ ¹³ C _{POC} (‰) | δ ¹⁸ O (‰) | δD (‰) | δ ¹³ C _{CaCO3} (‰) | | |
| 1 | spring near Peričnik waterfall, Julian Alps | 3.4 | 6.1 | 8.25 | 115 | 96.0 | 1.88 | 0.84 | 0.27 | 0.01 | 0.00 | 0.02 | 0.03 | 0.01 | -3.22 | 0.24 | -0.19 | -5.0 | -26.0 | -9.9 | -63 | 3.4 | | |
| 2 | Zmrzlek, Julian Alps | 13 | 6.0 | 7.77 | 156 | 96.0 | 2.53 | 1.42 | 0.19 | 0.02 | 0.00 | 0.02 | 0.03 | 0.02 | -2.61 | 0.1 | -0.84 | -9.9 | -27.3 | -11.0 | -67 | 3.4 | | |
| 3 | Lipnik, Julian Alps | 10 | 6.6 | 7.57 | 174 | 95.0 | 2.83 | 1.55 | 0.14 | 0.05 | 0.00 | 0.02 | 0.03 | 0.06 | -2.35 | -0.01 | -1.23 | -11.1 | -28.4 | -10.8 | -69 | 3.3 | | |
| 4 | Črna rečica, Julian Alps | 10 | 7.4 | 7.55 | 184 | 104.0 | 2.88 | 1.48 | 0.27 | 0.02 | 0.00 | 0.03 | 0.05 | 0.02 | -2.32 | -0.03 | -0.94 | -11.9 | -26.6 | -9.1 | -62 | 3.6 | | |
| 5 | Presušnik, Karavanke | 1.2 | 8.5 | 7.62 | 171 | 95.0 | 2.62 | 1.28 | 0.28 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.43 | -0.04 | -0.87 | -7.9 | -26.6 | -9.3 | -48 | 3.5 | | |
| 6 | Javorniški potok, Karavanke | 26 | 4.9 | 7.90 | 122 | 116.0 | 2.00 | 1.02 | 0.26 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.84 | -0.02 | -0.83 | -5.2 | -28.1 | -11.5 | -75 | 3.1 | | |
| 7 | Završnica, Karavanke | 17 | 6.3 | 7.87 | 131 | 100.0 | 2.08 | 1.08 | 0.17 | 0.01 | 0.00 | 0.02 | 0.04 | 0.01 | -2.79 | 0.02 | -0.95 | -5.5 | -27.6 | -9.7 | -60 | 2.8 | | |
| 8 | Mošenik, Karavanke | 22 | 7.0 | 7.97 | 153 | 100.0 | 2.09 | 0.98 | 0.37 | 0.05 | 0.00 | 0.13 | 0.04 | 0.04 | -2.88 | 0.08 | -0.42 | -4.6 | -22.5 | -9.7 | -57 | 2.9 | | |
| 9 | Perkova pušča, Karavanke | 1.2 | 7.4 | 6.53 | 64 | 75.0 | 0.95 | | | | 0.08 | 0.03 | 0.02 | 0.02 | -1.77 | -2.09 | -4.66 | -15.8 | -28.5 | -10.8 | -76 | | | |
| 10 | Črna, Kamniško-Savinjske Alps | 6.7 | 7.8 | 7.64 | 185 | 74.0 | 2.94 | 1.26 | 0.43 | 0.02 | 0.00 | 0.04 | 0.03 | 0.01 | -2.4 | 0 | -0.6 | -9.4 | -27.8 | -11.4 | -72 | 5.0 | | |
| 11 | Rogovlec, Kamniško-Savinjske Alps | 1.9 | 7.7 | 7.96 | 188 | 100.0 | 2.87 | 1.26 | 0.45 | 0.03 | 0.00 | 0.10 | 0.04 | 0.01 | -2.74 | 0.31 | 0.03 | -9.3 | -26.9 | -11.3 | -71 | 1.8 | | |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 180 | 5.4 | 8.09 | 100 | 102.0 | 1.67 | 0.81 | 0.15 | 0.01 | 0.00 | 0.01 | 0.02 | 0.01 | -3.1 | 0.02 | -0.88 | -2.2 | -27.8 | -11.1 | -67 | 2.4 | | |
| Autumn | | | | | | | | | | | | | | | | | | | | | | | | |
| Location on the map | | Discharge (l/s) | T (°C) | pH | Conductivity (µS/cm) | D. O. (%) | Alkalinity (mM) | Ca (mM) | Mg (mM) | Na (mM) | K (mM) | SO ₄ (mM) | NO ₃ (mM) | Cl (mM) | pCO ₂ (bars) | SI _{calcite} | SI _{gypsum} | δ ¹³ C _{DIC} (‰) | δ ¹³ C _{POC} (‰) | δ ¹⁸ O (‰) | δD (‰) | δ ¹³ C _{CaCO3} (‰) | ³ H (TU) | Age (years) |
| 1 | spring near Peričnik waterfall, Julian Alps | 3.4 | 6.4 | 8.00 | 187 | 95.0 | 2.04 | 0.95 | 0.30 | 0.01 | 0.00 | 0.02 | 0.03 | 0.01 | -2.93 | 0.08 | -0.51 | -5.1 | -27.7 | -11.0 | -76 | 3.4 | 7.4 | 2.7 |
| 2 | Zmrzlek, Julian Alps | 13 | 5.9 | 7.67 | 253 | 102.0 | 2.72 | 1.48 | 0.23 | 0.02 | 0.00 | 0.02 | 0.03 | 0.03 | -2.48 | 0.05 | -0.89 | -9.6 | -27.9 | -10.1 | -67 | 3.4 | 8.0 | 3.9 |
| 3 | Lipnik, Julian Alps | 10 | 6.7 | 7.48 | 297 | 94.0 | 3.05 | 1.83 | 0.16 | 0.07 | 0.00 | 0.03 | 0.03 | 0.10 | -2.23 | 0 | -1.21 | -10.9 | -26.5 | -9.8 | -64 | 3.3 | 7.9 | 3.8 |
| 4 | Črna rečica, Julian Alps | 10 | 7.5 | 7.48 | 316 | 97.0 | 3.42 | 1.64 | 0.52 | 0.02 | 0.00 | 0.03 | 0.04 | 0.02 | -2.18 | 0 | -0.64 | -11.7 | -26.2 | -9.6 | -61 | 3.6 | 6.4 | 0.1 |
| 5 | Presušnik, Karavanke | 1.2 | 4.9 | 7.89 | 244 | 93.0 | 2.61 | 1.41 | 0.27 | 0.01 | 0.00 | 0.04 | 0.04 | 0.01 | -2.72 | 0.2 | -0.5 | -7.0 | -26.6 | -11.1 | -77 | 3.5 | 8.4 | 4.8 |
| 6 | Javorniški potok, Karavanke | 26 | 4.8 | 7.94 | 189 | 112.0 | 1.96 | 0.96 | 0.27 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.89 | -0.02 | -0.78 | -4.9 | -27.1 | -11.1 | -74 | 3.1 | 8.4 | 4.8 |
| 7 | Završnica, Karavanke | 17 | 5.6 | 7.82 | 197 | 95.0 | 2.16 | 1.16 | 0.20 | 0.01 | 0.00 | 0.03 | 0.04 | 0.01 | -2.72 | 0 | -0.96 | -5.3 | -27.1 | -11.0 | -75 | 2.8 | 8.7 | 5.5 |
| 8 | Mošenik, Karavanke | 22 | 6.9 | 7.86 | 226 | 96.0 | 2.11 | 1.17 | 0.37 | 0.04 | 0.00 | 0.12 | 0.04 | 0.03 | -2.77 | 0.04 | -0.57 | -4.2 | -25.7 | -10.8 | -71 | 2.9 | 8.4 | 4.9 |
| 9 | Perkova pušča, Karavanke | 1.2 | 7.3 | 7.55 | 99 | 79.0 | 1.03 | | | | 0.09 | 0.03 | 0.02 | 0.02 | -2.76 | -1.03 | -2.51 | -15.4 | -28.1 | -10.9 | -74 | | 8.2 | 4.3 |
| 10 | Črna, Kamniško-Savinjske Alps | 6.7 | 7.1 | 7.94 | 262 | 120.0 | 2.77 | 1.22 | 0.43 | 0.01 | 0.00 | 0.04 | 0.03 | 0.01 | -2.73 | 0.25 | -0.1 | -8.5 | -29.1 | -10.2 | -69 | 5.0 | 7.9 | 3.8 |
| 11 | Rogovlec, Kamniško-Savinjske Alps | 1.9 | 7.6 | 8.12 | 302 | 105.0 | 3.09 | 1.47 | 0.46 | 0.04 | 0.00 | 0.19 | 0.04 | 0.02 | -2.87 | 0.55 | 0.45 | -9.4 | -25.6 | -9.6 | -65 | 1.8 | 9.8 | 7.7 |
| 12 | Kamniška Bistrica, Kamniško-Savinjske Alps | 180 | 5.5 | 7.88 | 164 | 106.0 | 1.67 | 0.88 | 0.16 | 0.01 | 0.00 | 0.01 | 0.02 | 0.01 | -2.89 | -0.16 | -1.23 | -2.4 | -26.6 | -10.5 | -69 | 2.4 | 8.3 | 4.7 |

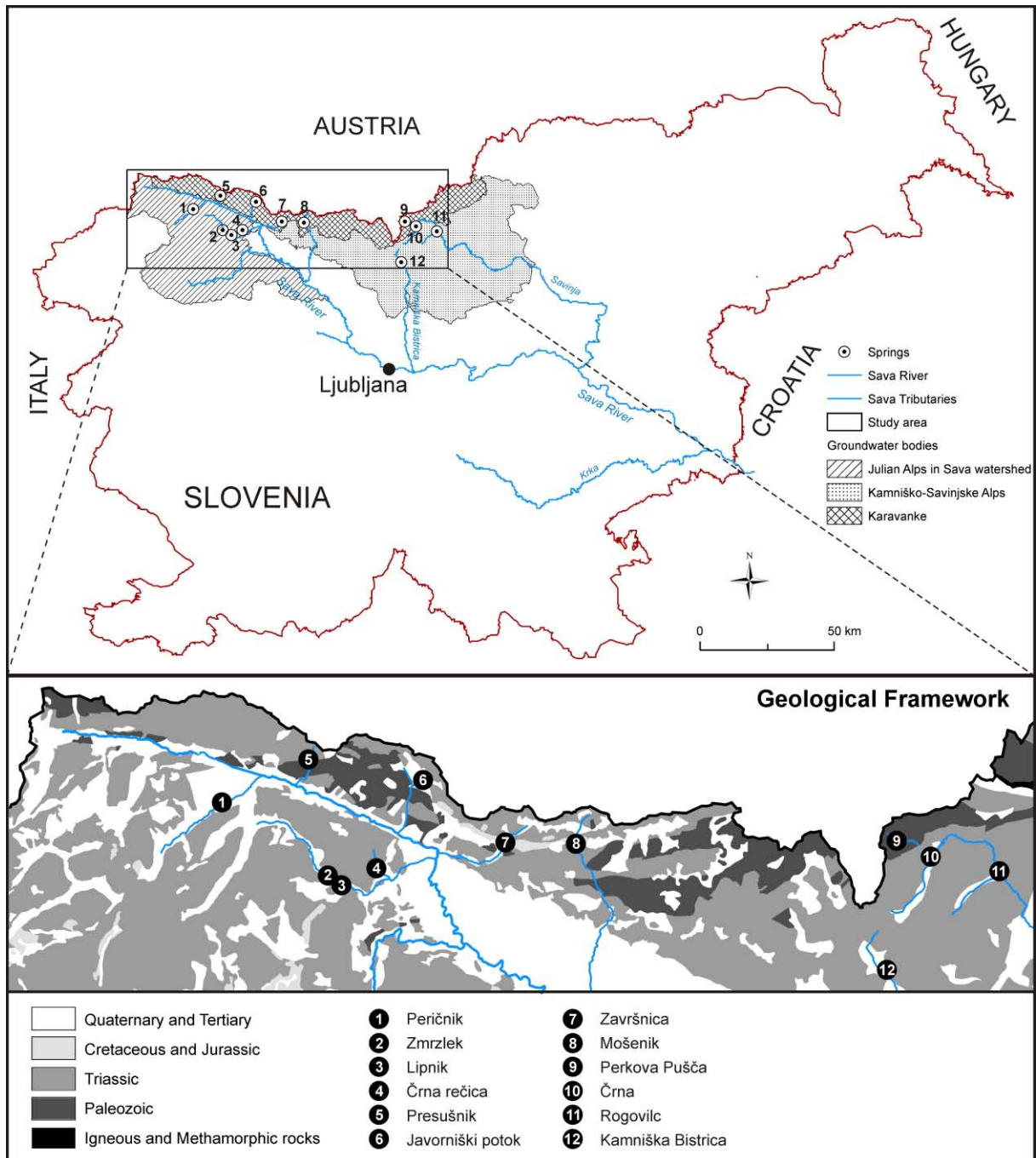


Figure 1

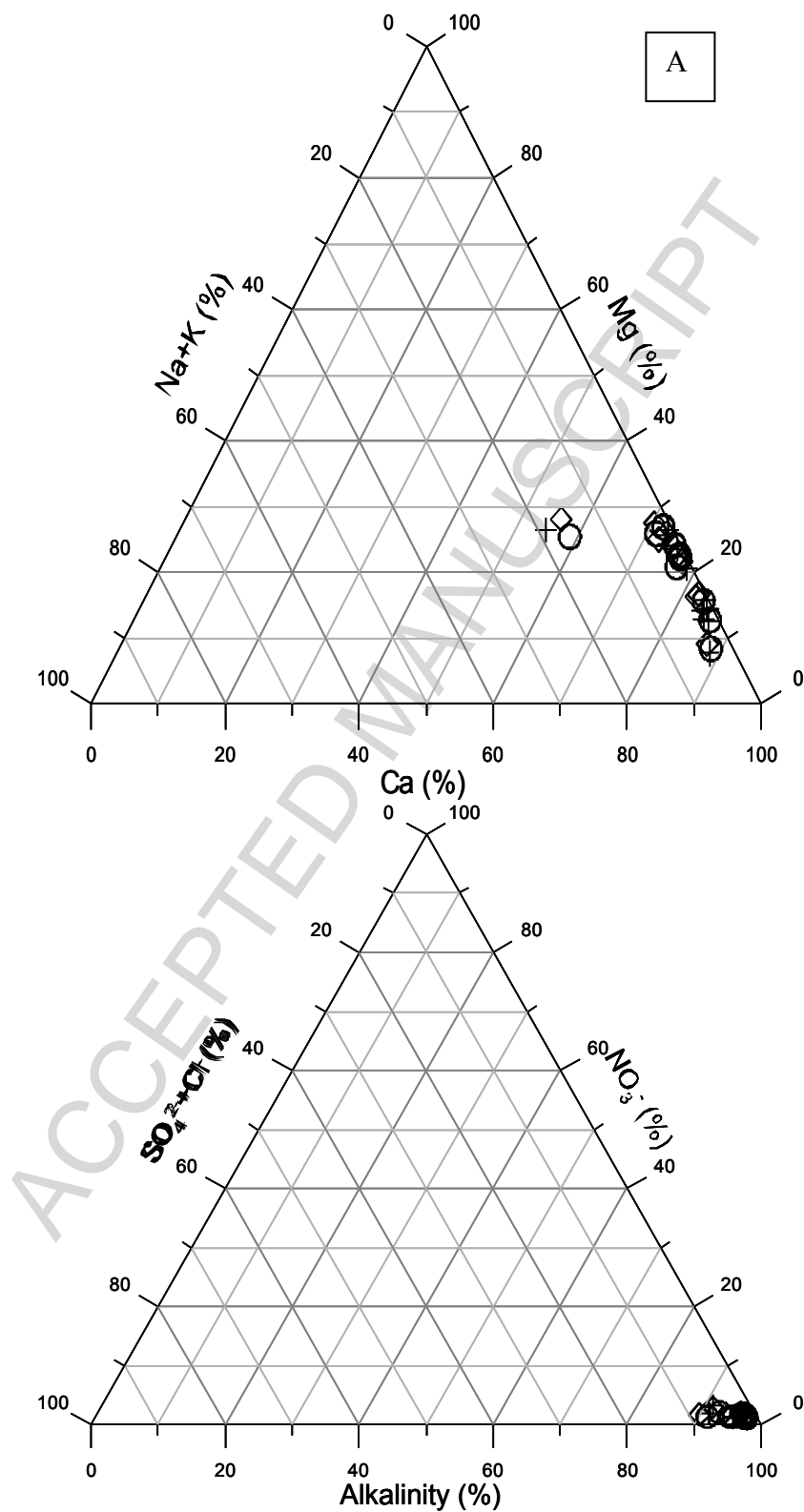


Figure 2 A

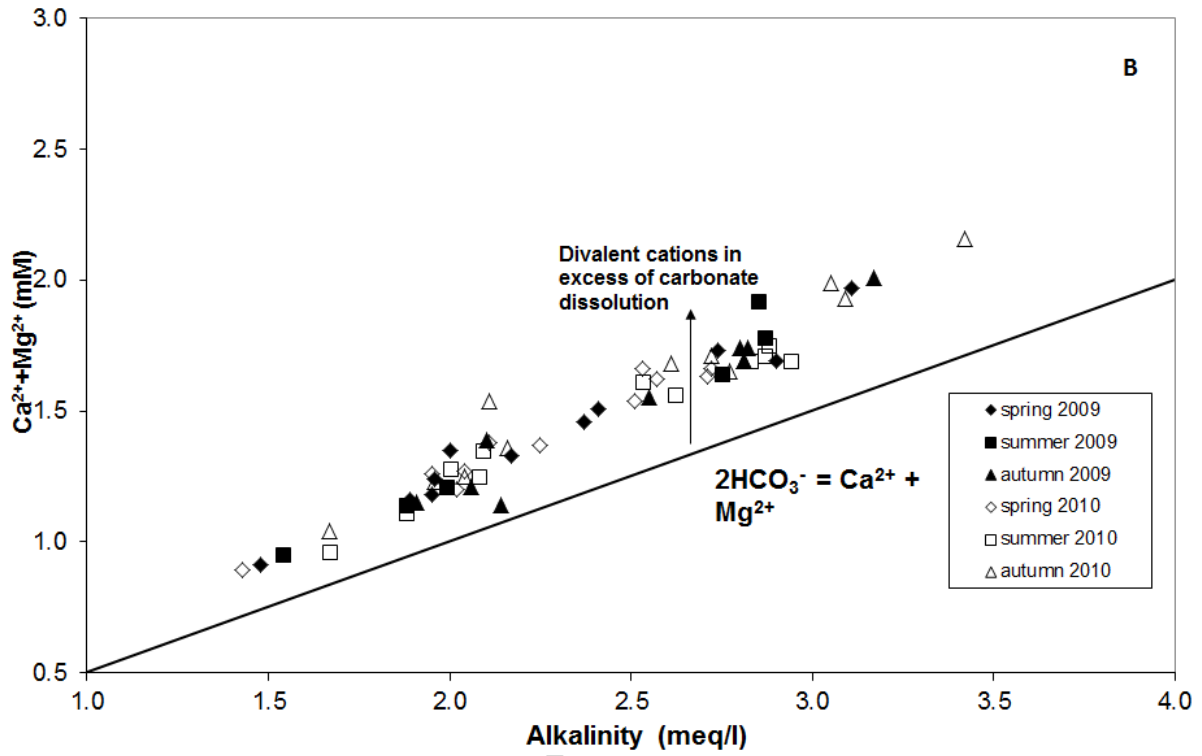


Figure 2 B

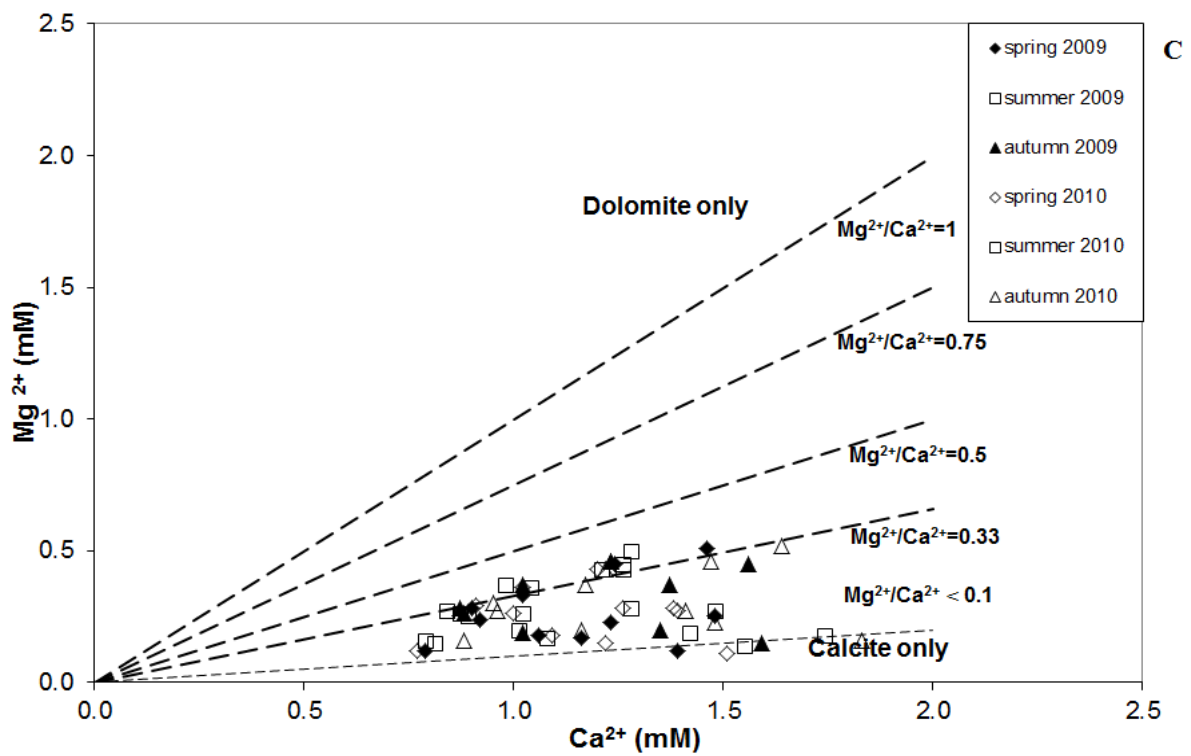


Figure 2 C

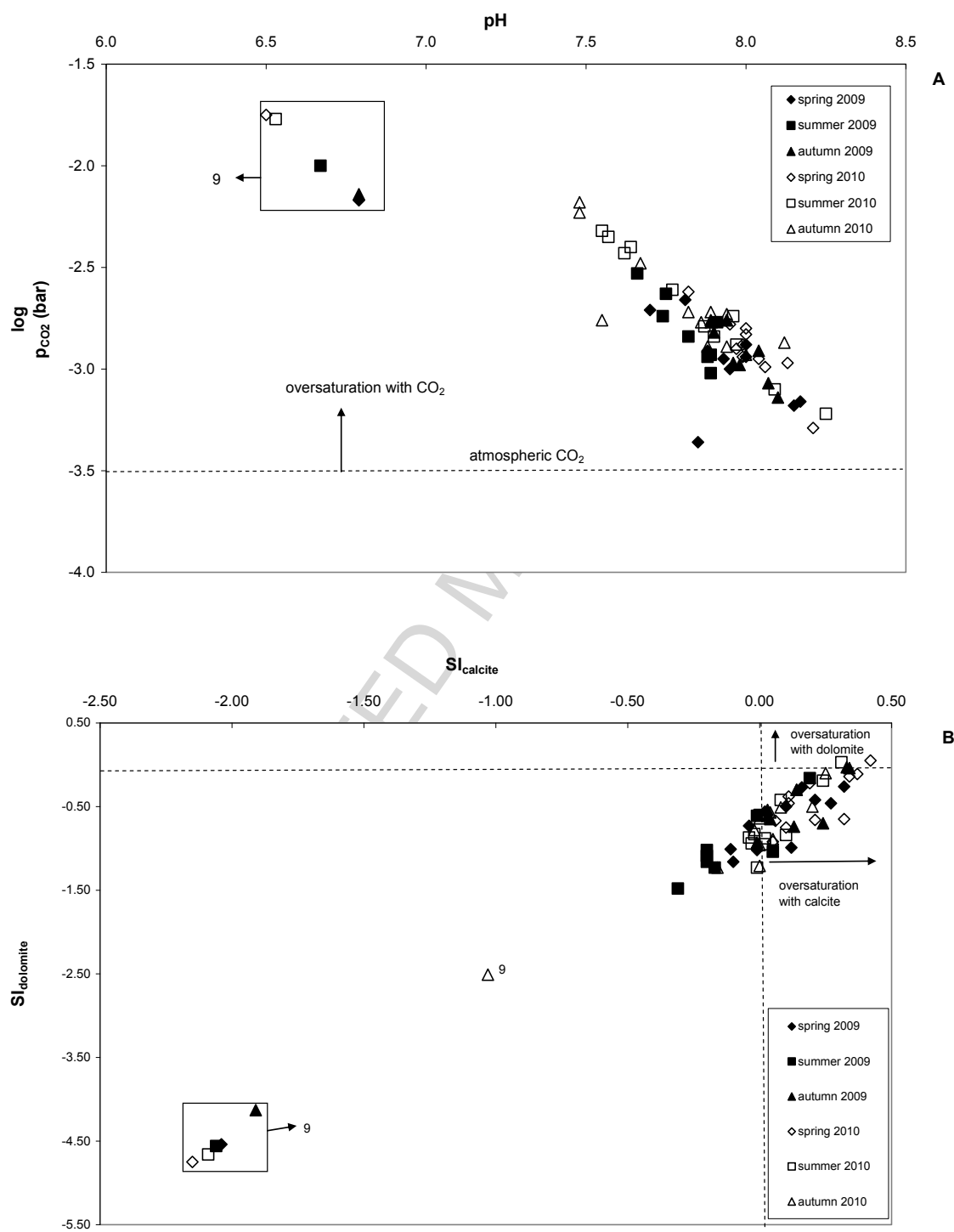


Figure 3

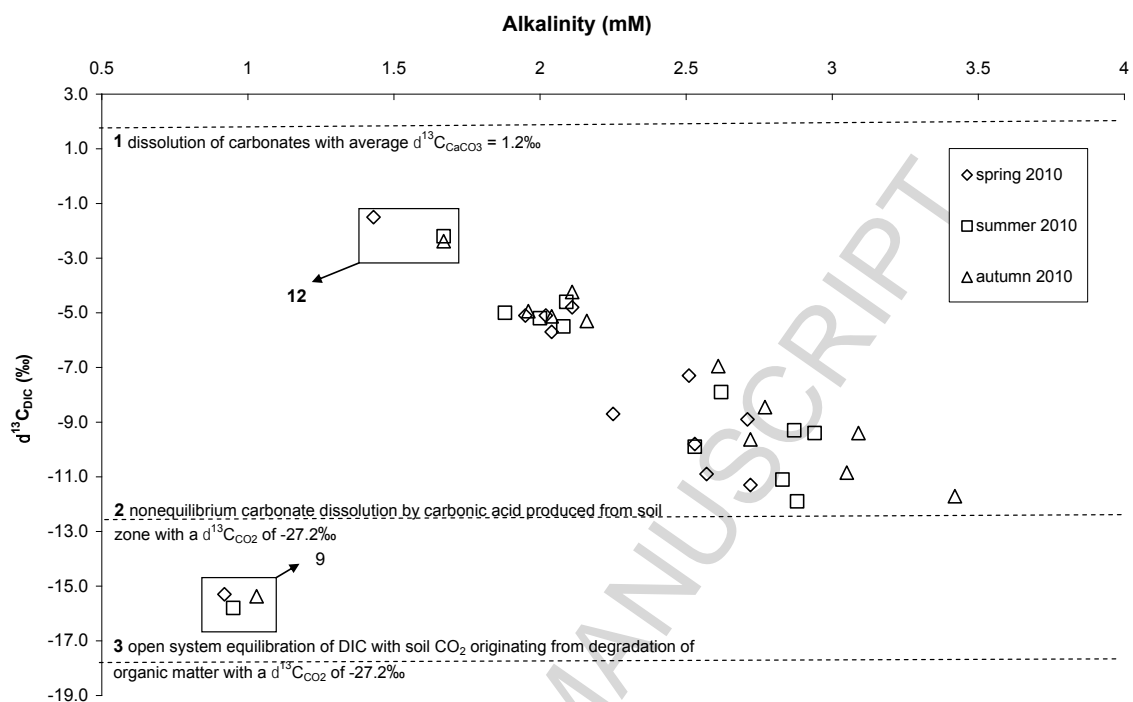


Figure 4

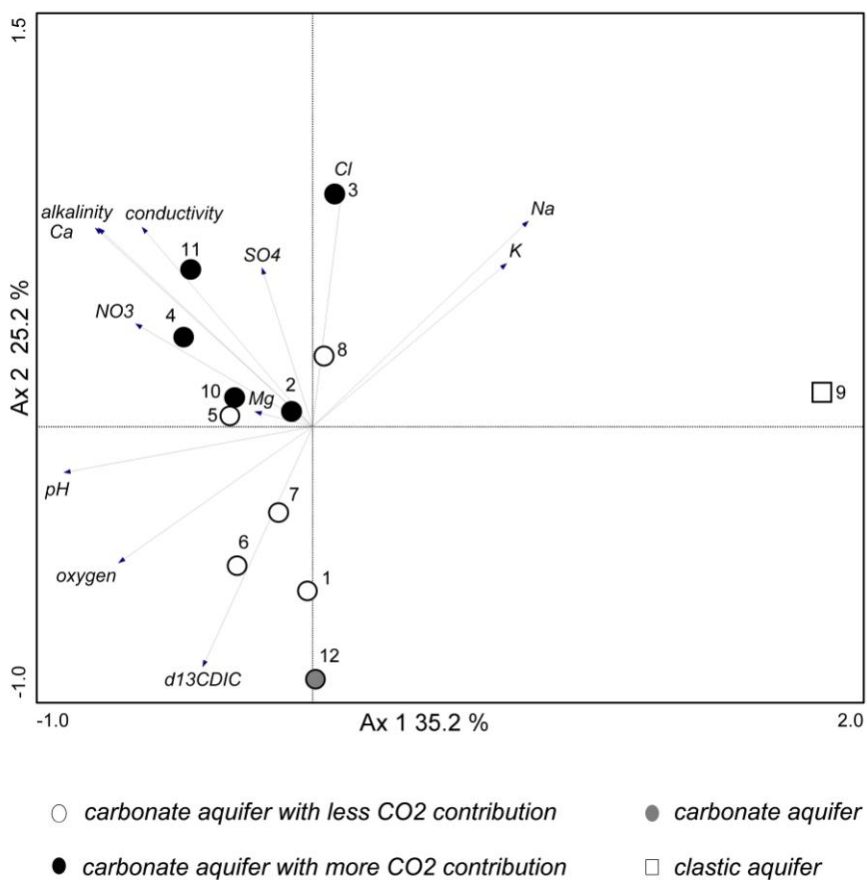


Figure 5

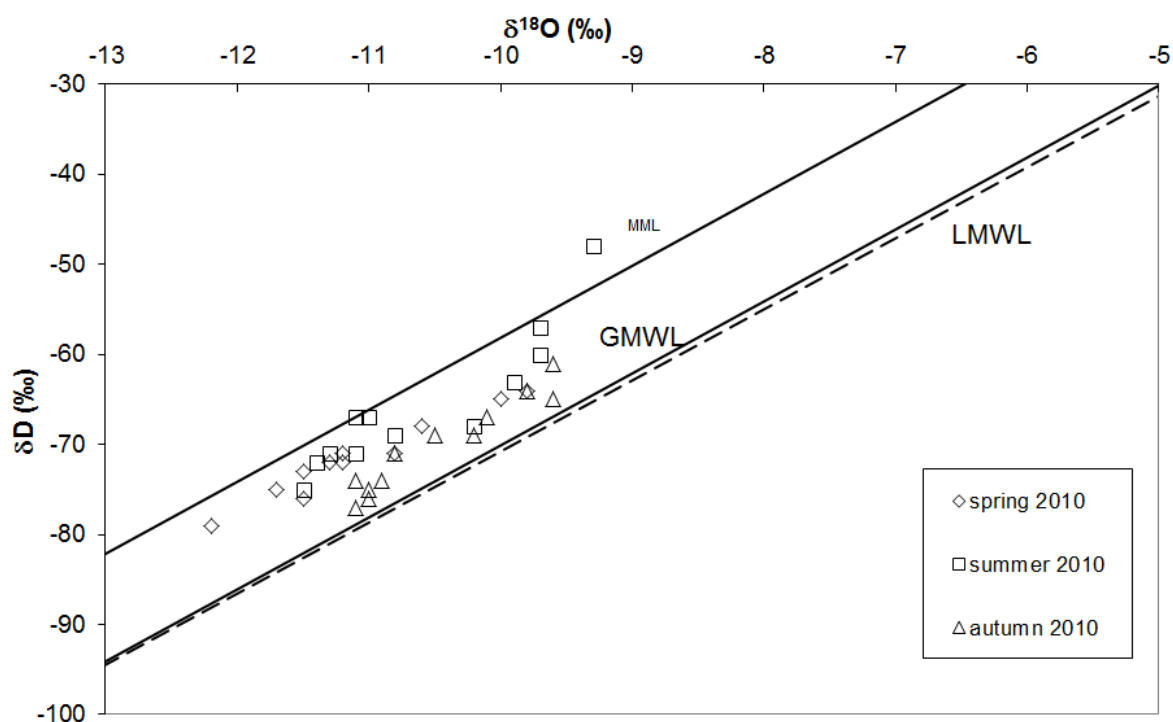


Figure 6

Highlights

- In this study we examine water chemistry and carbon cycling of Alpine springs.
- The major solute composition was dominated by dissolution of calcite.
- More negative $\delta^{13}\text{C}_{\text{DIC}}$ values indicated less vulnerable aquifers.
- Isotopic composition of oxygen indicates recharge from precipitation.
- The age of springs was estimated according to tritium up to 5 years.