GEOLOGIJA 53/1, 37-46, Ljubljana 2010
https://doi.org/10.5474/geologija.2010.003

Geochemical characteristics of surface waters and groundwaters in the Velenje Basin, Slovenia

Geokemične značilnosti površinskih in podzemnih vod v Velenjskem bazenu

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Prejeto / Received 1. 3. 2010; Sprejeto / Accepted 15. 5. 2010

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Key words: geochemistry, stable isotopes, carbon, surface waters, groundwaters, Velenje basin, Slovenia
Ključne besede: geokemija, stabilni izotopi, ogljik, površinske vode, podzemne vode, Velenjski bazen, Slovenija

Abstract

The geochemical and isotopic composition of surface water and groundwaters in the Velenje Basin, Slovenia, were investigated to gain a better understanding of the origin of surface and groundwaters. Surface waters and groundwaters from the Triassic aquifer are dominated by HCO_3^-, Ca^{2+}, and Mg^{2+} from dissolution of carbonate minerals, while groundwaters from the Pliocene and Lithotamnium aquifers have distinct geochemical signatures, enriched in Na^+ and K^+. Surface waters are controlled by calcite dissolution, while groundwaters from the Triassic aquifer are controlled by dolomite dissolution. The partial pressure of CO_2 in surface waters and groundwaters is well above atmospheric concentrations, indicating that these waters are a potential source of CO_2 to the atmosphere. The $\delta^{13}C_{DIC}$ values of surface waters are shown to be controlled by biogeochemical processes in the terrestrial environment, such as dissolution of carbonates, degradation of organic matter, and exchange with atmospheric CO_2, which is more pronounced in the lake waters. The $\delta^{13}C_{DIC}$ values of groundwater from the Triassic aquifer are consistent with degradation of CO_2 and dissolution of dolomite. Groundwaters from the Pliocene and Lithotamnium aquifers have $\delta^{13}C_{DIC}$ values suggestive of biogenic CO_2 reduction and degradation of organic matter.

Izvleček

Raziskane so bile geokemijske in izotopske značilnosti površinskih in podzemnih vod v Velenjskem bazenu. Površinske vode in podzemne vode, ki pripadajo triasnemu vodonosniku imajo kemijsko sestavo HCO_3^--Ca^{2+}-Mg^{2+}, medtem ko imajo podzemne vode, ki pripadajo pliocenskemu in litotamnijskemu vodonosniku drug vir napajanja in so obogatene z Na^+ in K^+. Kemijsko sestavo površinskih vod kontrolira raztapljanje kalcita, medtem ko je kemijska sestava triasnih podzemnih vod kontrolirana z raztapljanjem dolomita. Parcialni tlak je nad atmosferskim CO_2 v površinskih in podzemnih vodah in predstavlja vir CO_2 v ozračje. Vrednosti $\delta^{13}C_{DIC}$ v površinskih vodah so odvisne od biogeokemijskih procesov v terestričnem okolju: raztapljanje karbonatov, razgradnja organske snovi in izmenjava z atmosferskim CO_2, ki se odraža v jezerih. Na vrednosti $\delta^{13}C_{DIC}$ v triasnih vodonosnikih vplivajo razgradnja organske snovi in raztapljanje dolomita, medtem ko na vrednosti $\delta^{13}C_{DIC}$ v pliocenskih in litotamnijskih vodonosnikih vplivata razgradnja organske snovi in bakterijska CO_2 redukcija.

Introduction

The geochemical study of river water allows important information to be obtained on chemical weathering of rocks and soil and the chemical and isotopic compositions of the drainage basin (Gibbs, 1972; Reeder et al., 1972; Hu et al., 1982; Stallard & Edmond, 1983; Goldstein & Jacobsen, 1987; Elderfield et al., 1990; Zhang et al., 1995; Huh et al., 1998). Since carbonate weathering largely dominates the 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 to water solutes (Fairchild et al., 1999, 2000; Gaillardet et al., 1999; Liu & Zhao, 2000). Surface water hydrochemistry depends on multiple natural factors such as the intensity and composition of precipitation, chemical reactions between water and soil or sediment, biochemical reactions, and surface water-groundwater interactions, as well as on anthropogenic activities. The use of stable isotopes of carbon as an additional method is crucial to evaluate biogeochemical processes in rivers (Brunke & Gauser, 1997; Sophacleous, 2002; Wachinew, 2006).

Many hydrogeological studies use stable isotopes of the water molecule to determine groundwater quality, origin, recharge mechanisms, and rock-water interactions. Stable isotopes of carbon, nitrogen and sulphur can give valuable information about reactions involving these elements and to trace biogeochemical processes in aquatic systems (Adelana, 2005). The isotopic characterization of the groundwater is also needed to fully evaluate the processes and origin of gases in coal basins (Aravena et al., 2003).

This paper analyses several lines of evidence, including hydrogeological, chemical, and isotopic information on surface and groundwaters to evaluate different sources of fluids in the Velenje basin. This study represents the systematic study of geochemical (chemical and isotopic) variables of surface and groundwaters and is also a part of major project aimed at evaluating the hydrogeology and hydrochemistry of a coal seam gas (CSG) exploration area and searching for locations of the Velenje basin most appropriate for CO_2 sequestration.

Study area

The study area and geological sketch map are represented on Figure 1 A. The Velenje Basin is situated in the NE part of Slovenia. It is located at the junction of the WNW – ESE – trending Šoštanj Fault and the E – W trending Periadriatic Fault Zone, bounded to the south by the Smrekovec Fault segment. The Šoštanj and Smrekovec Faults were generated due to the collision of continental plates. The study area is within the Southern Karavanke. In the pre – Pliocene basement of the basin, Triassic limestones and dolomites prevail on the north-eastern side of the Velenje Fault. Oligocene to Miocene clastic strata, consisting predominantly of marls, sandstones and volcanoclastics prevail on the south-western side (Figure 1 A). More details about Velenje Basin geology, petrology and tectonics are presented in Brezigar et al., 1988; Markič & Sachsenhofer, 1997, Vrabec, 1999 and the references therein. The age of the groundwater in the Triassic section of the basin was previously investigated by Veselič & Pezdič, 1998, while statistical processing of chemical data of different groundwaters of the Velenje Basin was published in Mali, 1992.

The three artificial lakes investigated in this paper (Lake Velenje, 54 m deep on average; Lake Škale and Lake Družmirje) were formed due to excavation of coal and subsidence of the terrain (Figure 1 B). Lake Velenje was polluted by introduction of ash, transported from the Šoštanj power plant, up until 1983. The lake waters reached a pH of 12. Beginning in 1994, a closed system of deashing was constructed for the power plant, and the quality of surface waters has since improved (Šterbenk & Ramšak, 1995).

The headwaters of the River Paka are in the Volovica on Pohorje Mountain. The streams Bečovnica, Velunja and Toplica flow into the River Paka through Pliocene and Quaternary sediments (Figure 1 B). The River Paka tends to be characterized by flash floods (torrential runoff events), with the highest discharge in the spring (3.52 m^3/s) and the lowest discharge in the summer (1.86 m^3/s). Upstream of the cities of Velenje and Šoštanj, the River Paka is relatively pristine. Near Velenje and Šoštanj, the River Paka becomes highly polluted from sewage sludge discharge (Gams & Zupan,

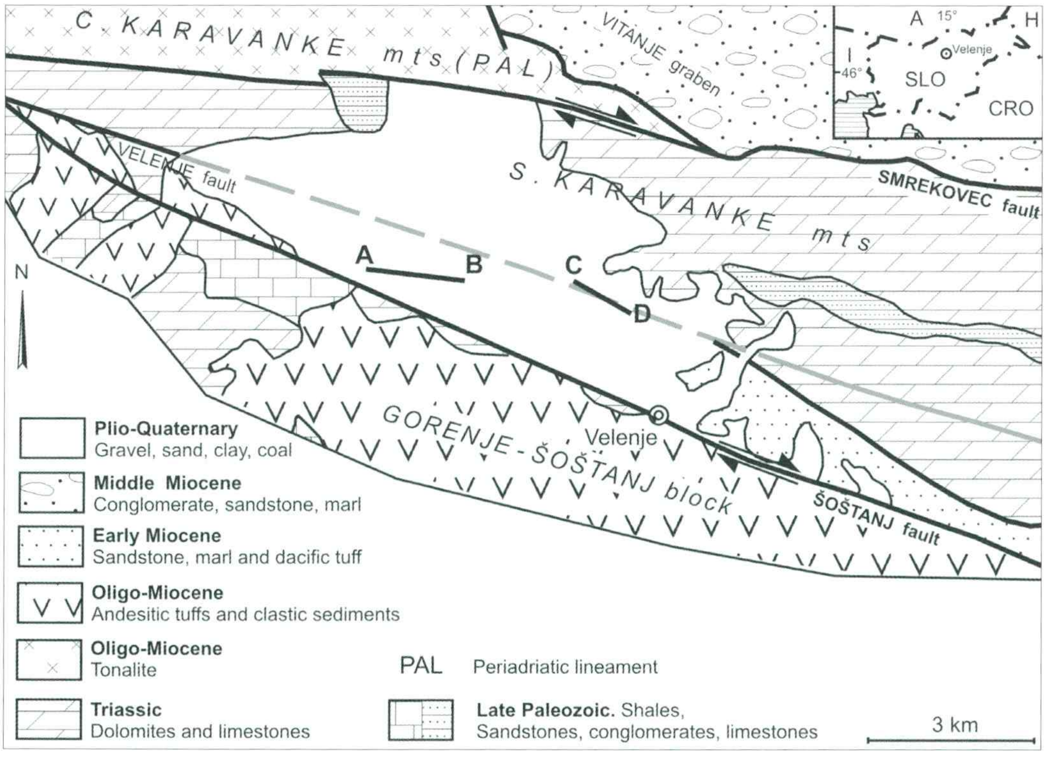


Figure 1 A. Geological sketch map of the Velenje Basin is also presented. Profiles A-B and C-D present locations of groundwater sampling.

1994). In the Velenje area the watershed of the River Paka is composed of Triassic limestone and Pliocene and Quaternary sediments.

The headwaters of the River Velunja drain rocks and sediments of the Velunja overthrust belt, composed of sericite and chlorite schist with sandstones and diabase of Ordovician and Devonian age. In the central part of the River Velunja drainage area, the watershed is composed of rocks of Miocene age, which were deposited on Devonian schist, composed of conglomerate, sandstones and clays. In its lower reach the River Velunja drains Pliocene and Quaternary sediments composed of sands, clays and gravels (Mioč & Žnidarčič, 1972). The gravels are composed of magmatic and metamorphic rocks, which were eroded from the upper part of the watershed.

The watershed of Rivers Bečovnica and Klančica are composed of limestone, breccias, and sandstones of Permian age and Pliocene and Quaternary sediments composed of gravel and sandy clays. The watersheds of streams Toplica, Lepena, Ljubela are composed of Triassic massive limestone in their upper reaches, while their lower reaches are composed of Pliocene and Quaternary gravels. Discharge from the Topolšica thermal spring contributes to Toplica stream waters. Thermal waters are 29 and 31 °C, discharge at approximately 28 l/s, and come to the surface at the section between the Smrekovec Fault and cross section faults between the contact of Triassic limestone and impermeable Tertiary sediments (Mioč & Žnidarčič, 1972).

Profiles A-B and C-D are presented on Figures 1 A and B. The Velenje coalmine in the Velenje Basin is separated into two parts: the Preloge coalmine and the Škale coalmine; the latter was closed for mining in the year 2008 (Figure 1 B). Groundwater in the Velenje coalmine is drained by hanging filters to prevent ingress of water into the mine. The average discharge of water from Pliocene sands varies from 490 l/min, the average discharge of water from Litotamnium limestone is 24 l/min and the average discharge from Triassic limestone is 236 l/min (Jamnikar & Fijavž, 2006). In the Velenje coal basin, the shallow aquifers are classified as Quaternary or Pliocene aquifers. Pliocene aquifers, found in the Preloge coalmine, are further divided into: 1) aquifers right above the coal (Pl 1), 2) aquifers 20-80 m above the coal (Pl 2), and upper Pliocene aquifers (Pl 3). The Pliocene aquifers are composed of clastic sediments, such as sand and gravel. The northern part of the Preloge coalmine, on the southern side of the Velenje Fault, is underlain by the Lithotamnium limestone (Oligocene and Miocene age) (Figures 1 A and C). The Lithotamnium limestone forms a local lens-shaped aquifer, which is confined by an impermeable barrier. The Škale coalmine contains a Triassic aquifer composed of Scythian and Anisian age limestone and dolomite (Figures 1A and C), which is of interest for water supply management (Fijavž, 2002).

Materials and methods

Sample collection

A map of the sampling locations of surface waters is presented on Figure 1 B. A map of sampling locations of groundwaters is presented on Figure 1 B. Sampling of surface waters and groundwaters was performed in October 2003. Water samples from 10 surface water locations, 3 lakes, and 7 streams were collected (Table 1, Fig. 1B). In addition, 31 groundwaters were collected from Pliocene aquifers (16 samples from P11 and P12 aquifers), 13 groundwaters were collected from Triassic aquifers and 2 groundwaters were collected from Litotamnium aquifers. All water samples were analyzed for geochemical and stable isotopic parameters (Table 2, Fig. 2A). Temperature and pH were measured in the field. Because pH is sensitive

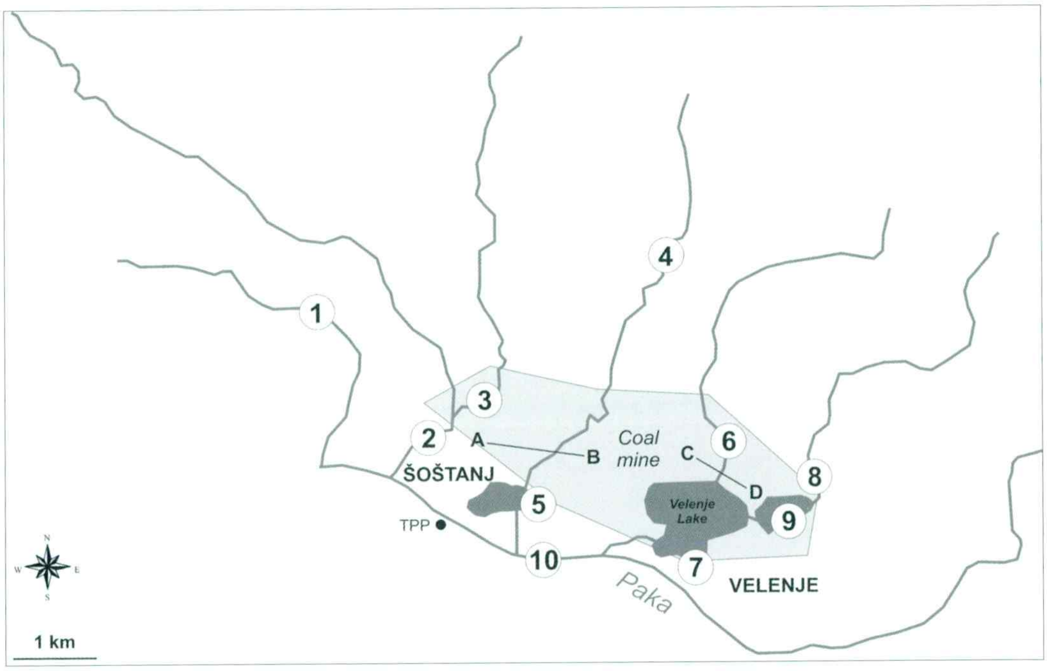


Figure 1 B. Map of surface water sampling locations. Numbers of location correspond to Table 1.

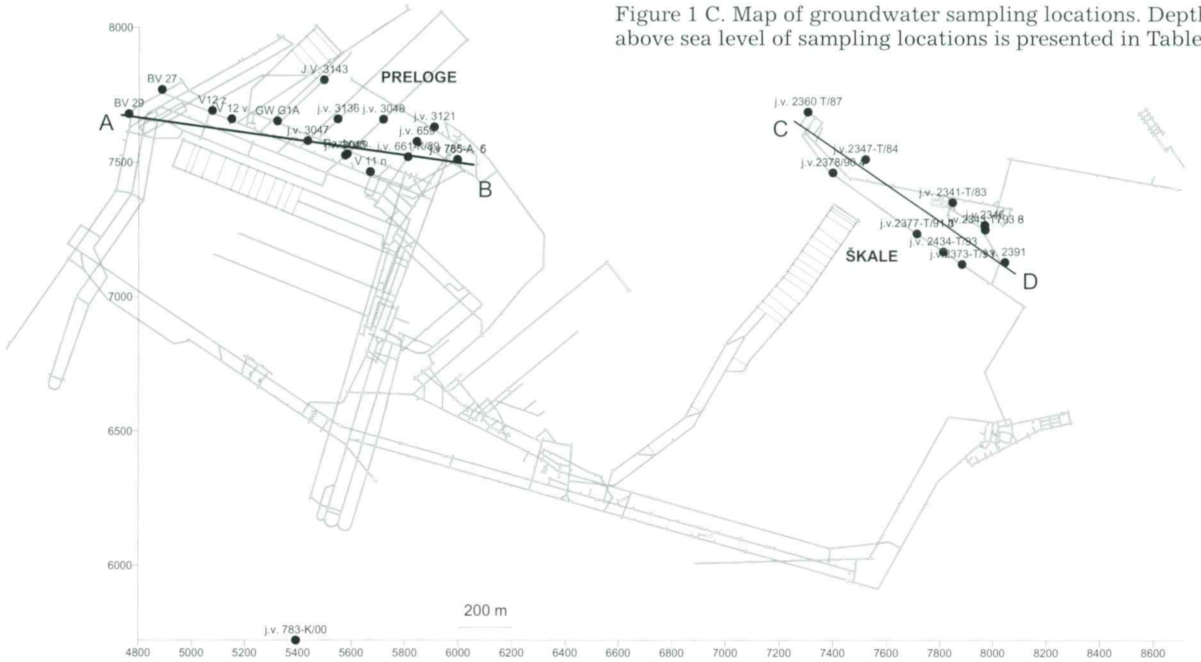


Figure 1 C. Map of groundwater sampling locations. Depth above sea level of sampling locations is presented in Table 2.

Table 1. Chemical and isotopic data for surface waters in the Velenje Basin

Sampling point	Location	T (°C)	pH	Total alkalinity (meq/l)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^{+} (mM)	K^{+} (mM)	Si (mM)	SO_4^{2-} (mM)	NO_3^{-} (mM)	Cl^{-} (mM)	DOC (mg/l)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{18}O$ (‰)
1	River Toplica	9.7	7.73	3.74	1.44	0.33	0.11	0.03	0.13	0.19	0.12	0.09	1.49	-12.6	-8.3
2	River Bečovnica	9.9	7.93	2.71	1.24	0.43	0.31	0.05	0.22	0.26	0.19	0.28	5.90	-11.7	-8.3
3	River Klančica	10.4	7.81	2.83	1.17	0.48	0.42	0.06	0.26	0.20	0.11	0.24	3.17	-12.8	-8.4
4	River Velunja	9.2	8.04	2.69	0.90	0.51	0.16	0.03	0.14	0.28	0.08	0.12		-11.0	-8.6
5	Lake Družmirje	15.0	8.30	2.29	1.01	0.60	0.32	0.07	0.04	0.45	0.04	0.14	6.20	-8.5	-9.8
6	River Ljubela	11.2	8.30	4.61	1.91	0.71	0.23	0.04	0.14	0.16	0.05	0.18		-12.0	-9.2
7	Lake Velenje	18.6	8.22	1.89	3.87	0.57	2.64	1.26	0.02	5.05	0.06	0.76	4.50	-6.6	n.a.
8	River Lepena	17.0	8.48	5.52	1.90	1.05	0.39	0.08	0.09	0.31	0.00	0.41		-10.9	-9.2
9	Lake Škale	16.1	7.95	3.91	1.27	0.99	0.52	0.07	0.03	0.50	0.04	0.27	6.42	-7.5	n.a.
10	River Paka	17.0	8.30	3.15	2.45	0.69	1.45	0.57	0.07	2.27	0.03	0.56	2.91	-8.7	-8.0

Table 2. Chemical and isotopic data for groundwaters dewatering different strata above the coal seam in the Velenje Basin

Location	Depth above sea level (m)	Geology	T (°C)	pH	Total alkalinity (meq/l)	Ca^{2+} (mM)	Mg^{2+} (mM)	Na^{+} (mM)	K^{+} (mM)	Si (mM)	SO_4^{2-} (mM)	NO_3^{-} (mM)	Cl^{-} (mM)	DOC (mg/l)	$\delta^{13}C_{DIC}$ (‰)	$\delta^{18}O$ (‰)
BV 29	417.0	Pliocene1,2	19.0	7.00	19.92	2.18	4.43	3.02	0.14	1.25	0.00	0.02	0.10	7.24	-2.5	n.a.
BV 27	413.0	Pliocene1,2	16.7	7.12	11.92	1.76	2.39	1.65	0.08	0.95	0.00	0.00	0.07	4.00	-3.2	-10.7
V 12 z	387.0	Pliocene1,2	18.6	6.70	32.44	3.61	8.46	4.55	0.19	1.37	0.00	0.00	0.19	6.93	-3.3	-11.3
V 12 v	385.0	Pliocene1,2	18.6	6.50	27.38	3.05	6.89	3.66	0.16	1.26	0.00	0.00	0.15	n.a.	-2.9	n.a.
GW G1A	-61.2	Pliocene 1	n.a.	n.a.	31.64	4.44	5.45	12.42	0.35	0.86	1.11	0.00	0.51	n.a.	-9.1	n.a.
j.v. 3121	-60.0	Pliocene 1	20.1	6.62	32.91	2.86	8.51	8.56	0.14	1.91	0.00	0.00	0.22	6.99	-2.4	-11.1
J.V. 3143	-45.0	Pliocene 1	20.1	6.35	33.53	4.17	8.16	7.30	0.14	1.71	0.00	0.00	0.20	8.22	0.2	-10.8
j.v. 783-K/00	-71.5	Pliocene 1	20.5	6.45	52.15	4.12	15.47	13.09	0.18	1.79	0.20	0.00	0.41	14.69	-2.6	-10.7
j.v. 3136	-63.9	Pliocene 1	20.5	6.49	38.19	3.18	10.11	9.98	0.15	1.84	0.00	0.08	0.23	9.75	-1.7	-10.4
j.v. 3048	-62.0	Pliocene 1	19.5	6.51	25.99	2.52	7.07	5.19	0.11	1.65	0.00	0.01	0.17	5.52	-3.6	-10.5
j.v. 3047	-79.0	Pliocene 1	21.4	6.43	43.09	3.63	12.65	10.33	0.16	1.81	0.01	0.01	0.41	12.56	-3.1	-10.0
j.v. 3045	-91.2	Pliocene 1	20.6	6.36	32.56	2.79	10.01	6.86	0.14	1.76	0.01	0.00	0.21	n.a.	-5.5	-10.4
razbremenilna	-60.0	Pliocene 1,2	20.8	6.53	51.59	3.60	16.34	12.79	0.20	1.91	0.00	0.00	0.40	n.a.	-4.8	-10.5
V 11 n	373.0	Pliocene 1,2	20.1	7.38	61.95	4.25	21.74	11.30	0.26	1.72	0.00	0.00	0.54	n.a.	-3.3	-10.4
j.v. 661-K/89	-106.6	Pliocene 1,2	20.8	7.01	59.78	4.50	20.77	11.45	0.25	1.83	0.01	0.08	0.53	11.99	-3.5	-10.4
j.v. 659	-106.0	Pliocene 1	21.0	6.93	44.33	3.53	13.60	9.47	0.19	1.82	0.00	0.00	0.33	11.44	-2.6	-10.9
j.v 785-A 6	-149.9	Litotamnium limestone	30.2	7.18	39.93	1.19	1.29	54.00	0.50	0.22	0.00	0.00	2.08	152.20	-2.6	-10.7
j.v 785-A 5	-149.7	Litotamnium limestone	30.0	7.30	38.06	1.29	1.22	50.73	0.48	0.23	0.00	0.00	2.01	n.a.	-1.9	-10.7
j.v.2373-T/93	85.9	Triass-anisian	18.4	7.08	9.88	2.37	2.02	0.42	0.03	0.16	1.98	0.01	0.03	2.17	-8.4	n.a.
j.v.2346	121.0	Triass-anisian	17.7	7.06	5.94	2.03	1.54	0.07	0.01	0.16	0.78	0.01	0.05	11.80	n.a.	-9.7
j.v.2343 T793 6	121.0	Triass -anisian	17.1	7.13	5.88	1.99	1.50	0.07	0.01	0.15	0.64	0.00	0.05	1.54	-11.0	n.a.
j.v. 2341-T/83	121.6	Triass-anisian	16.0	7.11	6.68	2.70	1.46	0.10	0.01	0.16	1.06	0.01	0.10	2.53	-17.4	-9.6
j.v.2347-T/84	73.7	Triass-anisian	18.9	6.90	5.79	2.68	1.76	0.17	0.03	0.17	1.81	0.01	0.12	n.a.	-8.7	-9.6
j.v. 2391	85.6	Triass-anisian	14.2	7.08	5.57	1.68	1.34	0.11	0.01	0.11	0.35	0.05	0.11	n.a.	-12.8	-9.5
j.v.2343 T793 3	121.0	Triass-anisian	16.4	7.11	5.79	2.15	1.46	0.07	0.01	0.14	0.56	0.00	0.06	n.a.	-12.5	-9.1
j.v. 2360 T/87	27.0	Triass-scythian	20.6	6.94	5.56	3.19	2.32	1.57	0.08	0.19	3.61	0.00	0.24	2.22	-9.3	-9.6
j.v.2378/90 1	30.2	Triass-scythian	20.1	6.74	6.66	4.46	3.16	1.51	0.08	0.17	5.37	0.01	0.15	n.a.	-8.3	-10.1
j.v.2378/90 4	30.2	Triass-scythian	19.8	6.61	7.65	4.63	2.36	0.91	0.17	0.16	n.a.	n.a.	n.a.	5.76	-10.1	-9.7
j.v.2377-T/91 1	33.6	Triass-scythian	15.3	6.91	6.89	3.68	1.73	0.18	0.02	0.15	2.07	0.00	0.12	2.05	-8.6	-9.8
j.v.2377-T/91 3	33.6	Triass-scythian	18.7	6.58	10.57	3.70	2.38	1.51	0.07	0.14	n.a.	n.a.	n.a.	8.17	-3.2	-9.3
j.v. 2434-T/93	50.0	Triass-scythian	20.0	6.66	n.a.	2.97	1.64	3.98	0.11	0.15	1.44	0.00	0.19	n.a.	-8.1	-9.6

to degassing and warming, water samples were collected in a large volume, air-tight container and the pH was measured at least twice to verify electrode stability. The field pH was determined on the NBS scale using two buffer calibrations with a reproducibility of ± 0.02 pH units.

Sample aliquots collected for chemical analysis were passed through a 0.45 μm nylon filter into bottles and kept refrigerated until analysed. 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 bottles and filled to the top, with no headspace. Samples for $\delta^{18}O$ analyses were collected in HDPE bottles.

Analytical methods

Total alkalinity was measured within 24 h of sample collection by Gran titration (Gieskes, 1974) with a precision of ± 1 %. Concentrations of dissolved Ca^{2+}, Mg^{2+}, Na^+, K^+ and Si were determined using a Jobin Yvon Horiba ICP-OES with an analytical precision of ±2 %. Anions (SO_4^{2-}, NO_3^-, Cl^-) were analyzed on a Dionex ICS-2500 with an analytical precision of ±2 %. Concentrations of DIC were determined on a UIC Coulometrics CO_2 coulometer with a precision of ±2 %. Dissolved organic carbon (DOC) concentrations were measured using high-temperature platinum-catalyzed combustion followed by infrared detection of CO_2 (Shimadzu TOC-5000A) with a precision of ±2 %.

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined with a Europa Scientific 20-20 continuous flow IRMS ANCA - TG preparation module. Phosphoric acid (100 %) was added (100-200 μl) to a septum-sealed vial which was then purged with pure He. The water sample (6 ml) was injected into the septum tube and headspace CO_2 was measured (modified after Miyajima et al. 1995; Spötl, 2005). In order to determine the optimal extraction procedure for surface water samples, a standard solution of Na_2CO_3 (Carlo Erba) with a known $\delta^{13}C_{DIC}$ of –10.8 ±0.2 ‰ was prepared with a concentration of either 4.8 meq/l (for samples with an alkalinity above 2 meq/l) or of 2.4 meq/l (for samples with alkalinity below 2 meq/l).

The isotopic composition of oxygen in water ($\delta^{18}O$) was measured after equilibration with reference CO_2 at 25 °C for 24 h (Epstein & Mayeda, 1953). The measurement was performed on a Varian MAT 250 mass spectrometer. Stable isotope results for O are reported using conventional delta (δ) notation $\delta^{18}O$, in permil (‰) relative to VSMOW. The precision of measurements was ±0.1 ‰ for $\delta^{18}O$.

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

Results and discussion

Major and stable isotope geochemistry of surface waters

Surface waters are primarily composed of HCO_3^-, Ca^{2+} and Mg^{2+} (Table 1). 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 (Figures 2A and 3A). Dissolved Na^+ and K^+ originate from the leaching of feldspars from clastics rocks also composing the watershed. The concentrations of alkalinity varied from 1.89 to 5.52 meq/l, concentrations of Ca^{2+} ranged from 0.9 to 3.87 mM, concentrations of Mg^{2+} from 0.33 to 1.05 mM (Table 1) and are comparable to sampling locations from the River Sava watershed (Kanduč et. al., 2007). Figure 2A presents Ca^{2+} + Mg^{2+} versus alkalinity. Most of the samples have a 2:1 mole ratio of HCO_3^- to Ca^{2+} + Mg^{2+} following the reactions:

Calcite: $CaCO_3 + CO_{2(g)} + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$
Dolomite: $CaMg(CO_3)_2 + 2CO_2 + 2H_2O \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$

Differences in HCO_3^- concentrations in carbonate-bearing watersheds are related to the geological composition of the watershed, relief, mean annual temperature, the depth of the weathering zone, the soil thickness and residence time in the system (Gaillardet et al., 1999). Most surface waters indicate that weathering of calcite is dominant (Figure 2B). A Mg^{2+}/Ca^{2+} ratio around 0.75, which is typical of weathering of dolomite with calcium, is characteristic only in location 9 (Lake Škale). Concentrations of K^+ and Na^+ in surface waters were low, except in Lake Velenje and the River Paka, where higher concentrations were observed (Figure 3). Na^+ and K^+ concentrations are derived from weathering of feldspars in the watershed.

Concentrations of dissolved organic carbon (DOC) ranged from 1.49 to 6.42 mg/l (Table 1), which is typical of unpolluted rivers (Tao, 1998). All of the surface water samples, except for Lake Velenje and River Paka, had low concentrations of dissolved sulfate (<0.50 mM; see Table 1). Sulfate concentrations in Lake Velenje were 5.05 mM, likely due to leaching of sulphur from nearby coal deposits. Sulphur in coal is found in both inorganic and organic forms (Davidson, 1993). Inorganic sulphur in coal is mostly pyrite (FeS_2), with minor amounts of marcasite and sulphates. The sulphate content of coal is usually low unless pyrite has been oxidized. Forms of organic sulphur are less well established (Davidson, 1993). River Boben, which is draining mining area district in Zasavje region (Kanduč, 2006) and River Paka (from this study) had slightly elevated sulfate values (1.13 and 2.27 mM, respectively). Sulfur and oxygen isotopes of SO_4^{2-}, although not measured as part of this study, could help to further elucidate the sources of sulfate to surface waters.

Oxygen isotope values of all surface water samples ranged from -9.8 ‰ to -8.0 ‰ (Table 1). $\delta^{18}O$ values in surface waters are dependent on several factors: precipitation, evaporation, evapotranspiration, infiltration and equilibration with run-off (Yee et al., 1990). Measured $\delta^{18}O$ values in river water are comparable with $\delta^{18}O$ values obtained in the River Sava ($\delta^{18}O$ ranged from -10.0 to -8.8 ‰) sampled in fall 2004 (Kanduč, 2006). More positive $\delta^{18}O$ values could be attributed to evaporation (Gonfiantini, 1986). Carbon isotope values of dissolved inorganic carbon (DIC) ranged from -12.8 ‰ to -6.6 ‰ (Table 1) and indicate different processes in the surface water system: dissolution of carbonates, degradation of organic matter and equilibration with atmospheric CO_2. Calculated CO_2 partial pressure (pCO_2) varied from near atmospheric values (354 ppmv) to values that are over 10-fold supersaturated (3388 ppmv), which is typical of surface water (Kanduč et al., 2007). Higher pCO_2 values are probably due to higher degradation of organic matter in surface waters (Dever et al., 1983).

The $\delta^{13}C_{DIC}$ values of surface waters were used to determine the contributions of organic matter decomposition, carbonate mineral dissolution, and exchange with atmospheric CO_2 to DIC in the watershed. An average $\delta^{13}C_{POC}$ value of –26.6 ‰ was assumed to calculate the isotopic composition of DIC derived from in-stream respiration (see Figure 4). Open system equilibration of DIC with CO_2 enriches DIC in ^{13}C by about 9 ‰ (Mook et al., 1974), thus yielding the estimate of –17.6 ‰ shown in Figure 4. Nonequilibrium dissolution of carbonates with one part of DIC originating from soil CO_2 (–26.6 ‰) and the other from carbonate dissolution with an average $\delta^{13}C_{Ca}$ of 2.0 ‰ (Kanduč et al., 2007) produces an intermediate $\delta^{13}C_{DIC}$ value of –12.3 ‰ (Figure 4). Given the isotopic composition of atmospheric CO_2 (–7.8 ‰; Levin et al., 1987) and equilibrium fractionation with DIC of +9 ‰, DIC in equilibrium with the atmosphere should have a $\delta^{13}C_{DIC}$ value of about 1.6 ‰ (Figure 4). Most surface water samples fall around the line of nonequilibrium carbonate dissolution by carbonic acid produced from soil zone with a $\delta^{13}C_{CO2}$ of -26.6 ‰. Higher $\delta^{13}C_{DIC}$ values were observed in lakes, indicating open system DIC equilibration with the atmosphere since the long residence time of water in lakes allows dissolved CO_2 to equilibrate with the atmosphere.

The calcite saturation index ($SI_{calcite} = \log([Ca^{2+}] \cdot [CO_3^{2-}])/K_{calcite}$; using the solubility products of calcite ($K_{calcite}$)) is near and well above equilibrium ($SI_{calcite} = 0$) and ranges from -0.03 to 1.55, indicating that calcite is supersaturated and precipitation is thermodynamically favoured in most of the surface waters.

Major and stable isotope geochemistry of groundwater

From the geochemical and stable isotope results of sampled groundwater (Table 2) three different aquifers can be identified: 1) A Pliocene aquifer with an alkalinity from 11.92 to 61.95 meq/l, concentrations of Ca^{2+} from 1.76 to 4.50 mM, concentrations of Mg^{2+} from 2.39-21.74 mM, concentrations of Na^+ from 1.65 to 13.09, concentrations of Si from 0.86 to 1.91 mM, $\delta^{13}C_{DIC}$ values from -9.1 to 0.2 ‰, and $\delta^{18}O$ values from -11.3 to -10.0 ‰; 2) A Triassic aquifer with an alkalinity from 5.56 to 10.57 meq/l, concentrations of Ca^{2+} from 1.68 to 4.63 mM, concentrations of Mg^{2+} from 1.34 to 3.16 mM, concentrations of Na^+ from 0.07 to 3.98 mM, concentrations of Si from 0.11 to 0.19 mM, $\delta^{13}C_{DIC}$ values from -17.4 to -3.2 ‰. and $\delta^{18}O$ values from -10.1 to -9.1 ‰; and 3) A Lithotamnium aquifer with an average alkalinity of 39.00 meq/l, an average concentration of Ca^{2+} of 1.24 mM, an average concentration of Mg^{2+} of 1.26 mM, an average concentration of Na^+ of 52.36 mM, an average concentration of Si of 0.23 mM, a $\delta^{13}C_{DIC}$ value of -2.2 ‰, and an average $\delta^{18}O$ value of -10.7 ‰ (Table 2).

Groundwaters from the Triassic aquifer have HCO_3^- to $Ca^{2+} + Mg^{2+}$ ratios close to 2, plotting along the 1:2 line shown in Figure 2A, indicating that weathering of carbonates is the major contributor of solutes, as seen for surface waters. Furthermore, it was found that the Mg^{2+}/Ca^{2+} ratio in the Triassic aquifer is higher than 0.5, indicating that weathering of dolomite is dominant (Figure 2 B). Groundwater from the Pliocene aquifer plots near the 2:1 line, but slightly below (Figure 2A) suggesting contribution of additional cations (Na^+) likely due to cation exchange. In contrast, groundwater from the Lithotamnium aquifer has no relationship to the 1:2 line, plotting with high HCO_3^- and low $Ca^{2+} + Mg^{2+}$ concentrations (Figure 2A). This suggests that carbonate weathering is not an important contributor of solutes to the Lithotamnium aquifer groundwaters.

Groundwaters from the Triassic aquifer have similar major ion chemistries, including K^+, Na^+, Si, Ca^{2+}, Mg^{2+}, and HCO_3^- concentrations as surface waters (Figures 2 and 3), whereas groundwater from the Pliocene and Lithotamnium aquifers display different chemical signatures. Groundwater from the Pliocene aquifer have relatively high K^+, Na^+ and Si concentrations (Figure 3), likely from leaching of feldspars in the aquifer sand, marl and mud units. It cannot be excluded that the water recharging Pliocene aquifers is discharged from the Periadriatic lineament. Groundwater from the Lithotamnium aquifer has low Si concentrations and high Na^+ and K^+ concentrations (Figure 3).

DOC (dissolved organic carbon) was investigated in the aquifers as it plays an important role in reduction-oxidation (redox) reactions. The most common soil–derived organic materials are humic substances, defined by their high molecular weight. In non-contaminated groundwaters, low molecular weight (LMW) compounds make up the remainder of the DOC. LMW DOC includes cellulose, proteins, and organic acids such as carboxylic, acetic and amino acids (Clark & Fritz, 1997). Concentrations of DOC in the Pliocene and Triassic aquifers in the Velenje basin are relatively low

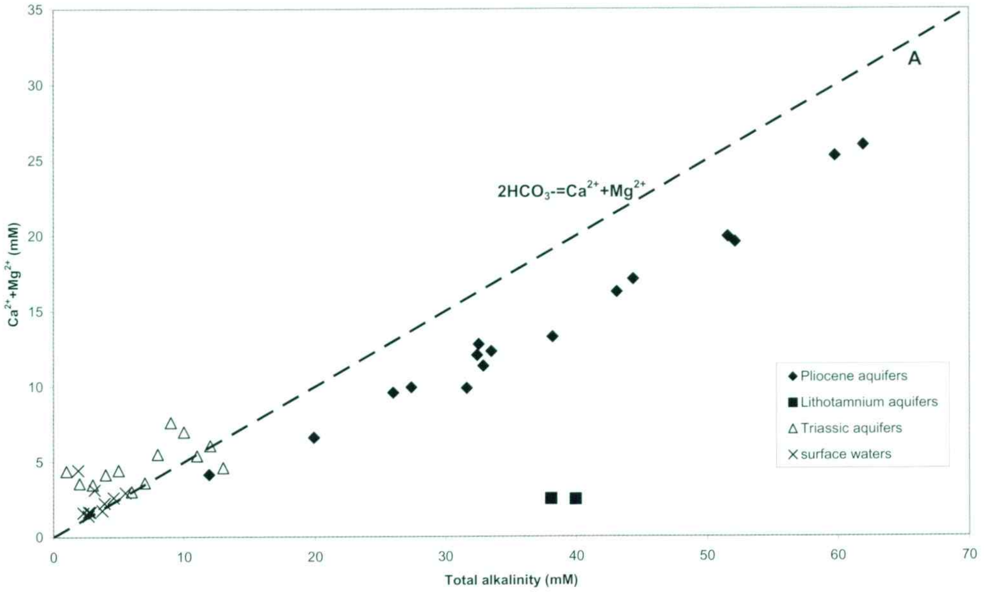
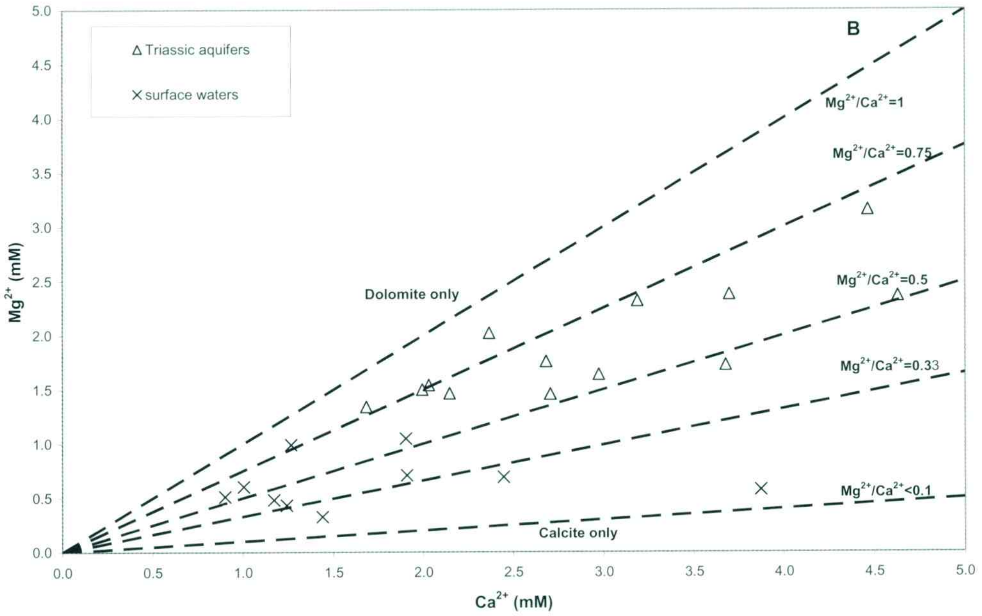


Figure 2. A. $Ca^{2+} + Mg^{2+}$ versus alkalinity concentrations; the dotted line indicates weathering of carbonates.



B. Mg^{2+} versus Ca^{2+} concentrations indicating the importance of dolomite versus calcite weathering.

(from 1.54 to 14.69 mg/l; Table 2). In comparison, groundwaters associated with organic-rich shales in the Michigan Basin contain DOC concentrations up to 840 mg/l (Martini et al., 1996). An elevated concentration of DOC (152.20 mg/l) was measured in the Lithotamnium aquifer, which is probably related to the higher organic matter content compared to the other aquifers.

Calculated CO_2 partial pressures (pCO_2) of groundwater varied from 22908 ppm to 870964 ppm (location j.v. 783-K/00), which is from 57 to 2180-fold supersaturated relative to atmospheric CO_2 (400 ppm; Clark & Fritz, 1997). The calcite saturation index ($SI_{calcite}$) of groundwater was generally well above equilibrium ($SI_{calcite} = 0$), indicating that calcite was supersaturated and precipitation was thermodynamically favoured in samples from the Pliocene and Lithotamnium aquifers ($SI_{calcite}$ ranged from -0.07 to 1.25), while Triassic aquifers were under saturated or close to saturation with respect to calcite ($SI_{calcite}$ ranged from -0.2 to 0.16). Groundwaters belonging to the Triassic aquifer have similar $\delta^{18}O$ values as surface waters, indicating similar water sources. In contrast, Pliocene and Lithotamnium aquifers had lower $\delta^{18}O$ values ranging from -11.3 to -10.0 ‰ (Table 2). $\delta^{18}O$ values from Pliocene and Lithotamnium groundwaters are lower in comparison with groundwaters in the Sava River Basin (Kanduč, 2006). Aravena et al., 2003 found very depleted $\delta^{18}O$ and δD values (around -20 ‰ for $\delta^{18}O$ and -150 ‰ for δD), which were attributed to CO_2 reduction processes.

Figure 4 indicates processes influencing the $\delta^{13}C_{DIC}$ value in groundwaters. It can be seen that groundwaters from the Triassic aquifer have similar $\delta^{13}C_{DIC}$ values as surface waters and fall around the line of nonequilibrium carbonate dissolution by carbonic acid produced from the soil zone with a $\delta^{13}C_{CO2}$ of -26.6 ‰. Groundwaters belonging to the Pliocene and Lithotamnium aquifers have higher $\delta^{13}C_{DIC}$ values, which could be attributed to bacterial CO_2 reduction, causing enrichment with ^{13}C. Investigation of origin of methane in the Elk Valley coalfield, southeastern British Columbia, Canada also confirmed bacterial origin of methane with $\delta^{13}C_{DIC}$ values from monitoring wells up

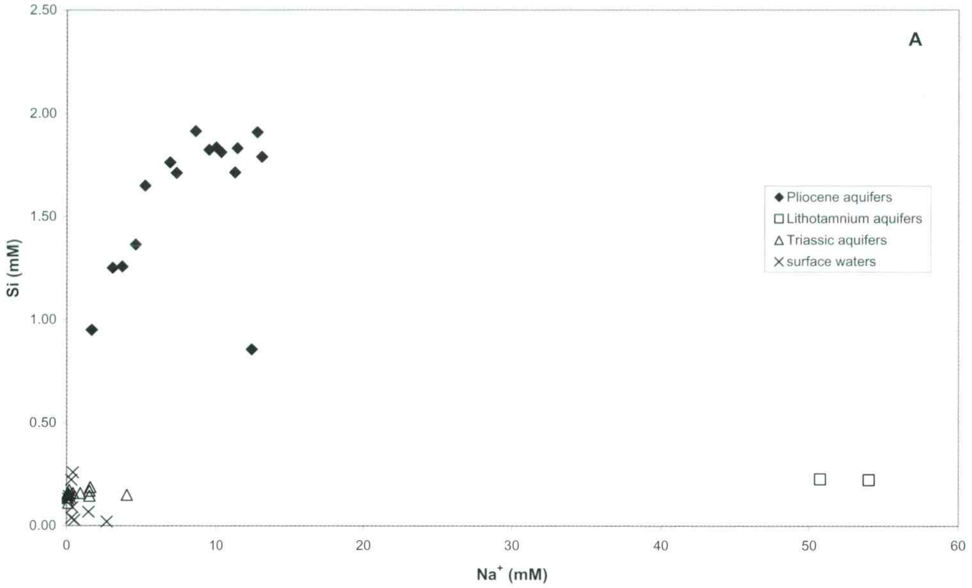
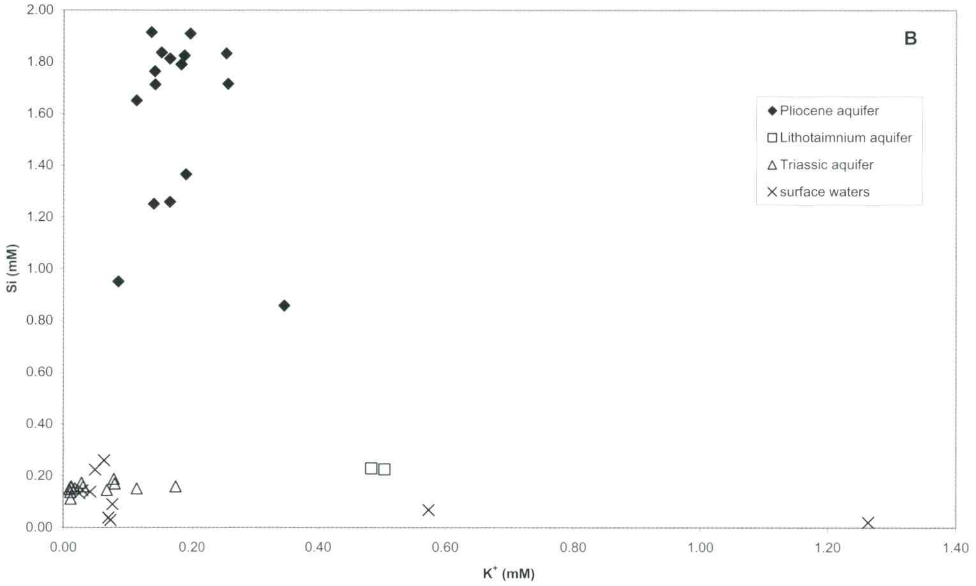


Figure 3. A. Si versus Na^+ concentration of surface waters and groundwaters from the Velenje Basin.



B. Si versus K^+ concentrations of surface waters and groundwaters from the Velenje Basin.

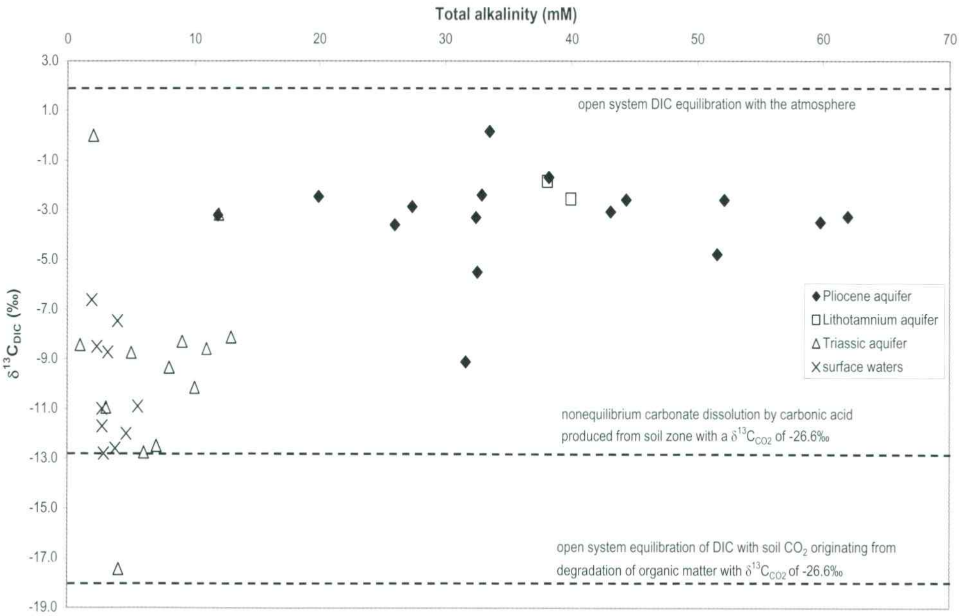


Figure 4. Variation in $\delta^{13}C_{DIC}$ values of surface waters and groundwaters compared to alkalinity concentrations, with lines indicating processes likely occurring in the Velenje Basin. These include values calculated for: 1) open system DIC in equilibration with the atmosphere, 2) nonequilibrium carbonate dissolution by carbonic acid produced from soil zone CO_2, and 3) open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{soil}$ = -26.6 ‰.

to +34.9 ‰ (Aravena et al., 2003). Since groundwaters represent a closed system, the process of open system equilibration with the atmosphere is negligible. The isotopic composition of CO_2 in the Velenje Basin also indicated a bacterial origin (besides endogenic CO_2) of CO_2 and is further discussed in Kanduč & Pezdič, 2005.

Conclusion

The major solute composition of surface waters in the Velenje Basin is dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Total alkalinity concentrations ranged from 2.69 to 5.52 mM in rivers, while in lakes concentrations of HCO_3^- ranged from 1.89 to 3.91 mM. The concentration of solutes decreases according to the sequence $HCO_3^- > Mg^{2+} > Na^+ > Ca^{2+}$ in the Pliocene aquifer, $Na^+ > HCO_3^- > Mg^{2+}$ in the Lithotamnium aquifer, and $HCO_3^- > Ca^{2+} > Mg^{2+}$ in the Triassic aquifer. Alkalinity values reached up to 61.95 mM in the Pliocene aquifer, 39.93 mM in the Lithotamnium aquifer, and 10.57 mM in the Triassic aquifer. Observed $\delta^{13}C_{DIC}$ values in lakes reached up to -7.5 ‰, which is related to longer equilibration time with atmospheric CO_2, while river water had lower $\delta^{13}C_{DIC}$ values similar to those observed in the Triassic aquifer. Higher $\delta^{13}C_{DIC}$ values up to 0.2 ‰ in the Pliocene and Lithotamnium aquifers could be attributed to the bacterial CO_2 reduction process.

Since the Velenje Basin is located in a tectonically complex system, the study confirms the different origins of groundwaters in this area. It seems that Pliocene groundwaters (Preloge mining area) recharging the Velenje Basin are related to coalbed gas generation in the coalbed seam, since waters with high alkalinities (mineralization) accelerate bacterial activity. It still remains a question how much bacterial gas in the Preloge mining area is of recent generation and how much bacterial gas remains trapped in the coalbed seam since formation of the basin. Triassic groundwaters (located in the Škale mining area) have similar chemical and isotopic composition as surface waters and are mostly controlled by dissolution of carbonates and degradation of CO_2.

This study was performed in the framework of a larger study called "Sequestration of CO_2 in geological media: criteria and approach for site selection as a response to climate change" in the Velenje Basin and represents the first results of a systematic study of the chemical and isotopic composition of surface waters and groundwaters in this area. It should be emphasized that the Velenje coalmine is located near Šoštanj power plant, which emits around 4 Mt/year of CO_2 into the atmosphere. Hence the question arises about sequestration of CO_2 in the Velenje Basin to satisfy the Kjoto protocol, which was ratified in the year 2002.

Acknowledgements

This study was conducted in the framework of the project Z1-2052 funded by the Slovenian Research Agency (ARRS) and the Velenje coalmine. The project was also financially supported by the National Science Foundation, USA (NSF-EAR#0208182). The authors are grateful to Mr. Marko Ranzinger and Mr. Igor Medved for technical support and assistance in the field sampling. Sincere thanks to Dr. Anthony Byrne for improving the English of the manuscript.

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