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Hydrogeochemistry and isotope geochemistry of Velenje Basin groundwater

Hidrogeokemija in izotopska geokemija podzemnih vod Velenjskega bazena

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Abstract

The geochemical and isotopic composition of groundwater in the Velenje Basin, Slovenia, was investigated between the years 2014 to 2015 to identify the geochemical processes in the major aquifers (Pliocene and Triassic) and the water–rock interactions. Thirty-eight samples of groundwater were taken from the aquifers, 19 in the mine and 19 from the surface. Groundwater in the Triassic aquifer is dominated by HCO_3^-, Ca^{2+} and Mg^{2+} with $\delta^{13}C_{DIC}$ values in the range from -19.3 to -2.8 ‰, indicating degradation of soil organic matter and dissolution of carbonate minerals. In contrast, groundwater in the Pliocene aquifers is enriched in Mg^{2+}, Na^+, Ca^{2+}, K^+, and Si, and has high alkalinity, with $\delta^{13}C_{DIC}$ values in the range of -14.4 to +4.6 ‰. Based on the $\delta^{13}C_{DIC}$ values in all the aquifers (Pliocene and Triassic), both processes influence the dissolution of carbonate minerals and dissolution of organic matter and in the Pliocene aquifers, methanogenesis as well. Based on Principal Component Analysis (PCA), and on geochemical and isotopic data we conclude that the following types of groundwater in Velenje Basin are present: Triassic aquifers with higher pH and lower conductivity and chloride, Pliocene, Pliocene 1 and Pliocene 2 aquifers with lower pH and higher conductivity and chloride contents, and Pliocene 3 and Pliocene 2, 3 aquifers with the highest pH values and lowest conductivities and chloride contents. $^{87}Sr/^{86}Sr$ tracer was used for the first time in Slovenia to determine geochemical processes (dissolution of silicate versus carbonate fraction) in Velenje Basin groundwater of different aquifers dewatering Pliocene and Triassic strata. $^{87}Sr/^{86}Sr$ values range from 0.70820 to 0.71056 in groundwater of Pliocene aquifers and from 0.70808 to 0.70910 in groundwater of the Triassic aquifer. This indicates that dissolution of the carbonate fraction prevails in both aquifers, while in Pliocene aquifers, an additional silicate weathering prevails with higher $^{87}Sr/^{86}Sr$ isotope ratios.

Izvleček

Raziskali smo geokemično in izotopsko sestavo podzemnih vod v Velenjskem bazenu, za določitev geokemičnih procesov v glavnih vodonosnikih (pliocenskih in triasnem) in interakcij voda–kamnina med letoma 2014 in 2015. Osemintrideset vzorcev podzemnih vod je bilo odvzetih iz vodonosnikov, od tega 19 iz jame in 19 s površine. V podzemni vodi triasnega vodonosnika prevladujejo ioni HCO_3^-, Ca^{2+}, Mg^{2+} , $\delta^{13}C_{DIC}$ vrednosti pa se gibljejo od -19.3 do -2.8 ‰, kar kaže na razgradnjo organske snovi in raztapljanje karbonatnih mineralov. Podzemna voda pliocenskega vodonosnika je obogatena z Mg^{2+}, Na^+, Ca^{2+}, K^+ in Si in ima višje alkalnosti ter vrednosti $\delta^{13}C_{DIC}$ v razponu od -14.4 do +4.6 ‰. Na $\delta^{13}C_{DIC}$ vrednosti v vseh vodonosnikih (pliocenskih in triasnem) vplivata raztapljanje karbonatnih mineralov in razgradnja organske snovi, v pliocenskih vodonosnikih pa še dodatno metanogeneza. Na osnovi analize glavnih osi (PCA) lahko zaključimo, da imamo v Velenjskem bazenu na osnovi geokemičnih in izotopskih podatkov sledeče tipe podzemnih vod: triasni vodonosnik z višjimi vrednostmi pH in nižjo elektroprevodnostjo ter klorom, pliocenski, pliocenski 1 in pliocenski 2 vodonosniki z nižjim pH in višjo elektroprevodnostjo in vsebnostjo klora, in pliocenski 3 in pliocenski 2, 3 vodonosniki z višjim pH in nizko elektroprevodnostjo in vsebnostjo klora. V tej študiji smo uporabili nov sledilec izotopskega razmerja $^{87}Sr/^{86}Sr$, katerega vrednosti se gibljejo od 0,70820 do 0,71056 v pliocenskem vodonosniku in od 0,70808 do 0,70910 v triasnem vodonosniku. $^{87}Sr/^{86}Sr$ kaže, da v obeh vodonosnikih prevladuje raztapljanje karbonatov, intenzivnejše pa je raztapljanje silikatnih mineralov v pliocenskem vodonosniku z višjim izotopskim razmerjem $^{87}Sr/^{86}Sr$.

Introduction

The Velenje Basin in Slovenia is one of the largest actively mined coal basins in central Europe, producing around 4 million tons of lignite per year (Mihelak, 2010). Large amounts of groundwater are extracted from Velenje Basin aquifers to facilitate underground mining of coal, and coal seam gas outbursts are a serious mine safety concern (Kanduč et al., 2011; Kanduč et al., 2015a). The main problem in the past production years of Velenje lignite mine has been the groundwater standing directly over the main production lignite strata inside the Pliocene's clastic rocks. In the 1970's many groundwater intrusions occurred in the mine. To reduce the hydrostatic pressure during the last four decades, advanced and massive dewatering works have been performed. As a result, constant water pumping in the production area and its surroundings has produced a typical dewatering groundwater cone (Vižintin et al., 2009).

Hydrogeochemistry and stable isotope compositions of groundwater provide critical information regarding water–rock interaction along flow paths, and mixing of distinct groundwater bodies (Cartwright et al., 2012). Groundwater geochemistry, especially where aquifers have contrasting mineralogy, is an effective method of determining regional scale inter-aquifer flow and patterns of recharge (Dogramaci & Herczeg, 2002; Edmunds, 2009; Cartwright, 2010). In this study we use major ion geochemistry and environmental isotopes to constrain geochemical processes in groundwater of Velenje Basin. In addition, characterization of geochemical properties of groundwater may further aid in understanding of hydrocarbon entrapment and mineral deposition, and help in identifying the origin of fluids (Aravena et al., 2003).

Concentrations of dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}C_{DIC}$) are governed by processes occurring in the water system. Changes of dissolved inorganic carbon concentrations result from addition or removal of carbon from the DIC pool (Atekwana & Krishnamurthy, 1998). The major sources of carbon to the groundwater DIC system are the dissolution of carbonate minerals, and soil CO_2 derived from root respiration and from microbial decomposition of organic matter. Constraining water-rock interaction, evapotranspiration, dissolution and precipitation of minerals, ion-exchange and groundwater mixing are all required to understand and manage hydrogeological systems (Cartwright et al., 2007).

The use of strontium isotopes in hydrogeological studies has many applications. First, minerals that interact with groundwater and surface water exhibit a wide and predictable range of $^{87}Sr/^{86}Sr$ ratios. ^{87}Sr is produced by the decay of ^{87}Rb with a half-life of 48.8 Ga (Faure, 1991). Strontium derived from K-rich minerals such as biotite and K-feldspar, have high $^{87}Sr/^{86}Sr$ ratios, minerals such as plagioclase that have lower K/Ca ratios will contain strontium with moderate $^{87}Sr/^{86}Sr$ ratios, while the strontium in Ca-rich minerals such as calcite or gypsum, have low $^{87}Sr/^{86}Sr$ ratios that remain essentially unchanged over time (Faure, 1991; Mcnutt, 2000). The geochemical and isotopic composition of carbon and $^{87}Sr/^{86}Sr$ isotopes of groundwater in the Velenje Basin, combined with mineralogical information, are applied to investigate the groundwater–rock interactions and geochemical processes that contribute to understanding the generation and source of coal seam gases, namely carbon dioxide and methane (Kanduč et al., 2012; Sedlar et al., 2014; Kanduč et al., 2015A).

Study area

The Velenje Basin and associated coal mines are situated in the NE part of Slovenia (Fig. 1). It is situated at the junction of the WNW–ESE trending Šoštanj fault and the E––W trending Periadriatic zone, bounded to the south by the Smrekovec fault segment. The Šoštanj and Smrekovec faults were generated by the collision of continental plates. In general, two hydrogeological systems can be distinguished in the Velenje coal mine (Fig. 1): (1) Plioquaternary and Pliocene aquifers, each composed of gravel, sand and silt, which are further divided to upper, middle and lower aquifers. Below the latter aquifers, Triassic carbonates are present as a basement of the basin. The upper aquifers are schematically divided into Plioquaternary alluvial sediments (not analyzed in this study) and at least three parts of the Pliocene aquifers (Pliocene 1, Pliocene 2, Pliocene 3) and (2) carbonate aquifers, which are further divided into Lower Triassic (Scythian) limestone and dolomite, Anisian dolomite and limestone, and Miocene Lithotamnium limestone (Vižintin et al., 2009 & references therein). Pliocene and Pliocene 2, 3 aquifers were introduced due to the fact that in some cases, it was not possible to attribute the water to a single aquifer, so a combination of all (Pliocene) or two aquifers (Pliocene 2, 3) was used instead. Hydrogeological properties of these dolomites are presented in detail in the works of Verbovšek & Veselič (2008) and Verbovšek (2008a, 2008b). Groundwater recharging the Velenje Basin is drained by hanging filters to prevent inrush of water into the mine. The average discharge of water from Pliocene sands is 800 l/min, while that from Triassic limestone aquifers is 3400 l/min (Supovec et al., 2012a, 2012b). In the Velenje coal basin, the shallow aquifers are part of the Quaternary and Pliocene sections. Pliocene aquifers are further classified as aquifers above the coal 0–20 m (Pl-1), aquifers 20–80 m above the coal, Pl-2, and upper Pliocene aquifers (Pl-3) (Fig. 1).

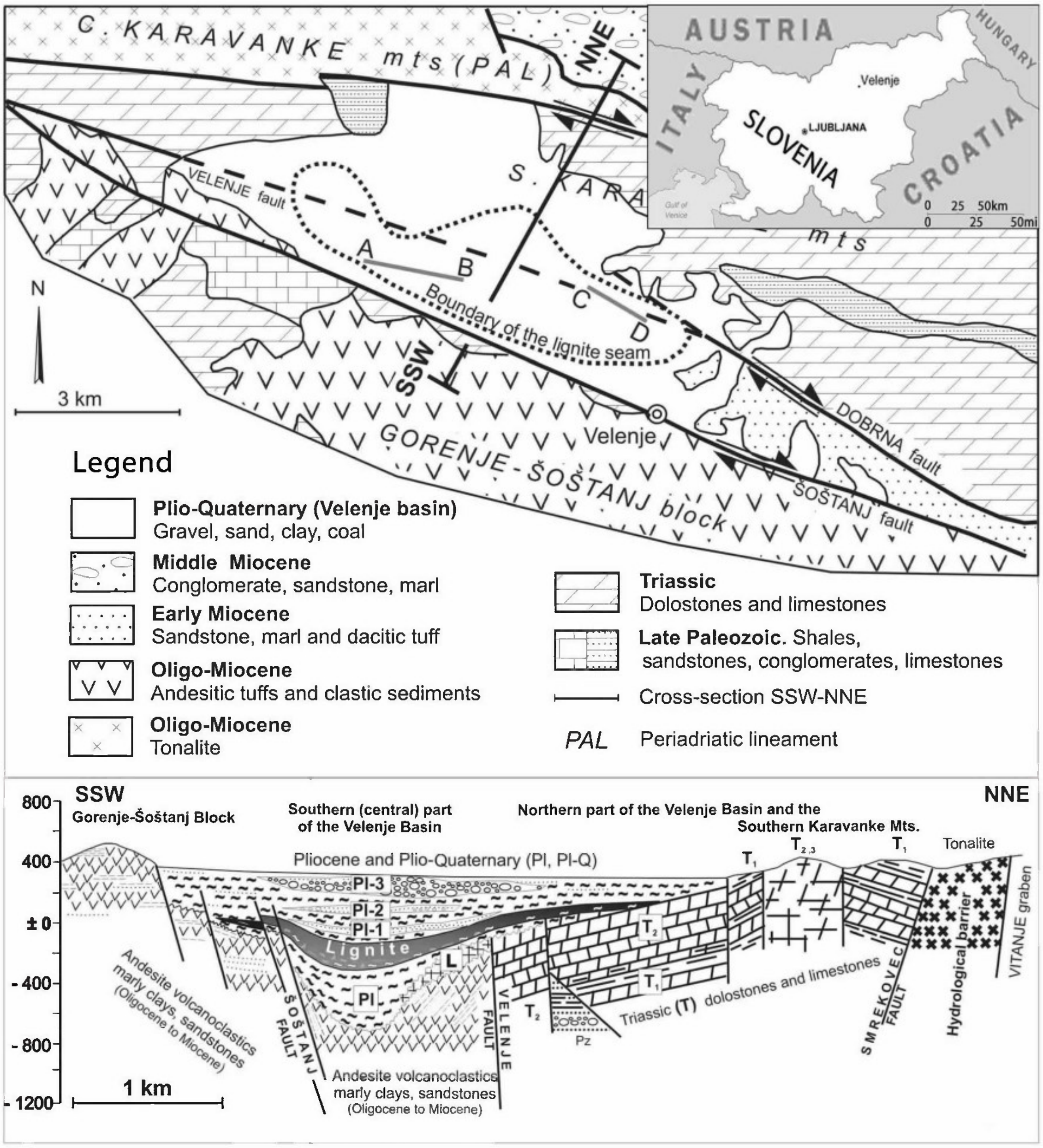

Fig. 1. Geological sketch map (Brezigar et al., 1988) of the Velenje Basin with a NNE-SSW cross section. Main aquifers are Pliocene (Pl$_1$, Pl$_2$ and Pl$_3$), and Triassic (T$_1$, T$_2$ and T$_{2,3}$) dolostones (prevailing) and limestones. Other Triassic and Paleozoic (Pz) lithologies are composed of relatively impermeable strata and therefore do not include significant aquifers. Profiles A-B and C-D show the locations of groundwater sampling in the study of Kanduč et al. (2014).

Materials and methods

In a previous study (Kanduč et al., 2014), only 14 groundwater samples were taken seasonally in Velenje Basin for geochemical and isotope characterization. Due to complex groundwater flow paths in the Velenje Basin, a more dense sampling network was established for investigation, in detail of spatial variability in hydrogeochemistry and isotope geochemistry.

Location of groundwater sampling location is presented on Figure 2. In this study, following locations of groundwater dewatering Triassic and Pliocene strata were sampled: groundwater dewatering Triassic strata (15 locations), Pliocene 2 (10 locations), Pliocene (1 location), Pliocene 1 (9 locations), Pliocene 3 (2 locations), Pliocene 2, 3 (1 location) (Fig. 2).

Samples were taken from: a) overflow piezometers from the surface, b) groundwater samples sampled with Solinst sampler and c) mine wells. Groundwater samples were taken wherever possible since the complete Velenje Basin is subsiding due to mining activity and piezometers are sheared. Altogether 38 samples were taken, 19 from the mine and 19 from the surface. Temperature, pH and electrical conductivity were measured in the field. Some groundwater samples (sampling b) were sampled with a Discrete Solinst Sampler (Kanduč et al., 2014, 2015a), modified for depth measurements and for sampling from depths to almost 400 m. Sample aliquots collected for

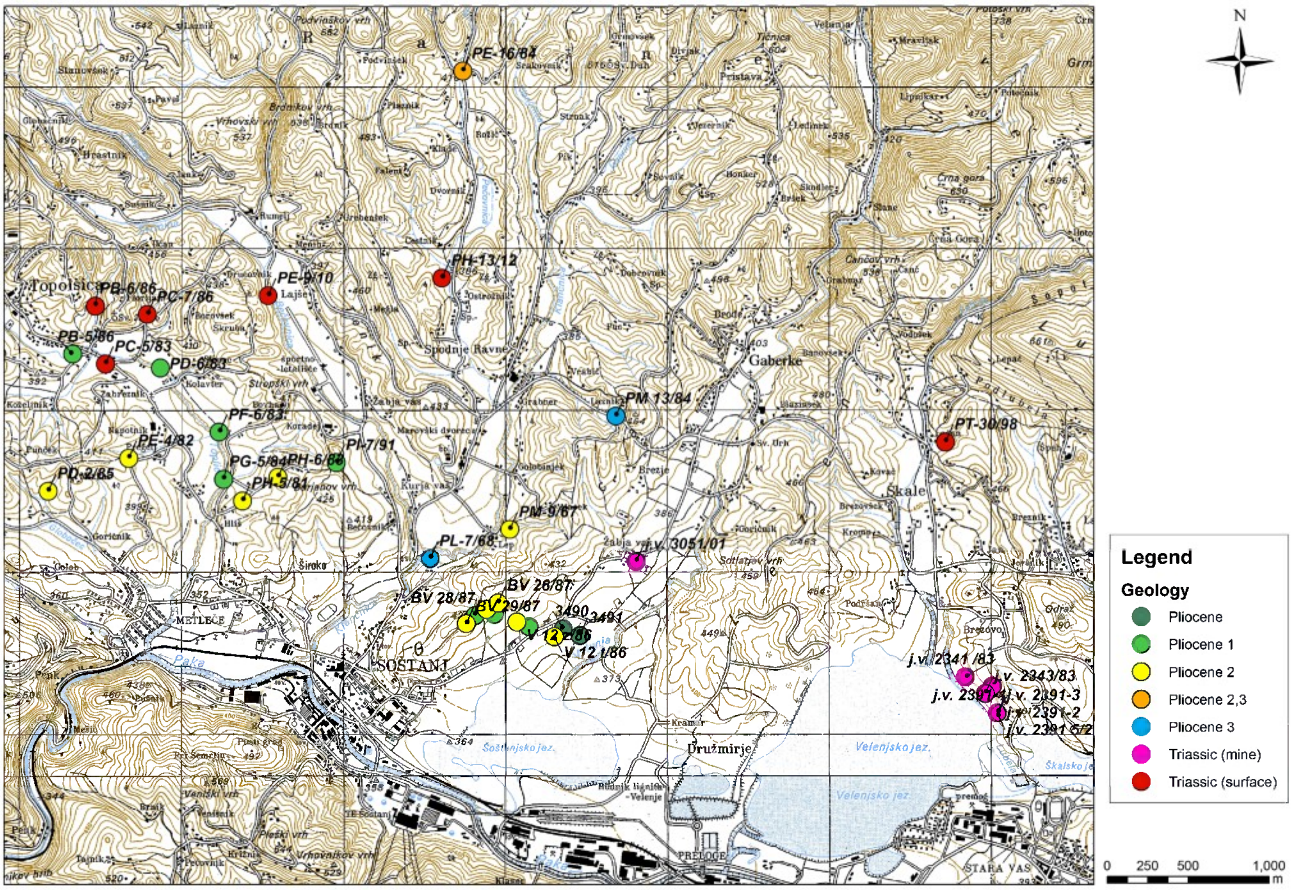

Fig. 2. Sampling locations (38 samples) of groundwater between years 2014 and 015 and located in the Velenje Basin: (a) overflow piezometers (red color) (b) groundwater sampling from the surface of Pliocene aquifers (green, yellow, and brown) and (c) from mining wells (purple color).

chemical analysis (major, trace elements, $^{87}Sr/^{86}Sr$) were immediately passed through 0.45 µ PTFE membranes, which were leached with 1-2 ml of dilute clean HCl, then 2–4 ml of MilliQ water (Millipore) and finally 1–2 ml of the sample itself before collecting the sample filtrate. For cations, $^{87}Sr/^{86}Sr$ and trace element analysis, 30 ml LDPE (Nalgene) bottles were used. The bottles were filled with 10 % HCl leaving some headspace and placed in in a zip lock bag in an oven at 70 °C for one day. The bag was then tightened and left for a second day. The bottles were then rinsed repeatedly with MilliQ water, and filled completely with MilliQ water and capped the bottles. They were finally emptied in a dust free place (fume cupboard) and left until dried. Samples for $\delta^{13}C_{DIC}$ analysis were stored in glass vials filled to the top, with no headspace. Total alkalinity was measured within 24 h of sample collection by Gran titration (Gieskes, 1974) with a precision of ±1 %. Major anions (Cl^-, SO_4^{2-} and NO_3^-) were analyzed (with ± 2 % precision) with a Dionex Ion Chromatograph (IC) Model 3000, using an AS23 analytical column in the Hydrology and Water Resources Department at the University of Arizona (UA).

Major and trace elements (Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}) in water were determined using a quadrupole inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500ce) with a double-pass spray chamber, PTFE 100 L/min nebulizer, platinum cones and sapphire injector within a quartz platinum-shielded torch. The instrument is located in a filtered air positive pressure lab and sample handling and chemistry was routinely performed on laminar flow benches. External calibration curves for all the elements reported were prepared from 1,000 mg/L single element standard solutions in HNO_3 (Inorganic Ventures). Both the samples, blanks and the calibration solutions were prepared in 2.4 % HNO_3 (BDH Aristair Plus). Standard Reference Material (SRM) 1643e ("Trace Elements in Water", National Institute of Standards and Technology, USA) was prepared at 1:20 dilution and run together with blanks, samples and calibration curve. Indium at a concentration of 20 ppb was added to the calibration curve, reference material, samples and blanks as internal standard. Samples were diluted in 1:5 and run with inductively coupled plasma mass spectrometer (MC-ICPMS) in blocks of five samples, two blanks and one SRM. This analysis were performed at University of Utah.

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined on Europa scientific TG isotope ratio mass spectrometer coupled with a ANCA-TG preparation module. Phosphoric acid (100 %) was added (100-200 µl) to a septum tube, then purged with pure He. The water sample (1 ml) was then injected into the septum tube and CO_2 measured directly from the headspace. Two standard solutions of Na_2CO_3

(Carlo Erba and Scientific Fisher) with known $\delta^{13}C_{DIC}$ values of -10.8±0.2 ‰ and -4.8±0.2‰ were used to calibrate $\delta^{13}C_{DIC}$ measurements (Spötl 2005; Kanduč, 2006). This analysis were performed at Jožef Stefan Institute.

Isotopic analysis of strontium was performed using an inductively coupled plasma mass spectrometer (MC-ICPMS) Neptune (ThermoFisher Scientific) at the Department of Geology and Geophysics, University of Utah. Purified fractions, with a strontium concentration around 30 ppb, were introduced in the mass spectrometer through a PTFE nebulizer, quartz double-pass spray chamber, quartz torch and nickel cones.

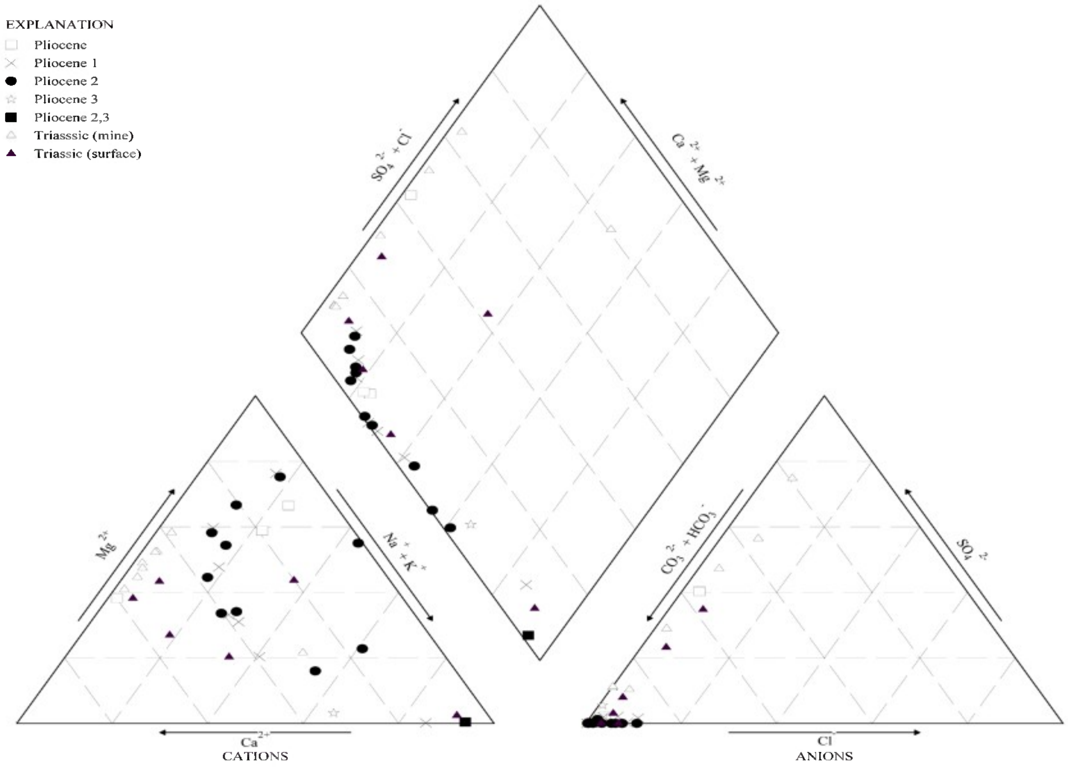

Fig. 3. Piper plot showing the major cation and anion geochemistry of the Velenje Basin groundwater.

Principal component analysis (PCA), based on correlation matrix was used to examine the variation of selected environmental variables (temperature, pH, conductivity, Na^+, K^+, Cl^-, Mg^{2+}, Ca^{2+}, nitrate (NO_3^-), sulphate (SO_4^{2-}) and HCO_3^- ions and $\delta^{13}C_{DIC}$) measured in 38 samples of Velenje Basin groundwater. The CANOCO software package (Ter Braak & Šmilauer, 2002) was applied, and the results presented as an ordination diagram, on which points represent samples and arrows the measured parameters.

Chemical speciation of the carbonate system-e.g. partial pressures of CO_2 (pCO_2), saturation indices of calcite ($SI_{calcite}$) – was evaluated using water composition, pH, alkalinity, and temperature as inputs to the PHREEQC speciation program and employing thermodynamic computations (Parkhurst & Appelo, 1999).

Results and discussion

Groundwater geochemistry of Velenje Basin groundwater

The pH of groundwater in the Triassic aquifers ranged from 6.8 to 8.7 and, in the Pliocene aquifers from 6.6 to 9.7 (Table 1). Dissolved oxygen (DO) was not measured in this study due to risk of explosion (from elevated methane concentration), but it ranges from 10 to 30 % in groundwater dewatering Pliocene strata and from 60 to 80 % in groundwater dewatering Triassic strata (Kanduč et al., 2014). Conductivity ranged from 205.4 to 4410 µS/cm in groundwater dewatering Pliocene strata, and from 232.8 to 4330 µS/cm in groundwater dewatering Triassic strata (Table 1). Only in one sample (j.v. 3051/01, Fig 2), from dewatering Pliocene strata, was very high conductivity found (Table 1). The very high alkalinities can be contributed to by the methanogenesis process, that occurs in the Pliocene groundwaters and are discussed below.

Concentrations of major and minor ions in Velenje Basin groundwater dewatering Pliocene strata and Triassic strata are presented on Figure 3. Groundwater in the Triassic aquifer is dominated by HCO_3^-, Ca^{2+}, Mg^{2+} (mostly water types Ca-Mg-HCO_3 and Mg-Ca-HCO_3), while groundwater in the Pliocene aquifers is enriched in Mg^{2+}, Na^+, Ca^{2+}, K^+ and Si. Total alkalinity of Pliocene aquifers ranges from 1.95 to 44.1 mM in groundwater dewatering Pliocene strata and from 1.3 to 10.4 mM in groundwater dewatering Triassic strata (Table 1). The highest alkalinity

Table 1. List of sampling locations with geochemical parameters (T, pH, conductivity) and selected major ion concentrations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Sr^{2+}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}) and isotopic composition of Sr^{2+} and dissolved inorganic carbon ($^{87}Sr/^{86}Sr$ and $\delta^{13}C_{DIC}$) in Velenje Basin groundwater during the sampling period 2014–2015.

Sample number	Date of sampling	Geology	T (°C)	Cond (µS/cm)	pH	Total alkalinity- (mM)	Total alkalinity- (mg/l)	Na^+ (mM)	Na^+ (mg/l)	Mg^{2+} (mM)	Mg^{2+} (mg/l)	K^+ (mM)	K^+ (mg/l)	Ca^{2+} (mM)	Ca^{2+} (mg/l)	Sr^{2+} (mM)	Sr^{2+} (mg/l)
V 12 t/86	1.4.2014	Pliocene 2	19.4	3340	6.63	42.4	2586.4	4.55	104.65	12.65	307.39	0.25	9.77	3.92	157.19	0.013	1.13
3490	1.4.2014	Pliocene	19.7	2305	6.85	28.0	1708	4.93	113.39	7.14	173.50	0.15	5.86	1.05	42.1	0.003	0.26
j.v. 2346 T/84	1.4.2014	Triassic	16.8	933.6	7.35	5.97	364.17	0.10	2.3	1.39	33.77	0.03	1.17	2.17	87.0	0.003	0.26
j.v. 2370 T/88	2.4.2014	Triassic	17.8	455.0	7.32	1.32	80.52	0.05	1.15	0.55	13.36	0.01	0.39	0.65	26.0	0.002	0.17
j.v.2343/83	2.4.2014	Triassic	16.6	759.6	7.35	5.65	344.65	0.095	2.185	1.66	40.33	0.03	1.17	1.67	66.96	0.005	0.43
BV 28/87	1.4.2014	Pliocene 1	17.3	1117	7.00	12.0	732	1.80	41.4	2.48	60.26	0.11	4.30	1.75	70.17	0.005	0.43
j.v.2391 5/2	2.4.2014	Triassic	14.2	581.4	7.38	5.45	332.45	0.14	3.22	1.43	34.74	0.02	0.78	1.21	48.52	0.002	0.17
j.v. 3051/01	1.4.2014	Triassic	26.7	4330	6.81	10.4	634.4	22.02	506.46	4.94	120.0	0.48	18.76	6.69	268.3	0.044	3.85
V 12 v/87	1.4.2014	Pliocene 1	18.7	2244	6.92	27.2	1659.2	2.41	55.43	6.90	167.67	0.20	7.82	3.35	134.3	0.009	0.78
j.v.2391-2	2.4.2014	Triassic	14.1	581.0	7.42	5.42	330.62	0.13	2.99	1.42	34.51	0.02	0.78	1.50	60.2	0.002	0.17
j.v. 2391-1	2.4.2014	Triassic	14.3	581.3	7.42	5.39	328.79	0.13	2.99	1.39	33.77	0.02	0.78	1.19	47.7	0.002	0.17
j.v. 2391-3	2.4.2014	Triasic	14.1	579.8	7.33	5.09	310.49	0.14	3.22	1.48	35.96	0.02	0.78	0.97	38.9	0.002	0.17
j.v. 2341/83	2.4.2014	Triassic	16.1	1094	7.39	6.30	384.3	0.173	3.979	2.06	50.05	0.03	1.17	2.86	114.7	0.004	0.35
BV 29/87	1.4.2014	Pliocene 2	18.5	2298	6.85	27.1	1653.1	3.31	76.13	7.59	184.4	0.23	8.99	0.72	28.9	0.006	0.52
BV 27/87	1.4.2014	Pliocene 2	16.4	900.7	7.22	9.64	588.04	1.43	32.89	1.92	46.65	0.09	3.51	1.62	64.9	0.005	0.43
V12z/86	1.4.2014	Pliocene 2	18.2	2252	6.89	27.1	1653.1	2.51	57.73	6.75	164.0	0.21	8.21	3.48	139.5	0.008	0.70
3491	1.4.2014	Pliocene	19.9	1848	6.80	21.6	1317.6	4.09	94.07	5.63	136.81	0.12	4.69	1.84	73.8	0.006	0.52
BV 26/87	1.4.2014	Pliocene 2	17.7	1200	7.19	14.2	866.2	1.87	43.01	3.25	78.97	0.12	4.69	1.73	69.4	0.006	0.52
j.v. 3378-K/08	1.4.2014	Pliocene 1	19.3	4410	6.88	44.1	2690.1	6.71	154.33	16.63	404.1	0.32	12.51	1.65	66.2	0.007	0.61
PC-5/83	6.6.2014	Triassic	15.7	616.2	8.14	5.26	320.86	5.78	132.94	0.08	1.94	0.06	2.34	0.21	8.42	0.001	0.08
PB-6/86	6.6.2014	Triassic	14.1	851.1	7.00	8.77	534.97	2.86	65.78	0.88	21.38	0.11	4.30	1.96	78.6	0.005	4.38
PH-13/12	6.6.2014	Triassic	16.2	232.8	8.66	1.50	91.5	0.80	18.4	0.53	12.87	0.067	2.61	0.24	9.6	0.0008	0.07
PT-30/98	6.6.2014	Triassic	14.0	469.9	7.80	4.70	286.7	0.41	9.43	1.21	29.4	0.048	1.87	1.35	54.1	0.006	0.52
PC-7/86	6.6.2014	Triassic	16.6	433.4	7.92	4.22	257.42	0.80	18.4	0.61	14.8	0.040	1.56	1.24	49.7	0.005	0.43
PE-9/10	6.6.2014	Triassic	14.9	388.3	7.57	2.74	167.14	0.16	3.68	0.79	19.19	0.063	2.46	1.18	47.3	0.005	0.43
PH-5/81	25.5.2015	Pliocene 2	16.1	1979	7.50	22.6	1378.6	4.95	113.85	3.02	73.38	0.186	7.27	3.27	131.1	0.011	0.96
PM13/84	26.5.2015	Pliocene 3	16.4	311.1	9.68	3.23	197.03	2.00	46	0.04	0.97	0.017	0.66	0.49	19.6	0.0029	0.25
PE-16/84	26.5.2015	Pliocene 2,3	16.4	205.4	9.68	1.95	118.95	1.82	41.86	0.004	0.097	0.02	0.78	0.05	2.0	0.00034	0.029
PG-5/84	26.5.2015	Pliocene 1	18.0	2276	7.42	27.6	1683.6	6.82	156.86	3.51	85.29	0.19	7.42	4.30	172.4	0.013	1.13
PM-9/67	27.5.2015	Pliocene 2	15.9	1667	8.17	18.9	1152.9	10.2	234.6	1.92	46.65	0.092	3.59	1.36	54.5	0.0125	1.09
Pl-7/68	27.5.2015	Pliocene 3	16.9	639.0	9.55	7.59	462.99	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PH-6/83	27.5.2015	Pliocene 2	17.6	1061	8.40	11.9	725.9	2.52	57.96	1.67	40.58	0.08	3.12	2.01	80.6	0.007	0.61
Pl-7/91	1.6.2015	Pliocene 1	15.8	1744	8.90	6.29	383.69	3.87	89.01	0.004	0.0972	0.51	19.94	0.36	14.4	0.002	0.17
PF-6/83	1.6.2015	Pliocene 1	17.9	1883	7.73	22.1	1348.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	n.a.
PD-6/83	1.6.2015	Pliocene 1	25.1	1811	7.45	20.6	1256.6	7.39	169.97	1.85	44.95	0.00012	0.00046	3.54	141.9	0.011	0.96
PB-5/86	2.6.2015	Pliocene 1	14.3	2617	7.69	30.5	1860.5	6.17	141.91	3.99	96.95	0.51	19.94	4.71	188.9	0.018	1.57
PD-2/85	2.6.2015	Pliocene 2	15.9	1300	8.00	8.01	488.61	3.30	75.9	0.49	11.9	0.06	2.34	0.90	36.1	0.0003	0.02
PE-4/82	2.6.2015	Pliocene 2	16.9	1117	8.10	12.4	756.4	1.52	34.96	1.02	24.8	0.11	4.30	0.017	0.68	0.008	0.70

Sample number	Date of sampling	Geology	Cl^- (mM)	Cl^- (mg/l)	SO_4^{2-} (mM)	SO_4^{2-} (mg/l)	NO_3^- (mM)	NO_3^- (mg/l)	pCO_2 (ppm)	$\delta^{13}C_{DIC}$ (‰)	$^{87}Sr/^{86}Sr$
V 12 t/86	1.4.2014	Pliocene 2	3.51	124.6	n.a.	n.a.	0.11	6.82	575439.9	-3.4	0.70919
3490	1.4.2014	Pliocene	0.87	30.88	0.31	29.8	n.a.	n.a.	245470.9	-0.9	0.70910
j.v. 2346 T/84	1.4.2014	Triassic	0.38	13.49	2.14	205.4	0.005	3.1	16595.9	-9.7	0.70822
j.v. 2370 T/88	2.4.2014	Triassic	0.29	10.29	1.04	99.8	n.a.	n.a.	4265.8	-10.9	0.70808
j.v.2343/83	2.4.2014	Triassic	0.20	7.1	1.19	114.2	n.a.	n.a.	15848.9	-10.7	0.70818
BV 28/87	1.4.2014	Pliocene 1	0.35	12.4	0.12	11.5	0.005	0.31	75857.8	-3.5	0.70931
j.v.2391 5/2	2.4.2014	Triassic	0.25	8.87	0.32	30.7	0.038	2.35	14125.4	-11.9	0.70846
j.v. 3051/01	1.4.2014	Triassic	3.19	113.2	20.2	1939.2	n.a.	n.a.	107151.9	-19.3	0.70869
V 12 v/87	1.4.2014	Pliocene 1	3.13	111.1	0.25	24	0.07	4.34	489778.8	-2.3	0.70925
j.v.2391-2	2.4.2014	Triassic	0.007	0.24	0.33	31.7	0.0006	0.0372	12989.3	-10.3	0.70846
j.v. 2391-1	2.4.2014	Triassic	0.007	0.24	0.32	30.7	0.030	1.86	12589.3	-11.4	0.70845
j.v. 2391-3	2.4.2014	Triasic	0.007	0.24	0.32	30.7	0.045	2.79	14791.1	-12.5	0.70843
j.v. 2341/83	2.4.2014	Triassic	0.56	19.88	3.07	294.7	n.a.	n.a.	15848.9	-9.5	0.70842
BV 29/87	1.4.2014	Pliocene 2	1.54	54.67	n.a.	n.a.	0.105	6.51	229086.8	-2.8	0.70923
BV 27/87	1.4.2014	Pliocene 2	0.18	6.39	0.06	5.8	0.002	0.124	36307.8	-3.5	0.70938
V12z/86	1.4.2014	Pliocene 2	3.26	115.7	n.a.	n.a.	0.063	3.906	208929.6	-1.2	0.70925
3491	1.4.2014	Pliocene	0.53	18.82	0.18	17.3	0.0079	0.4898	213796.2	0.0	0.70907
BV 26/87	1.4.2014	Pliocene 2	0.94	33.4	n.a.	n.a.	1.11	6.82	56234.1	-2.0	0.70820
j.v. 3378-K/08	1.4.2014	Pliocene 1	2.71	96.2	0.50	48	0.11	6.82	331131.1	-2.0	0.70924
PC-5/83	6.6.2014	Triassic	0.38	13.5	n.a.	n.a.	n.a.	n.a.	2041.7	-7.9	0.70912
PB-6/86	6.6.2014	Triassic	0.29	10.3	n.a.	n.a.	n.a.	n.a.	44668.4	-2.8	0.70862
PH-13/12	6.6.2014	Triassic	0.18	6.4	0.44	42.2	n.a.	n.a.	169.8	-6.9	0.70834
PT-30/98	6.6.2014	Triassic	0.20	7.1	0.21	20.2	n.a.	n.a.	3715.4	-8.0	0.70904
PC-7/86	6.6.2014	Triassic	0.19	6.7	0.07	6.72	n.a.	n.a.	2691.5	-9.6	0.70868
PE-9/10	6.6.2014	Triassic	0.201	7.1	0.44	42.2	0.0002	0.0124	3801.9	-6.7	0.70835
PH-5/81	25.5.2015	Pliocene 2	0.145	5.1	0.0139	1.33	n.a.	n.a.	34673.7	2.6	0.70958
PM13/84	26.5.2015	Pliocene 3	0.024	0.9	0.0961	9.2	n.a.	n.a.	46.8	-9.1	0.70972
PE-16/84	26.5.2015	Pliocene 2,3	0.023	0.8	0.002	0.192	n.a.	n.a.	15.8	-14.4	0.71056
PG-5/84	26.5.2015	Pliocene 1	0.2431	8.6	0.012	1.152	n.a.	n.a.	51286.1	4.3	0.70958
PM-9/67	27.5.2015	Pliocene 2	0.2913	10.4	n.a.	n.a.	n.a.	n.a.	6309.6	1.0	0.71002
Pl-7/68	27.5.2015	Pliocene 3	0.090	3.2	0.0065	0.624	0.003	0.186	398.1	1.0	n.a.
PH-6/83	27.5.2015	Pliocene 2	0.0697	2.5	n.a.	n.a.	n.a.	n.a.	2990.9	0.3	0.70975
Pl-7/91	1.6.2015	Pliocene 1	0.58	20.6	0.0059	0.56	n.a.	n.a.	398.1	-12.5	0.70867
PF-6/83	1.6.2015	Pliocene 1	0.187	6.6	n.a.	n.a.	n.a.	n.a.	n.a.	4.6	n.a.
PD-6/83	1.6.2015	Pliocene 1	0.547	19.4	0.00017	0.016	n.a.	n.a.	39810.7	1.8	0.70949
PB-5/86	2.6.2015	Pliocene 1	0.098	3.5	0.003	0.28	n.a.	n.a.	31623.8	4.3	0.70926
PD-2/85	2.6.2015	Pliocene 2	0.032	1.1	0.00078	0.074	n.a.	n.a.	4168.7	-0.3	0.70943
PE-4/82	2.6.2015	Pliocene 2	0.43	15.3	0.0019	0.18	n.a.	n.a.	5248.1	1.6	0.70942

n.a. - not analysed

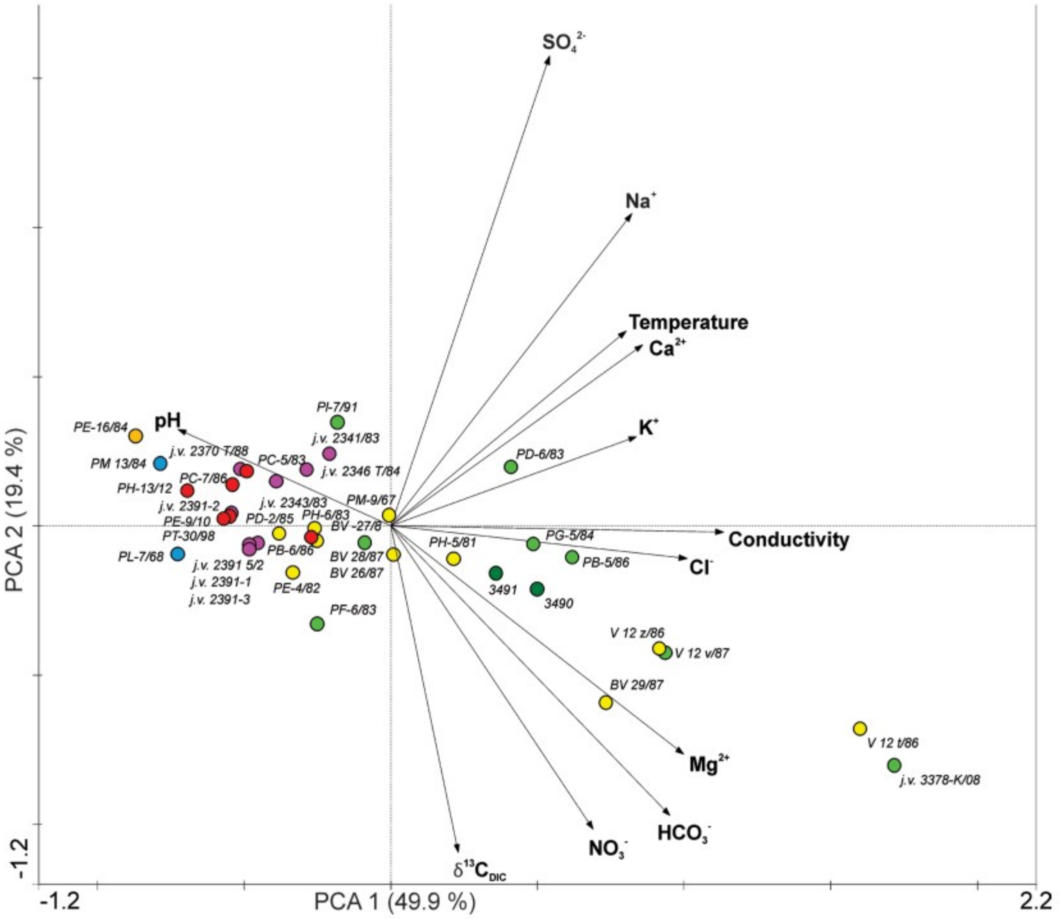

Fig. 4. PCA ordination diagram representing differences between groundwater samples taken during the years 2014-2015 (circles) and the gradients in environmental variables (arrows). Colors of the circles indicate the geology of the aquifer - for the legend see Fig. 2).

(44.12 mM = 2691.32 mg/l) was observed in well 3378-K/08 (Figs. 2, 3) and the lowest alkalinity of 1.32 mM (80.52 mg/l) at location j.v. 2370 T/88 (Figs. 2, 3). Na^+ concentrations range from 0.104 mM (2.38 mg/l) to 10.22 mM (234.0 mg/l), Mg^{2+} concentrations from 0.004 mM (0.097 mg/l) to 16.63 mM (4074. 1 mg/l), K^+ concentrations from 0.0001 mM (0.39 mg/l) to 0.51 mM (19.9 mg/l), and Ca^{2+} concentrations from 0.01 mM (0.401 mg/l) to 4.705 mM (188.5 mg/l) in Pliocene aquifers (Table 1). In groundwater from Triassic aquifer the following concentrations were obtained: Na^+ from 0.056 mM (1.28 mg/l) to 22.02 mM (504.3 mg/l), Mg^{2+} from 0.078 mM (1.89 mg/l) to 4.94 mM (120 mg/l), K^+ from 0.017 mM (0.66 mg/l) to 0.48 mM (18.7 mg/l) and Ca^{2+} from 0.21 mM (8.42 mg/l) to 6.69 mM (268.2 mg/l) mM (Table 1). SO_4^{2-} concentrations in groundwater from Pliocene aquifers are low due to reduction conditions in the aquifer (Kanduč et al., 2014) and range from 0.00078 mM (0.074 mg/l) to 0.50 mM (48 mg/l), NO_3^- concentrations range from 0.0002 mM (0.011 mg/l) to 0.11 mM (6.28 mg/l) mM in groundwater from Pliocene aquifers (Table 1). In addition, SO_4^{2-} and NO_3^- concentrations were low in the Pliocene aquifers (up to 0.5 mM (48 mg/l) and up to 0.11 mM (6.82 mg/l)) compared to groundwater from Triassic aquifer indicating sulfate and nitrate reduction (Kanduč et al., 2014), and consistent with microbial methanogenesis (Coetsiers & Walraevens 2009).

PCA analysis explained 49.9 % of all variability in data by the first, and an additional 19.4 % by the second axis (Fig. 4). Most of the samples are distributed along the first axis, described mostly as differences in pH and conductivity linked to chloride. Higher conductivity and chloride concentrations and lower pH were observed in the groundwater samples originating from Pliocene strata. The second axis represents mainly a gradient in sulfate and $\delta^{13}C_{DIC}$. Generally, the groundwater samples dewatering Triassic strata grouped together in the ordination diagram, while samples of groundwater dewatering Pliocene strata are scattered along both axes, indicating greater variation in measured variables. The outlier sample j.v. 3051/01 is from dewatering Triassic strata, having a high concentration of sulfate, 20.18 mM (1937 mg/l) (Table 1). The lowest $\delta^{13}C_{DIC}$ value of -19.3 ‰ in j.v. 3051/01 indicates greater soil CO_2 degradation in the groundwater. The other two outlier samples (V 12 t/86 and j.v. 3378-K/08) have high alkalinities and conductivities (Table 1).

Dissolution of calcite and dolomite produces groundwater with the molar ratio (Ca^{2+}+Mg^{2+}): HCO_3^- = 1:2. The weathering of dolomite in carbonate systems contributes the majority of the Mg^{2+}, in which Mg^{2+} : Ca^{2+} and Mg^{2+} : HCO_3^- molar ratios indicate the relative proportions of calcite and/or dolomite dissolution (Kanduč

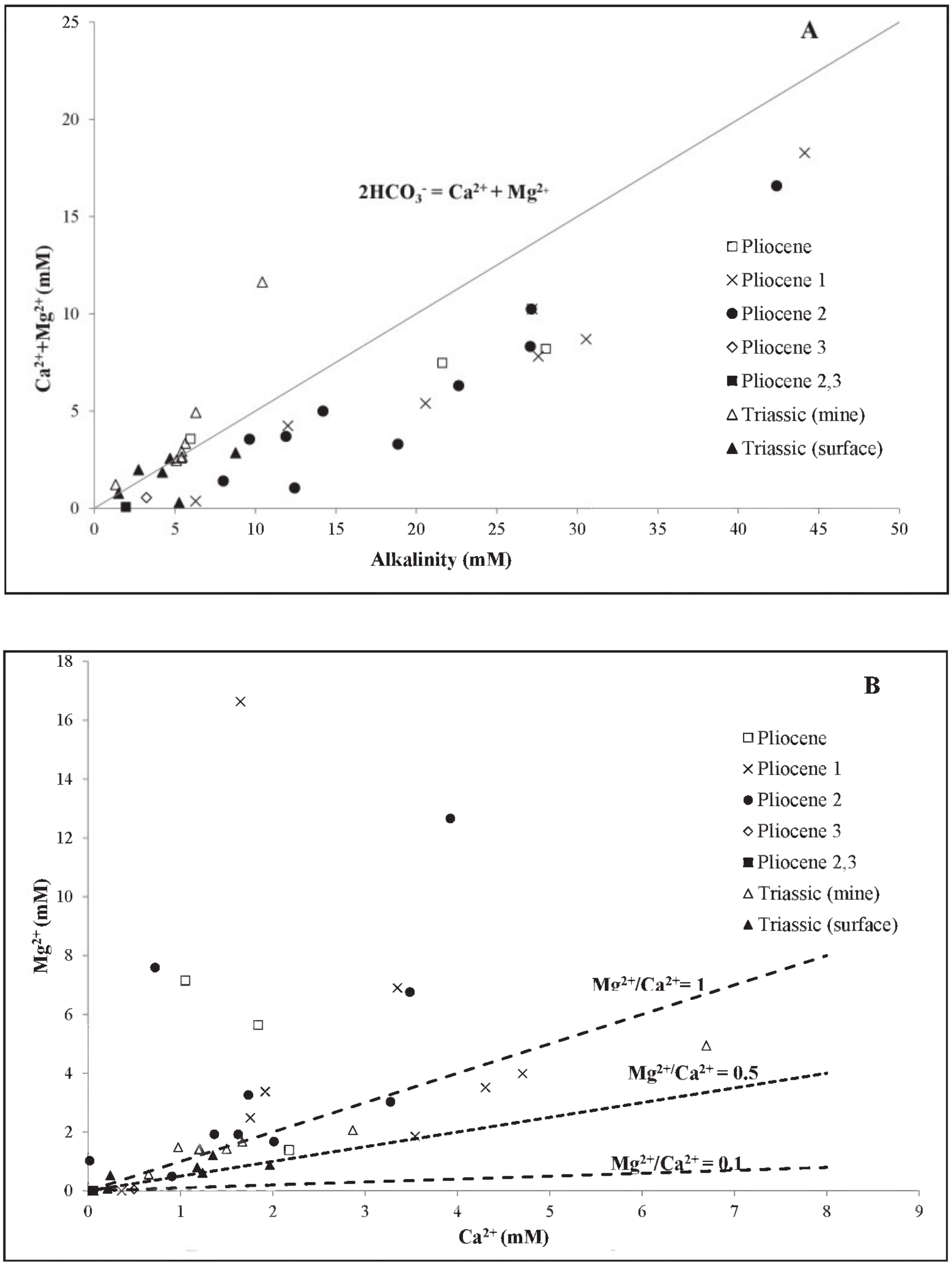

Fig. 5. A. Ca^{2+} + Mg^{2+} versus alkalinity concentrations. The line indicates the stoichiometry for weathering of carbonate minerals. B. Mg^{2+} versus Ca^{2+} concentrations in Velenje Basin groundwater.

et al., 2014). Groundwater dewatering Pliocene strata has higher alkalinity and deviates from the 2:1 groundwater line, while the groundwater in the Triassic aquifer falls along the 2:1 HCO_3^-:(Ca^{2+}+Mg^{2+}) line (Fig. 5A). Dissolution of calcite produces waters with a Mg^{2+} : Ca^{2+} molar ratio of less than 0.1, a ratio of 0.33 in the case of congruent dissolution of calcite and dolomite, and a ratio equal to 1 if only dolomite is dissolving (Szramek et al., 2011). Groundwater in the Triassic aquifer falls between lines 0.5 and 1, indicating weathering of dolomite (Fig. 5B), while groundwater in Pliocene aquifers deviates from the dolomite line (having a slope of 1) indicating that some other minerals (e.g. albite, plagioclase) contribute to alkalinity, already confirmed in previous studies by X-ray diffraction (Kanduč et al., 2014 and references therein).

Carbon cycling and strontium geochemistry of Velenje Basin groundwater

Partial pressures of CO_2 (pCO_2) in groundwater of Pliocene and Triassic aquifers ranged from 15.8 to 575,439.9 ppm and from 169.8 to 107,151.9 ppm, on average 80800 ppm, which is 202 times greater (supersaturated) than that of atmospheric CO_2 concentrations (400 ppm). $SI_{calcite}$ ranged from -0.8 to 1.48 and $SI_{dolomite}$ ranged from -0.32 to 2.93 in Pliocene aquifer. $SI_{calcite}$ ranged from -0.75 to 0.52 in groundwater dewatering Triassic aquifer and $SI_{dolomite}$ ranged from -1.54 to 1.06 in groundwater dewatering Triassic aquifer (Fig. 6). Groundwater samples from the Pliocene and Triassic aquifers therefore have calcite saturation indices ($SI_{calcite}$)

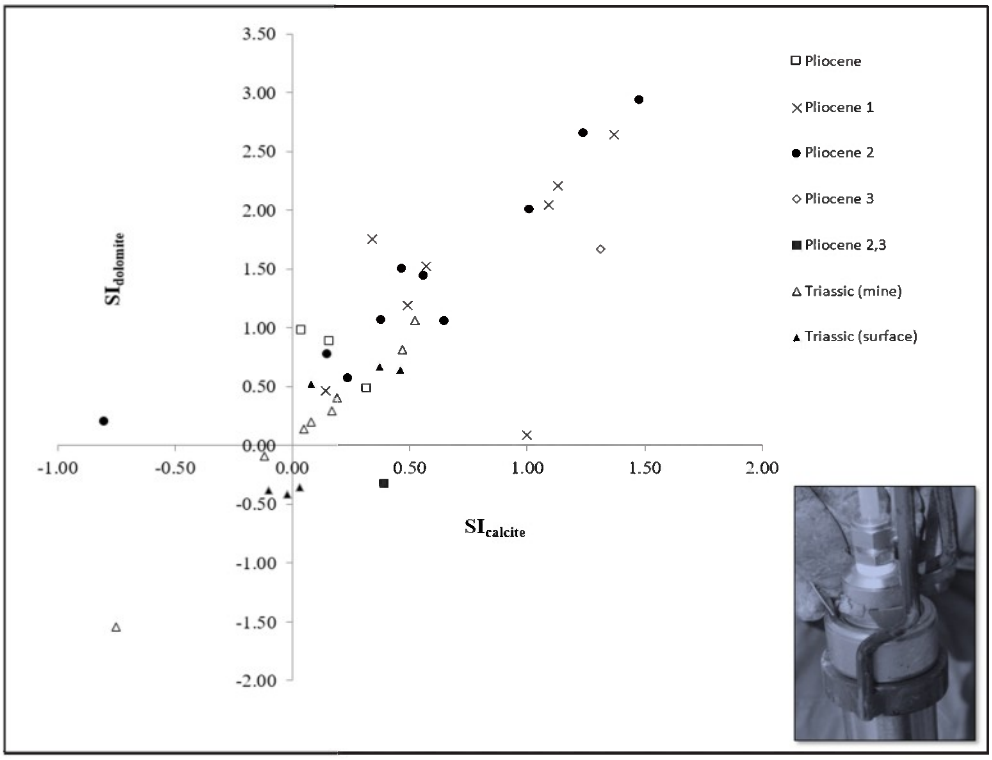

Fig. 6. Saturation index of calcite ($SI_{calcite}$) versus saturation index of dolomite ($SI_{dolomite}$) in the groundwater of the Velenje Basin. Photo on figure 6 represents precipitation of carbonates on a probe of "Solinst sampler".

generally well above the equilibrium ($SI_{calcite} = 0$), indicating that calcite is supersaturated and that precipitation is favored thermodynamically due to high alkalinities, especially in the Pliocene aquifer. Only two samples from mining wells and three samples that overflow dewatering Triassic strata are undersaturated with calcite and dolomite (Fig. 6). We also observed precipitates of dolomite/calcite as visible incrustations in some of the wells. Such incrustations have formed on the well casing, and were scratched from the casing walls when measuring with the Solinst Discrete Interval Probe (photo on Fig. 6).

Values of $\delta^{13}C_{DIC}$ for groundwater of dewatering Pliocene strata ranges from -14.4 to +4.6 ‰. Groundwater dewatering Triassic strata ranges from -19.3 to -2.8 ‰ (Table 1). Geochemical processes influencing the value of $\delta^{13}C_{DIC}$ in groundwater are presented on Figure 7. Groundwater samples from the Triassic aquifer have generally lower $\delta^{13}C_{DIC}$ and are similar to those investigated previously for surface waters (Kanduč et al., 2014). They fall approximately on the line of carbonate dissolution by carbonic acid produced from the soil zone with a $\delta^{13}C_{CO2}$ of -26.6 ‰ (Kanduč et al., 2007). Groundwater samples from the Pliocene aquifers have higher values of $\delta^{13}C_{DIC}$ (up to +4.6 ‰), which are attributed to microbial methanogenesis, causing enrichment in ^{13}C (Kanduč et al., 2012). Isotopic compositions of carbon in methane ($\delta^{13}C_{CH4}$) and of deuterium in methane (δD_{CH4}), analyzed directly from groundwater ranged from -77.7 to -51.4 ‰ and from -246.6 to -162.0 ‰, indicating bacterial gas (Kanduč et al., 2014; Kanduč et al., 2015b). Higher $\delta^{13}C_{DIC}$ values are due to methanogenesis within aquifer and are related to microbial methanogenesis associated with coal seam. We also found microbial gas collected from piezometers (as free gas) in previous studies and its $\delta^{13}C_{CH4}$ have values in the range of -70.5 to -34.2‰ (Kanduč et al., 2012; Kanduč et al., 2014).

Equilibration lines according to possible geochemical processes were calculated as follows:

- *Line 1.* Considering the isotopic composition of atmospheric CO_2 of -7.8 ‰ (Levin et al., 1987) and the equilibration fractionation with DIC of +9 ‰, DIC in equilibrium with the atmosphere should have a $\delta^{13}C_{DIC}$ about +1 ‰ (Fig. 7).
- *Line 2.* Given the average isotopic composition of carbonates ($\delta^{13}C_{CaCO3}$) with a value of -2 ‰ (Kanduč & Pezdič, 2005) and isotopic fractionation (and enrichment in ^{12}C) due to dissolution of carbonates, which is 1.0±0.2 ‰ (Romanek et al., 1992) (Fig. 7) would give a value of $\delta^{13}C_{DIC}$ of 1.0±0.2 ‰.
- *Line 3.* An average $\delta^{13}C$ value of particulate organic carbon (POC) of -26.6 ‰ was assumed to represent the isotopic composition of POC that was transferred to DIC by in stream respiration. Open system equilibration of DIC with CO_2 enriches DIC in ^{13}C by about 9 ‰ (MOOK et al., 1974), which corresponds to the value of -17.6 ‰ (Fig. 7).
- *Line 4.* This represents open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{CO2}$ of -26.6 ‰ (Fig. 7).

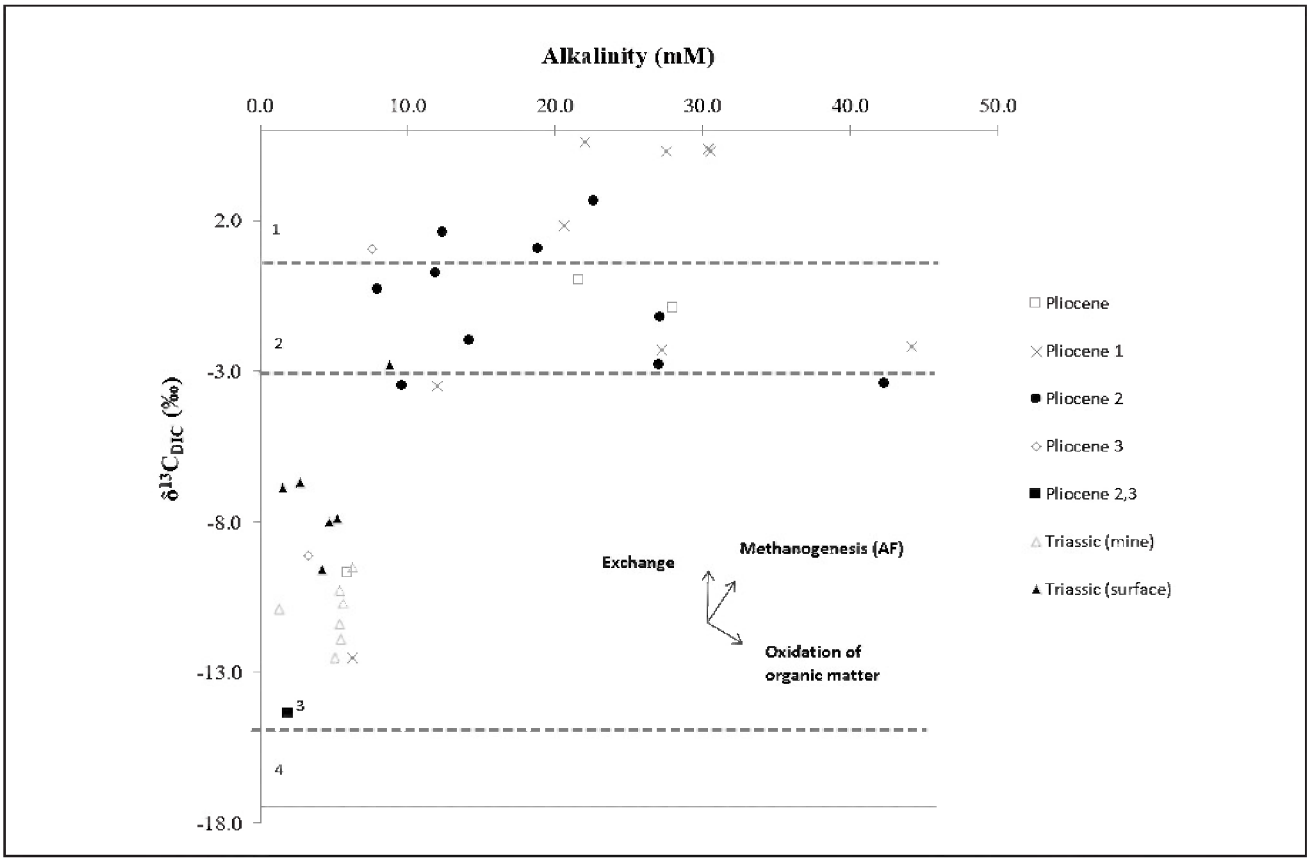

Fig. 7. $\delta^{13}C_{DIC}$ versus alkalinity in Velenje Basin groundwater. Variations in $\delta^{13}C_{DIC}$ values of groundwater samples compared to alkalinity concentrations, with lines indicating processes occurring in the Velenje Basin. Arrows show expected trends for a variety of processes. Lines indicate processes in aquifer as follows: 1: open system DIC equilibration with atmosphere (Exchange), 2: dissolution of carbonates with average $\delta^{13}C_{CaCO3}$ = -2 ‰, 3: nonequilibrium carbonate dissolution by carbonic acid produced from soil zone with a $\delta^{13}C_{CO2}$ of -26.6 ‰, 4: open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{CO2}$ of -26.6 ‰.

Groundwater in our study is considered as a closed system (Clark & Fritz, 1997), therefore any interactions with atmosphere are not possible.

It was found in previous studies that concentrations of dissolved organic carbon (DOC) in the Pliocene and Triassic aquifers in the Velenje basin are low, ranging from 1.54 to 14.69 mg/L (Kanduč et al., 2010), compared to groundwater associated with coalbeds in the Powder River Basin (Orem et al., 2010). In the latter, high DOC concentrations are related to methanogenesis and contact of groundwater with coal, but in Velenje Basin we can conclude that the methanogenesis (Fig. 7) in groundwater is probably related to the presence of low dissolved oxygen (DO), high alkalinity and high $\delta^{13}C_{DIC}$ values, occurring within the Pliocene aquifers (Kanduč et al., 2014).

The ratio $^{87}Sr/^{86}Sr$ ranges from 0.70820 to 0.71056 in groundwater dewatering Pliocene aquifers and from 0.70808 to 0.70910 in groundwater dewatering Triassic strata (Table 1). Figure 8 represents $^{87}Sr/^{86}Sr$ ratios and indicates characteristic values of $^{87}Sr/^{86}Sr$ isotopes in different environment with different geological composition e.g. marine limestone 0.711, while silicate fraction has higher $^{87}Sr/^{86}Sr$ ratio. The relations between $^{87}Sr/^{86}Sr$ ratios and $\delta^{13}C_{DIC}$ for groundwater in Pliocene and Triassic aquifers for Velenje Basin groundwater are presented on Figure 8. Based on the $^{87}Sr/^{86}Sr$ ratio in groundwater from both aquifers (Triassic and Pliocene), the carbonate fraction prevails (Fig. 8). The highest $^{87}Sr/^{86}Sr$ ratio was found in Pliocene 2, 3 strata, implying that more silicate fraction is leached in the aquifer. Generally, in Pliocene aquifers of Velenje Basin groundwater, higher $^{87}Sr/^{86}Sr$ ratios are observed than in Triassic aquifers (Table 1, Fig. 8). Given that carbonate dissolution rates are higher than those of silicates (Lasaga, 1984) as is the case for the Triassic and Pliocene aquifers of Velenje Basin carbonate dissolution may be important in controlling Sr isotope geochemistry (Harrington & Herzeg, 2003). However in the study of Murray Basin, Australia, $^{87}Sr/^{86}Sr$ ratios of groundwater lie between 0.71068 and 0.71905 (median = 0.71595), generally higher than values for potential carbonate sources (Cartwright et al., 2007). Trends in $^{87}Sr/^{86}Sr$ ratios versus $\delta^{13}C_{DIC}$ values for the mixing of groundwater from silicate and carbonate aquifers of Velenje Basin groundwater are shown schematically in Figure 8. Trends in $^{87}Sr/^{86}Sr$ ratios versus $\delta^{13}C_{DIC}$ values for the mixing of groundwater from silicate and carbonate aquifers or for the progressive dissolution of carbonates are shown in Figure 8. $^{87}Sr/^{86}Sr$ ratios of the silicate and carbonate fraction of aquifer

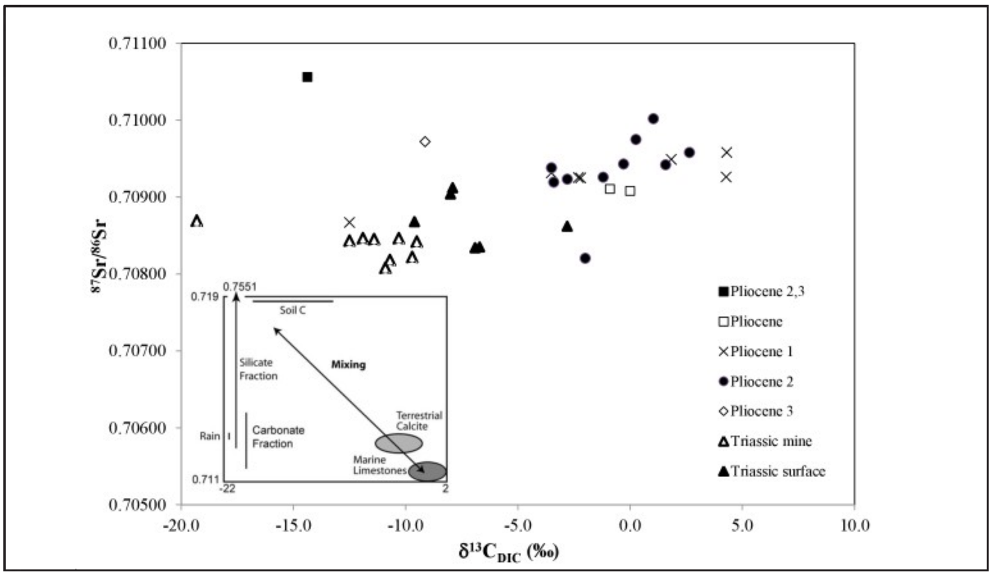

Fig. 8. $^{87}Sr/^{86}Sr$ versus $\delta^{13}C_{DIC}$ in Velenje Basin groundwater.

material in Velenje Basin groundwater, rainfall (Ullman & Collerson, 1994), typical $^{87}Sr/^{86}Sr$ ratios and $\delta^{13}C_{DIC}$ values of marine and terrestrial carbonates (Clark & Fritz, 1997; Faure, 1991), and typical $\delta^{13}C$ values of soil carbon (Clark & Fritz, 1997), are also shown.

Conclusions

Sampling in this study was performed only where possible due to the subsidence of the area, which destroyed some of the piezometers. New wells were sampled in the following three sampling campaigns during the period 2014–2015: a) overflow piezometers, b) groundwater and c) mine wells. Altogether, 38 wells were investigated for geochemical and isotopic analyses.

The major ion geochemistry and isotope geochemistry of the Velenje Basin groundwater are indicated in this study. The major ion geochemistry, isotopic composition of carbon and Sr ratios ($\delta^{13}C_{DIC}$, $^{87}Sr/^{86}Sr$) provides a new insight into geochemical processes (water - rock-interactions) in Velenje Basin groundwater.

The concentrations of dissolved ions and cations decreases in the order $HCO_3^- > Mg^{2+} > Na^+ > Ca^{2+}$ in the Pliocene aquifers and $HCO_3^- > Ca^{2+} > Mg^{2+}$ in the Triassic aquifer. Multivariate PCA analysis, based on "*in situ*" measured parameters (conductivity, pH, temperature), major geochemical parameters (Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_3^-, Cl^-, SO_4^{2-}) and $\delta^{13}C_{DIC}$ revealed that groundwater samples dewatering Triassic strata were grouped together in the ordination diagram, while the samples of groundwater dewatering Pliocene strata were scattered along both axes due mainly to variations in pH, conductivity, chloride, sulphate and $\delta^{13}C_{DIC}$.

The values of $\delta^{13}C_{DIC}$ and $^{87}Sr/^{86}Sr$, together with major ion geochemistry help explain geochemical processes in Velenje Basin groundwater. $\delta^{13}C_{DIC}$ values of groundwater in Pliocene aquifers range from -14.4 to +4.6 ‰ and in groundwater of Triassic aquifer from -19.3 to -2.8 ‰. Alkalinities range from 1.95 to 44.12 mM in Pliocene aquifers and from 1.32 to 10.43 mM in Triassic aquifer. $\delta^{13}C_{DIC}$ of groundwater in the Triassic aquifer indicate carbonate dissolution (dolostones and limestones) and organic matter degradation. In Pliocene aquifers, however methanogenesis (higher $\delta^{13}C_{DIC}$ values up to +4.6 ‰) is present in addition to degradation of organic matter and dissolution of carbonates, contributing to the very high alkalinity in these aquifers. Calculated value of pCO_2 in groundwater of Pliocene aquifers ranged from 15.8 to 575,439.9 ppm and in groundwater of Triassic aquifer from 169.8 to 107,151.9 ppm. Most groundwater in Pliocene and Triassic aquifers was oversaturated with calcite and dolomite. Pliocene groundwaters have much higher oversaturation values than the Triassic ones, also due to methanogenesis and high alkalinity.

The $^{87}Sr/^{86}Sr$ ratios in Pliocene aquifers range from 0.70820 to 0.71056 and, in groundwater of Triassic aquifer, from 0.70808 to 0.70912. $^{87}Sr/^{86}Sr$ isotopes in combination with $\delta^{13}C_{DIC}$, provide added value to the study in deciphering geochemical processes, water–rock interactions and silicate/carbonate weathering within the aquifers. The carbonate was found to have an $^{87}Sr/^{86}Sr$ ratio around 0.71120, the silicate fraction being in the range of 0.7120 to 0.7190. Groundwater from Pliocene aquifers has more positive $\delta^{13}C_{DIC}$ values and $^{87}Sr/^{86}Sr$ ratio, except for two samples located in the Pliocene 3 aquifer ($^{87}Sr/^{86}Sr$ ratio 0.70972, alkalinity 3.23 mM and $\delta^{13}C_{DIC}$ of -9.13 ‰, PM13/84) and Pliocene 2, 3 aquifer ($^{87}Sr/^{86}Sr$ ratio 0.71056 with low alkalinity of 1.95 mM and $\delta^{13}C_{DIC}$ of -14.37‰, PE 16/84 sample). Groundwater from Triassic aquifer has more negative $\delta^{13}C_{DIC}$ values and lower $^{87}Sr/^{86}Sr$.

From the hydrogeological (dewatering system) and geochemical (biogeochemical processes and age of groundwater) points of view it would be useful to investigate further the geochemical and hydrogeological relationships between shallow and deeper aquifers in different strata formations (Pliocene and Triassic). New observation objects (piezometers) will be drilled at northern part of the basin where mining activity is present.

As due to the mining activity, the basin is presently subsiding, a geochemical investigation in combination with hydrogeological studies is also necessary from the safety reasons and groundwater inrush into the mine.

Besides the groundwater investigations it would be useful to continue investigation of gases in groundwater and also geochemical characteristics of coalbed gases in coal matrix at active excavation fields. These investigations would be very useful for future development of CBM technology after the termination of mining activities in Velenje coal basin.

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