Overview of isotopic investigations of groundwaters in a fractured aquifer system near Rogaška Slatina, Slovenia

Pregled izotopskih raziskav podzemne vode v razpoklinskem vodonosnem sistemu na območju Rogaške Slatine

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Dedicated to Professor Jože Pezdič on the occasion of his 70th birthday

Abstract

The isotopic investigations of groundwaters stored in the Rogaška Slatina fractured aquifer system were performed in the periods 1978–1985 and 2007–2011 aiming at answering open questions on the groundwater recharge and dynamics, on connections between different types of aquifers and on solute transport. Environmental isotopes ^{2}H, ^{18}O, ^{3}H, ^{13}C of dissolved inorganic carbon and ^{14}C were analysed in mineral, thermo-mineral and spring waters. Results indicated the source and mechanism of groundwater recharge, its renewability, a transit time distribution, hydraulic interrelationships, the groundwater origin and its evolution due to effects of water-rock interaction. They proved the hypothesis that the Boča massif should be a catchment area of the Rogaška mineral waters. The estimates of the mean residence time of mineral waters in the aquifer system are between 7200 and 3400 years, depending on the location and depth. Thermo-mineral water is the oldest water in the study area with the mean residence time of 14000 years.

Izvleček

V obdobjih 1978–1985 in 2007–2011 so bile izvedene izotopske raziskave podzemne vode, uskladiščene v razpoklinskem vodonosnem sistemu na območju Rogaške Slatine, z namenom, da se odgovori na odprta vprašanja o napajanju podzemne vode in njeni dinamiki, o povezavi različnih vrst vodonosnikov in o prenosu snovi. V mineralnih, termomineralnih in izvirskih vodah smo analizirali ^{2}H, ^{18}O, ^{3}H, ^{13}C v raztopljenem anorganskem ogljiku in ^{14}C. V rezultatih smo opisali vire in mehanizme napajanja podzemne vode, njeno obnovljivost, zadrževalni čas v vodonosniku, izvor in geokemijski razvoj zaradi reakcij s kamninami. Potrdili smo hipotezo, da je masiv Boč napajalno območje Rogaških mineralnih vod, ki se zadržujejo v vodonosniku s povprečnim zadrževalnim časom od 7200 do 3400 let. Le ta je odvisen od lokacije in globine. Termomineralna voda je starejša – njen povprečen zadrževalni čas je 14000 let.

Introduction

Rogaška Slatina is famous by mineral water, which was discovered in this place in the time of ancient Rome. Numerous investigations of the Rogaška groundwaters were subject to balneology and to the larger exploitation quantities (Nosan, 1975), whereas information essential for the definition of the Rogaška aquifer system and for its protection has been still missing. Questions on the groundwater recharge area and dynamics, on connections between aquifers and on solute transport have remained open, which depends on the field geology and structure. The latter is very complicated – three regional faults intersect in this area, which is folded to anticlinal and synclinal folds. The nature of geological structures, their mutual relations and extent have not been

explained at a satisfactory level in many parts of the system. With regard to results of previous hydrogeochemical investigations (Nosan, 1973, 1975; Pezdič, 1986, 1997) it was presumed that the Boč massif near Rogaška Slatina is the catchment area of the Rogaška mineral waters, although geological data did not support this hypothesis (Aničić & Juriša, 1984).

Aiming at answering the discussed open questions also the isotopic investigations of groundwaters stored in the Rogaška Slatina fractured aquifer system were performed. The first studies took place in the period 1978–1985 (Pezdič, 1997), while the last studies were performed during a period 2007–2011 (Trček et al., 2010; Trček & Leis, 2011). The isotopic investigations based on the environmental isotopes of H, O and C, which were used as tracers of geological and hydrogeological processes.

The applications of stable isotope ratios of hydrogen and oxygen in groundwater hydrology are based primarily on isotopic variations in precipitation as the predominant groundwater source. After the infiltration of precipitation into the aquifer, only physical processes, such as diffusion, dispersion, mixing and evaporation, alter the groundwater isotopic composition (Clark & Fritz, 1997). The stable isotope content of water may be considered conservative under low-temperature and low-circulation groundwater systems, as long as the relative amount of water involved in chemical reactions remains limited (Clark & Fritz, 1997; Hoefs, 1997). The exchange with oxygen (possibly also hydrogen) bearing minerals of the host rocks is particularly important in geothermal environment. With low reaction rates in low-temperature environments a long time is needed for a significant exchange to take place and equilibrium will generally not be reached (IAEA, 1983). Another process, which may modify the initial stable isotope content of groundwater, is the isotopic exchange with a gas phase which is not initially in equilibrium with the environmental water (e.g. CO_2 or H_2S).

The stable carbon isotope composition of dissolved inorganic carbon (δ^{13}C-DIC) is not a conservative tracer. Nevertheless, the δ^{13}C can trace the carbon sources and reactions for numerous interacting organic and inorganic species. The isotope ratio ^{13}C/^{12}C is an important tool for quantifying the water-rock interactions, identifying the proportion of different CO_2 sources in

water, and determining the initial geological settings of the groundwater recharge (Hoefs, 1997; Kendall & McDonnell, 1998).

Groundwater dating is the main field of application of the ^{14}C and ^{3}H radioactive isotopes. Their input source functions, which describe the time-varying global fluxes of isotopes deduced from atmospheric, cosmogenic and anthropogenic production, are well known (Mook, 1980; Hoefs, 1997). The measured activity concentrations are compared with the input functions to get fairly informative age determinations over the past several decades. ^{3}H has a half-life of 12.3 years and is a very applicable tracer for determining spring residence times when recharge processes took place within a timescale of less than 50 years. Groundwaters seldom have more than 50 TU today and are typically in the 5–10 TU range (Criss et al., 2007; Rose, 2007). The recent ^{3}H study (Kovačič, 2015) indicated that Slovene groundwaters could be divided into four categories – groundwaters that are older than 100 years (^{3}H concentration is below the detection limit), groundwaters with the prevailing old component (^{3}H concentration is between 0 and 2.5 TU), groundwaters with the age between 30 and 60 years (^{3}H concentration is on average 8 TU) and recent groundwaters with age up to 15 years (^{3}H concentration is about 6 TU).

On the other hand ^{14}C with a half-life of 5,730 years is applicable for dating groundwaters recharged prior to 1,000–2,000 years (Bajjali et al., 1997) and as old as 30,000 years (Clark & Fritz, 1997).

Study area

The study area with its broader surroundings is geologically one of the most complex parts of Slovenia (Trček et al., 2010). It is the juncture of three major regional fault systems, separating three tectonic units (Figs. 1 and 2). The Boč massif belongs to the Southern Karavanke unit. It borders to the south with the Donat line to the narrow tectonic unit between the Donat line and Šoštanj fault close to which the town of Rogaška Slatina is situated. To the north, the Dravinja fault as part of the Periadriatic line separates the Southern Karavanke unit from the Upper Austro–Alpine unit. The ongoing dextral strike-slip zone along the Lavantal fault and the Šoštanj fault (Fig. 2) associates eastward extrusion of the Eastern Alps as a result of the northward shift

and the counter clockwise rotation of the Adria microplate. The complexity of the study area is reflected in a lithological heterogeneity as a result of faulting into many small tectonic blocks, which are relatively displaced and folded (Figs. 1 and 2). Most of the area is composed of massive limestones and dolomites of the Carnian age. They are capping the Boč mountain crest. The Oligocene and Miocene beds, covering the northernmost part of the territory and the lower slopes north of Rogaška Slatina, are composed of alternating sandstones, sands, shaly claystones and marlstones and conglomerates in the lower parts. A wide belt of volcanic rocks (andesite, its tuffs and volcanic breccias) is also present in within these units. The upper part is almost entirely composed of hard and bituminous marlstones (Aničić & Juriša, 1984).
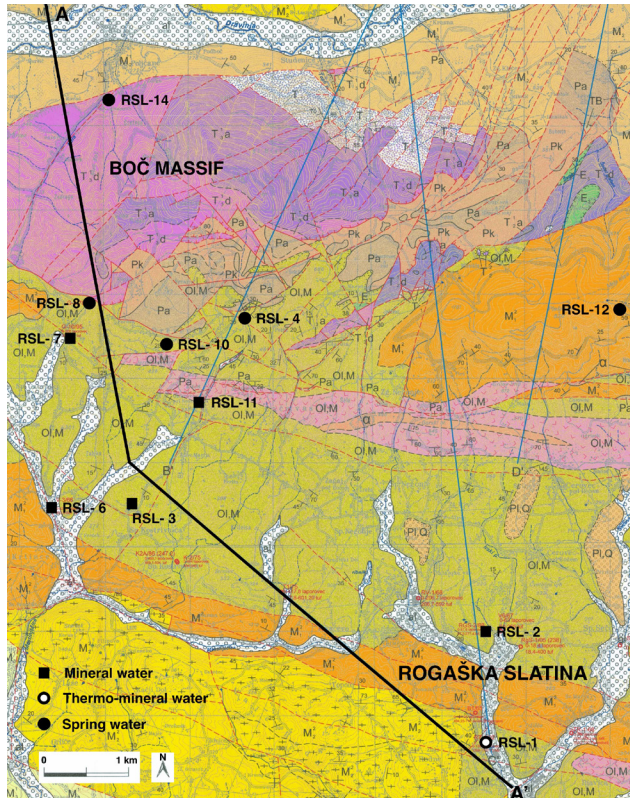
Mineral water is stored in fractured layers of the Oligocene tuff covered by the Upper Oligocene and Lower Miocene beds (Figs. 1 and 2). The discussed water belongs to the magnesium-sodium-hydrogen carbonate-sulphate facies. It was exploited from five boreholes that are 24 to 600 m deep (Fig. 1). Donat Mg is the most famous among Rogaška mineral waters. It has the highest mineral content (Tab. 1) and contains more than 1,000 mg/l of Mg. The content of gaseous CO_2 in the water is normally in the range of 2–30 g/l. Gas is practically pure CO_2 with minor share of nitrogen and negligible concentration of oxygen and methane (Pezdič, 1997).

Fig. 1. Study area with locations of boreholes with mineral, thermo–mineral and spring water (Trček et al., 2010).
Sl. 1. Raziskovalno območje z lokacijami vrtin z mineralno, termomineralno in izvirsko vodo (Trček et al., 2010)
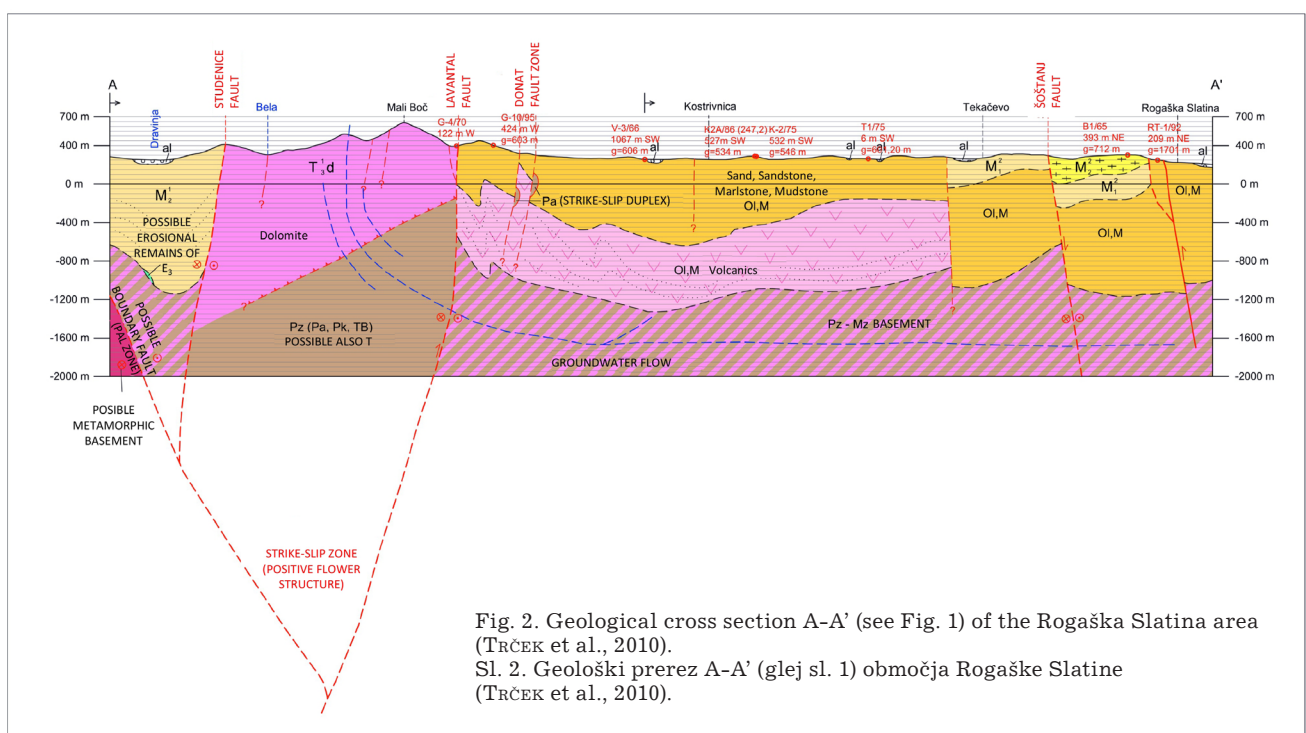

Fig. 2. Geological cross section A-A' (see Fig. 1) of the Rogaška Slatina area (Trček et al., 2010).
Sl. 2. Geološki prerez A-A' (glej sl. 1) območja Rogaške Slatine (Trček et al., 2010).

Table 1. Average values of sampled water discharges (Q), electroconductivity (SEC), mineralisation (M), temperature (T) and pH in the period 2007–2011

Tabela 1. Povprečne vrednosti pretoka vzorčenih vod ter njene elektroprevodnosti (SEC), mineralizacije (M), temperature (T) in pH v obdobju 2007–2011.

	Borehole name	Borehole depth (m)	Q (l/s)	M (g/l)	SEC (µS/cm)	T (°C)	pH
Mineral water	RSL-2	274	0.5	12.75	10999	14.6	6.8
	RSL-3	24	0.2	5.8	5165	11.9	6.4
	RSL-6	606	1	11.8	10539	28.4	6.9
	RSL-7	603	0.4	8.65	8627	15.1	6.5
	RSL-11	170	0.1	8.08	7102	12.0	6.5
Thermo-mineral water	RSL-1	1700	6	6	6418	55.4	7.1
Spring water from limestone	RSL-4	215	2.2		459	12.6	7.1
	RSL-10	130	2.1		379	11.0	7.5
Spring water from dolomite	RSL-8	170	1.4	0.5	570	11.7	7.3
	RSL-14	38	40		481	12.9	7.5
Spring water from sandstone	RSL-12	100	2		382	9.9	7.7

Spring water and thermo–mineral water are also exploited at the study area (Fig. 1, Tab. 1). The former is stored in fractured Triassic carbonate rocks and Miocene sandstones of the Boč massif and the latter in the dolomitized keratophyre at depths between 1,500 and 1,700 m.

The Rogaška mineral waters discharge with a help of a gas lift, thermo–mineral water discharges with a help of a thermo lift, while spring waters of boreholes RSL-4, RSL-8, RSL- 10 and RSL-14 are artesian.

Methods

Isotopic investigations were fundamental for studies of groundwater dynamics and solute transport in aquifers with mineral and spring water and among them. The recent investigations included the monitoring of 5 boreholes with mineral water (RSL-2, RSL-3, RSL-6, RSL-7 and RSL-11), 1 borehole with thermo–mineral water (RSL-1), 2 boreholes with spring water from a limestone (RSL-4, RSL-10), 2 boreholes with spring water from a dolomite (RSL-8, RSL-14) and 1 borehole with spring water from a sandstone (RSL-12; Fig. 1, Tab. 1). Besides the groundwater CO_2 was sampled and also precipitation at altitudes of 340, 530 and 710 m asl. The previous investigations involved only the sampling of mineral waters and spring water from carbonate rocks (PEZDIČ, 1997).

Recent isotopic analyses of stable isotopes of H and O were made in Laboratory Centre for Isotope Hydrology and Environmental Analytics, Joanneum Research, Graz, Austria. The oxygen isotopic composition ($\delta^{18}O$) of the water was measured by the classic $CO_2 – H_2O$ equilibrium technique (EPSTEIN & MAYEDA, 1953) with a fully automated device adapted from HORITA et al. (1989) coupled to a Finnigan DELTAplus Mass Spectrometer. Deuterium (δ^2H) was measured in a continuous flow mode by chromium reduction using a ceramic reactor slightly modified from MORRISON et al. (2001). Stable oxygen and hydrogen isotopic ratios are reported relative to the VSMOW (Vienna-SMOW) standard with an overall precision of 0.1 and 1 ‰, respectively.

The data of H and O stable isotopic composition in precipitation were applied to define the local meteoric waterline (LMWL) of the Rogaška Slatina area. Due to small number of samples (57) the ordinary linear regression analysis was conducted that based on the method of seasonally weighted mean values (ROZANSKI et al., 1993).

The ^{13}C content was also measured in the Stable Isotope Laboratory of the Institute of Water Resources Management, Joanneum Research, Graz, mass spectrometrically by Thermo Finnigan DELTA^{plus}XP (CF-IRMS). The values are reported as ‰ vs. V-PDB standard with an overall precision of 0.1 ‰.

Measurements of the radioactive isotopes ^{3}H and ^{14}C were performed in the Isotope laboratory HYDROSYS – Water and Environmental Protection Developing Ltd, Budapest, Hungary. ^{3}H was measured by counting β-decay events in a liquid scintillation counter (LSC). Values are reported in absolute concentrations as tritium units (TU), where one TU corresponds to one ^{3}H atom per 10^{18} atoms of hydrogen ^{1}H or to an activity of 0.118 Bq/kg in water.

^{14}C was measured by the super low level liquid scintillation analyser (PerkinElmer Tri-Carb 3170TR/SL) based on ASTM D6866-06 standard. The values are expressed in pmC (Percent Modern Carbon). Groundwater age (t) is determined using the radioactive decay equation (Eq. 1), employing the pre-industrial baseline ^{14}C activity of the soil CO_2 equal to 100 pmC as an initial concentration and the ^{14}C activity of the DIC (HCO_3^-) measured in the groundwater sample. However, the dissolved C mass balance of groundwaters is altered during the groundwater flow path due to geochemical reactions that take place within the aquifer. In such cases, a factor q is incorporated into the radioactive decay equation to take into account the ^{14}C dilution effect (other than radioactive decay) during the groundwater flow path caused by a dissolution of ^{14}C–free marine carbonates and incorporation of a geogenic ^{14}C–free CO_2 of the magmatic or metamorphic source. The groundwater age is thus determined:

$$t = -8267 \ln\left(\frac{a_t{}^{14}C}{qa_0{}^{14}C}\right) \qquad \text{(Eq. 1)}$$

where t is groundwater age, $a_0{}^{14}$C is a modern ^{14}C activity in the soil zone (100 pmC), $a_t{}^{14}$C is a ^{14}C activity of DIC in the groundwater sample and q is a dilution factor.

The chemical mass-balance correction (CMB model) has been used to quantify the ^{14}C dilution due to incorporation of ^{14}C–free geogenic CO_2, assuming that the carbonate dissolution in the recharge area evolves under the closed system condition. In such cases the ^{14}C dilution factor of

carbonate groundwaters is about 0.5. The subsequent ^{14}C dilution caused by the incorporation of ^{14}C–free geogenic CO_2 and resulting geochemical reactions has been determined as a ratio of the HCO_3^- concentration in the recharge area to the HCO_3^- concentration in samples of mineral and thermos-mineral waters. The HCO_3^- concentration in the recharge area is given as an average value of sampled spring waters that equals to 304 mg/l. The total ^{14}C dilution factor is thus the product of the ^{14}C dilution ensuing in the recharge area (0.5) and the subsequent ^{14}C dilution induced by the incorporation of ^{14}C-free geogenic CO_2.

The first analyses of O, H and C environmental isotopes were made at Institute Jožef Stefan, Ljubljana (Pezdič, 1997). For δ^{18}O determination from water the classic CO_2 – H_2O equilibrium technique was also applied (Epstein & Mayeda, 1953). Hydrogen gas was prepared by reducing water vapor on hot zinc wool at 400 °C or on zinc granules at 490 °C (Coleman et al., 1982). Precipitated DIC and carbonates reacted with 100 % orthophosphoric acid at 55 °C. Dissolved carbonate species are treated with phosphoric acid to measure just δ^{13}C. The isotopic composition of prepared gaseous compounds (H_2 and CO_2) were measured on the Varian MAT 250 mass spectrometer. Measuring accuracy exceeds ± 0.05 ‰ for oxygen and carbon and ± 0.5 ‰ for hydrogen. Results were given relative to the SMOW standard for oxygen and hydrogen and PDB for carbon.

The tritium content was measured with a liquid scintillation counter at Institute Jožef Stefan, Ljubljana (Pezdič, 1997). Concentrations were given in TU and Bq. The activity of radiogenic carbon (^{14}C) was measured at Rudjer Boikovic Institute in Zagreb using a gas proportional counter. ^{14}C data were presented as % Modern Carbon (pmC) vs. the activity of standard oxalic acid (Ox) formed before the nuclear period with a correction factor of 0.95 (Pezdič, 1997).

Results and discussion

Average values of sampled water discharges, electroconductivity, mineralisation, temperature and pH during a monitoring period 2008–2010 are presented in Table 1. The level of gaseous CO_2 in water is normally in the range 2-30 g/l, but in some areas is as high as 40 g/1 (Nosan, 1973). Gas analysis revealed that the gas is practically pure

CO_2 with a minor share of nitrogen (0.3 %) and negligible concentrations of oxygen and methane (below 0.01 %; PEZDIČ, 1997).

The relationship between O and H stable isotopic compositions of sampled water is illustrated in Figure 3. The average groundwater O and H isotopic composition approximately equals the weighted average of the precipitation O and H composition as a rule, while surface water is may be enriched more with heavier (more positive) isotopes than precipitation, due to the evaporation process (CLARK & FRITZ, 1997; ROZANSKI et al., 1992, 1993; TRČEK & ZOJER, 2010).

Mineral waters have [18]O in the range between -12.2 and -10.3 ‰ and δ^2H in the range between -80.5 and -63.9 ‰. The lowest δ values refer to waters with the highest mineralization, RSL-2 and RSL-6, and the highest to water of RSL-3 with the lowest mineralisation (Tab. 1), which reflects mixing processes of older and younger waters (Fig. 3).

The δ^{18}O and δ^2H values range in spring waters from carbonate rocks is -10.7 to -9.9 ‰ and -78.9 to -65.0 ‰, respectively. It is slightly different and more narrow in spring water from sandstone,

-10.9 to -10.6 ‰ and -76.9 to -67.2 ‰, respectively (Fig. 3). The δ^{18}O and δ^2H of thermo–mineral water is similar to spring water from a dolomite.

Similar δ^{18}O and δ^2H results were obtained in previous investigations (PEZDIČ, 1997). Mineral waters had a δ^{18}O range -11.2 to -9.55 ‰ and a δ^2H range -84.0 to -76.9 ‰, while the parameters ranged in spring waters from carbonate rocks from -10.25 to - 8.19 ‰ and from -78.6 to -63.6 ‰, respectively.

CRAIG (1961) firstly described the relationship of discussed isotopes in the precipitation by the global meteoric waterline (GMWL, Fig. 3). The local meteoric waterline (LMWL) of the Rogaška Slatina area slightly differs from the GMWL in both the slope and the intercept (Fig. 3). It is a function of temperature during the secondary evaporation as rain falls from a cloud, which results in effects of the isotopic fractionation with respect to the latitude, altitude, and climate. The isotopic composition of precipitation is affected by the season, latitude, altitude, precipitation amount, and distance from the coast (ROZANSKI et al., 1992, 1993). All sampled waters from recent and previous investigation (PEZDIČ, 1997) are distributed in the LMWL vicinity. The δ^{18}O and δ^2H values
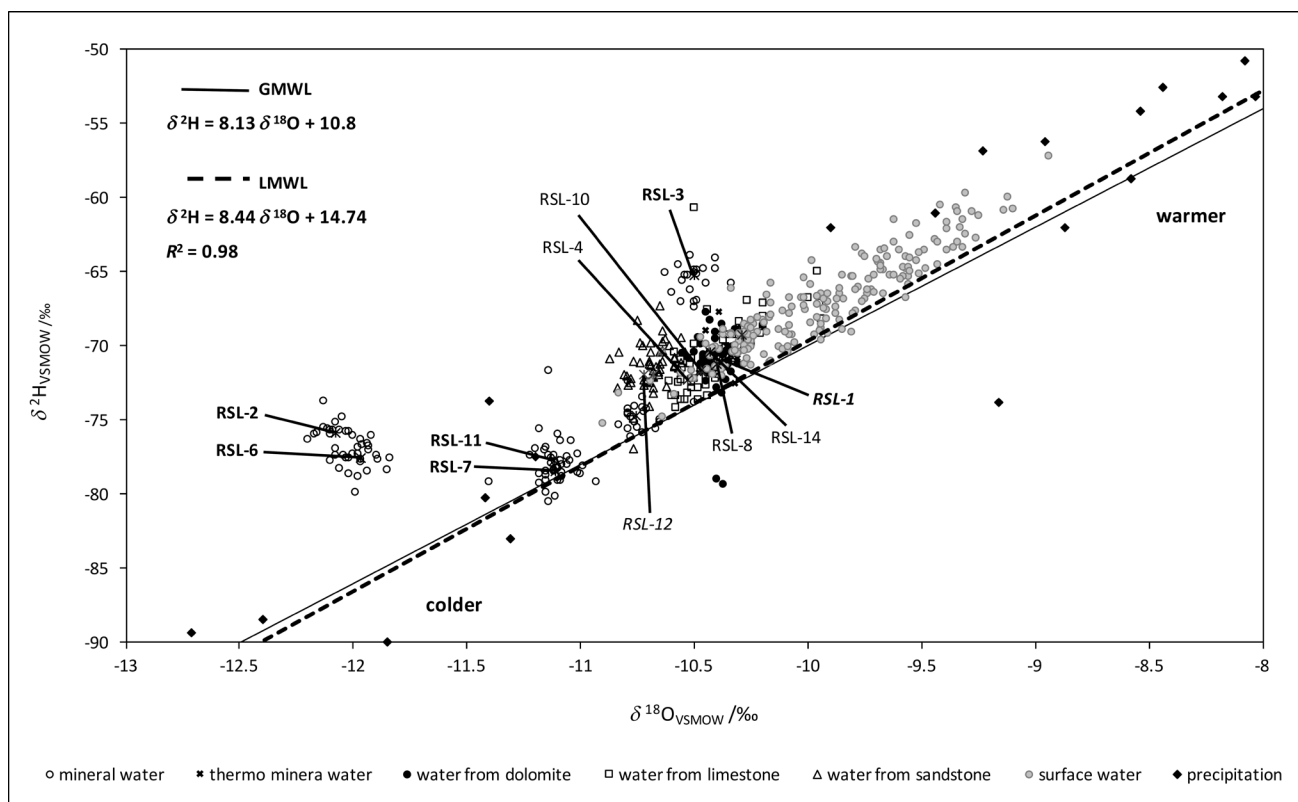

Fig. 3. The relationship between stable oxygen and hydrogen isotopic composition of sampled water in the period 2007-2011.
Sl. 3. Razmerje med sestavo stabilnih izotopov kisika in vodika v vzorčenih vodah v obdobju 2007-2011.

and their distribution indicate that sampled waters are of a meteoric origin, hence the Rogaška fractured aquifer system is recharged with local precipitation. The δ values of mineral waters fall on the same LMWL, but on its lower part with the depleted heavy isotopes (Fig. 3, Pezdič, 1997), which reflects colder climate conditions during the infiltration processes (Clark & Fritz, 1997; Hoefs, 1997; Iaea, 1983). The exception is the shallow RSL-3 mineral water (Tab. 1) that is mixed with surface waters (Figs. 3 and 4). The δ values of mineral waters sampled from RSL-2, RSL-6 and RSL-3 slightly deviate from LMWL (Fig. 3). The level of gaseous CO_2 in these waters is the highest (up to 40 g/1; Nosan, 1973), therefore it is assumed that ^{18}O is depleted due to the exchange of water with the geogenic CO_2 (Clark & Fritz, 1997; Hoefs, 1997; Iaea, 1983).

During the period of previous isotopic investigations (1978–1985) the ^3H contents of 1.9 to 176 TU were measured in mineral waters and of 37 to 150 TU in spring waters from carbonate rocks (Pezdič, 1997). The ^3H data of investigations in July 2008, when almost three half-lives of ^3H has passed, are illustrated in Figure 4. The precipitation had the ^3H content of 10.7 TU, which coincides with the summer values measured in Ljubljana (Kovačič, 2015). ^3H was not detected in mineral waters from boreholes RSL-6 and RSL-7, hence these waters are not in contact with recent precipitation infiltration. According to Kovačič (2015) mineral waters from boreholes RSL-6 and RSL-7 are older than 100 years. The samples of thermo–mineral and mineral waters from boreholes RSL-1, RSL-2 and RSL-11 contain 0.6 TU or less ^3H, which indicates the prevailing old water component (Kovačič, 2015). Evidently the recharge of these groundwaters occurred prior to the 1950s, therefore they are relatively unblemished by human activities. Similar findings were published in previous investigations (Pezdič, 1997).

Groundwater samples from RSL-3, RSL-4, RSL-8, RSL-10, RSL-12 and RSL-14 with tritium contents 4.6 to 9.4 TU (Fig. 4) should contain modern water that infiltrated predominantly after the 1960s, suggesting the vulnerability of these groundwater systems to man–made impacts. According to Kovačič (2015) the mean residence time of spring water of shallower boreholes RSL-10, RSL-12 and RSL-14 (Tab. 1) should be around 15 years, around 30 years for spring water of the deeper borehole RSL-4 and up to 60 years for spring water of the deeper borehole RSL-8.

Among listed waters only RSL-3 is mineralized. The water is captured from a depth of 20 m, where it should be mixed with young fresh water. Pezdič (1997) reported that spring waters from carbonate rocks are no more than 15 years old.

During the period 2007–2011 the $\delta^{13}C$ values of the dissolved inorganic carbon varied between –13 and +2 ‰ in sampled groundwater (Figs. 5 and 6). The parameter values between –2 and +2 ‰ are characteristic for groundwaters that are influenced by the volcanic CO_2: RSL-2, RSL-3, RSL-6, RSL-7 and RSL-11 (Clark & Fritz, 1997). These waters are highly mineralized, as it is evidenced in Table 1. The RSL-1 water has lower mineralization, which is reflected in $\delta^{13}C$-DIC values. On the other hand low $\delta^{13}C$ values (-12 to -13 ‰) are typical for spring waters, collected from RSL-4, RSL-8, RSL-10 and RSL-14. According to Clark & Fritz (1997) these values closely resemble the δ^3C content of carbonate groundwater that evolves under a closed system condition.
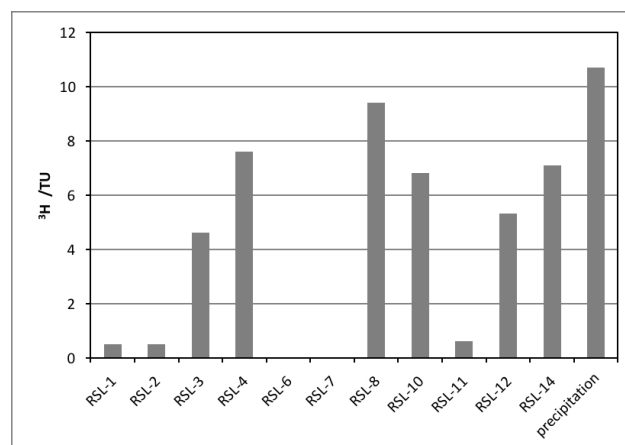

Fig. 4. Tritium concentrations in groundwater and in precipitation of the Rogaška Slatina area in the period 2007–2011.
Sl. 4. Koncentracije tricija v podzemnih vodah in padavinah na območju Rogaške Slatine v obdobju 2007–2011.

During the period 1978–1985 similar $\delta^{13}C$ values were detected in mineral waters, between –3.1 and +3.3 ‰, and between –16.9 and 13.1 ‰ in spring waters of carbonate rocks (Pezdič, 1997).

The main sources of the carbon dissolved in groundwater are soil CO_2, CO_2 of a geogenic origin or a magmatic CO_2 (from deep crustal or mantle sources), carbonate minerals, an organic matter in soils and rocks, fluid inclusions, and methane. Each of these sources has a different carbon isotopic composition and contribute to the totally dissolved carbon in various proportions. In the studied groundwater systems the total dissolved inorganic carbon (DIC) exists practically
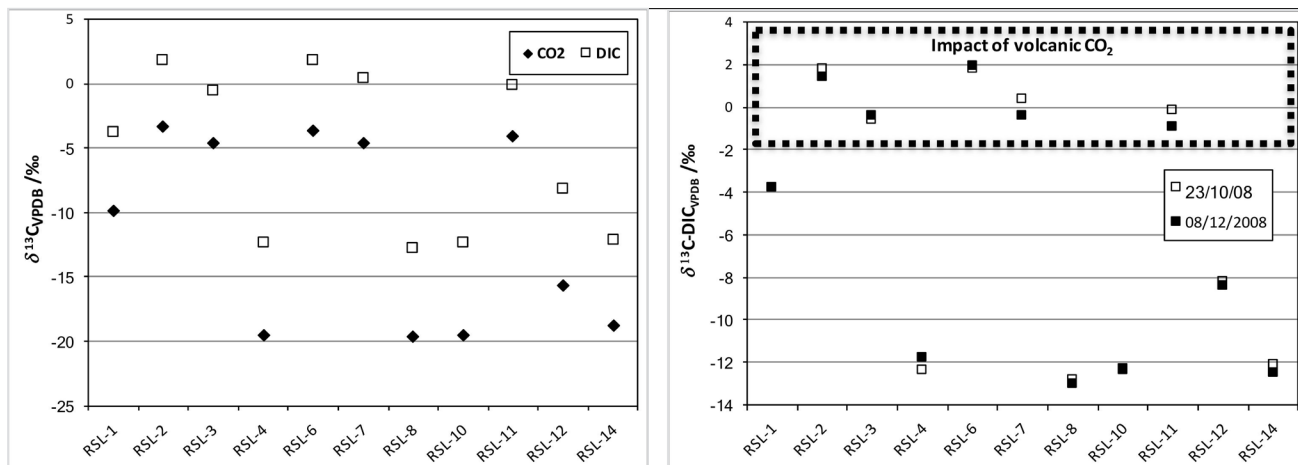
Fig. 5. Stable C isotopic composition of total dissolved inorganic carbon (DIC) in sampled water and its CO_2 in the period 2007–2011.
Sl. 5. Izotopska sestava ^{13}C raztopljenega anorganskega ogljika v vzorčenih vodah in v njihovem CO_2 v obdobju 2007–2011.

all in a HCO_3^- form. The HCO_3^- concentration varies between 224–382 mg/l in groundwater samples from RSL-4, RSL-8, RSL-10, RSL-12 and RSL-14, where the carbonate rocks were dissolute in the reaction with biogenic CO_2 in soil. The HCO_3^- concentration of mineral and thermo–mineral waters from RSL-1, RSL-2, RSL-3, RSL-6, RSL-7 and RSL-11 is increased to about 1950–8280 mg/l (Tab. 2). The hydrochemical composition was most probably altered to a great extent by the incorporation of the geogenic CO_2 influx that originates from a volcanic source (Fig. 5). The average δ^{13}C of CO_2 in mineral waters is -4.1 ‰ and -9.9 ‰ in thermo–mineral water, respectively. It induced the intensive rock-water interactions and consequently the dissolved solute contents increased significantly. It is well known that the δ^{13}C is about -25 ‰ in the soil CO_2 (similar to plants), -7 ‰ in the atmospheric CO_2, -8 ‰ to -3 ‰ in the CO_2 originating from the geothermal and volcanic systems and about 0 ‰ in marine carbonate rocks (KENDALL & MCDONNELL, 1998). δ values from -2.0 ‰ to +4.1 ‰, with an average of +2.2 ‰ were analysed in Slovene carbonate rocks

(KOCELI et al., 2013; OGORELEC et al., 2000). The relationship between δ^{13}C and HCO_3^- concentration in sampled water is illustrated in Figure 6.

The ^{14}C investigation was done on five groundwater samples of mineral and thermo–mineral waters collected from the boreholes RSL-1, RSL-2, RSL-3, RSL-6 and RSL-7 in 2009. Very low ^{14}C contents, ranging between 0.9 to 1.4 pmC, have been determined (Tab. 2), which reflects very long mean residence times of groundwaters. With the aim to determine the resident time of groundwater according to Equation 1 the geogenic CO_2 was characterised first based on the δ^{13}C value of the CO_2 gas phase of water samples. The δ^{13}C values show a very wide spread, between -10 and -3 ‰ (Fig. 5). They are within the range of δ^{13}C reported in the literature for magmatic CO_2, -12 to -1 ‰ (TRUESDELL & HUSTON, 1980; EXLEY et al., 1986; ROSE & DAVISSON, 1996). Further the chemical mass-balance correction (CMB model) has been used to quantify the ^{14}C dilution due to incorporation of the ^{14}C–free volcanic CO_2, assuming that the carbonate dissolution in the recharge area evolves under a closed system condition. From stoichiometry in such cases the initial ^{14}C concentration (~ 100 pmC) is expected to become diluted for about 50 %. It follows that the ^{14}C dilution factor is about 0.5. The subsequent ^{14}C dilution caused by the incorporation of the ^{14}C–free volcanic CO_2 and the resulting geochemical reactions has been determined as a ratio of the HCO_3^- concentration acquired in the recharge zone to the HCO_3^- concentration in the groundwater samples from RSL-1, RSL-2, RSL-3, RSL-6 and RSL-7. The HCO_3^- concentration acquired in the recharge zone is given as an average value from RSL-4, RSL-8, RSL-10 and RSL-14, which is about 304 mg/l. The ages of sampled mineral
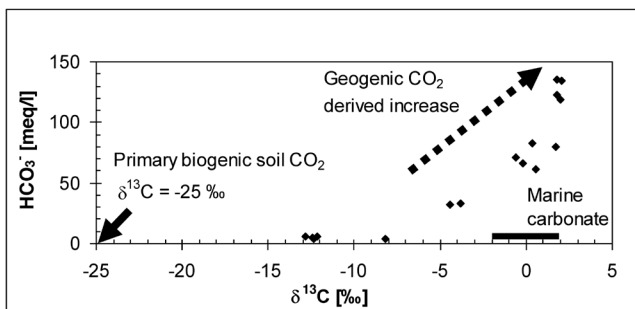

Fig. 6. The relationship between stable C isotopic composition and HCO_3^- concentration in sampled waters in the period 2007–2011.

Sl. 6. Razmerje med izotopsko sestavo ^{13}C in koncentracijo raztopljenega anorganskega ogljik v vzorčenih vodah v obdobju 2007–2011.

waters were calculated employing the total ^{14}C dilution factor, which is the product of the ^{14}C dilution ensuing in the recharge zone (= 0.5) and the subsequent ^{14}C dilution induced by the incorporation of the ^{14}C–free volcanic CO_2.

Table 2. HCO_3^- concentration, stable C isotopic compositions, ^{14}C content, dilution factor q_{total} and age estimates of the mineralized waters and thermos mineral water (RSL-1) sampled in 2009.

Tabela 2. Koncentracije HCO_3^-, izotopska sestava ^{13}C, vsebnost ^{14}C, faktor razredčenja q_{total} in ocena starosti mineralne in termomineralne vode, vzorčene leta 2009.

Sampling point	HCO_3^- (mg/l)	$\delta^{13}C$ (‰)	^{14}C (pmC)	q_{total}	Age (year)
RSL–1	1949.6	-4.37	1.43	0.078	14000
RSL–2	8176.7	2.05	1.23	0.019	3400
RSL–3	3771.0	0.53	0.95	0.040	----
RSL–6	7279.7	1,99	0.88	0.021	7100
RSL–7	4875.5	1,75	1.31	0.031	7200

The estimated ages of mineral waters are listed Table 2. The thermo–mineral water, captured from RSL-1 at depths 1500–1700 m exhibits a considerably high mean residence time – 14000 years, corresponding to the Pleistocene epoch, the Bølling-Allerød interglacial period that lasted from 14700 to 12900 years ago. During this period glaciers almost disappeared in many European mountain ranges, also in the Alps (Palacios et al., 2016; Dielforder & Hetzel, 2014; Hippe et al., 2014; Ivy-Ochs, 2015). The wormer climate during the infiltration process of thermo–mineral water is reflected also in the stable isotopic composition of O and H (Fig. 3).

The mean residence time of mineral waters RSL-6, RSL-7 and RSL-2 is 7200, 7100 and 3400 years, respectively. The first two correspond to the Holocene epoch, the end of the colder Boreal period that lasted from 8600 to 7200 years ago (Roberts, 2014). According to the ^{18}O and ^2H isotopic data (Fig. 3) waters from RSL-6 and RSL-2 should be recharged and discharged under similar conditions, but they are captured at different depths (606 and 274 m respectively, Tab. 1) and hence fallow different flow paths, which should result in age differences. It is also worth to note that despite the low ^{14}C concentration in the groundwater sample from RSL-3, no groundwater

age was calculated due to the presence of a higher tritium concentration (4.6 TU) in the groundwater sample. Most likely it represents mixing of recent and old groundwater, thus groundwater age dating using ^{14}C is not appropriate.

The ^{14}C was investigated in the RSL-7 mineral water also in 1980s (Pezdič, 1997). A content of 2 pmC was recorded. Two corrections were made to estimate the water mean residence time based on ^{14}C data: a) according to a dilution factor determined as the ratio between the predicted active and measured total DIC (equals to 0.037), which indicated that the mixture had about 3.7 pmC of initial ^{14}C activity (ICA) and measured 2 pmC and b) according to estimation that primary mineral water had become mixed with about 20 % of young meteoric water. The recalculation of values indicated the relative ^{14}C activity of primary RSL-7 mineral water to be approximately 35 pmC. This pointed to an estimated age of about 8000 years, which is compatible with the result of recent investigations.

Conclusions

The results of isotopic investigations of groundwaters in the Rogaška Slatina area performed in the period 1978–1985 (Pezdič, 1997) and 2007–2011 coupled with available information on a physical hydrogeology and a water chemistry help in understanding the source and mechanism of groundwater recharge, groundwater circulation and its renewability, groundwater transit time distribution, hydraulic interrelationships, the groundwater origin and its evolution due to effects of water-rock interaction.

The $\delta^{18}O$ and δ^2H values indicated the meteoric origin of mineral and thermos-mineral waters and proved the hypothesis that the Boč massif near Rogaška Slatina should be a catchment area of the Rogaška mineral waters. They reflected the mixing processes between younger and older waters or mineral and spring waters and hence contributed to the water body vulnerability assessment together with ^3H data. The latter pointed out waters that infiltrated predominantly after the 1960s, suggesting the vulnerability of these groundwater systems to man-made impacts.

The estimations of the mean residence time of mineral, thermos-mineral and spring waters based on ^3H, $\delta^{13}C$ and ^{14}C data provided additional information on groundwater recharge processes,

its renewability and vulnerability. Thermo-mineral water, captured from RSL-1 at depths 1500–1700 m is the oldest water in the study area with the mean residence time of 14000 years. The mean residence time of mineral waters captured at depth around 600 m from RSL-6 and RSL-7 is estimated to 7100 and 7200 years respectively. However, the residence time of mineral water captured at depth around 270 m from RSL-2 is shorter – 3400 years. Nevertheless, the ^{18}O and ^{2}H data indicated that mineral waters from RSL-6 and RSL-2 should be recharged and discharged under similar conditions. Based on ^{3}H data it was estimated that shallow spring waters are around 15 years old, while the age of deeper ones is 30 to 60 years.

The presented findings were integrated with the structural analysis of the study area (TRČEK et al., 2010; ŽIBRET, 2016). The results improved a conceptual hydraulic model of the Rogaška Slatina fractured aquifer system and are essential to determine the optimal balance between environmental protection and economic use of mineral and spring water resources in the study area.

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Pregled izotopskih raziskav podzemne vode v razpoklinskem vodonosnem sistemu na območju Rogaške Slatine

(daljši povzetek)

V obdobjih 1978–1985 in 2007–2011 so bile izvedene izotopske raziskave podzemne vode, uskladiščene v razpoklinskem vodonosnem sistemu na območju Rogaške Slatine z namenom, da se odgovori na odprta vprašanja o napajanju podzemne vode in njeni dinamiki, o povezavi različnih vrst vodonosnikov in o prenosu snovi. V mineralnih, termomineralni in izvirskih vodah so se analizirali ^{2}H, ^{18}O, ^{3}H, ^{13}C-DIC in ^{14}C (sl. 1). Mineralna voda je uskladiščena v razpokanih plasteh oligocenskega tufa, ki jih prekrivajo zgornje oligocenske in spodnje miocenske kamnine, izvirska voda pa v razpokanih zgornje triasnih karbonatnih Boča in miocenskih peščenjakih (sl. 1 in 2, tab. 1). Termomineralna voda je zajeta v vrtini RSL-1 na globinah 1500 do 1700 m, v dolomitiziranem keratofirju.

Razmerje med izotopsko sestavo ^{18}O in ^{2}H v vzorčenih vodah na območju Rogaške Slatine je predstavljeno na sliki 3. Lokalna meteorna premica (LMWL) ne odstopa dosti od globalne (GMWL). Vrednosti parametrov, izmerjenih v površinskih in podzemnih vodah, so razporejene v območju, ki ga pokrivajo vrednosti, izmerjene v padavinah. Na podlagi tega in sorodnih rezultatov predhodnih raziskav (PEZDIČ, 1997) lahko zaključimo, da so vse vzorčene vode meteornega izvora. Na sliki 3 odstopajo nekoliko vrednosti mineralnih vod, vzorčenih na vrtinah RSL-2, RSL-6 in RSL-3. Možnih je več vzrokov: drugačne klimatske razmere v času infiltracije padavin, drugačni pogoji napajanja vodonosnika in izotopska izmenjava s CO_2 v mineralni vodi. Razberemo, katere vode imajo podoben režim napajanja ali podobno napajalno območje. Med mineralnimi vodami je treba izpostaviti podobnost med vodami vzorčnih mest RSL-2 in RSL-6 oziroma RSL-11 in RSL-7. Iz tega sledi, da pripada par najverjetneje istemu vodonosniku. Termomineralna voda vrtine RSL-1 ima podobno izotopsko sestavo ^{18}O in ^{2}H kot dolomitne vode vrtin RSL-8 in RSL-14, kar kaže na podobno nadmorsko višino napajalnih zaledij vodonosnikov.

Rezultati analiz ^{3}H v vzorčenih vodah so prikazani na sliki 4. Mineralne in termomineralne vode vrtin RSL-1, RSL-2, RSL-6, RSL-7 in RSL-11 vsebujejo 0,6 TU ali manj, kar pomeni, da so se napajale pred letom 1960. Po drugi strani lahko sklepamo, da so omenjene vode zavarovane pred antropogenimi vplivi iz površja. Vsebnost ^{3}H v mineralni vodi RSL-3, več kot 4 TU, opozarja da se meša mineralna voda v vrtini z mlajšimi vodami, ki dotekajo s površja. Izvirske vode vrtin RSL-3, RSL-4, RSL-8, RSL-10, RSL-12 in RSL-14 vsebujejo 4,6 do 9,4 TU, kar pomeni, da so mlajše od 60 let. Ocenjujemo, da je starost plitvejših izvirskih vod okoli 15 let, medtem ko so globlje stare med 30 in 60 let.

Na podlagi podatkov δ^{13}C, HCO_3^- in ^{14}C se je določila starost mineralnih in termo mineralnih vod (sl. 5 in 6, tab. 2). Uporabila se je enačba radioaktivnega razpada (enačba 1), ki se ji doda faktor q, s pomočjo katerega se upošteva učinek razredčenja ^{14}C zaradi raztapljanja karbonatnih kamenin in geogenega CO_2 (vulkanskega izvora). Izotopska sestava ^{13}C-DIC v vzorčenih vodah je predstavljena na sliki 5. Le ta izpostavlja mineralne vode, ki so pod vplivom vulkanskega CO_2: RSL-2, RSL-3, RSL-6, RSL-7 in RSL-11. Omenjene vode so visoko mineralizirane, kar je

evidentirano v tabeli 1. Termomineralna voda RSL-1 ima nižjo mineralizacijo, kar se kaže tudi v vrednosti δ^{13}C-DIC. V izvirskih vodah RSL-4, RSL-8, RSL-10 in RSL-14 so bile izmerjene vrednosti δ^{13}C-DIC med -13 in -14 ‰. Te vrednosti so značilne za zaprt sistem raztapljanja karbonatnih kamnin v območju napajanja vodonosnika.

Za določitev vpliva vulkanskega CO_2 na merjene vrednosti ^{14}C se je uporabil model korekcije kemijske masne bilance (CMB model) ob predpostavki, da poteka proces raztapljanja karbonatnih kamenin v napajanem območju vodonosnika pod zaprtimi pogoji. V takih primerih se upošteva, da se zmanjša začetna koncentracija ^{14}C ($\sim$ 100 pmC) za okoli 50 %. Iz tega sledi, da je faktor razredčenja ^{14}C v karbonatnih podzemnih vodah raziskovalnega območja okoli 0,5. Dodatno razredčenje ^{14}C povzroči še vulkanski CO_2. Le-to se je ocenilo s pomočjo razmerja med koncentracijo HCO_3^- v vodah z območja napajanja vodonosnega sistema (karbonatne izvirske vode) in koncentracijo HCO_3^- v mineralnih in termo mineralnih vodah RSL-1, RSL-2, RSL-3, RSL-6 in RSL-7. Za koncentracijo HCO_3^- na območju napajanja vodonosnika z mineralno vodo se je upoštevala povprečna vrednost vzorčenih vod RSL-4, RSL-8, RSL-10 in RSL-14, 304 mg/l.

Opisani podatki in informacije so se upoštevali pri določitvi starosti mineralnih vod, podanih v tabeli 2. Najdaljši zadrževalni čas, 14000 let, je značilen za termomineralno vodo RSL-1, ki je zajeta v globinah 1500-1700 m. Povprečni zadrževalni časi mineralnih vod RSL-6, RSL-7 in RSL-2 so 7200, 7100 oziroma 3400 let. Glede na podatke δ^{18}O in δ^2H (sl. 3) imata vodi RSL-6 in RSL-2 isto napajalno območje in pripadata istemu vodonosnemu sistemu, kjer potekajo geokemijske reakcije pod podobnimi pogoji. Ker pa se zajemata obravnavani vodi na različnih globinah, 606 oziroma 274 m, je različen njun zadrževalni čas v vodonosniku. V predhodnih raziskavah je bilo ocenjeno, da je zadrževani čas mineralne vode RSL-7 okoli 8000 let (Pezdič, 1997).

Rezultati izotopskih raziskav so opisali vire in mehanizme napajanja podzemne vode, njeno obnovljivost, zadrževalni čas v vodonosniku, izvor in geokemijski razvoj zaradi reakcij s kamninami. Potrdili so hipotezo, da je masiv Boča napajalno območje Rogaških mineralnih vod, ki se zadržujejo v vodonosniku s povprečnim zadrževalnim časom od 7200 do 3400 let, ki je odvisen od lokacije in globine.

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