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Risk Assessment of Mineral Groundwater Near Rogaška Slatina

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Abstract. Groundwater resources of mineral and thermo–mineral water are invaluable for planning a sustainable spatial and economic development of the Rogaška Slatina area, which requires a protection of this natural heritage. Numerous previous investigations of Rogaška groundwaters were subjects to balneology and to demands for larger exploitation quantities, that is why information are missing that are essential for definition of the Rogaška fractured aquifer system with mineral and thermo–mineral water and for its protection. The isotopic investigations of groundwaters stored in the Rogaška Slatina fractured aquifer system were performed aiming at answering open questions on the groundwater recharge and dynamics, on connections between different types of aquifers and on solute transport. Environmental isotopes 2H, 18O, 3H, 13C of dissolved inorganic carbon and 14C 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. The mean residence time estimates of mineral and thermo–mineral water in the aquifer are between 3400 and 14000 years. On the other hand, the mixing processes between younger and older waters or mineral and spring waters are reflected as well as waters that infiltrated predominantly after the 1960s. These suggest the vulnerability of the research systems to man–made impacts. The presented results coupled with available information on a physical hydrogeology and water chemistry assess the optimal balance between the environmental protection and economic use of mineral water resources in the study area. They are essential for the protection strategy development of mineral and thermo–mineral water in the Rogaška Slatina area bringing together the state administration and local authorities and stakeholders.

1. Introduction
Rogaška Slatina (E Slovenia) is famous by mineral water, which was discovered in this place in the time of Ancient Rome. The spa tourism and the production of natural mineral waters are the powerful economic activities in the city, therefore the groundwater resources of mineral and thermo–mineral water are invaluable for planning a sustainable spatial and economic development of the area, which requires a protection of this natural heritage. Numerous investigations of the Rogaška groundwaters were subject to balneology and to the larger exploitation quantities [1], 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.

Besides, the management of mineral water faced with the organization and administrative problems during the last decades. Political changes in the nineties led to the ownership fragmentation of spa tourism and bottling companies of natural mineral water. The new companies very poorly cooperate among themselves. Each one obtained the concession and the water permit, however their programs are not harmonized and they base on old research results. The Bottling Company of Droga Kolinska was aware of the problem, therefore it initiated and co-financed the presented isotopic investigations.

The isotopic investigations of groundwaters stored in the Rogaška Slatina fractured aquifer system were performed aiming at answering open questions on the groundwater recharge and dynamics, on connections between different types of aquifers and on solute transport. 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 [2]. The stable isotope content of water may be considered conservative under low-temperature and low-circulation groundwater systems, if the relative amount of water involved in chemical reactions remains limited [2, 3]. 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 [4]. 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. CO₂ or H₂S).

The stable carbon isotopic composition of dissolved inorganic carbon (δ¹³C-DIC) is not a conservative tracer. Nevertheless, the δ¹³C can trace the carbon sources and reactions for numerous interacting organic and inorganic species. It is an important tool for quantifying the water-rock interactions, identifying the proportion of different CO₂ sources in water, and determining the initial geological settings of the groundwater recharge [3, 5].

Groundwater dating is the main field of application of the ¹⁴C and ³H 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 [3, 6]. The measured activity concentrations are compared with the input functions to get informative age determinations over the past several decades. ³H 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 [7, 8]. On the other hand, ¹⁴C with a half-life of 5730 years is applicable for dating groundwaters recharged prior to 1000 – 2000 years [9] and as old as 30000 years [2].

2. Study area

The study area is geologically one of the most complex parts of Slovenia [10]. It is the juncture of three major regional fault systems, separating three tectonic units (figure 1 and figure 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 complexity of the study area is reflected in a lithological
heterogeneity. 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 northermost 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.

Mineral water is stored in fractured layers of the Oligocene tuff covered by the Upper Oligocene and Lower Miocene beds (figure 1 and figure 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 (figure 1). Donat Mg is the most famous among Rogaška mineral waters. It has the highest mineral content (table 1) and contains more than 1000 mg/l of Mg. The content of gaseous CO₂ in the water is normally in the range of 2–30 g/l. Gas is practically pure CO₂ with minor share of nitrogen and negligible concentration of oxygen and methane [11].

Spring water and thermo–mineral water were also exploited at the study area (figure 1, table 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 1500 and 1700 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.

3. Methods
Isotopic 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; figure 1, table 1). Besides the groundwater CO₂ was sampled and also precipitation at altitudes of 340, 530 and 710 m asl.

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 (δ¹⁸O) of the water was measured by the classic CO₂ – H₂O equilibrium technique [12] with a fully automated device adapted from HORITA et al. [13] coupled to a Finnigan DELTAplus Mass Spectrometer. Deuterium (δ²H) was measured in a continuous flow mode by chromium reduction using a ceramic reactor slightly modified from MORRISON et al. [14]. 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 [15].

The ¹³C content was also measured in the Stable Isotope Laboratory of the Institute of Water Resources Management, Joanneum Research, Graz, mass spectrometrically by Thermo Finnigan DELTAplusXP (CF-IRMS). The values are reported as ‰ vs. V-PDB standard with an overall precision of 0.1 ‰.
Figure 1. Study area with locations of boreholes with mineral, thermo–mineral and spring water.

Figure 2. Geological cross section A-A’ (see Fig. 1) of the Rogaška Slatina area [10].
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 $\beta$-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 (equation 1), employing the pre-industrial baseline $^{14}$C activity of the soil CO$_2$ equal to 100 pmC as an initial concentration and the $^{13}$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 consider 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:

$$
t = -8267 \ln \frac{a_0^{14}C}{a^{14}C}$$  \hspace{1cm} (1)

where $t$ is groundwater age, $a_0^{14}C$ is a modern $^{14}$C activity in the soil zone (100 pmC), $a^{14}C$ 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 $^{13}$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 thermo–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$_2$.

4. Results and discussion

Average values of sampled water discharges, electroconductivity, mineralisation, temperature and pH during a monitoring period 2008 – 2015 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 40g/l [1]. 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 %; [11]).

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 isotopes than precipitation, due to the evaporation process [2, 16, 17].

Mineral waters have $\delta^{18}$O in the range between -12.2 and -10.3 %o and $\delta$ $^2$H in the range between -80.5 and -63.9 %o. The lowest $\delta$ 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 (table 2), which reflects mixing processes of older and younger waters (figure 3).
Table 1. Average values of sampled water discharges (Q), electroconductivity (SEC), mineralisation (M), temperature (T) and pH.

| Borehole name | Borehole depth (m) | Q (l/s) | M (g/l) | SEC (µS/cm) | T (°C) | pH |
|---------------|--------------------|---------|---------|-------------|-------|----|
| RSL-2         | 274                | 0.5     | 12.6    | 10995       | 14.55 | 6.9|
| RSL-3         | 24                 | 0.2     | 5.7     | 5171        | 11.8  | 6.5|
| RSL-6         | 606                | 1       | 11.8    | 10535       | 28.3  | 6.9|
| RSL-7         | 603                | 0.4     | 8.5     | 8630        | 15.2  | 6.4|
| RSL-11        | 170                | 0.1     | 8.2     | 7110        | 12.1  | 6.5|
| RSL-1         | 1700               | 6       | 6.1     | 6425        | 55.4  | 7.1|
| RSL-4         | 215                | 2.4     | 461     | 12.6        | 7.2   |    |
| RSL-10        | 130                | 2.1     | 376     | 11.1        | 7.6   |    |
| RSL-8         | 170                | 1.6     | 0.5     | 572         | 11.6  | 7.2|
| RSL-14        | 38                 | 42      | 483     | 12.7        | 7.6   |    |
| RSL-12        | 100                | 2.1     | 386     | 9.8         | 7.6   |    |

Mineral water

Thermo mineral water

Spring water from limestone

Spring water from dolomite

Spring water from sandstone

The δ¹⁸O and δ²H 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 narrower in spring water from sandstone, -10.9 to -10.6 ‰ and -76.9 to -67.2 ‰, respectively (figure 3). The δ¹⁸O and δ²H of thermo–mineral water is similar to spring water from a dolomite.

Craig [18] firstly described the relationship of discussed isotopes in the precipitation by the global meteoric waterline (GMWL, figure 3). The local meteoric waterline (LMWL) of the Rogaška Slatina area slightly differs from the GMWL in both the slope and the intercept (figure 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 [15, 16]. All sampled waters are distributed in the LMWL vicinity. The δ¹⁸O and δ²H values 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 (figure 3), which reflects colder climate conditions during the infiltration processes [2, 3, 4]. The exception is the shallow RSL-3 mineral water (table 1) that is mixed with surface waters (figure 3 and figure 4). The δ values of mineral waters sampled from RSL-2, RSL-6 and RSL-3 slightly deviate from LMWL (figure 3). The level of gaseous CO₂ in these waters is the highest (up to 40 g/1; [1]), therefore it is assumed that ¹⁸O is depleted due to the exchange of water with the geogenic CO₂ [2, 3, 4].

The ³H data are illustrated in figure 4. 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 [19] 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 [19]. Evidently the recharge of these groundwaters occurred prior to the 1950s, therefore they are relatively unblemished by human activities.
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 (figure 4) should contain modern water that infiltrated predominantly after the 1960s, suggesting the vulnerability of these groundwater systems to man–made impacts.

According to Kovčič [19] the mean residence time of spring water of shallower boreholes RSL-10, RSL-12 and RSL-14 (table 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.

**Figure 3.** The relationship between stable oxygen and hydrogen isotopic composition in sampled water

According to Kovčič [19] the mean residence time of spring water of shallower boreholes RSL-10, RSL-12 and RSL-14 (table 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.

**Figure 4.** Tritium concentrations in groundwater and in precipitation of the Rogaška Slatina area.
The $\delta^{13}C$ values of the dissolved inorganic carbon varied between -13 and +2‰ in sampled groundwater (figure 5 and figure 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 [2]. 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 [2] these values closely resemble the $\delta^{13}C$ content of carbonate groundwater that evolves under a closed system condition.

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 system, the total dissolved inorganic carbon (DIC) exists practically 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 dissolve 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 (table 2). The hydrochemical composition was most probably altered by the incorporation of the geogenic CO$_2$ influx that originates from a volcanic source (figure 5). The average $\delta^{13}C$ 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 $\delta^{13}C$ 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 [5]. $\delta$ values from -2.0‰ to +4.1‰, with an average of +2.2‰ were analysed in Slovene carbonate rocks [20, 21]. The relationship between $\delta^{13}C$ 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. Very low $^{14}$C contents, ranging between 0.9 to 1.4 pmC, have been determined (table 2), which reflects very long mean residence times of the groundwaters in the underground. With the aim to determine the resident time of groundwater according to equation 1 the geogenic CO$_2$ was characterised first based on the $\delta^{13}C$ value of the CO$_2$ gas phase of water samples. The $\delta^{13}C$ values show a very wide spread, between -10 and +3‰ (figure 5). They are within the range of $\delta^{13}C$ reported in the literature for magmatic CO$_2$, -12 to -1‰ [22, 23, 24]. Further the chemical mass-balance correction 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 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$_2$.

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 interglacial period of the Pleistocene epoch.

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. According to the $^{18}$O and $^2$H isotopic data (figure 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, table 1) and hence follow 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 groundwaters, thus groundwater age dating using $^{14}$C is not appropriate.

**Table 2.** HCO$_3^-$ concentration, stable C isotopic compositions, $^{14}$C content, dilution factor $q_{\text{total}}$ and age estimates of the mineralized waters (RSL-2, RSL-3, RSL-6 and RSL-7) and thermo–mineral water (RSL-1).

| Sampling point | HCO$_3^-$ (mg/l) | $\delta^{13}$C (‰) | $^{14}$C (pmC) | $q_{\text{total}}$ | 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       |

**Figure 6.** The relationship between stable C isotopic composition and HCO$_3^-$ concentration in sampled waters.
5. Conclusions
The results of isotopic investigations of groundwaters in the Rogaška Slatina area 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 $\delta^{2}H$ values indicated the meteoric origin of mineral and thermo–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 $^3$H 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, thermo–mineral and spring waters based on $^3$H, $\delta^{13}$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 $^3$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 results improve a conceptual hydraulic model of the Rogaška Slatina fractured aquifer system. They are essential to determine the optimal balance between environmental protection and economic use of mineral water resources in the study area and for their protection strategy development. The concession, the water permits and the related monitoring programmes should be harmonized with the presented results bringing together the state administration, local authorities and stakeholders.

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