Isotope studies of karst springs included in the water supply system of the City of Rijeka (Croatia)

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Abstract

Aim: To provide information about the results of isotopic analyses of karst springs, Rječina Spring and Zvir, which ensure potable water for more than 200,000 people in Rijeka County (Croatia)

Methods: Specific activities of selected radionuclides were determined by high resolution gamma spectrometric analysis and radiochemical separation method. Values of hydrogen and stable isotope contents were determined by water equilibration method on isotope ratio mass spectrometer in conjunction with dual inlet and equilibration peripheral unit.

Results: Anthropogenic radionuclides were detected in trace amounts. The results of the analysis show that the calculated yearly dose introduced to an adult human consuming 2 liters of water per day is approximately 20 μSv. Stable isotopes content of the spring waters indicates a dominant recharge of the analyzed hydrological system by winter precipitation. Different isotopic variations of spring water as a consequence of sudden precipitation inputs in summer and autumn indicate that water discharged at Rječina Spring mainly originates from a big water reservoir situated in the wide mountainous region in the hinterland of the spring.

Conclusion: The examined water is potable and radiologically safe. Stable isotope variations of the spring water show a fast reaction to sudden precipitation inputs, confirming the ecological vulnerability of karst springs. In light of recent heavy precipitation and flooding in different parts of Croatia, a more systematic research on isotopic water composition should be encouraged.

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Introduction

Rječina Spring (RJ) and Zvir (ZV) are the most important springs of the water supply system ensuring potable water for the City of Rijeka and its surroundings. These are springs with relatively similar annual average discharges but different flow dynamics. RJ springs at 325 m above sea level, has a mean annual output discharge of 7.38 m^3s^{-1} and regularly dries out for several months a year. Namely, RJ is a seasonal spring that functions as an overflow for high and medium groundwater discharges (1). It provides high quality water for the City of Rijeka and neighboring settlements through most of the year and its protection is of the highest priority. RJ average water supply rate measures 0.69 m^3s^{-1}. ZV springs at 3 m above sea level, has a mean annual distribution of 5.2 m^3s^{-1} and a nominal minimum discharge of 1.5 m^3s^{-1}. The pumping from ZV is activated, i.e. water from ZV is used for water supply, when the RJ discharge is reduced to 0.29 m^3s^{-1} or it dries out completely (2).

The two springs are under regular quality and health control checks by the Water Supply Company and the Teaching Institute of Public Health of Primorje & Gorski Kotar County (3), and have been subjects of many scientific investigations (1, 4). Nevertheless, isotopic studies of these spring waters are not as frequent. The need for better understanding of complex processes taking place in this ecologically and socially important karst area is often emphasized (5).

In order to expand the knowledge about RJ and ZV, we present the results of measurement for selected radionuclides in RJ and ZV water, as well as the results of monitoring hydrogen (^2H) and oxygen (^{18}O) stable isotope variations in RJ water as a reaction to precipitation input events.

To the best of the authors' knowledge, there have not been any reports about RJ and ZV from the radiological point of view. The first report about the results of a systematic analysis of a stable isotope composition of the springs was given by Mance et al. (6) and, before that, there were only sporadic reports (7, 8). The results presented here relate to short-term data collection, i.e. sampling during particular storm events, including observations related to rainfall inputs and stable isotope composition variations related to changes in RJ discharge. The results of this type of studies can contribute to identifying water storage processes and mechanisms of groundwater recharge and discharge in the karst aquifer (9). They are also important for public health as they reveal information about the reaction time of karst springs to potential pollutants.

Materials and Methods

Study area

RJ and ZV are the largest springs of the Rječina River (RR) basin, a typical Dinaric karst basin. The basin is located in the Dinarides of western Croatia and southern Slovenia (Figure 1A).

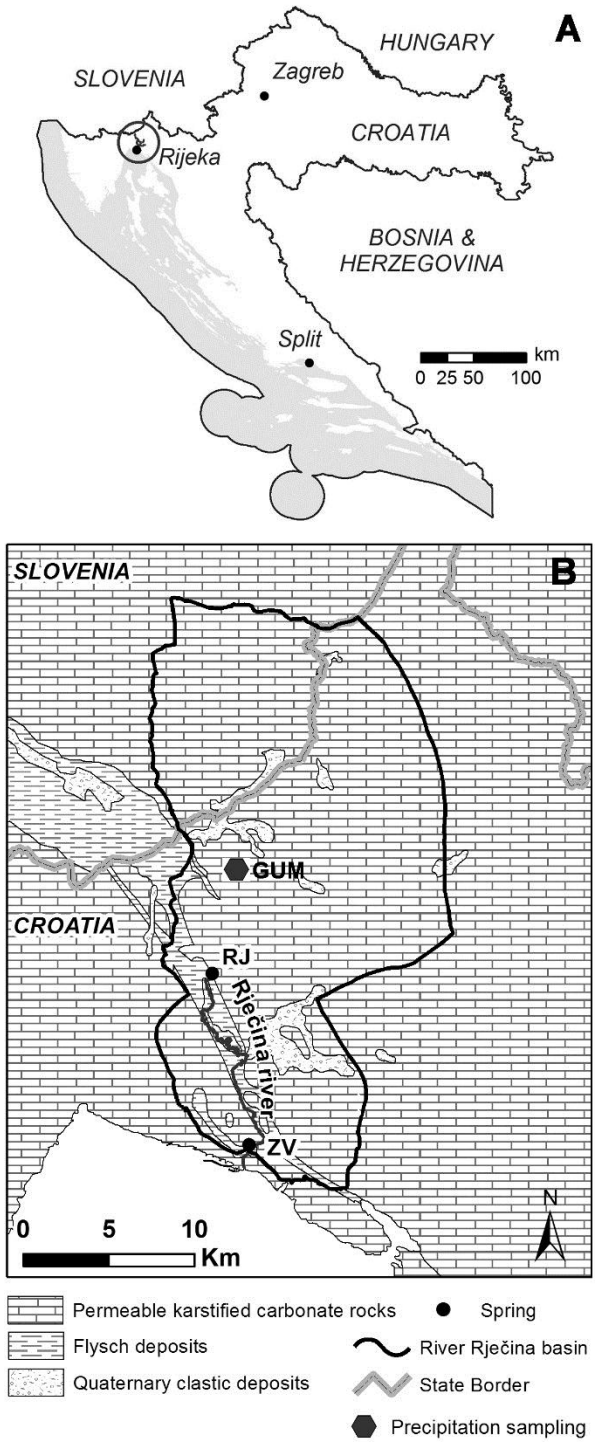
The RR basin covers approximately 500 km^2 and has its main recharge area in the mountains of Gorski Kotar (Croatia) and the Snežnik massif (Slovenia). The previous isotopic analysis found substantial evidence in favor of the conjecture that RJ and ZV are mainly recharged from the same average altitude and/or share the same groundwater reserves (6). The main lithological sedimentary units of the region are carbonate rocks, flysch and Quaternary clastic deposits (Figure 1B).

According to the Köppen-Geiger climate classification (10), the associated climate type for the study area changes from Cfa on the coast to Cfb in hinterland. These are temperate climates, with precipitation regimen without regular dry seasons, and with hot (Cfa) and warm summers (Cfb). The mountainous part of the study area has an annual rainfall greater than 3000 mm, making it one of the rainiest regions in Croatia (11).

Measurement methods and sampling

For the purpose of this study, spring water samples were collected at RJ and ZV, while

Figure 1. *A) Map of Croatia showing the study area (circle); B) sampling locations and distribution of the main lithological structures in the study area. RJ – Rječina Spring; ZV – Zvir; GUM – Gumance*



precipitation samples were collected at Gumance (GUM), the location that belongs to the recharge area of RJ and ZV basin. Precipitation sampling site can be seen on Figure 1B, while its coordinates and altitude are indicated in Table 1.

Table 1. *Coordinates and altitudes (in m above sea level) of precipitation sampling site*

Precipitation sampling site	Coordinates	Altitude (m a.s.l.)
Gumance (GUM)	N 45° 28' 4'' E 14° 24' 27''	688

Specific activity concentrations for natural (^{40}K, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{232}Th, ^{235}U, ^{238}U) and anthropogenic (^{134}Cs, ^{137}Cs, ^{241}Am) radionuclides have been determined for two samples collected in March 2012 at springs RJ and ZV. Activity concentrations were determined by high resolution gamma spectrometric analysis. Additionally, for the determination of ^{226}Ra activity concentration, the radiochemical separation method was also used (12). Measurements of activity concentrations were performed at the Institute for Medical Research and Occupational Health (Zagreb, Croatia). Effective dose calculation and results analysis were performed according to the regulation of Croatian Ministry of Health and recommendations of the World Health Organization (WHO) (13, 14). The annual effective dose *E* (mSv/year) resulting from water intake was estimated as (14):

$$E = q \cdot \sum_i C_i \cdot h_i$$

where:

q - annual ingested volume of drinking water, assumed to be 0.73 (m^3/year),

C_i - the activity concentration of radionuclide i (Bq/m^3),

h_i - dose coefficient for ingestion of radionuclide i by adults (mSv/Bq).

Drinking water is considered to be safe from the radiological point of view if the annual dose calculated based on the presence of radioactive isotopes in water, under the assumption of an average daily consumption of 2 liters, is below 0.1 mSv (14). Since there are no strict upper limits for activity of individual radionuclides in drinking

Table 2. *Results of gamma spectroscopic analysis of water samples*

Radionuclide	Activity concentration (Bq / m³)	
	Rječina Spring	Zvir
^{40}K	42.2 ± 2.5	44.7 ± 3.4
^{134}Cs	< 1.2 ± 0.2	4.4 ± 1.5
^{137}Cs	< 1.1 ± 0.2	< 1.4 ± 0.4
^{210}Pb	17.2 ± 4.2	32.5 ± 7.5
^{226}Ra (γγ)	< 25.6 ± 7.1	< 12.7 ± 4.2
^{226}Ra (αα)	21.1 ± 6.3	5.4 ± 2.8
^{228}Ra	3.4 ± 0.5	2.6 ± 0.7
^{232}Th	3.4 ± 0.5	2.6 ± 0.7
^{235}U	< 1.6 ± 0.8	< 2.0 ± 1.0
^{238}U	< 31.5 ± 5.3	30.2 ± 7.4
^{241}Am	< 3.5 ± 0.8	< 4.6 ± 1.1

water, screening for gross α and gross β radiation activity was also carried out (14).

In order to investigate the karst aquifer discharge response to sudden precipitation inputs, daily sampling during storm events at spring RJ was organized and precipitation samples were taken on GUM. Samples were taken during two storm events in late summer of 2013, followed by storm event sampling in the fall of 2013. On those occasions, both rain water (N = 10) and groundwater samples (N = 30) were collected. Stable isotope contents of collected samples were measured by the water equilibration technique in Stable Isotope Laboratory at the Physics Department of the Faculty of Medicine at University of Rijeka. For the measurement, an isotope ratio mass spectrometer (Delta^{plus} XP; Thermo Finnigan, Germany) coupled with equilibration unit and dual inlet system was used. Results were reported in δ-values (‰) on VSMOW scale (15). The measurement precision was < 1 ‰ for hydrogen (δ^2H), and < 0.1 ‰ for oxygen (δ^{18}O).

Globally, for natural waters that are not under the influence of evaporation, the linear relationship between δ^2H and δ^{18}O is represented by the Global Meteoric Water Line (GMWL): $\delta^2H = 8 \cdot \delta^{18}O + 10$ ‰ (16). There are local deviations from the GMWL, due to various different factors such as altitude, proximity to the sea, etc., which required the measurement of local meteoric water lines. One of these local meteoric water lines is the Western Mediterranean Meteoric Water Line (WMMWL): $\delta^2H = 8 \cdot \delta^{18}O + 13.7$ ‰ (17). Stable isotopes can be used as "fingerprints" to detect geographical origins of natural waters (18, 19). One of the ways to do this is by using d-excess, the hydrological parameter introduced by Dansgaard (20): d-excess = $\delta^2H - 8 \cdot \delta^{18}O$. Precipitation that originates from the Atlantic Ocean typically has d-excess values ≈ 10 ‰ and precipitation originating from the Mediterranean has d-excess values > 15 ‰ (21).

Results

Gamma spectrometric analysis proved the existence of natural as well as anthropogenic radionuclides in examined water samples. The latter were only found in trace amounts. Results of the analysis, i.e. activity concentration for radionuclides of interest, are presented in Table 2. Activity concentration of ^{226}Ra has been determined by using both gamma spectrometric method and radiochemical separation method, and results of these two methods do not differ significantly (Table 2).

Calculated gross α radiation activity for RJ is $2.831 \cdot 10^2$ Bq / m³, and for ZV it is $2.712 \cdot 10^2$ Bq / m³, while gross β radiation activity for RJ is $2.509 \cdot 10^2$ Bq / m³ and for ZV it is $2.443 \cdot 10^2$ Bq / m³. Estimated effective dose for an adult whose daily intake is 2 L of water, for RJ is 18 μSv / year and for ZV 23 μSv / year.

As it can be seen in Figure 2, δ^2H and δ^{18}O values of spring water correspond to WMMWL, while the majority of precipitation samples lie between GMWL and WMMWL. Figure 2 also shows spring water values corresponding to the lower part of value cluster of precipitation samples.

D-excess values of precipitation in our study range from a minimum of 6.98 ‰ to a maximum

Figure 2. *δ^2H versus $\delta^{18}O$ correlation diagram of Rječina Spring (RJ) samples and precipitation samples collected at Gumance (GUM). Global Meteoric Water Line (GMWL) and West Mediterranean Meteoric Water Line (WMMWL) are shown for comparison.*

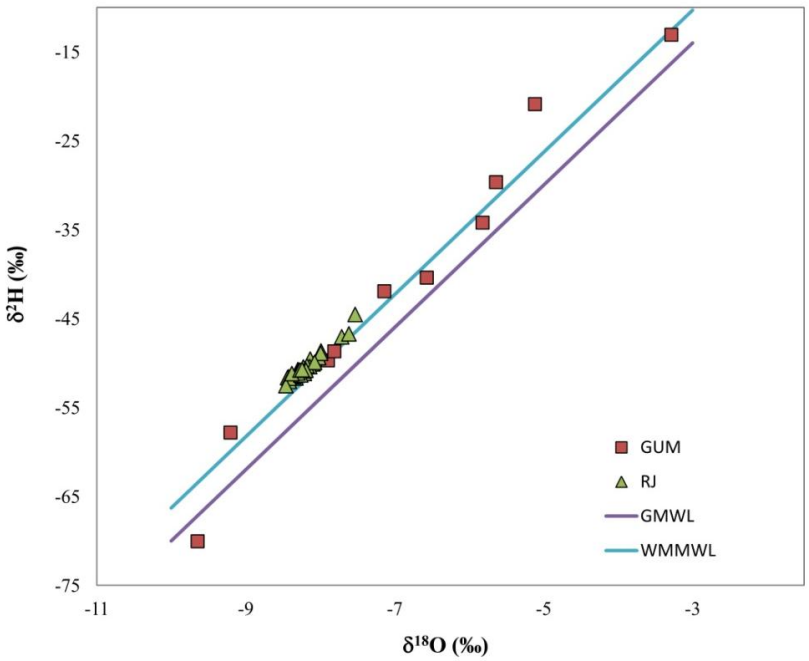


Figure 3. *Deuterium excess values of Rječina Spring (RJ) samples and precipitation samples collected at Gumance (GUM). The mean analytical uncertainty (± 1.04 ‰) was as indicated by the error bars.*

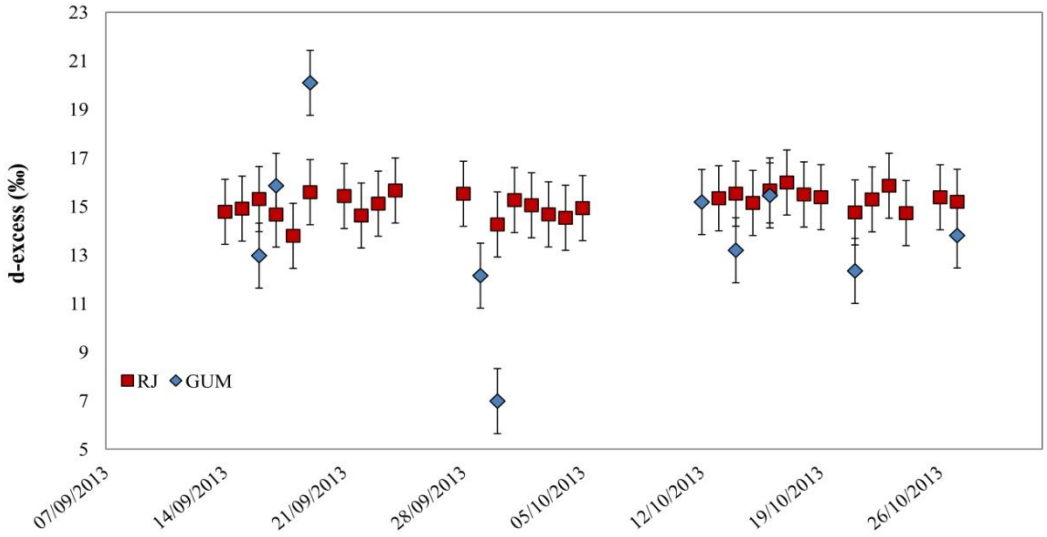
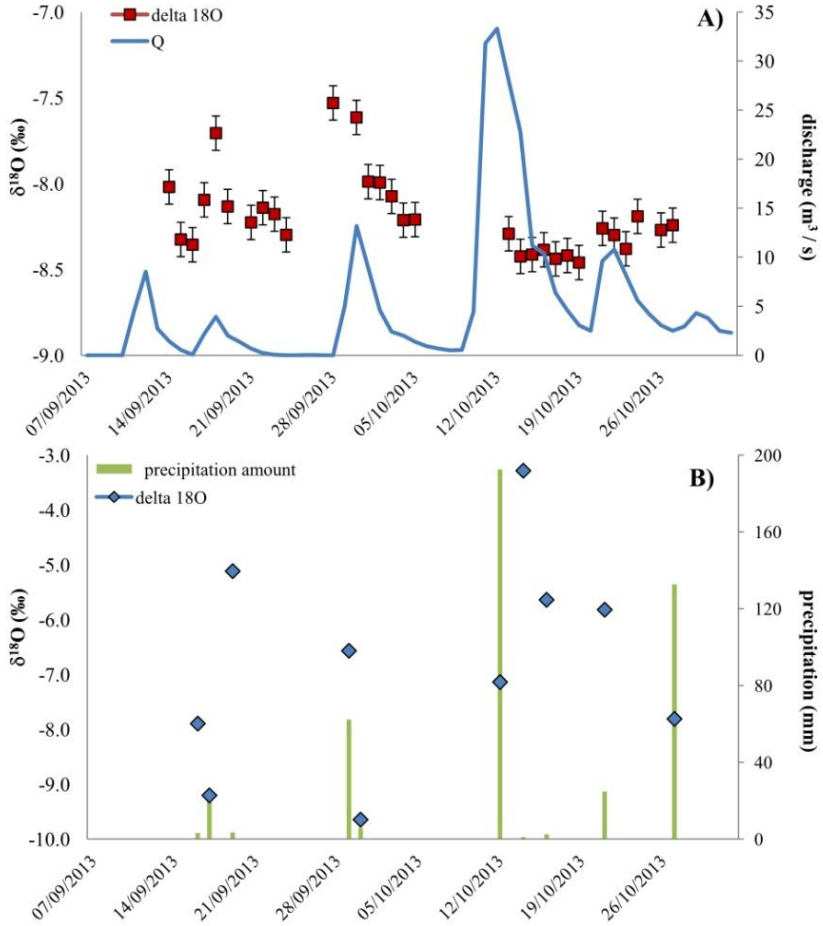


Figure 4. *A) Daily discharge and $\delta^{18}O$ groundwater series for samples collected at Rječina Spring; B) precipitation amounts and corresponding $\delta^{18}O$ values of samples collected at Gumance (GUM). The mean analytical uncertainty (± 0.1 ‰) is indicated by the error bars.*



deviation of 1.45 of 20.09 ‰ (Figure 3). Other precipitation d-excess values fluctuate about a mean value of 13.87 ‰, with standard deviation of 1.45 ‰. ~~‰~~. Unlike the precipitation samples, d-excess values of spring water are all within the measurement error with a mean value of 15.13 ‰ and a standard deviation of 0.49 ‰.

$\delta^{18}O$ time series of RJ spring water collected in September 2013 show shifts towards more positive values that coincide with an increase of RJ discharges (Figure 4). The first such shift occurred on 18th September (RJ, $\delta^{18}O$ = -7.71 ‰), although rain water collected on 17th of September had a lower value (GUM, $\delta^{18}O$ = -9.2 ‰) than values of RJ water sampled prior to that rain event (≈ -8.0 ‰ to -8.3 ‰).

Next significant rain event occurred between the 28th and 29th September 2013, with 62.3 mm of rain and $\delta^{18}O$ = -6.57 ‰. RJ sample collected on the 28th September had the value of -7.53 ‰, although the discharge was very low. The discharge reached the highest value on 30th September, with corresponding $\delta^{18}O$ = -7.61 ‰. During the following days, both discharge rates and $\delta^{18}O$ values continued to decrease (Figure 4A).

After the described events, RJ $\delta^{18}O$ values oscillations were not significant any more, although there were major precipitation events in October 2013. The two most important of those precipitation events took place on 12th and 27th October, with precipitation amounts of 192.6 mm and 132.7 mm, respectively. $\delta^{18}O$ value for the first event was -7.14 ‰, and for the second one -7.81 ‰ (Figure 4B), but a reaction to these events could not be detected in isotopic values of RJ (Figure 4A).

Discussion

Values of radionuclide activity in spring waters of RJ and ZV reported here are well below guidance levels for radionuclides in drinking water recommended by WHO (14). The calculated yearly effective doses, obtained by using the concentration values of radionuclide activity in spring waters of RJ and ZV, assuming that the water is introduced into the human body on a daily basis, are ≈ 20 μSv. This is significantly below the acceptable limit of a dose (13). The analyzed RJ and ZV samples are not radiologically contaminated and water may thus be considered radiologically safe and used for drinking.

Mance at al. (6) showed that RJ is under the influence of different hydrological conditions in comparison to other springs in the area. In order to provide some new, additional information about this complex system, samples of GUM precipitation and RJ groundwater were taken in late September 2013 and in the fall of 2013.

Both, an isotopic values correlation diagram (Figure 2) and d-excess values of the spring samples (Figure 3) indicate a Mediterranean origin of the analyzed water, confirming the dominant recharge of the system by winter precipitation (6).

An analysis of stable isotope dynamics shows a different composition of stable isotopes in groundwater during the three storm events. The first September storm event occurred after a relatively long period without significant precipitation. This event is difficult to comment given that a shift towards a more positive groundwater $\delta^{18}O$ value occurred one day prior to the rain event on GUM, and this rainfall had the second most negative $\delta^{18}O$ value of all rain samples collected during this study (Figure 4). A possible explanation is that a rain event that triggered the groundwater shift toward more positive $\delta^{18}O$ value had happened earlier than the one on GUM and that it had taken place deeper in the mountainous hinterland of the system, most probably on the Slovenian Snežnik massif.

The second September event had significantly less negative $\delta^{18}O$ precipitation values in comparison to RJ values collected previously during the month (with the exception of the value that corresponded to the highest RJ discharge of the previous event). As it already happened during the previous event, a shift towards less negative groundwater values occurred again a day prior to the event on GUM (Figure 4). Once more, this suggests that an earlier event, taking place further in the catchment area, had activated the system prior to the event on GUM. Also, this indicates a fast reaction of the hydrological system to sudden precipitation inputs and a short retention time of newly infiltrated water in the underground. This is very important from the environmental protection point of view as it indicates an area highly susceptible to contamination. The introduction of a pollutant to the system would probably cause an immediate pollution of drinking water.

Stable isotope composition of groundwater samples collected after the third storm event was without significant oscillations although the precipitation amount was considerable and its δ values were less negative than those for groundwater sampled prior to the storm. Bearing in mind that the system may be described by a dual porosity model (6), this situation might suggest that September storm events triggered the passage of groundwater through short and wide karst channels, while well mixed groundwater discharged in October originated from groundwater reservoirs. Accordingly, it can be concluded that there is a scant amount of groundwater in the vicinity of RJ, and the water discharged at RJ mainly originates from a large water reservoir located in the mountainous region in the hinterland of the spring.

The last precipitation event in this study occurred on 27th October, but the isotopic value of the collected precipitation was too close to the value of previously collected groundwater (Figure 4), so this event could not be used for further analysis.

Although we got new insights in the functioning of the system, such as the one indicating that precipitation from the hinterland has greater influence on RJ than precipitation occurring closer to it, there are still many unresolved questions. The reaction of the system to the precipitation inputs proved to be very fast, and daily sampling was probably not frequent enough to give a complete picture about the hydrological conditions. More frequent sampling, for example on an hourly basis, could give a better insight into the situation (9).

Conclusions

The authors present the results of radioactive and stable isotopes analyses for RJ and ZV, the two largest and most important water supply springs of the city of Rijeka, as well as precipitation samples collected at the assumed recharge areas of the two springs. The purpose of the paper is to provide a radiological analysis of their water quality and to expand the sources of available data for stable isotopes.

Measurements of radionuclides showed that the water is safe for human consumption. Stable isotope data indicates a rapid reaction of the system to sudden precipitation inputs, thus confirming vulnerability of karst springs to potential pollution. We can confirm that the main water reservoir of the system is situated in the mountainous region of the basin, and that in the vicinity of the Rječina Spring there are only scant amounts of groundwater.

The authors conclude that isotopic investigations of the spring water and precipitation collected on the assumed recharge area reveal some useful information on the hydrological system. Recently, there have been catastrophic floods in different parts of Croatia. We may treat the floods as indicators of a lack of detailed knowledge about the hydrological conditions in corresponding aquifers. Therefore, more systematic isotopic analyses are strongly encouraged.

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Competing interests: None to declare.

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