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# Study of the bank filtered groundwater system of the Sava River at Zagreb (Croatia) using isotope analyses

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Radioactive isotope tritium ( $^3\text{H}$ ) and stable isotopes of hydrogen ( $^2\text{H}/^1\text{H}$ ) and oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) were measured during 2010 in the Sava River, precipitation and groundwater at 3 monitoring wells and 1 production well of the Petruševac aquifer, close to the Sava River in the Zagreb area. Significant increase of  $^3\text{H}$  activity in the Sava River was observed in June, ( $200 \pm 20$ ) TU, and in groundwater of all wells with damped response (maximum 60 TU) and with delay of 3–5 months related to the Sava River. This increase was explained by release of tritiated water from the Krško Nuclear Power Plant, 30 km upstream from Zagreb in the beginning of June 2010. Stable isotope analyses showed similar range of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values for the Sava River and groundwater samples with higher variations in surface water. Differences in monthly variations of  $\delta^{18}\text{O}$  values between particular monitoring wells, together with  $^3\text{H}$  values, indicated different infiltration times of surface water of the Sava River to different wells of the Petruševac aquifer.

Key words: tritium  $^3\text{H}$ , stable isotopes  $^2\text{H}$  and  $^{18}\text{O}$ , Sava River, Petruševac aquifer

## Introduction

Measurements of radioactive isotope tritium ( $^3\text{H}$ ) and stable isotopes of hydrogen ( $^2\text{H}/^1\text{H}$ ) and oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) can give useful information in hydrogeological studies of (i) mixing of surface and groundwaters, (ii) water circulation in nature, especially in karst areas, and (iii) mean residence time of water in aquifers. Increased  $^3\text{H}$  activities in natural waters may indicate some contamination, such as global contamination of atmosphere with  $^3\text{H}$  due to

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atmospheric thermonuclear bomb tests (Rozanski et al. 1991), or local contamination due to release of tritiated waters from various nuclear facilities.

$^3\text{H}$  and stable isotope  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios in monthly precipitation of the Zagreb area have been measured since 1979, and the results have been included into the GNIP (Global Network of Isotopes in Precipitation) database (IAEA/WMO, 2011) of the International Atomic Energy Agency (IAEA). The investigation of the Petruševac aquifer in the Zagreb area is included in the *Regional IAEA Project RER/8/016 Using Environmental Isotopes for Evaluation of Streamwater/Groundwater Interactions in Selected Aquifers in the Danube Basin* with the aim to determine the influence of surface stream of the Sava River on the groundwater of aquifer used for water exploitation.

### Sampling and measurement

$^3\text{H}$ ,  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  were measured during 2010 in the Sava River, precipitation and groundwater at 3 monitoring wells (piezometers) and 1 production well of the Petruševac aquifer, close to the Sava River in Zagreb area. Groundwater samples were collected monthly and the Sava River weekly for stable isotopes. Details of the sampling sites are given in Table 1.

Measurements of  $^3\text{H}$  activities in waters were performed by the liquid scintillation counter Quantulus 1220 (Barešič et al. 2011). All samples were electrolytically enriched prior to LSC measurements. The system for electrolytic enrichment consists of 20 cells, the initial volume of water is 500 mL and the final

Table 1  
Sampling data

Location	Distance from the Save R. (m)	Depth (m)	Analysis and sampling frequency
Sava R., Zagreb, below the bridge "Domovinski most"			$^3\text{H}$ – monthly $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ – weekly
Precipitation, Zagreb Meteorological station Grič			$^3\text{H}$ , $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ – monthly integrated sample
Well B-5A, Petruševac	400	38.0	$^3\text{H}$ , $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ – monthly
Piezometer PP-23/5, Petruševac	200	16.4	$^3\text{H}$ , $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ – monthly
Piezometer PP-18/30, Petruševac	500	32.0	$^3\text{H}$ , $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ – monthly
Piezometer PP-19, Petruševac	500	41.6	$^3\text{H}$ , $^2\text{H}/^1\text{H}$ , $^{18}\text{O}/^{16}\text{O}$ – monthly

volume is  $19 \pm 1$  mL resulting in the mean enrichment factor of  $22.5 \pm 0.5$ . The limit of detection is 0.3 TU (TU – Tritium unit, 1 TU = 0.118 Bq/L).

The oxygen and hydrogen isotopic composition was analysed with a Liquid Water Isotope Analyser (LWIA-24d) by Los Gatos Research. The initial water sample volumes of 1 ml have been analyzed twice, with <10 microliter injected

into the instrument during each measurement. The uncertainty of the measurements is  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 0.6\text{‰}$  for  $\delta^2\text{H}$ .

**Results and discussion**

$^3\text{H}$  activity (Fig. 1) in precipitation showed slight seasonal fluctuation between 4 TU and 14 TU, with higher values in summer.  $^3\text{H}$  activity of the Sava River and groundwater of the Petruševac aquifer followed  $^3\text{H}$  of precipitation till May 2010. Significant increase of  $^3\text{H}$  activity in the Sava River,  $(200 \pm 20)$  TU, was observed in June and in the next month it fell down to 6 TU. This increase was explained by release of tritiated water from the Krško Nuclear Power Plant, 30 km upstream from Zagreb in the beginning of June 2010 (Stepišnik et al. 2011). Increase of  $^3\text{H}$  was also observed in groundwater of all monitoring wells and the production well with damped response and a delay of several months in relation to the Sava River. The maximum  $^3\text{H}$  activity ( $\sim 60$  TU) was observed in monitoring wells PP-23/5 and PP-18/30 with the delay of 3 and 5 months, respectively. The second peak activity in piezometer PP-23/5 in November could be resulted by the extremely high level of Sava River in September 2010. In the deepest groundwater of well B-5A and in piezometer PP-19 (Table 1) the rate of increase of  $^3\text{H}$  activity was slower and the maximum value was lower (30 TU).

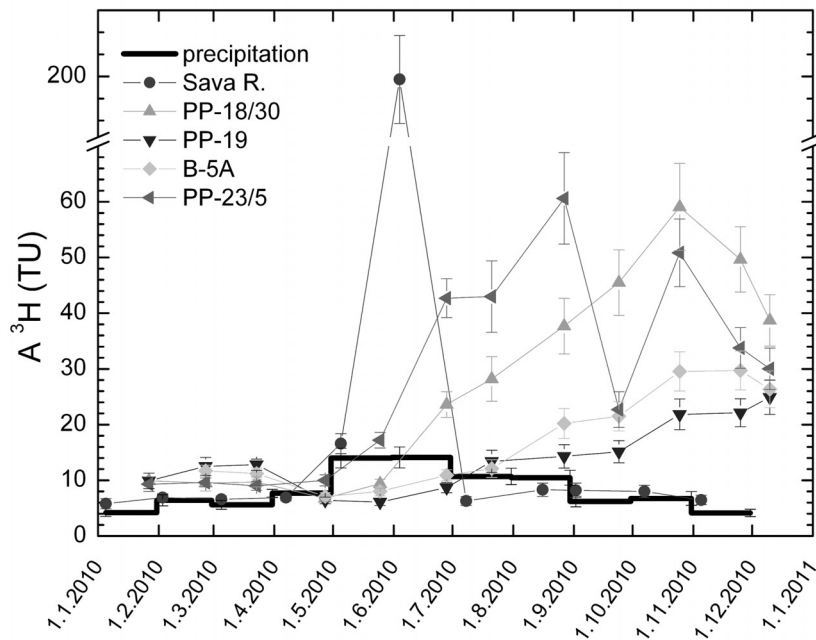


Fig. 1  $^3\text{H}$  activities in monthly precipitation and in the Sava River and groundwaters from the Petruševac aquifer (piezometers PP-23/5, PP-18/30, PP-19, well B-5A) during 2010

Stable isotope analyses of precipitation (Fig. 2) showed seasonal variations of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values typical for continental precipitation. The relation of  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  for Zagreb precipitation in 2010 (Fig. 3) is  $\delta^2\text{H} = (7.7 \pm 0.3) \delta^{18}\text{O} + (6.1 \pm 3.2)$ ,  $n = 12$ ,  $R = 0.992$ , and it is in agreement with the long-term (1980–2003) Local Meteoric Water Line (LMWL) for Zagreb:  $\delta^2\text{H} = (7.8 \pm 0.1) \delta^{18}\text{O} + (5.7 \pm 0.8)$ ,  $n = 271$ ,  $R = 0.98$  (Vreča et al. 2006).

The range of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values (Table 2) for the Sava River and groundwater samples was similar with higher variations in surface water. The regression line

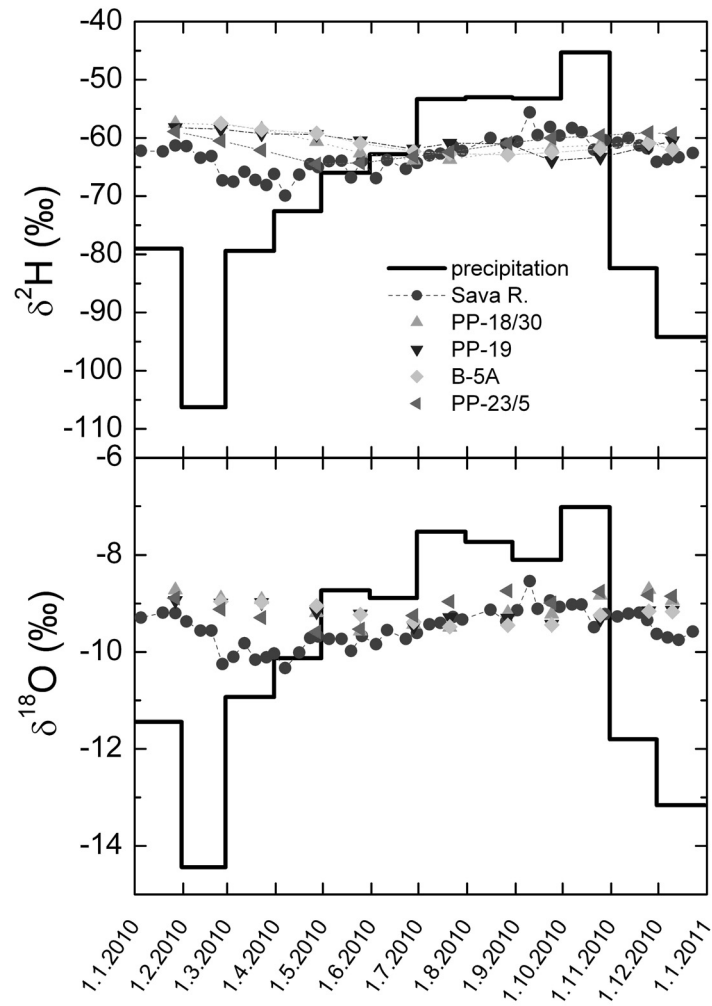


Fig. 2  
 $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in monthly precipitation and in the Sava River and groundwaters from the Petruševac aquifer during 2010

Table 2  
 $\delta^{18}\text{O}$  mean values with standard deviation and the minimum and maximum  $\delta^{18}\text{O}$  values in the Sava River and groundwater of the Petruševac aquifer during 2010

Location	$^{18}\text{O}$ (‰)		
	mean $\pm$	minimum	maximum
Sava River	$-9.5 \pm 0.4$	-10.33	-8.54
Well B-5A	$-9.2 \pm 0.2$	-9.48	-8.96
Piezometer PP-23/5	$-9.1 \pm 0.3$	-9.59	-8.74
Piezometer PP-18/30	$-9.1 \pm 0.3$	-9.57	-8.71
Piezometer PP-19	$-9.2 \pm 0.2$	-9.47	-8.94

$\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  in the Sava River and all groundwaters laid above the LMWL for Zagreb precipitation from 2010 (Fig. 3) and was described as  $\delta^2\text{H} = (7.5 \pm 0.3) \delta^{18}\text{O} + (8.2 \pm 2.6)$ ,  $n = 47$ ,  $R = 0.972$ . This relation could be compared with the long-term (1981–2006) LMWL for precipitation in Ljubljana, Slovenia:  $\delta^2\text{H} = (8.1 \pm 0.1) \delta^{18}\text{O} + (9.8 \pm 0.7)$ ,  $n = 290$ ,  $R = 0.99$  (Vreca et al. 2008). Ljubljana is geographically much closer to the springs of the Sava River than Zagreb and

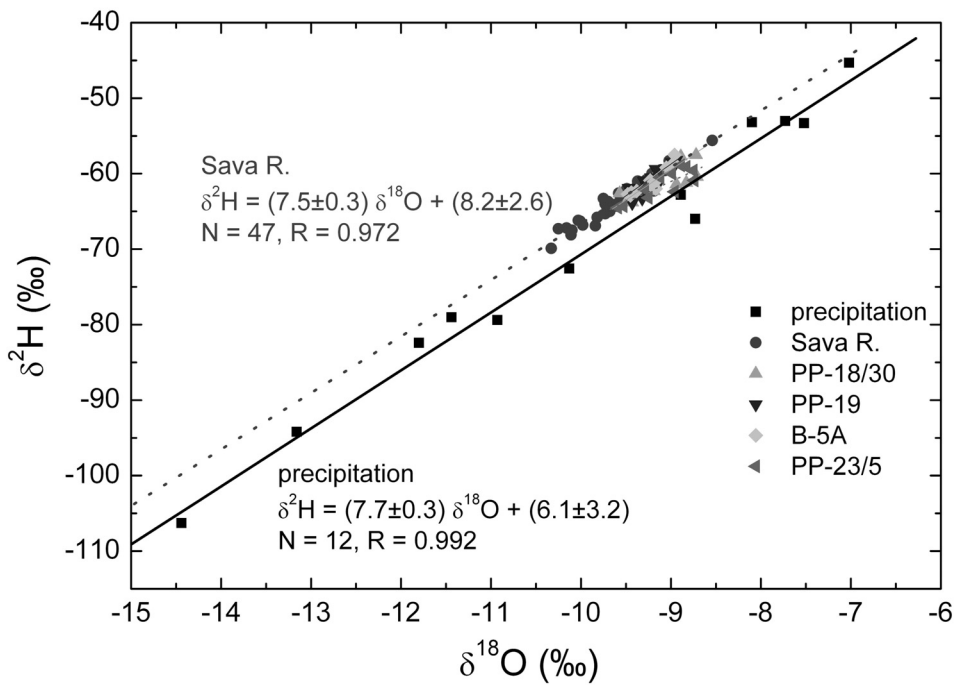


Fig. 3  
 Relation between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in the Sava River and in groundwaters of the Petruševac aquifer during 2010

therefore the LMWL for Ljubljana precipitation better describes the stable isotopic composition of the Sava River recharge area. All groundwater values laid very close to the correlation line of the Sava River (Fig. 3) showing direct influence of the Sava River on the groundwater of the Petruševac aquifer. Differences in monthly variations of  $\delta^{18}\text{O}$  values between particular wells (Table 2), together with  $^3\text{H}$  activities, indicated different infiltration times of surface water of the Sava River to different wells of the Petruševac aquifer: the wells B-5A and PP-19, which showed the slowest response to the changes in  $^3\text{H}$  in the Sava River, had also the smallest standard deviations and narrow range of the  $\delta^{18}\text{O}$  values.

### **Conclusions**

Results of measurements of  $^3\text{H}$  and stable isotopes  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  in precipitation, the Sava River and groundwaters from the Petruševac aquifer in the Zagreb area showed the following:

The isotopic water line ( $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  relation) of the Sava River was closer to the Local Meteoric Water Line for Ljubljana precipitation than that for Zagreb precipitation indicating the source of river water. The time series of stable isotope composition of groundwater followed that of the Sava River showing a direct influence of the river on the groundwater of the Petruševac aquifer.

Significantly higher  $^3\text{H}$  activity of the Sava River in June 2010 indicated the influence of the release of tritiated water from the Nuclear Power Plant Krško. Maximal  $^3\text{H}$  activity was detected 1–2 days after the release.

Increase in  $^3\text{H}$  activities in groundwater of the Petruševac aquifer was less pronounced and showed different time delay of 3 to 5 months for different wells. Intensity and time delay of the response could be correlated to the depth of the wells and the distance from the Sava River. This observation pointed to some differences in the infiltration time of the water from the Sava River to individual wells.

In this case  $^3\text{H}$  has been proven to be a good environmental tracer for determination of the transit time of the river water to the aquifer. The results of  $^3\text{H}$  and stable isotopes  $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$  will be used for modelling the transit time of the Sava River water to the groundwater reservoirs/aquifers.

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