

Use of nuclear power plant released tritium as groundwater tracer

Barešić, Jadranka; Parlov, Jelena; Kovač, Zoran; Sironić, Andreja

Source / Izvornik: **Rudarsko-geološko-naftni zbornik, 2020, 35, 25 - 34**

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

<https://doi.org/10.17794/rgn.2020.1.3>

Permanent link / Trajna poveznica: <https://urn.nsk.hr/urn:nbn:hr:169:854241>

Rights / Prava: [Attribution 4.0 International](#)/[Imenovanje 4.0 međunarodna](#)

Download date / Datum preuzimanja: **2024-07-02**



Repository / Repozitorij:

[Faculty of Mining, Geology and Petroleum
Engineering Repository, University of Zagreb](#)



Use of nuclear power plant released tritium as a groundwater tracer

The Mining-Geology-Petroleum Engineering Bulletin
UDC: 556.3
DOI: 10.17794/rgn.2020.1.3

Original scientific paper



Jadranka Barešić¹; Jelena Parlov²; Zoran Kovač³; Andreja Sironić⁴

¹ Ruder Bošković Institute, Bijenička 54, 10000 Zagreb, orcid.org/0000-0003-4634-5859

² University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, 10000 Zagreb, orcid.org/0000-0002-2862-7222

³ University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, 10000 Zagreb, orcid.org/0000-0001-8091-7975

⁴ Ruder Bošković Institute, Bijenička 54, 10000 Zagreb, orcid.org/0000-0001-7256-206X

Abstract

Tritium presents a natural radioactive isotope which can be used as a tracer in hydrology. This paper presents the usage of tritium in hydrogeological research of the Zagreb aquifer, which presents the country's strategic water reserves and is protected by the Republic of Croatia. In the research area, higher tritium content in surface water and groundwater is the result of releasing coolant water from the Nuclear power plant Krško. Tritium content was measured in 13 piezometers and one pumping well, in the wider area of the Petruševac and Kosnica well fields. It has been shown that tritium from cooling water is much more pronounced than its natural seasonal variability, and it can be very useful as a tracer. Also, results showed that the intensity and delay of responses in the aquifer depend on their distance from the Sava River and piezometer depth. Furthermore, the results suggest that variable hydrologic conditions can generate rapid change in the groundwater flow direction and affect tritium transport through the aquifer.

Keywords:

tritium, nuclear power plant, tracer, Zagreb aquifer

1. Introduction

Tritium (^3H) is a natural cosmogenic radioactive isotope of hydrogen which is created in the stratosphere by a reaction of thermal neutrons with atoms of nitrogen (^{14}N) and then decays to ^3He through the emission of beta particles (maximum of energy 18 keV). ^3H has low natural activity in the hydrosphere, measuring 0.1 – 0.9 Bq/L (Mook, 2001) and as a tracer, it became interesting after the introduction of a huge amount of man-made ^3H to the troposphere due to atmospheric thermonuclear bomb tests during the 1950s and 1960s. The concentration of ^3H increased by several thousand times and reached a maximum in 1963, of almost 1000 Bq/L (10000 TU (tritium unit); 1 TU = 0,118 Bq/L in the northern hemisphere precipitation. Tritium chemically behaves like other hydrogen isotopes (^1H and ^2H) and enters the water cycle as a part of H_2O , and, as such, represents the ideal tracer with a broad application in hydrogeology (Rozanski et al., 1991; Małoszewski and Zuber, 1996; Cartwright and Morgenstern, 2015; Nikolov et al., 2018). The increase of man-made ^3H activity prompted the World Meteorological Organization (WMO) and International Atomic Energy Agency

(IAEA) to establish a world-wide network for the monitoring of ^3H concentration in precipitation, named the Global Network of Isotopes in Precipitation (GNIP) (IAEA, 1979, 1983). Data from many meteorological stations are available to potential users through the IAEA web service WISER (IAEA/WMO, 2019). However, due to a short half-life of 12.32 years (Lucas and Unterwenger, 2000), the use of ^3H as a hydrological tracer has become more difficult nowadays since ^3H has almost reached its natural pre-bomb values (Krajcar Bronić et al., 1998; Horvatinčić et al., 2005; Vreća et al., 2006; Morgenstern and Daughney, 2012; Nikolov et al., 2018). Higher summer values that result from the introduction of ^3H from the stratosphere to the troposphere (jet stream) as well as electrolytic enrichment techniques enable the use of tritium in some hydrogeological studies. However, for the determination of aquifer vulnerability, especially in the case of riverbank filtration, seasonal variation of ^3H activity is not pronounced enough. Riverbank filtration is popularly used worldwide as a technique for drinking water supply, by the pumping of groundwater which is basically surface water that originated from lakes or rivers (Ray, 2002; Ray et al., 2002; Massman et al., 2008; Horvatinčić et al., 2011; Cartwright and Morgenstern, 2015; Gillefalk et al., 2018). Surface water is open to contaminants from the atmosphere and the surrounding area, while groundwater for

Corresponding author: Jelena Parlov
jelena.parlov@rgn.hr

drinking purposes produced from pumping wells must be free of contaminants. This is achieved by situating production wells in proper positions, depending on hydrogeological condition of the aquifer.

Characterization of the aquifer may be conducted by different tracers which must be clearly visible, measurable and conservative. Tritium is an ideal hydrological tracer since it is a part of the water molecule, but its use based solely on natural ^3H activity is very limited. As nuclear power plants (NPP) need coolant water, they are normally situated near water reservoirs such as seas, lakes or rivers from which water can be exploited as a coolant and released back to the water reservoir. Coolant water from NPPs is highly enriched with ^3H , and it is carefully released into environmental water reservoirs, so ^3H concentration in natural waters is very diluted and harmless for the environment (less than 100 Bq/L (1000 TU), the maximum allowed concentration for drinking water in the EU), but still high enough to use ^3H as an ideal hydrological tracer.

Croatia and Slovenia share the ownership of NPP Krško situated on the Sava River which is also the main recharge source of downstream aquifers and potable water for the Croatian capital Zagreb and a broader area of the Zagreb County, with almost 1 million inhabitants. Water has been exploited from several main well fields and it is naturally filtrated (bank filtration) due to the geological background of the aquifer (Velić and Saftić, 1991; Velić and Durn, 1993; Nakić et al., 2011, 2013). Demand for potable water in the Zagreb County has been constantly increasing. Due to the necessity for larger pumping quantities, the Water Supply Company started with the preparation of the new well field Kosnica. The Zagreb aquifer is a part of the country's strategic water reserves and is protected by the Croatian state. In such circumstances, it is very important to investigate the aquifer capacity and vulnerability, where ^3H released from NPP Krško can be used as a valuable tool.

This paper presents the investigation of the Zagreb aquifer by using ^3H released from NPP Krško, as a tracer. Monitoring of ^3H concentration in the Sava River and Zagreb aquifer was conducted within two IAEA projects: in 2010-2011 and in 2016-2017. Although these papers present case studies, methodology can be applied to any investigation of bank filtrated groundwater with NPP upstream from the aquifer.

2. Geological and hydrogeological settings

The NPP Krško lies on the gravel terrace of Krško polje, on the left bank of the Sava River southeast of Krško (Republic of Slovenia). In that area, the Sava River presents a regional hydrologic base, or such a surface river, into which all of the streams and brooks accumulate, along with all the natural groundwater outlets and fluxes. In a hydrogeological sense, Krško polje forms a Quaternary aquifer in which the changes of the ground-

water table are related to the water infiltration from the Sava River. In the western part of Krško polje, up to the NPP dam, the Sava River recharges the Krško aquifer. Downstream from the dam building, the Krško aquifer discharges into the Sava River most of the year, however some flood waves recharge the aquifer and cause oscillations of the water table in a wide riverbank area. The Sava River emerges out a valley near Krško and continues its flow towards the Pannonian Basin across the state border into the Republic of Croatia and Samobor-Zaprešić aquifer (see **Figure 1**). The Samobor-Zaprešić aquifer and Zagreb aquifer systems are located in north-west Croatia and include urban areas and their surroundings. The aquifers are composed mainly of Quaternary sediments where alluvial parts of the aquifers are directly connected with the Sava River.

The Zagreb aquifer is composed of Quaternary sediments deposited during the Middle and Upper Pleistocene and Holocene. Pleistocene deposits are lacustrine-marshy, while Holocene deposits are alluvial. At the beginning of Holocene, the Sava River started to flow and transport various materials from the Alps which was mainly carbonate. On the contrary, the Pleistocene deposits are mostly siliciclastic (Velić and Saftić, 1991). In general, Lower Pleistocene deposits are composed of silty clays and clayey silts with sporadic interbeds and lenses of gravelly sands. The lower and middle part of the Middle Pleistocene deposits are generally composed of sands, while silts and clays can occur in the upper part. In the Late Pleistocene, frequent lateral changes in gravels, sands, silts and clays can be found. On the other side, Holocene deposits are mainly composed of sand and gravels (Velić and Durn, 1993).

The Zagreb aquifer, from a hydrogeological perspective, consists of three main units: an unsaturated part of the alluvial deposits (overburden), a shallow Holocene aquifer layer and a deeper Pleistocene aquifer layer. The unsaturated zone thickness varies from two to eight meters (Ružičić et al., 2012), while during high waters, some parts of the Zagreb aquifer area can be flooded (Huljek et al., 2019). However, it must be emphasized that a great part of the unsaturated zone is disintegrated by the anthropogenic influence, especially in the urban part of the City of Zagreb. The shallow Holocene aquifer layer is composed of gravels and sand while its thickness varies from 5 to 40 m. The deeper Pleistocene aquifer is characterized by frequent lateral and vertical alternations of sand, gravel and clay, and it extends up to 60 m in depth (Nakić et al., 2011, 2013). Groundwater generally belongs to the CaMg-HCO₃ hydrogeochemical facies in the Holocene layer, while in the Pleistocene part CaMg-Na-HCO₃ facies can be additionally found. This is consistent with the hydrogeochemical stratification shown in the adjacent Samobor-Zaprešić aquifer (Vlahović et al., 2009; Marković et al., 2013). The Holocene aquifer layer is an unconfined aquifer which is in direct contact with the Sava River. General groundwater flow is from W/NW to E/SE, but it depends on the duration and inten-

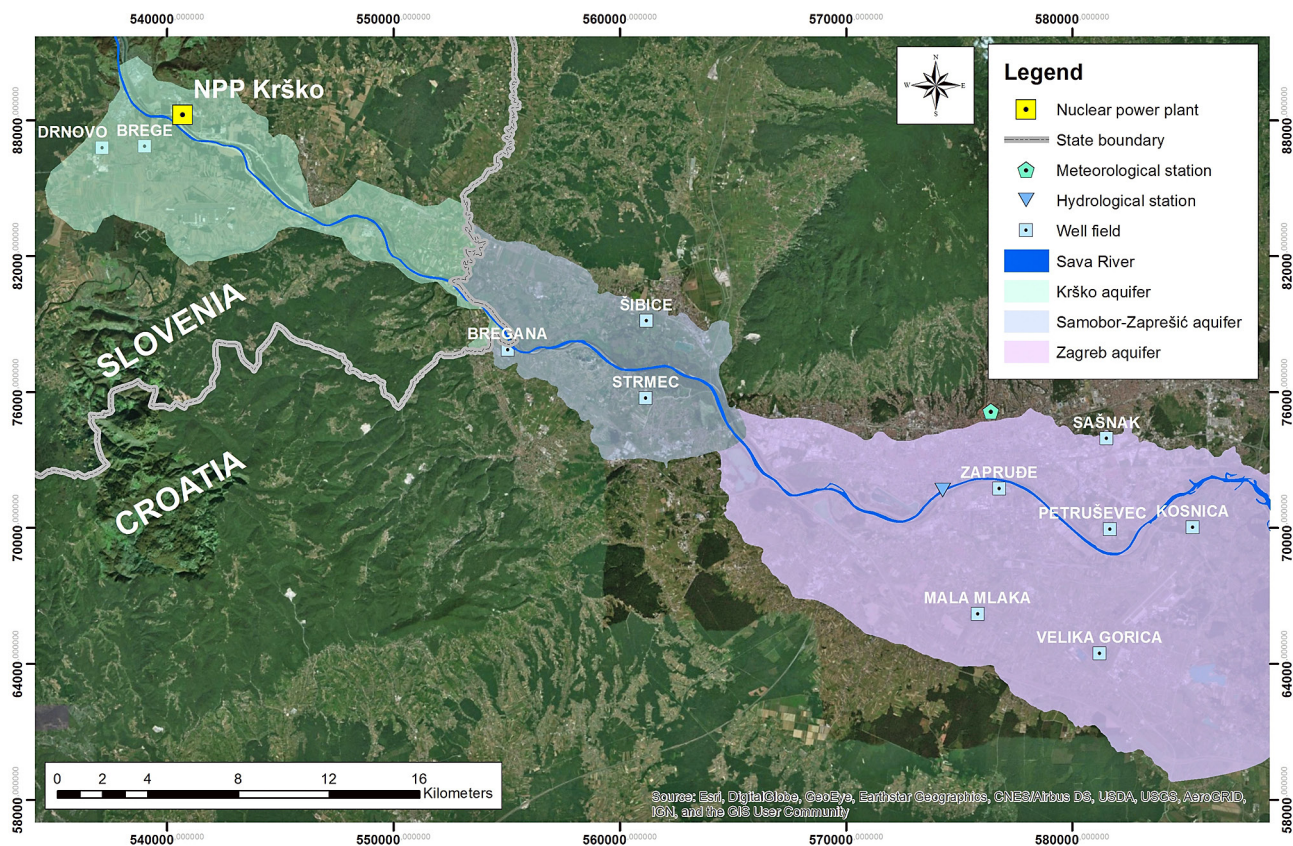


Figure 1: The geographical position of the Nuclear Power Plant Krško and aquifers connected with the Sava River

sity of hydrological conditions. It was shown that during low and medium waters, the Sava River drains the aquifer in some parts, while during high waters it gives water to the aquifer (Posavec, 2006). The Sava River has more influence on groundwater levels in the areas which are located in its vicinity (Posavec et al, 2017). For example, in the Petruševac and Kosnica well field areas, the flow directions of groundwater change significantly during low and high water periods (see Figure 2).

The development and fast growth of the City of Zagreb has resulted in quality and quantity groundwater issues. It has been shown that nitrates, pesticides, potentially toxic metals, pharmaceuticals and chlorinated aliphatic present the main contaminants of the Zagreb aquifer (Nakić et al., 2013). However, most of the research related to the groundwater quality issues has been focused only on nitrate contamination and potentially toxic metals. It was shown that nitrate concentrations are below 50 mg/l of NO_3^- , that nitrate origin is generally organic and trends are decreasing in most parts of the aquifer, and that the Zagreb aquifer presents an area with a generally high risk to nitrate contamination (Kovač et al., 2017a, 2017b; Kovač et al., 2018a, 2018b; Huljek et al., 2019). Also, it was shown that the landfill Jakuševac had an influence on groundwater quality due to increased concentrations of manganese, iron and arsenic (Bačani et al., 2012). Ružičić et al. (2016) have shown that risk of contamination with lead, cadmium

and zinc in the area of well field Kosnica is present, especially in the case of an accidental spill. Groundwater levels are declining approximately 1-2 meters every ten years which has resulted in a decrease of permanent groundwater reserves of about 4%, in the period from 1976 to 2006 (Bačani et al., 2010). Vujević and Posavec (2018) conducted a detailed analysis of historical groundwater levels in the area of the Zaprešić-Samobor aquifer where groundwater levels have generally declined by approximately 2 m while their decline in the area of the Zagreb aquifer amounted to approximately 1-2 m in its western part, approximately 2-5 m in its central part, and approximately 1-3 m in the eastern part of the aquifer. The most significant decline has been observed downstream from the weir of the Zagreb cogeneration plant TE-TO, more specifically, in the area of the Petruševac and Sašnak well fields and in the central and northern parts of the Mala Mlaka well field, where it amounted to 4-5 m and approximately 3 m, respectively. The main reasons for the decline in groundwater levels can be found in the deepening of the Sava riverbed, increased groundwater abstraction and the construction of dykes along the Sava River (Posavec, 2006).

3. Sampling and methods

Well fields Petruševac and Kosnica are situated in the alluvial Holocene deposits (thickness 5-40 m) and are

Table 1: Sampling locations of groundwater and sampling periods

Piezometers	Distance from Sava River (m)	Total depth (m)	Sampling period
PETRUŠEVEC			
Pumping well B-5A	400	38.0	2010-2012
PP-23/5	200	16.5	
PP-18/30	500	32.0	
PP-19	500	42.0	
KOSNICA			
MP-5	215	40.0	2016-2017
ČP-101	310	12.0	
ČDP-8/2	830	*56.0	
PKB-1/1/3	1205	28.0	
ČDP-13/1	1235	18.0	
PKB-3/1/3	1275	28.5	
PKB-5/1/3	1320	25.5	
A-2-1	1400	*64.0	
ČP-8	2100	30.0	
ČP-12/3	2470	24.0	

*Screen in shallow aquifer

close to the Sava River so their hydrological regime is governed by the hydrological regime of the river (Nakić et al., 2011, Marković et al., 2013, Posavec et al., 2017, Parlov et al., 2019). The Petruševac well field is the operating well field situated at the left bank of the Sava River and was investigated in 2010-2011 as a part of the project IAEA RER 8/016. Groundwater has been sampled from three piezometers and one pumping well for two years on a monthly basis (see Table 1, Figure 2). The Kosnica well field (the right bank of the Sava River) is not in operation yet, but it is in the testing and monitoring phase as it is designated as a main well field for the City of Zagreb and a broader area in the near future. Sampling was conducted by the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, within the IAEA TC Project CRO7001. 10 piezometers were sampled for one year on a monthly basis (see Table 1, Figure 2). Sampling of the Sava River started within the first IAEA project, in 2010, at the location Domovinski most (a bridge crossing the Sava River) and it has been continuing since then (see Figure 2). Precipitation has been sampled at the Ruđer Bošković Institute since 1978, and since 1995 at the meteorological station Zagreb – Grič, as a part of IAEA GNIP. The measurements of the Sava River water levels have been performed by the Meteorological and Hydrological Service of the Republic of Croatia (Croatian abbr. DHMZ) at the Zagreb

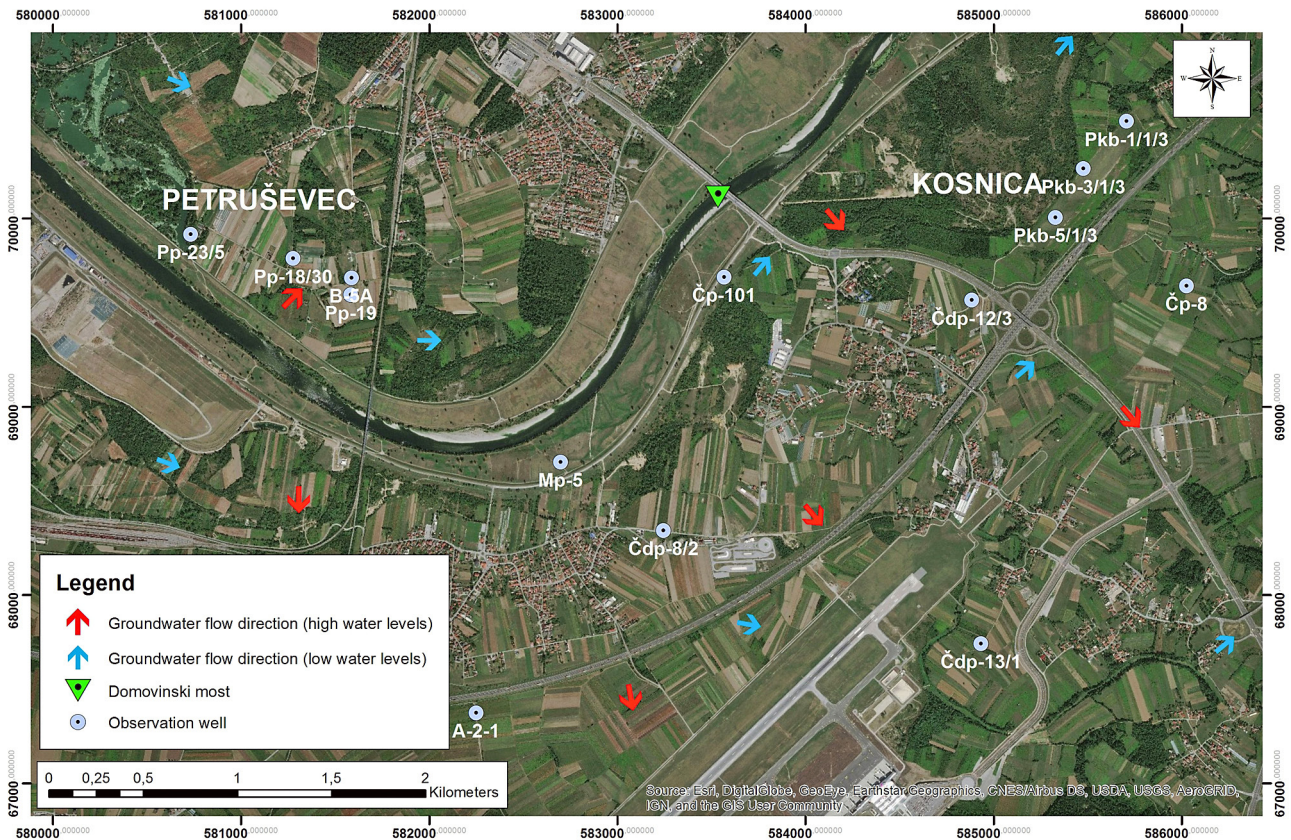


Figure 2: The sampling locations of groundwater and surface water from the Sava River (Domovinski most bridge) with groundwater flow directions

hydrological station continuously since 1849 (location in **Figure 1**).

Tritium activity was measured in the Laboratory for low-level radioactivity, Ruđer Bošković Institute, by the liquid scintillation counter Quantulus 1220. All samples were electrolytically enriched prior to the measurements. Within the enrichment procedure, the sample amount reduces so the sample became enriched with ^3H . The system for electrolytic enrichment consists of 20 cells of 500 ml volume (stainless steel anodes and mild steel cathodes) purchased from AGH University of Science and technology, Krakow, Poland. All samples have to be distilled prior to the enrichment procedure to reduce electrical conductivity to $<50 \mu\text{S/cm}$. An enrichment run consists of 15 samples of unknown activity, three spike samples of known activity (500 – 600 TU) necessary for the calculation of the enrichment factor and two dead-water (DW) samples used for system control. The enrichment procedure takes eight days (1420 Ah). The tritium enriched samples have been measured as scintillation cocktails that consist of 8 mL of sample and 12 mL of scintillant (Ultima Gold LLT; Perkin Elmer) in low diffusion polyethylene 20 mL disposable vials. Each measurement run consists of 20 enriched samples plus one nonenriched spike sample, one international standard and two nonenriched background samples. On the basis of the initial and final mass of water in cells, and individual count rates of spike water before and after enrichment, the sample enrichment factor, E_{SP} , has been calculated according to **Equations 1** and **2**, and finally, the tritium activity of unknown samples ($A^3\text{H}$) in tritium units (TU) has been calculated (see **Equation 3**) (**Rozanski and Groening, 2004; Stojković et al., 2018**).

$$P_{SP} = \frac{(W_i - W_f)}{Q / 2.975} \times \frac{\ln(E_{SP})}{\ln(W_i - W_f)} \quad (1)$$

$$E_s = \left\{ \frac{P_{AV} \times Q}{(W_i - W_f) \times 2.975} \ln \frac{W_i}{W_f} \right\} \quad (2)$$

$$A^3\text{H} = \frac{N_{SA} \times A_{ST}}{N_{ST} \times E_S} \quad (3)$$

Where:

W_i, W_f - initial/final effective mass of water in the given cell;

P_{SP} - enrichment parameter of each spike cell;

E_{SP} - enrichment factor of each spike cells;

P_{AV} - enrichment parameter obtained as an average of three individual spike cells P_{SP} values;

Q - total charge in [Ah] for the given enrichment run, 1420 at RBI;

2.975 - Faraday constant;

$A^3\text{H}$ - tritium content in the given sample;

N_{SA} - net count rate of the sample (counts per minutes, cpm);

N_{ST} - net count rate of the standard (cpm);

A_{ST} - tritium activity in the standard on the counting date in TU.

The average enrichment factor for the measured samples (E_s) was 26 ± 2 , while the average enrichment parameter (P_{AV}) at the Ruđer Bošković Institute is 0.953 ± 0.013 (close to 1) and indicates high tritium retention during electrolysis.

4. Results and discussion

Tritium activity in precipitation shows a typical pattern with almost natural values (3 – 10 TU) with higher values in warmer months with spring/summer maxima (14 – 20 TU at Zagreb) due to the lowering of the stratosphere in the spring (jet stream) and due to the breaking of the tropopause which happens each spring in northern latitudes between 30 and 60° (**Gat et al., 2001; Yasunary and Yamazaki, 2009**) (**Figure 3**). Tritium naturally forms in the stratosphere, and a certain amount is a residue from thermonuclear bomb tests. Differences between summer and winter values can hardly be used as a tracer tool in the case of the Sava River where several times a year, cooling water from NPP is being realised (see **Figure 3**). The peak from cooling water is much more pronounced and very useful as a tracer so tritium in precipitation will not be discussed any further.

During investigation of the Petruševac well field, a tritium peak of 198.7 ± 20.9 TU was observed in the Sava River and the same peak was observed in three piezometers (PP-23/5, PP-18/30 and PP-19) and in the producing well (B-5A) (see **Table 1, Figure 4**). The maximum value of tritium activity was registered in May 2010 during average Sava River water levels without the occurrence of larger flood waves (see **Figure 5**). Peaks observed in piezometers were delayed and damped, and it is clearly that the intensity and delay of responses depend on both, distance from the Sava River and piezometer depth, as shown in **Horvatinić et al. (2011)** based on data collected within 2010.

In 2011, additional sampling was organized, and a tritium activity peak in the Sava River was noticed, but its intensity was much smaller than in the previous year (see **Table 2, Figure 4**). Peak intensities were calculated as a ratio of response peak observed in s piezometer and a peak observed in Sava River for both sampling periods (see **Table 2**), but only the results obtained in 2010 gave a clear time/intensity relation which was expected according to distance/depth positions of the piezometers. Peak intensities calculated for the sampling period in 2011 gave confusing results, contrary to results from 2010 showing that a second peak of 30.9 ± 4.1 TU (value close to natural tritium activities), observed in the Sava River was not strong enough to produce clear responses in piezometers. Peak activities in piezometers PP-23/5 and PP-18/30 were barely visible (11.1 ± 1.6 TU, 10.9 ± 1.5 TU, respectively), and in piezometer PP-19 and pump-

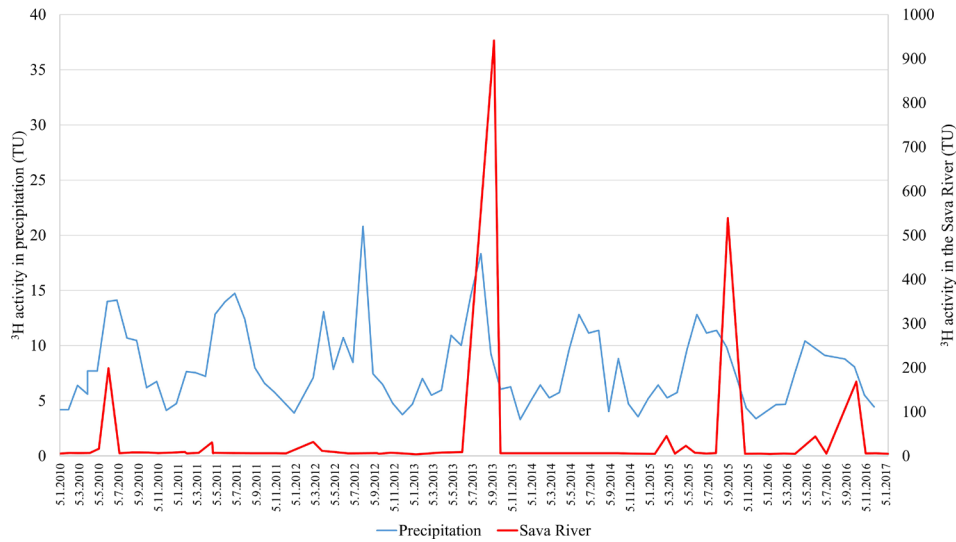


Figure 3: Tritium concentrations in precipitation at Zagreb (monthly samples) and in the Sava River (grab samples)

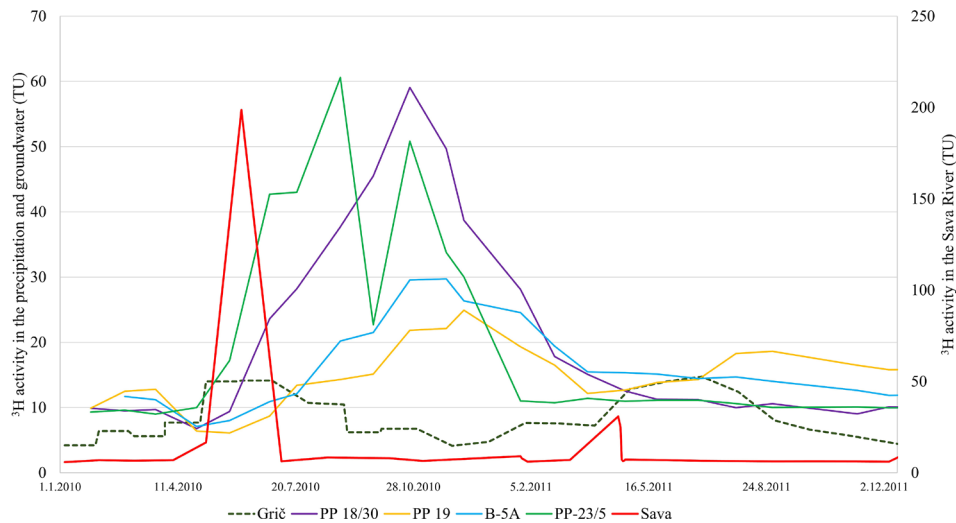


Figure 4: Tritium concentrations in precipitation in Zagreb (monthly samples), groundwater (Petruševac well field) and the Sava River (grab samples)

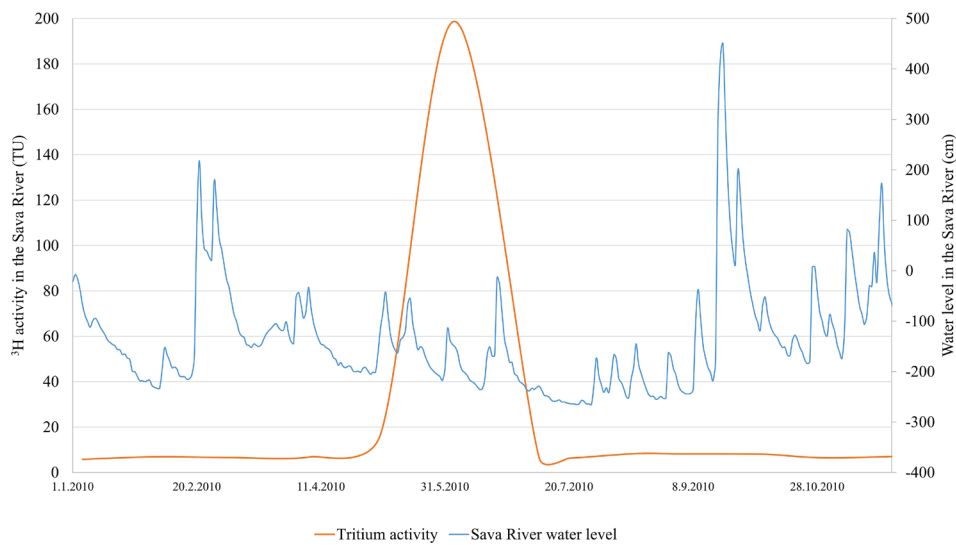
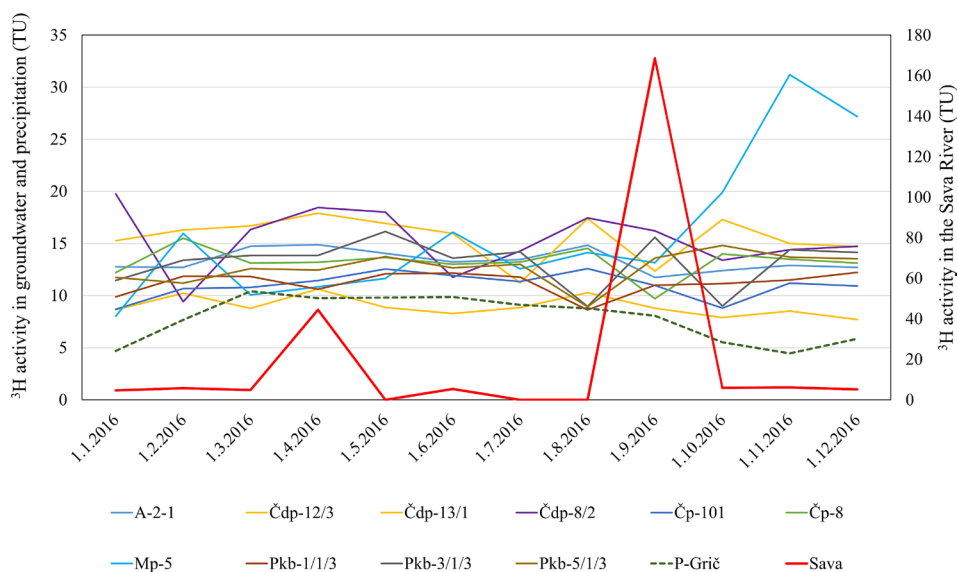


Figure 5: Tritium concentrations and water levels in the Sava River during 2010

Table 2: Tritium activities peaks in the Sava River and piezometers

	Distance from Sava River (m)/ depth (m)	Peak ^3H activity (TU) (2010)	Time delay (months) (2010)	Peak ^3H activity (TU) (2011)	Time delay (months) (2011)	Peak intensity (2010) (%)	Peak intensity (2011) (%)	Peak ^3H activity (TU) (2016)	Time delay (months) (2016)	Peak intensity (2016) (%)
Sava River		198.7±20.9		30.9±4.1				168.6±20.9		
PETRUŠEVEC										
Pumping well B-5A	400/38.0	29.7±3.5	5.5	14.7±2.2	3.5	14.9	49.0			
Monitoring well PP-23/5	200/32.0	60.6±8.2	2.5	11.1±1.6	2.5	30.5	37.1			
Monitoring well PP-18/30	500/16.4	59.1±7.8	4.5	10.9±1.5	3.5	29.7	36.3			
Monitoring well PP-19	500/41.6	24.9±3.1	7.5	18.6±2.4	4.5	12.5	62.1			
KOSNICA										
Monitoring well Mp-5	215/40.0							31.2±4.0	2.5	18.5

**Figure 6:** Tritium concentrations in precipitation at Zagreb (monthly samples), groundwater (Kosnica well field) and Sava River (grab samples)

ing well B-5A the observed tritium activities were higher than expected according to results obtained in 2010 (18.6±2.4 TU, 14.7±2.2 TU, respectively), meaning that in some point/moment, a peak in the Sava was probably much higher, but was not caught. Due to these reasons, the time/intensity relation for 2011 gave quite different results and probable results in comparison with the results from 2010 (see **Table 2**).

The results of ^3H measurements from the Kosnica well field (10 piezometers), Sava River and precipitation for 2016 are presented in **Figure 6**. A ^3H peak (168.6±20.9 TU) in the Sava River was observed in September 2016, and it was followed by a less intense peak in the piezom-

eter Mp-5 (31.2±4.0 TU) two months later. A peak in other piezometers was not observed by the end of the monitoring. The tritium peak in the Sava River was registered during low and medium river water levels without major oscillations, but in less than a month, water levels were increased significantly (see **Figure 7**). These variable hydrologic conditions generate rapid change in the groundwater flow direction (see **Figure 2**) and affect tritium transport. The peak intensity for piezometer Mp-5 was 18.5%, similar to the intensity of the first peak observed in the producing well B-5A from the Petruševac well field (14.9%, **Table 2**). The distance of piezometer Mp-5 (Kosnica) from the Sava River is 215 m, and a

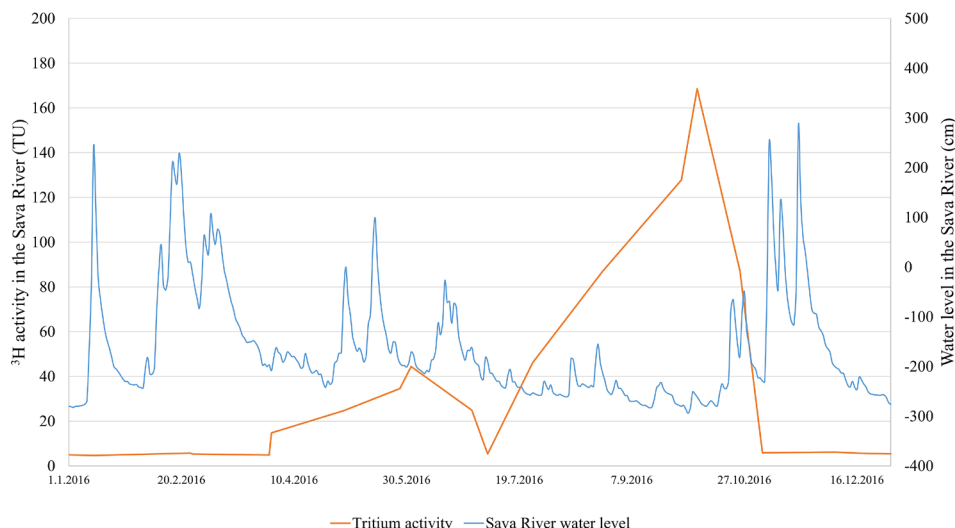


Figure 7: Tritium concentrations and water levels in the Sava River during 2016

peak was observed after 2.5 months. The distance of the B-5A well (Petruševac) from the Sava River is 400 m and its peak of bit smaller intensity was observed after 5.5 months. On the other hand, a peak of high intensity of 30.5% was observed in a piezometer 200 m away from the Sava River PP-23/5 (Petruševac) with 2.5 months delay regarding the Sava River peak.

It should be noticed that peak activity should be high enough to leave a response in groundwater such as in the case with peaks from the Sava River in 2010 (198.7 ± 20.9 TU) and 2016 (168.6 ± 20.9 TU) and these activities can be easily measured without the time consuming electrolytic enrichment of samples. A small peak in surface water such as the peak from 2011 (30.9 ± 4.1 TU) did not produce clear response peaks in the monitored piezometers.

5. Conclusions

The investigation presented within this paper showed that a release of cooling water enriched with ^3H can be very useful for the determination of aquifer characteristics in the case of using a groundwater obtained by river-bank filtration for drinking purposes in cases similar to the Zagreb County. This kind of water supply is common in many cities worldwide, and it is often the case that NPPs have been built upstream from water well fields. However, investigation has to be planned properly as a ^3H activity peak in surface water has a velocity of the river and escapes within several hours. This can be avoided by cooperation with the NPP authorities which plan and monitor the amount of releasing tritiated water from the plant, and the concentration of ^3H in liquid effluent as well as concentrations in river/lake acceptors of the effluent. These types of monitoring are usually conducted on a daily basis and a sample with peak activity can be easily caught. The next step is the sampling of groundwater from piezometers of interest and which can

be done on a monthly basis since the response peak is dumped and visible for a longer period. It is of the utmost importance that the sampling period is long enough to catch response peaks in monitored piezometers so the sampling should not be stopped before obtaining measurement results, or at least two years after spotting the peak in surface water. The responses in monitored piezometers are also dependent on the hydrological regime of surface water and groundwater and a short observing period could be meteorologically extreme and the obtained results could lead to a wrong perception of the aquifer characteristics.

The first sampling period (2010-2011) conducted at the Petruševac well field gave satisfying results as all piezometers showed time delays and peak intensities depending on piezometer depth and distance from the Sava River. These results were obtained on the basis of the first peak in the Sava River (198.7 ± 20.9 TU) while the second peak (30.9 ± 4.1 TU) was not high enough to produce responses in piezometers. In the case of second monitored period, clear peak in Sava River was observed in September 2016 (168.6 ± 20.9 TU), but the sampling was stopped before obtaining measurement results (January 2017) and only one peak response was caught in the piezometer closest to the Sava River (Mp-5) after 2.5 months. However, even this short period gave preliminary information on aquifer characteristics, i.e. approximate velocities of groundwater (2.8 m/day). The results obtained from this research provide a good basis for the spatial set up and temporal monitoring network for future investigations of the Zagreb aquifer characteristics. This step is necessary because only good monitoring plans result in precise groundwater velocities which are unavoidable for development of the sanitary protection zones of the well fields. This research confirmed that velocities of groundwater could be determined by using isotope techniques, i.e. tritium released from NPP can be used as a hydrogeological tracer.

Acknowledgment

Research presented in this paper was conducted within two IAEA projects: 2010-2011 (RER 8/016 Using Environmental Isotopes for Evaluation of Streamwater/Groundwater Interactions in Selected Aquifers in the Danube Basin) and 2016-2017 TC CRO7001 project (Isotope Investigation of the Groundwater-Surface Water Interaction at the Well Field Kosnica in the Area of the City of Zagreb).

The authors kindly thank Ines Krajcar Bronić for reviewing the paper and her useful comments.

6. References

Papers:

- Bačani, A., Posavec, K. and Parlov, J. (2010): Groundwater quantity in the Zagreb aquifer. – In: Zuber, A., Kania, J. & Kmiecik, E. (eds.): XXXVIII IAH Congress Groundwater Quality Sustainability, Krakow, September 12–17, 2010, 87–92.
- Bačani, A., Posavec, K., Parlov, J. and Bačani, L. (2012): Jakuševac Landfill Impact on the Groundwater Quality. 34th International Geological Congress, Brisbane, Australia.
- Cartwright, I. and Morgenstern, U. (2015): Transit times from rainfall to baseflow in headwater catchments estimated using tritium: the Ovens River, Australia - *Hydrol. Earth Syst. Sci.*, 19, 3771–3785, doi: 10.5194/hess-19-3771-2015.
- Gat, J. R., Mook, W. G. and Meijer, H. A. J. (2001): Atmospheric Water (Volume II). Mook, W. G., ed., *Environmental Isotopes in the Hydrological Cycle: Principles and Applications*. Paris: UNESCO/IAEA.
- Gillefalk, M., Massmann, G., Nützmann, G. and Hilt, S. (2018): Potential Impacts of Induced Bank Filtration on Surface Water Quality: A Conceptual Framework for Future Research. - *Water*, 10, 1-25. doi: 10.3390/w10091240
- Horvatinčić, N., Barešić, J., Krajcar Bronić, I., Obelić, B., Kármán, K. and Főrizs, I. (2011): Study of the bank filtered groundwater system of the Sava River at Zagreb using isotope analyses. *Central European Geology* 54, pp. 121–127
- Horvatinčić, N., Krajcar Bronić, I., Barešić, J., Obelić, B. and Vidič, S. (2005): Tritium and stable isotope distribution in the atmosphere at the coastal region of Croatia. *Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate*, TECDOC Series No. 1453, IAEA, Vienna, pp. 37–50
- Huljek, L., Perković, D. and Kovač, Z. (2019): Nitrate contamination risk of the Zagreb aquifer. *Journal of Maps* 15, 2, doi: 10.1080/17445647.2019.1642248.
- International Atomic Energy Agency, Guide Book on Nuclear Techniques in Hydrology, Technical Report Series No.91, IAEA, Vienna, 1983
- International Atomic Energy Agency, Behavior of Tritium in the Environment (Proc. Symp. San Francisco, 1978), IAEA, Vienna, 1979
- Kovač, Z., Nakić, Z. and Pavlić, K. (2017a): Influence of groundwater quality indicators on nitrate concentrations in the Zagreb aquifer system. *Geologica Croatica* 70, 93-103, doi: 10.4154/GC.2017.08.
- Kovač, Z., Cvetković, M. and Parlov, J. (2017b): Gaussian simulation of nitrate concentration distribution in the Zagreb aquifer. *Journal of Maps* 13, 2, 727–732, doi: 10.1080/17445647.2017.1354786.
- Kovač, Z., Nakić, Z., Barešić, J. and Parlov, J. (2018a): Nitrate Origin in the Zagreb Aquifer System. *Geofluids* 15, doi: 10.1155/2018/2789691.
- Kovač, Z., Nakić, Z., Špoljarić, D., Stanek, D. and Bačani, A. (2018b): Estimation of nitrate trends in the groundwater of the Zagreb aquifer. *Geosciences* 8, 5, doi: 10.3390/geosciences8050159.
- Leibundgut, C., Maloszewski, P. and Kulls, C. (2009): *Tracers in Hydrology*. Wiley-Blackwell, John Wiley and Sons Ltd, West Sussex, UK. p. 415.
- Lucas, L.L. and Unterwiesing, M.P. (2000): Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Stand. Technol.* ; 105 (4): 541-549.
- Maloszewski, P. and Zuber, A. (1996): Lumped parameter models for the interpretation of environmental tracer data, In: *Manual on Mathematical Models in Isotope Hydrology*. IAEA-TECDOC-910 with Supplement, IAEA, Vienna, pp. 9–58.
- Marković, T., Brkić, Ž. and Larva, O. (2013): Using hydrochemical data and modelling to enhance the knowledge of groundwater flow and quality in an alluvial aquifer of Zagreb, Croatia”, *Science of the Total Environment*, vol. 458-460, no. 508-516,. Doi: 10.1016/j.scitotenv.2013.04.013.
- Massmann, G., Sueltenfuss, J., Duennbier, U., Knappe, A., Taute, T. and Pekdeger, A. (2008): Investigation of groundwater residence times during bank filtration in Berlin: Multi-tracer approach. - *Hydrol. Process.*, 22, 788–801.
- Mook, W.G. (2001): *Environmental Isotopes in the Hydrological Cycle. Principles and Applications*. UNESCO/IAEA Series 2001, p.164.
- Morgenstern, U. and Daughney, C.J. (2012): Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification – The National Groundwater Monitoring Programme of New Zealand. *Journal of Hydrology* 456–457; 79–93
- Nakić, Z., Posavec, K., Parlov, J. and Bačani, A. (2011): Development of the Conceptual Model of the Zagreb Aquifer System. *The Geology in Digital Age: Proceedings of the 17th Meeting of the Association of European Geological Societies*, MAEGS 17 / Banjac, N. (ed.). – Belgrade: Serbian Geological Society, 2011. 169–174 (ISBN: 978-86-86053-10-7).
- Nakić, Z., Ružičić, S., Posavec, K., Mileusnić, M., Parlov, J., Bačani, A. and Durn, G. (2013): Conceptual model for groundwater status and risk assessment—Case study of the Zagreb aquifer system. *Geologica Croatica* 66, 55–76, doi: 10.4154/GC.2013.05.
- Nikolov, J., Krajcar Bronić, I., Todorović, N., Stojković, I., Barešić, J. and Petruvić-Pantić, T. (2018): Tritium in Water: Hydrology and Health Implications. In: *Tritium - Advances in Research and Applications*, ed. Janković, M. M. New York: NOVA Science Publishers, pp. 157-211.

- Parlov, J., Kovač, Z., Nakić, Z. and Barešić, J. (2019): Using Water Stable Isotopes for Identifying Groundwater Recharge Sources of the Unconfined Alluvial Zagreb Aquifer (Croatia). *Water* 11, 2177, doi: 10.3390/w11102177.
- Posavec, K., Vukojević, P., Ratkaj, M. and Bedeniković, T. (2017): Cross-correlation modelling of surface water—groundwater interaction using the Excel spreadsheet application. *The Mining-Geology-Petroleum Engineering Bulletin* 32, 1, 25–32, doi: 10.17794/rgn.2017.1.4.
- Ray, C. (Ed.) *Riverbank Filtration: Understanding Contaminant Biogeochemistry and Pathogen Removal*; Springer Science & Business Media: Berlin, Germany, 2002; ISBN 978-1-4020-0954-9
- Ray, C.; Melin, G.; Linsky, R.B. (Eds.) *Riverbank Filtration: Improving Source-Water Quality*; Water Science and Technology Library; Kluwer Acad. Publ: Dordrecht, The Netherlands, 2002; ISBN 978-1-4020-1133-7.
- Rozanski, K., Gonfiantini, R. and Araguas-Araguas, L. (1991): Tritium in the global atmosphere: distribution patterns and recent trends. – *J Phys G: Nucl Part Phys* 17, pp. 523–536.
- Rozanski, K. and Groening, M. (2004): Tritium assay in water samples using electrolytic enrichment and liquid scintillation spectrometry. In: *Quantifying uncertainty in nuclear analytical measurements*, IAEA-TECDOC-1401; p.195–217.
- Ružičić, S., Mileusnić, M. and Posavec, K. (2012): Building conceptual and mathematical model for water flow and solute transport in the unsaturated zone at Kosnica site. *The Mining-Geology-Petroleum Engineering Bulletin*, 25, 21–31.
- Ružičić, S., Mileusnić, M., Posavec, K., Nakić, Z., Durn, G. and Filipović, V. (2016): Water flow and solute transport model of potentially toxic elements through unsaturated zone at regional wellfield Kosnica. *Hydrological processes* 30, 4113–4124, doi: 10.1002/hyp.10914.
- Stojković, I., Todorović, N., Nikolov, J., Krajcar Bronić, I., Barešić, J. and Kozmidic Luburić, U. (2018): Methodology of tritium determination in aqueous samples by Liquid Scintillation Counting techniques. In *Tritium - Advances in research and applications*, ed.: Janković, M. M., New York : NOVA Science Publishers, pp. 99–156.
- Velić, J. and Saftić, B. (1991): Subsurface Spreading and Facies Characteristics of Middle Peistocene Deposits between Zaprešić and Samobor. *Geološki vjesnik* 44, 69–82.
- Velić, J. and Durn, G. (1993): Alternating Lacustrine-Marsh Sedimentation and Subaerial Exposure Phases during Quaternary: Prečko, Zagreb, Croatia. *Geologia Croatica* 46/1, 71–90, doi: 10.4154/GC.1993.06.
- Vlahović, T., Bačani, A. and Posavec, K. (2009): Hydrogeochemical stratification of the unconfined Samobor aquifer (Zagreb, Croatia). *Environmental Geology* 57/8, 1707–1722, doi: 10.1007/s00254-008-1452-4. Vreča, P., Krajcar Bronić, I., Horvatinčić, N. and Barešić, J. (2006): Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations. – *J. Hydrology*, 330, pp. 457–469.
- Vujević, M. and Posavec, K. (2018): Identification of Groundwater Level Decline in the Zagreb and Samobor-Zaprešić Aquifers since the Sixties of the Twentieth Century. *The Mining-Geology-Petroleum Engineering Bulletin*, 4, 55–64.
- Yasunari, T. J. and Yamazaki, K. (2009): Impacts of Asian dust storm associated with the stratosphere-to-troposphere transport in the spring of 2001 and 2002 on dust and tritium variations in Mount Wrangell ice core, Alaska, *Atmos. Environ.*, 43, 16, 2582–2590.

Books/thesis written in non-English language:

- Posavec, K. (2006): Identifikacija i prognoza minimalnih razina podzemne vode zagrebačkoga aluvijalnog vodonosnika modelima recesijskih krivulja [engl. Identification and prediction of minimum ground water levels of Zagreb alluvial aquifer using recession curve models – in Croatian]. – Unpub. PhD Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, 89 p.

Internet sources:

- URL: <http://www.iaea.org/water>. IAEA/WMO (2019). Global Network of Isotopes in Precipitation. The GNIP Database. (accessed 20th June 2019)

SAŽETAK

Korištenje tricija ispuštenoga iz nuklearne elektrane kao trasera

Tricij je prirodni radioaktivni izotop koji se može koristiti kao traser u hidrologiji. Ovim radom prikazuje se korištenje tricija u hidrogeološkim istraživanjima zagrebačkoga vodonosnika koji je Republika Hrvatska zaštitila i uvrstila u strateške zalihe vode. Na istraživanome području povišen sadržaj tricija u površinskoj i podzemnoj vodi posljedica je ispuštanja rashladne vode iz nuklearne elektrane Krško u rijeku Savu. Sadržaj tricija mjeren je u 13 piezometara i u jednome zdencu na području crpilišta Petruševac i Kosnica. Pokazano je da je tricij podrijetlom iz rashladne vode naglašeniji od njegove sezonske varijabilnosti te može biti korišten kao traser. Također, rezultati su pokazali da intenzitet i zakašnjenje reakcije u vodonosniku izravno ovisi o udaljenosti od rijeke Save i dubini piezometra. Nadalje, rezultati upućuju na to da promjenjivi hidrološki uvjeti uzrokuju brze promjene u smjeru tečenja podzemne vode i utječu na transport tricija kroz vodonosnik.

Ključne riječi:

tricij, nuklearna elektrana, traser, zagrebački vodonosnik

Authors contribution

Jadranka Barešić (Senior Research Associate, PhD, Earth Sciences) participated in one part of the field work, conducted the sample preparation and measurements, and participated in data analyses and interpretation. **Jelena Parlov** (Associate Professor, PhD, Hydrogeology) performed one part of the field work and provided the hydrogeological interpretation of the results. **Zoran Kovač** (Assistant Professor, PhD, Hydrogeology) participated in the manuscript writing, data interpretation and figure construction. **Andreja Sironić** (Research Associate, PhD, Earth Sciences) conducted one part of the field work, participated in sample preparations and data analyses.