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Isotopic signature of the Sikirevci well field and its connection with the Sava River

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Abstract

The Sikirevci well field is one of the most important well fields in the eastern Slavonia used for the public water supply. In this study, stable isotopes of water were used to determine the origin of water from pumped aquifer, but also to test its connection with the Sava River. From August 2020 till July 2021, groundwater samples were collected from four pumping wells, while historical chemical analyses were used to determine the hydrogeochemical facies. The isotopic signature of the Sava River was found to be different from that of the sampled aquifer. The stable isotopes of hydrogen and oxygen (δ^2H and $\delta^{18}O$) of the groundwater are more negative than those of the Sava River, indicating that the Sikirevci well field pumps water from the deeper part of the aquifer where Sava River does not have such a strong influence, although the d-excess values do not show such a large difference. Moreover, the isotopic composition of the groundwater is very stable and does not change over time. This is consistent with the presence of iron, manganese and arsenic concentrations in groundwater, which indicate reductive conditions. However, the variations in the concentrations of the observed potentially toxic metals indicate that different geochemical conditions prevailed during the study period. Most of the water samples had hydrogeochemical facies CaMg-HCO_3, while two samples had slightly higher levels of sodium and magnesium. Results of this research indicate different conclusions when observing main isotopic composition with respect to d-excess values. Although d-excess is observed as a second order parameter, it can greatly help in data interpretation.

Keywords: stable water isotopes; Sikirevci well field; Sava River; hydrogeochemical facies

1. Introduction

The Sikirevci well field is located in the Brodsko-Posavska County, in the eastern part of Croatia, between the settlement of Sikirevci and the Sava River. It has four active pumping wells (Z2-Z5, Figure 1). It is located in the zone of typical lowland relief. The climate is temperate continental, characterized by a variety of weather conditions with frequent and intense changes throughout the year. The inflow area of the Sikirevci well field extends over the territory of the Republic of Croatia and the Federation of Bosnia and Herzegovina (Kopić, 2016; Kopić et al., 2016).

The wellfield Sikirevci captures Quaternary deposits with transmittivities ranging from 3000 to 6000 m^2/day. It is a gravelly-sandy aquifer, semi-confined to unconfined type, with a thickness of over 90 m. Pumping wells capture three aquifer layers (29 - 36 m, 51 - 57 m and 69 - 75 m), while the total thickness of aquifers and less permeable interlayers between them is 50 to 60 m. The aquifer belongs to the alluvial sediment of the Bosna River. The Sikirevci wellfield has a very high pumping capacity (about 1000 l/s) and exceptional water quality (**Kopić, 2016; Kopić et al., 2016**). The average hydraulic conductivity is about 150 m/day (**Briški et al., 2013**), which is in accordance with the lithological composition of the aquifer. The shallow, semi-permeable layers of the Sava plain consist of alternations of clay, silt and

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sand deposits whose lithologic diversity and individual permeability cause varying infiltration into the aquifer layers. Due to small thickness of semi-permeable layers, the riverbed is cut into the shallowest aquifer, resulting in direct contact between surface water and groundwater, so that the Sava maintains a high piezometric level at high water levels (**Brkić et al., 2009**). At high water levels, the aquifer is fed by the Sava River, and at low and medium water levels the Sava River drains the groundwater, especially in the downstream parts (**Briški et al., 2013**).

In recent years, isotope hydrology research in Croatia was mainly focused to the unconfined aquifers in the northwestern part of Croatia, especially in Zagreb (**Kovač et al., 2018; Parlov et al., 2019; Barešić et al., 2020**) and in the Varaždin aquifer (**Marković et al., 2020**), as well as on soil hydrology related to hillside vineyards (**Kovač et al., 2022**). On the other side, in the eastern part of Croatia, conduction of isotope hydrology research is not that common.

The main objectives of this research were to evaluate the isotopic signature of the groundwater and the Sava River in the area of the Sikirevci well field and to study their relationship using the water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$). In addition, we used the concentrations of major ions to define the hydrogeochemical facies and evaluate whether it changes over time.

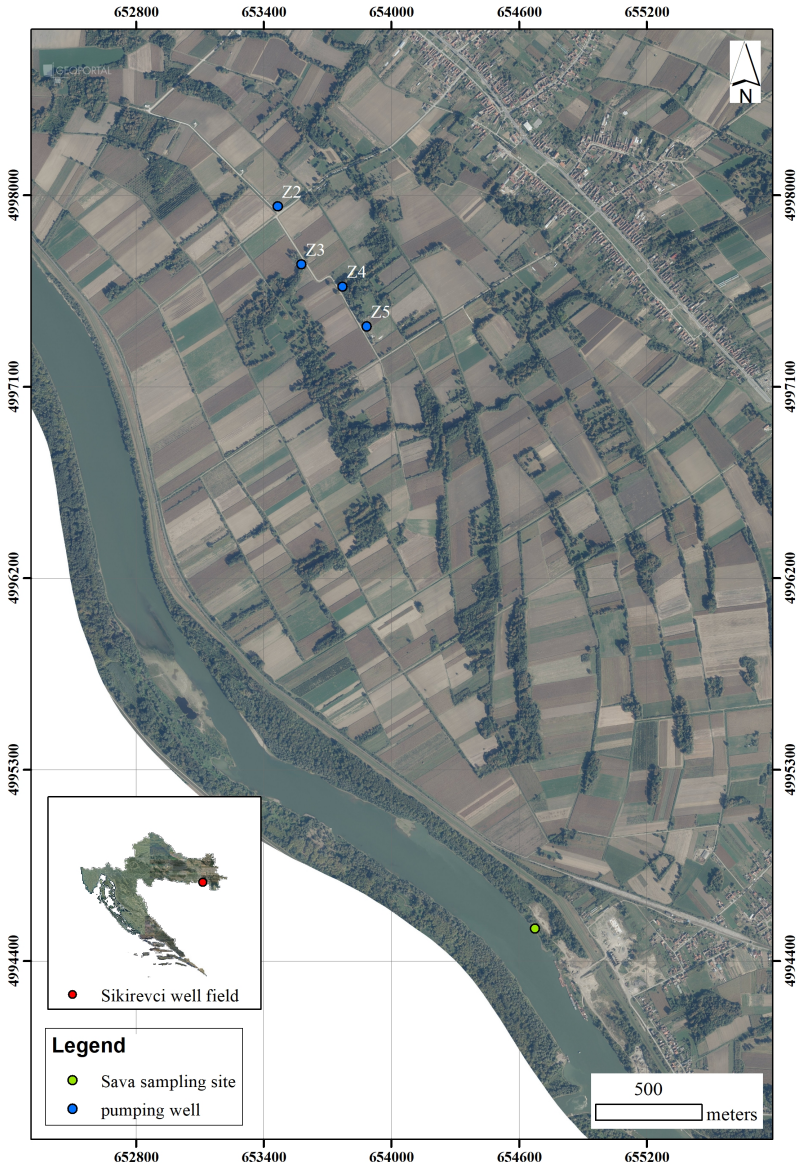

Figure 1: Location of sampled pumping wells and Sava River sampling site in the research area

2. Methods and data

Monthly sampling of groundwater and Sava River water was conducted between August 2020 and July 2021. All four pumping wells were sampled, as well as the Sava River (**Figure 1**). Due to the COVID-19 epidemiological situation and related technical problems, samples were not taken in all months, which primarily refers to the Sava River. Stable isotopes of groundwater and Sava River (δ^2H and $\delta^{18}O$) were determined at the Laboratory for Spectroscopy of the Faculty of Mining, Geology, and Petroleum Engineering, University of Zagreb, using a Liquid Water Isotope Analyzer (LWIA-45-EP, Los Gatos Research). Data preparation and interpretation were performed using the Laboratory Information Management System (LIMS for lasers 2015; **Coplen and Wassenaar, 2015**). The measurement precision of duplicate samples was ±0.19‰ for $\delta^{18}O$ and ±0.9‰ for δ^2H, while all results are presented with respect to VSMOW (Vienna Standard Mean Ocean Water). Hydrogeochemical facies were determined based on available historical data from 2012 to 2020. The chemical analyses were performed at the Teaching Institute for Public Health of Osijek-Baranja County, while the data are available on the website of the Vinkovci Waterworks and Sewage Company.

Data interpretation was done in four steps. First, the isotopic signature of the Sava River and groundwater is compared with the LMWLs (Local Meteoric Water Lines) of Zagreb and Ljubljana based on the available data from GNIP (Global Network of Isotopes in Precipitation; **IAEA/WMO, 2021 – URL 1**). In the second step, the change of $\delta^{18}O$ of the Sava River and groundwater over time is evaluated, while in the third step the d-excess value is investigated. In the fourth step, the hydrogeochemical facies was determined together with the concentrations of iron, manganese, and arsenic. Analyses of major ion concentrations were available only for mixed water from all pumping wells.

3. Results and discussion

In **Figure 2** isotopic composition of the Sikirevci well field and the Sava River, together with the LMWLs of Zagreb and Ljubljana are presented. It can be clearly seen that the isotopic signature of the Sava River is different from that of the groundwater pumped from the Sikirevci well field. This corresponds to the evaluation of the $\delta^{18}O$ in time (**Figure 3**). Furthermore, the results suggest that the isotopic signature of the Sava River is primarily related to the precipitation which falls in Slovenia (**Filipović, 2021**), which corresponds to the results of previous studies in the Zagreb area (**Parlov et al., 2019**). Groundwater from the well field Sikirevci is more negative than the Sava River, indicating that well field Sikirevci pumps water from deeper aquifer layers that are not in the direct contact with the Sava River. This is consistent with previous research (**Kopić et al., 2016**). Furthermore, it is evident from all results that the isotopic composition of the Sava River varies more than that of the groundwater, which is generally very stable.

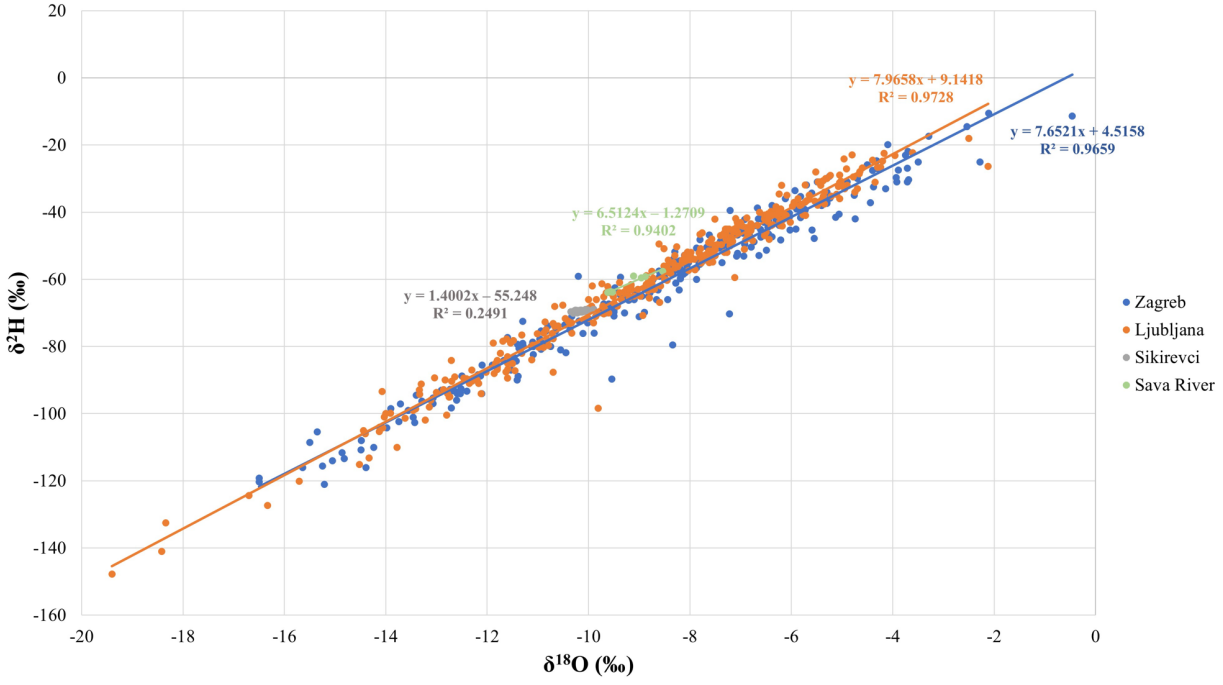

Figure 2: Isotopic composition of the well field Sikirevci and Sava River with respect to LMWLs of Zagreb and Ljubljana (modified from **Filipović, 2021**)

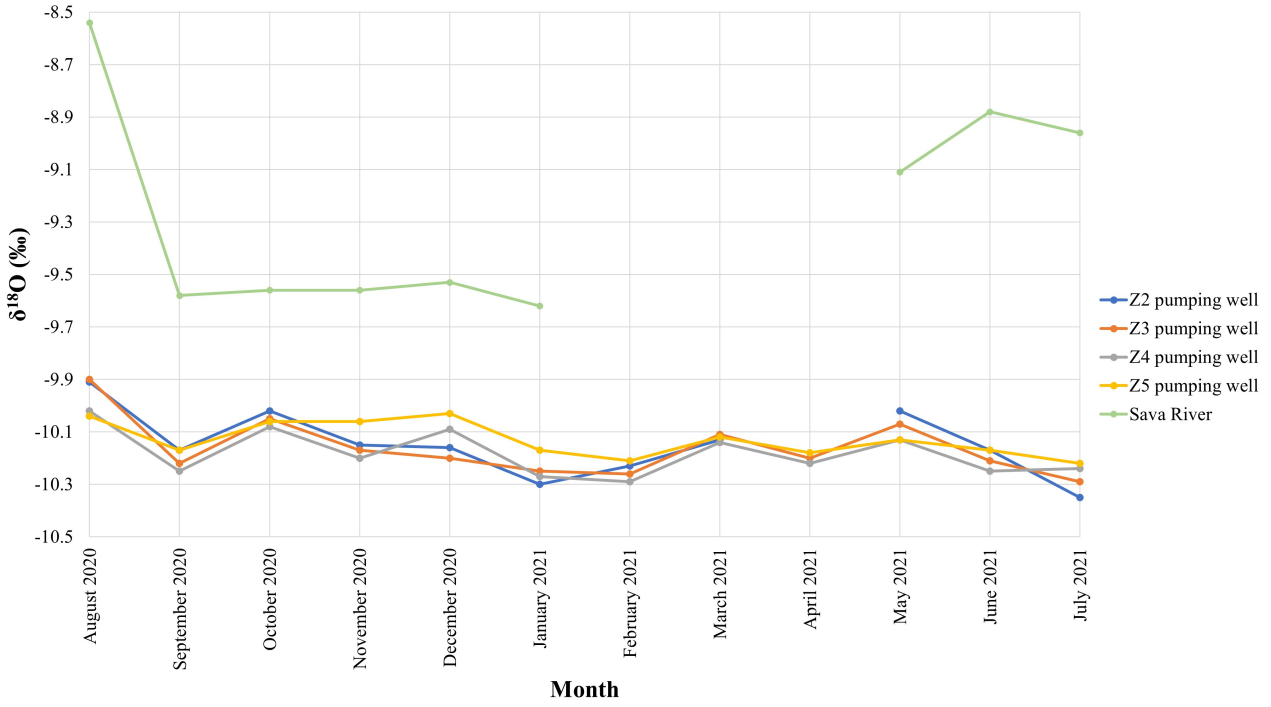

Figure 3: Variability of the $\delta^{18}O$ values of the well field Sikirevci and Sava River in time

Although the primary evaluation of the isotopic signature shows a difference between the Sava River and the groundwater, the d-excess values, as a second order parameter, have similar average values, while the minimum and maximum values are not so different (**Table 1; Figure 4**). The d-excess values indicate that connection between Sava River and groundwater from deeper layers exist. **Figure 4** shows that the d-excess values of the groundwater follow a similar pattern to those of the Sava River. In this case, without evaluating the d-excess, the isotopic composition would likely lead to incorrect conclusions. This is consistent with other soil hydrology research where d-excess was defined as a better tracer (**Lee et al., 2007**). The initial isotopic results suggest that the relationship between the Sava River and groundwater is complicated and needs to be studied in much more detail, including the influence of the Bosna River.

Parameter	Groundwater			Sava River		
	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	d-excess (‰)
Average	-69.44	-10.15	11.80	-61.58	-9.26	12.50
Minimum	-70.11	-10.35	10.10	-63.90	-9.62	10.75
Maximum	-68.94	-9.90	13.19	-57.57	-8.54	13.90
Standard deviation	0.25	0.10	0.71	2.67	0.40	0.88

Table 1: Statistical parameters of water isotope composition of groundwater from the well field Sikirevci and Sava River

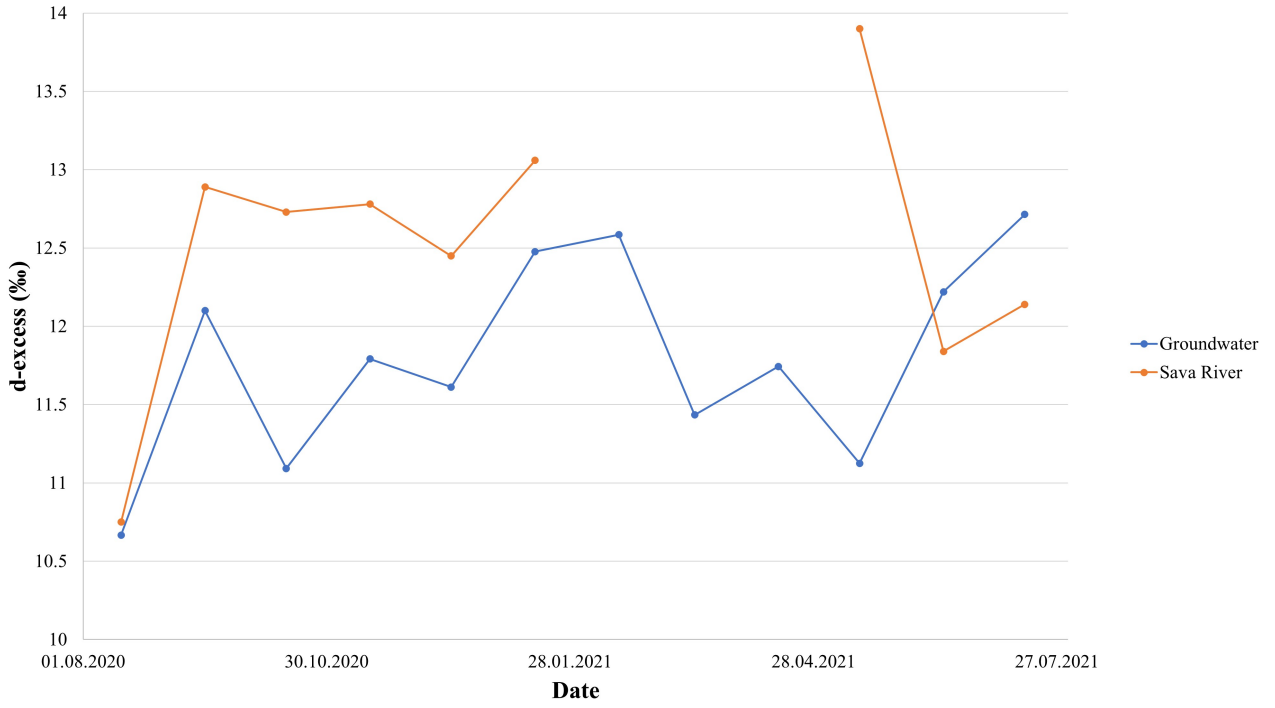

Figure 4: Variability of average d-excess values between groundwater and Sava River

The hydrogeochemical facies of the groundwater from the Sikirevci well field is shown in **Figure 5**. In general, CaMg-HCO_3 facies was detected in almost all samples. In 2016, slightly higher sodium values were observed, which resulted in the CaMgNa-HCO_3 hydrogeochemical facies. In 2020, magnesium concentrations were the highest in all analyses which resulted in MgCa-HCO_3 hydrogeochemical facies (**Filipović, 2021**). In the previous research (**Kopić et al., 2016**) cluster analysis showed that the groundwater quality parameters are a consequence of the dissolution of alumosilicates, mostly clay minerals, organic matter, but also an anthropogenic input (probably related to the agriculture influence). One of the subgroups was defined as a group of complex parameter affinities of different origin, more or less related to geochemical processes, which include the presence of organic matter and its decomposition. Within that group, sodium concentrations were defined, while the origin of the concentrations was defined as anthropogenic or/and natural. Third subgroup, where one of the parameters was magnesium, was defined as non-reactive group which origin was probably natural. From this point of view, it is still unclear why higher sodium and magnesium concentrations were observed and whether they were of natural or anthropogenic origin. If higher sodium concentrations are the consequence of human influence, they probably represent further evidence that infiltration from the surface into deeper aquifer layers is possible. The concentrations of potentially toxic metals are very interesting: iron, manganese, and arsenic (group **Figure 6**). While arsenic concentrations (**Figure 6a**) do not vary much over time, i.e., are generally very stable, concentrations of iron (**Figure 6b**) and manganese (**Figure 6c**) show much greater variation. Iron concentrations vary from about 11 µg/l to about 91 µg/l. Manganese concentrations vary from about 1 µg/l up to 20 µg/l. The observed concentrations of potentially toxic metals are consistent with those observed in previous studies (**Kopić et al., 2016**). In general, they are lower than the maximum contaminant levels (MCLs) defined by Croatian law. However, this variation suggests the presence of a different geochemical environment that changes over time (probably dominantly reductive), possibly leading to mixing of water between different aquifer layers and possible infiltration of surface water. It must be emphasised that in this case the limited amount of data does not allow strict and reliable conclusions. From that perspective detail hydrogeological and hydrogeochemical investigations, which include determination of stable isotopes on all types of water (surface water, precipitation and groundwater), should be done. This applies not only to the Croatian part, but also to the part located in the Federation of Bosnia and Herzegovina, which is primarily related to the Bosna River and its influence on the Sikirevci well field.

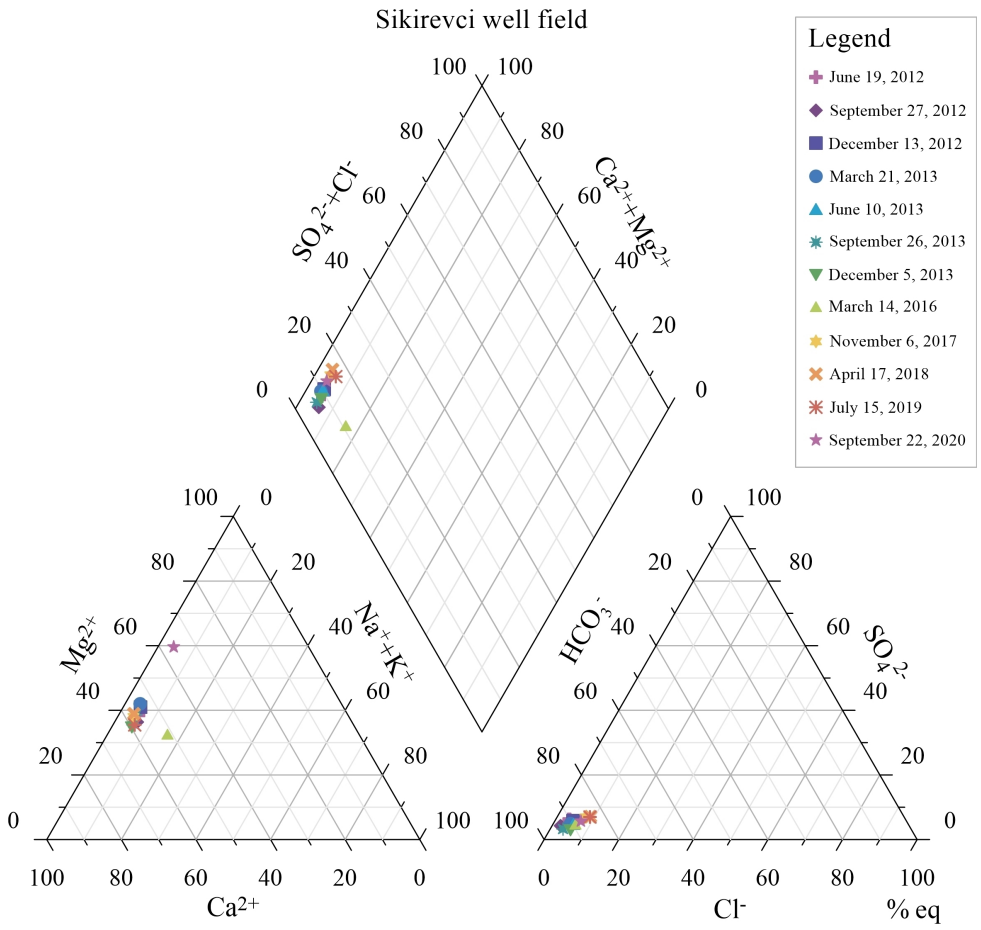

Figure 5: Hydrogeochemical facies at the well field Sikirevci (modified from **Filipović, 2021**)

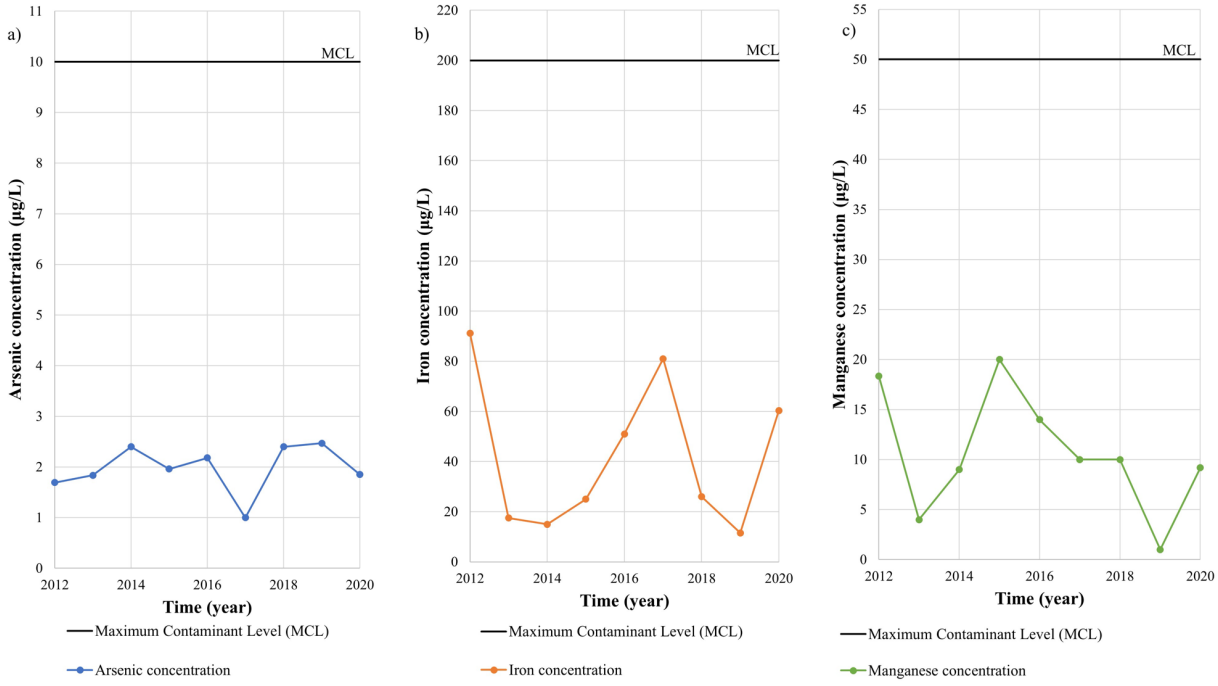

Figure 6: Concentrations of potentially toxic metals at the well field Sikirevci: a) arsenic concentration, b) iron concentration, c) manganese concentration (modified from **Filipović, 2021**)

4. Conclusions

The wellfield Sikirevci presents one of the main and most important well fields in the eastern part of the Slavonia. In this paper, the isotopic composition of the Sava River and groundwater from the Sikirevci well field is studied. Although the primary isotopic signature has shown a different isotopic composition between the two compartments, the d-excess values suggest that there is a connection between the Sava River and the deeper groundwater. However, this connection is not very strong, probably because the pumping wells of the Sikirevci well field pump water from deeper aquifer layers, while the Sava River is in direct contact only with the shallow aquifer layer. In addition, the hydrogeochemical composition showed a dominant $CaMgHCO_3$ facies, while the variations in iron and manganese concentrations indicate a possible change in the geochemical environment, which is mostly reductive. All results suggest the need for more detailed hydrogeological and hydrogeochemical research which should include both the Republic of Croatia and Federation of Bosnia and Herzegovina, as they are transboundary aquifers very important for public supply in both countries, in order to achieve sustainable groundwater management and provision of potable water for future generations.

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Sažetak

Izotopni sastav crpilišta Sikirevci i njegova povezanost sa rijekom Savom

Crpilište Sikirevci jedno je od najvažnijih crpilišta u istočnoj Slavoniji koje se koristi za javnu vodoopskrbu. U ovom istraživanju korišteni su stabilni izotopi vode za određivanje porijekla vode iz crpljenog vodonosnika, ali i za ispitivanje njegove povezanosti s rijekom Savom. Od kolovoza 2020. do srpnja 2021. godine uzorci podzemne vode prikupljeni su iz četiri zdenca, dok su povijesne kemijske analize korištene za određivanje hidrogeokemijskog facijesa. Utvrđeno je da se izotopni sastav rijeke Save razlikuje od uzorkovanog vodonosnika. Stabilni izotopi vodika i kisika (δ^2H i $\delta^{18}O$) podzemne vode imaju negativnije vrijednosti od onih u rijeci Savi, što ukazuje na to da zdenci crpilišta Sikirevci crpe vodu iz dubljeg dijela vodonosnog sloja na koji rijeka Sava nema tako jak utjecaj, iako vrijednosti viška deuterija ne pokazuju tako veliku razliku. Štoviše, izotopni sastav podzemne vode je vrlo stabilan i ne mijenja se tijekom vremena. To je u skladu s prisutnošću koncentracija željeza, mangana i arsena u podzemnoj vodi, što ukazuje na postojanje dominantno reduktivnih uvjeta. Međutim, varijacije u koncentracijama promatranih potencijalno toksičnih metala ukazuju na to da su tijekom razdoblja istraživanja prevladavali različiti geokemijski uvjeti. Većina uzoraka vode imala je CaMg-HCO_3 hidrogeokemijski facijes, dok su dva uzorka imala nešto više koncentracija natrija i magnezija.

Ključne riječi: stabilni izotopi vode; crpilište Sikirevci; rijeka Sava; hidrogeokemijski facijes

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Author’s contribution

Vedrana Filipović (student in the graduate studies of Geological Engineering) participated in writing of original draft, data interpretation and presentation of the results. **Zoran Kovač** (PhD, Assistant Professor, hydrogeology, hydrogeochemistry and isotope hydrology) made the isotope analysis, and participated in conceptualization, writing of the original draft and data interpretation. **Jasna Kopić** (PhD, hydrogeology), performed the field work (sampling of groundwater and Sava River) and participated in data interpretation. **Zoran Nakić** (PhD, Full Professor, hydrogeology, hydrogeochemistry) participated in conceptualization, review, and editing. **Jelena Parlov** (PhD, Associate Professor, hydrogeology, isotope hydrology) participated in the interpretation and presentation of the results, as well as review and editing. **Ferid Skopljak** (PhD, hydrogeology, geology) participated in data interpretation and review and editing.