

# Hazardous substances in karst aquifer waters - one of the results of the operational monitoring of groundwater in Serbia

Zoran Stevanović, Veljko Marinović, Branislav Petrović



Дигитални репозиторијум Рударско-геолошког факултета Универзитета у Београду

[ДР РГФ]

Hazardous substances in karst aquifer waters - one of the results of the operational monitoring of groundwater in Serbia | Zoran Stevanović, Veljko Marinović, Branislav Petrović | Geoloski anali Balkanskoga poluostrva (Annales geologiques de la Peninsule balkanique) | 2020 | |

10.2298/GABP201107010S

<http://dr.rgf.bg.ac.rs/s/repo/item/0006013>

Дигитални репозиторијум Рударско-геолошког факултета Универзитета у Београду омогућава приступ издањима Факултета и радовима запослених доступним у слободном приступу. - Претрага репозиторијума доступна је на [www.dr.rgf.bg.ac.rs](http://www.dr.rgf.bg.ac.rs)

The Digital repository of The University of Belgrade Faculty of Mining and Geology archives faculty publications available in open access, as well as the employees' publications. - The Repository is available at: [www.dr.rgf.bg.ac.rs](http://www.dr.rgf.bg.ac.rs)

## Hazardous Substances in Karst Aquifer Waters – One of the Results of the Operational Monitoring of Groundwater in Serbia

ZORAN STEVANOVIĆ<sup>1</sup>, VELJKO MARINOVIĆ<sup>1</sup>  
& BRANISLAV PETROVIĆ<sup>1</sup>

**Abstract.** Hydrogeological survey of wider Majdanpek mining area in the Carpathian mountain arch of eastern Serbia, including open mine pits, tailings sites, and major karstic springs and caves has been undertaken in order to estimate environmental conditions in groundwater body (GWB) “Krš–sever”, groundwater quality, and to investigate causes of their earlier indicated poor chemical status. Bearing in mind that Majdanpek copper mine field is directly bordering the karst aquifer and delineated GWB “Krš–sever”, the two karst springs namely Valja Fundata and Kaludjerica were *in situ* measured and sampled in high and low-water periods (spring 2019, late autumn 2019 and spring 2020). Sampling and analysis of groundwater were carried out under the frame of project “Operational Monitoring of Groundwater of the Republic of Serbia”, established by the Ministry of Environmental Protection of Serbia. The field measurements of unstable chemical components and physical properties as well as laboratory analyses confirmed very poor and even hazardous water quality of both surveyed springs Valja Fundata and Kaludjerica. Registered concentrations of some ions, such as  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  are high above maximal permitted level for potable water in Serbia. High turbidity rate also confirms impact of colloidal suspensions from the tailing which is located in karstic blind valley. Leakage of mine water passes through joints, open cavities and even large cave system Valja Fundata. Results of undertaken survey confirm that low-water period results with worse water quality and much higher concentration of hazardous substances than that characterized high-water season when infiltrated rainy water and/or melted snow dilute tailing’s wastewater. Strict application of environmental protection measures and design/construction of the smaller water treatment facility at both surveyed springs should possibly mitigate the impacts of mining activities to karst groundwater and dependant ecosystem.

### Key words:

*Hazardous substances,  
karst aquifer, copper, tailing,  
Majdanpek, Serbia.*

**Апстракт.** У циљу оцене стања животне средине и разумевања потенцијалних узрока још раније евидентираног лошег хемијског статуса водног тела подземних вода „Крш–север“, извршена је хидрогеолошка проспекција шире околине лежишта бакра Мајданпек, која је укључила истраживање површинског копа, флотационог језера и главних карстних врела и пећина. Имајући у виду да се експлоатационо поље рудника

<sup>1</sup>University of Belgrade – Faculty of Mining and Geology, Department of Hydrogeology, Centre for Karst Hydrogeology, Djušina 7, 11000 Belgrade, Serbia. E-mail: zstev\_2000@yahoo.co.uk

бакра Мајданпек директно граничи са карстном издани и водним телом подземних вода „Крш–север“, параметри квалитета подземне воде су анализирани (*in situ* и лабораторијски) на два главна карстна врела – Ваља Фундата и Калуђерица у периодима високих и ниских вода (пролеће 2019, касна јесен 2019. и пролеће 2020.), у циљу оцене утицаја рударских активности на квалитет подземних вода. Узорковање и анализа подземних вода извршена је у оквиру пројекта „Оперативни мониторинг подземних вода Републике Србије“, иницираног од стране Министарства заштите животне средине Републике Србије. Теренска мерења нестабилних хемијских компоненти и физичких карактеристика, као и лабораторијске анализе потврдиле су веома лош, па чак и опасан квалитет вода оба осматрана карстна врела. Регистроване концентрације неких јона, као што су  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$  далеко су изнад максимално дозвољених концентрација за воду за пиће у Србији. Знатно повећане вредности мутноће указују на продор вода из флотације Ваља Фундата лоциране у дубокој карстној депресији слепе долине истог имена. Процуривање и активна филтрација отпадних вода флотације остварује се преко пукотина, каверни и крупних пећинских канала Ваља Фундате. Резултати спроведених истраживања потврђују да периоди ниских вода резултирају лошијим квалитетом воде и много већом концентрацијом опасних материја, него што је случај у периоду високих вода када долази до разблажења услед повећане инфилтрације вода од кише и/или топљења снега. Доследном применом мера заштите животне средине и изградњом мини постројења за пречишћавање вода на оба осматрана извора, могуће је ублажити утицај рударских активности на подземне карстне воде и низводни еко-систем.

### Кључне речи:

Опасне супстанце,  
карстна издан, бакар,  
флотацијско језеро,  
Мајданпек, Србија.

## Introduction

Mining has a very long history in eastern Serbia. Traces of extraction of copper minerals, malachite and azurite and early metallurgy at the archaeological site Rudna Glava date back to five millennia B.C. Although exploitation of copper minerals continued during the Roman and Ottoman Empires, the period that lasted from the middle to the end of the 19<sup>th</sup> century was marked by the opening of new and modern copper mines. One of them, Majdanpek (meaning: *Mine at River Pek*) is still in active operation with two open pit mines and a flotation tailing lake. The main ore resource is copper, and, to a lesser extent, silver and gold.

The geological setting of the Majdanpek ore field (Fig. 1) is complex. The area belongs to the Carpathian-Balkanides, a geologically heterogeneous and morphologically very dissected orogenic belt of the Alpine system (PETKOVIĆ, 1935; GRUBIĆ, 1974). The oldest metamorphic rocks, gneisses and schists of

Pre-Cambrian to Early Paleozoic age are locally intruded by granites (Hercynian orogeny). The big transgression, which started in Middle Jurassic, resulted in thick carbonate deposits of mostly Upper Jurassic–Tithonian age (ANTONIJEVIĆ, 1979). During the period between Turonian and Paleogene, a volcanogenic-sedimentary series called Timok Magmatic Complex (TMC) were formed in the eastern part, in a tectonic trough. The TMC is about 85 km long, and up to 25 km wide (BANJEŠEVIĆ, 2010), with the Majdanpek area in its northernmost part. Andesites, pyroclastics and tuffa rocks, followed by rich porphyry-type copper deposits, prevail in this complex which is more than 2,000 metres thick (JANKOVIĆ, 1990; KARAMATA et al., 1994; JELENKOVIĆ & KOŽELJ, 2002). There were several phases (at least two) of volcanism, and the volcanic processes were sub-aerial to submarine eruptive, with hypabyssal intrusion and rarely explosive (BANJEŠEVIĆ, 2010). The regional tectonic pattern is composite. Long regional faults elongate in the direction of NNW–SSE, in

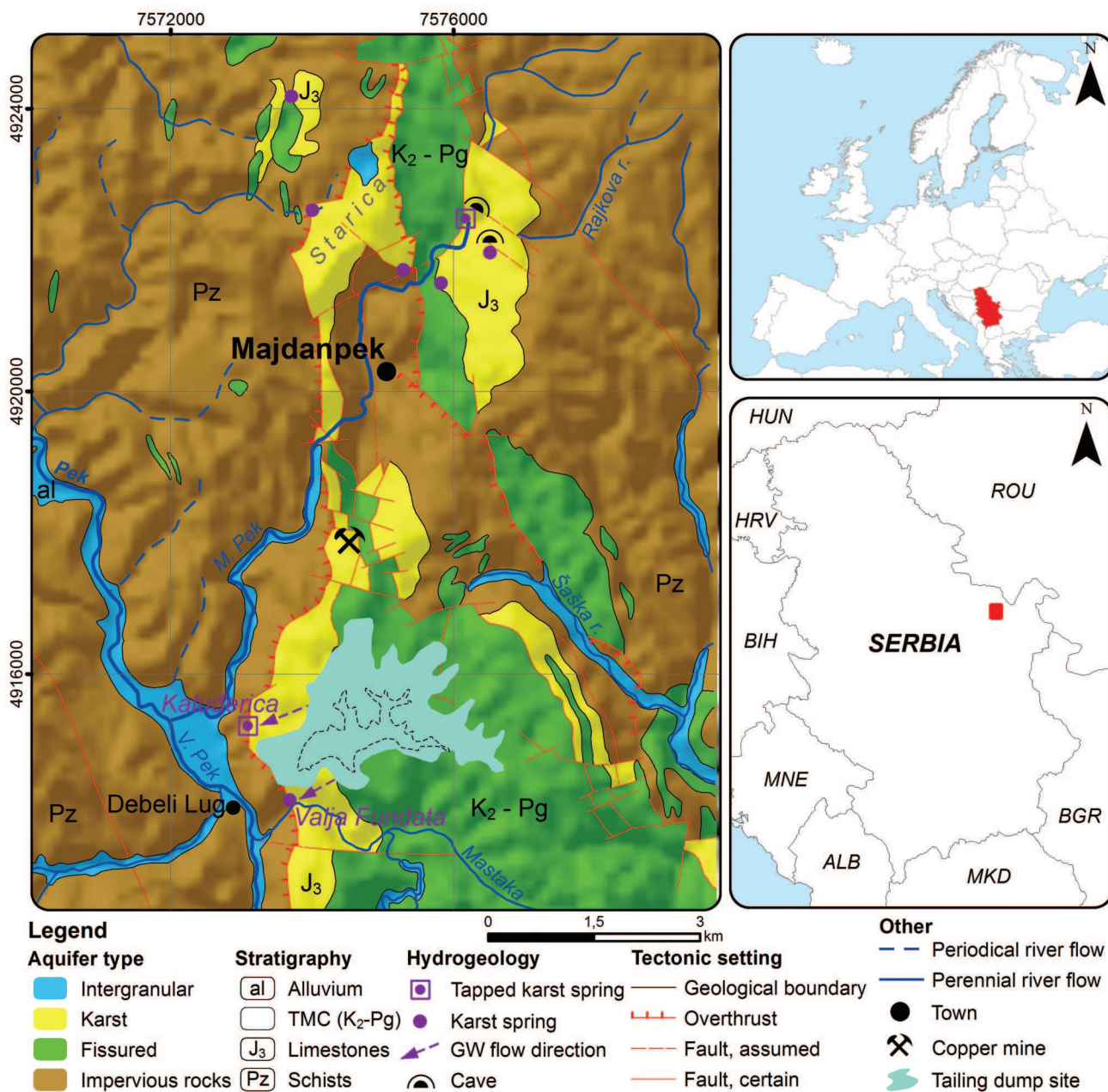


Fig. 1. Location and hydrogeological maps of the studied Majdanpek mining area.

parallel to the main geological structure (longitudinal) and are intersected by a group of perpendicular (transversal) faults that are younger and shorter (Fig. 1).

The karstification process in the Carpathian karst was intensive and, in the Majdanpek area, it resulted in specific landscapes (sinkholes, blind valleys, ponors, stone bridges) and long caves (Rajkova, Paskova, Valja Fundata) (LAZAREVIĆ, 1976). The karst aquifer formed in the carbonate rocks of Upper

Jurassic (Tithonian) is rich in groundwater, and is recharged mainly by rainfall and by sinking flows that gravitate from higher altitudes and impermeable Paleozoic rocks toward lower-positioned Mesozoic limestones (STEVANOVIĆ, 1991). The springs issuing from the three above-mentioned caves and a few others (Kaludjerica, Baščao, Štameta; Fig. 1) are the main drainage points of the karst aquifer and are used for local potable water supply (FILIPOVIĆ et al., 1975).



The fissure aquifer of TMC is not rich in groundwater. The groundwater flow pattern is linked to joint and fissure systems as well as main faults. Paleozoic formations, magmatic and metamorphic rocks mostly represent aquitards or aquifuges and in most cases act as a barrier to groundwater flow (FILIPOVIĆ et al., 1975).

## Methodology

The ongoing process of the Republic of Serbia's (RS) European Union (EU) accession requires many steps toward improving environmental conditions, primarily in the water sector. Adaptation to the Water Framework Directive (WFD, 2000) and EU standards, especially in the area of environmental regulations, has thus become one of the priorities. The project of the Ministry of Environmental Protection of Serbia – “Operational Monitoring of Groundwater of the Republic of Serbia”, which aims to create new bases, expand the groundwater monitoring network and improve the protection of water resources in the RS (STEVANOVIĆ et al., 2020), has been completed (2017–2020).

The Serbian Environmental Protection Agency (SEPA) is in charge of systematic monitoring of the quality of groundwater in the RS, while monitoring the quantity of groundwater falls within the competence of the Republic Hydrometeorological Service of Serbia (RHSS). However, the monitoring situation is far from satisfactory. Only about 30 delineated groundwater bodies (GWB), or 20% of the total, are subjected to systematic observation. Moreover, there is a noticeable disproportion in the spatial distribution of relatively dense piezometers located in alluviums or large rivers and the Vojvodina province, and karst aquifers and artesian aquifers in Neogene sedimentary basins, which are both largely unobserved.

The undertaken project of operational monitoring has increased the number of observed groundwater bodies, comprising – in the last stage - 50 additional groundwater bodies, including the one located in the Majdanpek area (GWB “Krš-sever”).

Operational monitoring consists of field visits, *in situ* measurements and laboratory analyses. All the

selected sites are visited in both high-water and low-water periods, in order to assess the differences in water discharge, groundwater table position and physical-chemical composition. Two springs – Valja Fundata and Kaludjerica – were visited in an attempt to assess the impact of mining activities on the quality of groundwater of GWB “Krš-sever”. The water quality of these springs was measured *in situ* and sampled for laboratory analyses.

Groundwater samples were collected on three occasions: in the spring of 2019, in late autumn of 2019 and in the spring of 2020. The low-water season (smallest discharge at the springs) corresponded with the late autumn period of 2019. Standard procedures for sampling, transport and storage of groundwater samples were applied.

Field parameters such as turbidity, water temperature, electrical conductivity (Ec), pH, oxidation-reduction potential (Eh) and dissolved oxygen (DO) were measured by use of WTW measuring instruments 355 Turb IR and 340i SET (pH/Conductivity/Oxi), while the total hardness and total alkalinity of water were measured using the instrument called Exact Micro 20 (ITS Inc.). Concentration of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  was measured using the MColorTest (Merck Millipore). Groundwater samples were collected when the measured field parameters of fresh groundwater at the karst springs were stable. Groundwater samples were taken in PVC bottles for the purpose of conducting the analyses of relevant major ions and pesticides, and in glass bottles preserved with acid (2 ml of conc.  $\text{HNO}_3$ ) for metal ions analyses.

Major ions, metal ions and pesticides were analysed in the accredited laboratory of the Institute of Public Health in Kragujevac (ATC 01-169 SRPS ISO/IEC 17025:2006; IQ NET Certified Management System; ISO 9001: Q-1644-IVR). Volumetric titrimetry was used to determine the concentration of chlorides and to quantitatively determine the total oxidisable organic material. The concentration of nitrites was determined using the molecular absorption spectrometric method. The spectrophotometric method was used to determine the amount of nitrates and ammonia. Sulphate was determined using the method of liquid chromatography. Determination of elements, by inductively coupled

plasma optical emission spectrometry (ICP-OES), has been used for selected ions: iron, manganese, cadmium, nickel, zinc, copper, mercury and arsenic. Gas chromatography-mass spectrometry (GC-MS) was the analytical method that was used to determine organochlorine pesticides (OCPs) in groundwater samples.

Several earlier studies were collected and evaluated for the purpose of assessing the environmental conditions. Some available information on previous pollution accidents were studied as well.

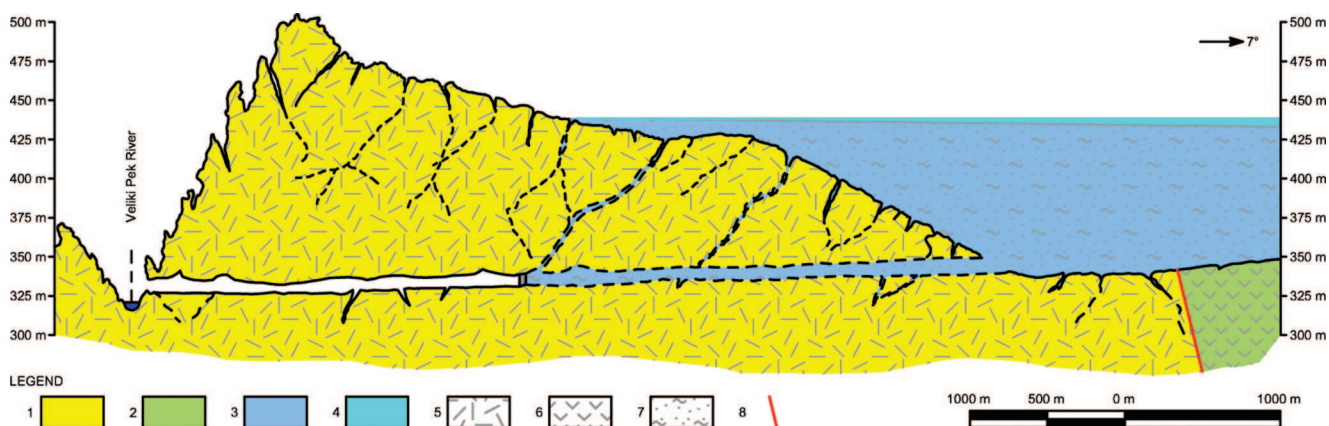
This analysis and the assessment of pressure on the quality of water in GWB “Krš-sever” required an important step in the form of hydrogeological conceptualisation. Therefore, hydrogeological exploration of the wider Majdanpek area was undertaken, including a survey of open mine pits and tailings, while visits to major karstic springs and caves were steps that were necessary for the creation of the conceptual model and the assessment of the environmental conditions and groundwater status.

## Results

### Conditions on Site

In the previous period, very thick TMC deposits required a combination of underground mining works and removal of rocks and minerals in the

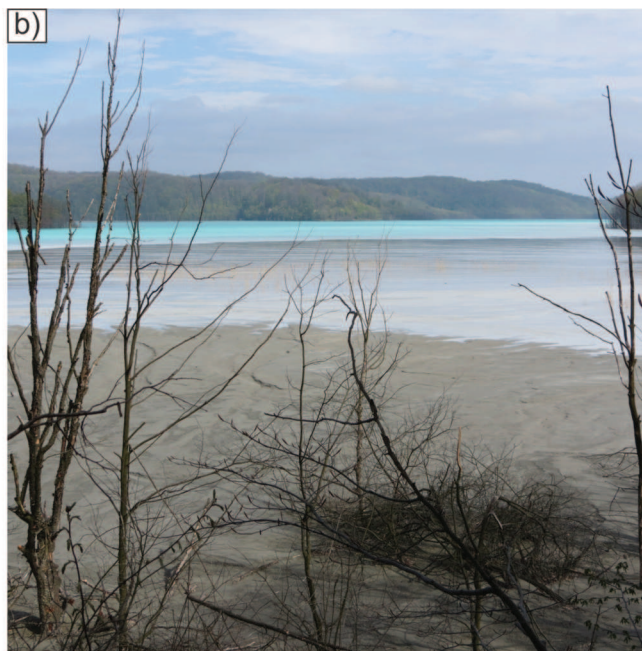
open pits. The former method has in the meantime been completely abandoned. The two open pits – “Northern” and “Southern” – were caused by long and intensive exploitation at great depth. The bottom of the latter is more than 200m deeper than the surrounding terrain and the riverbed of the nearby stream Mali Pek, which in natural conditions and prior to the deepening of the open mine used to represent the erosional base. The flotation tailing is located above the “Southern” pit, in the hill with an altitude of approximately 500 m a.s.l. The site was chosen in the late 1960s, to be closer to the underground mine works and the then newly opened pit. Deep and blind valley Valja Fundata, formed in Jurassic karstified limestone, was found to be a suitable place for the deposition and flotation of extracted ore material and rocks (Fig. 2). On the southern side of the Valja Fundata valley lies the valley of the perennial stream Valja Mastaka (Fig. 1). Some 25 m above the valley there is a large orifice of the Valja Fundata cave (Fig. 3a), which is passable for a few dozen of metres (FILIPOVIĆ et al., 1975). This cave also functions as a permanent spring which is most probably connected with the blind valley of Valja Fundata (Fig. 2). Aware of this fact, to prevent leakage from the tailing, the mining engineers of the Majdanpek Mine have constructed a form of a barrage gate inside the cave, in its last accessible part. Initially, some registered larger faults, fissures and ponors in the blind valley were also plugged with



**Fig. 2.** Hydrogeological cross-section of the Valja Fundata tailing and cave. 1, Karst aquifer; 2, Fissured aquifer; 3, Intergranular aquifer; 4, Tailing's water table; 5, Jurassic limestones; 6, Andesites; 7, Ore and crushed – fragmented rocks and clays; 8, Fault (according to FILIPOVIĆ et al., 1975).

clays or cement. Further deposited excavated andesite material in tailing today is more than 100 m thick and is fully saturated. The floatation tailing Valja Fundata is a mixture of crushed fragments and particles with copper and magnetite minerals and fluid mass. The solid phase of the tailing has a fine grain distribution, with diameters ranging between 0.002 to 0.6 mm (DRAGIŠIĆ, 1992).

Due to the presence of sulphide mineralisation, groundwater is often acidic (low pH), with a high content of  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  ions and several metallic micro-constituents. Mine waters, pumped out directly to riverbeds, pollute the surface waters and dependent eco-systems (DRAGIŠIĆ, 1992; ATANACKOVIĆ, 2018). Nicely coloured water (light green to azure-blue), such as that of the Valja Fundata tailing, is the result of oxidation of pyrite minerals and sulfidation (Fig. 3b).



**Fig. 3. a**, Valja Fundata a large cave orifice; **b**, Valja Fundata tailing dump site (springtime 2019).

### Earlier Accidents

The first big accident happened in 1974, after several years of the tailing's operation, when the activation of some of Valja Fundata ponors at the bottom (or banks?) of the tailing provided a path for the flow of the tailing's dense fluid, which resulted in

the contamination of karst groundwater draining at the speleological site of Valja Fundata. Discharged from the cave, the tailing's fluid entered the Valja Mastaka stream, reaching the river Veliki Pek near Debeli Lug (Fig. 1). Rapid waste water outflow killed the entire river's fauna for several tens of kilometres, all the way to its confluence with the Danube (STEVANOVIĆ & DRAGIŠIĆ, 1995). Information about this accident was published in one of the most-cited books on karst, written by FORD & WILLIAMS (2007).

Another accident took place in 1996. After the Valja Fundata accident, the management of Majdanpek decided to create a new tailing, smaller in size, in the head watershed of the Šaška River. This area is away from the karstic rocks, and not very far from the open pit, which made ore transportation feasible. However, after a long and heavy rain on 8 and 9 May 1996, the flotation dam broke and 100,000 m<sup>3</sup>

of waste fluid came out, polluting Šaška River downstream, and later Porečka reka all the way to its confluence with the Danube (DRAGIŠIĆ et al., 1997). The water intake used for the downstream tourist town Donji Milanovac and several villages in the Majdanpek municipality was abandoned as a direct consequence of polluted alluviums. The Šaška tailing site



has not been in use since this accident, and only Valja Fundata is used now for the flotation process. In the meantime, the volume and surface of the lake expanded; in Fig. 1, is possible to see the contour of the lake in its earlier stage (mid 1970s) and how it looks today.

### Groundwater Quality of the Two Observed Springs

Field measurements of unstable chemical components and physical properties, as well as laboratory analyses, confirmed very poor and even hazardous water quality of the two surveyed karst springs – Valja Fundata and Kaludjerica.

Registered concentrations of some ions are high above the maximum permitted level (MPL) for potable water in Serbia (SL. GLASNIK RS, 1999, 2019). Electrical conductivity in all the samples (3+3 of each spring) was above 1000  $\mu\text{S}/\text{cm}$ . Table 1 shows only components with concentrations above MPL.

riod, reaching the value of 12 NTU (MPL = 1 NTU), which is very rare for karst springs and their often dynamic regimes.

The low-water period results in worse water quality than the high-water period, as evidenced by the concentration of several other chemical constituents. For instance, the concentration of ammonium ion ( $\text{NH}_3^-$ ) is above MPL during the periods of low-water (0.71 mg/l), similar as  $\text{NO}_2^-$  0.036 mg/l. The content of the  $\text{SO}_4^{2-}$  ion, which is dominant in anion composition, is regularly high above MPL (250 mg/l), reaching its maximum value of 1152 mg/l again during the low-water season (Fig. 4a). Water of the Valja Fundata spring is characterised by a high concentration of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions throughout the year, but the highest value is noted once again during the low-water season, when the concentration of  $\text{Fe}^{2+}$  is six times higher than permitted (1870  $\mu\text{g}/\text{l}$  vs. 300  $\mu\text{g}/\text{l}$ ), while that of  $\text{Mn}^{2+}$  is even ten times higher than permitted (504  $\mu\text{g}/\text{l}$  vs. 50  $\mu\text{g}/\text{l}$ ) (Fig. 4b).

In high-water periods, water samples from the Kaludjerica spring had turbidity values of 25.99 and 122.2 NTU in 2019 and 2020, respectively. However,

**Table 1.** Chemical composition of spring water of Valja Fundata and Kaludjerica.

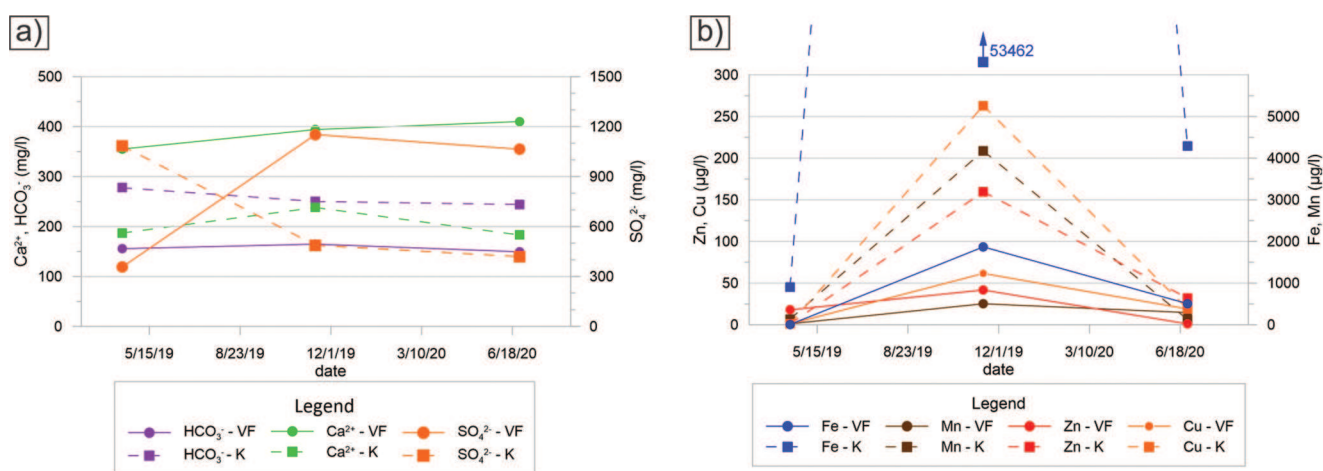
Component	Max. Perm Level	Valja Fundata			Kaludjerica		
		High-water 2019	Low-water 2019	High-water 2020	High-water 2019	Low-water 2019	High-water 2020
NTU	1	2.31	12	5.54	25.99	694.8	122.2
El. Conductivity ( $\mu\text{S}/\text{cm}$ )	2500	1945	1888	1934	1056	1138	963
$\text{Ca}^{2+}$ (mg/l)	200	355	394	410	187	238	83
$\text{NH}_3^-$ (mg/l)	0.5	0.18	0.71	<0.05	<0.05	1.27	<0.05
$\text{NO}_2^-$ (mg/l)	0.03	0.027	0.036	0.039	0.016	0.059	0.025
$\text{SO}_4^{2-}$ (mg/l)	250	356.2	1152	1064	1084.3	487.2	419.3
$\text{Fe}^{2+}$ ( $\mu\text{g}/\text{l}$ )	300	<15	1870	506	828	53462	3937
Mn ( $\mu\text{g}/\text{l}$ )	50	23	504	293	135	4175	126
Ni ( $\mu\text{g}/\text{l}$ )	20	<15	<15	<15	<15	47.5	<15
Zn ( $\mu\text{g}/\text{l}$ )	3000	17.9	35.5	<10	<14	159.6	32
Cu ( $\mu\text{g}/\text{l}$ )	2000	<17	55.0	17	<17	234.8	17

Examined during periods of high-water, turbidity of water of the Valja Fundata spring has values of 2.31 and 5.54 Nephelometric Turbidity Units (NTU) in 2019 and 2020, respectively. It is interesting that turbidity is even higher during the low-water pe-

as in case of Valja Fundata, the water's turbidity is the highest during the low-water season, reaching all of 694.8 NTU (Fig. 5).

During low-water periods, four chemical components of the Kaludjerica water are above MPL. They





**Fig. 4. a**, Concentration of major ions ( $HCO_3$ ,  $Ca$ ,  $SO_4$ ) in water of karst springs Valja Fundata (VF) and Kaludjerica (K); **b**, Concentration of Fe, Mn, Zn, Cu ions in water of karst springs Valja Fundata (VF) and Kaludjerica (K).



**Fig. 5.** Muddy, heavily polluted water of the Kaludjerica spring during low water season (December 1<sup>st</sup> 2019).

are:  $Ca^{2+}$  and all three Nitrogen ions  $NH_3^-$ ,  $NO_2^-$  and  $NO_3^-$  (Table 1). The content of  $SO_4^{2-}$  is regularly above MPL, varying from 419.3 to 1084.3 mg/l (Fig. 4a). The

concentration of  $Fe^{2+}$  and  $Mn^{2+}$  ions in the Kaludjerica spring water is enormous, especially during the low-water season:  $Fe^{2+}$  is 200 times higher than permitted (53462  $\mu g/l$ ), while  $Mn^{2+}$  is 80 times higher than permitted (4175  $\mu g/l$ ) (Fig. 4b).

The heavily polluted water of these two karst springs pollutes the streams Valja Mastaka and Veliki Pek. The impact of the poor quality of river water can be observed far downstream. For instance, in the alluvial groundwater of the latter river, which is tapped to supply water to the town of Kučevo, the concentration of  $SO_4^{2-}$  during the low-water period is about two times higher than permitted (363 mg/l). This could be the result of old accidental pollution, but it could also mean that new waves are “refreshing” the pollution of this alluvial aquifer.

In contrast, other examined karst springs, which belongs to other karstified blocks such as those issuing from Rajkova and Paskova caves (Fig. 1) characterized by very good water quality and are utilized for potable water supply. No treatment process except chlorination is applied. The dislocation from mining activity and pure catchments are main factors of such water quality.

## Discussion

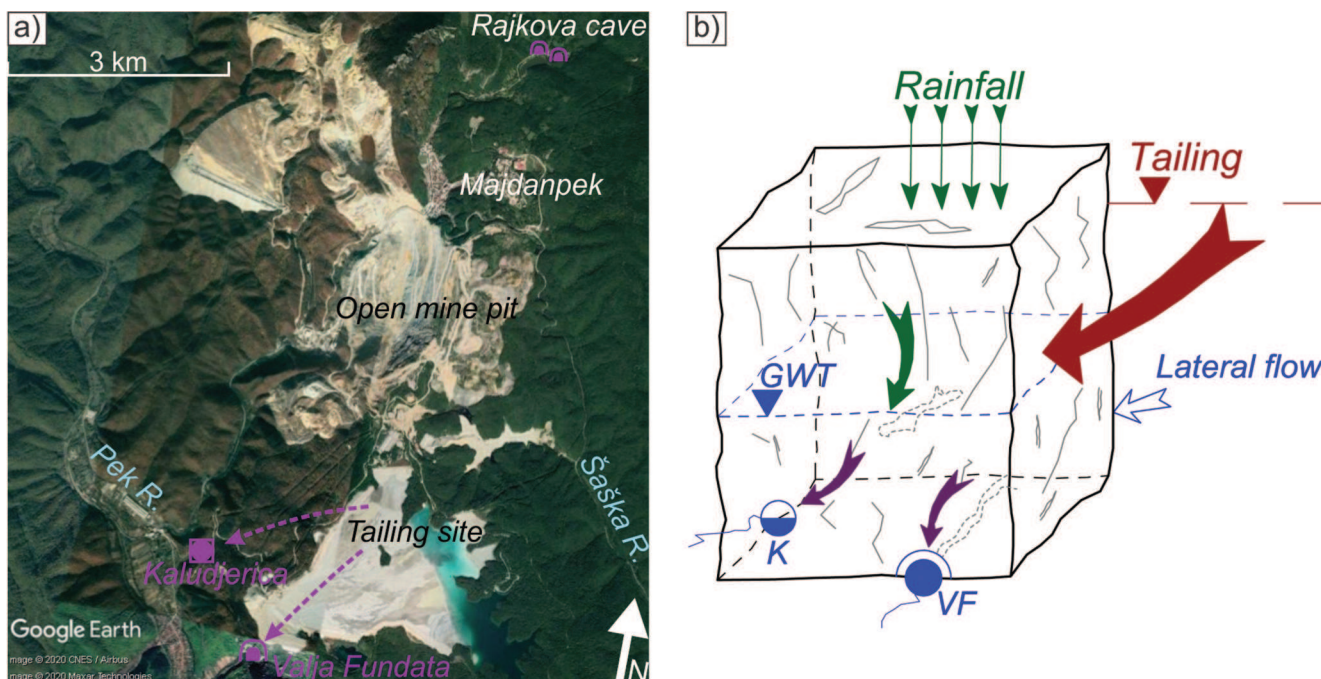
The Majdanpek copper minefield is directly bordering the karst aquifer and the delineated GWB of

“Krš-sever”. Waste consisting of crushed and defragmented rocks mixed with pre-processed low-copper ore, disposed in the Valja Fundata tailing, are in the catchment area of the Valja Fundata cave and spring and the Kaludjerica karst spring. The distance is very short, as the total catchment area of this tectonically relatively isolated limestone block is only about 3 km<sup>2</sup>. Such conditions enable direct hydraulic communication of the waste mine and tailing’s waters with karst groundwater. An attempt to close this communication by a barrage gate inside the cave or by plugging some ponors on the tailing side would be “a mission (that is almost) impossible” in the case of the karst aquifer in question. Due to permeability of karst, developed large cavities, limited attenuation capacity and a high gradient, remedial measures to prevent leakage can only partly amortize and slow this undesired flow from the tailing.

The natural chemistry of karst groundwater in the Carpathian karst is of high quality. Within open karst structures groundwater is just slightly mineralised, with intensive water exchange and rapid filtration. The developed channels and caverns of the karst system provide a short contact between water and rock, and the geogenic factors are therefore in

favour of good water quality. This was confirmed at numerous sources, where local waterworks apply only chlorination for water distributed to consumers (STEVANOVIĆ, 1995). In contrast, groundwater in the zone of oxidation of copper deposits depends primarily on geologic and hydrogeologic conditions, chemical-mineralogic composition of the deposits and the existing climatic factors (DRAGIŠIĆ, 1992; DRAGIŠIĆ et al., 1994). Complex physical-chemical processes take place during the interaction between water and sulphide ore bodies. They are reflected in the change of anion-cation composition, the decrease of pH values, and the increase of the values of mineralisation (electrical conductivity) and enrichment of microelements (NDORO & WITIKA, 2007; SCHULTZE et al., 2011).

Rock wastes in Majdanpek consist of fragments and blocks of mineralised hydrothermally altered volcanic rocks and crystalline schists (DRAGIŠIĆ et al., 1994). Degradation of sulphide minerals in waste rocks provides groundwater with specific physical and chemical properties. In parts with waste dumps, mine water directly percolates into karstified limestones, mixing with original karst aquifer’s waters of the GWB “Krš-sever” (Fig. 6a). Tailing fluid con-



**Fig. 6. a**, Position of main objects in Majdanpek area on satellite image (Source Google Earth); **b**, Conceptual model of mixture of fresh groundwater and tailing water in Majdanpek area.



taminates fresh groundwater to a certain extent, endangering the local habitat and biocenose. The conceptual model of this mixing mechanism is shown in Figure 6b.

Earlier accidents confirmed that the higher the pressure in the aquifer system, the higher the risk of pollution. For instance, high-water level in the tailing, plus intensive rainfall which fully saturates the aquifer and increases the water table, are definitely factors that could initiate a new wave of pollution. However, intensive rainfall dilutes hazardous substances and reduces their concentration. Further survey and monitoring should be focused on establishing more precisely the ratio/equilibrium between these two aquifer recharge components.

Results of the undertaken survey confirmed that low-water periods are more problematic, resulting in lesser quality water and a much higher concentration of hazardous substances than that which characterises the high-water season. Moreover, the main threats to the dependent and sensitive riverine eco-system are the low flow in the downstream rivers (Valja Mastaka, Veliki Pek) and the higher pollution rate.

Although there are not too many topographically suitable locations surrounding the mine works in Majdanpek, the decision to choose a blind valley in a karstic terrain that is not completely fossilised (still with temporary flows) for a dumping site is absolutely unfeasible and dangerous from the environmental point of view. This was confirmed in the years that followed. Unfortunately, remediation and rehabilitation of the existing tailing, even if a new location is found, is not only very expensive but also difficult to implement. For instance, drying the lake and installing an impervious cover with new soil layers and forestation may be possible in certain situations, but not in the case of Valja Fundata, because of its dimensions. However, mitigation is possible at two water outlets of the flotation lake - sources Valja Fundata and Kaludjerica. A small treatment plant, including a retention pit, a filtration chamber and an aeration facility, could improve the quality of water or at least prevent pollution peaks during period of low-water.

This example of “poor practice” is, however, a lesson learned and should be conveyed to technical

staff involved in similar projects and environmental impact assessment studies related to mining.

## Conclusions

In Serbia and former Yugoslavia, the period after the World War II was marked by intensive development of the industrial and mining sectors. Many new mines were opened, and ore extraction and metal production were stressed. The Majdanpek mine functioned with two open pits, a waste dump and a flotation lake – the Valja Fundata tailing. Many decisions taken during that period of fast industrialisation aimed to increase employment and support the economic development of the then socialist country. Not only in Majdanpek and Bor mining centres in eastern Serbia, but all across ex-Yugoslavia, not much attention was being paid to the environment and the consequences of intensive mining on natural resources and local eco-systems. Today, when the approach involving sustainability and environmentally safe activities is dominant in the entire Europe, locating a mine tailing directly on karst and in a deep depression with a blind valley on the bottom would not be considered justifiable under any circumstances.

Great damage suffered by the water, environment and local biocenose as a result of two major accidents in 1974 and 1996 in the Valja Fundata and Šaška tailings was never completely remedied. Groundwater stored in alluviums of upper watersheds of Veliki Pek and Porečka reka and their tributaries Valja Mastaka and Šaška is not usable, or is used just for individual water supply (dug wells) and with caution. Permanent seepage from the tailing to the adjacent karst aquifer and springs Valja Fundata and Kaludjerica, evidenced during the survey campaigns in 2019/2020, requires special attention and systematic monitoring beyond the project “Operational Monitoring of Groundwater of the Republic of Serbia”.

If EU WFD is fully transposed in Serbian legislation, with strictly applied one of its main principles – “the polluter pays”, many industrial and mining factories will be obliged to pay more attention to their technological processes, and to construct their



facilities in line with environmentally friendly requirements. As for the Majdanpek Mine, it should be mandatory to have a water treatment facility designed and installed at the two surveyed springs – Valja Fundata and Kaludjerica.

## Acknowledgments

The research was carried out using the funds provided by the Ministry of Environmental Protection of Serbia and the Ministry of Education, Science and Technology Development of Serbia through the OI 176022 project, for which the authors express their gratitude.

## References

- ANTONIJEVIĆ, I. 1979. *Stratigraphy and tectonics of Veliki Krš and Stol in eastern Serbia*. Rasprave "Geozavoda", X, Beograd (in Serbian).
- ATANACKOVIĆ, N. 2018. Procena rizika od zagadjivanja vodnih resursa pod uticajem napuštenih rudarskih radova na prostoru Srbije [*Risk assessment of water pollution caused by abandoned mining operations in Serbia – in Serbian, with an English Abstract*]. Unpubl. PhD Thesis, Faculty of Mining and Geology, University of Belgrade, 295 pp.
- BANJEŠEVIĆ, M. 2010. Upper Cretaceous magmatic suites of the Timok Magmatic Complex. *Geološki anali Balkanskoga poluostrva*, 71: 13–22.
- DRAGIŠIĆ, V. 1992. *Hydrogeology of the copper deposits of Eastern Serbia*. Spec ed. of the Institute of Hydrogeology, The Faculty of Mining and Geology, Belgrade (in Serbian), 211 pp.
- DRAGIŠIĆ, V. MILADINOVIĆ, B. & MILENIĆ, D. 1997. Pollution of ground water in Donji Milanovac. *Proceedings of the XXVII IAH Congress "Groundwater in the Urban Environment", Nottingham*, 1: 395–399.
- DRAGIŠIĆ, V., FILIPOVIĆ, B., STEVANOVIĆ, Z., VUJASINOVIĆ, S. & MILADINOVIĆ, B. 1994. Influence of mine waters on ground water quality on example of copper deposits in eastern Serbia. *Proceedings of Intern. Symp. "Impact of Industrial Activities on Ground Water Quality", IAH, AHR University press, Constanza*, 139–148.
- FILIPOVIĆ, B., DIMITRIJEVIĆ, N. & TOMIĆ, V. 1975. *Hydrogeological study of copper ore field „Majdanpek”, Zbornik radova RGF, Spec. ed., vol. 2, The Faculty of Mining and Geology, Beograd*, 108 pp. (in Serbian).
- FORD, D. & WILLIAMS, P. 2007. *Karst hydrogeology and geomorphology*. J. Wiley & sons, Chichester.
- GRUBIĆ, A. 1974. Eastern Serbia in light of new global tectonics and reflection of such model to explanation of tectonics of northern branch of Alpides. In: Janković S. (Ed.). *Mineral material complex of Serbia and Montenegro at the crossing of two millenniums*. MARGO-ART, Belgrade, 368–378. (in Serbian with a Summary in English).
- JANKOVIĆ, S. 1990. *Ore deposits of Serbia*. Fond za geološka istraživanja i zajednica nauke. Beograd, 760 pp. (in Serbian).
- JELENKOVIĆ, R. & KOŽELJ, D. 2002. Morphogenetical types of porphyry copper mineralization in the Bor metallogenic zone. *Proceedings of the Intern. Symp. "Geology and metallogeny of copper and gold deposits in the Bor metallogenic zone". RTB Bor holding company, Copper institute, Bor*, 29–56.
- KARAMATA, S., VASKOVIĆ, N., CVETKOVIĆ, V. & KNEŽEVIĆ-ĐORĐEVIĆ, V. 1994. Upper Cretaceous and Tertiary magmatites of central and eastern Serbia and their metalogeny *Geološki anali Balkanskoga poluostrva*, 58 (1): 159–175.
- LAZAREVIĆ, R. 1976. *Rajkova cave*. MZ. Boža Stojanović, Majdanpek, 61 pp. (in Serbian).
- NDORO, O.T. & WITIKA, K.L. 2007. A Review of the Flotation of Copper Minerals. *International Journal of Sciences: Basic and Applied Research*, 34 (2): 145–165.
- PETKOVIĆ, V. 1935. *Geology of eastern Serbia*. Pos. izd. SKA, Beograd (in Serbian).
- SCHULTZE, M., BOEHRER, B., FRIESE, K., KOSCHORRECK, M., STASIK, S. & WENDT-POTTHOFF, K. 2011. Disposal of Waste Materials at the Bottom of Pit Lakes. *Proceedings of the Sixth Intern. Conf. on Mine Closure, 18-21 September 2011, Lake Louise, Alberta*, Vol. 1: Mine Site Reclamation, Australian Centre For Geomechanics (Acg), Nedlands, 555–564.
- SL. GLASNIK RS 1999, 2019. *Statutory act on drinking water standard of the Republic of Serbia*, no. 44/99 and 28/2019.
- STEVANOVIĆ, Z. 1991. *Hydrogeology of karst aquifer of Carpathian-Balkanides of Eastern Serbia and water supply possibilities*. Spec ed. of the Institute of Hydrogeology, The Faculty of Mining and Geology, Belgrade. 245 pp. (in Serbian).

- STEVANOVIĆ, Z. 1995. Karst ground waters in Serbia – present and potential uses in regional water supply. In: STEVANOVIĆ Z. (Ed.). *Lithospheric water mineral resources in Serbia*. Spec ed. of the Institute of Hydrogeology, The Faculty of Mining and Geology, Belgrade, 77–120.
- STEVANOVIĆ, Z. & DRAGIŠIĆ, V. 1995. Some cases of accidental karst water pollution in the Serbian Carpathians, *Theoretical and applied Karstology*, 8: 137–144.
- STEVANOVIĆ, Z., PETROVIĆ, B. & MARINOVIĆ, V. 2020. *Operational monitoring of groundwater in Serbia*. Final Report of 3-year research (2017–2020). Ministry of Environmental Protection, Belgrade. (<https://www.ekologija.gov.rs/dokumenti/>)
- WFD, 2000. Water Framework Directive, Official Journal of EU, 2000/60, L 327/1, Brussels.

## Резиме

### Опасне супстанце у водама карстних издани – један од резултата оперативног мониторинга подземних вода у Србији

Рударска активност на подручју Мајданпека има дугу традицију. Тренутно се експлоатише руда бакра и у мањој мери руде сребра и злата. Шира околина лежишта бакра Мајданпек у геолошком (Слика 1) и морфолошком смислу представља део Карпато-Балканида (РЕТКОВИЋ, 1935; GRUBIĆ, 1974). На истражном терену су присутни прекамбријумски и старије палеозојски гнајсеви и шкриљци, местимично испробијани гранитима херцинске орогенезе. Дебели комплекс карбонатних седимената формиран је највећим делом током горње јуре (титон) (АНТОНИЈЕВИЋ, 1979). Источни делови терена су настали током дугог периода турон–палеоген, када је формиран тзв. Тимочки вулканогено-седиментни комплекс (ТВК) од андезита, пирокластита, туfoва и порфирита богатих рудом бакра који достиже дебљине и до 2000 m (JANKOVIĆ, 1990; KARAMATA et al., 1994; JELENKOVIĆ & KOŽELJ, 2002; BANJEŠEVIĆ, 2010).

Формирање бројних површинских и подземних карстних облика (Рајкова и Паскова пећина, Ваља Фундата) и карстне издани у оквиру титонских кречњака шире области Мајданпека резул-

тат је интензивног процеса карстификације (LAZAREVIĆ, 1976; STEVANOVIĆ, 1991). Карстна издан се прихрањује падавинама, али и понирућим површинским токовима који се формирају на водонепропусним палеозојским стенама и стенама ТВК. Значајнији извори и карстна врела (Калуђерица, Ваља Фундата, Башчао, Штамета, врела Рајкове и Паскове пећине) настала су на контакту титонских кречњака и слабопропусних палеозојских и вулканогено-седиментних стена.

У циљу креирања квалитетнијих подлога за приступне преговоре са Европском Унијом (ЕУ) у области животне средине, као и проширења мониторинг мреже подземних вода ради примене Оквирне директиве о водама ЕУ (WFD, 2000), реализован је пројекат „Оперативни мониторинг подземних вода Републике Србије“ који је подржало Министарство за заштиту животне средине Србије (STEVANOVIĆ et al., 2020). У склопу поменутог пројекта два карстна врела – Ваља Фундата и Калуђерица, у оквиру водног тела подземних вода „Крш–север“, била су укључена у тзв. оперативни мониторинг у циљу оцене утицаја рударских активности на квалитет подземних вода.

Утицај рударских активности на подземне воде настао је услед остварене хидрогеолошке везе између следеће карстне долине Ваља Фундата (FILIPović et al., 1975), која је одабрана као локација за формирање флотацијског одлагалишта/језера и истоимене пећине (Слика 2, 3), односно врела Калуђерица (Слика 5). Теренска мерења параметара квалитета, као и извршене хемијске анализе у акредитованој лабораторији Института за јавно здравље Крагујевац (Табела 1, Слика 4), потврдиле су да постоји значајан антропогени утицај на квалитет подземних вода у оквиру истраживане карстне издани. Концентрације нитрита, амонијака, сулфата, гвожђа, мангана и никла забележене су изнад максимално дозвољених концентрација (МДК) за воду за пиће (SL. GLASNIK RS, 1999, 2019). Знатно повећане вредности мутноће указују на продор висококолоидног флуида из флотације Ваља Фундата лоциране у карстној депресији следеће долине за коју је још 1974. констатовано да је главни узрочник еколошког инцидента који је довео до уништења флоре и фауне у водотоку

Велики Пек све до његовог ушћа у Дунав (STEVANOVIĆ & DRAGIŠIĆ, 1995). Процуривање и активна филтрација отпадних флуида флотације остварује се и данас преко пукотина, каверни и крупних пећинских канала Ваља Фундате. Резултати спроведених истраживања, такође, указују да је квалитет подземних вода лошији у периоду ниских вода, него што је то случај у периоду високих вода. Разлог је разблаживање подземних вода инфилтрираним водама од падавина и од топљења снега. Током спроведених истраживања подземна вода врела Ваља Фундата је у свим узорцима имала високе концентрације јона гвожђа и мангана, док је у узорку, који је узет у периоду ниских вода, концентрација гвожђа била шест пута, а мангана десет пута виша од МДК (Слика 4). Још неповољнија ситуација је забележена за подземне воде врела Калуђерица, у периоду ниских вода концентрација гвожђа је била чак 200 пута, а мангана 80 пута већа од МДК (Слика 4).

У неизмењеним природним условима подземна вода карстне издани је обично одличног квалитета (STEVANOVIĆ, 1995), међутим, у контакту са рудним телом долази до њене измене услед комплексних физичко-хемијских реакција измене јона, смањења рН вредности, повећања минерализације (DRAGIŠIĆ, 1992; DRAGIŠIĆ et al., 1994; NDORO & WITKA, 2007; SCHULTZE et al., 2011; АТАНАСКОВИЋ, 2018). У случају флотацијског језера рудника Мајданпек долази до оксидације сул-

фидних минерала, који погоршавају квалитет флуида која се инфилтрира у карстну издан и затим појављује на врелима Ваља Фундата и Калуђерица (Слика 6).

Висок ниво флотацијског језера у комбинацији са интензивним падавинама повећава ризик од продора загађења у карстну издан, што је забележено у претходним инцидентима из 1974. и 1996. године (STEVANOVIĆ & DRAGIŠIĆ, 1995; DRAGIŠIĆ et al. 1997). Иако у околини рудника не постоји много погодних локација за флотацијско језеро, својевремена одлука да се оно лоцира у слепу карстну долину, која је и даље хидрогеолошки активна, показала се као неоправдана и у данашње „еколошко“ време сигурно не би уопште била могућа. У садашњим условима ремедијација постојећег јаловишта Ваља Фундата, осим што би изискивала огромна финансијска средства, скоро је и технички неизводљива. Али би могло и требало да буде реализовано пројектовање и изградња мини система за третман вода контаминираних карстних извора. У циљу ублажавања утицаја рударских активности на подземне карстне воде треба применити и принцип Оквирне директиве о водама ЕУ која је транспонована и у нашу легислативу, али се не примењује доследно - „загађивач плаћа“.

*Manuscript received November 07, 2020*

*Revised manuscript accepted December 05, 2020*