

## Groundwater pollution with heavy metals in the Ibar alluvium near Raška (Serbia)

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**Abstract.** As a result of the operation of an ore flotation facility at Donja Rudnica near Raška, Serbia, during the period from 1972 to 2002, flotation tailings and wastewater of highly complex chemical compositions were deposited in the alluvial plain of the Ibar River. Due to the excellent groundwater flow characteristics of the alluvial formations underlying the tailings dump, the groundwater and soil over an extended area were continually polluted. High concentrations of heavy metals (Fe = 7.38 mg/L, Zn = 4.04 mg/L, Pb = 2.17 mg/L) in the soil and concentrations of sulfate as high as 3709 mg/L, and pH levels of 4.2 in the groundwater have been recorded at some locations. This paper draws attention to the potential risk this site poses for the conservation of biodiversity over the extended area.

**Key words:** flotation tailings dump, alluvium, groundwater pollution, Serbia.

**Апстракт.** Као резултат рада постројења за флотацију руде у Доњој Рудници код Рашке, у периоду од 1972. до 2002. године, депонована је у алувијоној равници реке Ибар, флотацијска јаловина и отпадне флотацијске воде веома сложеног хемијског састава. Услед добрих филтрационих својстава алувијалних творевина које се налазе у подини јаловишта, врши се стално загађење подземних вода и земљишта на ширем подручју. У земљишту су одређене високе концентрације тешких метала (Fe = 7.38 mg/L, Zn = 4.04 mg/L, Pb = 2.17 mg/L) а у подземним водама и високе концентрације сулфата (достигу 3709 mg/L), као и рН вредности у неким водама од 4,2. Овим радом се указује на потенцијалне ризике које овај простор може имати на очување биодиверзитета шире околине.

**Кључне речи:** загађење подземних вода, алувијон, флотацијско јаловиште, Србија.

### Introduction

The Ibar is one of the most important rivers in southwest Serbia. In geological terms, a portion of its catchment area, from Donja Rudnica (or from the administrative border between Serbia and Kosovo) to the downstream location of Biljanovac (along the road to Kraljevo), belongs to the so-called “Raška” Ore-bearing Area.

The ore-bearing capacity of this area was known back in the Middle Ages but intensive mining took place only in the latter half of the past century. In 1972, a magnetite separation and copper flotation plant was built in Donja Rudnica. This plant processed a total of 2858100 tons of ore until the year 1986.

Following the opening of new lead and zinc mines at Sastavci and Kiževak on the western slopes of Mt.

Kopaonik, the Donja Rudnica plant began floating these ores as well in 1986. Until the year 2002, when the flotation plant was decommissioned, a total of 2064956 tons of Pb/Zn ores had been processed.

During the period of operation of the flotation plant from 1972 to 1986, flotation tailings were deposited at several sites along the Ibar River. The most significant flotation tailings dump was formed in the alluvial plain of the Ibar, at Veliko Polje near Donja Rudnica.

The development of a new flotation tailings dump in the Kukanjica Creek upstream from the Donja Rudnica plant began in mid-1991. By the year 2002, some one million tons of tailings had been deposited at this site (from 1991 to 1996, a portion of the tailings were disposed of at the Veliko Polje site).

In addition to flotation tailings, flotation wastewater was also disposed of at these landfills. The che-

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mical composition of the wastewater was highly complex, given that the flotation reagents NaCN, ZnSO<sub>4</sub>, CuSO<sub>4</sub>, FeSO<sub>4</sub>, NaSO<sub>3</sub>, etc. were used in the ore flotation process. For example, the plant used 170 tons of sodium cyanide (NaCN) from 1986 to 2001. The soil and groundwater over an extended area were polluted through infiltration of this wastewater from the flotation tailings dump. Additionally, flotation wastewater was occasionally discharged directly into the Ibar River via tailings dump collectors.

Given that the Village of Donja Rudnica does not have a public water supply system, its inhabitants withdraw groundwater from shallow dug wells for their daily needs, and that there is active farming at Veliko Polje immediately adjacent to the flotation tailings dump, pilot tests of environmental substrates were conducted from 2002 to 2004. The objective of this paper is to present the results of the tests performed in the Veliko Polje Plain, in view of the fact that they showed that there was considerable environmental pollution, with the Ibar River potentially spreading the pollution over a much greater area. The exposure of the local population to health risks is highlighted.

## General geological and hydrogeological characteristics of the extended area of Donja Rudnica

The extended area of Donja Rudnica is made up of Tertiary volcanics that are found over a large area, from Ušće in the north to Leposavić in the south. The volcanic rocks are underlain by Paleozoic shales (the

oldest rocks), ophiolitic rocks (peridotites and a diabase–chert formation), Kopaonik granodiorites and other rocks.

Tertiary volcanism began in the Lower Miocene, lasted through the Neogene (albeit with certain interruptions) and began to cease at the end of the Pliocene. Its nature was distinctly explosive and it underwent several stages and pulsations (UROŠEVIĆ *et al.* 1973).

The volcanic rocks are made up of dacite–andesites ( $\alpha\alpha$ ), quartzlatite, basaltoids (to a lesser extent), as well as volcanic pyroclastics ( $\Theta\alpha\alpha$ ) represented by volcanic breccias, tuffs and agglomerates (Fig. 1). The thickness of the volcanic rocks varies but is about 300 m on average, depending on the paleorelief morphology, the nature of the volcanic activity and the proximity of supply channels.

The youngest formations are Quaternary and are represented by alluvials (al), which are found along the course of the Ibar. They are made up of sands, gravels and clays the total thickness of which occasionally exceeds 10 m, as is the case in the alluvial plain at Veliko Polje near Donja Rudnica (Fig. 1).

From a structural perspective, the terrain is heavily tectonically faulted and deformed. There are many faults of different sizes and orientations. Aerial photographs east of Raška also show circular (ring-like) structures. In the andesites, the faults feature a better continuity and longer dip elements than those of the poorly consolidated pyroclastites.

In hydrogeological terms, the volcanic rocks are characterized by fracture veins and a fractured rock aquifer formed within them (Fig. 1). Given that the fractures are heavily squeezed and packed with secondary fillings, the permeability of the volcanic rocks is poor and they hold relatively modest amounts of groundwater.

A confined aquifer was formed in the alluvial formations, due to their intergranular porosity. The largest extent of these formations is found in the alluvial plain at Veliko Polje. The groundwater flow characteristics of the alluvial formations is good, with permeability coefficients of  $k = 2.5 \times 10^{-3}$  m/s (KB-1), Fig. 2, and  $k = 8.1 \times 10^{-4}$  m/s (KB-8), MILADINOVIĆ (2005).

The fluctuations of the groundwater level in the alluvial formation were continuously monitored in 2004, and the mean of these measurements are shown in Fig. 3. Evident jumps of groundwater levels were observed in the spring after snow melt and heavy rains. The difference

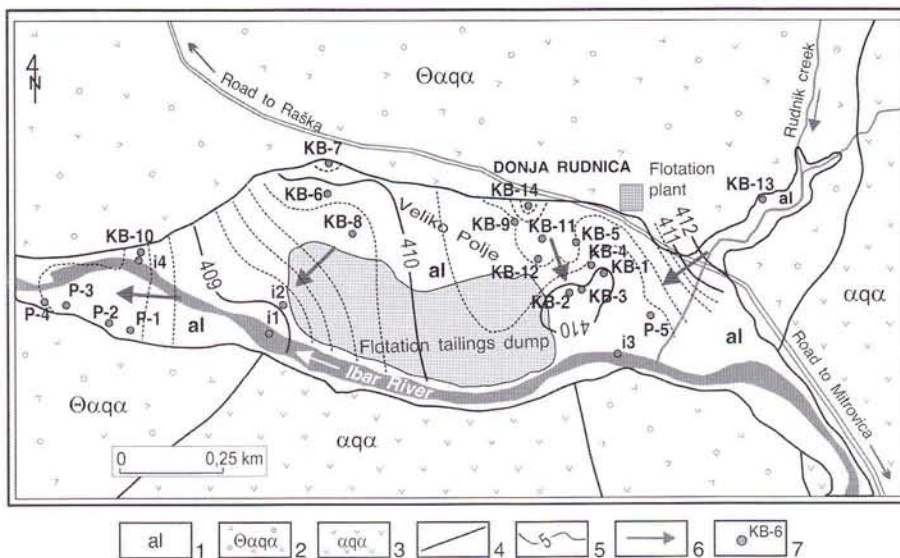


Fig. 1. Hydrogeological map of the extended area of Veliko Polje near Donja Rudnica. 1, Alluvial sands, gravels and clays (intergranular aquifer); 2, dacite–andesite pyroclastites (fractured rock aquifer); 3, dacite–andesites (fractured rock aquifer); 4, geological boundary; 5, water-table contour lines of confined aquifer (as of 20 December 2004); 6, direction of groundwater flow; 7, dug well.

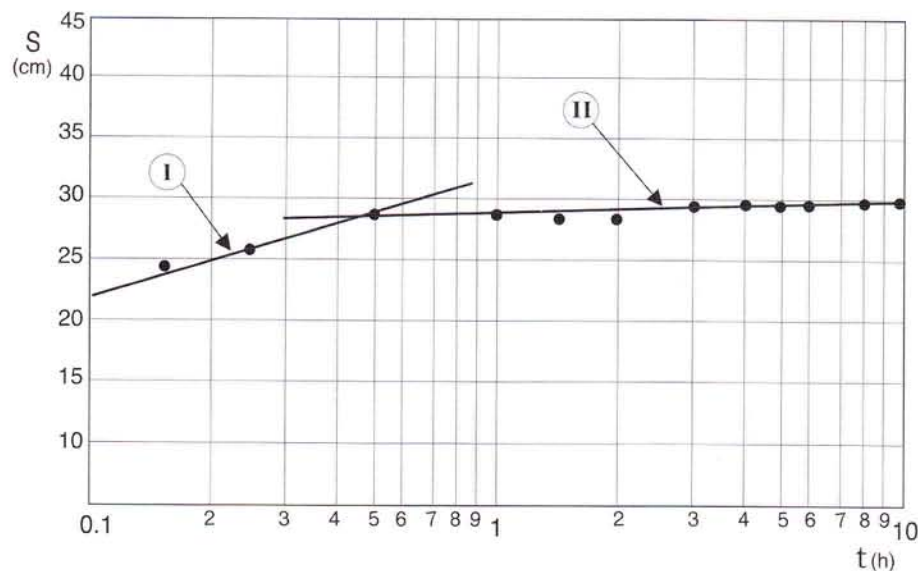


Fig. 2. Dynamic groundwater level of the confined aquifer in the Ibar alluvium during a pumping test at the dug well KB-1 in Veliko Polje.

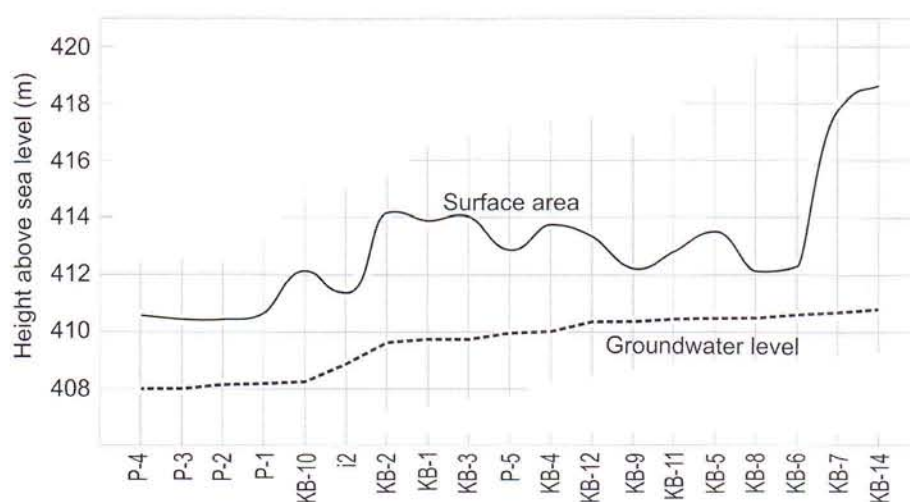


Fig. 3. Diagram of the groundwater levels in the alluvial formations near Donja Rudnica (the mean fluctuation levels for 2004).

between the minimum and maximum levels varied according to location; the lowest was registered at the locations of P-1, P-2, P-3 and P-4 (1.58 to 1.72 m) and the largest at KB-7 (3.46 m) and KB-14 (3.95 m). The aquifer is in good hydraulic contact with the Ibar River, which flows along the southern edge of the Veliko Polje alluvial plain (Fig. 1).

The direction of groundwater flow in the alluvial formations of Veliko Polje are directly dependent on the stages of the Ibar River, but it is generally from the northern edges to the central portions of the alluvial plain, or to the most downstream profiles of the Ibar at Veliko Polje (MILADINOVIĆ 2005).

At low water stages of the Ibar, the confined aquifer is discharged directly into the River and is partly drained by groundwater abstraction from the wells

dug by the local population. The confined aquifer is recharged by precipitation and from surface streams, but only at high water stages of the Rudnik Creek and the Ibar River relative to the groundwater level.

## Methods

In order to determine the impact of the flotation tailing in Veliko Polje on the surrounding soil and groundwater, laboratory tests of the substrate environment were conducted.

Sampling of the loose soil was performed by taking samples that consisted of three individual samples with a surface area of 2 m<sup>2</sup> at a depth of 10 cm. The collected samples were air-dried and milled to a particle size < 2 mm.

The soil samples were prepared for metals analysis by measuring 1 g a dry sample and digestion by the addition of portions of concentrated HNO<sub>3</sub> and HCl and 30% H<sub>2</sub>O<sub>2</sub>. The determinations were performed by flame atomic absorption spectroscopy (AAS) using a Varian Spectra AA200 instrument, and hydride AAS using a Varian Spectra AA20+ instrument, according to the manufacturer's instructions (Institute of Public Health of Belgrade).

Groundwater was sampled from privately dug wells, the levels of which are shown in Fig. 3. The samples were taken at the end of autumn when the level of the Ibar River was lower than the groundwater level, shown in Fig. 1

Samples from the River were taken from the middle part of the flow at a depth of 0.5 m and samples were taken from the same depth from the excavation site by the flotation tailings. All water samples were acidified with HNO<sub>3</sub> to pH < 2.

Water samples with turbidity < 1 NTU were analyzed directly. The other samples were prepared by the addition of HNO<sub>3</sub> and HCl, reduction of the volume and refluxing, and subsequent dilution to the start volume. The determinations were realized by AAS.

A standard QA/QC protocol was adopted throughout this research. For example, in the analysis of each

metal, the slope of the calibration curve was verified by analyzing every fourth concentration of the calibration standards used for the construction of the curve after the analysis of every 20th sample and by analyzing QC standards with concentrations in the middle of the calibrated range immediately after completion of the analysis of each batch of samples. In addition, duplicate samples of both field and laboratory blank samples were included in each analytical batch.

## Results

### Environmental substrates

Laboratory tests of environmental substrates in the Donja Rudnica area revealed considerable pollution of the alluvial soil and groundwater (DALMACIJA 2000).

As a result of particles from the tailings dump being carried by winds into the neighboring areas, as well as due to the infiltration of flotation tailings leachate into the permeable alluvial formations (Fig. 4), heavy metals were detected in the soils at Veliko Polje in concentrations which were several times higher than the regulation standards.

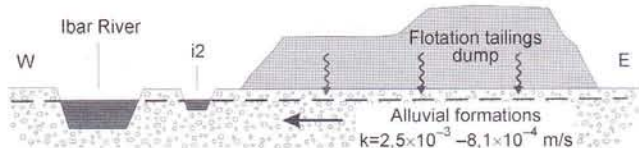


Fig. 4. Schematic view of the impact of flotation tailings on groundwater pollution in the alluvial formations.

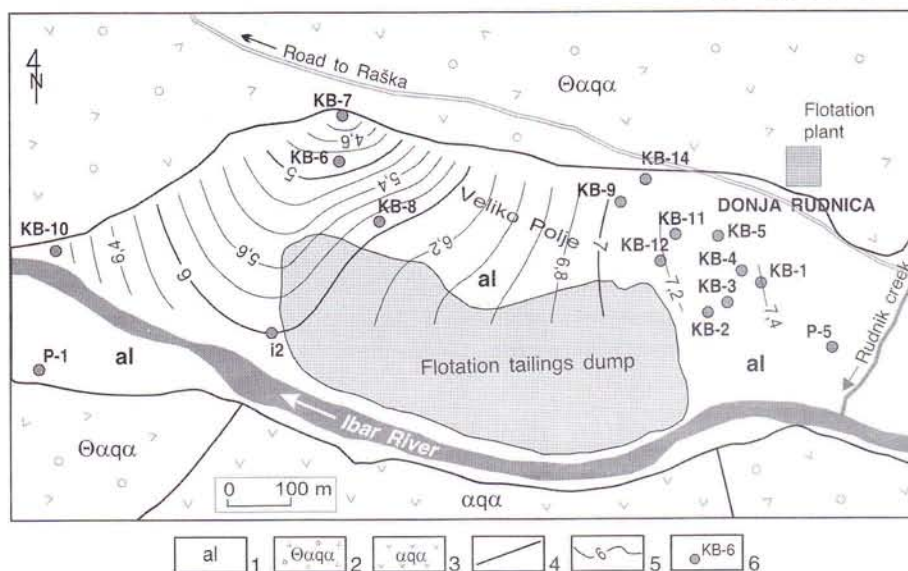


Fig. 5. Contour chart of the pH values in the groundwater in the Ibar alluvium near Donja Rudnica. 1, Alluvial formations; 2, dacite-andesite pyroclastites; 3, dacite-andesites; 4, geological boundary; 5, pH values contour lines; 6, dug well.

The results of the analysis of the groundwater from the private wells were compared with maximum allowed concentration (*MAC*) values defined in the Regulations on the Hygiene of Drinking Water (Official Gazette of the FRY 42/98). The obtained values for the surface water were compared with the Ordinance on Hazardous Substances in Water / Official Gazette SRS 31/82, and the results for the soil samples were compared with the *MAC* values given in Regulations on Permitted Amounts of Hazardous and Harmful Substances in Soil and Water for Irrigation and Methods of their Testing (Official Gazette of RS 23/94).

Significant deviation from the allowed values were found for the content of heavy metal in the soils west of the tailings (Fig. 1 and Fig. 4), primarily lead ( $Pb = 335.5 \text{ mg/kg}$ , *MAC* – 100 mg/kg), arsenic ( $As = 44.3 \text{ mg/kg}$ , *MAC* – 25 mg/kg), chromium ( $Cr = 104.7 \text{ mg/kg}$ , *MAC* – 100 mg/kg) and nickel ( $Ni = 79.7 \text{ mg/kg}$ , *MAC* – 50 mg/kg). The zinc concentrations were similar to the reference value ( $Zn = 249.7 \text{ mg/kg}$ , *MAC* – 300 mg/kg).

This research devoted special attention to groundwater pollution in the alluvial formations of Veliko Polje, or the so-called "first" aquifer. Laboratory tests of the groundwater were conducted using samples collected from six dug wells (KB-1, KB-6, KB-7, KB-8, KB-10 and KB-11), as well as from a gravel excavation site located on the western edge of the tailings dump (i2), Fig. 1. These tests revealed elevated concentrations of both major ions and micro-components in the groundwater.

The concentration of sulfate ( $SO_4$ ) in four samples exceeded the drinking water standard and ranged from 579.6 mg/l to as much as 3709 mg/l (*MAC* – 250 mg/L, REGULATION ON HYGIENIC STANDARDS OF WATER 1998).

The maximum allowable concentration (*MAC*) values of heavy metals in the tested groundwater of samples from the dug wells were exceeded in the central and northern parts of Veliko Polje: lead ( $Pb = 2.17 \text{ mg/L}$ , *MAC* – 0.010 mg/L), cadmium ( $Cd = 0.1 \text{ mg/L}$ , *MAC* – 0.003 mg/L), zinc ( $Zn = 4.04 \text{ mg/L}$ , *MAC* – 3.0 mg/L), aluminum ( $Al = 2.5 \text{ mg/L}$ , *MAC* – 0.2 mg/L), total iron ( $Fe = 7.38 \text{ mg/L}$ , *MAC* – 0.3 mg/L) and manganese ( $Mn = 2.04 \text{ mg/L}$ , *MAC* – 0.05 mg/L). The lowest pH values were found in wells KB-7 (4.2), KB-6 (4.9) and KB-8 (5.9), Fig. 5.

The most important groundwater pollution was recorded

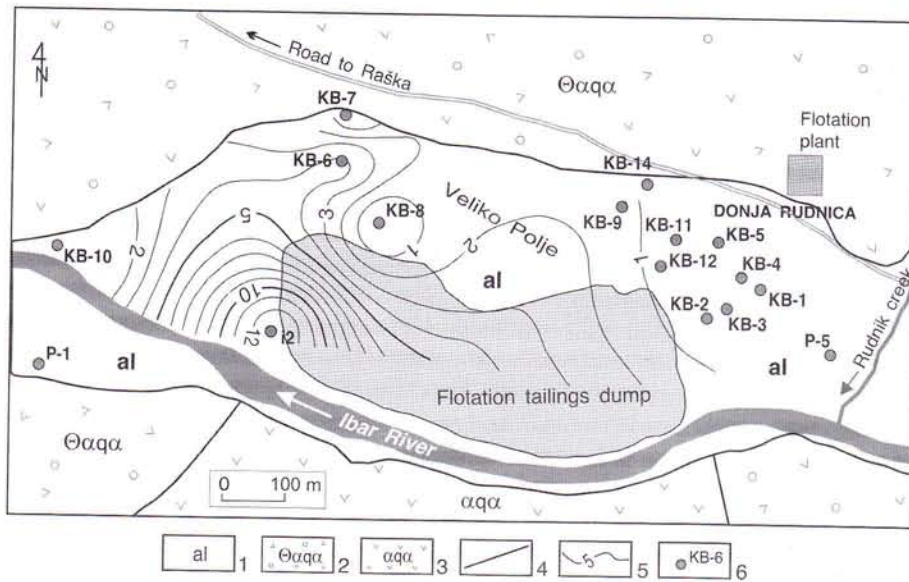


Fig. 6. Contour chart of the zinc (Zn) concentrations in the groundwater of the Ibar alluvium near Donja Rudnica. 1, Alluvial formations; 2, dacite-andesite pyroclastites; 3, dacite-andesites; 4, geological boundary; 5, zinc concentration (mg/L) contour lines; 6, dug well.

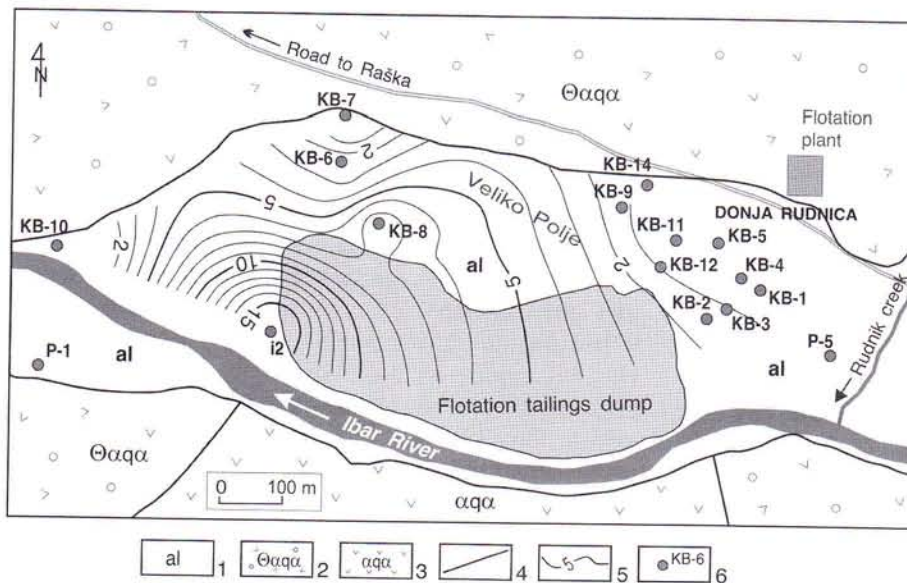


Fig. 7. Contour chart of the iron (Fe) concentrations in the groundwater in the Ibar alluvium near Donja Rudnica. 1, Alluvial formations; 2, dacite-andesite pyroclastites; 3, dacite-andesites; 4, geological boundary; 5, total iron concentration (mg/L) contour lines; 6, dug well.

in the south-western part of Veliko Polje, immediately adjacent to the western perimeter of the tailings dump (i2), primarily as a result of the direction of groundwater flow (or the prevailing direction of the plume) from the tailings dump source at Veliko Polje to the downstream profiles of the Ibar in the western part of Veliko Polje. Samples of this groundwater had the maximum concentrations of zinc  $Zn = 12.7$  mg/L (Fig. 6), nickel  $Ni = 0.6$  mg/L, manganese  $Mn = 10.6$  mg/L and

iron  $Fe = 16.0$  mg/L (Fig. 7). The total dissolved solids (TDS) value was 8010 mg/L and the pH level was 6.0 (Fig. 5).

## Discussion

Before the construction of the ore separation plant in 1972, the residents of Donja Rudnica used only groundwater drawn from wells dug for their daily needs. Even after 30 years of heavy environmental pollution in this area, the inhabitants of Donja Rudnica customarily continue to use groundwater for their household needs and, in some cases, to even drink this water.

The use of groundwater from the wells dug in Donja Rudnica, based on the evidenced by the determined concentrations and their deviations from standards, constitutes a major health risk if used not only as drinking water, but also other household needs and water for domestic animals, given that over a protracted period of time, some of the inorganic pollutants are likely to enter the food chain (WHO 2008).

A sulfate ion ( $SO_4$ ) concentration higher than the MAC value for drinking water results in a tart taste and can also have a laxative effect on sensitive individuals if the sulfate concentrations exceed 500 mg/L.

Manganese (Mn) concentrations in excess of the MAC value alter the taste of water, leave stains and deposits, and foster the growth of manganese bacteria. Prolonged use

of drinking water with high manganese concentrations leads to poisoning, the symptoms of which are related to the central nervous system, where manganese psychosis is typical but not lethal.

The use of water from well KB-7, featuring a high lead (Pb) concentration (2.17 mg/L) would pose a considerable health risk, particularly for children who absorb 50 % of lead ingested with water, compared to adults whose absorption rate is 10–15 %. Lead has an

adverse effect on nearly all body systems, but in accumulates in the central nervous system and, in children, affects intelligence, growth and development.

## Conclusion

The environment of the Village of Donja Rudnica near Raška has been considerably polluted by an ore processing industry. The local population is exposed to health risks, given that environmental substrates (soil and groundwater) were found to be polluted.

Measures should be undertaken without delay to seek out alternative sources of healthy water supply from neighboring areas for Donja Rudnica, as well as to remediate the soils of Donja Rudnica, which were found to be polluted by a tailings dump, in order that environmentally acceptable conditions be restored for life in this area.

## Acknowledgments

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## Резиме

### Загађење подземних вода тешким металима у алувијону Ибра, близу Рашке (Србија)

До изградње постројења за сепарацију, мештани Доње Руднице, Рашка, користили су искључиво подземне воде из својих копаних бунара за основне животне потребе. После 30 година интензивног загађења животне средине на овом простору, становништво и даље користи ове воде за потребе својих домаћинстава, а неки и за пиће. Коришћење подземних вода из копаних бунара, представља велики ризик по здравље људи, не само ако се користе за пиће, већ и за друге потребе. Ово може довести до уласка неких загађујућих супстанци неорганског порекла у ланац исхране. Концентрација сулфатних јона која прелази максимално дозвољену вредност утиче на горак укус, а у већим концентрацијама од 500 mg/l, могу деловати и лексативно. Узорци подземних вода имају максималне концентрације цинка од 12,7 mg/l, никла од 0,6 mg/l, мангана од 10,6 mg/l и гвожђа од чак 16 mg/l. Укупно растворене материје су чак 8 g/l, а вредност рН индекса је 6. Коришћење воде из бунара KB-7, која садржи олово у концентрацији од 2,17 mg/l, представља велики ризик по здравље, нарочито за децу која апсорбују 50% олова из воде, у поређењу са одраслима који апсорбују само 10–15% олова из воде за пиће. Овај метал има негативно дејство на све системе у људском организму. Водоснабдевање становника Доње Руднице, захтева неодложне мере за изналажење алтернативних изворишта из околних подручја, како би се обезбедиле здравствено исправне воде за пиће. Такође, неопходно је одредити и ремедијационе поступке за довођење животне средине у предходно стање квалитета, које је угрожено флотацијским јаловиштем.