



Geochemical characteristics and estimation of groundwater pollution in catchment areas of Timok and Pek Rivers, Eastern Serbia: Determination of early-stage groundwater pollution in mining areas

Dragana Adamovic^{a,b,*}, Daizo Ishiyama^a, Hiroshi Kawaraya^a, Yasumasa Ogawa^a, Zoran Stevanovic^b

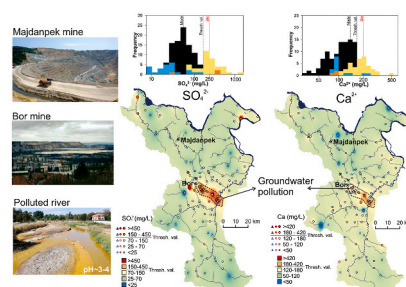
^a Graduate School of International Resource Sciences, Akita University, Tegatagakuen-machi 1-1, Akita Pref., 010-8502, Japan

^b Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, Bor, 19210, Serbia

HIGHLIGHTS

- Groundwater threshold values are derived for the first time in Eastern Serbia.
- Early-stage groundwater pollution by mining activities was defined.
- SO_4^{2-} and Ca^{2+} are good indicators for monitoring early-stage groundwater pollution.
- The evaluation method is widely applicable to the environmental assessment of groundwater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Bor mine
Copper
Early-stage groundwater pollution
Geochemical maps
Sulfate
Threshold value

ABSTRACT

Long-term mining activities in the Bor and Majdanpek porphyry copper mining areas located in Eastern Serbia have led to serious environmental problems, the most notable being surface water pollution by heavy metals downstream of the mining sites. However, the geochemical characteristics and environmental impact on groundwater in the mining areas are not clear. This study clarified the geochemistry of groundwater in catchment areas of Timok and Pek Rivers including the Bor and Majdanpek mining areas. In this study, it was also examined whether the combination of geochemical maps and threshold values is appropriate for determination of early-stage groundwater pollution associated with mining activities.

Groundwater in the study area was characterized by pH values from 6.4 to 8.8 and a high concentration of HCO_3^- . Groundwater outside the Bor mining area was of good quality and had a low content of trace elements. High concentrations of Ca^{2+} and SO_4^{2-} in groundwater were distributed along polluted rivers with mining wastes such as tailings downstream of the Bor mining area, especially in the area along Bela River. The actual concentrations of Ca^{2+} and SO_4^{2-} in those groundwater samples exceeded the threshold values that were estimated in this study as the highest natural background concentrations. The anomalous concentrations of Ca^{2+} and SO_4^{2-} in groundwater along the polluted rivers are therefore thought to have been caused by mining activities of the Bor mine. Calcium and sulfate anomalies that were estimated by the combination of geochemical maps and threshold values are good indicators for monitoring of early-stage groundwater pollution caused by mining

* Corresponding author. Graduate School of International Resource Sciences, Akita University, Tegatagakuen-machi 1-1, Akita Pref., 010-8502, Japan.

E-mail address: dragana.adamovic@irmbor.co.rs (D. Adamovic).

<https://doi.org/10.1016/j.gsd.2021.100719>

Received 9 October 2021; Received in revised form 18 December 2021; Accepted 22 December 2021

Available online 30 December 2021

2352-801X/© 2021 Elsevier B.V. All rights reserved.

activities in the study area. The procedure of evaluation for early-stage groundwater pollution used in this study is appropriate and widely applicable for the environmental assessment of groundwater having neutral pH in many mining areas.

1. Introduction

Pollution of river water, in many mining areas, can be identified by naked eye observation and is relatively easy to identify based on water coloration (Abramov et al., 2020; Adamovic et al., 2021a). Groundwater, on the other hand, does not often appear directly on the surface of the ground, and pollution of groundwater may not be detected until after the groundwater contamination has become serious, especially when groundwater has good buffering capacity. Groundwater generally has a long residence time. Once the groundwater is contaminated, it is difficult to restore the environment. Therefore, it is necessary to determine contamination at an early stage of groundwater pollution.

In Serbia, over 70% of the population uses groundwater for drinking purposes (Devic et al., 2014; Polomcic et al., 2018; Pesic et al., 2020). The territory of Eastern Serbia is one of the most resourceful areas for groundwater based on the density of occurrences of groundwater. Much of the groundwater resources in Eastern Serbia occurs in karst aquifers (Kortatsi, 2007; Stevanovic et al., 2007; Petrovic et al., 2010). Groundwater in karst aquifers has the potential to contain good quality drinking water (Hartmann et al., 2014; Pesic et al., 2020). However, both industrial (mainly mining) and agricultural activities which can affect groundwater quality are present in the study area.

Areas with mining activities in the study area are the Bor mining area and Majdanpek mining area. In both mining areas, porphyry copper ores are mined. The Bor mining area and Majdanpek mining area are located in the Serbian part of the Carpathian-Balkan belt (Fig. 1). Mining development in the Bor mining area started in 1903. In 1961, operations started in the Majdanpek mine. Mining activity has been the main economic activity in Eastern Serbia. The mining and ore processing activities have generated large amounts of tailings and overburdens

(Stevanovic et al., 2011; Markovic, 2012). The smoke from the smelter and dust from the overburden pollute the air, soil and watercourses in its vicinity. In previous studies, air pollution in the vicinity of Bor City, where copper is produced, was characterized as an environmental hot-spot in Serbia based on concentrations of metals, As and SO₂ (Dimitrijevic et al., 2009; Kovacevic et al., 2010; Serbula et al., 2017, 2021). The size of the area with soil pollution caused by pollutants transported by air was estimated to be about 15 km in the north-west directions and 5 km in the east and south-east direction from Bor City. The soil in this region has been shown to contain high concentrations of As (Pejovic et al., 2017). Soil contamination by surface water was also observed based on elevated concentrations of heavy metals in plants (Filimon et al., 2021; Petrovic et al., 2021). However, there has been no study carried out to determine the effects of soil pollutants on groundwater. Oxidation of sulfide minerals such as pyrite in tailings and overburdens results in the production of acidic, metal-rich wastewater that contaminates local surface water and groundwater (Ozunu et al., 2009; Marin et al., 2010). Many studies have been conducted on the chemical characterization of river water in the Bor mining area, showing strong pollution of river water by heavy metals (Milijasevic et al., 2011; Ishiyama et al., 2012, 2016; Serbula et al., 2016; Milijasevic Joksिमovic et al., 2018). Mobility and natural attenuation of metals and arsenic were also examined (Dordievski et al., 2018). Adamovic et al. (2021a) showed that the lengths of polluted rivers downstream of the Bor and Majdanpek mining areas are about 100 km and that the pollution reaches the Danube River based on the total concentrations of heavy metals and sulfates. Based on the current conditions of pollution of air, soil and surface water in the Bor and Majdanpek mining areas and the risk of groundwater pollution caused by historical mining activities in Serbia (Atanackovic et al., 2016), there is a possibility that groundwater is also

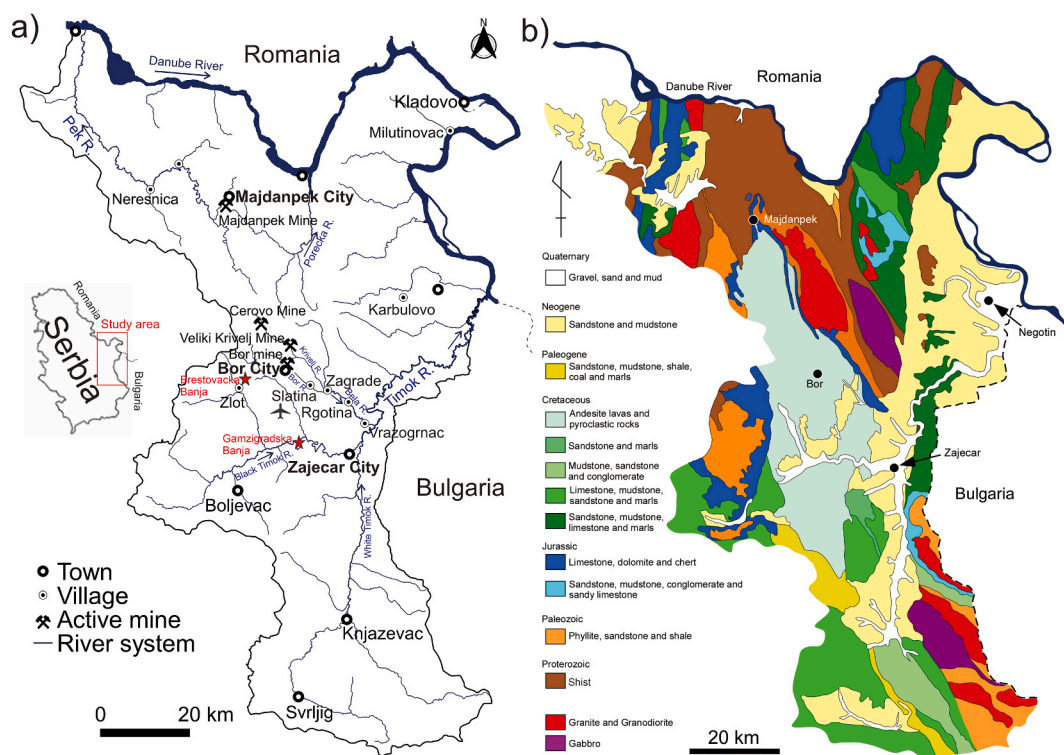


Fig. 1. a) Map showing the distribution of towns, villages, active mines and river system b) geological map of the study area (IGT, 1970).

affected by the mining activities, because shallow groundwater is linked to the surface where severe pollution occurred.

There were some studies in which assessment of the environmental impact of groundwater contamination was carried out in base metal and precious metal mining areas in the world based on heavy metal and arsenic concentrations (Santos et al., 2002; Herbert Jr, 2006; Liang-qi et al., 2010; Gong et al., 2014; Esteller et al., 2015; Mehrabi et al., 2015; Ekemen Keskin and Ozler, 2020; Popugaeva et al., 2020). Contamination is severe in groundwater that has acidic pH and high concentrations of heavy metals and arsenic. To prevent serious pollution of groundwater, detection of early-stage groundwater pollution is important. Galhardi and Bonatto (2016) showed that SO_4^{2-} content in groundwater in coal mining areas is important for groundwater monitoring. However, it is not clear if this applies to other mining areas.

There had been no comprehensive study on the geochemistry of groundwater in the study area. Determination of the pristine composition of groundwater is a key issue for assessing any modification that may be caused by anthropogenic activities and is, therefore, an important issue for environmental evaluation. The aims of this study were to determine the geochemical characteristics of groundwater in the study area, to determine whether groundwater pollution is present or not and to find appropriate chemical species for detection of early-stage groundwater pollution on the basis of 1) creation of geochemical maps to know if there are vulnerable areas for groundwater contamination and 2) estimation of threshold values for discrimination of background and anomalous concentrations of elements in groundwater. In this study, it was also examined whether the procedure for environmental evaluation of groundwater based on the combination of geochemical maps and threshold values is appropriate for estimation of early-stage groundwater pollution.

2. Study area

2.1. Outline of the study area

The study area is located in Eastern Serbia, Balkan Peninsula, south-eastern Europe. The area of Eastern Serbia borders Romania on the north and north-east side and Bulgaria on the east side (Fig. 1). The extent of the study area is about 8320 km². Geologically, Eastern Serbia belongs to the Carpathian-Balkan belt. Mining areas located in the Carpathian-Balkan belt are one of the world's oldest mining areas and played a major role in the history of European civilization (Lips et al., 2004; Gallhofer et al., 2015). The study area is characterized by mountain terrains in the central, western and southern parts and by plain terrains in the eastern and northwestern parts. Agriculture fields are present in plain areas and river valleys. The study area includes watersheds of Timok River, which is located in the southern part of the study area, and Pek River and Porecka River, which are located in the northern part of the study area. In the upstream of Timok River, there are Bor River, Krivelj River and Bela River receiving wastewater from the mines located in the Bor mining area (Fig. 1). While in the upstream of Pek River there is Small Pek River which receives wastewater from the Majdanpek mine (Fig. 1). Large amounts of tailings are present along polluted rivers in the Bor mining area. After the collapse of a tailings dam in the 1950s, a large amount of tailings was transported downstream in the Bor mining area (Paunovic, 2010; Bogdanovic et al., 2014). Due to this accident, the level of the river bed of Bela River may be higher than the level of groundwater in the lower reach of Bela River. Failure of the flotation tailings dam may cause serious environmental problems for groundwater downstream of the Bor mining area. On the other hand, tailings are not present along Small Pek River and Pek River. All of the rivers in the study area belong to the drainage system of the transboundary Danube River (Fig. 1).

2.2. Geology

Geology of the study area consists of Proterozoic schists, Paleozoic metamorphic rocks and sedimentary rocks, Jurassic sedimentary rocks, Cretaceous sedimentary rocks and volcanic rocks, Paleogene sedimentary rocks, Neogene sedimentary rocks, Quaternary sediments, and Paleozoic granitic rocks and gabbro (Fig. 1b) (IGT, 1970). Limestone and dolomite cover about 25% of the study area (Dragicevic et al., 2011). The Bor and Majdanpek mining areas, which are porphyry copper deposits, are located in an area composed of Cretaceous volcanic rocks that is called the Timok Magmatic Complex (Jelenkovic et al., 2016; Banjesevic et al., 2019). The Timok Magmatic Complex is a part of the Carpathian-Balkan belt and is distributed in the central part of the study area. The Timok Magmatic Complex is 60 km long and 20 km wide. Volcanic rocks in Timok Magmatic Complex were formed within three stages during the Upper Cretaceous (Jelenkovic et al., 2016). The volcanic rocks in the complex are composed of andesitic lava and andesitic pyroclastic rocks, while dacite occurs sporadically (Fig. 1b). The radiometric age of the magmatic complex is from 90 to 80 Ma (Von Quadt et al., 2002; Clark and Ullrich, 2004). Neogene sedimentary rocks are found in plain terrains of the study area. They are widely distributed in the eastern part and to a lesser extent in the north-western part of the study area. The Neogene sedimentary rocks consist of sandstone and mudstone. Quaternary sediments, which consist of gravel, sand and mud, are distributed along the river system in the study area.

2.3. Hydrogeological and lithological features

In the study area, there are two different hydrogeological regions, the Dacian Basin and Carpatho-Balkanides of Serbia (Fig. 2) (Petrovic et al., 2010; Polomcic et al., 2011; Krunic and Sorajic, 2013). The lithology of aquifers is also shown in Fig. 2. The types of aquifers in the study area are classified as follows: karst aquifer, fractured aquifer, sedimentary aquifer, low productive aquifer and alluvial aquifer (Polomcic et al., 2011). The hydrogeological region of Carpatho-Balkanides of Serbia is characterized by a large distribution of Upper Jurassic and Lower Cretaceous carbonate rocks. There is a large number of karst aquifers as significant groundwater reserves within these carbonate rocks (Fig. 2) (Stevanovic et al., 2007; Petrovic et al., 2010; Polomcic et al., 2011; Zivanovic et al., 2016; Vasic et al., 2020). There are about 1360 springs in the hydrogeological region of Carpatho-Balkanides of Serbia, which represent the highest frequency of karst groundwater bodies in the Balkan Peninsula (Djurovic and Zivkovic, 2013). There is almost no pollution of groundwater in karst aquifers in the area consisting of carbonate rocks due to the low population density and lack of anthropogenic causes such as industry and agriculture. Fractured aquifers are present in volcanic rocks and basement rocks in the hydrogeological region of Carpatho-Balkanides (Fig. 2). These aquifers are also a significant source of groundwater (Dokmanovic et al., 2007, 2012). In addition, alluvial aquifers are present to a lesser extent in the Dacian Basin and Carpatho-Balkanides of Serbia (Fig. 2). The alluvial aquifers have the possibility of being vulnerable to anthropogenic activities due to the higher population density.

Groundwater samples for this study were collected from wells in a shallow aquifer, cold springs and hot springs. The average depth of the water table was 4 m in this study (Fig. 2b). The alluvial aquifer in the Dacian Basin along Danube River in the northeastern part of the study area is deeper with a level of the water table of more than 10 m (Fig. 2b). An exception was the sample collected in Zajecar City from a deep borehole with a depth of 382 m. Groundwater samples from the Bor mining area were mainly collected from fractured aquifers and alluvial aquifers, while groundwater samples in the Majdanpek mining area were collected from karst aquifers and low productive aquifers.

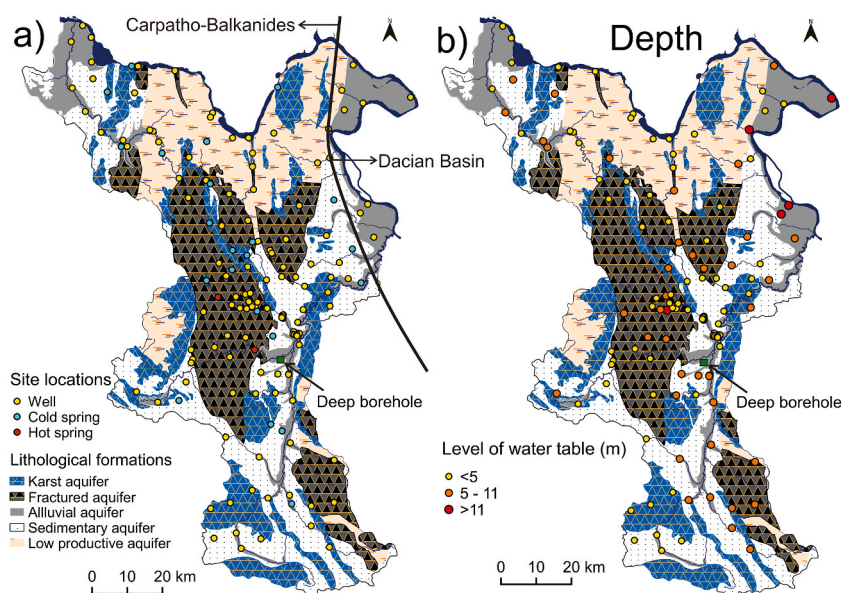


Fig. 2. Maps showing types of aquifers at sampling sites according to the hydrogeochemical map of Polomcic et al. (2011). a) Map showing hydrogeological regions of Dacian Basin and Carpatho-Balkanides in addition to well, cold spring, hot spring and borehole sampling sites; b) Map showing the depths of water tables of wells where samples were taken.

3. Materials and methods

A field survey was carried out for field observation and sample collection from August 6 to September 20 in 2019. The sampling sites are shown in Fig. 2. The total number of groundwater samples collected in the study area was 172. The kinds of groundwater samples that were collected are shown in Table 1. Samples of groundwater were collected all around the study area with a distribution of two to three samples per 10 km². A larger number of groundwater samples were collected along polluted rivers by mining activities having acidic pH and high concentrations of heavy metals in settlements Slatina, Zagrade, Rgotina and Vrazogrnac. These rivers belong to the catchment area of Timok River (Fig. 1a). Eighteen, two, nine and ten groundwater samples were collected in Slatina Village (fractured aquifer), Zagrade settlement (fractured aquifer), Rgotina Village (alluvial aquifer) and Vrazogrnac Village (alluvial aquifer), respectively.

The coordinates of sampling sites were determined using GPS. Groundwater samples from wells were collected using a sampling bailer, while spring water samples were collected directly from the spring. The level of the water table was measured using a water level measure (YAMAYO Million) at each well. The color and odor were checked and in situ measurements of pH, Eh, water temperature and bicarbonate ion concentration were carried out immediately after sampling. Values of pH and oxidation-reduction potential of water (ORP) were determined by using a hand-held ion/pH meter (TOA DKK, Model IM-32P). The ORP values were converted to Eh values following the manual given by the instrument. The temperature of water samples was measured using a thermometer and confirmed by a hand-held ion/pH meter. Bicarbonate ion concentrations were determined by using a water test kit based on the neutralization titration method (Kyoritsu Chemical-Check Lab.,

Corp.). At each sampling site, two samples were collected for measurements of major cations, major anions and trace elements. All samples were filtrated using cellulose acetate hydrophilic filters with a pore size of 0.20 µm. For measurements of major cations and anions, samples were collected in 100 mL polypropylene bottles. Each polypropylene bottle was rinsed with the filtrated water sample three times before actual sample collection. For measurement of trace elements, water samples were collected in 50 mL polypropylene bottles prewashed with a solution of 3% HNO₃. A volume of 2.5 mL of concentrated ultrapure HNO₃ was added to each 50 mL polypropylene bottle to prevent precipitation.

The concentrations of major cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺), major anions (F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) and trace elements (Cu, As, Mn and Fe) were measured at Akita Industrial Technology Center in Akita City, Japan. Non-acidified water samples were analyzed for major cations and major anions using ion chromatography (IC), Thermo Scientific Dionex Ion Chromatography system, ICS-3000 for anions and ICS-2100 for cations. Acidified water samples were analyzed for total dissolved trace elements by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent 7500ce. Certificate reference material JSAC 0302-3, The Japan Society for Analytical Chemistry, was used to verify the accuracy of the results obtained for major cations and trace elements. Reference materials made in the laboratory were used to verify the accuracy of the results obtained for major anions. The accuracies of measurements for major elements were estimated to be within ±5%, while the accuracies of measurements for trace elements were within ±2% except for Fe. Accuracies of measurements of Fe concentrations were estimated to be ±10%.

A charge balance between major cations and anions was calculated to estimate the reliability of HCO₃⁻ measurements conducted in the field. The difference between HCO₃⁻ concentrations obtained by field measurements and HCO₃⁻ concentrations obtained by calculations based on the charge balance was ±5%.

Geochemical maps were created using QGIS software (free software, available at: <https://qgis.org/en/site/forusers/download.html>). The base map of the geochemical maps consists of the river system and the boundary of the study area. Sampling points are shown on each geochemical map. Log-transformed data of chemical composition were used for intensive distance weighting (IDW) interpolation. After completion of the interpolation of data, the values showing

Table 1
Kinds of groundwater samples.

Groundwater sample	Number
Well	145
Cold spring	22
Hot spring	3
Borehole	2
Total	172

concentrations in the legend are back-transformed from logarithms into the original values.

Threshold values for discrimination of background population and anomalous population were estimated by the method described by Sinclair (1974, 1986, 1991) that is used in geochemical exploration and environmental research (Reimann et al., 2005; Panno et al., 2006; Masetti et al., 2009; McIlwaine et al., 2016; Rahman et al., 2020). Estimation of threshold values was conducted by the following steps: 1) values (172 values for concentrations of the components) were converted to logarithms, 2) the values converted to logarithms were classified into 16 to 20 groups, 3) histograms were created to confirm the presence of background and anomalous populations, 4) after calculation of the cumulative percentage, plotting the data of the cumulative frequency distribution was carried out on a probability paper (log concentration-probability plot), 5) the cumulative frequency distribution was divided into two or more groups showing background and anomalies, and 6) the threshold value was estimated as the value of $\mu + 2\sigma$, where μ is the mean value of a normal distribution in the background group and σ is the standard deviation. The detailed procedure is shown in Rose et al. (1979).

4. Results

4.1. Characteristics of water samples

A summary of the physical and chemical parameters including pH, Eh, water temperature, concentrations of major cations and anions, and concentrations of trace elements in groundwater samples is shown in Table 2. All of the data sets are shown in the supplementary material (Tables A.1 and A.2). Most of the groundwater samples were achromatic (colorless) and odorless. The temperatures of water samples collected from wells, boreholes and cold springs ranged from 10 °C to 20 °C. The temperatures of water samples collected from hot springs ranged from 34 °C to 37.3 °C.

Geochemical maps showing the distributions of pH and Eh values in groundwater from the study area are presented in Fig. 3. Water samples collected from wells, cold springs and hot springs had pH values ranging from 6.6 to 7.9, 6.4 to 7.8 and 7.3 to 8.8, respectively. The groundwater sample collected from the deep borehole (382 m) in Zajecar City had a pH value of 8.8. Most groundwater samples showed a neutral character with an average pH value of 7.2. This is to be expected in areas like Eastern Serbia where the bedrocks are predominantly carbonates. The bedrocks have the ability to neutralize the acidity and keep the pH near neutral (Gomez et al., 2010; Ma et al., 2011). A slightly acidic pH (6.4) was found in water from a cold spring located at Neresnica in the

north-western part of the study area, while alkaline pH was found in hot spring water and the deep borehole groundwater in Zajecar City.

The Eh values for groundwater samples collected from wells, cold springs and hot springs range from −66 to 502 mV, 225–710 mV and 242–362 mV, respectively. Groundwater samples collected from the borehole in Slatina Village and the deep borehole in Zajecar City had Eh values of 297 and 142 mV, respectively.

4.2. Concentrations of major ions

The variation of concentrations of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} and HCO_3^- in groundwater samples is given in Table 2. Major components of groundwater in this study were Ca^{2+} , Mg^{2+} and HCO_3^- (Fig. 4). The groundwater in the study area was classified as Ca–Mg– HCO_3^- -dominant type. Ca–Mg– HCO_3^- -dominant type groundwater is typical in areas where carbonate bedrocks are present (Appelo and Postma, 2005; Tanaskovic et al., 2012). Four groundwater samples were different from the majority of groundwater samples. These groundwater samples (a sample from Zajecar City, two samples from Brestovacka Banja and a sample from Milutinovac) were Na-rich groundwater (Fig. 4). The sample collected from the deep borehole (382 m deep) in Zajecar City was classified as (Na + K)– HCO_3^- -dominant type of water. The other three water samples, collected in Brestovacka Banja and Milutinovac, are plotted in the field of (Na + K)–Ca– SO_4 -dominant water type. Groundwater collected along polluted rivers downstream of the Bor mine (catchment area of Timok River) is different from the majority of groundwater samples. Groundwater collected in the vicinity of polluted rivers was classified as either Ca–Mg– HCO_3^- -dominant type water or Ca–Mg– SO_4 -dominant type water (Fig. 4). Those groundwater samples are plotted in the Piper diagram between unpolluted Ca–Mg– HCO_3^- -dominant type water in the study area and river water samples of polluted rivers, which are Ca–Mg– SO_4 -dominant type water, in the Bor and Majdanpek mining areas (Adamovic et al., 2021a), indicating the possibility of pollution by mining activities in this area (Fig. 4). Regarding groundwater samples collected downstream of the Majdanpek mine in the catchment area of Pek River, no differences from the majority of groundwater samples collected outside the mining areas were observed (Fig. 4).

Distributions of the concentrations of major cations and anions are shown as histograms (Fig. 5). Sodium concentrations show a bimodal distribution. The group in the histogram showing higher Na^+ concentrations, over 100 mg/L, corresponds to Na^+ -rich groundwater. Groundwater samples collected from wells outside the Bor mining area and in the Bor mining area had a similar range of Na^+ concentrations. These groundwater samples had higher Na^+ concentrations compared

Table 2
Composition of groundwater samples.

Parameter	Unit	LOD	Min	Max	Mean	Med	MAC	Estimated concentration
pH			6.4	8.8	7.2	7.1	6–8–8.5	
Eh	mV		−66	710	396	410	–	
T	°C		10	37.3	15.4	14.7	–	
Na^+	mg/L	0.01	0.04	244	31.3	24.6	200	100
K^+	mg/L	0.01	0.2	275	9.5	3.7	12	40
Mg^{2+}	mg/L	0.01	0.3	81.1	21.9	19.8	50	40
Ca^{2+}	mg/L	0.01	8.0	511	122	114	200	180
F^-	mg/L	0.01	<0.01	11.4	0.2	0.1	1.2	
Cl^-	mg/L	0.01	0.01	247	28.4	20.5	250	70
NO_3^-	mg/L	0.01	<0.01	254	41.6	25.6	50	70
SO_4^{2-}	mg/L	0.01	0.5	1111	116	68.7	250	150
HCO_3^-	mg/L		30	930	375	380	–	
Mn	µg/L	0.01	<0.01	2585	30	1.1	50	40
Fe	µg/L	0.1	<0.1	6387	20	5.6	300	50
Cu	µg/L	0.005	0.3	151	6.3	2.9	2000	15
As	µg/L	0.01	<0.01	97.5	3.8	0.9	10	10

LOD, the limit of detection; Min, minimum value; Max, maximum value; Mean, mean value; Med, median value; MAC, maximum admissible concentration according to the Serbian standards for drinking water (Republic of Serbia, 2019); –, not specified.

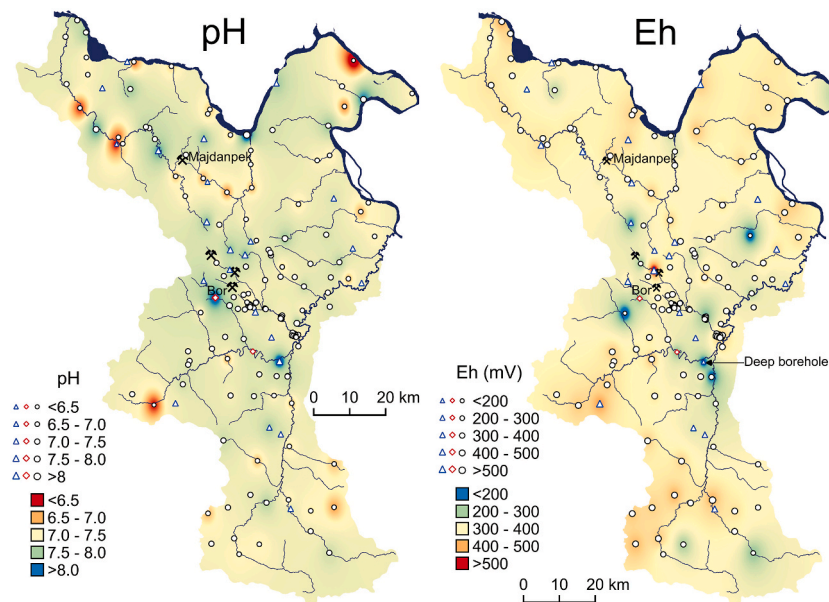


Fig. 3. Geochemical maps showing the distribution of pH and Eh values in groundwater of the study area. In the geochemical maps, samples collected from wells, cold springs and hot springs are marked by circles, triangles and diamonds, respectively.

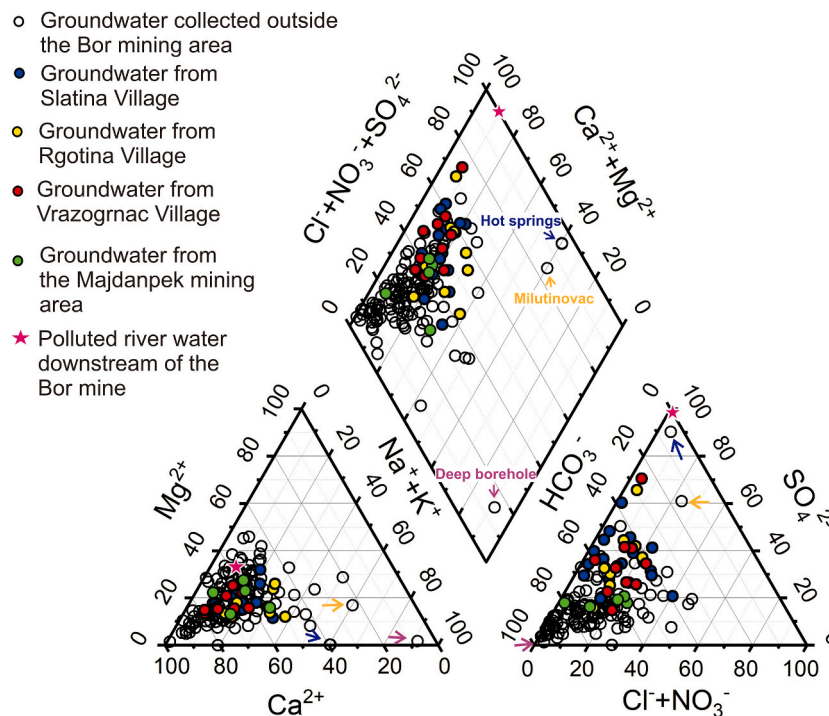


Fig. 4. Piper diagram showing the chemical composition of groundwater. The sample marked by a pink star corresponds to polluted river water (Adamovic et al., 2021a,b) in the study area.

with Na^+ concentrations in samples collected in cold springs in the mountainous areas (Fig. 5a). There is one sample in which the concentrations of Na^+ exceeded the maximum admissible concentration for drinking water of the Serbian standards (Republic Serbia, 2019).

Cold spring water samples were characterized by low concentrations of K^+ (Fig. 5b). There was no difference in the range of K^+ concentrations in groundwater collected from wells outside and in the Bor mining area. However, the concentration of K^+ in many samples collected from wells exceeded the standard value for drinking water in Serbia. The high K^+ content is considered to be a high background concentration rather

than contamination since samples with elevated concentrations are found all around the study area without systematic distribution in agriculture fields.

Concentrations of Mg^{2+} generally showed a unimodal distribution. Concentrations of Mg^{2+} in cold spring samples were lower than concentrations of Mg^{2+} in well groundwater samples collected in the Bor mining area. The range of concentrations of Mg^{2+} in well samples collected outside the Bor mining area included the ranges of Mg^{2+} concentrations in cold springs, hot springs and well samples from the Bor mining area (Fig. 5c).

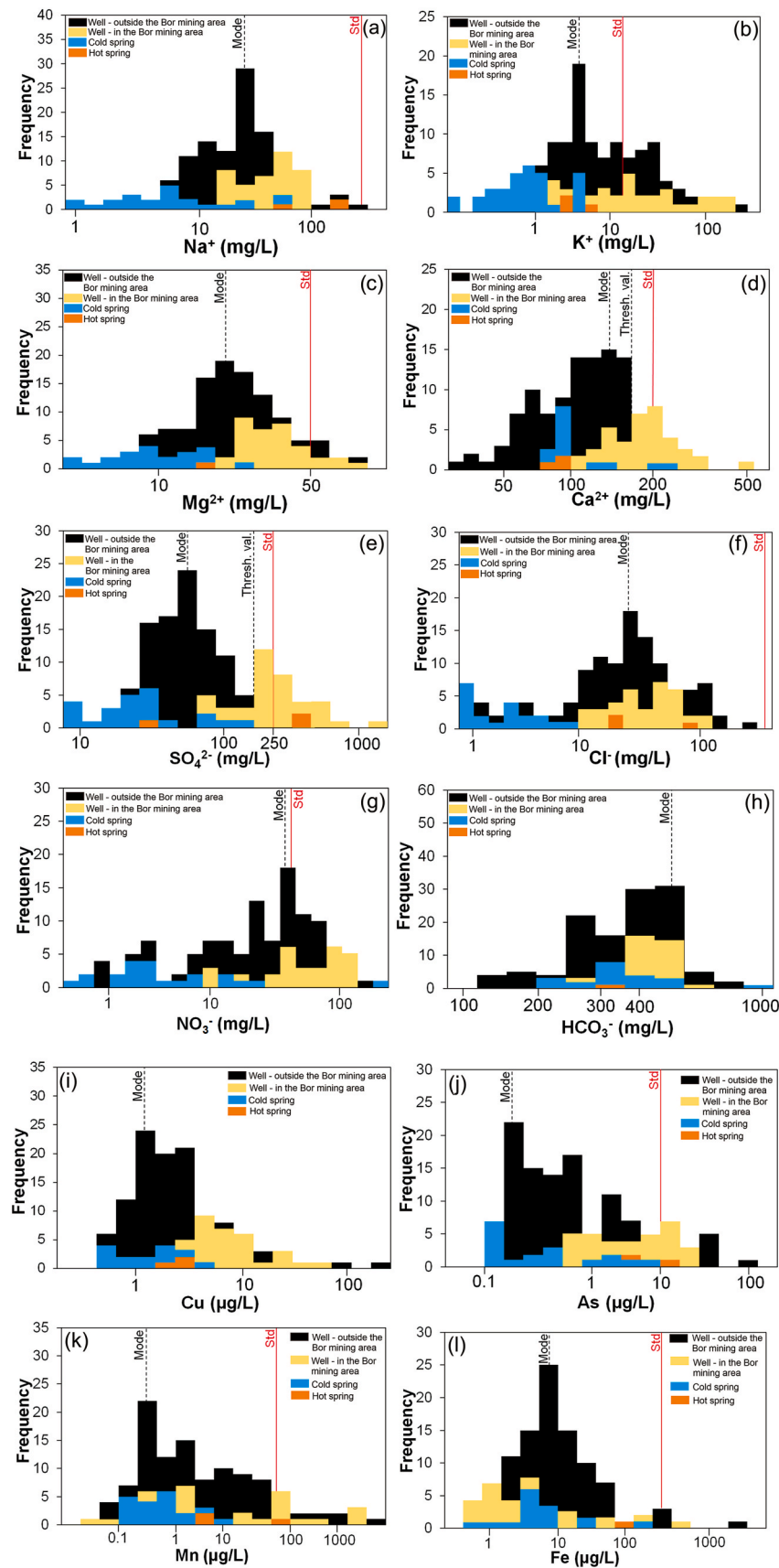


Fig. 5. Histograms showing distributions of data for major elements (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , NO_3^- and HCO_3^-) and trace elements (Cu, As, Mn and Fe) in groundwater from the study area. Mode, the value that appears the most; Thresh. val., threshold value; Std, maximum admissible concentration for drinking water according to the Serbian standards (Republic of Serbia, 2019).

Calcium concentrations had a bimodal distribution (Fig. 5d). Groundwater samples collected in limestone-poor areas had lower Ca^{2+} concentrations (less than 100 mg/L). Concentrations of Ca^{2+} measured in well samples collected outside the Bor mining area, cold springs and hot springs overlapped each other. On the other hand, groundwater samples collected in the Bor mining area had higher concentrations of Ca^{2+} than the concentrations of Ca^{2+} in groundwater samples collected outside the Bor mining area. Concentrations of Ca^{2+} in several groundwater samples collected in the Bor mining area exceeded the maximum admissible concentration for drinking water (Fig. 5d).

Sulfate concentrations in groundwater in the study area showed a bimodal distribution. Low concentrations of SO_4^{2-} were found in water samples collected from cold springs, both in the mountainous and plain areas. On the other hand, groundwater samples collected in the vicinity of polluted rivers in the Bor mining area had higher SO_4^{2-} concentrations (Fig. 5e). Groundwater samples collected from wells outside the Bor mining area are plotted between cold spring samples and well samples from the Bor mining area. Concentrations of SO_4^{2-} in some well samples from the Bor mining area exceeded the standard value for drinking water. The bimodal distribution of SO_4^{2-} concentrations corresponds to the presence of anomalous values, indicating the possibility of groundwater pollution.

Chloride concentrations had a unimodal distribution. However, water samples collected from cold springs and wells in mountainous areas, where there are less anthropogenic activities, had lower concentrations of Cl^- than those in samples collected from other parts of the study area (Fig. 5f). No differences in Cl^- concentrations were observed between well samples collected outside and in the Bor mining area.

In the case of NO_3^- and HCO_3^- , a negative skewness was observed in histograms (Fig. 5g and h). Nitrate concentrations were low in water samples collected from cold springs and wells in mountainous areas. On the other hand, groundwater samples from the plain areas had higher concentrations. Groundwater samples from the Bor mining area also had higher concentrations of NO_3^- than those in samples collected from mountainous areas. Despite this, the concentrations of NO_3^- in the Bor mining area were similar to concentrations in groundwater samples from the plain areas. The concentrations of NO_3^- in most of the samples exceeded the maximum admissible concentration of NO_3^- for drinking water of the Serbian standards (Fig. 5g). Since the elevated NO_3^- concentrations were present in the plain areas where agriculture is the main activity, therefore, this is considered to be the reason for the higher concentrations.

The ranges of HCO_3^- concentrations in all groundwater types in the study area were similar (Fig. 5h). The ranges of HCO_3^- concentrations in groundwater from cold springs and groundwater from wells in the Bor mining area were included in the range of HCO_3^- concentrations in groundwater from wells outside the Bor mining area.

4.3. Concentrations of trace elements

Four trace elements (Cu, As, Mn and Fe) were considered in this study. A summary of the results is shown in Table 2. The concentrations of trace elements in groundwater samples collected from the study area are shown by histograms (Fig. 5).

Histograms of Cu, As and Mn concentrations in groundwater from the study area showed a unimodal distribution with positive skewness, suggesting that a larger number of groundwater samples contain low concentrations of these elements (Fig. 5i, j and k). Low concentrations of Cu, As and Mn were found in groundwater samples collected from cold springs, both in mountainous and plain areas, and in well samples collected outside the Bor mining area. Groundwater samples collected from wells along polluted Bor River and Bela River in the Bor mining area had higher concentrations of Cu, As and Mn than those in other samples (Fig. 5i, j and l).

Groundwater samples containing the highest concentrations of Cu and As were collected around the Bor ore deposits at Brestovac (Cu =

151.2 $\mu\text{g/L}$; As = 25.5 $\mu\text{g/L}$) and a location near the area of Bor airport (Cu = 84 $\mu\text{g/L}$; As = 97.5 $\mu\text{g/L}$), where copper ore deposits are present in the deeper part between 400 m below the surface to more than 2 km (Banjesevic and Large, 2014; Jelenkovic et al., 2016). These data indicate the possibility of water-rock interaction between groundwater and rocks showing the signature of Cu mineralization in the shallow part of the mineralized areas. On the other hand, the highest concentrations of Mn were found in two locations outside the mining areas in Zlot (Mn = 1268 $\mu\text{g/L}$) and Karbulovo (Mn = 1077 $\mu\text{g/L}$). The distance between these two sampling sites is about 50 km. Moreover, these two sampling sites are far from the Bor mining area (Fig. 1a). Therefore, the higher concentrations of Mn in Zlot and Karbulovo are thought to be caused by some local effects. Concentrations of Cu did not exceed the maximum admissible concentrations for drinking water according to the Serbian standards, while a small number of samples had concentrations of As and Mn above the maximum admissible concentrations.

Bimodal distributions were observed for concentrations of Fe (Fig. 5l). Groundwater from the study area was characterized by low concentrations of Fe. There were no differences in concentrations of Fe among samples collected from wells, cold springs and hot springs both in the Bor mining area and outside the mining area. Several samples had Fe concentrations higher than 50 $\mu\text{g/L}$, which makes an anomalous population of samples. However, these samples were collected outside the mining area and had lower Eh values (<250 mV) than those in other samples, enabling Fe to be present in the solution (Figs. 2 and 4o). It is thought that these anomalous concentrations correspond to some local effects due to different redox conditions.

Groundwater samples collected in the Majdanpek mining area had ranges of trace element concentrations similar to those in groundwater samples collected outside the Bor mining area. Therefore, no signatures of groundwater pollution by trace elements were present in the Majdanpek mining area.

5. Discussion

5.1. Spatial distributions of studied components in groundwater

Distributions of the concentrations of major cations and anions (Na^+ , Ca^{2+} , SO_4^{2-} , Cl^-) and concentrations of trace elements (Cu, As, Mn and Fe) are shown in geochemical maps (Fig. 6). The geochemical maps show areas in which groundwater has higher concentrations of the components. Moreover, it was observed that groundwater samples collected from cold springs contain the lowest concentrations of studied components (Fig. 5). The reason why the concentrations in this kind of samples are low is that the cold springs occur at the higher altitudes where anthropogenic activities are present to a lesser extent.

A comparison of the distributions of concentrations of major cations and anions showed that concentrations of Ca^{2+} and SO_4^{2-} in groundwater have similar spatial distributions (Fig. 6c and d). Groundwater samples having high concentrations of Ca^{2+} and SO_4^{2-} were mostly collected in the vicinity of the Bor mine and along polluted rivers in the catchment area of Timok River containing high concentrations of these components at Slatina Village, Rgotina Village and Vrazogrnac Village downstream of the Bor mine (Fig. 6c and d) (Adamovic et al., 2021a). Heikkinen et al. (2002) reported that elevated concentrations of SO_4^{2-} in groundwater were observed in an area within a diameter of 2 km in one of the nickel mining areas in Western Finland. In this study, the highest concentrations of Ca^{2+} and SO_4^{2-} were found in groundwater collected from wells located in the vicinity of Bela River in Rgotina Village and Vrazogrnac Village that are located more than 20 km downstream of the Bor mine. Groundwater samples collected in Vrazogrnac Village, located 30 km downstream of the Bor mine, had higher SO_4^{2-} concentrations than the concentrations in groundwater samples collected in Rgotina Village, located 20 km downstream of the Bor mine. The concentrations of Ca^{2+} and SO_4^{2-} in groundwater collected at Slatina Village, Rgotina Village and Vrazogrnac Village are high near the

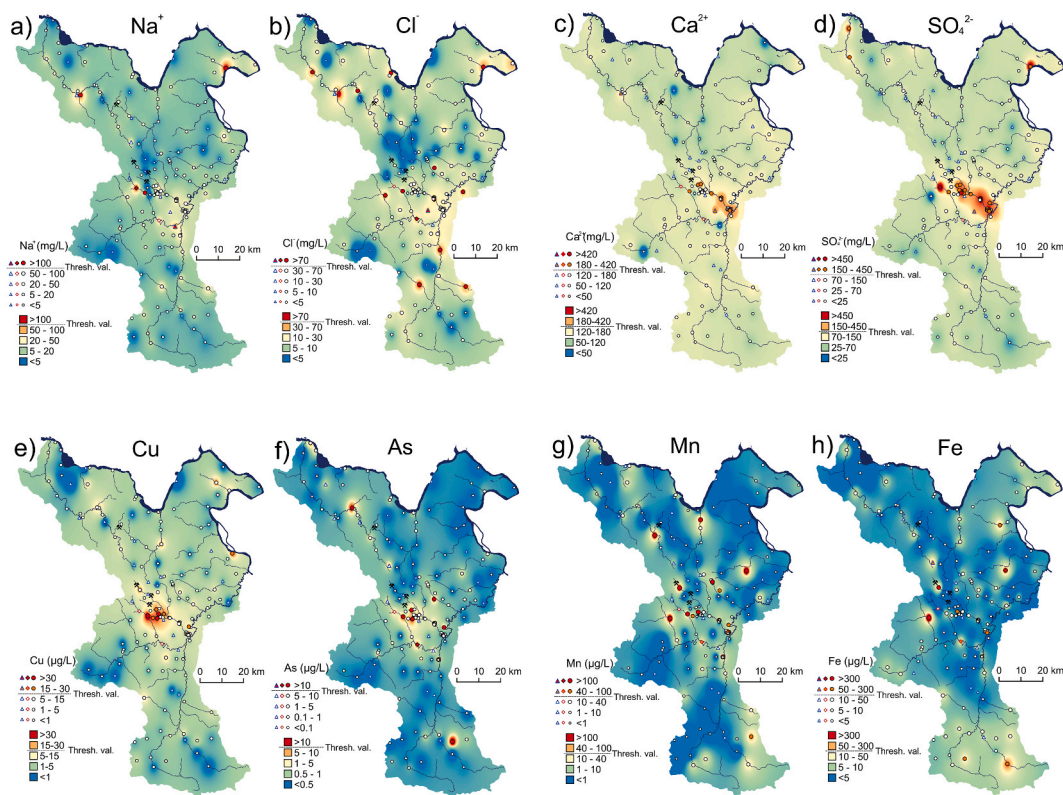


Fig. 6. Geochemical maps showing the distributions of concentrations of major elements (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , NO_3^- and HCO_3^-) and trace elements (Cu, As, Mn and Fe) in groundwater from the study area. In the geochemical maps, samples collected from wells, cold springs and hot springs are marked by circles, triangles and diamonds, respectively. Thresh. val., threshold value.

river and decrease away from the Bor River and Bela River (Fig. 6c and d) (Adamovic et al., 2021b). Therefore, there is no possibility that geological factors can affect groundwater composition just near the polluted rivers. Slightly higher concentrations of SO_4^{2-} were also found in groundwater samples collected in the area downstream of Pek River near the confluence between Pek River and Danube River. The area is located away from the Majdanpek mine, and the river water in the area is polluted with SO_4^{2-} (Adamovic et al., 2021a). There is a possibility that the river water of Pek River affects groundwater in its vicinity. However, SO_4^{2-} concentrations in this groundwater do not exceed the standard value for drinking water and are significantly lower than the concentrations measured in groundwater along polluted rivers in the Bor mining area. For these reasons, it is considered that groundwater in this area is not at high risk of pollution.

Most of the groundwater from the study area had low concentrations of Cu and As that were below the maximum admissible concentrations for drinking water. Elevated concentrations of Cu and As were found in groundwater in the vicinity of the Bor deposits, in which orebodies are massive sulfides in porphyry copper deposits where the predominant metals and metalloids are Cu, Au, Fe and As, and along polluted rivers in the area downstream of the Bor mine (Fig. 6e and f). It is known that groundwater in mineralized areas, especially in fractured aquifers, contains elevated concentrations of Cu and As (Armienta et al., 2001; Sako et al., 2016; Bonda et al., 2017). Groundwater near the Bor deposits, also had elevated concentrations of SO_4^{2-} , which can be released by water-rock interaction. Therefore, the high concentrations of Cu and As near ore deposits of the Bor mine are thought to be due to high background concentrations generated by water-rock interaction between groundwater and mineralized rocks in the mineralized area rather than pollution caused by mining activities. The concentrations of Cu and As in groundwater at Slatina Village, Rgotina Village and Vrazognac Village along Bor River, Bela River and Timok River after the confluence

of river water from the upper Timok River and the polluted Bela River were higher than the concentrations of Cu and As in groundwater outside the Bor mining area (Fig. 6e and f). The mere fact that the concentrations of Cu and As in such groundwater are higher than the concentrations of these elements in groundwater outside the Bor mining area does not indicate the presence or absence of contamination. Therefore, a threshold value is needed to distinguish between an anomalous population and a background population.

Regarding groundwater in the Majdanpek mining area (catchment area of Pek River), there was no distinct difference in the concentrations of Ca^{2+} , SO_4^{2-} , Cu and As between groundwater in the Majdanpek mining area and groundwater outside the Bor and Majdanpek mining areas (Fig. 6). In the Majdanpek mining area, a signature showing groundwater pollution was not found.

5.2. Estimation of threshold values for examination of groundwater pollution

Groundwater in mining areas is known to be vulnerable to quality problems (Von der Heyden and New, 2004; Leybourne and Cameron, 2008; Davis et al., 2010; Ibrahima et al., 2015). Therefore, determination of the maximum concentrations of chemical components in groundwater without pollution, i.e., background concentrations, is essential for knowing whether mining activities have affected the environment of groundwater or not (Runnells et al., 1992). Determination of background maximum concentrations is also necessary for distinguishing polluted areas. One appropriate way for estimating natural background concentrations is estimation of threshold values by the method of Sinclair (1974, 1986, 1991) (Reimann et al., 2005). In that method, all of the data for one component are classified into one or more groups in histograms and probability diagrams. If data are classified in one group it means that all of the considered concentrations belong to

the background group. On the other hand, if all of the data are classified into two or more groups, the group with the highest concentrations corresponds to the group showing pollution based on other information such as distribution of mining facilities and geochemical maps. A threshold value to discriminate anomalous populations from background populations is defined according to this procedure.

Threshold values for river water in the study area were estimated and the distribution of polluted areas was clarified (Adamovic et al., 2021a). Based on those results, there is a possibility that groundwater in the study area is contaminated. Therefore, there is a necessity for estimation of threshold values in groundwater in this study area.

Probability diagrams used for the classification of data to separate a group having the highest concentrations for all components are shown in Fig. 7. The estimated values for the classification in probability diagrams of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , NO_3^- , Cu, As, Mn and Fe are shown in Table 2.

Regarding Na^+ , the data classified into a separated group having higher concentrations had no systematic distribution in mining facilities and polluted rivers downstream of the Bor mine (Fig. 6a). The data in the group with the highest concentrations correspond to Na^+ -rich groundwater from the study area. Therefore, no pollution by Na^+ is present in the study area.

Based on histograms created for Cu and As, it is difficult to distinguish groups because data show a distribution having positive skewness (Fig. 5i and j). However, in the probability diagrams, the presence of different groups was noticeable (Fig. 7i and j). The groups with the highest concentrations of Cu and As in probability diagrams include groundwater samples with concentrations higher than 15 $\mu\text{g/L}$ and 10 $\mu\text{g/L}$, respectively. In geochemical maps showing the distributions of the concentrations of Cu and As, it can be easily seen that there is an area where groundwater has higher concentrations of these elements near the Bor deposits (massive sulfides in porphyry copper deposits) (Fig. 6e and f). However, these higher concentrations of Cu and As are thought to be caused by water-rock interaction because there are no mining facilities or other pollution sources. For that reason, elevated concentrations of Cu and As around Bor deposits are considered to be natural anomalies. There were also higher concentrations of Cu and As in several groundwater samples collected in Slatina Village compared with the concentrations of threshold values of Cu and As. Therefore, there is a possibility that groundwater in Slatina Village is affected by pollutants transported by air (Serbula et al., 2021). However, in groundwater collected in Rgotina Village and Vrazognac Village, which are located farther from the mining facilities, there were no concentrations of Cu and As that exceeded the estimated concentrations as threshold values.

According to probability diagrams of Mn and Fe, concentrations of Mn and Fe can be separated into three groups and two groups, respectively (Fig. 6k and l). However, the high concentrations of these elements in geochemical maps do not show a systematic distribution associated with mining facilities of the Bor mine (Fig. 6g and h). Therefore, the concentrations of Mn and Fe do not indicate groundwater pollution caused by mining activities in the study area.

Components showing anomalous values caused by mining activities are thought to be Ca^{2+} and SO_4^{2-} . These two components are also found to have high concentrations in Bor River and Bela River polluted by mining activities (Adamovic et al., 2021a). Moreover, along these rivers, tailings are deposited. Based on probability diagrams of Ca^{2+} and SO_4^{2-} , the distribution of data in the probability diagrams consists of two groups having different slopes (Fig. 7d and e). The presence of different slopes suggests that all of the data for Ca^{2+} and SO_4^{2-} were separated into two groups. The values divided into two groups were estimated for Ca^{2+} and SO_4^{2-} (Table 2). On the basis of geochemical maps, the area showing high Ca^{2+} and SO_4^{2-} concentrations is located along polluted rivers downstream of the Bor mine (Fig. 6c and d). Therefore, the estimated values of Ca^{2+} and SO_4^{2-} are threshold values for discriminating anomalous values caused by mining activities in the study area. The threshold values of Ca^{2+} and SO_4^{2-} are 180 mg/L and 150 mg/L,

respectively. The estimated threshold values of Ca^{2+} and SO_4^{2-} are below the maximum admissible concentrations according to the Serbian standards for drinking water. However, the concentrations of Ca^{2+} and SO_4^{2-} in groundwater along Bor River and Bela River in Slatina Village, Rgotina Village and Vrazognac Village, which are areas that are considered to be affected by mining activities, exceeded the threshold values. Unlike Cu and As, a stronger impact was observed for groundwater in the downstream area of Bela River in Vrazognac Village (located 30 km downstream of the Bor mine) compared with groundwater in Slatina Village (located 7 km downstream of the Bor mine), which is relatively close to the Bor mine based on the concentrations of Ca^{2+} and SO_4^{2-} .

Groundwater anomalies could be detected even though the actual concentrations of Ca^{2+} and SO_4^{2-} were lower than the maximum admissible concentrations for drinking water by Serbian standards (Republic of Serbia, 2019). On the other hand, heavy metals including Cu, Fe and Mn as well as As, which are present in extremely high concentrations in acidic river water of Bor River and Bela River (Dordievski et al., 2018; Adamovic et al., 2021a), do not show obvious evidence of groundwater pollution in the same area. Therefore, it is thought that groundwater in the Bor mining area is in an early stage of pollution.

In this study, early-stage groundwater pollution was detected by a procedure that included the use of geochemical maps and threshold values estimated by using histograms and probability diagrams. In studies on groundwater pollution in mining areas, due to high concentrations of toxic elements, the presence of pollution could be determined by using various methods for assessment of pollution such as estimation of threshold values, statistical methods, Water Pollution Index, and GIS modeling based on concentrations of toxic elements (Bathrellos et al., 2008; Molinari et al., 2012; Gong et al., 2014; Cruz and Andrade, 2015; Reagan et al., 2015; Moye et al., 2017; Giri and Singh, 2019; Bulut et al., 2020; Popugueva et al., 2020). In addition to these studies, our study showed that the use of just one method may not be sufficient to detect early-stage groundwater pollution. Therefore, to determine early-stage pollution of groundwater in the study area, a combination of threshold values and geochemical maps showing the systematic distribution of higher concentrations of appropriate components regarding the source of pollution was used in this study. If these methods are used separately, it would be difficult to evaluate the early stage of groundwater pollution. The procedure used in this study for estimation of the existence of early-stage groundwater pollution was as follows: 1) examination of data for separation of groups using histograms (Examination of the bimodal distribution and unimodal distribution with positive skewness is important.), 2) creation of geochemical maps and examination of the distribution of areas having high concentrations, 3) separation of the groups in probability diagrams, and 4) examination of the relation between the distribution of areas having high concentrations of components and the presence of possible sources of pollution such as mining or other anthropogenic activities. Based on this procedure, it is possible to determine whether the anomalies are of anthropogenic or natural origin, even if actual concentrations of toxic elements are below the maximum admissible concentrations for drinking water.

This study showed the importance of Ca^{2+} and SO_4^{2-} concentrations for the determination of early-stage groundwater pollution in mining areas such as the Bor mining area, where groundwater has a near-neutral character. Although large amounts of heavy metals and arsenic are discharged into Bor River and Bela River (Ishiyama et al., 2012; Stevanovic et al., 2013; Gardic et al., 2015; Adamovic et al., 2021a), it seems that river water does not have a large impact on groundwater because the concentrations of heavy metals and arsenic in groundwater are very low. The main difference observed between the Majdanpek mining area, where groundwater pollution was not detected, and the Bor mining area, in which there is groundwater pollution, is the absence and presence of tailings along polluted rivers. Based on these observations, there is a possibility that tailings along Bor River and Bela River are the source of groundwater pollution in this area. Since there are several potential