令和３年度博士論文

Geochemical and stable isotope studies of groundwater and river water in the Bor and Majdanpek porphyry copper mining areas in Eastern Serbia: Implications for the environmental impact on groundwater

（セルビア国東部ボール・マイデンペック鉱山地域の地下水と河川水の地球化学的・安定同位体的研究：地下水への環境負荷の意味）

ドラガナ　アダモビッチ

Dragana Adamović

6518107

秋田大学大学院

国際資源学研究科博士後期課程

資源学専攻

Abstract

Contamination of water bodies is a large problem in many mining areas in the world. A similar problem exists in Eastern Serbia, where mining activities have been carried out for about 120 years. Currently, in Eastern Serbia, there are four active copper mines, three in the Bor mining area and one in the Majdanpek mining area. The long history of mining in the Bor mining area has led to serious environmental problems, which are most pronounced on water pollution downstream of the mining sites. This research aims to clarify the geochemistry of river water and groundwater in the study area and to estimate the environmental impact on groundwater in the Bor and Majdanpek mining areas.

River water of Bor River, Krivelj River and Bela River located in the Bor mining area showed acidic pH ranging from 2.9 to 5.1, from upstream to downstream direction, with high concentrations of SO_4^{2-}, Fe, As, Cu and Mn. River water of Small Pek River and the upper reach of Pek River are characterized by weakly alkaline pH and high concentrations of SO_4^{2-}, Fe, As, Cu and Mn, although lower than the concentrations of these components in river water in the Bor mining area. The acidic river water in the Bor mining area transports large quantities of heavy metals and arsenic downstream, including 6900 t/year of Fe, 42 t/year of As, 910 t/year of Cu and 187 t/year of Mn. On the other hand, the weakly alkaline river water in the Majdanpek mining area transports smaller quantities of heavy metals and arsenic downstream (160 t/year of Fe, 0.1 t/year of As, 6 t/year of Cu and 272 t/year of Mn). This indicates that the environmental impact in the Bor mining area is significantly larger than that in the Majdanpek mining area. However, concentrations of SO_4^{2-}, Fe, As, Cu and Mn in Bela River in the Bor mining area have greatly decreased after mixing of acidic polluted water of Bela River with water of Timok River containing a high bicarbonate concentration. This fact suggests that river water in the study area including Bor and Majdanpek mining areas has sufficient capacity for neutralization.

Stable isotope ratios of groundwater are typical for the moderate continental climate. However, groundwater samples collected in mountainous areas are relatively depleted in δD and $\delta^{18}O$ compared with samples that are collected in plain areas of the

study area. This difference is thought to be caused by the altitude effect due to the Rayleigh process, which means that precipitations enriched in stable isotopes, that form groundwater in the study area, will occur first in the plain areas, and going towards higher altitudes precipitations will become depleted in stable isotopes.

Groundwater in the study area is characterized by pH values ranging from 6.4 to 8.8 and a high concentration of HCO_3^-. The groundwater is Ca-Mg-HCO_3-dominant type water. In general, groundwater from the study area has good quality with low content of trace elements, which are below maximum admissible concentrations according to the Serbian standard for drinking water. Trace elements that are mainly present in groundwater are Ba and Sr. Barium and strontium concentrations are especially high in limestone-rich areas.

To determine whether mining activities are causing groundwater pollution in the study area, geochemical maps were created and threshold values for discrimination of anomalous populations from background populations were estimated for Ca^{2+}, SO_4^{2-}, and 24 other components. Geochemical maps created for Ca^{2+} and SO_4^{2-} show that groundwater with high concentrations of these components is found along polluted rivers downstream of the Bor mining area, especially in the area along the Bela River. The actual concentrations of Ca^{2+} and SO_4^{2-} exceeded the threshold values, although the concentrations in some groundwater samples in the area downstream of the Bor mine were below the standard values. Pollution of the groundwater along the polluted rivers is therefore thought to have been caused by mining activities of the Bor mine. Elevated concentrations of the studied components in groundwater from the Majdanpek mining area were not detected.

Based on the mixing analysis between interstitial water present in tailings along strongly polluted rivers and unpolluted groundwater, it is thought that interstitial water in tailings along Bor River and Bela River is causing pollution of groundwater in the vicinity of those rivers. While river water does not directly affect groundwater in the study area.

Calcium and sulfate concentrations were shown to be good indicators for monitoring of early-stage groundwater pollution caused by mining activities in the

study area, this evaluation is mainly suitable for groundwater with a near-neutral pH. In addition to this, the evaluation method used in this study, which is based on geochemical maps, threshold values and mixing analysis considering geochemical reactions, is widely applicable to environmental assessment in mining areas.

Table of contents

1. Introduction

Pollution of river water and soil can be identified by naked eye observation and is relatively easy to identify. 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. 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 (Djurovic and Zivkovic, 2013; Devic et al., 2014; Polomčić et al., 2018; Pešić et. al., 2020). The territory of Eastern Serbia is one of the most resourceful areas based on the density of occurrences of groundwater. Much of the groundwater resources in Eastern Serbia occur in karst aquifers (Kortatsi, 2007; Stevanović et al., 2007; Petrović et al., 2010). Groundwater in karst aquifers in Serbia and worldwide has been shown to have good quality for drinking water (Hartmann et al., 2014; Pešić et. al., 2020). However, both industrial and agricultural activities, which can affect groundwater quality, are present in the study area.

Geologically, Eastern Serbia belongs to the Carpathian-Balkan belt, which is one of the world's oldest mining areas. Mining areas located in the Carpathian-Balkan belt played a major role in the history of European civilization (Ciobanu et al., 2002; Popov et al., 2002; Lips et al., 2004; Kolb et al., 2013; Mao et al., 2014; Gallhofer et al., 2015). In the Serbian part of the Carpathian-Balkan belt, there are two mining areas, namely the Bor mining area and Majdanpek mining area. Modern and organized mining started in Bor as underground mining in 1903 after the discovery of high-grade copper ore deposits when a French company opened the mine (Kovačević et al. 2010; Šerbula et al., 2010; Šerbula et al., 2016). After World War II, mining company became state property (Milijašević et al., 2011). The enterprise was state property until December 2018, when a Chinese mining company bought it. Approximately 60 years after the opening of the mine in the Bor mining area (1961) surface ore extraction started in the Majdanpek mining area (Armstong et al., 2005; Šerbula et al., 2015). Operations are

still being carried out in both mines and today mining represents the main economic activity in this part of the country (Milijašević et al., 2011; Panias, 2006). The Bor and Majdanpek mines have ores of porphyry copper deposits around Bor City and Majdanpek City, respectively. The currently remaining ore reserves in the Bor and Majdanpek mining areas are estimated to be about 379.2 million tons and 144.5 million tons, respectively. The estimated average contents of Cu in ore reserves in the Bor and Majdanpek mining areas are 0.57% and 0.38%, respectively (Jelenković et al., 2016). The mineral assemblage of both deposits is characterized by chalcopyrite, pyrrhotite and magnetite with trace amounts of molybdenite, enargite, galena and sphalerite (Stevanovic et al., 2011).

Environmental problems have become major issues since operations were started in the Bor mining area (Corsi & Sacco, 2006). The mining and ore processing activities have generated large amounts of tailings and overburdens (Stevanovic et al., 2011; Markovic, 2012). Oxidation of sulfide minerals such as pyrite in tailings and overburdens produces acidic, metal-rich wastewater that contaminates local surface water and groundwater (Ozunu et al., 2009; Marin et al., 2010). The dust from smelter and overburden can contaminate soil and watercourses in its vicinity. The current mining activities in the study area have a large impact on the quality of air, surface water and soil. Air pollution in the mining area is caused by the operation of the smelter for pyrometallurgical copper production located in Bor City. Previous studies characterized air pollution in the vicinity of Bor City as an environmental hotspot in Serbia and beyond based on concentrations of SO_2, as well as metals and As in PM particles (Dimitrijević et al., 2009; Kovačević et al., 2010, Pejović et al., 2017; Serbula et al., 2017, 2021). The size of the area polluted by pollutants transported through the air is about 15 km in the north-west direction and 5 km in the east and south-east direction from Bor City (Pejović et al., 2017; Serbula et al., 2017). Soil pollutants are transported either through the air or through polluted surface water (Nikolić et al., 2011; Avramović et al., 2016; Nikolic et al., 2016; Pejović et al., 2017; Filimon et al., 2021; Petrovic et al., 2021). The water chemistry of river water in the Bor mining area is also thought to be affected by the physical transport of pollutants through the air. However, the environmental impact of wastewater from the Bor mine on river water is very strong

compared with the effects of air pollution. Therefore, it is important to consider the relations between the chemical characteristics of wastewater from the mines (wastewater from mining facilities, overburdens and flotation tailings) and the chemical characteristics of river water and groundwater in the mining areas. Also, along the polluted rivers in the Bor mining area, tailings transported from the Bor mine during an accident event that happened in the 1950s are present (Paunović, 2010; Bogdanović et al., 2014). However, there is no study to know the effects on groundwater caused by air, soil, surface water and tailings. Based on the current conditions of quality of air, surface water and soil in the Bor and Majdanpek mining areas and the risk of groundwater pollution induced by historical mining activities in Serbia (Atanacković et al., 2016), there is a possibility that groundwater is also affected by the mining activities, because shallow groundwater is linked to surface where strong pollutions occurred. However, up to the present, there is no comprehensive study on the geochemistry of the groundwater in the study area. The determination of the pristine composition of groundwater is a key issue to assess any modification that may be caused by anthropogenic activities, therefore an important issue for environmental evaluation.

There is an intense environmental impact on river water downstream of the Bor and Majdanpek mines, which might affect groundwater quality. In addition, a large number of studies have been conducted on the quality of polluted river water (Milijašević et al., 2011; Ishiyama et al., 2012; Atanacković et al., 2013; Gardić et al., 2015; Šerbula et al., 2016; Đorđievski et al., 2018; Milijaševic-Joksimovic et al., 2018). Ishiyama et al. (2012) showed that the environmental impact on Danube River water is small based on the chemical composition of filtered river water in the Bor mining area. However, surveys for environmental evaluation by government agencies are often carried out for total concentrations of elements in unfiltered samples. In the Bor mining area, there has been no systematic investigation of the total concentrations of heavy metals in river water. In addition, there is not sufficient information about the environmental impact in the Majdanpek mining area. Moreover, an estimation of the sizes of polluted areas based on total concentrations of heavy metals in river water in the Bor and Majdanpek mining areas needs to be determined through the evaluation of the sizes of areas with pollution and evaluation of the environmental impact based on

the threshold values to discriminate background and anomalous concentrations of elements for environmental reclamation (Reiman and de Caritat, 2017). Regarding groundwater, usually, it has neutral pH, and when such groundwater has high concentrations of heavy metals and arsenic, the contamination is often severe. Given this problem and the long residence time of groundwater, detection of early-stage groundwater pollution is necessary. Therefore, it is important to find aqueous species that can be present in groundwater having neutral pH for the detection of early-stage groundwater pollution. Since there is no comprehensive study on groundwater geochemistry as well as on the assessment of their pollution, it is important to determine whether there is groundwater pollution or not, based on appropriate components. It is also important to know the size of the vulnerable area of pollution if pollution is present. Estimation of background concentrations and threshold values for discrimination between background and anomalous values of elements in groundwater and creation of geochemical maps are useful for the assessment of the degree of pollution. Based on these backgrounds, this PhD thesis was carried out to: 1) estimate the threshold values for discrimination of background and anomalous concentrations of elements in groundwater and river water, 2) create the geochemical maps to delineate vulnerable areas for groundwater and river water contamination, 3) compare environmental impacts in the Bor and Majdanpek mining areas based on the sizes of areas with pollution estimated by threshold values and quantities of elements transported by river water, 4) estimate the effect of environmental impact from the Bor and Majdanpek mining areas to Danube River, and 5) determine if there is an effect of pollution on groundwater in the vicinity of highly polluted Bor River and Bela River in the Bor mining area. It is also necessary to find the appropriate chemical species for groundwater monitoring and to establish a method for detecting early-stage of pollution of groundwater having neutral pH. The procedure of environmental evaluation of groundwater combining geochemical maps and threshold values was also examined whether is appropriate for the estimation of early-stage of groundwater pollution or not.

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. 2.1). The size of the study area is about 8320 km^2. The study area is characterized by mountain terrains in the central, western and southern parts. On the other hand, the eastern and northwestern parts of the study area are characterized by plain terrains (Fig. 2.1).

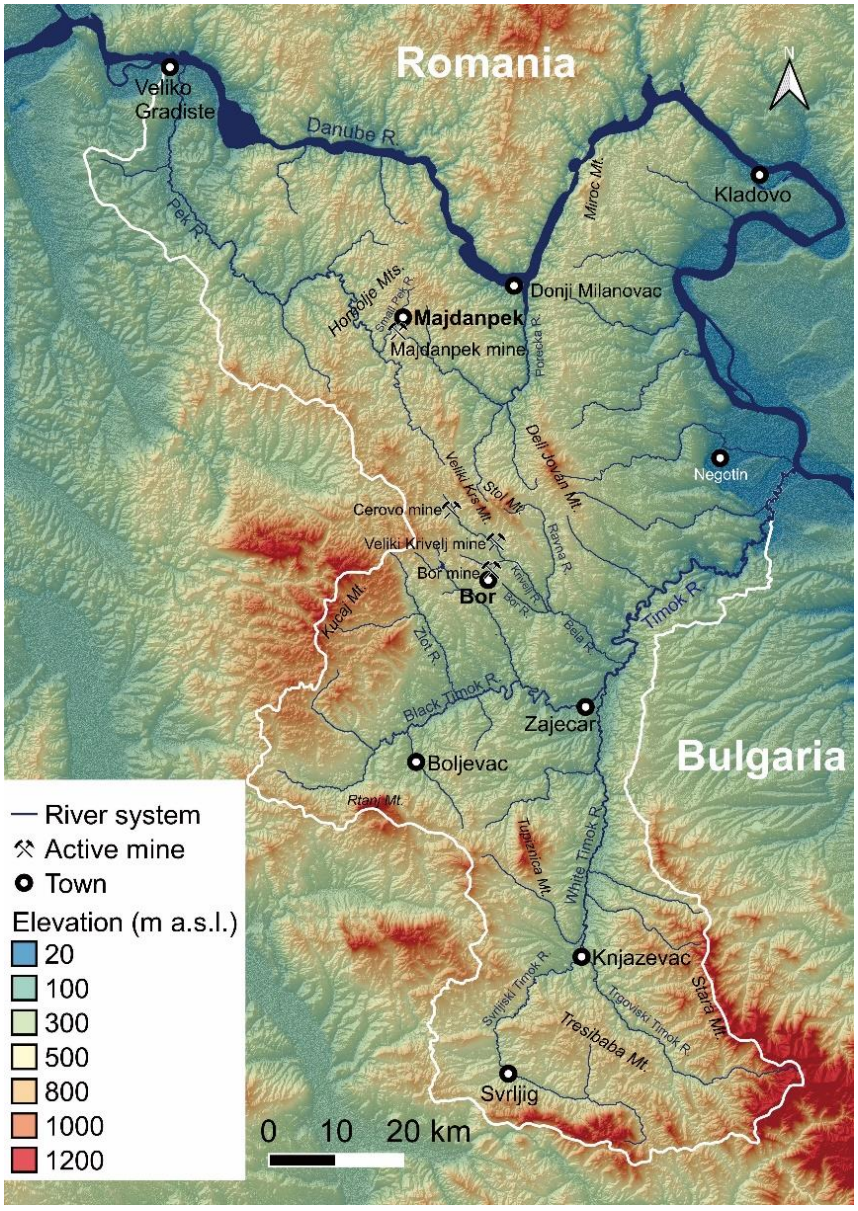


Fig. 2.1 Geographic map of the study area.

2.2. Meteorological conditions

The study area is characterized by a moderate continental climate with extreme temperature changes (from -30ºC to 40ºC) during a year. For the plain terrains, the typical continental climate is characteristic. The mountainous terrains are characterized by the mountain climate, where snow lasts about five months a year. The distribution of annual precipitation in the study area is shown in Fig. 2.2.

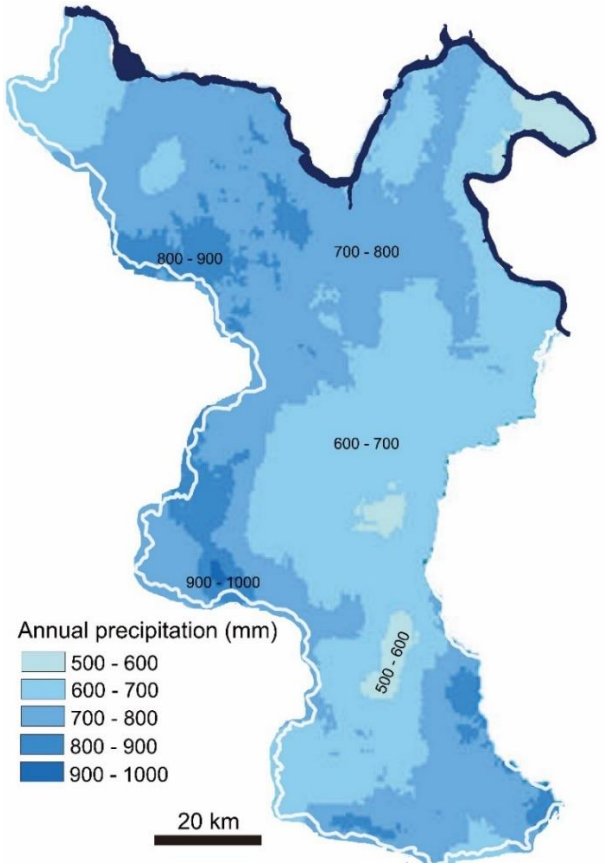


Fig. 2.2 Map showing annual precipitation in the study area. Modified according to Milovanović et al., 2017.

In the whole study area, snow is mainly present from December to March. The season of snowmelt is during March and April. May and June are the months with the frequent occurrence of rain. While August and September are the driest months. In this study, data from the Hydrometeorological Institute of Serbia were used (Republic of Serbia, 2011, 2012a, 2013-2018, 2019a, 2020).

Sample collection was carried out during the hottest period of the year and without significant amounts of precipitations, both in 2015 and 2019.

2.3. Hydrological settings and mine locations

The study area includes watersheds of Timok River, which is present in the southern part, Pek River and Porecka River, which are present in the northern part of the study area (Fig. 2.3).

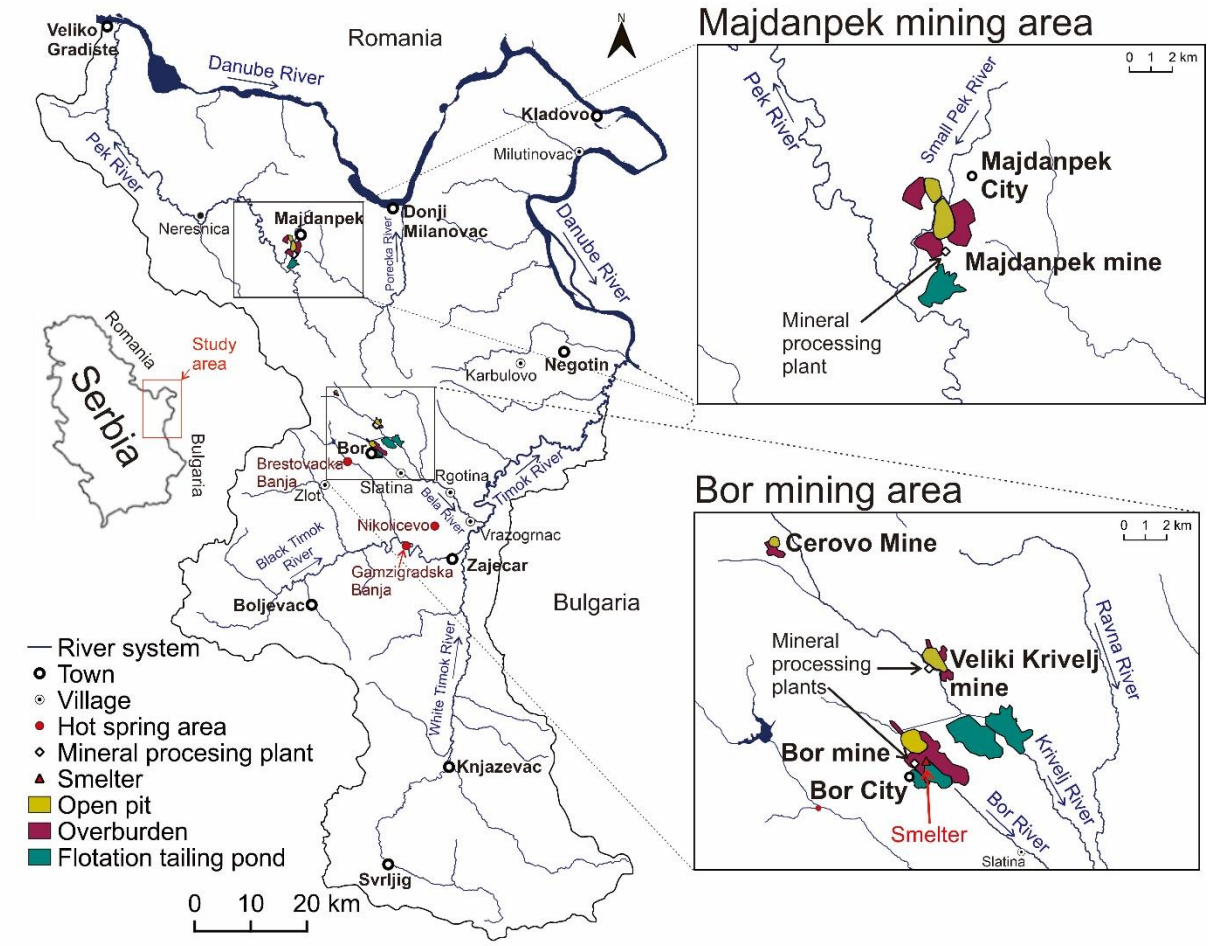


Fig. 2.3 Map showing distributions of towns, villages, hot spring areas, open pits, overburdens and flotation tailing ponds in the study area including Bor and Majdanpek mining areas.

The Bor and Majdanpek mining areas belong to the riverine systems of Timok River watershed and Pek River watershed, respectively. Large amounts of tailings are present along polluted rivers in the Bor mining area. After the collapse of a tailings dam in the 1950s, large amounts of tailings were transported downstream in the Bor mining area (Paunović, 2010; Bogdanović et al., 2014). Due to this accident, the river bed of Bela River may be higher than the groundwater level in the lower reach of Bela River. Failure

of the flotation tailings dam may cause serious environmental problems on groundwater downstream of the Bor mining area. On the other hand, along with Small Pek River and Pek River tailings are not present. All of the rivers in the study area belong to the drainage system of Danube River, which is the second longest river in Europe and flows for about 2850 km from southern Germany through Central and Eastern Europe to the Black Sea.

The Majdanpek mine is located near Small Pek River, which is one of the tributaries of Pek River. Two open pits, overburdens and flotation tailings of the Majdanpek mine are located in the watershed of Small Pek River (Figs. 2.3 and 2.4). Concentrates after mineral processing in the Majdanpek mine are transported to the smelter in the Bor mine and are refined to metals. Small Pek River contains mine drainage water from the Majdanpek mine and municipal wastewater from Majdanpek City. The river water of Small Pek River flows into the mainstream of Pek River downstream of the Majdanpek mine. Pek River flows into Danube River in the northern part of the study area (Fig. 2.3).

Fig. 2.4 Photographs showing open pit, mine waste materials and flotation tailing in the Majdanpek mining area.

White Timok River, which flows from the south of the study area, and Black Timok River, which flows from the west to east in the study area, are located in the upstream area of Timok River system. These rivers merge to the mainstream of Timok River near Zaječar City (Fig. 2.3). The Bor mining area is located upstream of Bela River, which is one of the tributaries of Timok River downstream of Zaječar City. Bor River and Krivelj River are located in the Bor mining area as tributaries of Bela River. Bor River flows into Krivelj River and the name of Krivelj River changes to Bela River (Fig. 2.3). Along Bor River, Bor open pit, facilities for ore processing (ore flotation) and metallurgical facilities of the Bor mine, overburdens and old flotation tailings are present. Cerovo open pit with an overburden is located in the upper reaches of the Krivelj River watershed and active Jama underground mine (a part of the Bor mine) and Veliki Krivelj open pit with facilities for ore flotation plant, overburdens and flotation tailings are located in the middle course of the Krivelj River watershed (Figs. 2.3 and 2.5).

Fig. 2.5 Photographs showing the open pit, overburden, flotation tailings and metallurgical facilities located in the Bor mining area.

Based on the classification of wastewaters in the Bor mining area, there are three types of wastewater that have an impact on the environment: 1) acid mine drainage

waters from the Jama underground mine, Veliki Krivelj open pit, overburdens and flotation tailings of the Bor mine, 2) wastewater from metallurgical facilities of the Bor mine that is released into Bor River without any pretreatment before discharging and 3) municipal wastewater from Bor City. These wastewaters are discharged into the natural river water of Bor River and Krivelj River, resulting in polluted river water (acid mine drainage-bearing river water). Acid mine drainage-bearing river water flows into unpolluted river water of Timok River, and Timok River flows into Danube River in the eastern part of the study area (Fig. 2.3).

2.4. Geology

The 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 (IGT, 1970). The Proterozoic schists occur in the northern part of the study area. The schists are chlorite schist, chlorite albite schist and actinolite schist. The Paleozoic metamorphic rocks and sedimentary rocks occur in the western part of the study area. The Paleozoic metamorphic rocks and sedimentary rocks are Ordovician phyllite and Silurian and Devonian sandstone and shale, respectively. The Jurassic sedimentary rocks are distributed widely in the northern and western parts of the study area. The Jurassic sedimentary rocks consist of a large amount of limestone and dolomite with lesser amounts of chert, sandstone, mudstone and conglomerate. The Cretaceous sedimentary rocks occur in the southern and northeastern parts of the study area. They are mainly composed of sandstone, mudstone, conglomerate, limestone and marls. The Cretaceous volcanic rocks, which are named Timok Magmatic Complex, are distributed in the central part of the study area. The volcanic rocks are composed of andesitic lava and pyroclastic rocks (Fig. 2.6). The radiometric age of the magmatic complex is estimated to be from 90 to 80 Ma (Von Quadt et al., 2002; Clark & Ullrich, 2004; Banješević, 2010; Banješević et al., 2019). The Paleogene sedimentary rocks occur locally in the southern part of the study area and are composed of sandstone, mudstone,

shale, coal and marls. The Neogene sedimentary rocks are widely distributed in the eastern part of the study area and consist of sandstone, mudstone, conglomerate and limestone. The Quaternary sediments are distributed along the river system in the study area. The Paleozoic granitic rocks are mainly distributed in the northern part of the study area. The Paleozoic gabbro also occurs in central and southeastern parts (IGT, 1970).

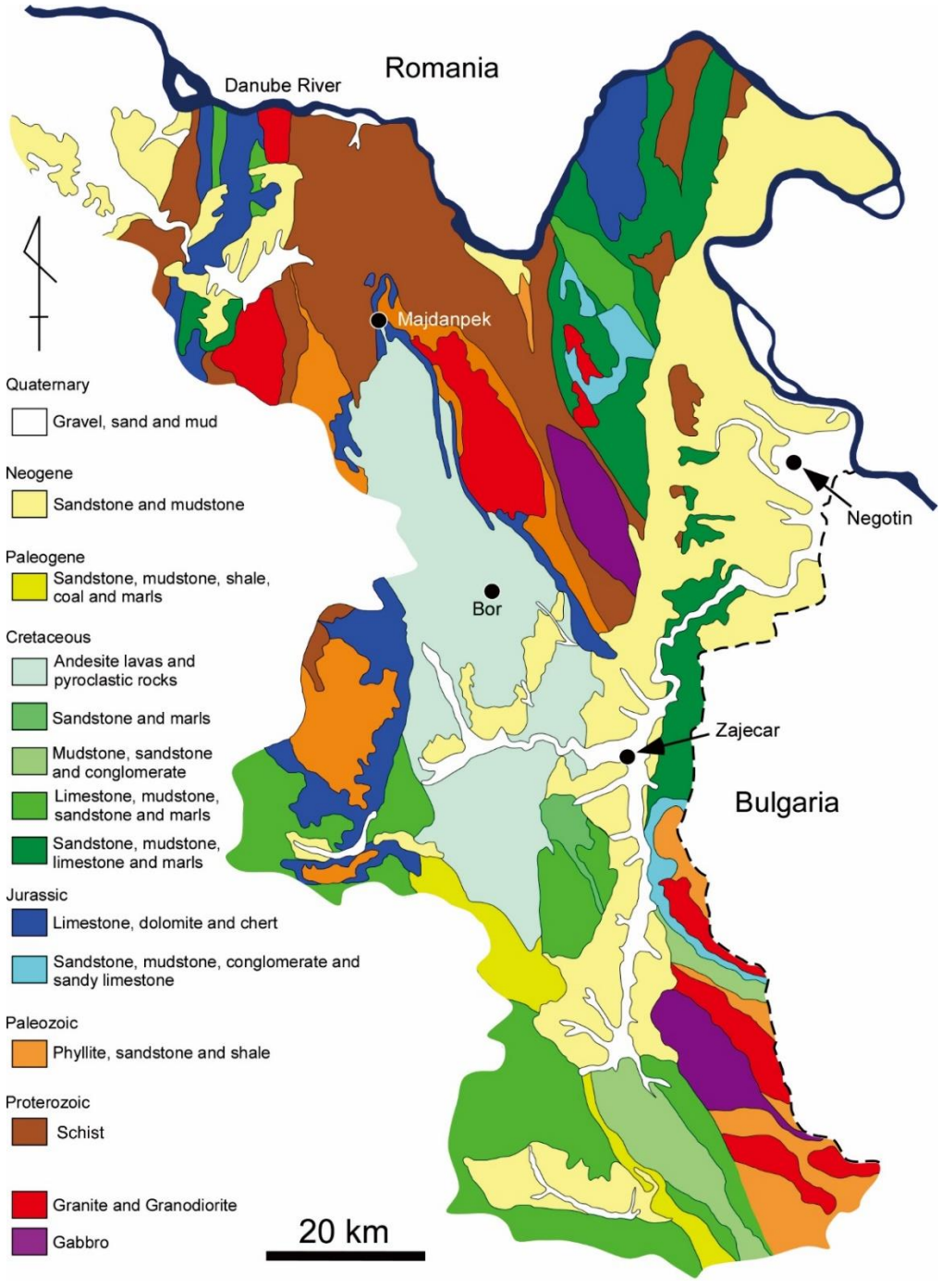


Fig. 2.6 Geological map of the study area.

Porphyry copper deposits in the Bor mining area are hosted in the Timok Magmatic Complex. In the Bor mining area, there is a small amount of Jurassic limestone near the porphyry copper deposits (a few small limestone bodies near the Veliki Krivelj open pit). On the other hand, porphyry copper deposits of the Majdanpek mining area are present at the boundary zone between Jurassic limestone and andesitic lava and pyroclastic rocks of Timok Magmatic Complex. The limestone is present close to orebodies of the Majdanpek deposit. The positional relation between limestone and porphyry copper deposits in the Bor mining area is different from that in the Majdanpek mining area (Fig. 2.6).

2.5. Hydrogeological and lithological features

The study area contains different permeable and semi-permeable aquifers beneath the surface of the ground upon the previous geological description (Chapter 2.4). In the study area, there are two different hydrogeological regions, the Dacian Basin and Carpatho-Balkanides of Serbia (Fig. 2.7a) (Petrović et al., 2010; Polomčić et al., 2011; Krunić and Sorajić, 2013). The lithology of aquifers and sampling locations are also shown in Fig. 2.7. The type of aquifer in the study area is classified as followed: karst aquifer, fractured aquifer, sedimentary aquifer, low productive aquifer and alluvial aquifer. 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. 2.7) (Stevanović et al., 2007; Petrović et al., 2010; Polomčić et al., 2011; Živanovic et al., 2016; Vasić 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 for groundwater in karst aquifers in the area consisting of carbonate rocks due to 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. 2.7). These aquifers are also a significant source of groundwater

(Dokmanović et al., 2007, 2012). In addition, alluvial aquifers are present to a lesser extent in the Dacian Basin and Carpatho-Balkanides of Serbia (Fig. 2.7). The alluvial aquifers have a possibility to be vulnerable to anthropogenic activities due to higher population density.

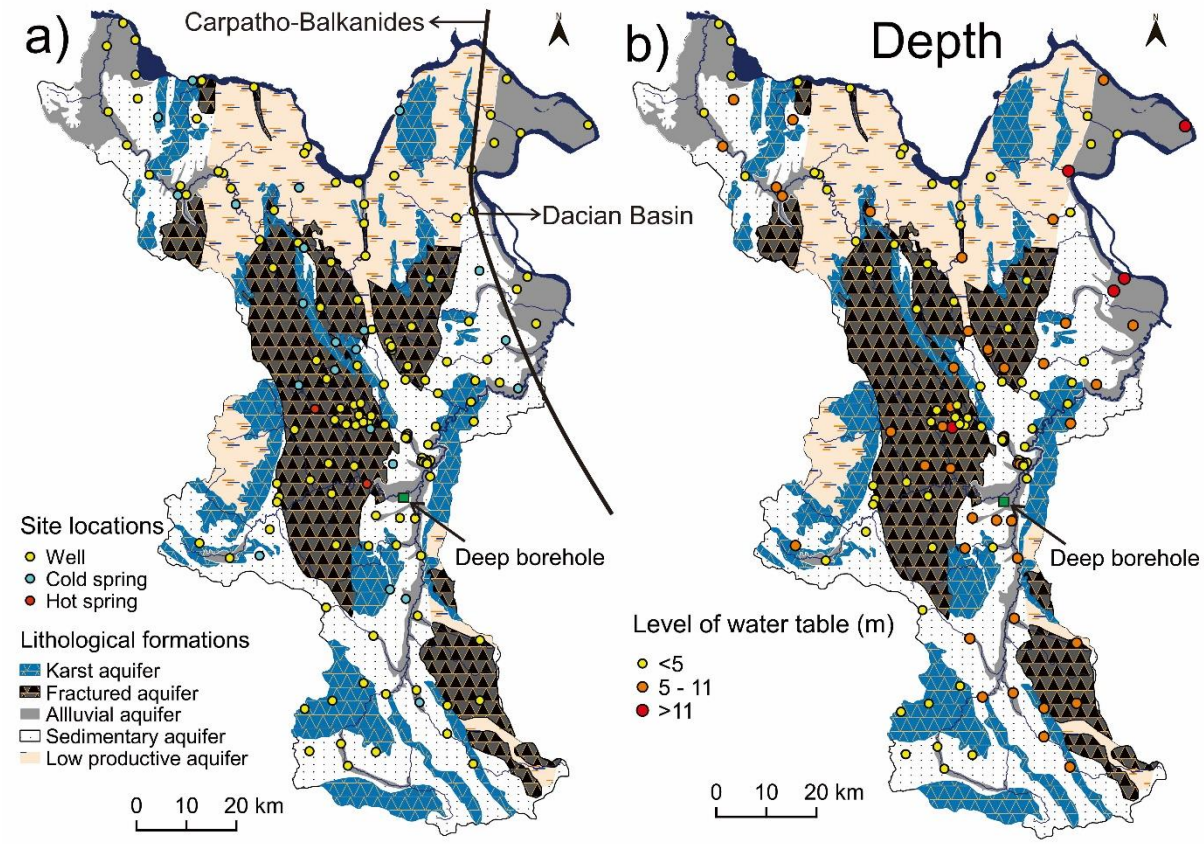


Fig. 2.7 Maps showing lithological formations for aquifers at sampling sites according to the hydrogeochemical map of Polomčić et al., (2011). a) Map showing hydrogeological regions of Dacian Basin and Carpatho-Balkanides in addition to locations of well, cold spring, hot spring and borehole samples; b) Map showing the depth of water table of wells where the samples were taken.

Intensive tectonic activity in the study area has created dislocation lines and faults of large dimensions, which enables favorable conditions for groundwater circulation (Goldscheider et al., 2010). Andesite and other igneous rocks erupted along the faults. In these terrains, the occurrence of groundwater with elevated temperature is present (Brestovačka Banja, Gamzigradska Banja and Nikoličevo) (Fig. 2.3) (Petković, 1976).

Groundwater samples considered in this study were collected from shallow aquifer wells, cold springs and hot springs. The average depth of the water table was 4 m in this study (Fig. 2.7b). The depth of the alluvial aquifer along Danube River on the north-east part of the study area is deeper having the level of water table more than 10 m (Fig. 2.7b). The depth of groundwater sample collected from a deep borehole in Zaječar City is 382 m. Groundwater samples from the Bor mining area were mainly collected in the fractured aquifer and alluvial aquifer. While groundwater samples in the Majdanpek mining area were collected in the karst aquifer and low productive aquifer.

3. Materials and methods

The research methodology included field and laboratory methods during sample collection and data analysis, while statistical methods were applied during data processing.

3.1. Sampling collection and field measurements

3.1.1. River water samples collected in 2015

A field survey was carried out from summer to fall in 2015 to determine the geochemical characteristics and environmental impact of polluted river waters in the Bor and Majdanpek mining areas. The sampling sites are shown in Fig 3.1. The total number of samples, including samples of polluted river water and unpolluted river water, was 198. The color and odor of river water were recorded at each site. The coordinates of sampling sites were determined in the field by GPS. The pH and Eh values were determined using a hand-held ion/pH meter. The flow rates of river water were determined at some sampling sites in the Bor and Majdanpek mining areas. At each sampling site, two kinds of samples were collected. One kind was non-acidified filtrated samples for measurements of the concentrations of anions by ion chromatography analysis. The other kind were acidified samples. Two kinds of acidified samples were prepared: unfiltrated and filtrated samples for measurements of total concentrations and measurements of concentrations of the dissolved fractions of elements. Water samples were filtrated on-site using cellulose acetate hydrophilic filters with a pore size of 0.20 μm. Total concentrations include concentrations of particulate and dissolved fractions of the elements. The filtered samples may include dissolved and colloidal fractions (Tang et al., 2001; Waeles et al., 2015). Some studies showed that the colloidal fraction is small compared with the dissolved fraction (Guéguen and Dominik, 2003; Ogawa et al., 2012, 2013). Therefore, the filtered samples are considered to correspond to dissolved fractions of elements. The samples were acidified with concentrated nitric acid in situ. The final concentration of HNO_3 in acidified samples was 3%. All of the water samples were collected in 50 mL polypropylene bottles prewashed with a solution

of 3% HNO_3 except for non-acidified samples for ion chromatography analysis. After completion of field work, the samples were transported to Canada.

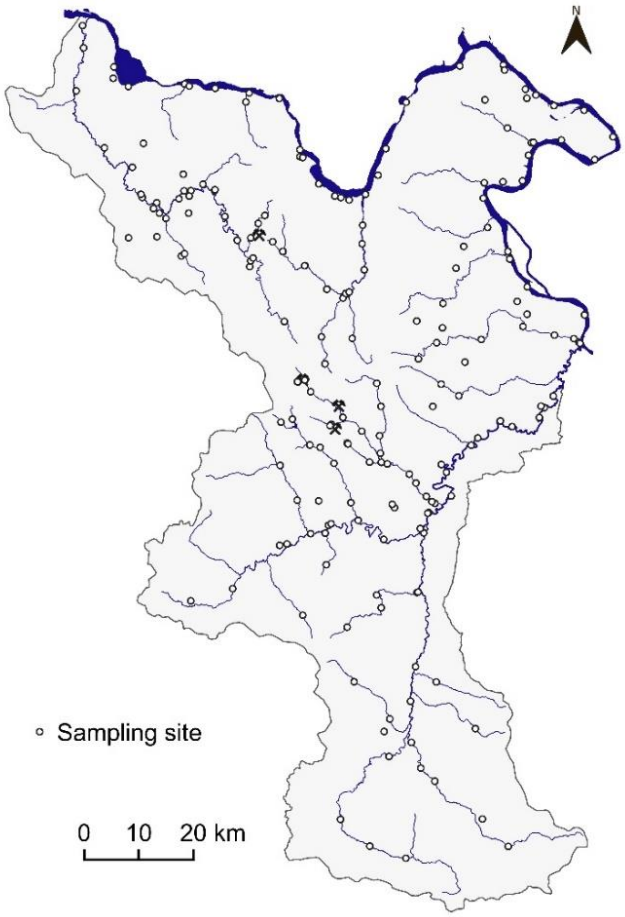


Fig. 3.1. Maps showing the distribution of river water samples collected in 2015.

3.1.2. Groundwater samples and river water samples collected in 2019

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. 3.2. The total number of groundwater samples collected in the study area was 172. The groundwater samples collected in the study area included water samples from wells (145 samples), boreholes (2 samples), cold springs (22 samples) and hot springs (3 samples). Samples of groundwater were collected all around the study with a distribution of two to three samples per 10 km^2. In addition, many groundwater samples were collected in settlements (Slatina, Zagrađe, Rgotina and Vražogrnac) that are located downstream of

the Bor mine. Eighteen, two, nine and ten groundwater samples were collected in Slatina Village (fractured aquifer), Zagrađe settlement (fractured aquifer), Rgotina Village (alluvial aquifer) and Vražogrnac Village (alluvial aquifer), respectively. These samples are located in the vicinity of rivers with pollution caused by the mining activities of the Bor mine. Additionally, 13 river water samples, including 9 samples of polluted river water and 4 samples of unpolluted water samples, were collected to compare water chemistry between river water and groundwater (Fig. 3.2b).

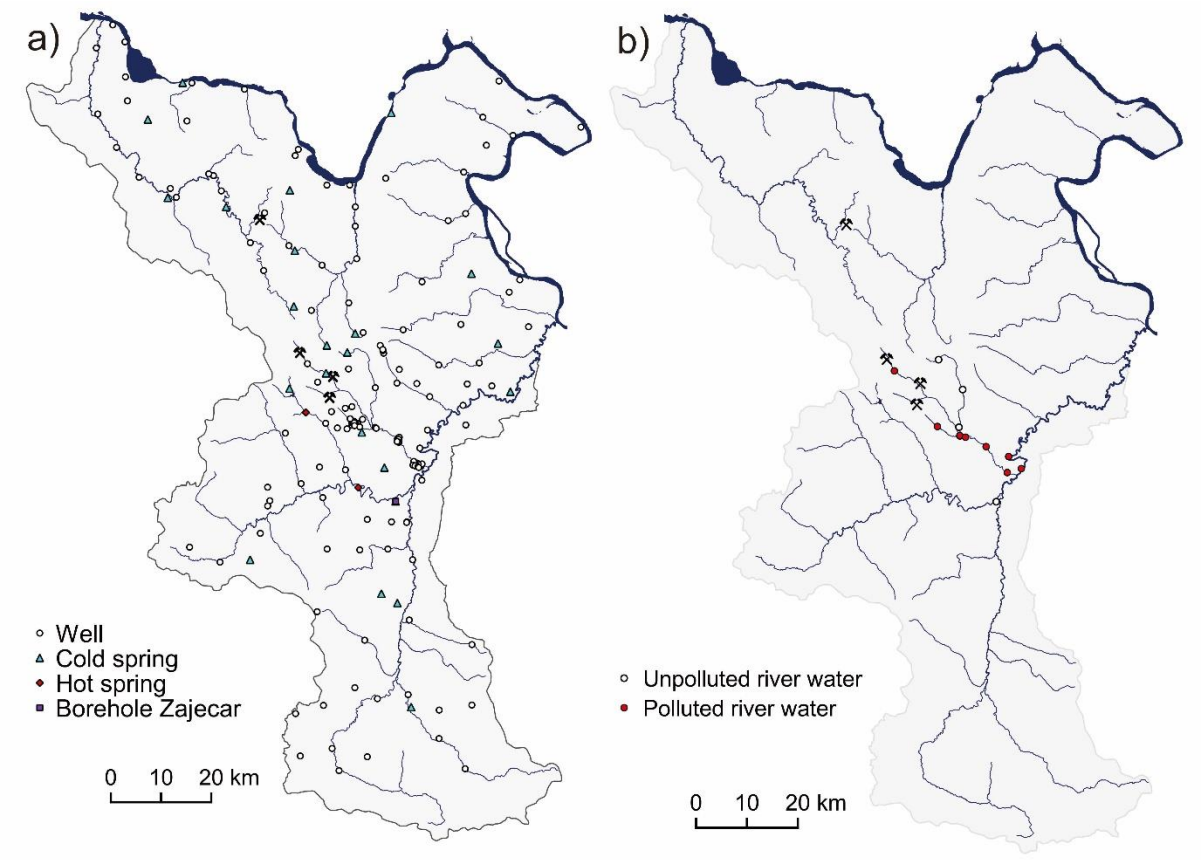


Fig. 3.2 Maps of the study area showing the distribution of a) groundwater samples collected from wells, cold springs, hot springs and deep borehole, b) unpolluted and polluted river water.

The coordinates of sampling sites were determined using GPS. Groundwater samples from wells were collected using a sampling bailer, while spring water samples and river water samples were collected directly from the spring and river, respectively. The level of the water table was measured using water level measure (YAMAYO Million) at each well. Wells were not purged before the actual sample collection for the

reason that those wells are used for local people. 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 Eh were determined by a hand-held ion/pH meter (TOA DKK, Model IM-32P). The temperature of water samples was measured using a thermometer. 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 measurement 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% HNO_3. A volume of 2.5 mL of concentrated ultrapure HNO_3 was added to the 50 mL polypropylene bottles to prevent precipitation.

After completion of field work, the samples were transported to Japan.

Fig. 3.3 Sampling collection and field measurements during summer 2019.

3.2. Laboratory analysis

All chemical analyses, for water samples collected in 2015, including ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS) were carried out in Activation Laboratories Ltd., Canada. Chemical analyses, for water samples collected in 2019, including ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS) were carried out at Akita Industrial Technology Center in Akita City, Japan. Iron and copper concentrations of river water collected in 2019 were measured by atomic absorption spectrometry (AAS) at Akita University, Japan, due to high concentrations in samples from the Bor mining area. In 2015, major anions (F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) were measured by IC, while major cations (Na, K, Mg, Ca) and trace elements (Fe, As, Cu, Mn, Zn, Cd and Pb) were measured by ICP-MS. Water samples collected in 2019 were analyzed for major anions (F^-, Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) by using IC and for trace elements (Li, Be, B, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Cd, In, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Tl, Pb, Bi, Th and U) by using ICP-MS.

Blanks were run to verify clean and uncontaminated conditions, while certified reference materials were used to verify the accuracy of the results. The accuracies for measurements in 2015 were estimated to be within ±4% except for measurements of Zn and Pb, which had accuracies of ±6% and ±7%, respectively. In 2019, the accuracies for major element measurements were estimated to be within ±5%, while the accuracy of trace elements was within ±2%, except Fe and Zn. Accuracy for measurement of Fe and Zn concentrations was estimated to be ±10%.

3.3. Determination of bicarbonate concentrations

In 2015, the concentrations of bicarbonate ion (HCO_3^-) were estimated based on the charge balance between major cations such as Na^+, K^+, Mg^{2+} and Ca^{2+} and major anions such as F^-, Cl^-, SO_4^{2-}, NO_3^- and PO_4^{3-}. In order to know the reliability of estimation of HCO_3^- concentrations based on the calculation of charge balance, HCO_3^-

concentrations of two unpolluted river water samples that were collected outside the mining areas were measured in the field using a water test kit (Kyoritsu Chemical-Check Lab., Corp.) based on the neutralization titration method in summer 2019 at the same sampling points as those in 2015. The measured bicarbonate ion concentrations were 350 mg/L (Black Timok River) and 240 mg/L (Ravna River). Bicarbonate ion concentrations in these samples were also calculated on the basis of charge balance between major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and major anions (F-, Cl-, NO3-, and SO_4^{2-} without HCO_3^-) and were estimated to be 330 mg/L (Black Timok River) and 230 mg/L (Ravna River). These concentrations are similar to the measured concentrations (Table 4.2). Therefore, it is thought that estimation of bicarbonate concentrations by charge balance provided appropriate concentrations of bicarbonate ions to some degree in this study.

In 2019, bicarbonate ion concentrations were measured in the field using a water test kit (Kyoritsu Chemical-Check Lab., Corp.). A charge balance between major cations and anions was calculated to estimate the reliability of HCO_3^- measurements conducted in the field. The difference between HCO_3^- concentrations obtained by field measurement and HCO_3^- concentrations obtained by calculation based on the charge balance was ±5%.

3.4. Data processing

3.4.1. Creation of geochemical maps

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 was used for intensive distance weighting (IDW) interpolation. After completion of the interpolation of data, the values showing concentration in the legend are back-transformed from logarithms into the original values.

3.4.2. Determination of threshold values

Threshold values for discrimination of background values and anomalous values 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).

3.4.3. Two end-member mixing model and mixing ratio

In order to determine if mixing of groundwater with polluted river water and infiltration of pollutants from the surface is present, two end-members, two-component mixing lines were created (Clark, 2015). Three polluted end-members were established, average concentrations of components measured in polluted river water, interstitial water in tailings that are present along the banks of polluted rivers and groundwater collected from a drill hole in the overburden of the Bor mine were used. For unpolluted end-member, concentrations of components measured in groundwater collected outside the mining areas were used. In addition, for each groundwater sample collected in settlements near polluted rivers mixing ratio was calculated. The mixing ratio was calculated using a simple mass balance equation, where the sum of the end-member contributions (f) is equal to 1.

$$f_{pw} + f_{upw} = 1$$

$$C = f_{pw} \cdot C_{pw} + f_{upw} \cdot C_{upw}$$

Where:

f_{pw} – polluted water end-member

f_{upw} – unpolluted water end-member

C – concentration of components in the sample for which the mixing ratio is to be calculated

C_{pw} – concentration of component measured in polluted water end-member

C_{upw} - concentration of component measured in unpolluted water end-member

Regarding and substituting one equation into the other:

$$f_{pw} = 1 - f_{upw}$$

$$C = (1 - f_{upw}) \cdot C_{pw} + f_{upw} \cdot C_{upw}$$

4. Estimation and comparison of the environmental impacts of acid mine drainage-bearing river water in the Bor and Majdanpek mining areas

4.1. Sampling sites for comparison

For estimation and comparison of the environmental impacts in the Bor mining area and Majdanpek mining area, 30 sampling points were used. Seventeen sampling points are located in the Bor mining area and thirteen sampling points are located in the Majdanpek mining area (Fig. 4.1, Table 4.1).

Table 4.1 Sampling points used for estimation and comparison of the environmental impacts in the Bor and Majdanpek mining areas.

Sample name	River name	Location
B1	Bor River	
B2	Bor River	
K1	Krivelj River	
K2	Krivelj River	
K3	Krivelj River	
K4	Krivelj River	
B3	Bela River	
B4	Bela River	
B5	Bela River	Bor mining area
B6	Bela River	
B7	Bela River	
B8	Bela River	
B9	Timok River	
B10	Timok River	
B11	Timok River	
B12	Timok River	
B13	Timok River	
M1	Small Pek River	
M2	Pek River	
M3	Pek River	
M4	Pek River	
M5	Pek River	
M6	Pek River	
M7	Pek River	Majdanpek mining area
M8	Pek River	
M9	Pek River	
M10	Pek River	
M11	Pek River	
M12	Pek River	
M13	Pek River	

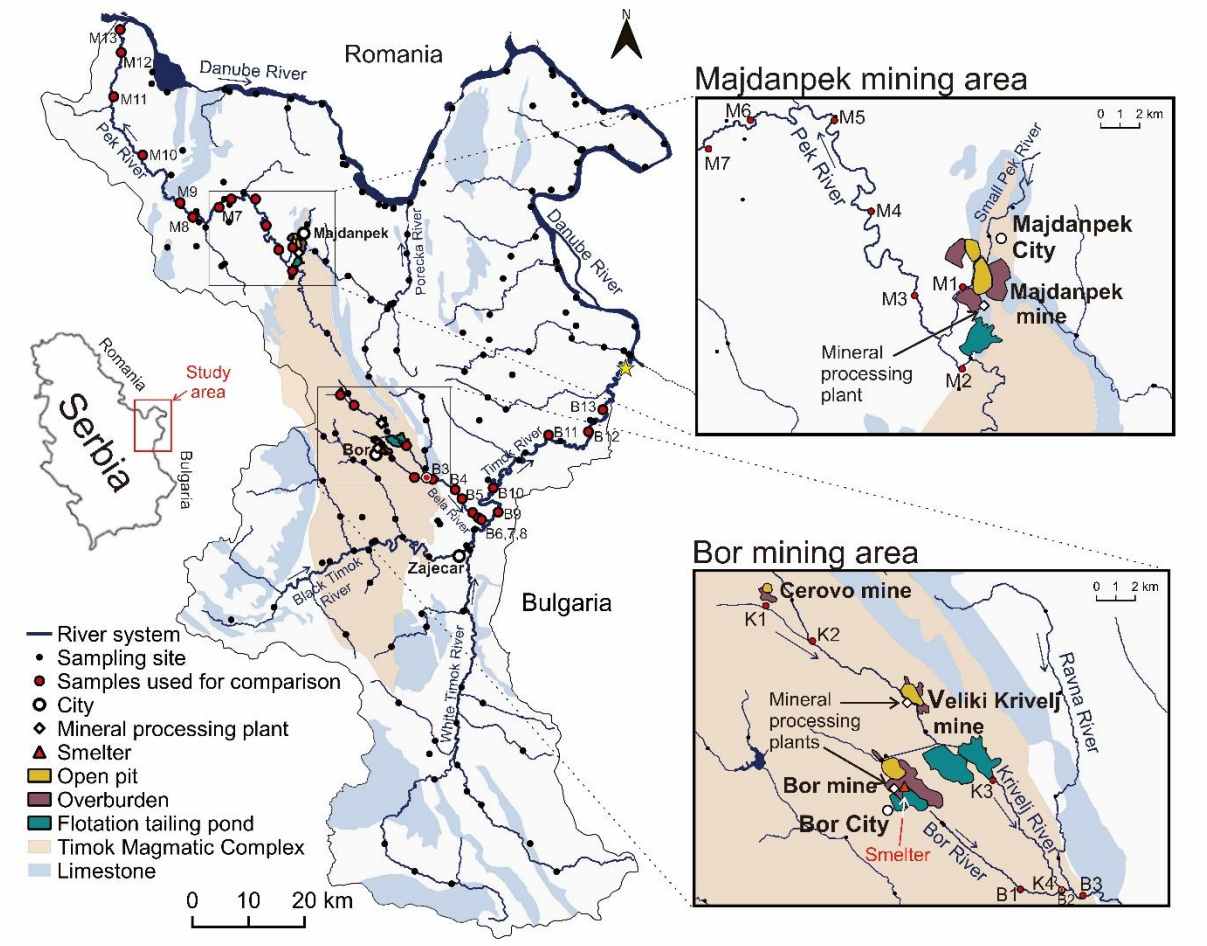


Fig. 4.1 Map showing distributions of sampling sites, open pits, overburdens, flotation tailing ponds, Timok Magmatic Complex and limestone in the study area including Bor and Majdanpek mining areas. Locations of sampling sites in Tables 4.1, 4.2 and 4.3 are shown as larger circles in red with labels on the map. The yellow star mark on the lower reach of Timok River represents the location of the sampling site described by Bird et al. (2010).

4.2. Characteristics of river water

The river water samples collected far from the Bor and Majdanpek mining areas were achromatic (transparent) (Fig. 4.2a) and had no odor. On the other hand, the color and odor of polluted river water samples in both mining areas differed depending on the sampling sites. The color of Bor River water samples varied from dark brown to yellow from upstream to downstream (Fig. 4.2b). In the lower reaches of Krivelj River (downstream of a flotation tailing pond), the color of the river water varied from yellowish to milky gray from K3 to K4 (Figs. 4.1 and 4.2c). The color of Bela River

water changed from light brown to orange and to yellowish in downstream (Figs. 4.2d, e, f). The color of Timok River water from the point of confluence of Bela River and Timok River changed from light brown to transparent in the downstream direction (Fig. 4.2g). The color of Small Pek River water and the mainstream water of Pek River in the Majdanpek mining area varied from gray to pale orange and from light brown to transparent in the downstream direction (Figs. 4.2h, i), respectively. The colors of Small Pek River and Pek River water in the Majdanpek mining area were similar to the colors of Bela River and Timok River water in the Bor mining area, respectively. Water samples from Bor River, Krivelj River and Bela River had a sewage odor, while water samples from Timok River, Small Pek River near the Majdanpek mine and Pek River were odorless. Thus, there was a difference in odor between water samples collected in the Bor mining area and those collected in the Majdanpek mining area.

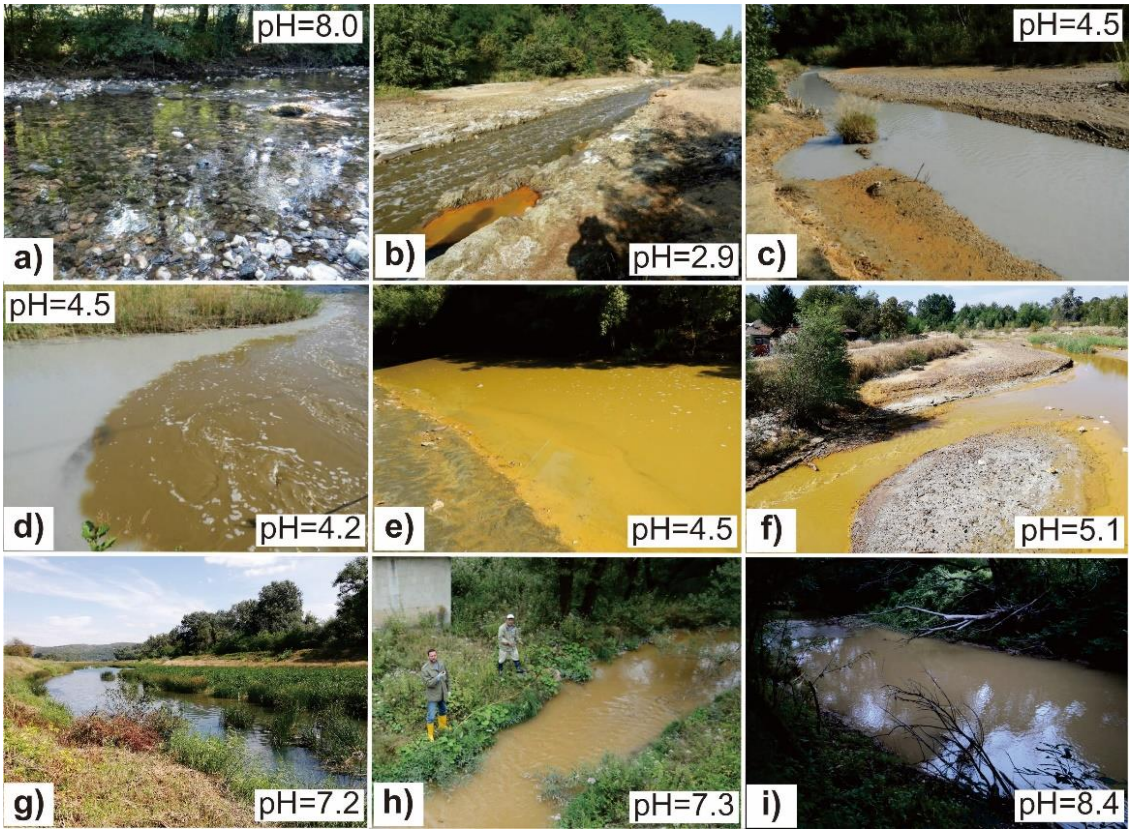


Fig. 4.2 Pictures of rivers with pollution caused by mining activities in the Bor and Majdanpek mining areas and one of the unpolluted rivers outside the mining areas: a) one of the unpolluted rivers outside the mining areas, b) Bor River (site B1), c) Krivelj River (site K4), d) confluence of Bor River and Krivelj River, e) Bela River (site B3), f) lower reach of Bela River (site B6), g) Timok River (site B10), h) Small Pek River (site M1), and i) Pek River (site M3).

Flow rates of rivers in the Bor and Majdanpek mining areas are shown in Table 4.2. Flow rates of Bor River and Small Pek River, which contains mine wastewater, are about 30000 L/min (at sites B1, B2 and B3). Flow rates of Bela River and the upper reach of Pek River are about 50000 L/min (at sites B3-B8 and M2). There is no notable difference in the flow rates of rivers in the Bor and Majdanpek mining areas.

The distribution of pH values in rivers in the study area is shown in Fig. 4.3. The pH values in rivers in the study area ranged from 2.9 to 9.0. In a watershed far from the mining areas, the pH value of all river water samples ranged from 7.5 to 9.0. The pH values of river water samples collected downstream of the Bor and Veliki Krivelj mines were acidic. The pH values of Bor River, Krivelj River and Bela River ranged from 2.9 to 4.2, from 4.4 to 6.2 and from 4.5 to 5.4, respectively (Table 4.2). After the confluence of Bela River with Timok River, the pH of Timok River changed from 6.9 in the middle reach of the river to 8.1 in the lower reach of the river. In the Majdanpek mining area, the pH value of Small Pek River, which receives wastewater from the Majdanpek mine, was close to neutral (pH=7.3, Table 4.2). The pH value of Pek River ranged from 8.4 in the upper reaches to 7.3 in the lower reaches. The values of pH of river water around the Bor and Majdanpek mines differ greatly, though the flow rates of river water in both mining areas are similar.

Table 4.2 Location of sampling sites, flow rates, pH values, Eh values and concentrations of major cations and anions in river water in the Bor and Majdanpek mining areas and maximum, minimum and mean measured values of these items in 146 samples of river water from unpolluted areas.

Sample name	Location	Flow rate	pH	Eh	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	PO_4^{3-}
		(L/min)		(mV)	(mg/L)									
B1	Bor River	28300	2.9	657	45.8	6.1	95.8	279	6.9	29.8	2010	-	1.2	<0.02
B2**		34950	4.2	492	49.9	7.8	79.4	277	1.0	32.3	1510	-	0.9	<0.02
K1*	Krivelj River	3600	7.7	370	11.7	2.1	12.9	54.9	0.1	2.1	196	-	0.6	<0.02
K2*		9900	8.8	357	16.6	2.0	17.3	91.7	0.2	4.8	254	100	1.0	<0.02
K3		36000	6.2	623	72.5	7.3	84.1	344	10.4	28.7	2360	-	1.1	<0.02
K4**		33750	4.5	498	89.2	10.9	75.5	454	2.2	41.1	2060	-	1.4	<0.02
B3**	Bela River	43400	4.5	480	60.6	10.0	74.3	327	1.8	33.1	1590	-	1.1	<0.02
B4**		55600	4.7	478	52.6	7.0	68.0	284	1.0	29.4	1360	-	1.7	<0.02
B5		47900	5.4	434	41.2	5.3	66.9	164	1.5	18.1	924	-	1.7	<0.02
B6		53750	5.1	445	38.5	5.2	64.7	260	1.3	18.5	935	-	1.2	<0.02
B7		44100	4.5	608	52.1	7.1	59.4	263	1.2	30.8	1430	-	1.5	<0.02
B8		55000	4.5	538	53.8	7.3	67.7	304	1.3	30.3	1440	-	1.4	<0.02
B9	Timok River	nd	6.9	383	23.2	3.5	24.8	113	0.3	19.0	316	100	0.3	<0.02
B10**		nd	7.2	335	30.8	4.5	24.4	112	0.2	20.3	348	-	3.7	<0.02
B11**		nd	7.9	437	9.0	2.0	10.5	89.7	0.1	7.9	118	200	1.3	<0.02
B12		nd	8.1	406	8.4	1.9	9.2	88.4	0.1	7.9	98.5	200	2.0	<0.02
B13**		nd	8.0	405	8.3	2.1	9.4	91	0.1	6.8	111	200	1.9	<0.02
Black Timok River[1]*		54700	7.2	70	38.7	5.8	11.1	55.0	0.1	6.8	55.0	220	<0.3	0.8
Black Timok River[2]*		nd	7.5	42	29.5	4.1	10.0	76.9	0.02	28.2	8.2	350[f]	<0.3	nd
Black Timok River[2]*												330[c]		
M1	Small Pek River	34200	7.3	232	35.0	6.4	167	335	0.3	19.8	1630	-	2.3	<0.02
M2*	Pek River	53900	8.2	359	10.8	2.7	12.0	85.3	0.1	11.7	155	150	<0.02	<0.02
M3		nd	8.4	364	20.2	5.8	62.2	183	0.1	5.0	680	-	<0.02	<0.02
M4		nd	8.3	360	7.2	6.2	18.5	62.0	<0.01	9.8	142	120	<0.02	<0.02
M5		nd	8.2	334	5.3	13.4	10.6	37.1	<0.01	11.2	51	120	<0.02	<0.02
M6		nd	8.0	391	6.4	3.8	15.2	51.5	<0.01	3.8	111	100	<0.02	<0.02
M7		nd	8.0	361	6.4	4.6	14.5	51.9	<0.01	4.6	105	120	<0.02	<0.02
M8		nd	7.7	427	7.8	2.5	19.1	64.5	<0.01	3.0	135	150	<0.02	<0.02
M9		nd	7.9	359	9.0	3.1	21.3	75.6	<0.01	3.9	153	200	<0.02	<0.02
M10		nd	7.3	349	8.9	3.0	19.4	69.0	<0.01	4.3	151	150	<0.02	<0.02
M11		nd	7.9	404	8.6	3.2	20.4	76.1	<0.01	4.4	140	200	<0.02	<0.02
M12		nd	7.5	421	11.5	3.6	31.0	97.5	0.1	7.8	265	150	<0.02	<0.02
M13		nd	7.6	388	10.6	36.0	28.8	104	0.1	8.1	157	150	<0.02	<0.02
Ravna River[1]*		1300	8.3	360	11.5	0.8	22.1	59.8	0.03	7.6	44.2	250	0.6	<0.02
Ravna River[2]*		nd	8.3	380	10.1	0.9	17.6	80	0.01	5.9	46.8	240[f]	1.1	nd
Ravna River[2]*												230[c]		
Typical unpolluted river water outside the mining areas (146 samples)														
MAX			9.0	500	45.0	23.5	43.6	151	1.8	30.4	154	550	6.0	0.8
MIN			7.5	64	2.1	0.4	2.4	13.1	<0.01	0.9	7.3	50	<0.3	<0.02
Mean			8.0	370	10.5	3.2	12.0	69.0	0.2	10.5	45.7	250	1.2	0.02

*, Unpolluted river water; **, Đorđievski et al. (2018); nd, no data; -, not present; [1], sample collected in 2015; [2], sample collected in 2019; [c], estimated concentrations of HCO_3^- by charge balance calculation; [f], actual measured concentrations of HCO_3^- in the field; MAX, maximum measured values in river water from unpolluted areas; MIN, minimum measured values in river water from unpolluted areas; Mean, mean values in river water from unpolluted areas; detection limits: F^-=0.01 mg/L, NO_3^-=0.3 mg/L, PO_4^{3-}=0.02 mg/L.

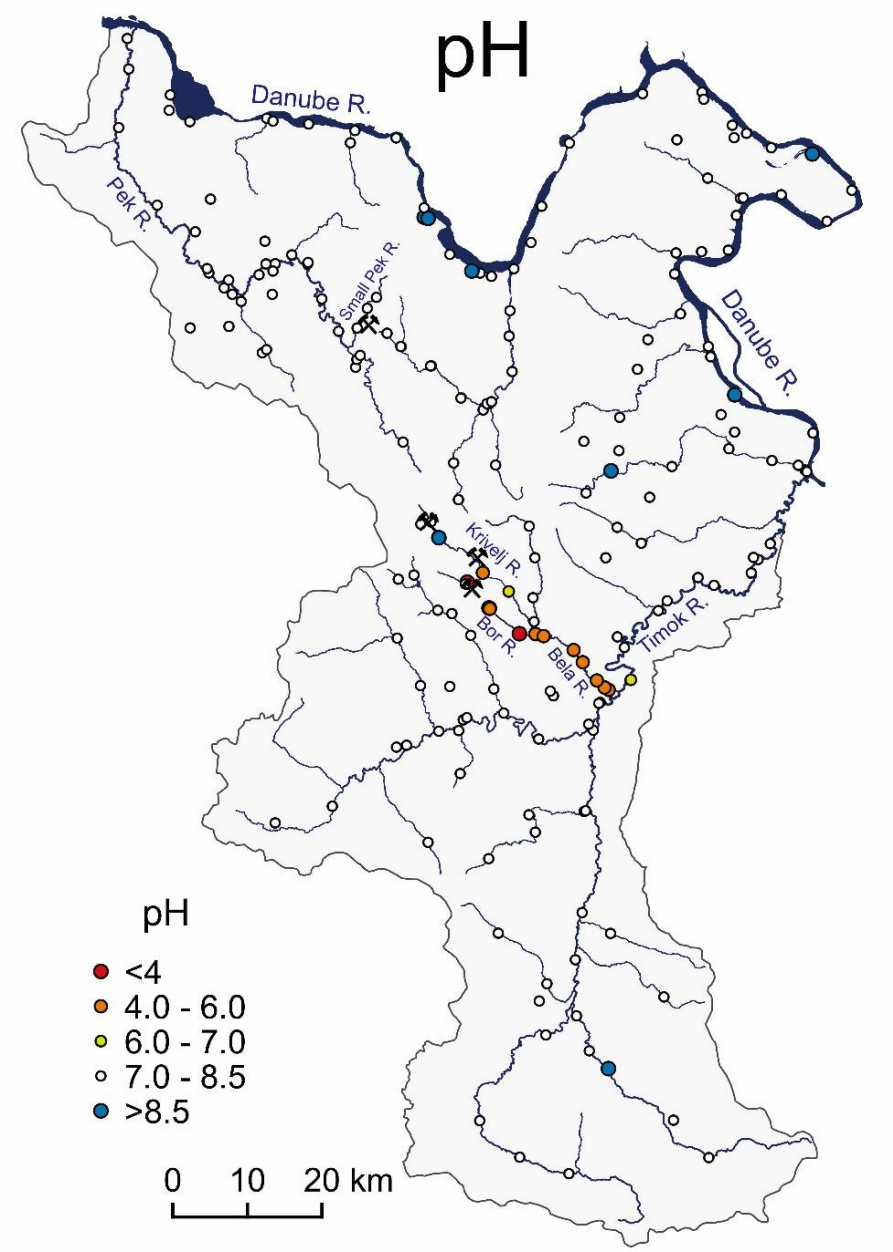


Fig. 4.3 Geochemical map showing the distribution of pH values in rivers.

4.3. Concentrations of major ions in river water

Concentrations of Na, K, Mg and Ca in river water samples collected in unpolluted areas ranged from 2.1 to 45 mg/L, from 0.4 to 23.5 mg/L, from 2.4 to 43.6 mg/L and from 13.1 to 151 mg/L, respectively. Concentrations of Na, K, Mg and Ca in polluted river water samples collected in the Bor and Majdanpek mining areas (Bor River, Krivelj River, Bela River, Small Pek River and the upper reach of Pek River)

ranged from 20.2 to 89.2 mg/L, from 5.2 to 10.9 mg/L, from 59.5 to167 mg/L and from 183 to 454 mg/L, respectively. In most of the water samples, both unpolluted and polluted river water samples, Ca and Mg were dominant cations (Fig. 4.4). Concentrations of those major cations in water samples from Timok River and lower reaches of Pek River were similar to concentrations of those cations in river water samples collected in unpolluted areas. On the other hand, concentrations of Na, Mg and Ca in water samples from Bor River, Bela River, Krivelj River, Small Pek River and the upper reach of Pek River were higher than those of Na, Mg and Ca in water samples from Timok River, lower reaches of Pek River and unpolluted rivers (Fig. 4.5), although concentrations of K in river water samples collected in unpolluted and polluted areas were similar.

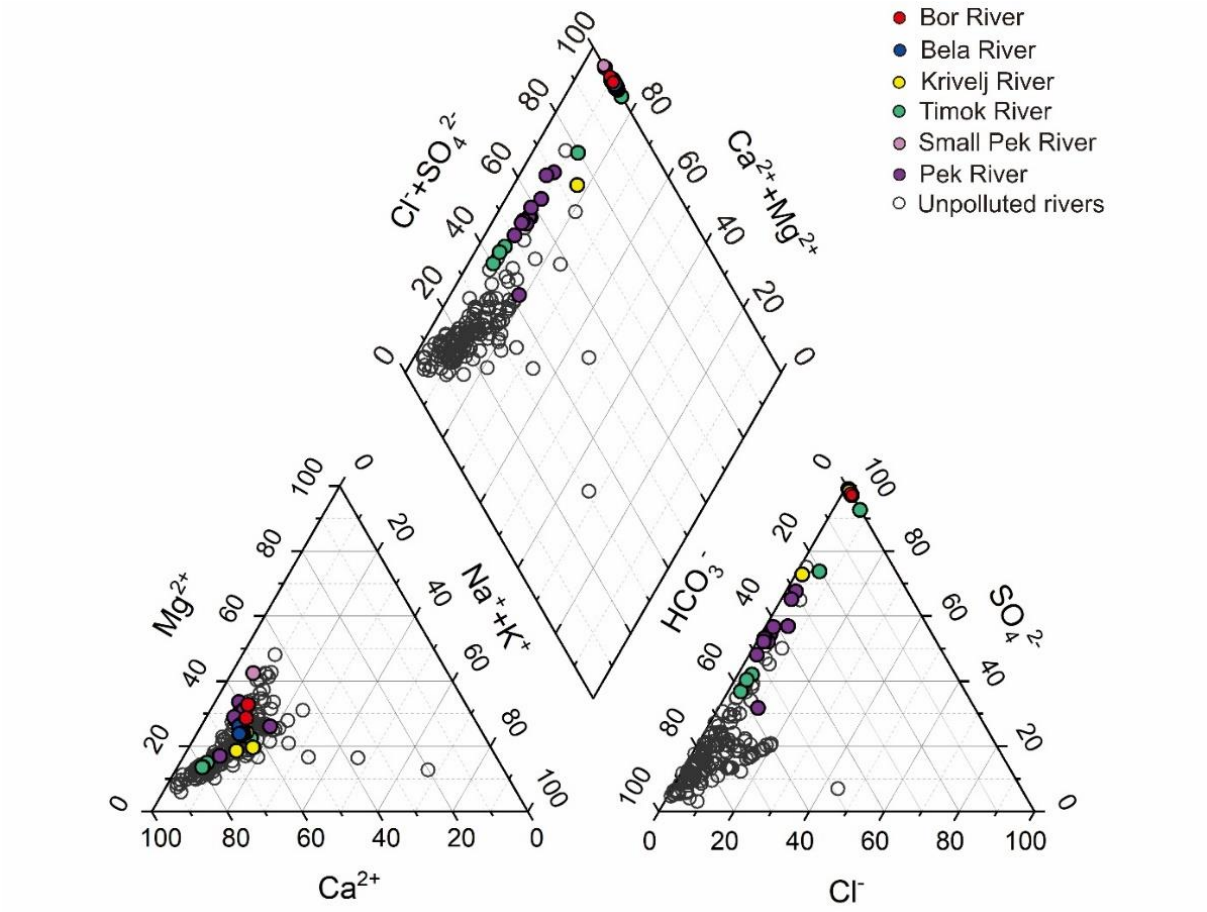


Fig. 4.4 Piper diagram showing chemical compositions of polluted river water and unpolluted river water in the study area.

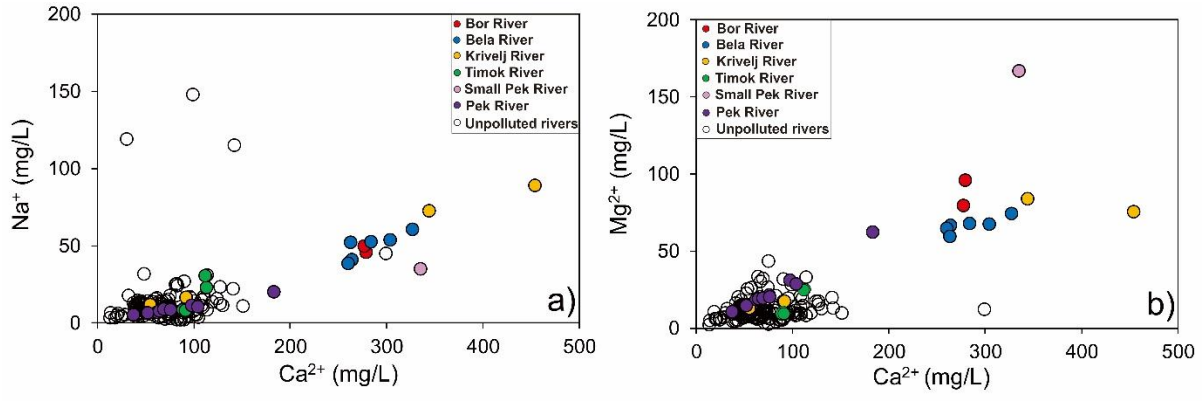


Fig. 4.5 Diagrams showing correlations between major cations in river water in the Bor and Majdanpek mining areas and those in unpolluted river water outside the mining areas: a) Ca^{2+} and Na^{+}, b) Ca^{2+} and Mg^{2+}.

Concentrations of Cl^{-}, SO_4^{2-} and HCO_3^{-} in river water samples collected in unpolluted areas ranged from 0.9 to 30.4 mg/L, from 7.3 to 154 mg/L and from 50 to 550 mg/L, respectively. In polluted water samples from Bor River, Krivelj River, Bela River, Small Pek River and the upper reach of Pek River, concentrations of Cl^{-} and SO_4^{2-} ranged from 9.8 to 41.1 mg/L and from 680 to 2360 mg/L, respectively. In these river water samples, HCO_3^{-} concentration was extremely low. There was no notable difference between concentrations of chloride in unpolluted and polluted river water samples. Concentrations of Cl^{-}, SO_4^{2-} and HCO_3^{-} in water samples from Timok River and lower reaches of Pek River ranged from 2.1 to 20.3 mg/L, from 51 to 348 mg/L and from 100 to 200 mg/L, respectively. Concentrations of SO_4^{2-} and HCO_3^{-} in water samples from Timok River and Pek River were intermediate values between those concentrations in polluted river water samples and unpolluted river water samples, although the concentrations in Timok River and Pek River were close to the concentrations in water of unpolluted rivers in the study area. River water in the unpolluted area outside the mining areas and river water in the polluted area in the Bor and Majdanpek mining areas are characterized by low SO_4^{2-} and high HCO_3^{-} concentrations and by high SO_4^{2-} and low HCO_3^{-} concentrations, respectively (Fig. 4.4). The unpolluted river water and polluted river water are classified into Ca-Mg-HCO_3-dominant type water and Ca-Mg-SO_4-dominant type water, respectively (Fig. 4.4).

4.4. Concentrations of heavy metals and arsenic in river water

In this study, two fractions of elements were considered: dissolved and particulate fractions. Filtrated samples contain colloidal and dissolved fractions. Based on some researches, the colloidal fraction is smaller compared with the dissolved fraction (Guéguen and Dominik, 2003; Ogawa et al., 2012, 2013). Therefore, concentrations of heavy metals and arsenic measured from filtrated samples are expected to be dissolved fractions. Concentrations of particulate fractions were calculated by subtracting the dissolved concentration from the total concentration. Dissolved, particulate and total concentrations of Fe, As, Cu, Mn, Zn, Cd and Pb in river water are summarized in Table 4.3.

The maximum concentrations of Fe, As, Cu, Mn, Zn, Cd and Pb as total concentrations in typical unpolluted river water samples ranged up to 350 µg/L, 5 µg/L, 30 µg/L, 70 µg/L, 20 µg/L, 0.05 µg/L and 1.5 µg/L, respectively. On the other hand, concentrations of those elements in polluted river water samples collected in the Bor and Majdanpek mining areas (Bor River, Krivelj River, Bela River and Small Pek River) were extremely high compared to the concentrations in river water samples collected in unpolluted areas. For example, total concentrations of Fe, As, Cu and Mn in river water samples collected downstream of mines ranged from 8960 to 302000 µg/L, from 5 to 2920 µg/L, from 337 to 52500 µg/L and from 4190 to 15100 µg/L, respectively. Elements with high concentrations in polluted river water in the Bor and Majdanpek mining areas were Fe, Cu and As, reflecting the types of ore deposits, which are porphyry copper deposits (Banješević et al., 2019). Concentrations of those elements in river water samples from Timok River and Pek River were lower compared with the concentrations in polluted river water samples. However, the concentrations of those elements in Timok River and Pek River were higher than the concentrations in river water samples collected in unpolluted areas.

Table 4.3 Total concentrations and concentrations of dissolved and particulate fractions of metals and arsenic in river water in the Bor and Majdanpek mining areas and maximum, minimum and mean values of total concentrations of metals and arsenic in 146 river water samples from unpolluted areas.

Sample name	Location	Fe (µg/L)			As (µg/L)			Cu (µg/L)			Mn (µg/L)			Zn (µg/L)			Cd (µg/L)			Pb (µg/L)		
		T	D	P	T	D	P	T	D	P	T	D	P	T	D	P	T	D	P	T	D	P
B1	Bor River	260000	219000	41000	2920	1740	1180	52500	52500	<0.2	8190	7940	250	6970	6130	840	224	219	5.0	313	224	89.0
B2**		79800	26400	53400	253	17.7	335	23600	24200	2100	7770	6650	1120	2500	3190	<0.5	21.9	20.4	1.5	54.9	20.4	34.5
K1*	Krivelj River	4600	100	360	1.5	1.0	0.6	12.0	5.4	6.6	28.0	13.4	14.6	4.3	66.1	<0.5	0.1	0.1	0.04	0.3	1.0	<0.01
K2*		360	100	260	1.5	1.5	<0.03	268	165	103	114	119	0.2	45.9	54.9	<0.5	0.5	0.8	<0.01	0.2	4.2	<0.01
K3		97000	26400	70600	98.7	2.9	96.0	37000	28400	8600	9700	3540	3160	1550	1770	<0.5	12.3	14.1	<0.01	2.7	10.5	<0.01
K4**		43900	11600	32300	57.3	1.3	56.0	30000	29000	1000	7100	5600	1500	680	951	<0.5	5.7	6.1	<0.01	1.1	0.4	0.7
B3**	Bela River	302000	19300	282700	1830	28.6	1801	39900	24200	15700	8190	6020	2170	3160	3010	<0.5	18.1	15.1	3.0	218	9.4	208
B4**		48000	11200	37700	395	8.3	387	2100	18900	2100	5040	5530	<0.1	1680	1840	<0.5	13.7	13.5	0.2	62.8	8.9	53.9
B5		47300	23700	23600	573	25.6	547	15600	13900	1700	4680	5070	<0.1	1640	1460	<0.5	25.5	25.8	<0.01	64.9	5.0	59.9
B6		50900	18700	22200	715	36.0	679	19700	18000	1700	4190	4770	<0.1	1640	1680	<0.5	32.8	32.2	0.6	81.9	15.4	66.5
B7		45400	240	45160	373	2.4	371	23100	17200	5900	5010	4620	390	1540	2020	<0.5	12.7	14.3	<0.01	43.1	7.8	35.3
B8		48000	2660	45340	528	1.5	527	5250	23100	29400	5250	5280	<0.1	1770	1760	10.0	14.9	15.0	<0.01	50.6	7.8	42.8
B9	Timok River	540	350	<10	5.4	2.9	2.5	645	249	366	1330	1230	100	164	261	<0.5	1.7	1.9	<0.01	0.3	0.9	<0.01
B10**		670	50	620	7.2	2.9	4.3	536	114	422	1490	1100	390	127	87.5	39.5	1.4	2.5	<0.01	0.5	0.8	<0.01
B11**		500	40	460	5.0	1.6	3.4	228	117	111	296	298	<0.1	36.6	41.9	<0.5	1.2	1.1	0.1	0.3	0.1	0.2
B12		660	10	650	7.3	3.3	4.0	185	54.4	130.6	205	155	50	23.9	15	8.9	0.4	0.3	0.1	0.7	0.2	0.5
B13**		430	10	420	6.2	3.5	2.7	125	49.7	75.3	128	111	17	20	15.5	4.5	0.4	0.3	0.1	0.5	0.1	0.4
M1 Small Pek River		8960	300	8660	4.8	0.3	4.5	337	22.3	315	15100	11400	3700	2260	1790	470	12.6	10.0	2.6	10.3	2.7	7.6
M2*	Pek River	360	100	260	1.8	1.3	0.4	8.0	4.9	3.2	53.6	20.2	33.4	7.1	10.1	<0.5	0.1	0.1	<0.01	0.4	4.5	<0.01
M3		3630	50	3580	4.1	1.0	3.1	126	13.3	113	3710	3580	130	496	202	294	3.8	2.5	1.3	28.6	0.5	28.1
M4		7830	170	7660	12.7	1.4	11.3	287	32.4	246	773	522	251	205	27.9	177.1	1.1	0.4	0.8	26.6	0.9	25.7
M5		2470	80	2390	3.9	1.3	2.6	70.4	12.6	57.8	186	102	84.0	79.2	9.1	40.1	0.2	0.1	0.2	5.6	0.4	5.3
M6		6730	120	6610	10.4	1.4	9.0	218	17.9	200	531	249	282	172	15.6	156.4	0.8	0.2	0.6	20.5	0.6	20.0
M7		5800	90	5710	10.5	1.5	9.0	163	17.2	146	426	208	218	140	14.6	125.4	0.6	0.2	0.4	20.4	0.5	19.9
M8		1830	40	1790	3.3	1.2	2.1	74.7	12.5	62.2	313	232	81.0	69.3	15.2	54.1	0.4	0.2	0.2	6.3	0.5	5.8
M9		1850	30	1820	3.2	1.2	2.0	78.6	11.0	67.6	307	211	96.0	69.5	15.0	54.5	0.4	0.2	0.2	7.5	0.3	7.2
M10		1460	30	1430	3.0	1.1	1.9	53.6	9.2	44.4	188	88.4	100	54.7	12.6	42.1	0.3	0.1	0.2	5.0	0.4	4.6
M11		1640	30	1610	3.2	1.2	2.0	52.6	9.2	43.4	153	32.9	120	50.4	9.2	41.2	0.3	0.1	0.2	7.8	0.2	4.6
M12		1910	10	1900	3.1	0.8	2.3	60.9	21.0	39.9	140	59.3	80.7	68.0	15.6	52.4	0.3	0.2	0.2	9.0	1.0	8.0
M13		2370	20	2350	3.8	0.9	2.9	71.4	7.5	36.9	155	36.3	118	79.8	13.9	65.9	0.4	0.1	0.3	12.8	0.1	12.7
Typical unpolluted river water outside the mining areas (146 samples)																						
MAX		350			5.0			30			70			20			0.05			1.5		
MIN		<10			0.1			0.8			0.9			0.7			<0.01			<0.01		
Mean		206			2.0			5.7			36.7			6.1			0.04			0.4		

*, Unpolluted river water; **, Đorđievski et al. (2018); T, total concentrations; D, concentrations of dissolved fractions; P, concentrations of particulate fractions; MAX, maximum concentrations in river water from unpolluted areas; MIN, minimum concentrations in river water from unpolluted areas; Mean, mean concentrations in river water from unpolluted areas; Detection limit: Fe=10 µg/L, As=0.03 µg/L, Cu=0.2 µg/L, Mn=0.1 µg/L, Zn=0.5 µg/L, Cd=0.01 µg/L, Pb=0.01 µg/L

Abundances of dissolved and particulate fractions of Fe, As, Cu and Mn in polluted river water in the Bor and Majdanpek mining areas were examined. Dissolved fractions of Fe and As were dominant at sampling site B1 in acidic river water (pH=2.9) of Bor River near the source of pollution (Fig. 4.2b, Fig. 4.6). The amounts of the particulate fraction of Fe in total Fe in river water samples from Timok River, Small Pek River and Pek River having a neutral to alkaline signature were larger than those in water samples from Bor River, Krivelj River and Bela River having an acidic signature. The amounts of particulate Fe and As in water samples from Timok River (pH=6.9 to 8.1) downstream of the confluence of Bela River and Timok River (B9 to B13) were similar to the amounts of particulate Fe and As in Pek River (Fig. 4.6). The amounts of particulate Fe and As in strongly polluted river water (Bor River, Krivelj River and Bela River) in the Bor mining area were different from those of particulate Fe and As in river water (Small Pek River and the upper reach of Pek River) in the Majdanpek mining area due to the difference in degrees of acidic signatures of river water in the Bor mining area. Based on the colors and chemical compositions of dissolved and particulate fractions of river water (Figs. 4.2e, f, h and i, Fig. 4.6), Fe and As in river water in the Bor and Majdanpek mining areas are thought to be transported as a particulate fraction, not Fe-bearing gangue minerals, although there are differences in the amounts of Fe and As as particulate and dissolved fractions.

The dominant chemical fraction of Cu in acidic river water of Bor River, Bela River and Krivelj River (B1-B7 and K3-K4) was the dissolved fraction (Fig. 4.6). On the other hand, the particulate Cu was dominant in water having a neutral to alkaline signature in Timok River downstream of the confluence of Bela River and Timok River (B9-B13) (Đorđievski et al., 2018). The chemical fraction of Cu differed greatly before (B8) and after (B9) mixing of acidic water of Bela River (Ca-Mg-SO_4-dominant type water) with weakly alkaline water of Timok River (Ca-Mg-HCO_3-dominant type water). The dominant chemical fraction of Cu in alkaline river water at site M1 of Small Pek River and site M3 at the upper reach of Pek River was particulate even though these rivers are near the Majdanpek mine. Manganese was mainly present as the dissolved fraction in Bor River, Krivelj River and Bela River in the Bor mining area and Small Pek River and Pek River in the Majdanpek mining area (Fig. 4.6). However, the

percentages of the dissolved fraction of Mn in total Mn in Bor River, Krivelj River and Bela River in the Bor mining area were larger than those in Small Pek River and Pek River in the Majdanpek mining area.

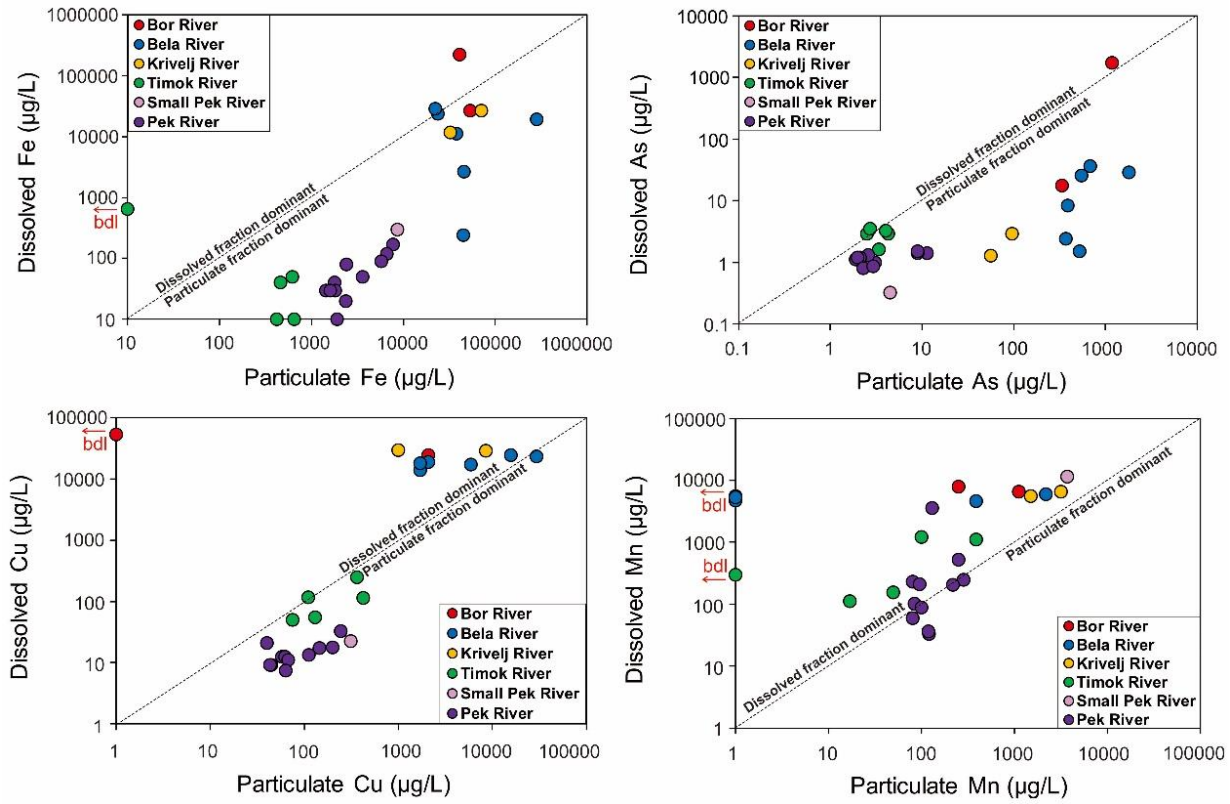


Fig. 4.6 Diagrams showing correlations between concentrations of particulate and dissolved fractions of Fe, As, Cu and Mn in river water in the Bor and Majdanpek mining areas. bdl: below the detection limit.

Based on the general features of the chemical fractions of Fe, As and Cu in rivers in the Bor and Majdanpek mining areas, the chemical fractions of those elements in rivers having an acidic signature in the Bor mining area (Bor River, Krivelj River and Bela River) is different from that of those elements in Small Pek River and Pek River having neutral to weakly alkaline signature in the Majdanpek mining area. On the other hand, the general features of the chemical fractions of those elements in Small Pek River and Pek River are similar to those of the chemical fraction of these elements in Timok River after the confluence of Bela River and Timok River, because of neutral to a weakly alkaline signature.

4.5. Estimation of environmental impact

4.5.1. Estimation of threshold values based on total concentrations and distribution of polluted areas

The occurrence of metal-rich water is common in mining areas. Therefore, it is necessary to know the natural background of elements in unpolluted areas that surround impacted areas to discriminate against the polluted area. Data for natural background concentrations should be helpful for monitoring and remediation (Runnels et al., 1992). One of the appropriate ways to estimate background concentrations is the determination of threshold values by Sinclair (1974, 1986, 1991) (Reimann et al., 2005). The threshold value was estimated as the background of $\mu+2\sigma$ (see chapter 3.4.2.). In this study, determination of threshold values for eight components (SO_4^{2-}, Fe, As, Cu, Mn, Zn, Cd and Pb) was performed. In Figs 4.7 and 4.8., histograms and probability diagrams used for the determination of threshold values for SO_4^{2-}, Fe, As, Cu, Mn, Zn, Cd and Pb are shown.

Estimated threshold values of SO_4^{2-}, Fe, As, Cu, Mn, Zn, Cd and Pb are shown in Table 4.4 with the environmental limits of surface water in Serbian regulations (Republic of Serbia, 2012b). The estimated threshold values for SO_4^{2-}, Fe, As, Cu, Mn, Zn, Cd and Pb were 180 mg/L, 350 µg/L, 10 µg/L, 35 µg/L, 100 µg/L, 100 µg/L, 0.1 µg/L and 2 µg/L, respectively. The distributions of concentrations above and below the threshold values are shown in geochemical maps (Fig. 4.9). The geochemical maps show areas where there is a pollution of the river water. In the maps, background concentrations (concentrations below threshold values) and anomalous concentrations (concentrations above threshold values) are indicated by open and colored closed circles, respectively. Based on the chemical composition of river water in the Bor and Majdanpek mining areas, it is evident that mining activities in the Bor and Majdanpek mines have had a great environmental impact on river water. However, the sizes of areas in which there has been an environmental impact have not been clarified until now. One of the methods for determining the size of an area in which there has been an environmental impact is the estimation of the length of a river with pollution based on

threshold values to separate anomalous concentrations from background concentrations of elements in the river water

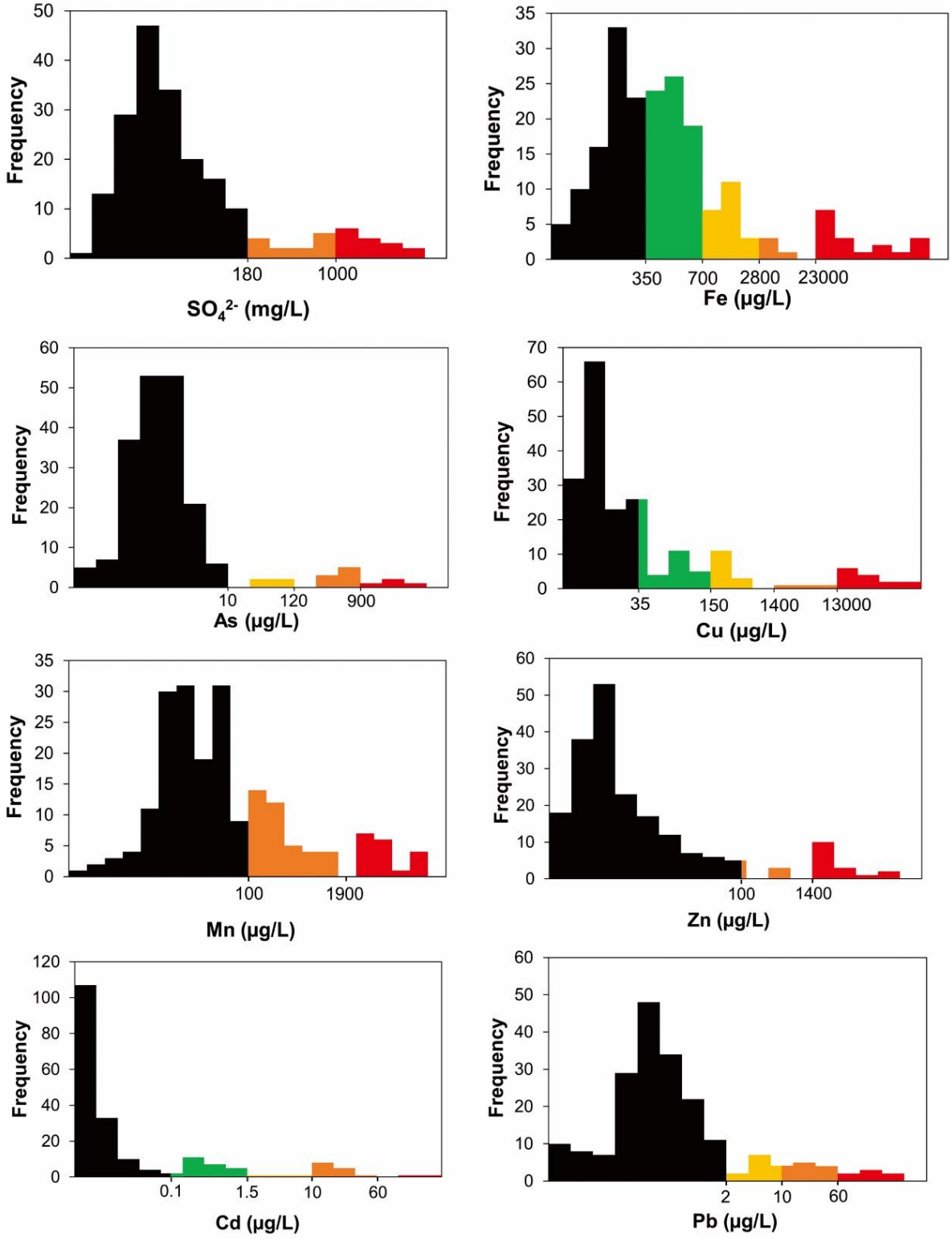


Fig. 4.7 Histograms used for estimation of threshold values of SO_4^{2-}, Fe, As, Cu, Mn, Zn, Cd and Pb in river water. Background values on histograms are shown in black, while anomalous values are marked by different colors.

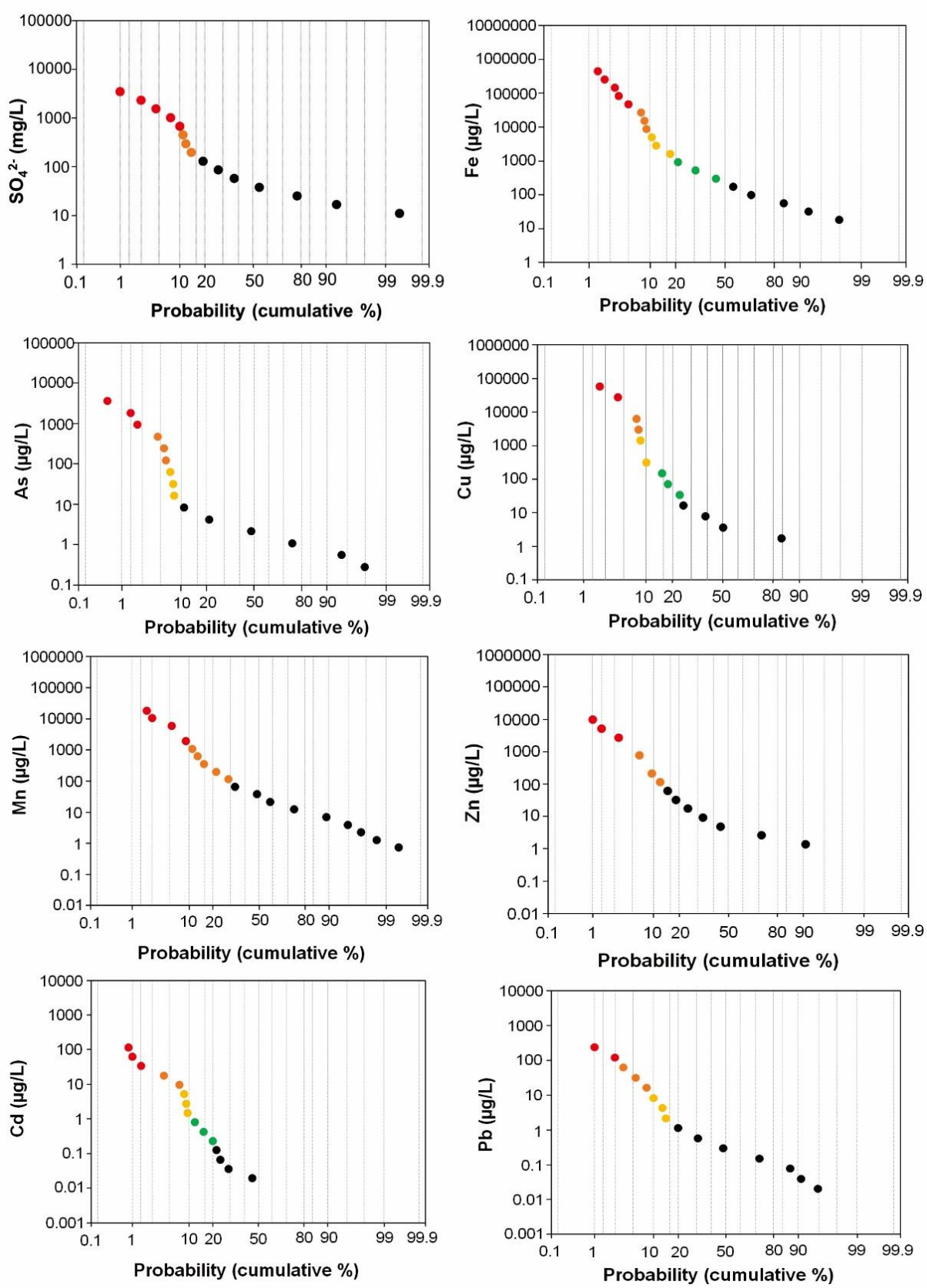


Fig. 4.8 Probability diagrams used for estimation of threshold values of SO_4^{2-}, Fe, As, Cu, Mn, Zn, Cd and Pb in river water. Background values on probability diagrams are shown in black, while anomalous values are marked by different colors.

Table 4.4 Estimated threshold values and classification of river water by Serbian regulations for quality of surface water.

Class Ecological status	I Excellent	II Good	III Moderate	IV Weak	V Bad	Threshold value
SO_4^{2-} (mg/L)	50	100	200	300	>300	180
Fe (µg/L)	200	500	1000	2000	>2000	350
As (µg/L)	<5	10	50	100	>100	10
Cu (µg/L)	40	40	500	1000	>1000	35
Mn (µg/L)	50	100	300	1000	>1000	100
Zn (µg/L)	300	1000	2000	5000	>5000	100
Cd (µg/L)	-	-	-	-	-	0.1
Pb (µg/L)	-	-	-	-	-	2

-, not specified. Surface waters of classes I and II correspond to excellent and good ecological status, respectively. Waters classified in these classes can be used for drinking purposes with prior treatment by filtration and disinfection. Water classified into class III corresponds to moderate ecological status. Surface water in this class can be used for drinking water supply with prior treatment by coagulation, flocculation, filtration and disinfection. Water of class IV corresponds to weak ecological status. Water in this class can be used for drinking water supply after using a combination of the above-mentioned treatments and advanced treatment methods and is also appropriate for irrigation and industrial use. Water classified in class V corresponds to bad ecological status and cannot be used for any purpose (Republic of Serbia, 2012b).

Lengths of rivers in the Bor and Majdanpek mining areas containing high concentrations of SO_4^{2-}, Fe, Cu, Mn, Zn and Pb were estimated. The concentrations of SO_4^{2-}, Fe and Cu at site B8 of Bela River, 30 km from the Bor mine, were 1440 mg/L, 48000 µg/L and 52500 µg/L, respectively. On the other hand, the concentrations of SO_4^{2-}, Fe and Cu at site M3 of Pek River, 5 km from the Majdanpek mine, were 680 mg/L, 3630 µg/L and 126 µg/L, respectively (Tables 4.2 and 4.3, Figs. 4.9 a, b, d). A similar tendency was found in the relationship between the lengths of rivers and concentrations of As, Mn, Zn, Cd and Pb in river water for Bela River and Pek River. The lengths of highly polluted rivers in the Bor mining area (Bor River and Bela River) were greater than those of highly polluted rivers in the Majdanpek mining area (Small Pek River and upstream of Pek River). Therefore, the area of pollution in the Bor mining area is larger than the area of pollution in the Majdanpek mining area.

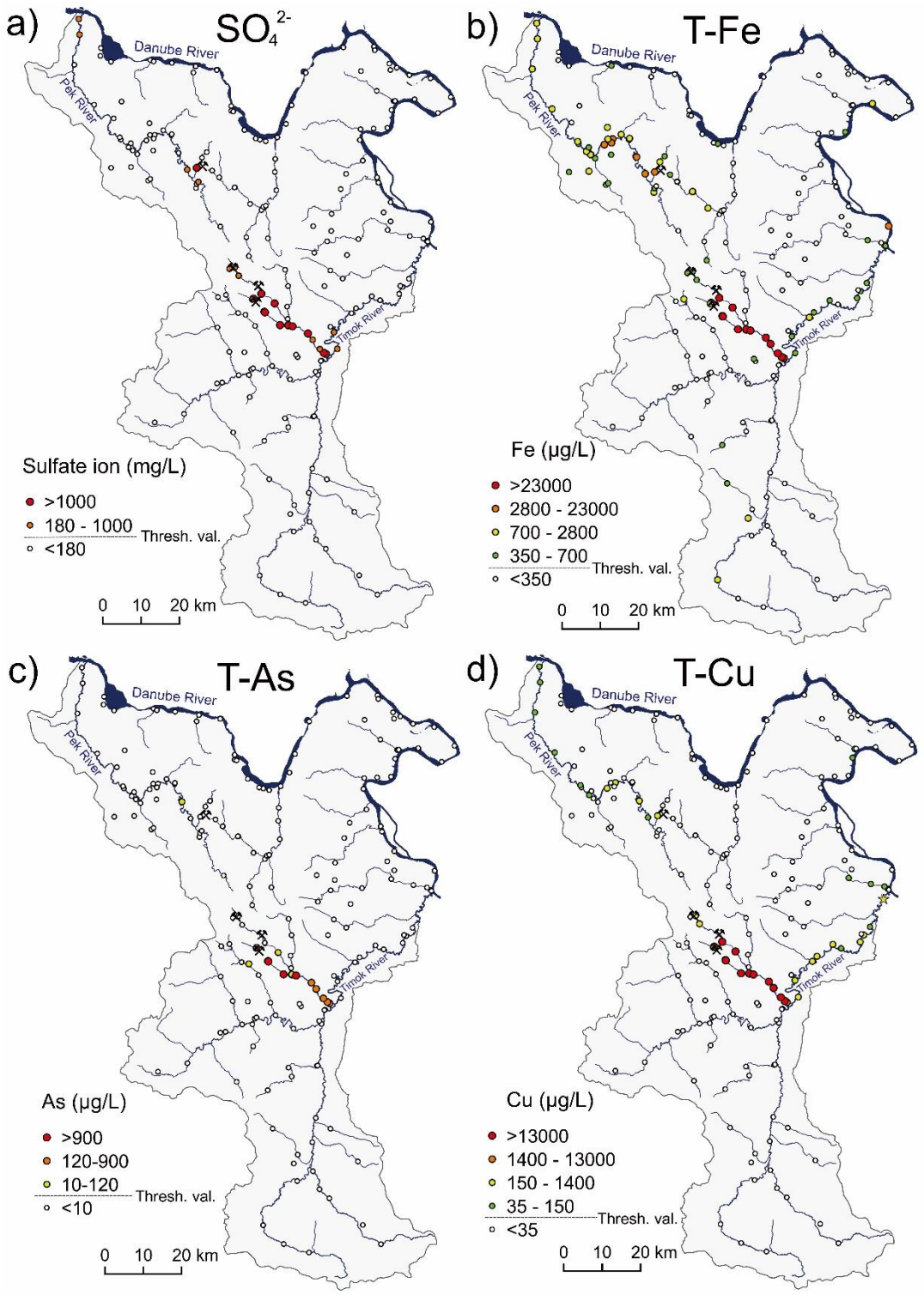


Fig. 4.9 Geochemical maps showing distributions of sulfate, heavy metals and arsenic in river water. The geochemical maps show areas where there is a pollution of the river water. Open circles indicate concentrations below the estimated threshold values. Colored closed circles indicate concentrations above the estimated threshold values. a) SO_4^{2-}, b) total Fe, c) total As, d) total Cu (yellow star mark: location of the sampling point and data described by Bird et al. (2010)), e) total Mn, f) total Zn, g) total Cd, h) total Pb.

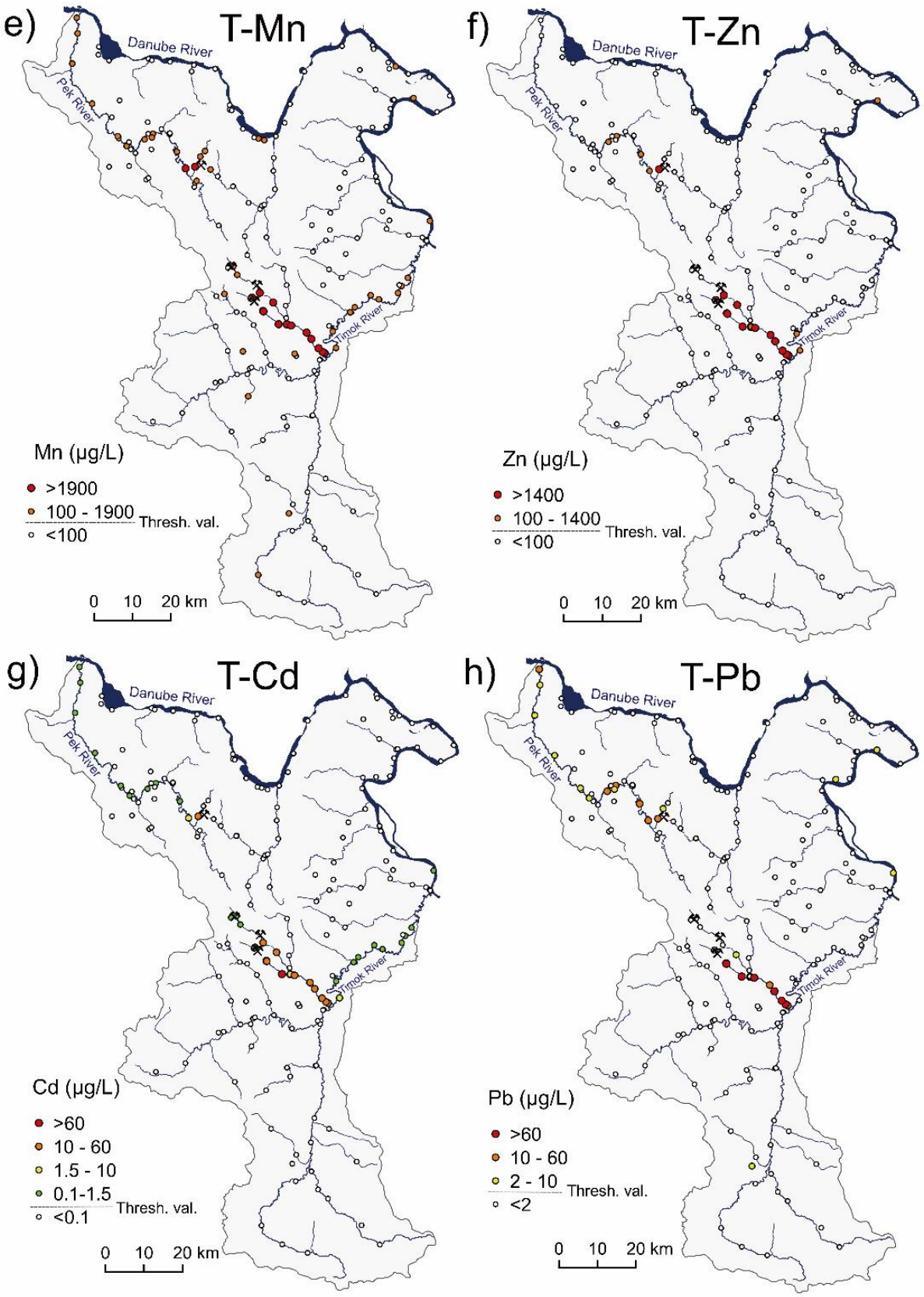


Fig. 4.9 (continued)

Lengths of rivers with higher concentrations of Fe and Cu than the estimated threshold values were also examined to determine the effects of mining activities on pollution in Danube River. Lengths of rivers with anomalous concentrations of Fe and Cu were more than 100 km in the Bor and Majdanpek mining areas (Fig. 4.9). The same results were obtained for Mn and Cd. These results suggest that the pollution caused by mining activities reaches the Danube River. However, due to the large flow rate of water in Danube River, the effect of dilution of the river water of Pek River by the water of Danube River is large. Therefore, anomalous values of elements caused by pollution from the Majdanpek mining area are not observed in the water of Danube River (Fig. 4.9). On the other hand, there is a high Cu concentration in the river water of Timok River near the confluence with Danube River (within 2 km) (Fig. 4.9d) based on Bird et al. (2010). In addition, contamination of soil and riverbed sediments of Danube River after the confluence with Timok River by tailings that were transported from the Bor mining area has been reported (Bird et al., 2010; Pavlović et al., 2016). There is a possibility that mining activities of the Bor mining area have an environmental impact on the river water of Danube River.

4.5.2. Estimation of quantities of heavy metals and arsenic involved in the environmental impact

For a comparison of the environmental impact in the Bor mining area and that in the Majdanpek mining area, the quantities of heavy metals and arsenic that are transported through river water to the downstream area were estimated. Based on the concentrations of elements in river water and flow rate, quantities of Fe, As, Cu and Mn in Bela River and Small Pek River were estimated at site B3 of Bela River and site M1 of Small Pek River on an annual basis (Figs. 4.1 and 4.10). The estimated quantities of Fe and As transported downstream through river water were about 6900 and 42 t/year, respectively, for Bela River (B3) and 160 and 0.1 t/year, respectively, for Small Pek River. The estimated quantities of Cu and Mn transported by river water of Bela River (B3) were 910 and 187 t/year, respectively. The quantities of Cu and Mn transported by Small Pek River (M1) were estimated to be about 6 and 272 t/year, respectively.

The acidic water of the Bela River in the Bor mining area transports large quantities of the elements downstream compared with the quantities of these elements in the water of Small Pek River except for Mn (Fig. 4.10). The ore reserves in the Bor mining area are 2.6-times larger than those in the Majdanpek mining area (Jelenković et al., 2016). However, the quantity of Cu that is transported to river water downstream of the Bor mine is about 150-times larger than that transported in river water downstream of the Majdanpek mine. The environmental impact on Bela River in the Bor mining area is larger than that on Small Pek River in the Majdanpek mining area. In the Bor mining area, there are some open pits, an underground mine, mineral processing plants and smelter. On the other hand, in the Majdanpek mining area there are two open pits and mineral processing plants, however, there is no smelter. In addition, ores from the Majdanpek mine are transported to the smelter in the Bor mine as concentrates and refined into metals with ores used from the ore deposits in the Bor mining area. The wastewater from metallurgical facilities (including a smelter) of the Bor mine contains high concentrations of heavy metals and arsenic (Đorđievski et al., 2018). In the Bor mining area, the wastewater from metallurgical facilities (including a smelter) is discharged into Bor River without any treatment. The difference between the environmental impact in the Bor mining area and the Majdanpek mining area was probably caused by the discharge of the untreated wastewater from the metallurgical facilities of Bor mine. Therefore, for environmental reclamation of the Bor mining area, the priority is countermeasures of environmental reclamation for the wastewater from the mining facilities of the Bor mine.

Đorđievski et al. (2018) suggested that particulate fractions of heavy metals and arsenic precipitated in an area downstream of the confluence of Timok River having a neutral signature and Bela River having an acidic signature. Accumulation of particulate fractions of copper and arsenic in riverbed sediments in Timok River after the confluence with Bela River (Bor mining area) and the upper reach of Pek River (Majdanpek mining area) was also reported by Ishiyama et al. (2016). If there are events such as floods, riverbed sediments containing high concentrations of heavy metals and

arsenic might be transported to downstream areas. Therefore, there is a risk of pollution of Danube River.

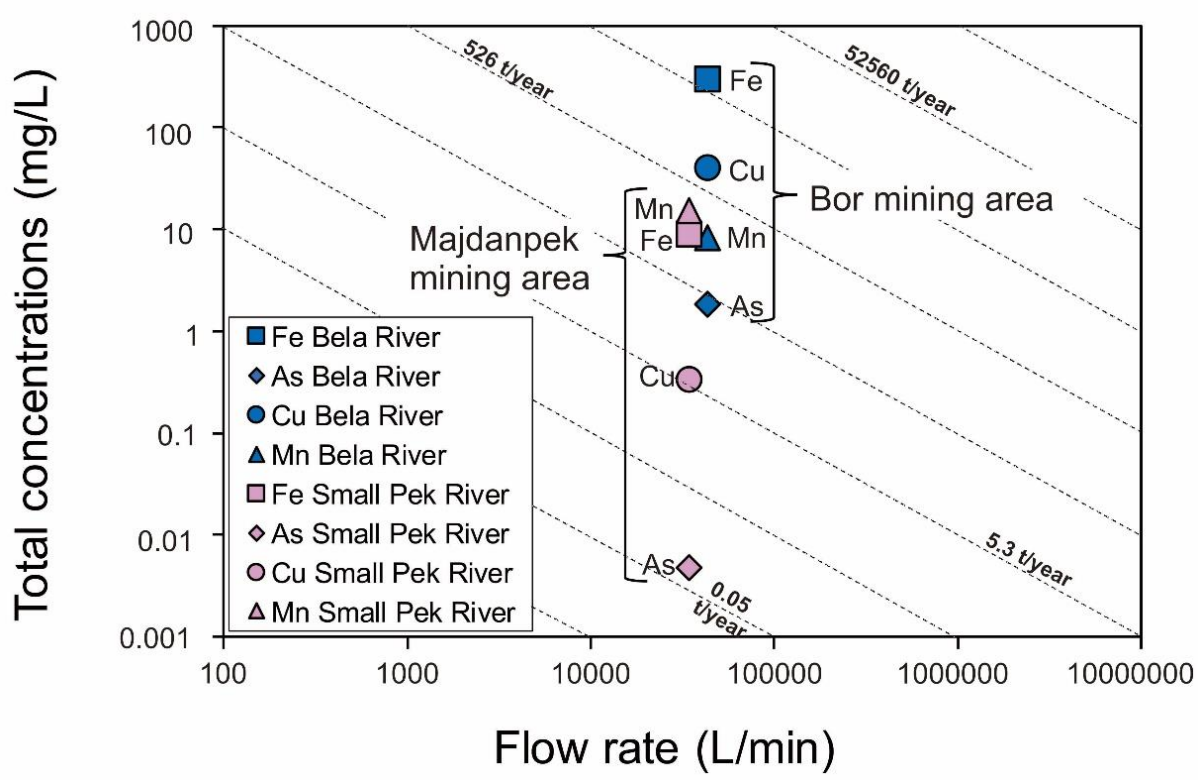


Fig. 4.10 Diagram showing degrees of environmental impact based on quantities of Fe, As, Cu and Mn transported downstream in the Bor and Majdanpek mining areas.

All the results are obtained for river water samples collected during the summer season which is the dry season, there is the possibility that the results may be different during the rainy season. Environmental impact in all seasons should be investigated in the future.

4.6. General features of the chemical composition of river water for environmental reclamation

To determine the limits of reduction in concentrations of SO_4^{2-}, Fe, As, Cu, Mn and Zn after environmental countermeasures, it is necessary to consider the relations between estimated threshold values and Serbian regulations for quality of surface water.

The estimated threshold values for Cu and Zn belong in class I, while the estimated threshold values for Fe, As and Mn belong to class II of the Serbian regulations for quality of surface water. The estimated threshold value for SO_4^{2-} belongs in class III of the Serbian regulations for quality of surface water (Table 4.4). Based on these relations, a reduction in the concentrations of these components in river water in the Bor and Majdanpek mining areas would be possible if appropriate environmental countermeasures such as artificial neutralization for these mining areas are carried out.

For environmental reclamation of the Bor and Majdanpek mining areas, remediation of wastewater prior to releasing the wastewater is necessary. It is also important to determine whether the river water has remediation ability in the natural system or not. In order to determine the remediation ability of river water in the Bor and Majdanpek mining areas in the natural system, a comparison of acid mine drainage-bearing river water under different geological settings was carried out to determine how geological factors can contribute to the reduction of pollution. Therefore, a comparison of the chemical composition of river water in the Bor mining area, where limestone is dominant, and the chemical composition of river water in mining areas in the Iberian Pyrite Belt in Spain, in which there is no limestone, was carried out. Polluted water of Bor River and Bela River containing high concentrations of SO_4^{2-}, Fe, As, Cu and Mn flows into Timok River, 30 km downstream from the Bor mine (Figs. 4.1 and 4.9). The concentrations of these components in the water of Timok River were greatly decreased after mixing the polluted water of Bela River (Ca-Mg-SO_4-dominant type water) with unpolluted water of Timok River having neutral pH and a high bicarbonate concentration (Ca-Mg-HCO_3-dominant type water). On the other hand, in the Iberian Pyrite Belt in Spain, acidic polluted river waters (Odiel River; pH of about 3) from the mining area flows into the Atlantic Ocean more than 140 km away without a major change in the pH value (Sainz et al., 2003; Sánchez España et al., 2005; Nieto et al., 2007). The lengths of rivers having acidic pH in the Bor mining area are smaller than the length of Odiel River in the Iberian Pyrite Belt. The geology of the Iberian Pyrite Belt is composed predominantly of volcanic rocks, shale and sandstones without limestone (Saez et al., 1999). The bicarbonate ion content in Odiel River is low due to the absence of limestone and acidic pH of the river water. In addition, the average

bicarbonate ion concentration of unpolluted water in natural streams from the tributaries of Odiel River is about 70 mg/L (Sánchez España et al., 2005). The average concentration is only about one-third of the average bicarbonate ion concentration in unpolluted river water in the study area in Eastern Serbia, where limestone is dominant (Ciobanu et al., 2002; Koželj, 2002; Jelenković et al., 2016). Moreover, the concentration of bicarbonate ion in river water in the study area in Eastern Serbia is also higher than the world average of bicarbonate ion concentration (92 mg/L) in river water in areas where igneous rocks are dominant without limestone (Oyarzún et al., 2013; Đorđievski et al., 2018). Due to the presence of a high concentration of bicarbonate ion in unpolluted water of Timok River (Ca-Mg-HCO_3-dominant type water), the polluted water of Bela River is neutralized by the buffering reaction shown below:

$$HCO_3^- + H^+ \rightleftarrows H_2CO_{3(aq)} (= CO_{2(g)} + H_2O).$$

Therefore, the length of strongly polluted rivers in Eastern Serbia including the Bor mining area is shorter than that of strongly polluted river water in the Iberian Pyrite Belt. Unpolluted river water in the study area in Eastern Serbia has the ability for environmental reclamation under natural conditions. If there are appropriate countermeasures such as artificial neutralization for wastewater from metallurgical facilities (including a smelter) with reduction of the quantity of wastewater from flotation tailings and overburdens, there is a possibility that the quality of river water in the Bor mining area will be greatly improved.

5. Stable isotopes, geochemistry and pollution of groundwater

5.1. δD and $\delta^{18}O$ values of groundwater

Results of δD, $\delta^{18}O$ and d-value (deuterium excess) in groundwater and river water samples, collected in 2019, in the study area are shown in appendices 10, 11 and 12. The results of stable isotopes are reported as δD and $\delta^{18}O$ values relative to the VSMOW (Vienna Standard Mean Ocean Water, Fig. 5.1) and in per mil (‰) according to the formula of McKinney et al. (1950):

$$\delta D = \frac{\left(\frac{D}{H}\right)_{sample} - \left(\frac{D}{H}\right)_{Std}}{\left(\frac{D}{H}\right)_{Std}} \times 1000$$

$$\delta^{18}O = \frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample} - \left(\frac{^{18}O}{^{16}O}\right)_{Std}}{\left(\frac{^{18}O}{^{16}O}\right)_{Std}} \times 1000$$

The meaning of the d-value is shown in Fig. 5.1. Deuterium excess (d-value) was proposed by Dansgaard (1964), the value is defined for a slope 8, and is calculated by the following equation:

$$d = \delta D - 8 \times \delta^{18}O.$$

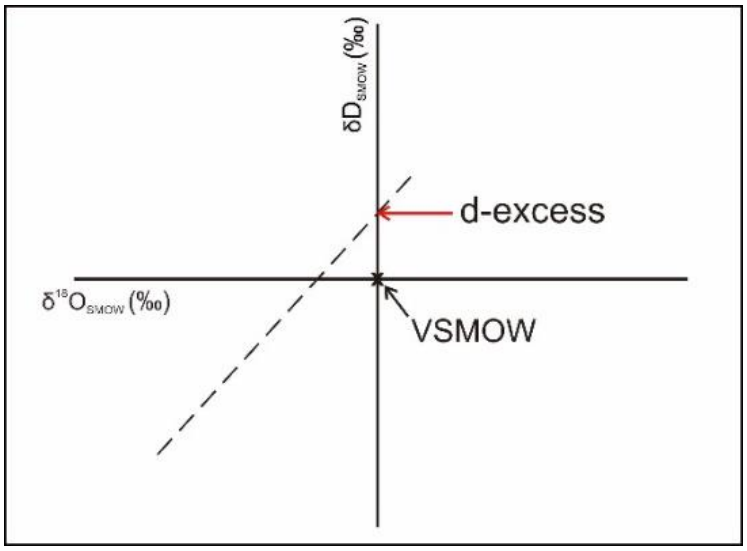


Fig. 5.1 Diagram showing the meaning of d-value (deuterium excess) and position of VSMOW.

Based on the previous study, δD and $\delta^{18}O$ values of groundwater are similar to average annual values of δD and $\delta^{18}O$ in precipitations. For examination of δD and $\delta^{18}O$ values of groundwater, the distribution of average annual values of δD and δ18O in precipitations in a wide area is necessary. Due to the lack of data of stable isotopes of precipitation in and around the study area, δD and $\delta^{18}O$ values of average values of annual precipitations in European countries were summarized in Fig. 5.2.

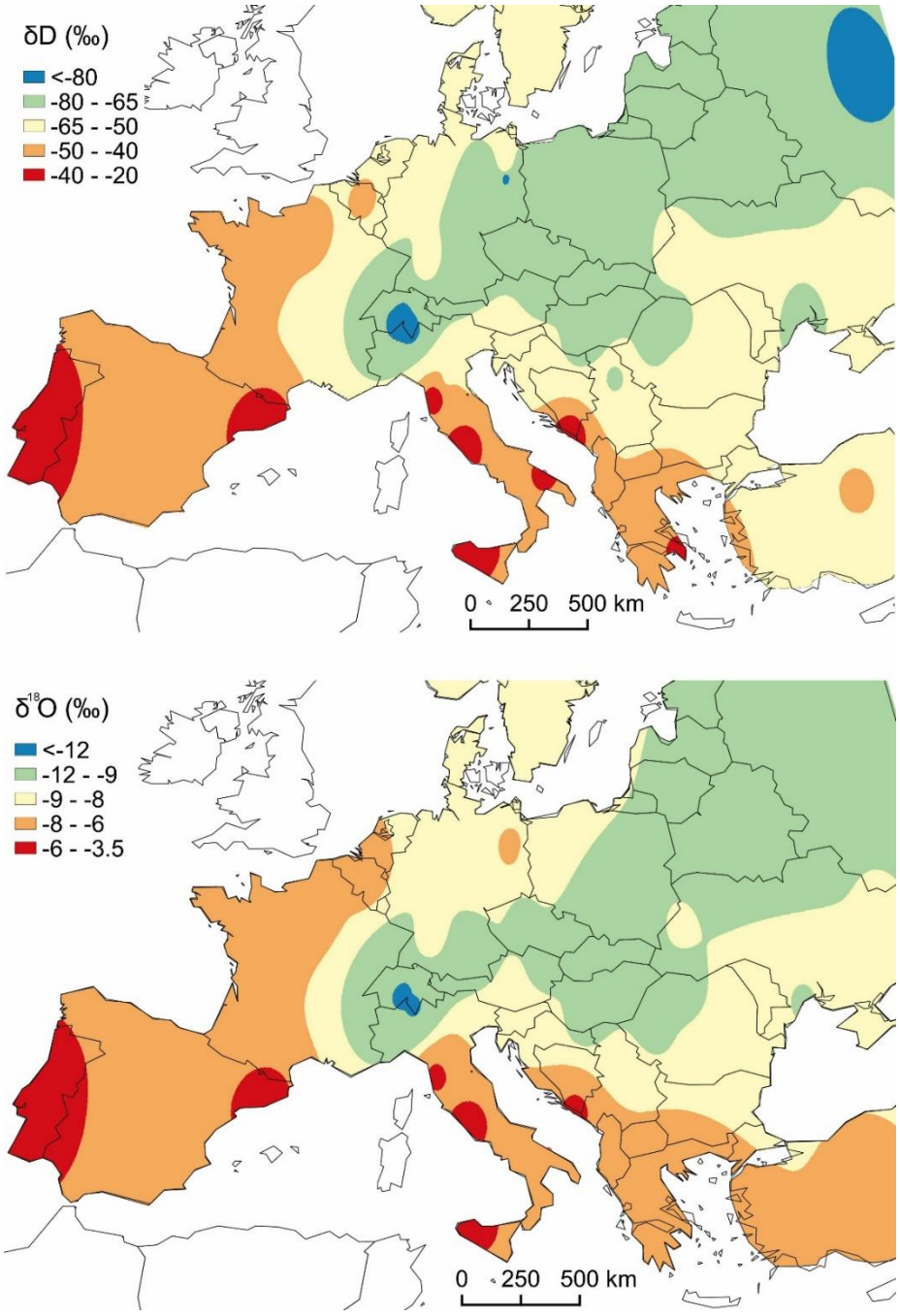


Fig. 5.2 The distribution of long-time average values of δD and $\delta^{18}O$ in precipitation in Europe (IAEA, 2021).

The European continent is under the influence of four main air masses in a year, Atlantic Ocean air mass, Mediterranean Sea air mass, East Europe air mass and North Europe air mass (Bădăluța et al., 2018). In the regions of the Atlantic Ocean and the Mediterranean Sea, precipitations have higher δD and $\delta^{18}O$ values. On the other hand, in the region of the Alps and the Carpathian Mountains, precipitations show lower δD and $\delta^{18}O$ values, as well the north-eastern part of the European continent. Based on some researches in eastern and central Europe, the Mediterranean Sea and the Atlantic Ocean are the main sources of precipitation and fewer amounts of precipitations are coming from Northern and Eastern Europe (Bottyán et al., 2017; Nagavciuc et al., 2019). However, precipitations in the Carpathian region (study area corresponds to the southern part of the Carpathian region) are depleted in δD and $\delta^{18}O$ values compared with the precipitations in coastal regions of the Atlantic Ocean and the Mediterranean Sea. Moreover, it was observed that precipitations in areas of higher altitudes are characterized by lower δD and $\delta^{18}O$ values compared to precipitations in areas of lower altitude in the same regions (Holko, et al., 2012; Nagavciuc et al., 2019). The model of the altitude effect is shown in Fig. 5.3. Therefore, δD and $\delta^{18}O$ values of precipitations in eastern and central Europe are affected by both different air masses and altitude effects.

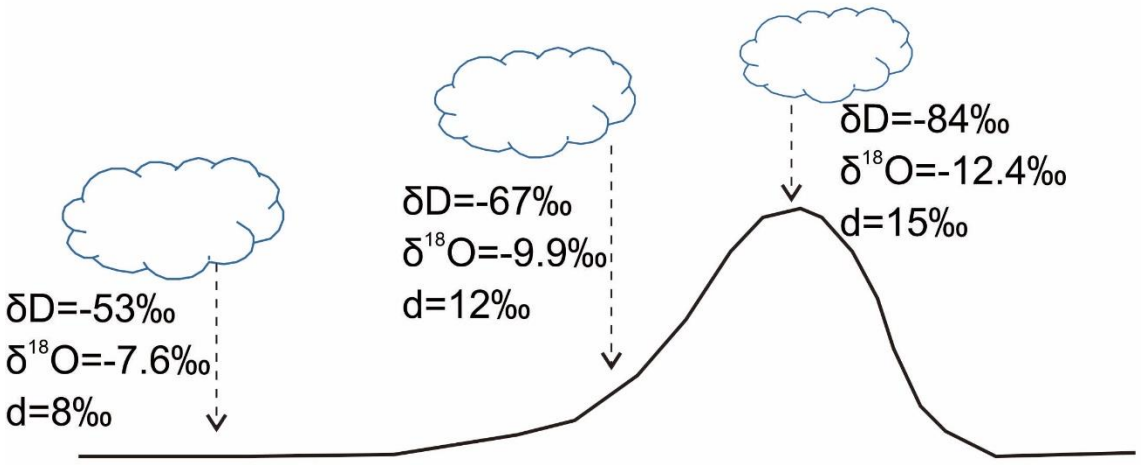


Fig. 5.3 Diagram showing the model of the altitude effect on δD and $\delta^{18}O$ isotopic ratios.

Regarding δD and $\delta^{18}O$ values of groundwater in the study area, for samples collected from wells data ranged from -84 to -54‰ for δD and from -12 to -7.6‰ for $\delta^{18}O$. The ranges of δD and $\delta^{18}O$ in water samples collected from cold springs were from -78 to -67‰ and from -11.5 to -9.6‰, respectively. Hot spring water samples collected from Brestovačka Banja had a δD value of -80‰ and a $\delta^{18}O$ value of -11.8‰, while the sample collected in Gamzigradska Banja had a δD value of -74‰ and a $\delta^{18}O$ value of -10.9‰. Values of δD and $\delta^{18}O$ measured in groundwater sample collected from the deep borehole in Zaječar City were -98‰ and -14.1‰, respectively. The ranges of d-value in water samples collected from wells and cold springs were from 6 to 15‰ and from 10 to 16‰, respectively. Groundwater samples collected from hot springs and a deep borehole had a d-value of 14‰ and 17‰, respectively. Values obtained for δD and $\delta^{18}O$ in groundwater samples are typical for the moderate continental climate. On a global basis, d-value has an average value of 10‰, but regionally it can vary due to various factors such as wind speed, humidity and sea surface temperature (Clark and Fritz, 1997).

Distributions of δD, $\delta^{18}O$ and d-value in groundwater of the study area are shown in geochemical maps (Fig. 5.4). As a general trend, groundwater samples collected from mountainous regions in the study area have lower δD and $\delta^{18}O$ values compared with the groundwater samples collected in plain areas. The d-value is higher in groundwater from mountainous regions than in groundwater from plain terrains (Fig. 5.4).

A diagram of δD and $\delta^{18}O$ values is shown in Fig 5.5. Sampling points are plotted along Global Meteoric Water Line (GMWL) described by Craig (1961), suggesting that collected groundwater samples have a meteoric origin. Most of the samples are plotted above the global meteoric water line (GMWL). Differences between samples collected from wells, springs and the deep borehole, as well as from mountainous and plain areas are observed. The most depleted sample in δD and $\delta^{18}O$ was groundwater from the deep borehole in Zaječar City, followed by hot spring samples and groundwater samples from mountainous areas, while the most enriched sample was collected in the plain area near to the Danube River. The groundwater in the study area consists of two end-members.

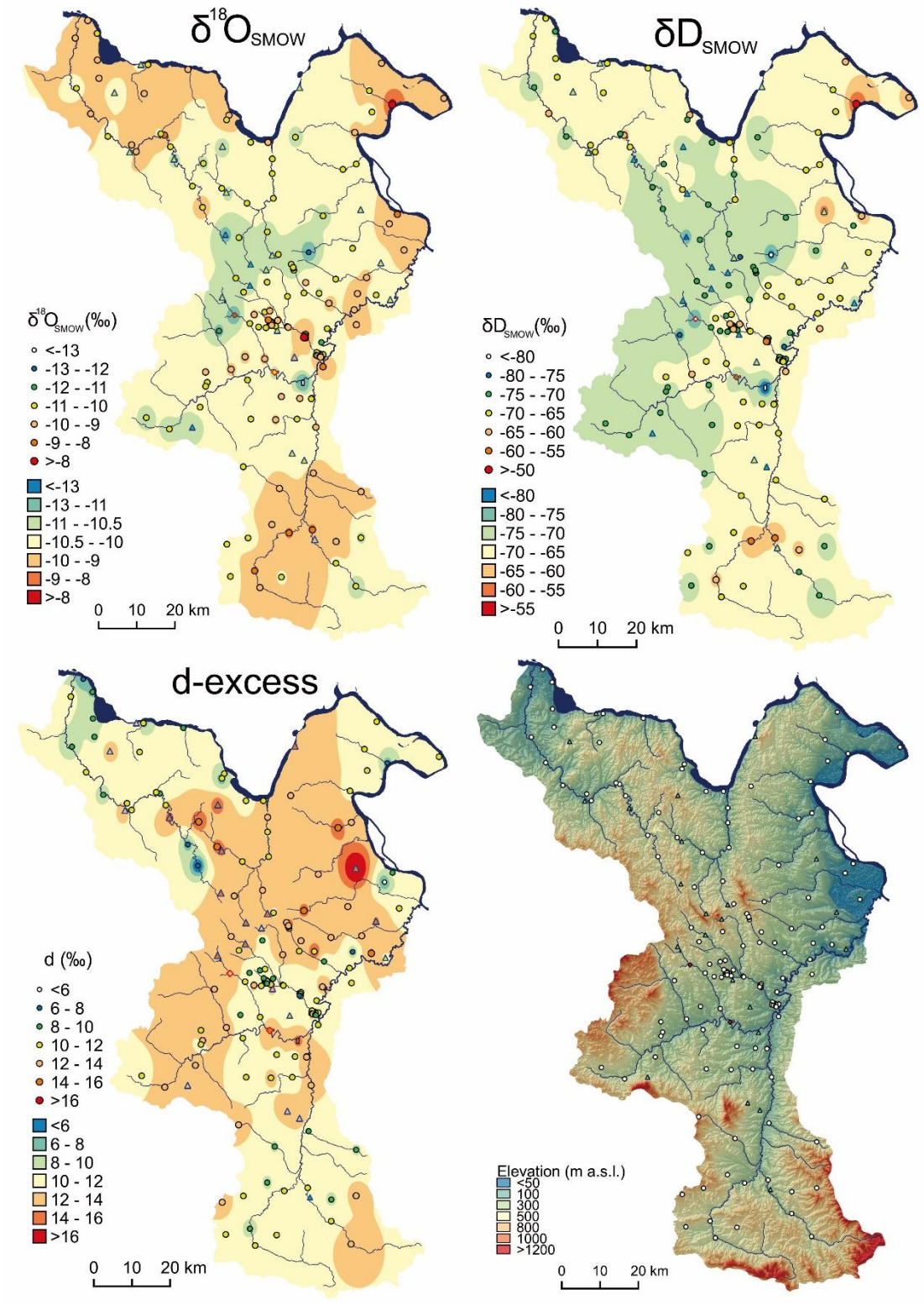


Fig. 5.4 Geochemical maps showing the distribution of $\delta^{18}O$, δD and d-value (d-excess) in groundwater of the study area and topographic map of the study area with sampling sites. On the maps sampling sites corresponding to groundwater samples collected from wells, cold springs, hot springs and a deep borehole are shown by circles, triangles, diamonds and a rectangle, respectively.

They are groundwater having lower δD and $\delta^{18}O$ values (δD<-70‰, $\delta^{18}O$<-10.3‰) and higher δD and $\delta^{18}O$ values (δD>-65‰, $\delta^{18}O$>-9.7‰). Differences between stable isotope ratios in mountainous areas and plain areas may be caused by different types of precipitations caused by the altitude effect. However, there is a possibility that groundwater is also a mixture of precipitation influenced by different air masses because the residence time of groundwater is long. Nagavciuc et al, 2019 showed that pressure above the continent is a very important factor for air masses circulation in Europe, and depending on that, different vapor sources can be present in south-eastern Europe. In most cases, precipitations in south-eastern Europe reach by Mediterranean and Atlantic cyclones (Nagavciuc et al., 2019). Based on the distribution of δD and altitude of sampling points (Fig. 5.4), there is a good correlation between them. Therefore, the difference in stable isotope ratios of groundwater samples in the study area is due to the difference in altitude effects rather than the difference in air masses.

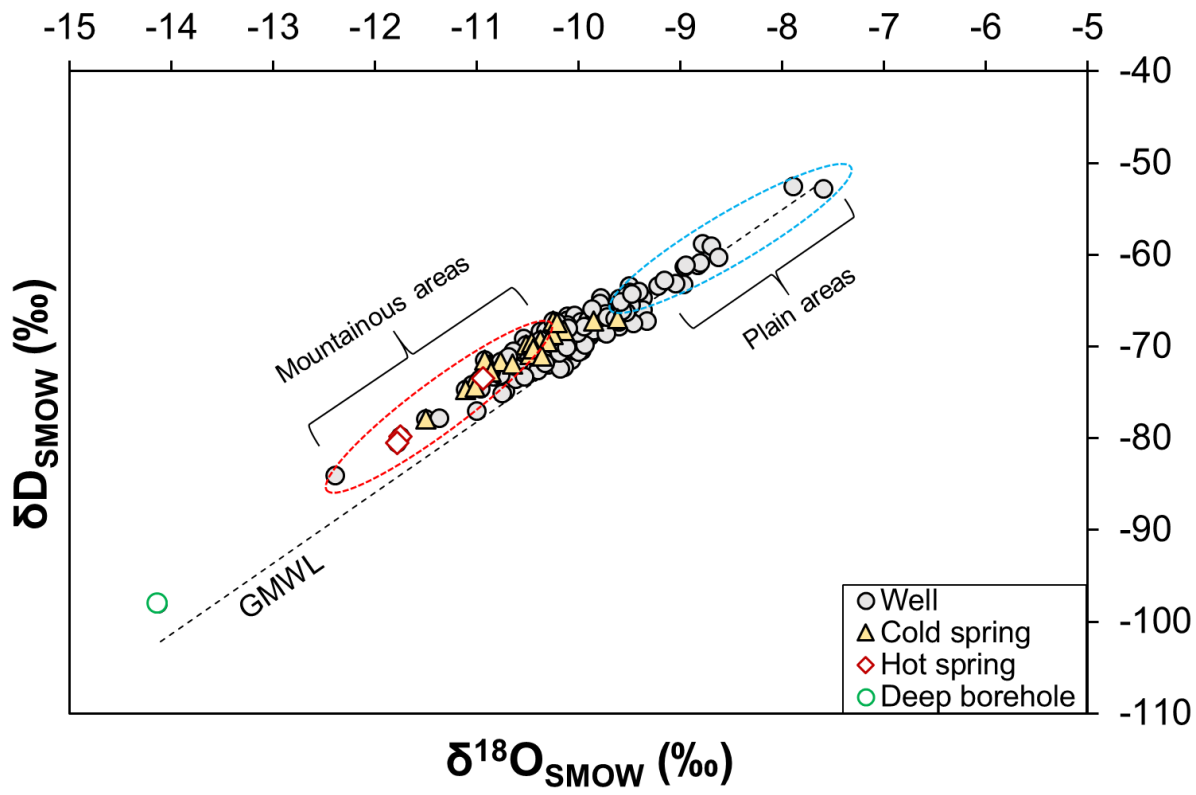


Fig. 5.5 Diagram showing the correlation between $\delta^{18}O$ and δD in groundwater of the study area. GMWL, $\delta D=8\delta^{18}O+10$ (Craig, 1961).

5.2. General characteristics of groundwater

A summary of the physical and chemical parameters including pH, Eh, water temperature, depth of the water table, concentrations of major cations and anions, and concentrations of trace elements in groundwater samples is shown in Table 5.1. All of the data sets are shown in the appendix (Appendices 4, 5, 6, 7, 8 and 9). Most of the groundwater samples were achromatic (colorless) and odorless. The temperatures of water samples collected from wells, boreholes and cold springs ranged from 10ºC to 20ºC. The temperatures of water samples collected from hot springs ranged from 34ºC to 37.3ºC.

Table 5.1. Statistical summary of physical and chemical parameters in groundwater.

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	ºC		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	-	
Li	µg/L	0.004	0.02	78.5	6.9	3.8	-	20
B	µg/L	0.1	3.7	876	87	42.6	300	300
Al	µg/L	0.01	0.5	44.5	4.2	3.0	200	10
V	µg/L	0.002	0.01	22.6	2.6	1.1	-	10
Cr	µg/L	0.01	<0.01	23.4	0.4	0.2	50	3
Mn	µg/L	0.01	0.03	2585	30	1.1	50	40
Fe	µg/L	0.1	<0.1	6387	20	5.6	300	50
Co	µg/L	0.003	<0.003	9.6	0.2	0.06	-	0.7
Ni	µg/L	0.007	<0.007	15.6	2.4	1.8	20	6
Cu	µg/L	0.005	0.3	151	6.3	2.9	2000	15
Zn	µg/L	0.01	0.2	287	17.4	6.4	3000	75
Ga	µg/L	0.004	0.03	22.2	3.0	2.3	-	10
As	µg/L	0.01	0.04	97.5	3.8	0.9	10	10
Rb	µg/L	0.002	0.06	28.4	1.3	0.5	-	7
Sr	µg/L	0.001	32	3231	602	447	-	1000
Sb	µg/L	0.002	<0.002	11.8	0.3	0.1	3	3
Ba	µg/L	0.002	2.7	383	57.3	36.5	700	200
U	µg/L	0.003	0.01	33.6	2.8	1.3	-	8

LOD, the limit of detection; Min, minimum value; max, maximum value; Mean, mean value; Med, median value; MAC, maximum admissible concentrations according to Serbian standard for drinking water (Republic of Serbia, 2019b); -, not specified.

Geochemical maps showing the distributions of pH and Eh values in groundwater from the study area are presented in Fig. 5.6. Water samples collected from shallow 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 borehole (5 m) in Slatina Village had a pH value of 6.9. The groundwater sample collected from the deep borehole (382 m) in Zaječar 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 Zaječar City. There is a possibility that different pH values correspond to different types of groundwater in the study area.

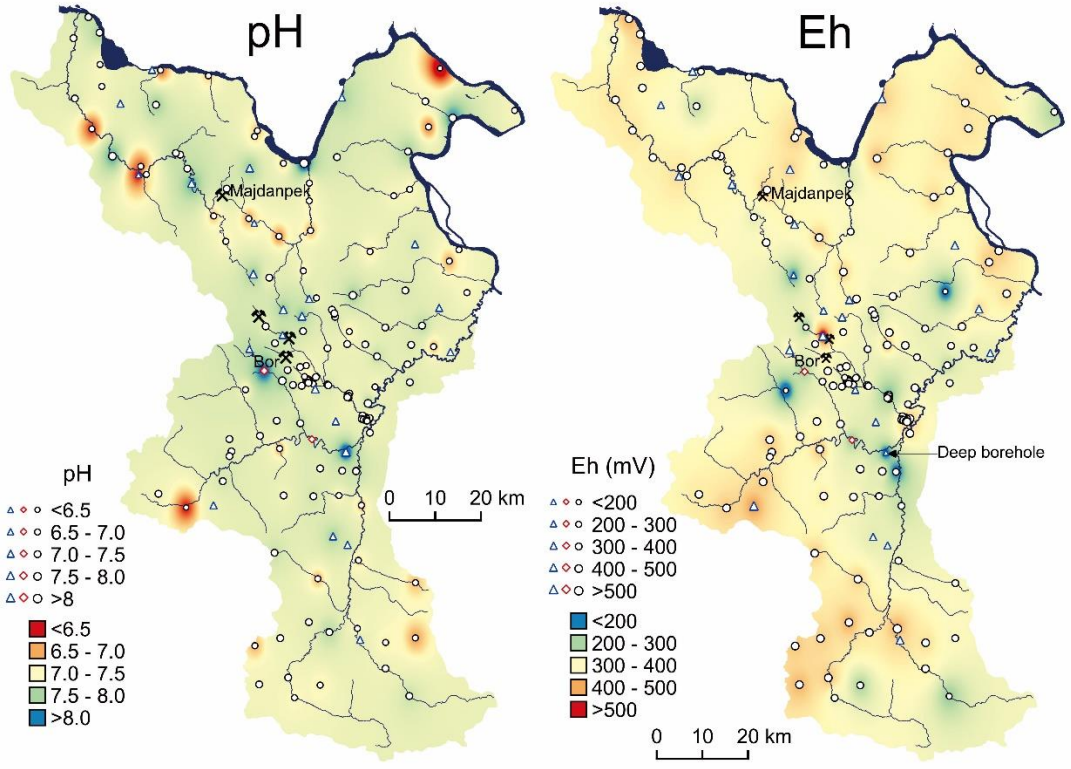


Fig. 5.6 Geochemical maps showing the distribution of pH and Eh values in groundwater of the study area. On the geochemical maps sampling sites corresponding to groundwater samples collected from wells, cold springs and hot springs are shown by circles, triangles and diamonds, respectively.

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

5.3. Concentrations of major ions in groundwater

Concentrations of Na^+, K^+, Mg^{2+} and Ca^{2+} in groundwater samples collected from the study area ranged from 0.04 to 244 mg/L, <0.01 to 275 mg/L, <0.01 to 81.1 mg/L and 8 to 511 mg/L, respectively. Concentrations of SO_4^{2-}, Cl^-, NO_3^- and HCO_3^- in groundwater samples from the study area ranged from 0.5 to 1111 mg/L, 0.01 to 247 mg/L, <0.01 to 254 mg/L and 30 to 930 mg/L, respectively.

Major components of groundwater in this study were Ca^{2+}, Mg^{2+} and HCO_3^- (Fig. 5.7). The groundwater in the study area was classified as Ca-Mg-HCO_3-dominant type water. The Ca-Mg-HCO_3-dominant type water groundwater is typical in areas where carbonate bedrocks are present (Appelo and Postma, 2005; Tanasković et al., 2012). Several groundwater samples were different from the majority of groundwater samples. Four groundwater samples (a sample from Zaječar City, two samples from Brestovačka Banja and a sample from Milutinovac) were Na-rich groundwater (Fig. 5.7). The sample collected from the deep borehole (382 m deep) in Zaječar City was classified as (Na+K)-HCO_3-dominant type of water. The other three water samples, collected in Brestovačka Banja (2 samples) and Milutinovac, are plotted in the field of Na+K-Ca-SO_4-dominant water type. Groundwater collected from the area downstream of the Bor mine is different from the majority of groundwater samples. Groundwater collected in the vicinity of polluted rivers located downstream of the Bor mine was classified either in Ca-Mg-HCO_3-dominant type water or Ca-Mg-SO_4-dominant type water (Fig. 5.7). 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, indicating the possibility of pollution by mining activities in this area (Fig. 5.7).

Regarding groundwater samples collected downstream of the Majdanpek mine, no differences from the majority of groundwater samples collected outside the mining areas were observed (Fig. 5.7).

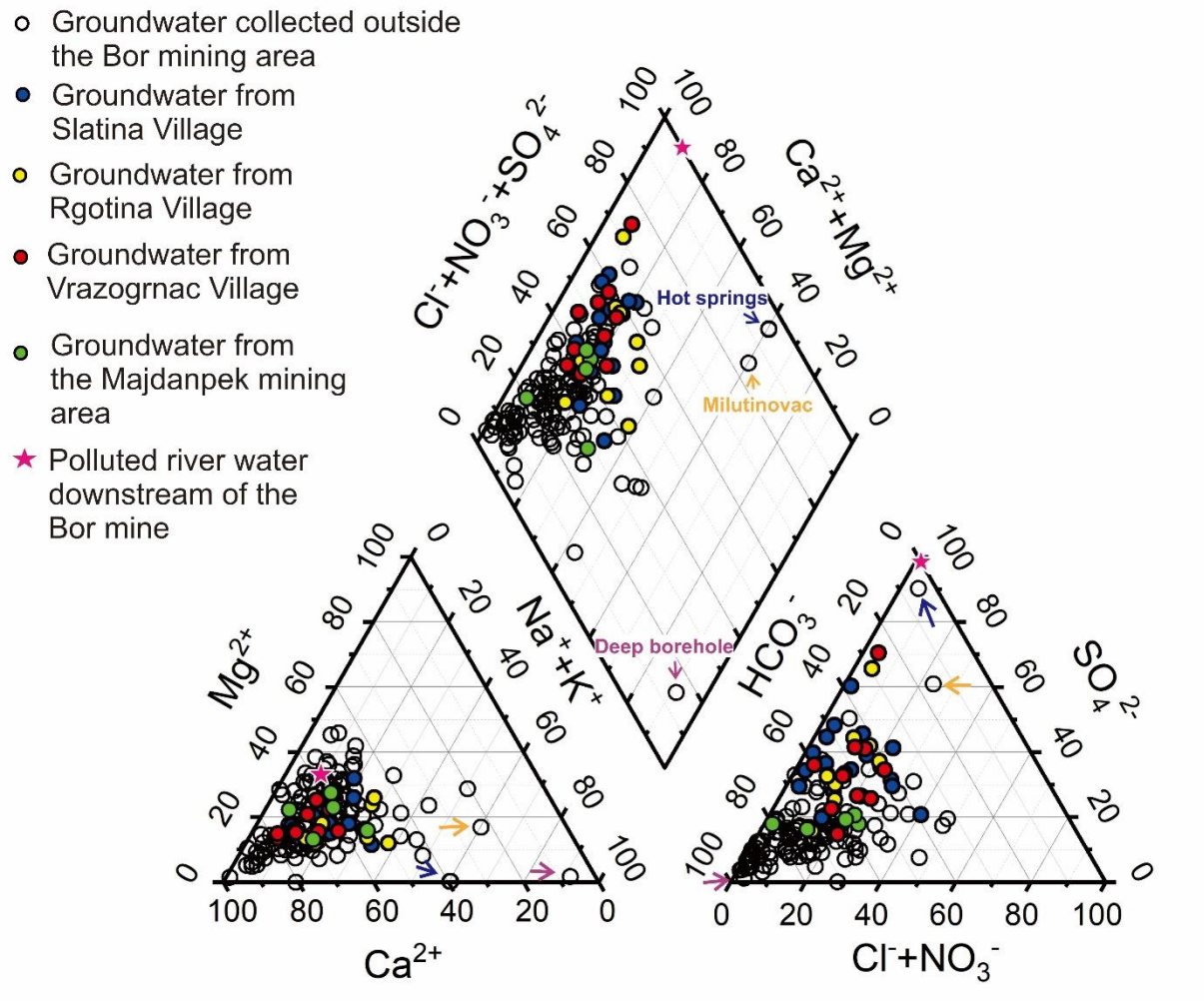


Fig. 5.7 Piper diagram showing the chemical composition of groundwater in the study area. Blue arrow, groundwater samples collected from Brestovačka Banja hot springs; yellow arrow, groundwater sample collected in Milutinovac; pink arrow, groundwater sample collected from the deep borehole in Zaječar City.

Distributions of the concentrations of major cations and anions are shown as histograms (Fig. 5.8). Sodium concentrations show a bimodal distribution. The lower concentrations of Na^+ correspond to water samples collected from cold springs in the

mountainous areas (Fig. 5.8a). On the other hand, the group in the histogram showing higher Na^+ concentrations (over 100 mg/L) compared with other samples corresponds to Na^+-dominant type groundwater. Sodium concentrations in groundwater collected from wells outside the Bor mining area and in the Bor mining area were higher than Na^+ concentrations in samples collected in cold springs. Groundwater samples collected from wells outside the Bor mining area and in the Bor mining area had similar ranges of Na^+ concentrations. There were no samples in which the concentration of Na^+ exceeded the maximum admissible concentration for drinking water of the Serbian standards (200 mg/L) (Republic of Serbia, 2019b).

Cold spring water samples were characterized by low concentrations of K^+ (Fig. 5.8). There was no difference in the range of K^+ concentrations in groundwater collected from wells outside and in the Bor mining area. However, the concentrations of K^+ in many samples collected from wells exceeded the standard value for drinking water in Serbia (12 mg/L).

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. 5.8c).

Calcium concentrations had a bimodal distribution (Fig. 5.8d). 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, from cold springs and hot springs, overlapped. 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 (200 mg/L) (Fig. 5.8d).

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. 5.8e). Concentrations of SO_4^{2-} in some well samples from the Bor mining area exceeded the standard value for drinking water (250 mg/L). Groundwater samples collected from wells outside the Bor mining area are plotted between cold spring samples and well samples from the Bor mining area. 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. 5.8f). 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. 5.8g 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 described by the Serbian standards (50 mg/L) (Fig. 5.8g).

The ranges of HCO_3^- concentrations in all groundwater types in the study area were similar (Fig. 5.8h). 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.

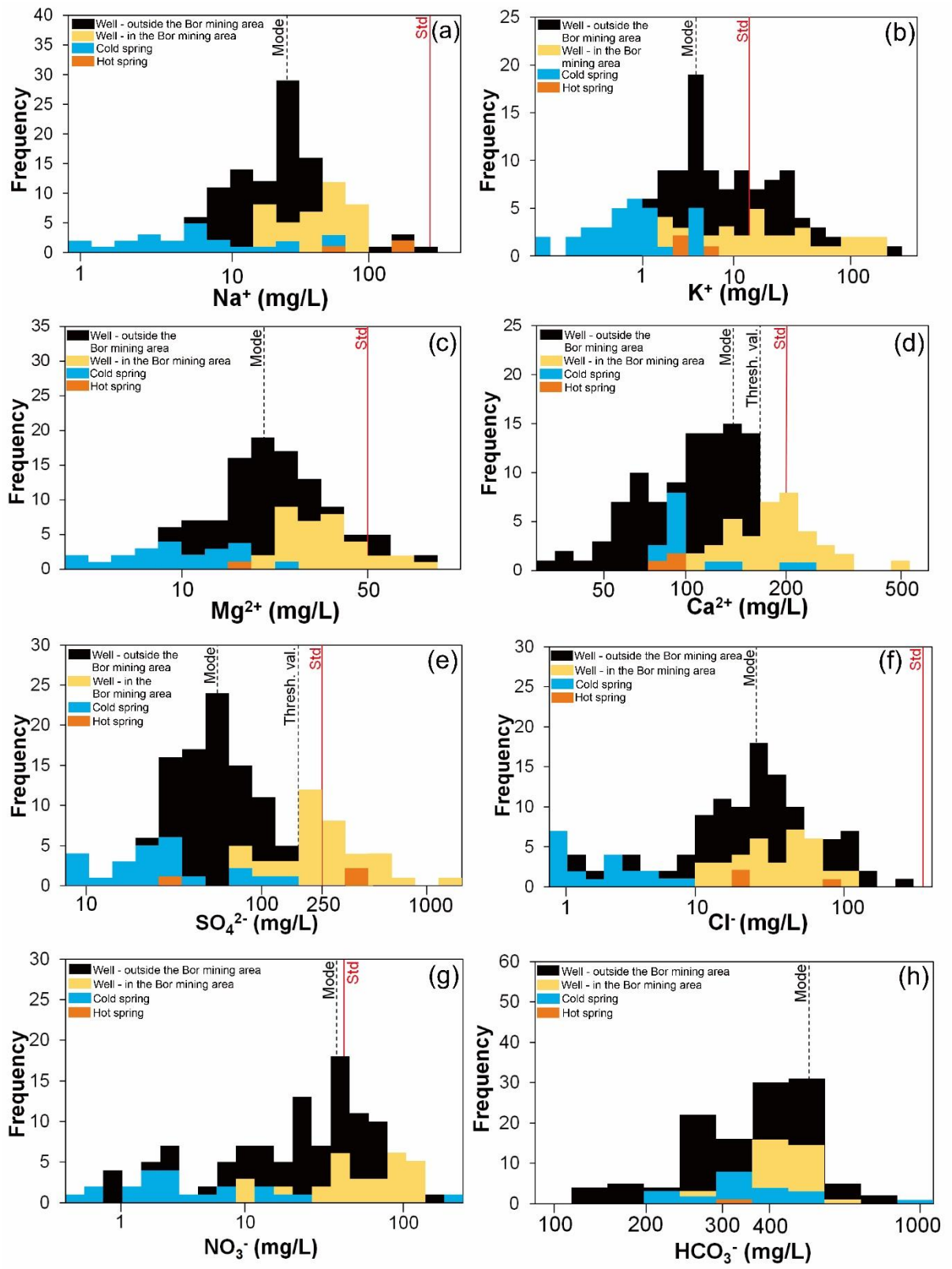


Fig. 5.8 Histograms showing distributions of data for major elements (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-) in groundwater from the study area. Mode, the value that appears the most; Thresh. val., threshold value; Std, maximum admissible concentration for drinking water according to Serbian standards (Republic of Serbia, 2019b).

5.4. Concentrations of trace elements in groundwater

Eighteen trace elements (Li, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Sb, Ba and U) were detected in groundwater from the study area. A summary of the results is shown in Table 5.1. The concentrations of trace elements in groundwater samples collected from the study are shown by histograms (Fig. 5.9).

The ranges of concentrations of the 18 trace elements in groundwater samples from the study area were 0.3 to 151 µg/L for Cu, 0.04 to 97.5 µg/L for As, <0.1 to 6387 µg/L for Fe, 0.03 to 25858 µg/L for Mn, <0.003 to 9.6 µg/L for Co, <0.007 to 15.6 µg/L Ni, 0.2 to 287 µg/L for Zn, 0.01 to 22.6 µg/L for V, <0.01 to 23.7 µg/L for Cr, 3.7 to 879 µg/L for B, 0.02 to 78.5 µg/L for Li, 0.5 to 44.5 µg/L for Al, 32 to 3231 µg/L for Sr, 0.5 to 383 µg/L for Ba, 0.03 to 22.6 µg/L for Ga, 0.06 to 28.4 µg/L for Rb, <0.002 to 11.8 µg/L for Sb and 0.01 to 33.6 µg/L for U. The data set for all of these elements is shown as appendix (Appendices 6, 7, 8 and 9).

Histograms of Cu, As, Mn, Ni, Rb and Sb 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 (Figs. 5.9a, b, c, d, e and f). Low concentrations of Cu, As, Mn and Ni 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, Mn and Ni than those in other samples (Figs. 5.9a, b, c and d).

Groundwater samples containing the highest concentrations of Cu and As were collected around the Bor ore deposits at Brestovac (Cu=151.2 µg/L; As=25.5 µg/L) and a location near the area of Bor airport (Cu=84 µg/L; As=97.5 µg/L), where copper ore deposits are present in the deeper part, between 400 m below the surface to more than 2 km (Banješević and Large, 2014; Jelenković 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 µg/L) and Karbulovo (Mn=1077 µg/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. 2.2). Therefore, the higher concentrations of Mn in Zlot and Karbulovo are thought to be caused by some local effects. There was no large difference in the concentrations of Rb and Sb among the different kinds of groundwater from the study area (Figs. 5.9e and f). Concentrations of Cu and Ni did not exceed the maximum admissible concentrations for drinking water according to the Serbian standards (Cu=2000 µg/L; Ni=20 µg/L), while a small number of samples had concentrations of As, Mn and Sb above the maximum admissible concentrations (As=10 µg/L; Mn=50 µg/L; Sb=3 µg/L).

Bimodal distributions were observed for concentrations of Fe, Co, V, B and U (Figs. 5.9g, h, i, j and k). 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 µg/L, which makes an anomalous group 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. 5.1 and 5.9g). It is thought that these anomalous concentrations correspond to some local effects due to different redox conditions. In histograms of V and B concentrations, the ranges of concentrations of these elements in groundwater samples from cold springs, wells along polluted rivers and wells outside the Bor mining area overlapped (Figs. 5.9i and j). However, samples collected from wells along polluted Bor River and Bela River had higher concentrations of V and B, while cold spring samples had lower concentrations of these elements. The ranges of U concentrations were similar for all kinds of groundwater samples collected in the study area (Fig. 5.9k). The concentrations of Fe and B in a small number of groundwater samples exceeded the maximum admissible concentrations of Fe and B according to the Serbian standards for drinking water (Fe=300 µg/L; B=300 µg/L).

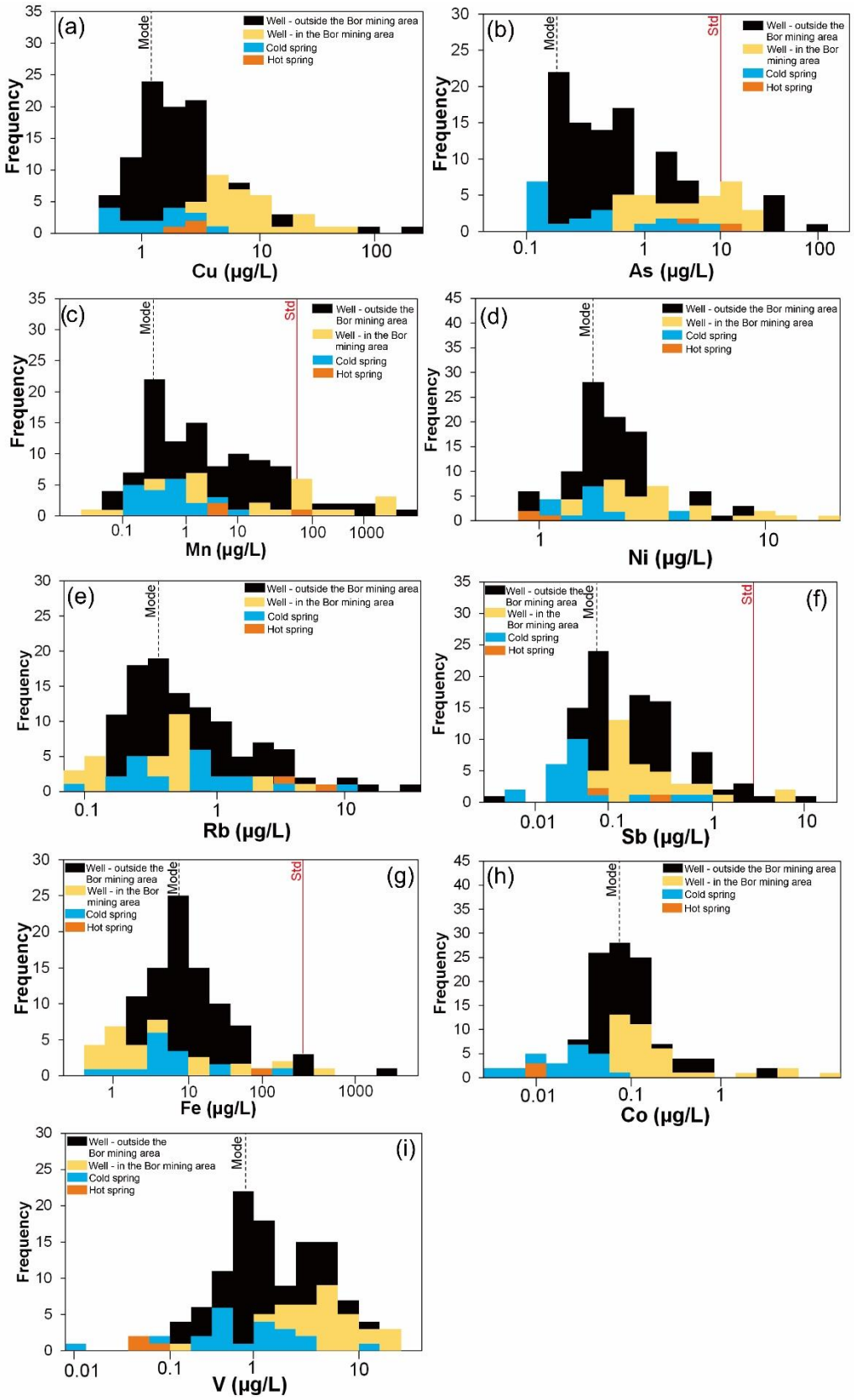


Fig. 5.9 Histograms showing distributions of data for trace elements (Cu, As, Mn, Ni, Rb, Sb, Fe, Co, V, B, U, Sr, Zn, Cr, Al, Li, Ba and Ga) in groundwater from the study area. Mode, the value that appears the most; Thresh. val., threshold value; Std, maximum admissible concentration for drinking water according to Serbian standards (Republic of Serbia, 2019b).

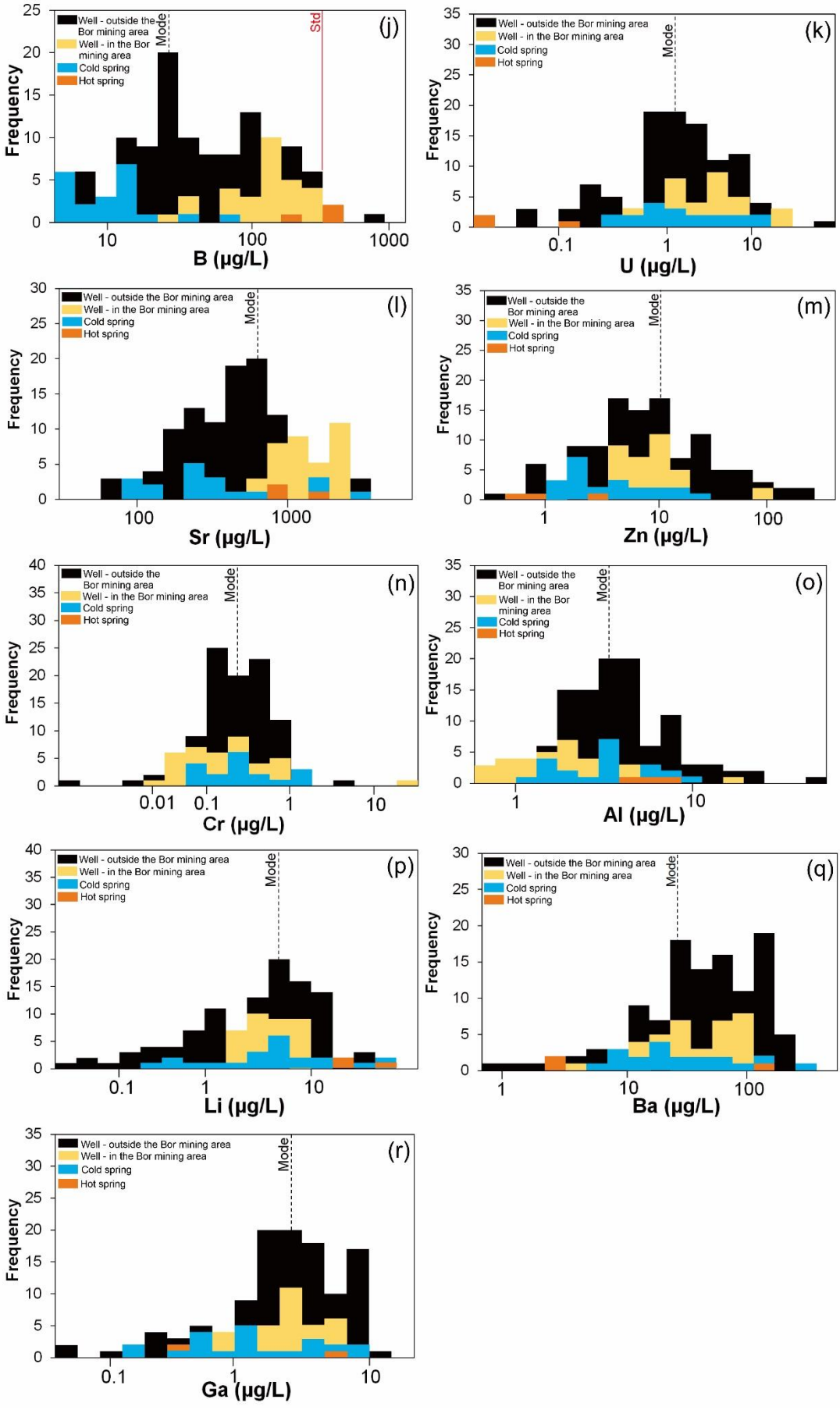


Fig. 5.9 (continued)

Unimodal distributions were observed for Sr, Zn, Cr, and Al concentrations in groundwater (Figs. 5.9l, m, n and o). Concentrations of Sr in groundwater samples collected from cold springs and wells outside the Bor mining area had similar ranges. However, groundwater from wells in the Bor mining area had higher concentrations (Fig. 5.9l). There was no difference in the ranges of Zn and Cr concentrations in cold spring samples and well samples from both the Bor mining area and outside the mining area (Figs. 5.9m and n). Groundwater samples from wells in the Bor mining area had lower concentrations of Al than the concentrations in other groundwater samples (Fig. 5.9o). The concentrations of Zn, Cr and Al in groundwater samples did not exceed the maximum admissible concentrations for drinking water in the Serbian standard (Zn=3000 µg/L; Cr=50 µg/L; Al=200 µg/L).

Distributions of the concentrations of Li, Ba and Ga showed a negative skewness (Figs. 5.9p, q and v). There were no differences in the ranges of concentrations in groundwater samples collected from cold springs and wells outside and in the Bor mining area. Slightly higher concentrations of Li were found in samples collected from hot springs and three cold springs than the concentrations in other samples (Fig. 5.9p).

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.

5.5. Spatial distributions of studied components in groundwater

Distributions of the concentrations of major cations and anions (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-) and concentrations of trace elements (Li, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Sb, Ba and U) are shown in geochemical maps (Fig. 5.10). The geochemical maps show areas in which groundwater had higher concentrations of the components.

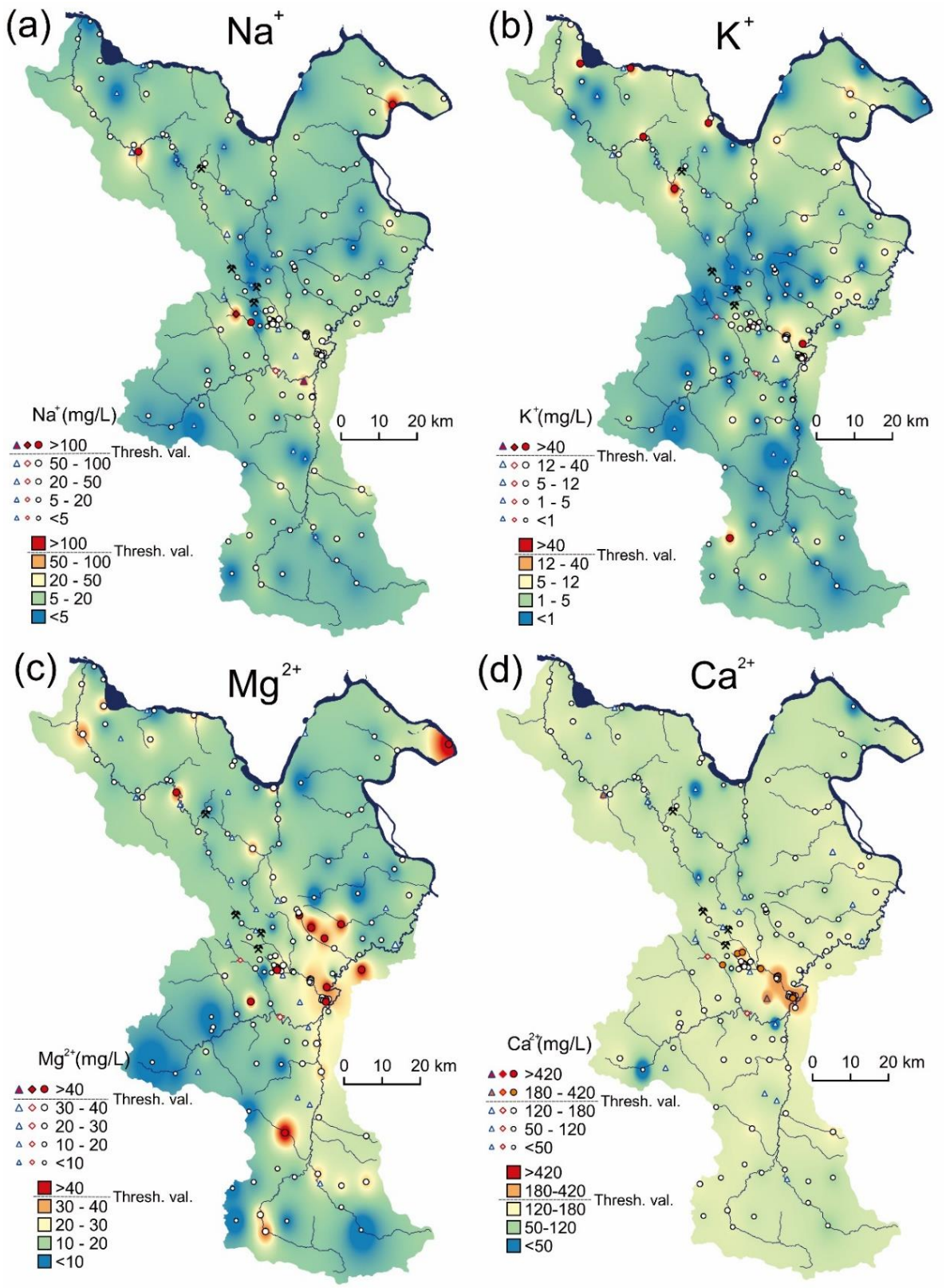


Fig. 5.10 Geochemical maps showing the distributions of concentrations of major elements (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-) and trace elements (Cu, As, Mn, Ni, Rb, Sb, Fe, Co, V, B, U, Sr, Zn, Cr, Al, Lu, Ba and Ga) in groundwater from the study area. In the geochemical maps, samples collected from wells, cold springs and hot springs are marked by circles, triangles and diamonds, respectively. Thresh. val., threshold value.

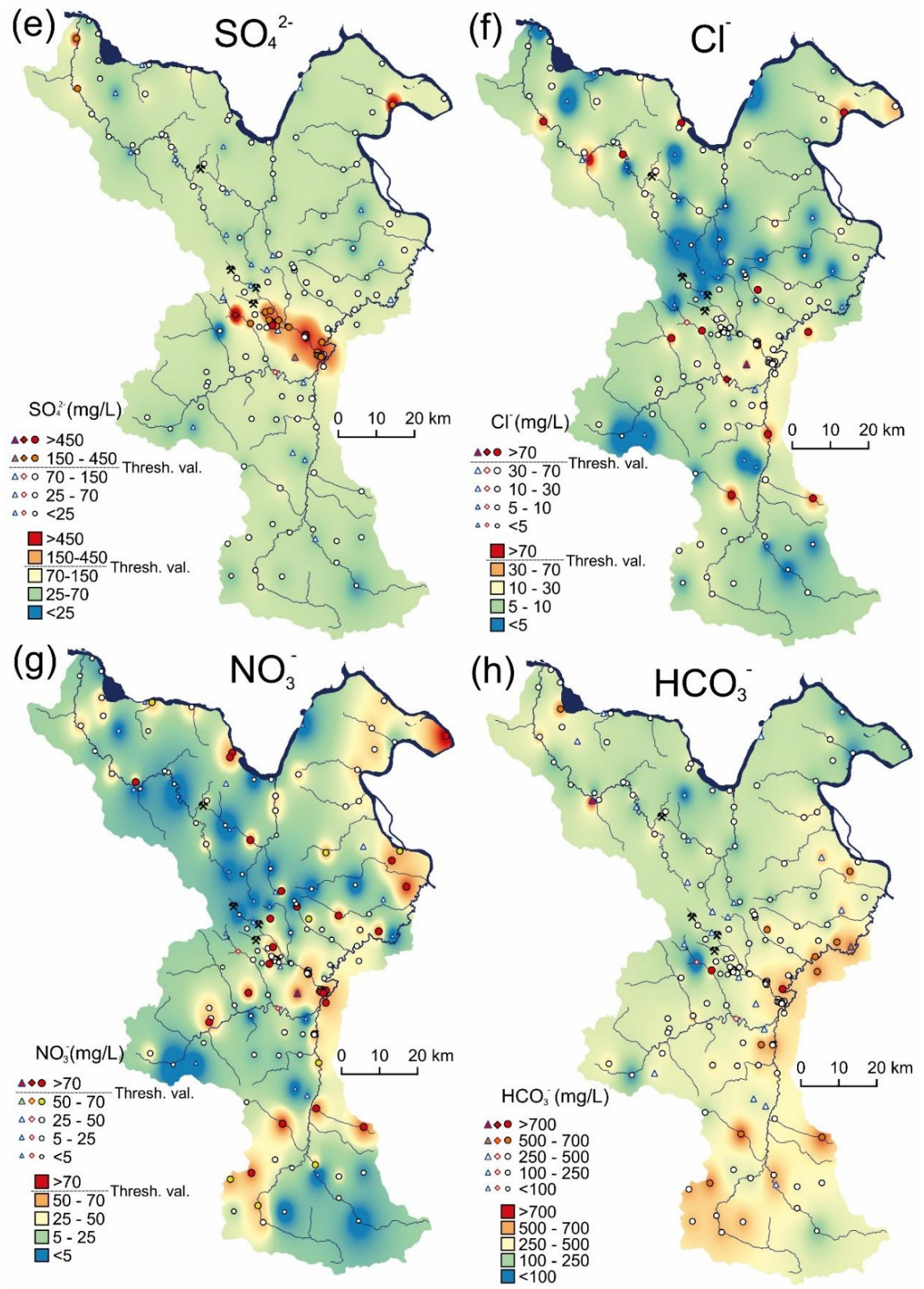


Fig. 5.10 (continued)

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 (Figs. 5.10d and e). 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 (Bor River and Bela River) downstream of the Bor mine (Figs. 5.10d and e). 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 Vražogrnac Village. Groundwater samples collected in Vražogrnac Village, located 30 km downstream of the Bor mine, had higher SO_4^{2-} concentrations than the concentrations in the groundwater samples collected in Rgotina Village, located 20 km downstream of the Bor mine. High concentrations of SO_4^{2-} in groundwater are also present 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 is polluted with SO_4^{2-} (Chapter 4). The cause of the high concentration of SO_4^{2-} in groundwater is thought to be different from contamination by mining activity.

Magnesium concentrations in groundwater from an area located east of the Bor mining area were slightly high (Fig. 5.10c). The area located east of the Bor mining area corresponds to the area where Gabbro is present (Fig. 2.1a). This fact suggests that water-rock interaction between groundwater and gabbro also plays an important role in groundwater composition in this area.

Higher concentrations of K^+ and NO_3^- were mainly found in areas of plain terrains where there are agriculture activities (Figs. 5.10b and g). In the mountainous areas where there are less anthropogenic activities, K^+ and NO_3^- concentrations were low. Therefore, the sources of K^+ and NO_3^- are thought to be fertilizers and livestock manure used in agriculture.

The distribution of bicarbonate ion concentrations in groundwater from the study area is shown in Fig. 5.10h. Concentrations of HCO_3^- in groundwater were higher in the southern, south-eastern and eastern parts of the study area. The geology of the southern

and south-eastern parts of the study area is dominated by Cretaceous limestone (Fig. 2.6). The source of HCO_3^- in groundwater is thought to be limestone. On the other hand, there is no limestone in the eastern part of the study area. Therefore, the source of HCO_3^- in the eastern part of the study area is thought to be different.

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 and along polluted rivers in the area downstream of the Bor mine (Figs. 5.10i and j). 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 Vražogrnac 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 (Figs. 5.10i and j). 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 show the presence or absence of contamination. Therefore, a threshold value is needed to distinguish between an anomalous population and a background population.

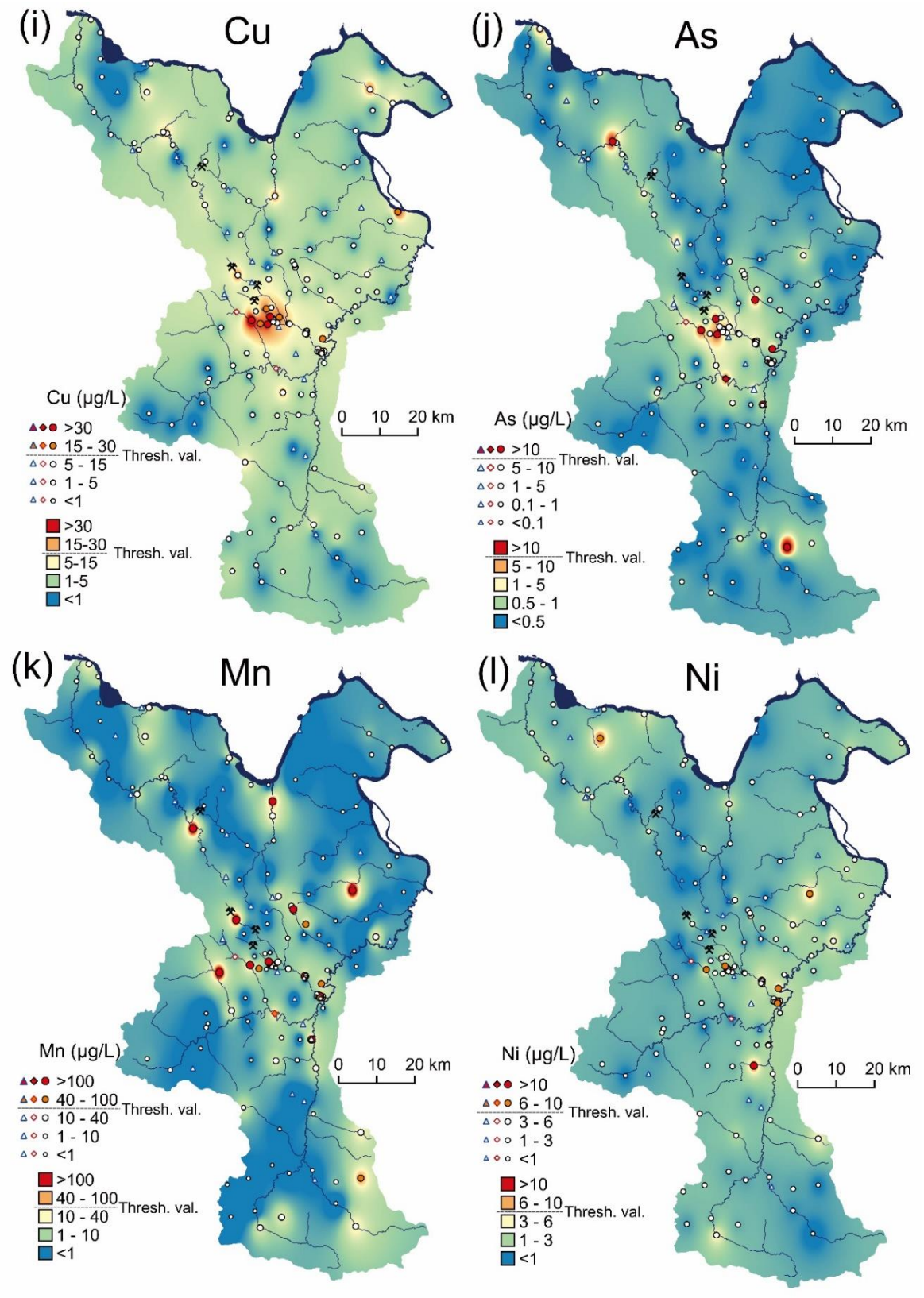


Fig. 5.10 (continued)

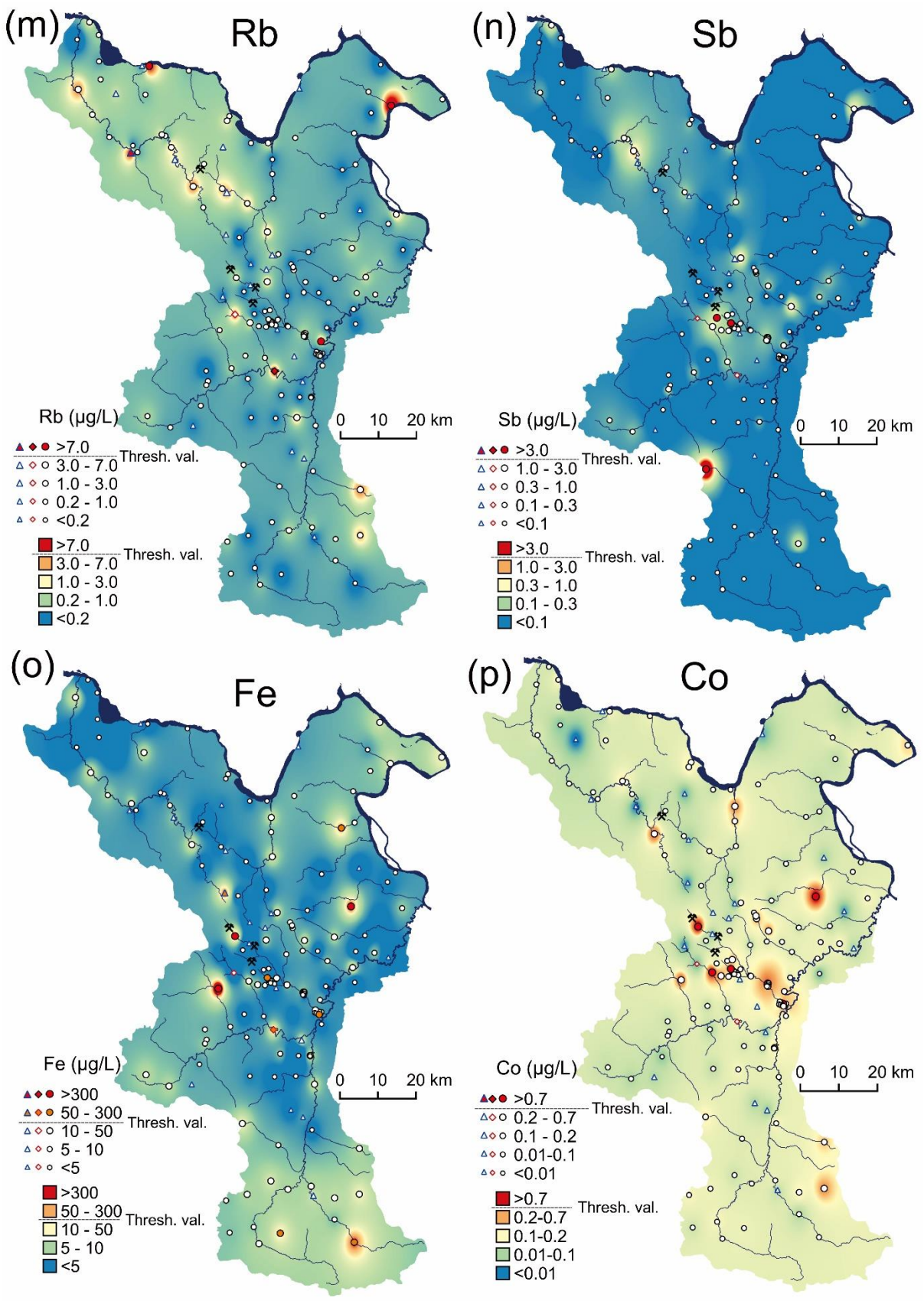


Fig. 5.10 (continued)

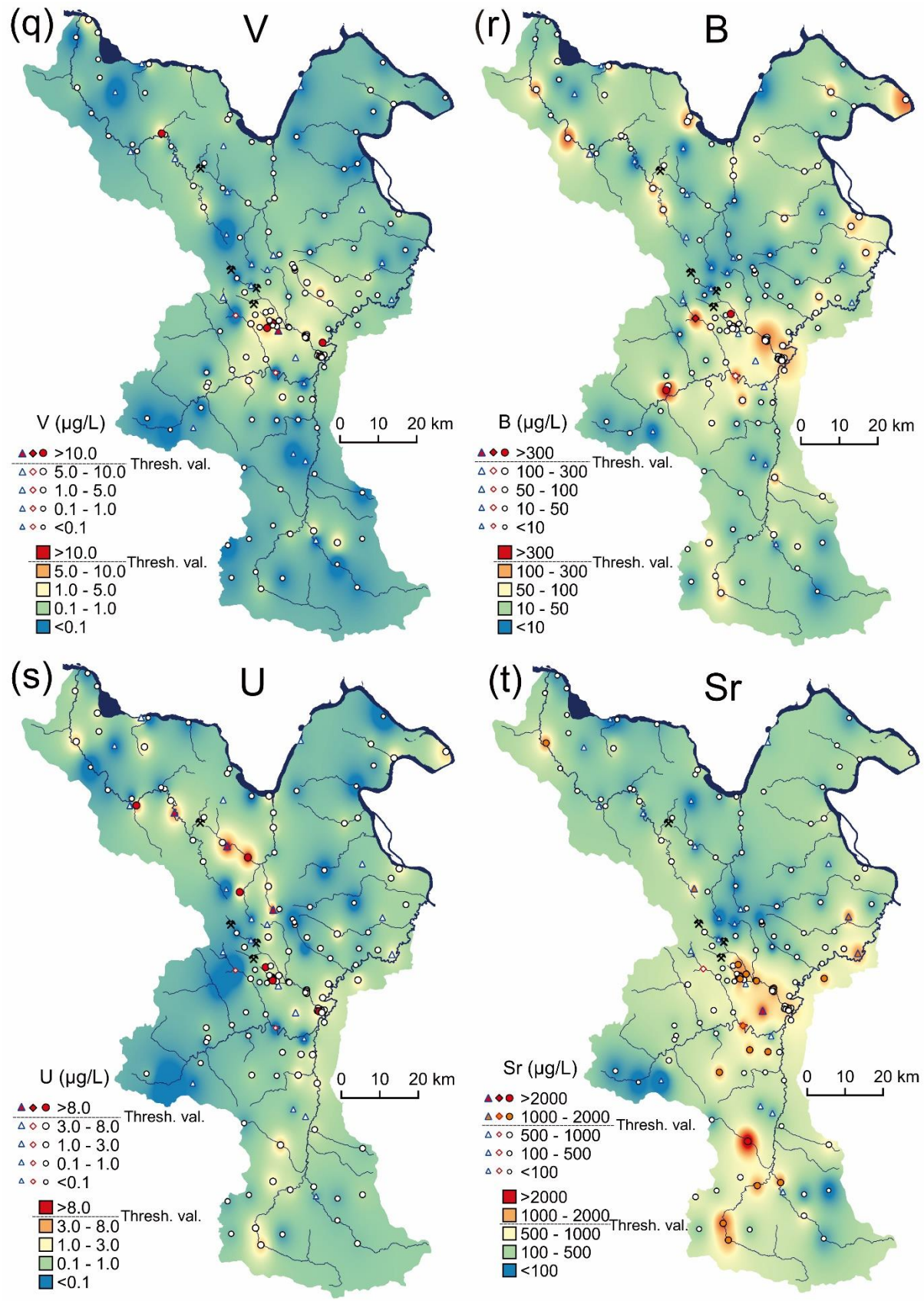


Fig. 5.10 (continued)

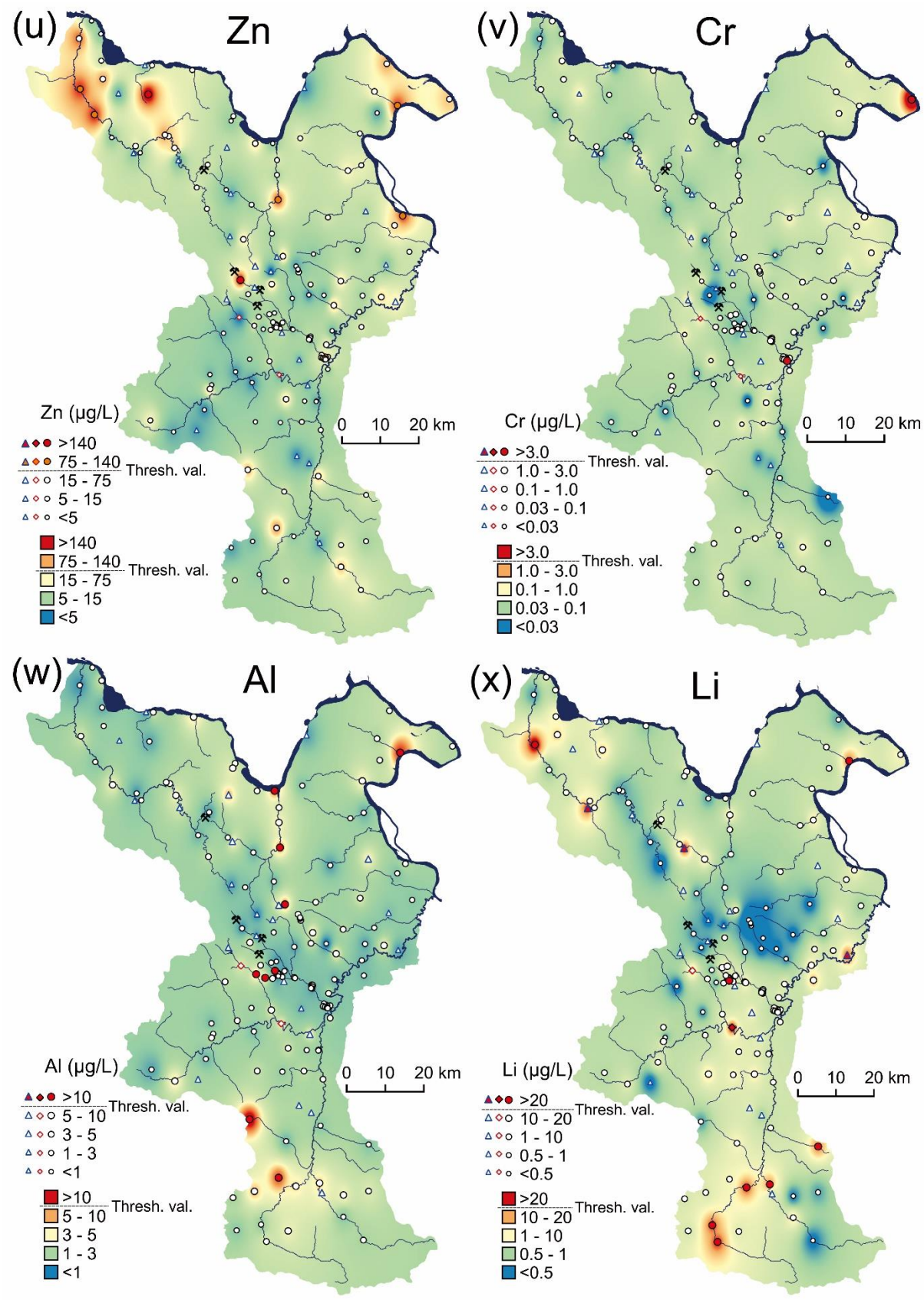


Fig. 5.10 (continued)

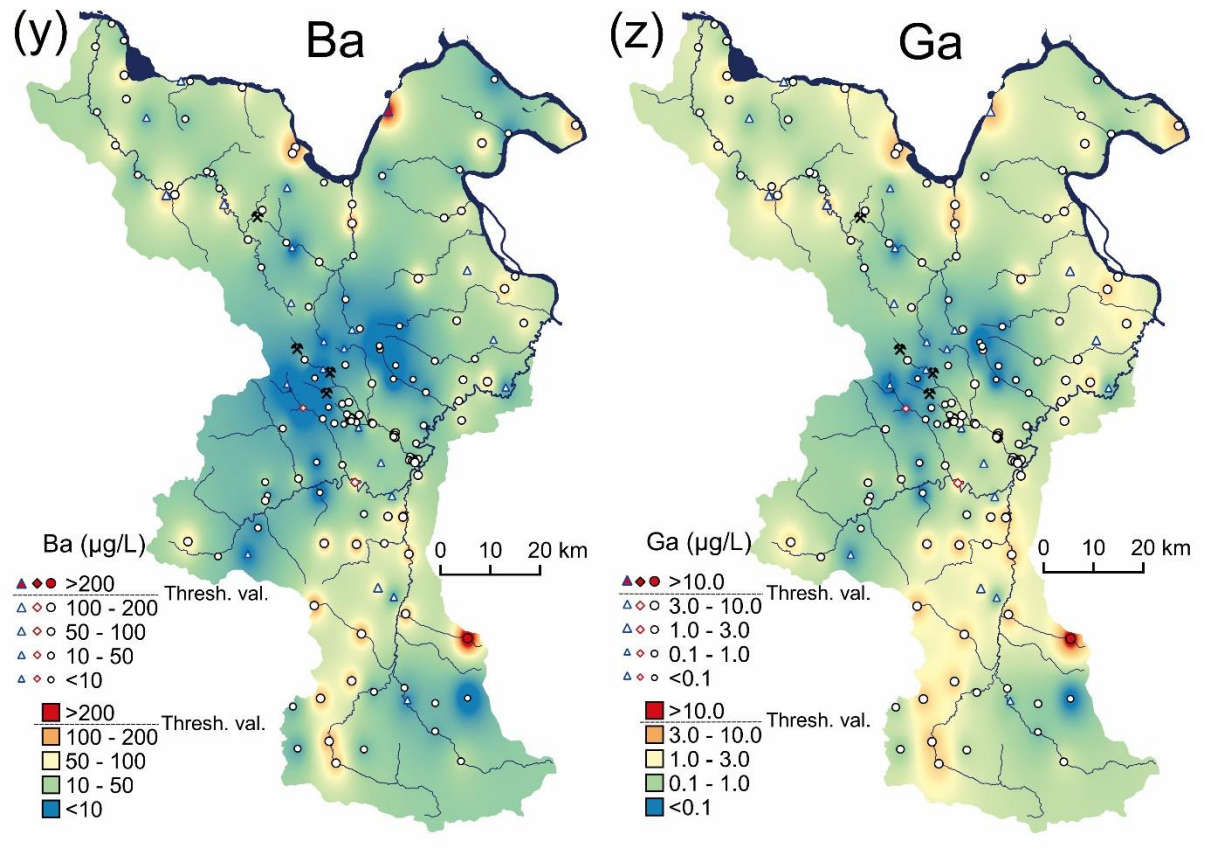


Fig. 5.10 (continued)

Groundwater from the study area was generally characterized by low concentrations of Mn and Fe (Figs. 5.10k and o). Elevated concentrations of Mn and Fe were found in a small number of groundwater samples collected in areas downstream of the Bor mining area. However, groundwater samples having the highest concentrations of Fe and Mn were collected from locations outside the mining areas without systematic distributions. These groundwater samples also had low Eh values (reducing environmental conditions). Therefore, elevated concentrations of Fe and Mn in areas far from the mining activities are thought to be caused by different effects according to the redox condition of the groundwater.

The concentrations of other heavy metals including Ni, Co and V in groundwater from the study area were significantly lower than the concentrations of Cu, As, Fe and Mn. However, concentrations of Ni, Co and V were slightly higher in the Bor mining area than in other parts of the study area (Figs. 5.10l, p, and q).

The spatial distribution showing the presence of high concentrations of Sr corresponds to the Cretaceous limestone-rich areas and an area near the Bor mine (Figs. 2.6 and 5.10t). Based on this distribution, one of the sources of Sr in groundwater is thought to be limestone. This possibility is supported by a similar distribution of HCO_3^- in the study area (Fig. 5.10h). Therefore, groundwater chemistry in these parts of the study area is controlled by water-rock interaction between groundwater and limestone.

A comparison of the spatial distributions of components including Ca^{2+}, SO_4^{2-}, Cu, As, Ni, and Co showed that there is a difference between the Bor and Majdanpek mining areas. Groundwater collected in the Bor mining area showed higher concentrations of these components, while there was no distinct difference in the concentrations of these components between groundwater in the Majdanpek mining area and groundwater collected outside the Bor mining area (Fig. 5.10). In the Majdanpek mining area, a signature showing groundwater pollution was not found.

5.6. 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 the 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 of many components are classified into one or more groups. 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.

In a previous chapter (Chapter 4), threshold values for river water in the study area were estimated and the distribution of polluted areas was clarified. Based on those results, there is a possibility that groundwater in the study area is contaminated. Therefore, there is a necessity for the estimation of threshold values in groundwater in the 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. 5.11. The estimated values for the classification in probability diagrams of Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^{-}, NO_3^{-}, Li, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Sb, Ba and U are shown in Table 5.1 (Estimated concentration). Data obtained for some components were classified into two or more groups.

Regarding Na^{+}, HCO_3^{-}, V, U, Sr and Ba, elevated concentrations of these components had no systematic distribution in mining facilities and polluted rivers downstream of the Bor mine (Figs. 5.10a, h, q, s, t and y). For example, higher concentrations of HCO_3^{-}, Sr and Ba are present in Cretaceous limestone-rich areas, indicating the occurrence of strong water-rock interaction. Therefore, these estimated concentrations to separate the group with the highest concentration from a group with a lower concentration are not threshold values for discriminating anomalous values indicating pollution from background values. The estimated concentrations correspond to concentrations that are used to divide the background group into several groups.

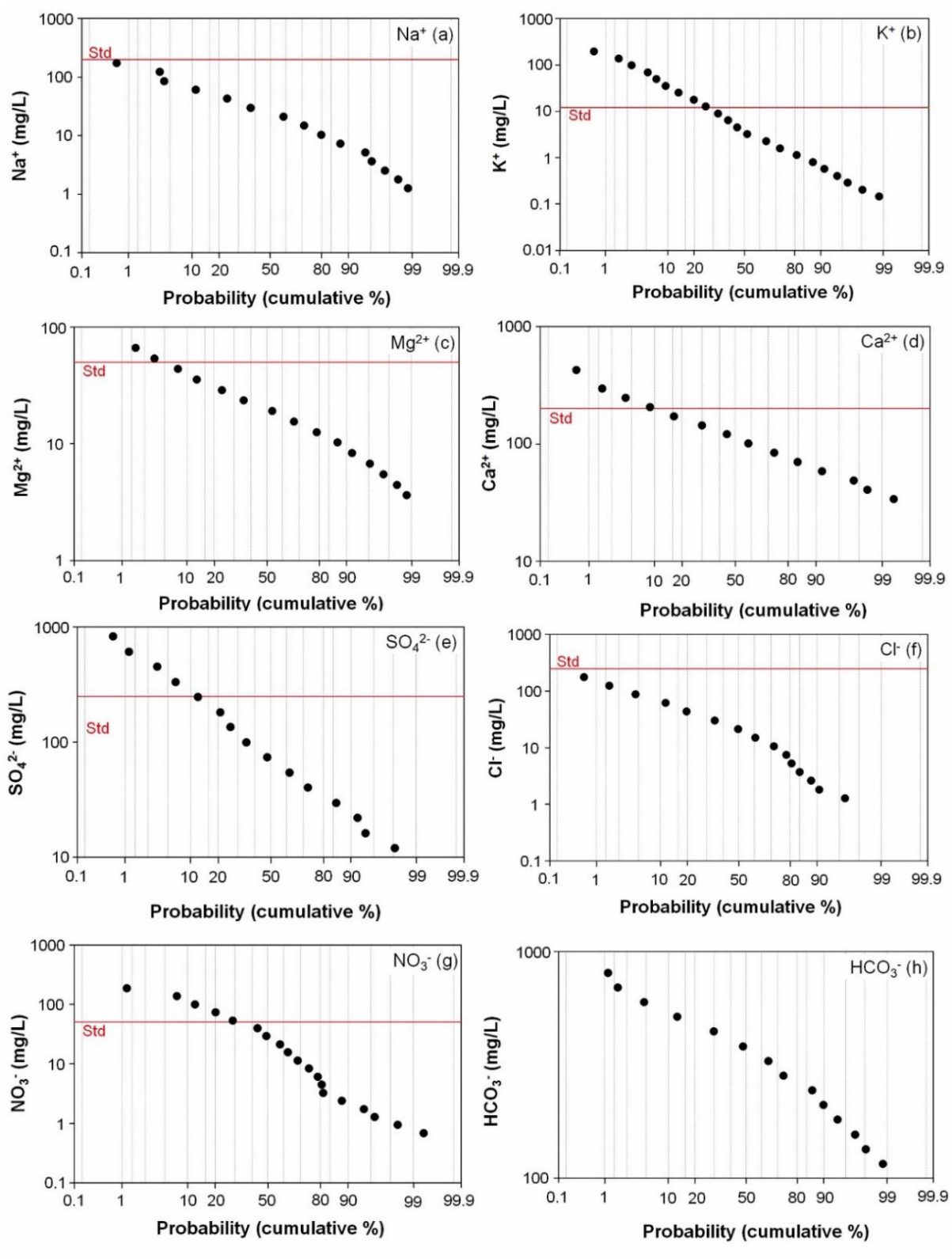


Fig. 5.11 Probability diagrams for major elements (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^- and HCO_3^-) and trace elements (Cu, As, Mn, Ni, Rb, Sb, Fe, Co, V, B, U, Sr, Zn, Cr, Al, Lu, Ba and Ga) in groundwater from the study area.

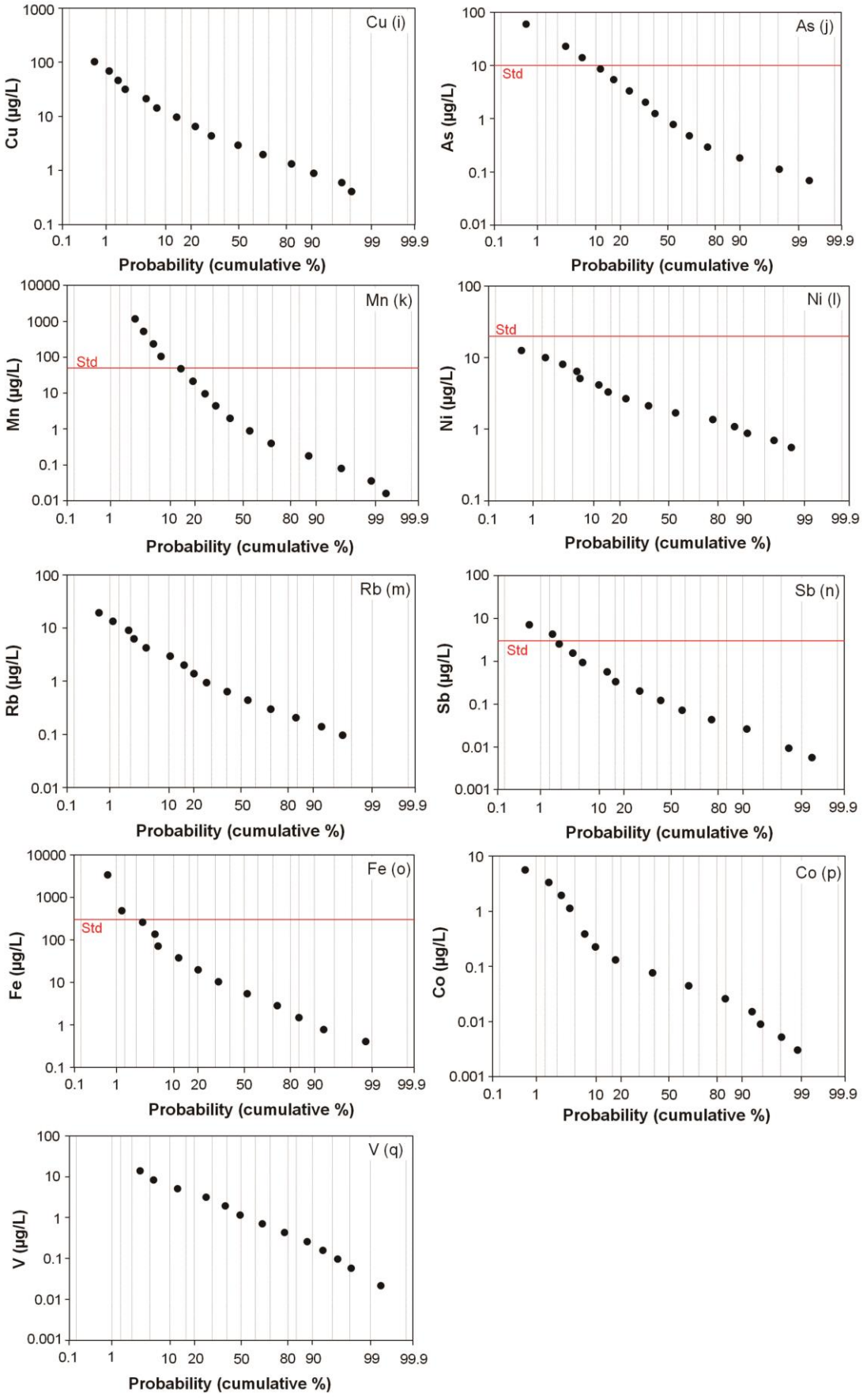


Fig. 5.11 (continued)

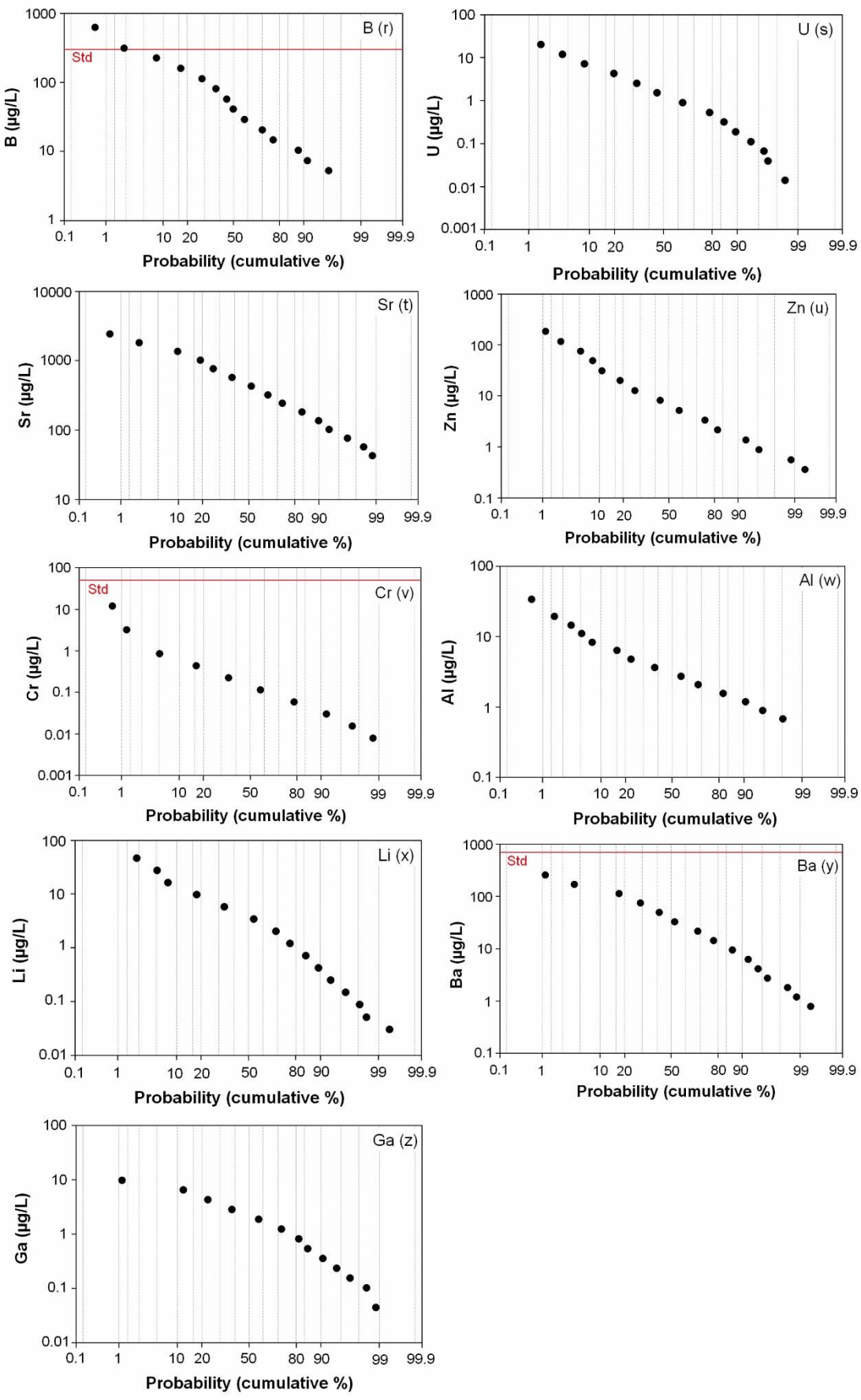


Fig. 5.11 (continued)

Based on histograms created for Cu and As, it is difficult to distinguish groups because data show a distribution having positive skewness (Figs. 5.9a and b). However, in the probability diagrams, the presence of different groups was noticeable (Figs. 5.11i and j). The groups with the highest concentrations of Cu and As in probability diagrams include groundwater samples with concentrations higher than 15 µg/L and 10 µg/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 (Figs. 5.10i and j). However, these higher concentrations of Cu and As are also thought to be caused by water-rock interaction between groundwater and mineralized ores showing Cu mineralization 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 along the Bor River 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 mining activities. However, in groundwater collected in Rgotina Village and Vražogrnac Village, there were no concentrations of Cu and As that exceeded the estimated concentrations as threshold values.

According to probability diagrams of Mn and Fe, data can be separated into three groups and two groups, respectively (Figs. 5.11k and o). However, the high concentrations of these heavy metals in geochemical maps do not show a systematic distribution with the mining areas (Figs. 5.10k and o). Therefore, the concentrations of Mn and Fe do not indicate groundwater pollution 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-}. 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 (Figs. 5.11d and e). The presence of different slopes suggests that all of the data of 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 5.1). 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 (Figs. 5.10d and e). Therefore, estimated values of Ca^{2+} and SO_4^{2-} are threshold values for discriminating pollution 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 Vražogrnac Village, which are areas that are considered to be affected by mining activities, exceeded both the standard values and the threshold values. Unlike Cu and As, a stronger impact was observed for groundwater in the downstream area of Bela River in Vražogrnac 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 pollution 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, 2019b). 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 (Đorđievski et al., 2018), do not show obvious evidence of groundwater pollution in the same area.

5.7. Pollution of groundwater

Groundwater pollution in the Majdanpek mining area was not observed. Hence, only the pollution of groundwater in the Bor mining area will be discussed below.

Geochemical maps of Ca^{2+} and SO_4^{2-} indicate the presence of groundwater pollution in the area along the polluted Bor River and Bela River downstream of the Bor mine where the tailings transported from the Bor mine are present. However, not all groundwater samples collected from this region are polluted. In order to determine

groundwater samples affected by the pollution, stiff diagrams showing major ions concentrations in groundwater and river water in Slatina Village, Rgotina Village and Vražogrnac Village were created. Since Ca^{2+} is the dominant cation in all groundwater samples in villages located downstream of the Bor mine, it is necessary to observe SO_4^{2-} concentrations for identification of the presence of pollution. Maps showing locations of sampling sites and stiff diagrams for groundwater samples and river water samples collected in Slatina Village, Rgotina Village and Vražogrnac Village are shown in Figs. 5.12, 5.13 and 5.14. In the stiff diagrams, groundwater close to the polluted rivers is shown in the top row and groundwater far from the polluted rivers is shown in the bottom row.

Stiff diagrams of groundwater samples collected at Slatina Village show that concentrations of SO_4^{2-} and HCO_3^- in groundwater collected from wells near the Bor River (wells 18, 10, 11, 3 and 4) are similar. On the other hand, groundwater samples collected far from the Bor River (wells 6, 7, 9, 15, 16 and cold spring 13) are characterized by lower concentrations of SO_4^{2-} and higher concentrations of HCO_3^- (Fig. 5.12). Exceptions are groundwater samples from wells 8 and 17 which contain higher concentrations of SO_4^{2-} than HCO_3^-. However, the cause of higher SO_4^{2-} concentrations in those groundwater samples is most probably different from pollution by the polluted river water or tailings because these wells are located far from the Bor River and on the higher elevations. Therefore, contamination of these groundwater samples by pollutants that are transported by river water is not possible. Since Slatina Village is located near the mining facilities, there is a possibility that pollutants that affect groundwater quality in this part of the study area are transported through the air.

In Rgotina and Vražogrnac Villages, which are located in the downstream area of the Bor mine, the nearest wells to Bela River (well 47 in Rgotina and well 5 in Vražogrnac) contain the highest concentrations of SO_4^{2-} in the groundwater in each settlement (Figs. 5.13 and 5.14). In the wells located in intermediate parts between the polluted river and hilly area along the polluted river (Rgotina: wells 42, 48, 49 and 45; Vražogrnac: wells 4 and 1), concentrations of SO_4^{2-} and HCO_3^- are similar. In groundwater samples collected from wells located far from the Bela River in Rgotina

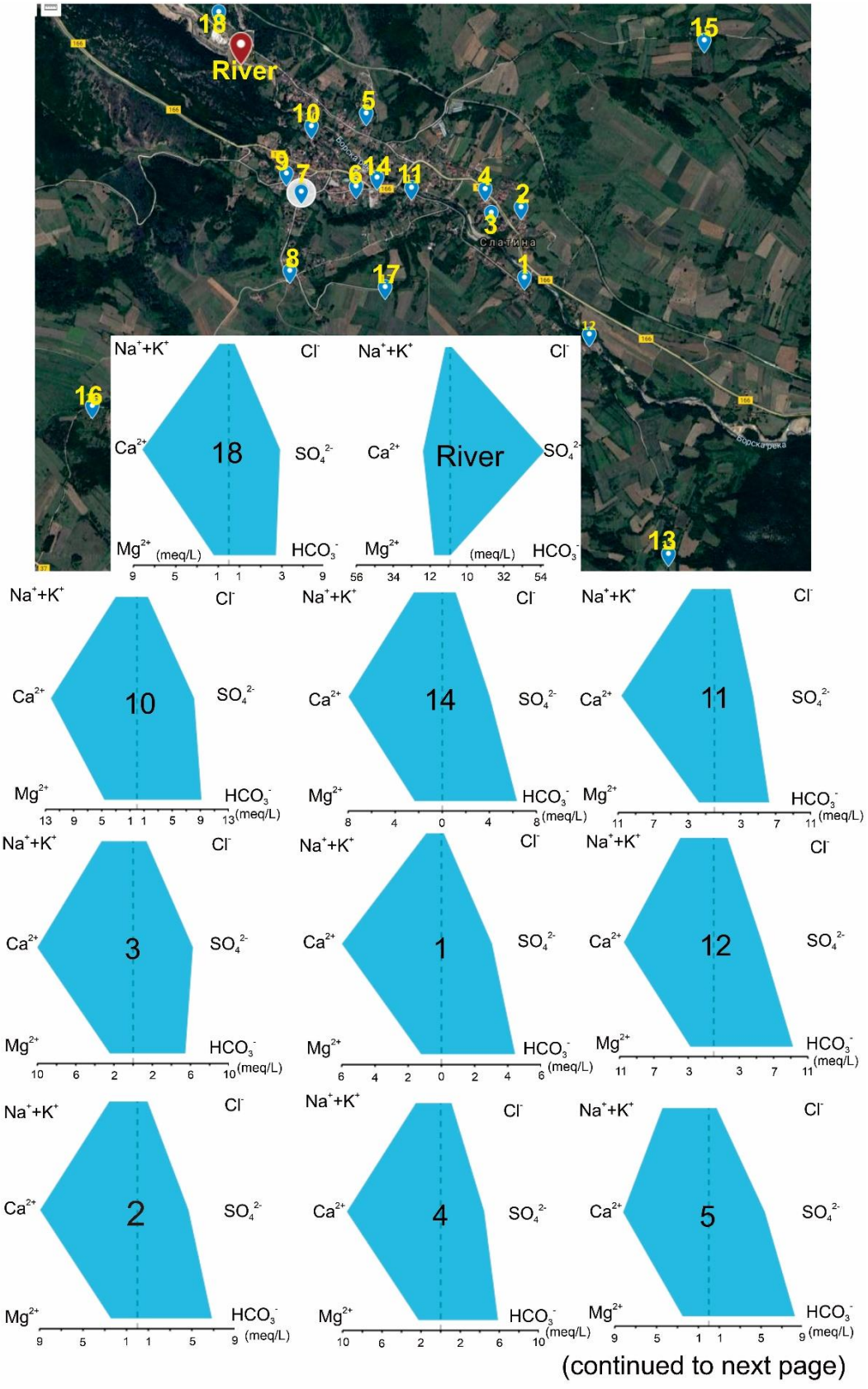


Fig. 5.12 Map of Slatina Village showing the location of sampling points and stiff diagrams for each groundwater sample and river water sample in the village. On the map, groundwater sampling sites are marked by blue and river water sampling site is marked by red.

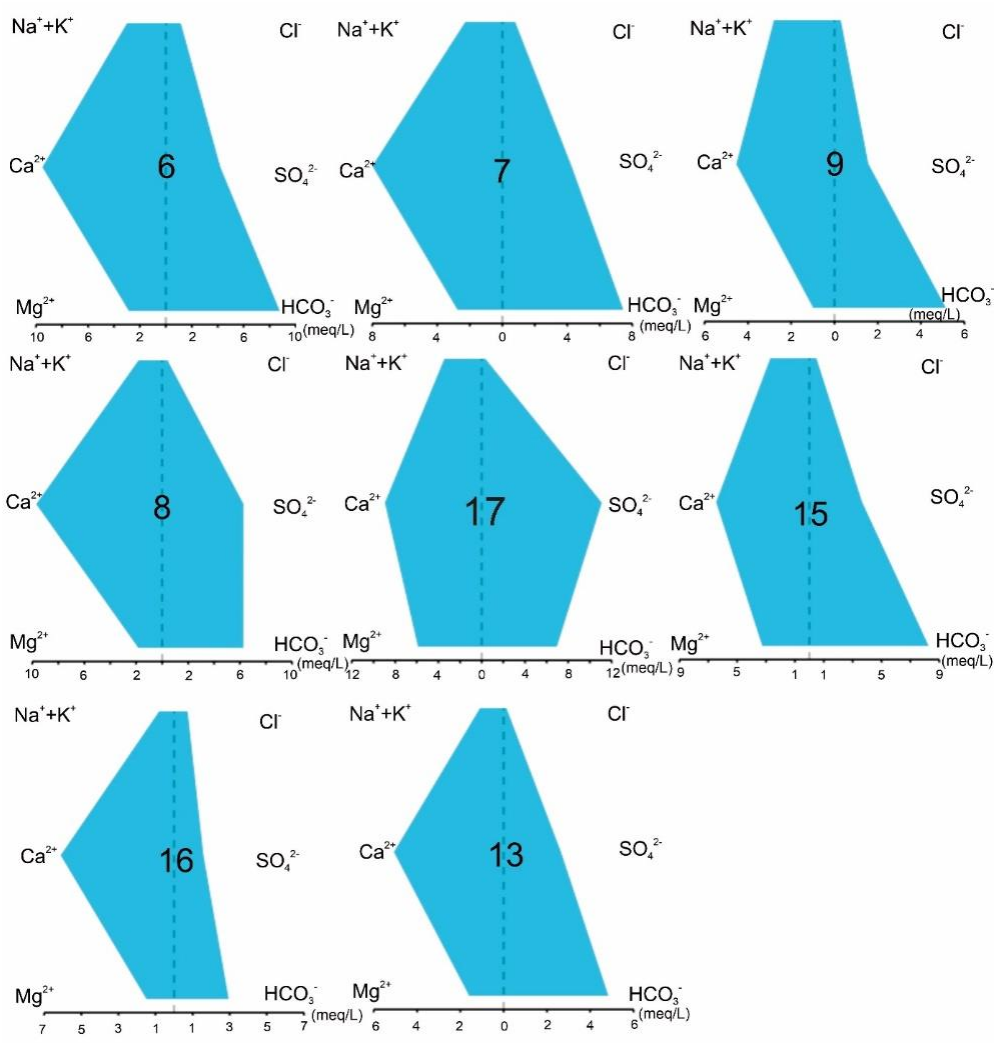


Fig. 5.12 (continued)

Village and Vražogrnac Village, concentrations of HCO_3^- are higher than concentrations SO_4^{2-} (Figs. 5.13 and 5.14). Therefore, a systematic distribution along polluted rivers in Rgotina and Vražogrnac Villages of groundwater having higher concentrations of SO_4^{2-} was observed.

Based on these data, groundwater in wells located near the polluted river in the Bor mining area is Ca-Mg-SO_4-dominant type water showing signature of pollution, while groundwater from wells in the same area that are located far from the polluted rivers is Ca-Mg-HCO_3-dominant type water without the signature of pollution by mining activities.

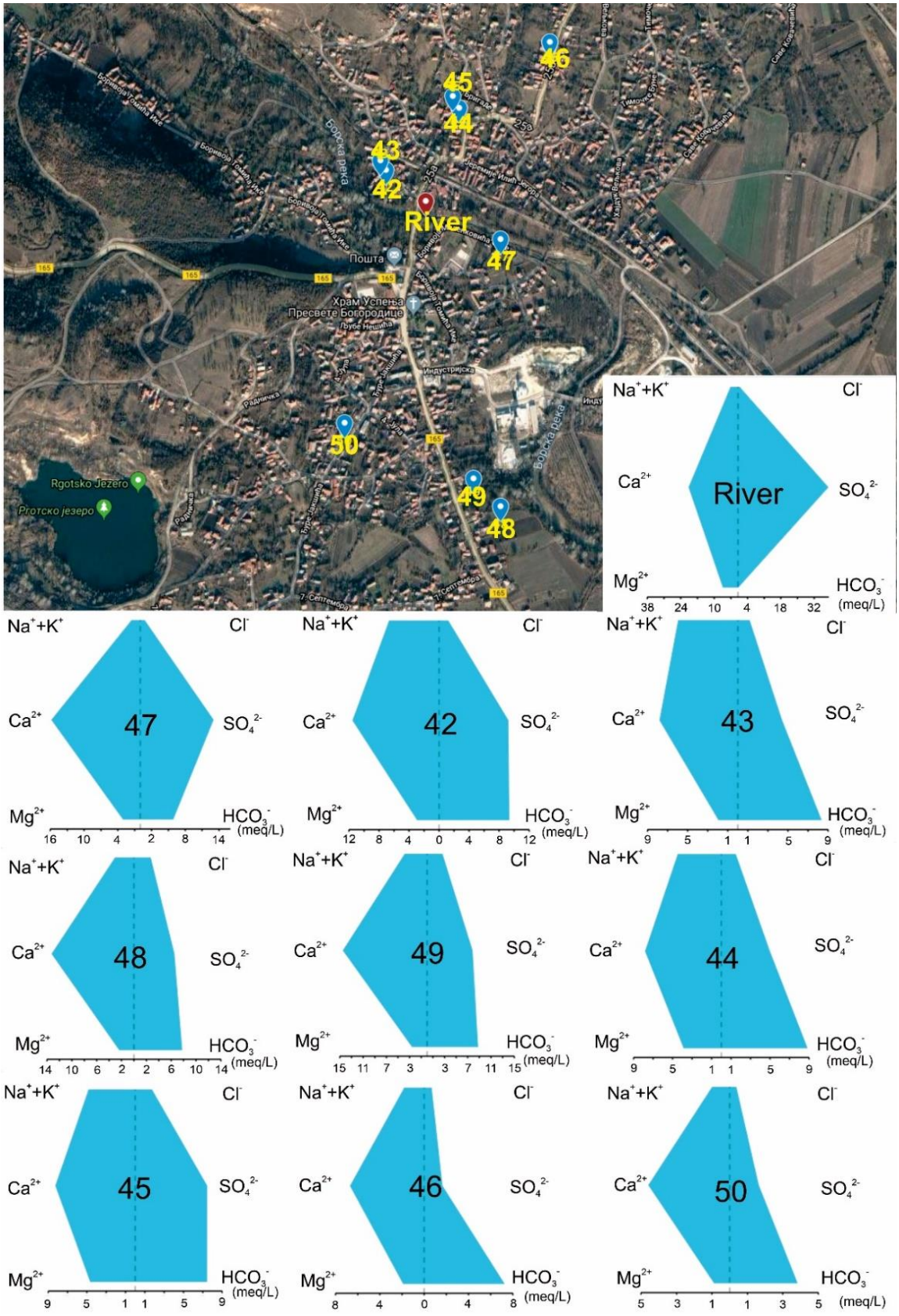


Fig. 5.13 Map of Rgotina Village showing the location of sampling points and stiff diagrams for each groundwater sample and river water sample in the village. On the map, groundwater sampling sites are marked by blue and river water sampling site is marked by red.

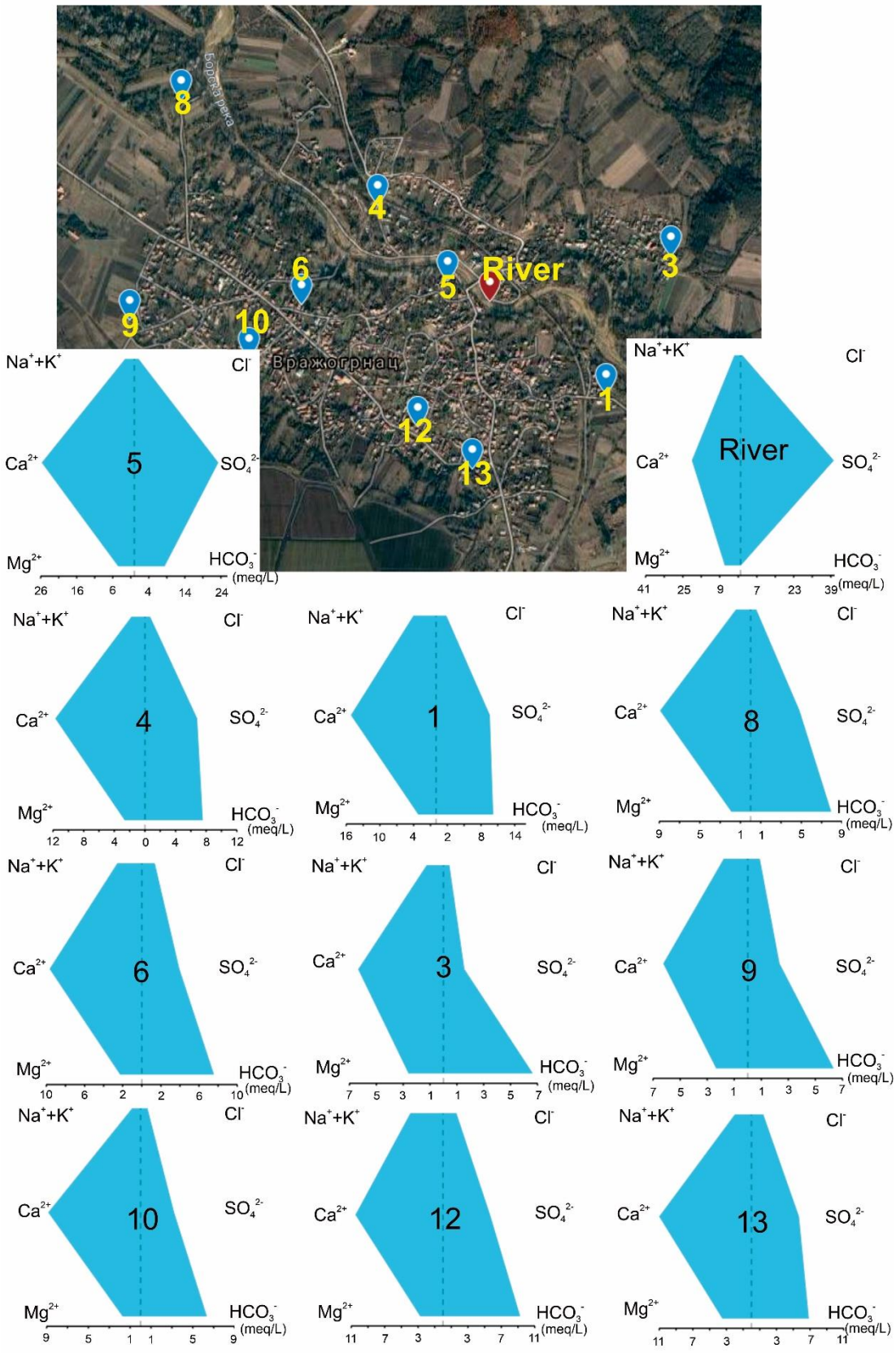


Fig. 5.14 Map of Vražogrnac Village showing the location of sampling points and stiff diagrams for each groundwater sample and river water sample in the village. On the map, groundwater sampling sites are marked by blue and river water sampling site is marked by red.

5.8. Mechanism of groundwater pollution

5.8.1. Examination of groundwater pollution by Ca^{2+} and SO_4^{2-}

Groundwater collected from wells near polluted rivers in the Bor mining area is mainly Ca-Mg-SO_4-dominant type water (Fig. 5.7, 5.12, 5.13 and 5.14). There are two possible explanations for high concentrations of Ca^{2+} and SO_4^{2-} in groundwater collected in the vicinity of polluted rivers, they are:

Case 1: mixing between polluted river water and groundwater, and

Case 2: infiltration of interstitial water in tailings along the banks of polluted rivers into groundwater.

5.8.1.1. Case 1: Mixing between polluted river water and groundwater

To understand the process of groundwater pollution, it is necessary to know the river channel slope and lateral valley slope i.e. lateral cross-section of the river (Larkin and Sharp, 1992; Sophocleous, 2002). The river channel slope of Bor River and Bela River is shown in Fig. 5.15. In the case of Slatina Village, a steeper river channel slope was observed, indicating that the speed of river water is fast. While in Rgotina Village and Vražogrnac Village, a gentler river channel slope was observed, suggesting that the speed of river water is slow. The retention time of river water in Rgotina Village and Vražogrnac Village is longer compared with the retention time of river water in Slatina Village. This means that on the territory of these villages, the potential pollutants will last longer.

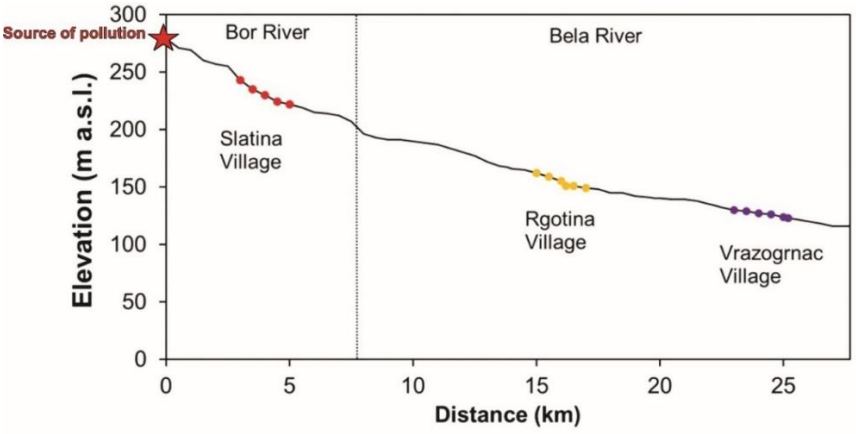


Fig. 5.15 Gradient (the river channel slope) along polluted rivers in the Bor mining area from the source of pollution to the confluence of Bela River with Timok River.

Mixing of river water and groundwater in an aquifer is possible in the case that the river channel slope is virtually small (gentle slope) and the lateral valley slope is negligible (Larkin and Sharp, 1992). In addition, in the case that the level of the water table of groundwater is lower than the level of river water (losing stream) the river water can affect groundwater in its vicinity (Sophocleous, 2002).

The lateral valley slope (lateral cross-section of the river) of Bor River in Slatina Village and Bela River in Rgotina and Vražogrnac Villages together with differences of levels of the water table and river water are shown in Figs. 5.16, 5.17 and 5.18, respectively.

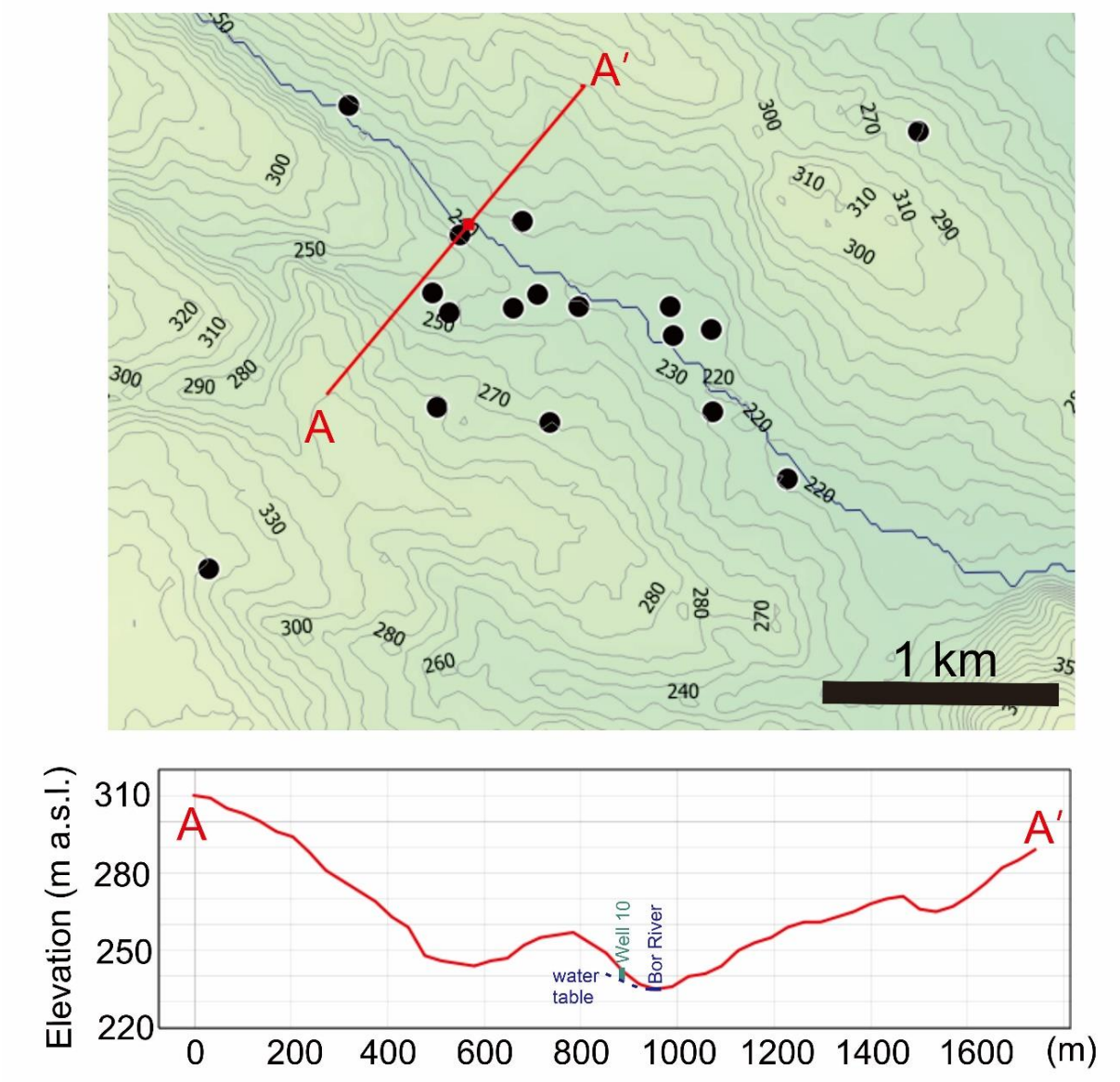


Fig. 5.16 Lateral cross-section of Bor River in Slatina Village.

The lateral cross-section of Bor River in Slatina Village indicates that the level of river water of Bor River is lower than the level of the water table (Fig. 5.16). Moreover, Slatina Village is located in the intermountain basin. On the other hand, Rgotina and Vražogrnac Villages are located in plain areas and based on the lateral cross-section of Bela River in these villages, the level of the river water is higher than the level of the water table of wells located close to the river (Figs. 5.17 and 5.18). Based on the topography of villages in the area downstream of the Bor mine and slope of the river channel as well as the level of the water table, there is a low possibility of direct mixing between polluted river water and groundwater in Slatina Village. On the other hand, in Rgotina and Vražogrnac Villages there is a possibility that polluted river water can affect groundwater. Due to the large amounts of tailings that were transported

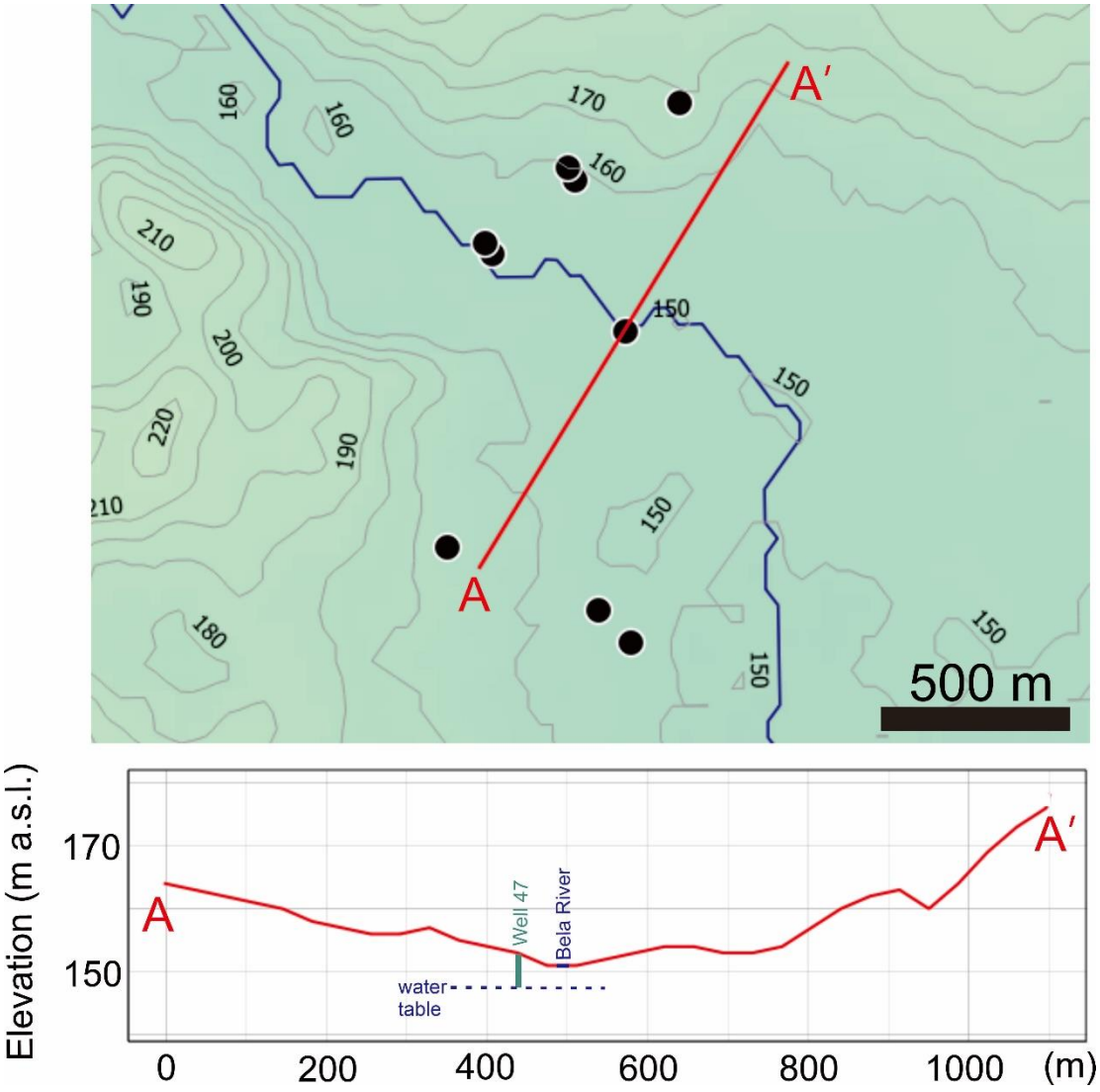


Fig. 5.17 Lateral cross-section of Bela River in Rgotina Village.

during the dam collapse event (see chapter 2.3) the river bed increased which may be the reason why the level of the water table in Rgotina and Vražogrnac Villages is lower than the level of Bela River.

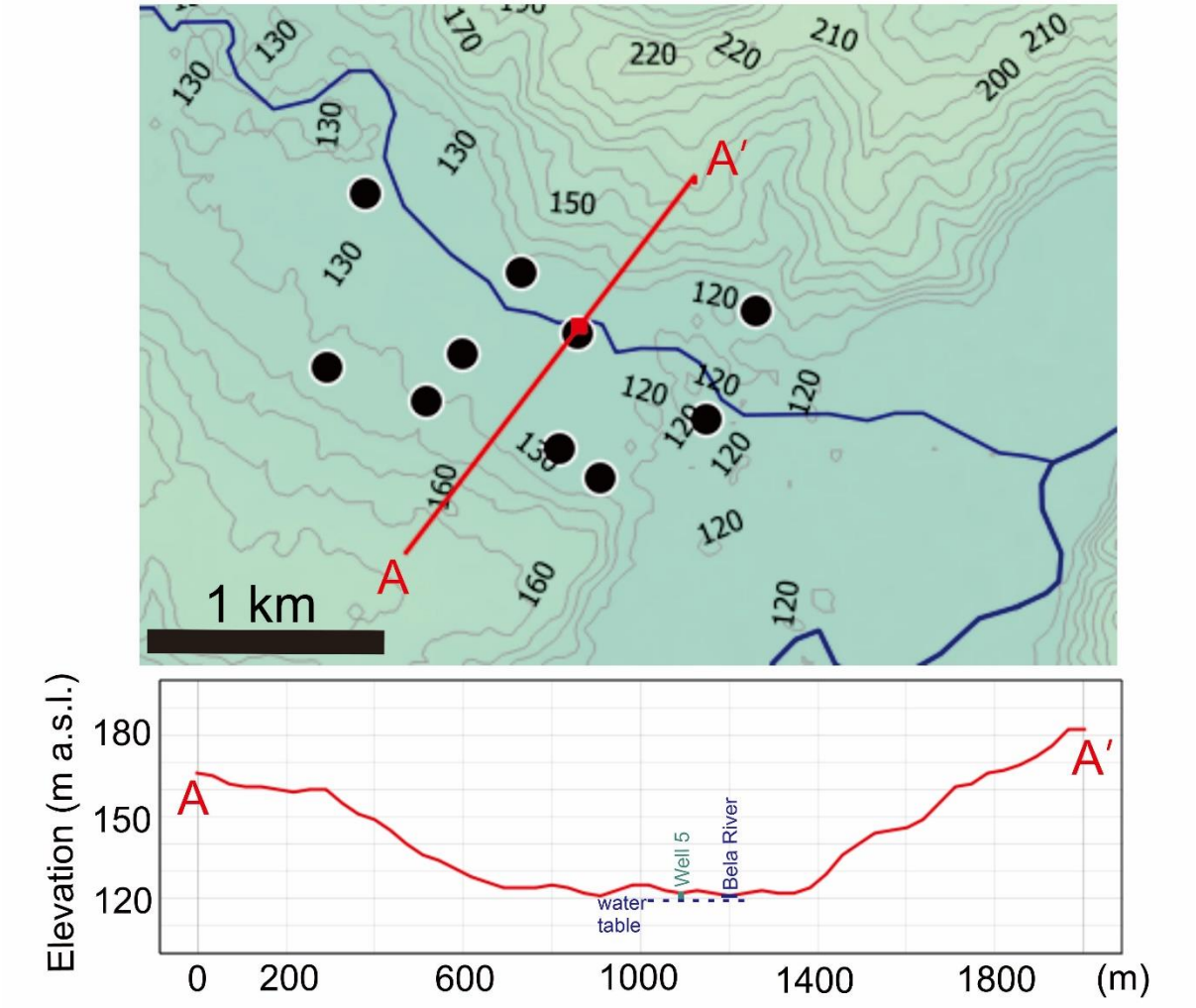


Fig. 5.18 L[a]teral cross-sections of Bela River in Vražogrnac Village.

Based on the relation between the level of the polluted river water and the level of groundwater in Rgotina and Vražogrnac Villages, a mixing between polluted river water and groundwater could be a possible process of groundwater contamination. To confirm a concept of mixing calculations, mixing models were created between polluted water samples and unpolluted water samples collected in the study area. Polluted water samples included polluted river water samples, interstitial water in tailings that are present along polluted rivers and groundwater from a drill hole in the overburden. The

pH values, Eh values and concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, Fe, As, Cu and Mn in polluted water samples from the Bor mining area are shown in Table 5.2. Unpolluted water samples included groundwater samples collected outside the mining areas, results obtained for these groundwater samples are shown in Appendices 4, 5, 6 and 7.

Table 5.2 The pH values, Eh values, concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-}, dissolved Fe, dissolved As, dissolved Cu and dissolved Mn in polluted river water, unpolluted river water sample, a drill hole in the overburden and interstitial water from tailings.

Sampling site	pH	Eh (mV)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	SO_4^{2-} (mg/L)	Fe (µg/L)	As (µg/L)	Cu (µg/L)	Mn (µg/L)
Bor River, S1[1]	2.9	650	317.8	111.1	2679	252800	651	100500	8566
Bor River, S2[1]	2.9	655	356.0	112.5	2831	261900	500	102800	8776
Krivelj River, S3[1]	7.8	439	554.2	84.5	1796	21.3	0.6	68.6	5300
Bela River, S4[1]	3.1	635	373.5	90.0	2112	113620	96.6	60180	6316
Ravna River, S5[2]	8.3	400	95.4	6.1	27.0	6.6	1.7	1.4	1.3
Bela River, S6[1]	3.7	533	409.7	74.1	1807	74240	35.3	46360	5097
Bela River, S7[1]	3.1	652	416.2	80.0	1921	36550	19.8	50320	5313
Timok River, a.c. S8[1]	6.5	416	146.2	25.1	377	9.5	11.0	1582	1008
Timok River, b.c. S9[2]	7.5	42	76.9	10.0	8.2	44.1	2.5	4.8	25.0
Ravna River, S10[2]	8.3	364	78.7	17.6	46.8	4.3	2.7	0.9	1.5
Timok River, a.c. S11 [1]	7.1	467	135.6	24.1	344	9.8	10.5	1007	977
Ravna River, S12[2]	8.0	382	80.1	2.5	21.5	8.0	0.7	0.9	2.0
Krivelj River, S13[1]	7.9	402	130.0	38.5	427	6.5	0.9	325	2204
Drill hole[3]	6.8	369	700	110	1700	30000	20	4000	10000
Interstitial water[4]	4.5	530	500	40	1670	11500	100	4200	20000

[1], polluted river water by mining activities; [2], natural river water; [3], groundwater collected from a drill hole in the overburden; [4], interstitial water collected from shovel near Bor River at Slatina Village; a.c., after the confluence with polluted river water; b.c., before the confluence with polluted river water.

To ascertain if the mechanism of groundwater pollution in the study area is by direct mixing between polluted river water and groundwater, a mixing line was created. In this case, a polluted end-member consisted of concentrations of Ca^{2+} and SO_4^{2-} obtained for polluted river water, while an unpolluted end-member consisted of concentrations of Ca^{2+} and SO_4^{2-} obtained for groundwater samples that were collected outside the mining areas. In the mixing diagrams together with mixing lines, actual concentrations of Ca^{2+} and SO_4^{2-} in groundwater samples collected at Slatina Village (Fig. 5.19), Rgotina Village (Fig. 5.20) and Vražogrnac Village (Fig. 5.21) were plotted.

Groundwater samples that were collected near polluted rivers (within 100 m) are shown as solid circles in red, groundwater samples from the intermediate part are solid circles in orange and groundwater samples collected far from the polluted rivers are solid circles in yellow. End-members in the mixing diagrams are shown in different colors.

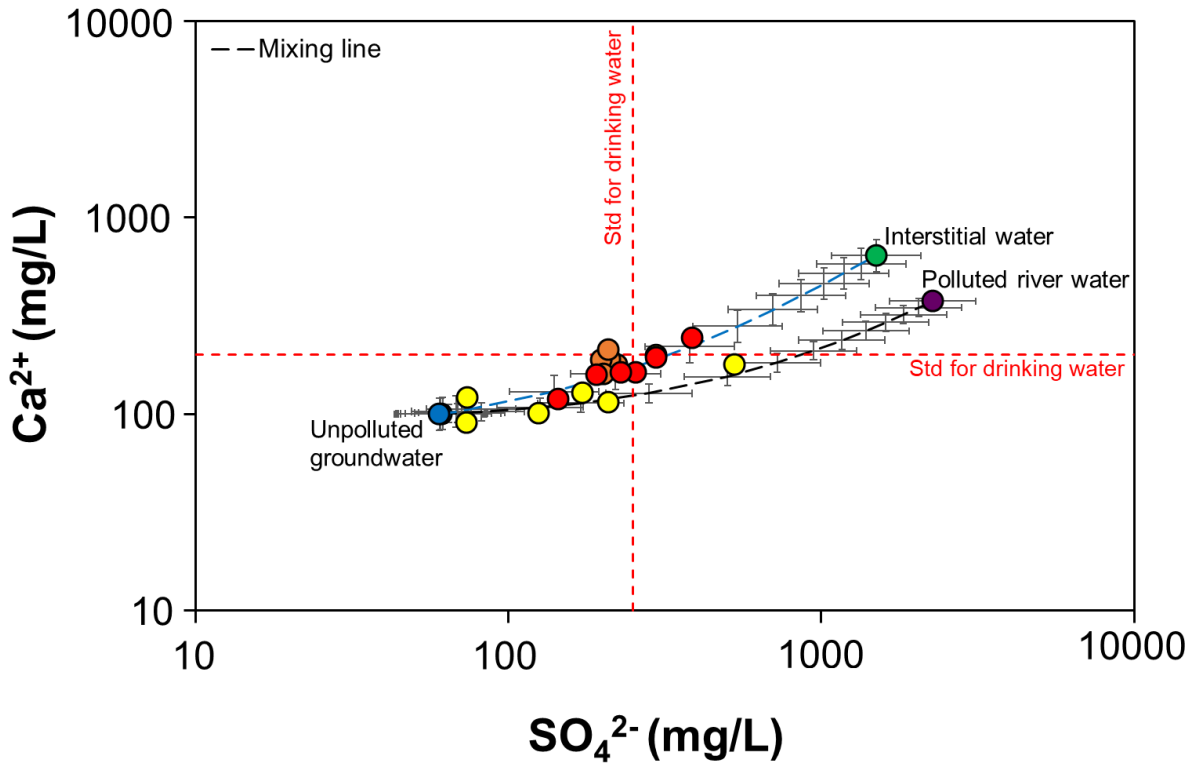


Fig. 5.19 Diagram showing two end-members/two components mixing lines for groundwater samples collected in Slatina Village. Solid circles in red correspond to groundwater samples collected near the Bela River, orange solid circles correspond to intermediate groundwater samples and yellow solid circles correspond to groundwater samples collected far from the Bor River. The black dashed line corresponds to the mixing model between polluted river water and groundwater, while the blue dashed line corresponds to the mixing model between interstitial water and groundwater.

Based on the distribution of actual concentrations of Ca^{2+} and SO_4^{2-} in groundwater, direct mixing between polluted river water and groundwater is not the mechanism of pollution of groundwater because samples are plotted outside the mixing line. Several samples collected at Slatina Village are plotted on the mixing line.

However, these samples were collected far from the Bor River. Therefore, mixing of groundwater from that region and polluted river water is not possible. In addition, the highest concentrations of Ca^{2+} and SO_4^{2-} were found in groundwater collected at Vražogrnac Village, which is located relatively far from the source of pollution. For this reason, attention should be also paid to areas far from the mine areas not just in the mine vicinity.

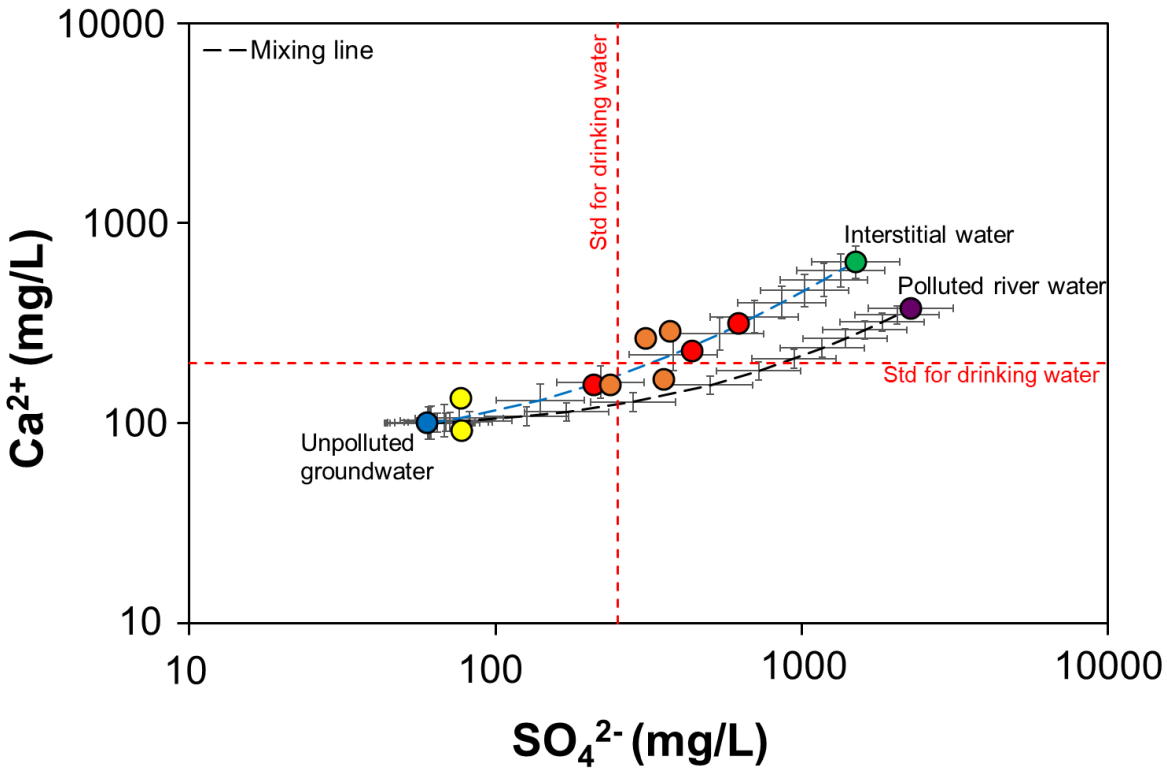


Fig. 5.20 Diagram showing two end-members/two components mixing lines for groundwater samples collected in Rgotina Village. Solid circles in red correspond to groundwater samples collected near the Bela River, orange solid circles correspond to intermediate groundwater samples and yellow solid circles correspond to groundwater samples collected far from the Bela River. The black dashed line corresponds to the mixing model between polluted river water and groundwater, while the blue dashed line corresponds to the mixing model between interstitial water and groundwater.

A similar examination was carried out using H^+ and SO_4^{2-} concentrations. The diagrams showing mixing relation based on pH and SO_4^{2-} are shown in Figs 5.22, 5.23

and 5.24. For these mixing diagrams, the end-members used were the same as those used for the mixing model for Ca^{2+} and SO_4^{2-} concentrations. Polluted river water samples of Bor River and Bela River have acidic character, while all groundwater samples are characterized by a near-neutral pH. Hence, all groundwater data is plotted far from the mixing line created for the mixing model between polluted river water and groundwater. Based on these results, it is difficult to explain the pollution of groundwater near the Bor River and Bela River in these villages based on the process of mixing between polluted river water and unpolluted groundwater.

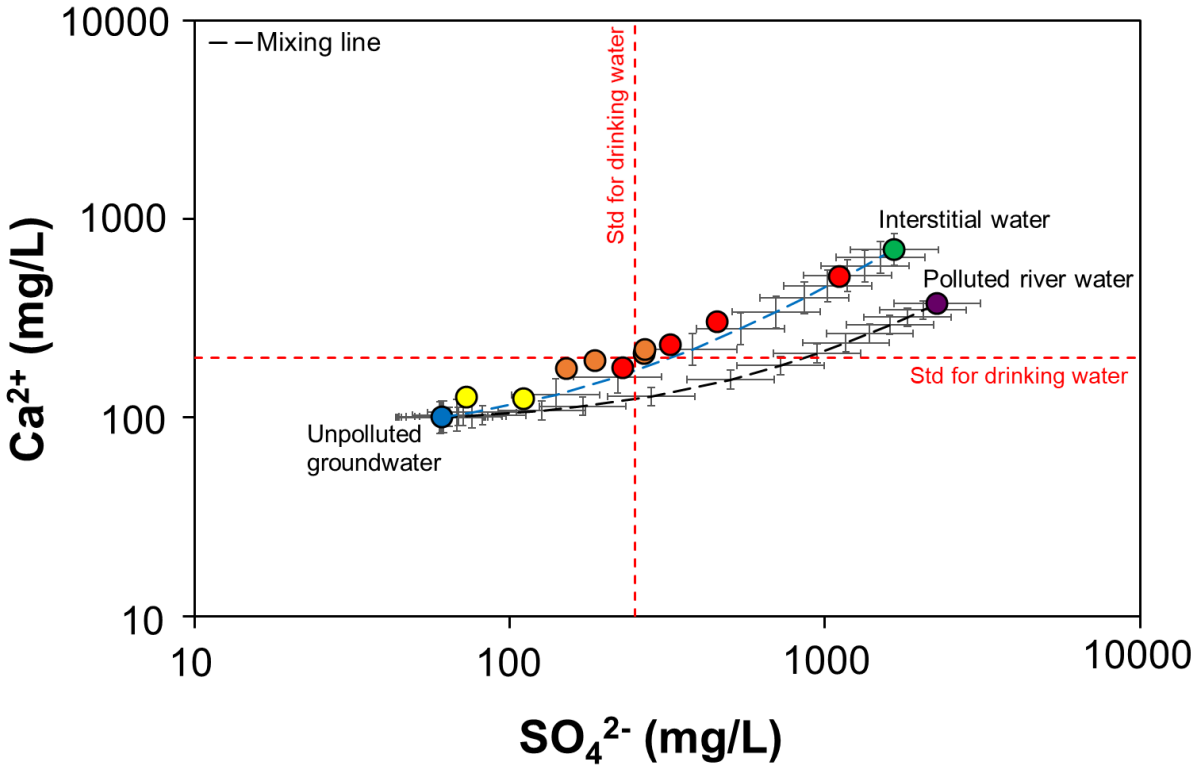


Fig. 5.21 Diagram showing two end-members/two components mixing lines for groundwater samples collected in Vražogrnac Village. Solid circles in red correspond to groundwater samples collected near the Bela River, orange solid circles correspond to intermediate groundwater samples and yellow solid circles correspond to groundwater samples collected far from the Bela River. The black dashed line corresponds to the mixing model between polluted river water and groundwater, while the blue dashed line corresponds to the mixing model between interstitial water and groundwater.

5.8.1.2. Case 2: Infiltration of interstitial water in tailings along the banks of polluted rivers into groundwater

Mixing between interstitial water in tailings and groundwater may be possible in rainy seasons and snow-melting seasons when water from the surface can percolate into the aquifer. To investigate the possibility of groundwater pollution by interstitial water from the tailings deposited on the floodplains of rivers downstream of the Bor mine, the chemical composition of these pore waters was determined. In addition, the chemical composition of groundwater collected from a drill hole in the overburden was examined. The results are shown in Table 5.2. Concentrations of major elements in interstitial water and groundwater from the drill hole in the overburden were found to be similar. Based on these results, the second mixing line was created. The mixing line for this case is shown in blue in Figs. 5.19, 5.20 and 5.21. For a polluted end-member, concentrations of Ca^{2+} and SO_4^{2-} measured in interstitial water present in tailings along polluted rivers and groundwater from a drill hole in the overburden were used (Table 5.2). For unpolluted end-member concentrations of Ca^{2+} and SO_4^{2-} measured in groundwater outside the mining areas were used.

Data obtained for groundwater samples collected close to the polluted Bor and Bela Rivers and from intermediate parts are plotted on the mixing line created for the mixing model between interstitial water and unpolluted groundwater (Figs. 5.19, 5.20 and 5.21.). This fact suggests that interstitial water in tailings has an effect on groundwater in the area downstream of the Bor mine. Therefore, the mechanism of groundwater pollution in the area downstream of the Bor mine is mixing between interstitial water in tailings and groundwater.

The most affected groundwater was collected from well 5 in Vražogrnac Village. The mixing ratio for this groundwater sample is estimated to be 65% of polluted water and 35% of unpolluted water.

A similar examination was carried out regarding the interstitial water and unpolluted groundwater using H^+ and SO_4^{2-} concentrations. The mixing diagrams of pH values and SO_4^{2-} concentrations are shown in Figs. 5.22, 5.23 and 5.24. For this

consideration, four mixing lines were created, showing a wider range of pH values in interstitial water in tailings. If the pH values of interstitial water ranged between 5.5 and 8.0, pollution of groundwater may be caused by interstitial water in tailings.

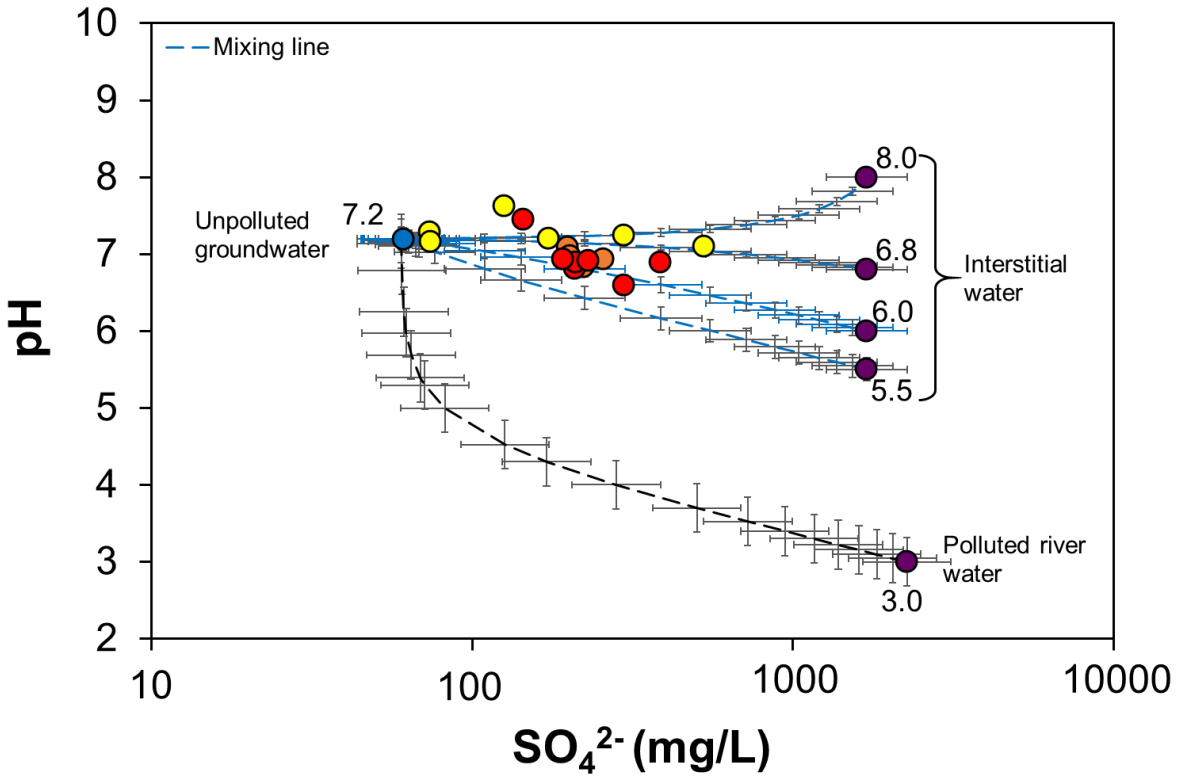


Fig. 5.22 Diagram showing two end-members/two components mixing lines for groundwater samples collected in Slatina Village. Solid circles in red correspond to groundwater samples collected near the Bela River, orange solid circles correspond to intermediate groundwater samples and yellow solid circles correspond to groundwater samples collected far from the Bela River. The black dashed line corresponds to the mixing model between polluted river water and groundwater, while the blue dashed lines correspond to the mixing model between interstitial water and groundwater.

Based on the relation of Ca^{2+} and SO_4^{2-}, as well as pH values and SO_4^{2-} concentrations of groundwater on mixing diagrams (Figs. 5.19, 5.20, 5.21, 5.22, 5.23 and 5.24), if the interstitial water in tailings along polluted rivers percolate into the aquifer, pollution of groundwater may occur (Fig. 5.25). In the snow melting season

and rainy season, the level of surface water increases, and water from the surface percolate into the aquifer (Ćatović, 2018-2020; Republic of Serbia, 2018, 2019a, 2020).

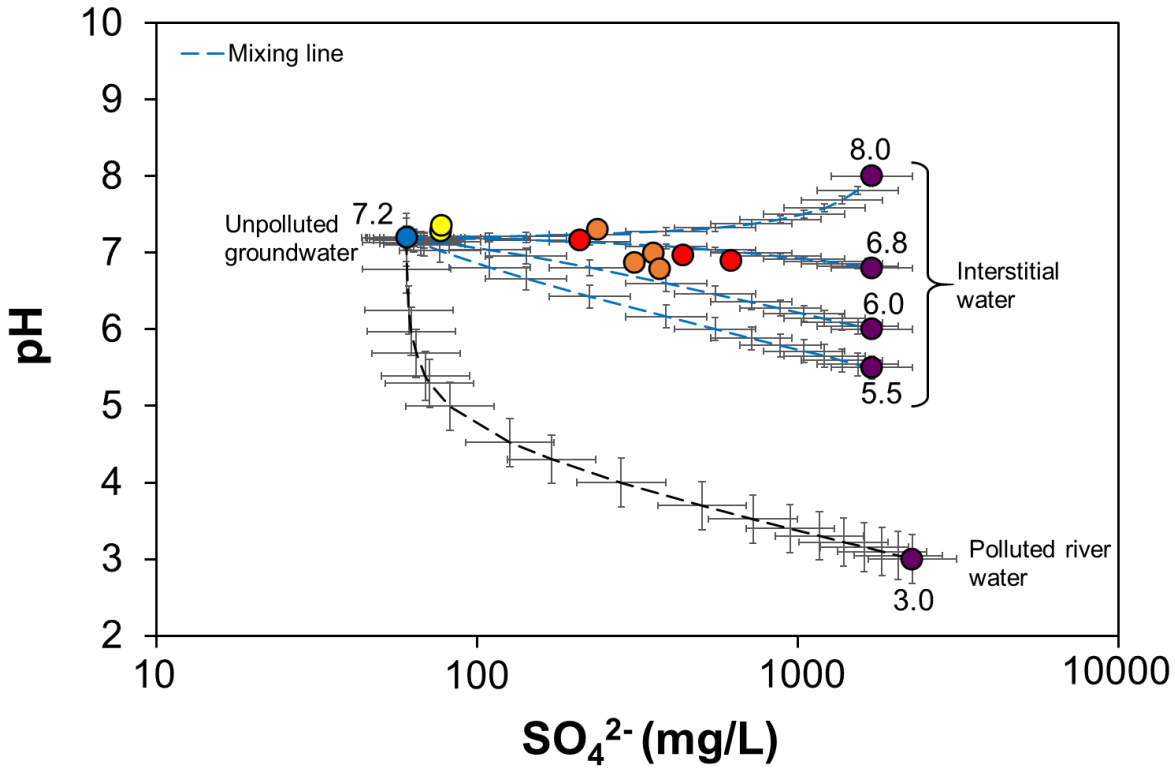


Fig. 5.23 Diagram showing two end-members/two components mixing lines for groundwater samples collected in Rgotina Village. Solid circles in red correspond to groundwater samples collected near the Bela River, orange solid circles correspond to intermediate groundwater samples and yellow solid circles correspond to groundwater samples collected far from the Bela River. The black dashed line corresponds to the mixing model between polluted river water and groundwater, while the blue dashed lines correspond to the mixing model between interstitial water and groundwater.

Concentrations of Ca^{2+} and SO_4^{2-} in groundwater at Rgotina and Vražogrnac Villages were high in the vicinity of polluted rivers. With increasing distance from the river, concentrations of these components were lower. Moreover, pollution is consistent with the presence of tailings along the rivers. Therefore, the mechanism of groundwater pollution in Rgotina and Vražogrnac Villages is primarily the percolation of interstitial water in tailings into groundwater. The model of groundwater pollution in these villages

is shown in Fig. 5.25. On the other hand, the highest concentrations of SO_4^{2-} in Slatina Village are found farther from the Bor River at a higher altitude. Therefore, there is a possibility that groundwater in Slatina Village might be affected by a combination of pollutants transported by dust and smoke from the Bor mine and downward movement of interstitial water containing high SO_4^{2-} derived from the dust and smoke. The model of groundwater pollution in Slatina Village is shown in Fig. 5.25. This idea is supported by the following evidence:

1) Air pollution in Slatina village is intense (Serbula et al., 2021),
2) The distribution of polluted groundwater is not restricted near the polluted Bor River,

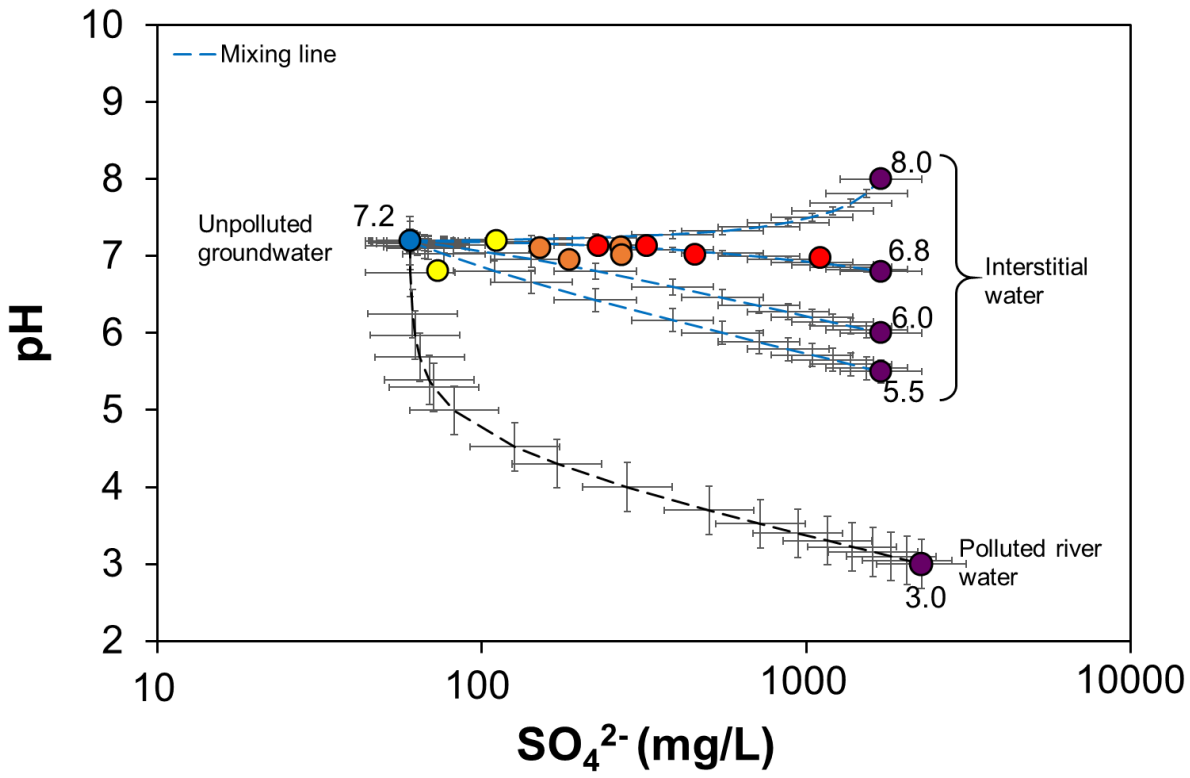


Fig. 5.24 Diagram showing two end-members/two components mixing lines for groundwater samples collected in Vražogrnac Village. Solid circles in red correspond to groundwater samples collected near the Bela River, orange solid circles correspond to intermediate groundwater samples and yellow solid circles correspond to groundwater samples collected far from the Bela River. The black dashed line corresponds to the mixing model between polluted river water and groundwater, while the blue dashed lines correspond to the mixing model between interstitial water and groundwater.

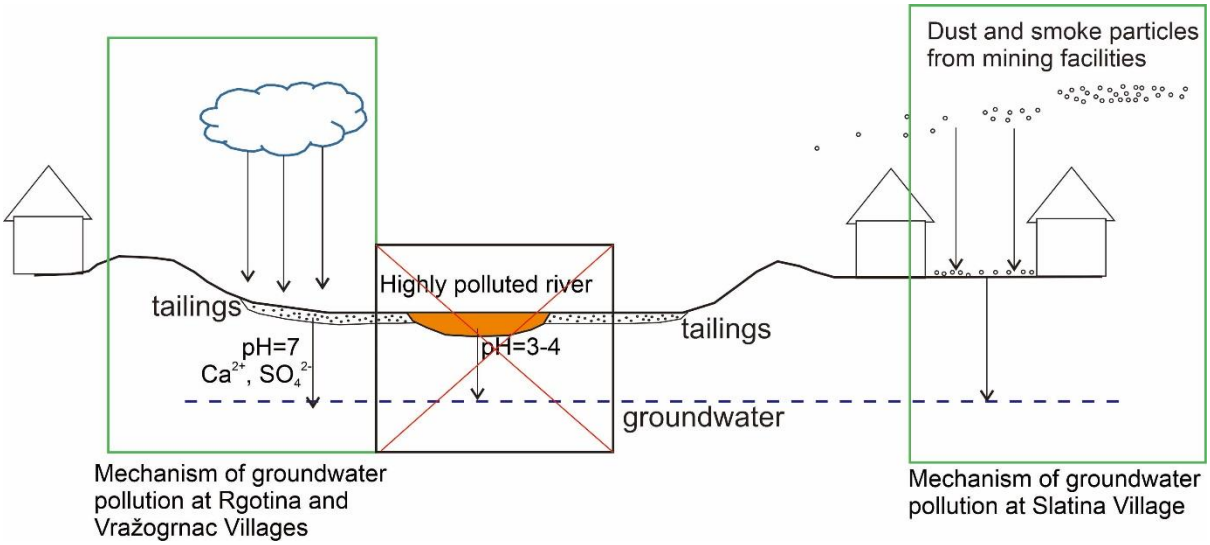


Fig. 5.25 Diagram showing different mechanisms of groundwater pollution in the Bor mining area.

5.8.2. Examination of groundwater pollution by heavy metals and arsenic

To examine if groundwater is affected by heavy metals and arsenic, mixing diagrams were created for concentrations of Cu, Fe, Mn and As that are present in high concentrations in the acid mine drainage-bearing river water in the study area (Fig. 5.26). In this case, two mixing lines were also used. The three polluted end-members included polluted river water, interstitial water from shovel near Bor River and groundwater from a drill hole in the overburden of the Bor mine. Unpolluted end-member consisted of unpolluted groundwater collected outside the mining areas. Heavy metal and arsenic concentrations in polluted end-members were much higher than actual concentrations of groundwater samples collected at Slatina Village, Rgotina Village and Vražogrnac Village. Therefore, the mixing relation between polluted water and unpolluted water was not observed among these components. This is because Cu, Fe, Mn and As will precipitate and co-precipitate in tailings and could not be present as aqueous species in water having a near-neutral pH, which is the case of groundwater from the study area.

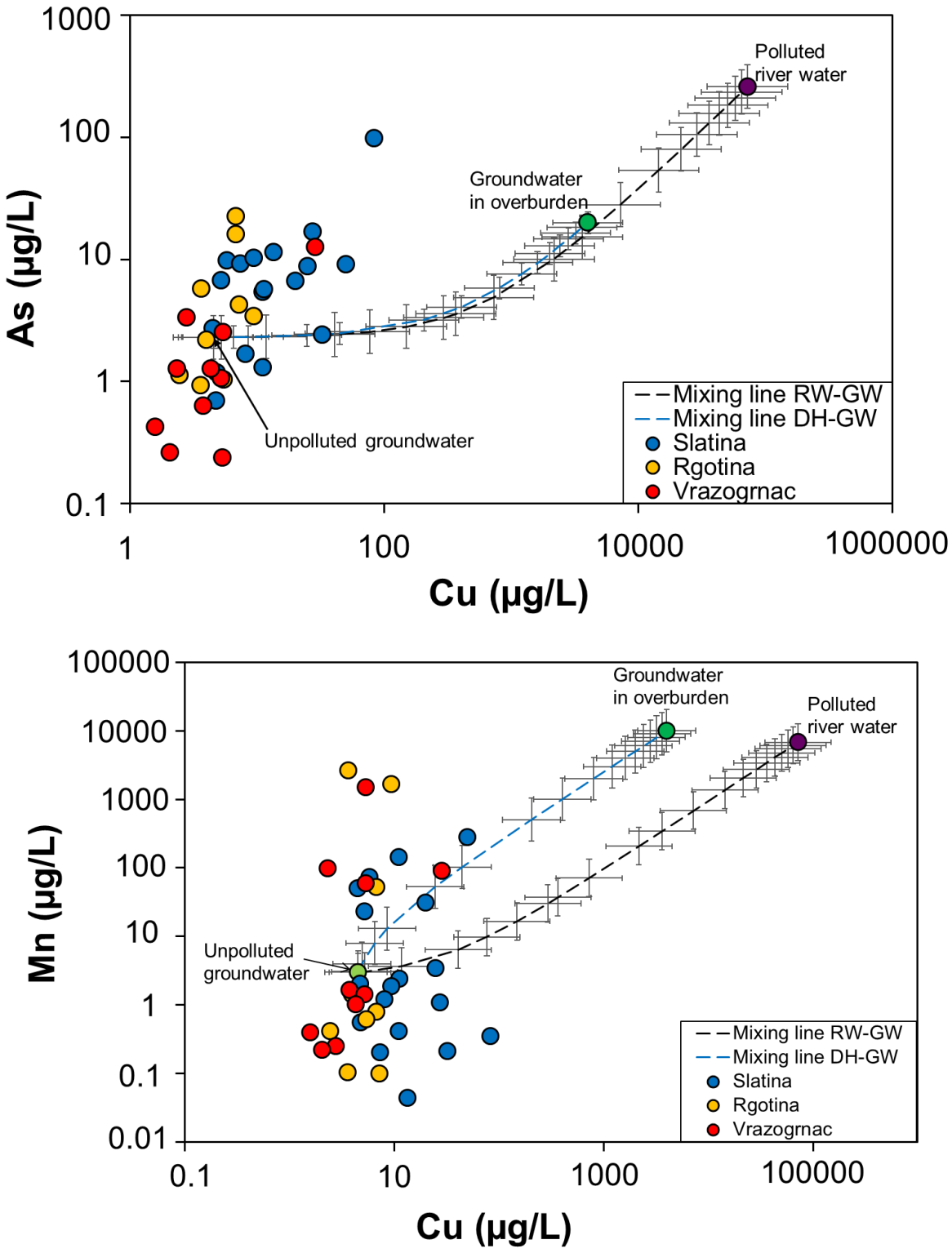


Fig. 5.26 Mixing diagrams obtained for heavy metals and arsenic in groundwater samples from Slatina Village, Rgotina Village and Vražogrnac Village.

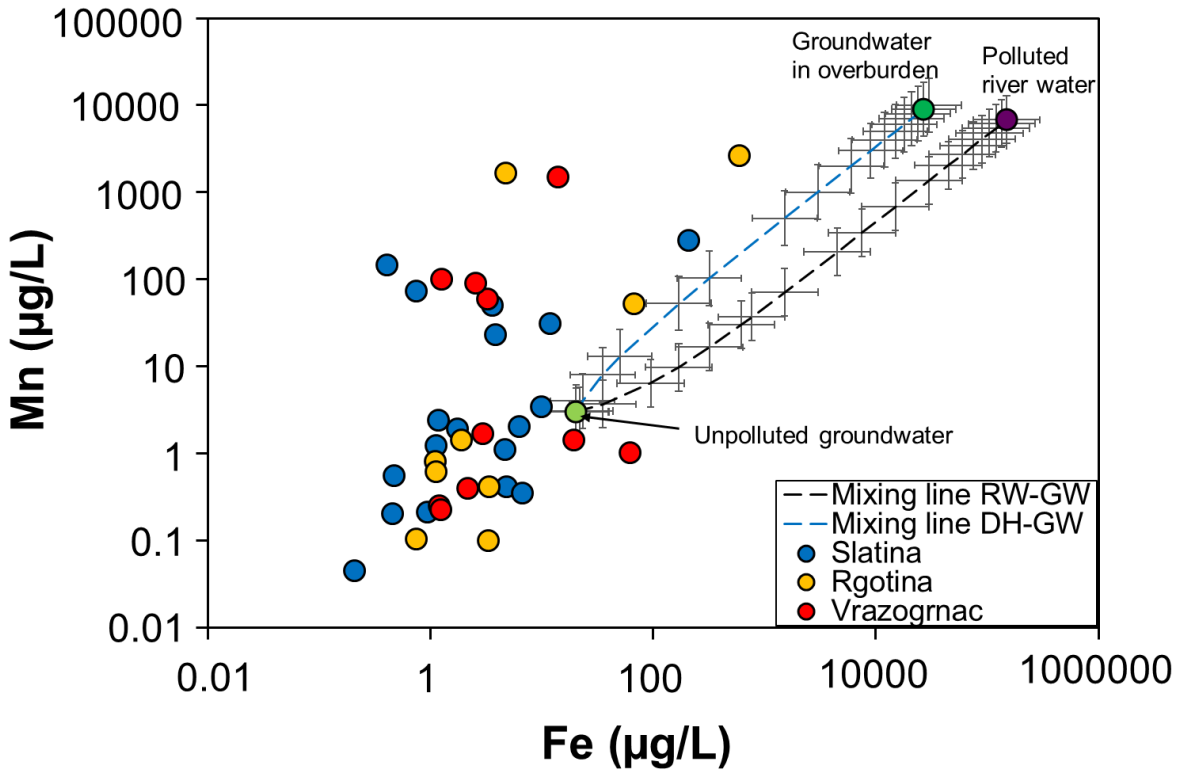


Fig. 5.26 (continued)

5.9. Evaluation method and appropriate components for groundwater monitoring

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; Moyé et al., 2017; Giri and Singh, 2019; Bulut et al., 2020; Popugaeva 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. Calcium and sulfate can be present as aqueous species in a solution having a near-neutral character, while heavy metals precipitate in this kind of solution. Although large amounts of heavy metals and arsenic are discharged into Bor River and Bela River (Ishiyama et al., 2012; Stevanović et al., 2013; Gardić et al., 2015), groundwater is not affected by heavy metals and arsenic. Moreover, the 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 all observations in this study, that tailings that are present along Bor River and Bela River are the source of groundwater pollution in this area.

6. Summary

In this study, a geochemical investigation of river water and groundwater in Eastern Serbia was conducted. Mining activities that have been carried out for more than a century in this area have had a severe environmental impact on rivers, especially rivers that are located downstream of mining sites. Results of the geochemical analysis showed that river water in the Bor and Majdanpek mining areas has been affected by mining activities. This study indicated that groundwater was less affected compared with river water from the same area.

The results obtained in this study are summarized below.

1. Based on the estimations of threshold values and lengths of rivers with pollution, there is a possibility that the pollution caused by mining activities reaches the Danube River, which is located more than 100 km from the sources of pollution in the Bor and Majdanpek mines.
2. The environmental impact in the Bor mining area, which has metallurgical facilities (including a smelter), was shown to be larger than that in the Majdanpek mining area, which has no metallurgical facilities, by a comparison of water chemistry in the Bor mining area and that in the Majdanpek mining area. There is a possibility that the presence of limestone bodies in the Majdanpek mining area also contributes to the remediation of the water chemistry of river water in the mining area.
3. Considering appropriate countermeasures of environmental reclamation such as artificial neutralization at some important sources of wastewater before discharging the wastewater from the mining sites, there is a possibility for environmental reclamation in both mining areas because unpolluted water in the study area has sufficient capacity for neutralization in a natural system.
4. Results of the geochemical analysis showed that groundwater in the study area has a good quality in general. Groundwater samples are characterized by circumneutral pH values. In most of the groundwater samples, all heavy metals

and hazardous element concentrations are below the maximum admissible concentrations according to the Serbian standards for drinking water.

5. Geology has a strong influence on groundwater composition, especially in the area around Bor deposits where higher concentrations of Cu and As are present and in the Cretaceous limestone-rich areas where higher concentrations of HCO_3^- and Sr are present.
6. The distributions of Ca^{2+} and SO_4^{2-} concentrations in geochemical maps show that the area downstream of the Bor mine along strongly polluted rivers has groundwater contamination, even though the area is located in the plain area, about 30 km downstream of the Bor mine. Threshold values estimated for Ca^{2+} and SO_4^{2-} are below the standard values for drinking water. However, the actual concentrations of these components in groundwater samples from the area downstream of the Bor mine exceed the threshold values, suggesting an impact of mining activities by the Bor mine. In the Majdanpek mining area, groundwater pollution was not detected.
7. Calcium and sulfate concentrations were shown to be good indicators for monitoring of early-stage groundwater pollution caused by mining activities such as those in Eastern Serbia. Evaluation using Ca^{2+} and SO_4^{2-} concentrations is mainly suitable for groundwater with a near-neutral pH. In addition, due to high concentrations of heavy metals and arsenic in potential groundwater pollutants, it is recommended to monitor their concentrations as well to prevent serious groundwater pollution.
8. Mixing calculations showed that the mechanism of groundwater pollution is infiltration of interstitial water in tailings along the banks of polluted rivers into groundwater, not direct mixing between polluted river water and groundwater.
9. The evaluation method used in this study, which is based on geochemical maps, threshold values and mixing analysis considering geochemical reactions, is widely applicable to environmental assessment in mining areas.

References

Appelo, C. and Postma, D., 2005. Geochemistry, groundwater and pollution. Boca Raton: CRC Press, p.668.

Armienta, M.A., Villasenor, G., Rodriguez, R., Ongley, L.K., Mango, H., 2001. The role of arsenic-bearing rocks in groundwater pollution at Zimapan Valley, Mexico. Environmental Geology. 40(4-5), 571-581.

Armstong, R., Kozelj, D., Herrington, R., 2005. The Majdanpek Cu-Au Porphyry Deposit of Eastern Serbia: A Review. In: Porter, T.M. (Ed.) Super Porphyry Copper & Gold Deposits: A Global Perspective. PGC Publishing: Adelaide, Vol. 2, pp. 453-466.

Atanacković, N., Dragišić, V., Stojković, J., Papić, P., Živanović, V., 2013. Hydrochemical characteristics of mine waters from abandoned mining sites in Serbia and their impact on surface water quality. Environmental Science and Pollution Research, 20, 7615-7626. https://doi.org/10.1007/s11356-013-1959-4.

Atanacković, N., Dragišić, V., Živanović, V., Gardijan, S., Magazinović, S., 2016. Regional-scale screening of groundwater pollution risk induces by historical mining activities in Serbia. Environ. Earth Sci. 75, 1152. https://doi.org/10.1007/s12665-016-5983-9.

Avramović, Lj., Stevanović, Z., Bugarin, M., Jonović, R., Marković, R., Gardić, V., Jonović, M., Đorđević, J., 2016. Characterization of soil in the coastal area of the Bor River. Zaštita Materijala. 57(3), 378-382. https://doi.org/10.5937/ZasMat1603378A.

Bădăluța, C.A., Perișoiu, A., Ionita, M., Nagavciuc, V., Bistricean, P.I., 2018. Stable isotope investigation of groundwater recharge in the Carpathian Mountains, East-Central Europe. Hydrology and Earth System Sciences Discussions. https://doi.org/10.5194/hess-2018-6.

Banješević, M. and Large, D., 2014. Geology and mineralization of the mew copper and gold discovery south of Bor Timok magmatic complex. Proceedings of the XVI Serbian Geological Congress, Serbian Geological Society, Donji Milanovac. 739-741.

Banješević, M., 2010. Upper Cretaceous magmatic suites of the Timok Magmatic Complex. Geoloski Anali Balkanskog Poluostrva, 71, 13-22. https://doi.org/10.2298/GABP1071013B.

Banješević, M., Cvetković, V., von Quadt, A., Ljubović Obradović, D., Vasić, N., Pačevski, A., Peytcheva, I., 2019. New constraints on the main mineralization event inferred from the latest discoveries in the Bor Metallogenetic Zone (BMZ, East Serbia). Journal Minerals. 9,672. https://doi.org/10.3390/min9110672.

Bathrellos, G.D., Skilodimov, H.D., Kelepertsis, A., Alexakis, D., Chrisanthaki, I., Archonti, D., 2008. Environmental research of groundwater in the urban and suburban area of Attica region, Greece. Environmental Geology. 56, 11-18. https://doi.org/10.1007/s00254-007-1135-6.

Bird, G., Brewer, P. A., Macklin, M. G., Nikolova, M., Kostev, T., Mollov, M., Swain, C., 2010. Dispersal of contaminant metals in the mining-affected Danube and Maritsa Drainage Basins, Bulgaria, Eastern Europe. Water, Air, & Soil Pollution. 206, 105-127. https://doi.org/10.1007/s11270-009-0090-0.

Bogdanović, D., Obradović, L., Miletić, S., 2014. Selection of the optimum method of rehabilitation the degraded areas around the Bor river downstream from the flotation tailing dump Bor. Mining & Metallurgy Engineering Bor, 4, 137-156. https://doi.org/10.5937/MMEB1404137B.

Bonda, R., Cloutier, V., Benzaazova, M., Rosa, E., Bouzahzah, H., 2017. The role of sulfide minerals in the genesis of groundwater with elevated geogenic arsenic in bedrock aquifer from western Quebec, Canada. Chemical Geology. 474, 33-44. https://dx.doi.org/10.1016/j.chemgeo.2017.10.021.

Bottyán, E., Czuppon, G., Weidinger, T., Haszpra, L., Kármán, K., 2017. Moisture source diagnostics and isotope characteristics for precipitation in east Hungary: implications for their relationship. Hydrological Science Journal. 60(12), 2049-2060. https://doi.org/10.1080/02626667.2017.1358450.

Bulut, O.F., Duru, B., Çakmak, O., Günhan, O., Dilek, F.B., Yetis, U., 2020. Determination of groundwater threshold values: A methodological approach. Journal of Cleaner Production. 253, 120001. https://doi.org/10.1016/j.jclepro.2020.120001.

Ciobanu, C.L., Cook, N.J., Stein, H., 2002. Regional settings and geochronology of the Late Cretaceous Banatitic Magmatic and Metallogenic Belt. Mineralium Deposita. 37, 541-567. https://doi.org/10.1007/s00126-002-0272-9.

Clark, H. A. & Ullrich, D. T., 2004. $^{40}Ar/^{39}Ar$ age data for andesitic magmatism and hydrothermal activity in the Timok Massif, eastern Serbia: implications for metallogenic relationships in the Bor copper-gold subprovince. Mineralium Deposita. 39, 256-262.

Clark, I., 2015. Groundwater Geochemistry and Isotopes. CRC Press Boca Raton, Fl, USA.

Clark, I.D. and Fritz, P., 1997. Environmental isotopes in hydrogeology. Boca Raton: CRC Press LLC. p. 311.

Corsi, R. and Sacco, C., 2006. Environmental Assessment of RTB Bor Operations-Final Report. The Privatization Agency-Republic of Serbia ERM's Milan Office, Environmental Resources Management. Final report.

Craig. H., 1961. Isotopic variations in meteoric waters. Science. 133, 1702-1703.

Cruz, J.V. and Andrade, C., 2015. Natural background groundwater composition in the Azores archipelago (Portugal): A hydrogeochemical study and threshold value determination. Science of the Total Environment. 520, 127-135. https://doi.org/10.1016/j.scitotenv.2015.03.057.

Ćatovoić, S., 2018. Hydrological yearbook, 1 Surface water 2017. Republic of Serbia. Republic Hydrometeorological Institute: Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia Sector for hydrological observation system and analysis (in Serbian).

Ćatovoić, S., 2019. Hydrological yearbook, 1 Surface water 2018. Republic of Serbia. Republic Hydrometeorological Institute: Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia Sector for hydrological observation system and analysis (in Serbian).

Ćatovoić, S., 2020. Hydrological yearbook, 1 Surface water 2019. Republic of Serbia. Republic Hydrometeorological Institute: Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia Sector for hydrological observation system and analysis (in Serbian).

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus. 5, 461-469.

Davis, A., Heatwole, K., Greer, B., Ditmars, R., Clarke., 2010. Discriminating between background and mine-impacted groundwater at the Phoenix mine, Nevada USA. Applied Geochemistry. 25, 400-417. https://doi.org/10.1016/j.apgeochem.2009.12.007.

Devic, G., Djordjevic, D., Sakan, S., 2014. Natural and anthropogenic factors affecting the groundwater quality in Serbia. Science of the Total Environment. 468-469, 933-942. https://dx.doi.org/10.1016/j.scitotenv.2013.09.011.

Dimitrijević, M., Kostov, A., Tasić, V., Milošvić, N., 2009. Influence of pyrometallurgical copper production on the environment. Journal of Hazardous Materials. 164, 892-899. https://doi.org/10.1016/j.jhazmat.2008.08.099.

Djurovic, P. and Zivkovic, N., 2013. Morphological and hydrological characteristics of the Serbian border zone towards Bulgaria. Bulletin of the Serbian geographical society. 4, 51-69. https://doi.org/10.2298/GSGD1304051D.

Dokmanović, P., Dragišić, V., Špadijer, S., 2007. Thermomineral water of Nikoličevo Spa (eastern Serbia). Geoloski anali Balkanskog poluostrva. 68, 91-96. https://doi.org/10.2298/GABP0701091D.

Dokmanović, P.B., Krunić, O.Ž., Martinović, M.K., Magazinović, S.M., 2012. Hydrothermal resources in spa areas of Serbia main properties and possible improvement of use. Thermal Science. 16(1), 21-30. https://doi.org/10.2298/TSCI1201021D.

Đorđievski, S., Ishiyama, D., Ogawa, Y., Stevanović, Z., 2018. Mobility and natural attenuation of metals and arsenic in acidic waters of the drainage system of Timok River from Bor copper mines (Serbia) to Danube River. Environmental Science and Pollution Research. 25, 25005-25019. https://doi.org/10.1007/s11356-018-2541-x.

Filimon, M.N., Caraba, I.V., Popescu, R., Dumitrescu, G., Verdes, D., Petculescu Ciochina, L., Sinitean, A., 2021. Potential ecological and human health risks of heavy metals in soils in selected copper mining areas-a case study: the Bor area. International Journal of Environmental Research. Public Health. 18, 1516. https://doi.org/10.3390/ijerph18041516.

Gallhofer, D., von Quadt, A., Peycheva, I., Schmid, S.M., Heinrich, C.A., 2015. Tectonic, magmatic, and metallogenic evolution of the Late Cretaceous arc in the Carpathian-Balkan orogen. Tectonics. 34(9), 1813-1836. https://doi.org/10.1002/2015TC003834.

Gardić, V.R., Petrović, J.V., Đurđevac-Ignjatović, L.V., Kolaković, S.R., Vujović, S.R., 2015. Impact assessment of mine drainage water and municipal wastewater on the surface water near the City of Bor. Hemijska Industrija, 69(2), 165-174. (in Serbian with English abstract). https://doi.org/10.2298/HEMIND140128031G.

Giri, S. and Singh, A.K., 2019. Assessment of metal pollution in groundwater using a novel multivariate metal pollution index in the mining areas of the Singhbhum copper belt. Environmental Earth Sciences. 78, 192. https://doi.org/10.1007/s12665-019-8200-9.

Goldscheider, N., Mádl-Szőnyl, J., Erőss, A., Scgill, E., 2010. Review: Thermal water sources in carbonate rock aquifers. Hydrogeology Journal. 18, 1303-1318. https://doi.org/10.1007/s10040-010-0611-3.

Gomez, M.E.P., Antunes, I.M.H.R., Silva, P.B., Neiva, A.M.R., Pacheco, F.A.L., 2010. Geochemistry of waters associated with the old mine workings at Fonte Santa (NE of Portugal). Journal of Geochemical Exploration. 105, 153-165. https://doi.org/10.1016/j.gexplo.2010.05.001.

Gong, X., Chen, Z., Luo, Z., 2014. Spatial distribution, temporal variation, and sources of heavy metal pollution in groundwater of a century-old nonferrous metal mining and smelting area in China. Environmental Monitoring and Assessment. 186, 9101-9116. https://doi.org/10.1007/s10661-014-4069-y.

Guéguen, C. and Dominik, J., 2003. Partitioning of trace metals between particulate, colloidal and truly dissolved fractions in a polluted river: the Upper Vistula River (Poland). Applied Geochemistry. 18, 457-470.

Hartmann, A., Goldscheider, N., Wagener, T., Lange, J., Weiler, M., 2014. Karst water resources in a changing world: Review of hydrological modeling approaches. Reviews of Geophysics. 52(3), 218-242. https://doi.org/10.1002/2013RG000443.

Heikkinen, P.M., Korkka-Niemi, K., Lahti, M., Salonen, V., P., 2002. Groundwater and surface water contamination in the area of the Hitura nickel mine, Western Finland. Environmental Geology. 42, 313-329. https://doi.org/10.1007/s00254-002-0525-z.

Holko, L., Dóša, M., Michalko, J., Kostka, Z., Šanda, M., 2012. Isotopes of Oxigen-18 and deuterium in precipitation in Slovakia. Journal of Hydrology and Hydromechanics. 60(4), 265-276. https://doi.org/10.2478/v10098-012-0023-2.

IAEA, 2021. Water Isotope System for data analysis visualization and Electronic Retrieval. Available at https://nucleus.iaea.org/wiser/index.aspx.

Ibrahima, M., Moctar, D., Maguette, D.N., Diakher, M.H., Malick, N.P., Serigne, F., 2015. Evaluation of water resources quality in Sabodala gold mining region and its surrounding area (Senegal). Journal of Water Resource and Protection. 7, 247-263. https://doi.org/10.4236/jwarp.2015.73020.

Institute for geological and mining exploration and investigation of nuclear and other mineral raw materials, Belgrade, 1970. SFR Yugoslavia, geologic map 1:500000. National government publication. Federal Geological Survey, Beograd. p. 1.

Ishiyama, D., Kawaraya, H., Sato, H., Obradovic, L., Blagojević, B., Petrovic, J., Gardic, V., Stevanovic, Z., Shibayama, A., Masuda, N., Takasaki, Y., 2012. Geochemical characteristics of mine drainage water and river water in Bor mining area, Serbia: results of study in 2011. Scientific and Technical Reports od Graduate School of Engineering and Resource Science, Akita University, 33, 41-49.

Ishiyama, D., Obradović, Lj., Marinković, V., Đorđievski, S., Sato, H., Gardić, V., Petrović, J., Kawaraya, H., Ogawa, Y., Masuda, N., Shibayama, A., Stevanović, Z., 2016. Recent advance of environmental evaluation on mining activity based on combination of different types of geochemical maps: An example in Bor mining area, Serbia. 48th International October Conference on Mining and Metallurgy, Sep. 28th-Oct. 1st, Bor, Serbia. Proceedings. 1, 204-207.

Jelenković, R., Milovanović, D., Koželj, D., Banješević, M., 2016. The mineral resources of the Bor metallogenic zone: A review. Geologia Croatica, 69(1), 143-155. https://doi.org/10.4154/GC.2016.11.

Kolb, M., von Quadt, A., Peytcheva, I., Heinrich, C. A., Fowler, S. J., Cvetković, V., 2013. Adakite-like and normal arc magmas: Distinct fractionation paths in the East Serbian segment of the Balkan-Carpathian arc. Journal of Petrology. 54(3), 421-451. https://doi.org/10.1093/petrology/egs072.

Kortatsi, B.K., 2007. Hydrochemical framework of groundwater in the Ankobra Basin, Ghana. Aquatic Geochemistry. 13, 41-74. https://doi.org/10.1007/s10498-006-9006-4.

Kovačević, R., Janošević-Stojanović, M., Tasić, V., Milošević, N., Petrović, N., Stanković, S., Matić-Besarabić, S., 2010. Preliminary analysis of level of arsenic and other metallic elements in PM_{10} sampled near copper smelter Bor (Serbia). Chemical Industry & Chemical Engineering Quarterly, 16(3), 269-279. https://doi.org/10.2298/CICEQ091225049K.

Koželj, D. I., 2002. Epithermal gold mineralization in the Bor metallogenic zone-morphogenic types, structural-texture varieties and potentiality. Institut za Bakar Bor, Bor (in Serbian, English summary).

Krunić, O. and Sorajić, S., 2013. Balneological classification of mineral waters of Serbia. Srpski Arhiv za Celokupno Lekarstvo. 141(1-2), 72-80. https://doi.org/10.2298/SARH1302072K (in Serbian with English abstract).

Larkin, R.G. and Sharp, J.M. Jr., 1992. On the relationship between river-basin geomorphology, aquifer hydraulics, and ground-water flow direction in alluvial aquifers. Geological Society of America Bulletin. 104, 1608-1620.

Leybourne, M.I. and Cameron, E.M., 2008. Source, transport, and fate rhenium, selenium, molybdenum, arsenic, and copper in groundwater associated with porphyry-Cu deposits, Atacama Desert, Chile. Chemical Geology. 247, 208-228. https://doi.org/10.1016/j.chemgeo.2007.10.017.

Lips, A.L.W., Herrington, R.J., Stein, G., Kozelj, D., Popov, K., Wijbrans, J. R., 2004. Refined timing of porphyry copper formation in the Serbian and Bulgarian portions of the Cretaceous Carpatho-Balkan belt. Economic Geology. 99(3), 601-609. https://doi.org/10.2113/gsecongeo.99.3.601.

Ma, R., Wang, Y., Sun, Z., Zheng, C., Ma, T., Prommer, H., 2011. Geochemical evolution of groundwater in carbonate aquifers in Taiyuan, northern China.

Applied Geochemistry. 26, 884-897. https://doi.org/10.1016/j.apgeochem.2011.02.008.

Mao, J., Pirajno, F., Lehmann, B., Luo, M., Berzina, A., 2014. Distribution of porphyry deposits in the Eurasian continent and their corresponding tectonic settings. Journal of Asian Earth Sciences. 79, 576-584. https://doi.org/10.1016/j.jseaes.2013.09.002.

Marin, C., Tudorache, A., Moldovan, O. T., Povara, I., Rajka, G., 2010. Assessing the contents of arsenic and of heavy metals in surface flows and in the hyporheic zone of the Aries stream catchment area Romania. Carpathian Journal of Earth and Environmental Sciences. 5, 13-24.

Markovic Z.S., 2012. Sustainability of Mining Waste in Basin Bor, Serbia. In: Vitale K. (eds) Environmental and Food Safety and Security for South-East Europe and Ukraine. NATO Science for Peace and Security Series C: Environmental Security. Springer, Dordrecht. https://doi.org/10.1007/978-94-007-2953-7_12.

Masetti, M., Sterlacchini, S., Ballabio, C., Sorichetta, A., Poli, S., 2009. Influence of threshold value in the use of statistical methods for groundwater vulnerability assessment. Science of the Total Environment. 407, 3836-3846. https://doi.org/10.1016/j.scitotenv.2009.01.055.

McIlwaine, R., Cox, S.F., Doherty, R., 2016. Determining geochemical threshold values from the Tellus data sets: the examples of zinc and iodine, in: Young, M.E. (Eds.), Unearthed: impacts of the Tellus surveys of the north of Irland. Dublin. Royal Irish Academy. https://doi.org/10.3318/978-1-908996-88-6.ch21.

McKinney, C.R., McCrea, J.M., Epstein, S., Allen, H.A., Urey, H.C., 1950. Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios. Review of Scientific Instruments. 21, 724-730. https://doi.org/10.1063/1.1745698.

Milijaševič, D., Milanov, A., Brankov, J., Radovanović, M., 2011. Water quality assessment of the Borska Reka River using the WPI (water pollution index) method. Archives of Biological Sciences Belgrade, 63(3), 819-824. https://doi.org/10.2298/abs1103819m.

Milijašević-Joksimović, D., Gavrilović, B., Lović-Obradović, S., 2018. Application of the water quality index in the Timok River Basin (Serbia). Journal of Geographical Institute Cvijic, 68(3), 333-344. https://doi.org/10.2298/IJGI180610007M.

Milovanović, B., Schuster, P., Radovanović, M., Ristić Vakanjac, V., Schneide, C., 2017. Spatial and temporal variability of precipitation in Serbia for the period 1964-2010. Theoretical and Applied Climatology. 130, 687-700. https://doi.org/10.1007/s00704-017-2118-5.

Molinari, A., Guadagminini, L., Marcaccio, M., Guadagnini, A., 2012. Natural background levels and threshold values of chemical species in three large-scale groundwater bodies in Northern Italy. Science of the Total Environment 425, 9-19. https://doi.org/10.1016/j.scitotenv.2012.03.015.

Moyé, J., Picard-Lesteven, T., Zouhri, L., El Amari, k., Hibiti, M., Benkaddour, A., 2017. Groundwater assessment and environmental impact in the abandoned mine of Kettara (Morocco). Environmental Pollution 231, 899-907. https://doi.org/10.1016/j.envpol.2017.07.044.

Nagavciuc, V., Bădăluța, C.A., Ionita, M., 2019. Tracing the relationship bete=ween precipitation and river water in the northern Carpathian base on the evaluation of water isotope data. Geosciences. 9, 198. https://doi.org/10.3390/geosciences9050198.

Nieto, J. M., Sarmiento, A. M., Olías, M., Canovas, C. R., Riba, I., Kalman, J., Delvalls, T. A., 2007. Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environment International. 3, 445-455. https://doi.org/10.1016/j.envint.2006.11.010.

Nikolic, N., Böcker, R., Nikolic, M., 2016. Long-term passive restoration following fluvial deposition of sulphidic copper tailings: nature filters out solutions. Environmental Science and Pollution Research. 23, 13672-13680. https://doi.org/10.1007/s11356-015-5205-0.

Nikolić, Đ., Milošević, N., Živković, Ž., Mihajlović, I., Kovačević, R., Petrović, N., 2011. Multi-criteria analysis of soil pollution by heavy metals in the vicinity of the Copper Smelting Plant in Bor (Serbia). Journal of the Serbian Chemical Society. 76(4), 625-641. https://doi.org/10.2298/JSC100823054N.

Ogawa, Y., Ishiyama, D., Shikazono, N., Iwane, K., Kajiwara, M., Tsuchiya, N., 2013. Fractionation and deposition of indium and arsenic from the Kusatsu and Tamagawa acidic hot springs, Japan: Possible man-made analogues for rare metal concentrations onto lake beds? Economic Geology, 108, 1641-1656.

Ogawa, Y., Ishiyama, D., Shikazono, N., Iwane, K., Kajiwara, M., Tsuchiya, N., 2012. The role of hydrous ferric oxide precipitation in the fractionation of arsenic, gallium, and indium during the neutralization of acidic hot spring water by river water in the Tama River watershed, Japan. Geochimica et Cosmochimica Acta. 86, 367-383. https://dx.doi.org/10.1016/j.gca.2012.03.009.

Oyarzún, J., Carvajal, M. J., Maturana, H., Núñez, J., Krestschmer, N., Amezaga, J. M., Rötting, T. S., Strauch, G., Thyne, G., Oyarzún, R., 2013. Hydrochemical and isotopic patterns in a calc-alkaline Cu- and Au-rich arid Andean basin: the Elqui River watershed, north Central Chile. Applied Geochemistry. 33, 50-63. https://doi.org/10.1016/j.apgeochem.2013.01.014.

Ozunu, A., Stefanescu, L., Costan, C., Miclean, M., Modoi, C., Vlad, S. N., 2009. Surface water pollution generated by mining activities. Case study: Aries River middle catchment basin, Romania. Environmental Engineering and Management J. 8, 809-815.

Panias, D., 2006. Consequences of environmental issues on sustainability of metal industries in Europe: The case study of Bor. Journal of Metallurgy. 4, 29-250.

Panno, S.V., Kelly, W.R., Martinesc, A.T., Hackley, K.C., 2006. Estimating background and threshold nitrate concentrations using probability graphs. Groundwater. 44(5), 697-709. https://doi.org/10.1111/j.1745-6584-2006-00240.x.

Paunović, P, 2010. Unsuccessful attempt of regulation of Timok in order to prevent destruction of the land from industrial waste from Bor copper mine. In: Proceedings of XVIII International Scientific and Professional Meeting "Ecological Truth" Eco-Ist'10, 1-4 June, Spa Jankovic, Apatin, Serbia, Publisher: Univ. Of Belgrade – Technical Faculty in Bor, Serbia, pp 224-251.

Pavlović, P., Mitrović, M., Đorđević, D., Sakan, S., Slododnik, J., Liska, I., Csanyi, B., Jarić, S., Kostić, O., Pavlović, D., Marinković, N., Tubić, B., Paunović, M., 2016. Assessment of the contamination of riparian soil and vegetation by trace metals–A Danube River case study. Science of the Total Environment. 540, 396-409. https://dx.doi.org/10.1016/j.scitotenv.2015.06.125.

Pejović, M., Bajat, B., Gospavić, Z., Saljnikov, E., Kilibarda, M., Čakmak, D., 2017. Layer-specific spacial prediction of As concentration in copper smelter vicinity considering the terrain exposure. Journal of Geochemical Exploration. 179, 25-35. https://doi.org/10.1016/j.gexplo.2017.05.004.

Pešić, M., Milić, S., Nujkić, M., Marić, M., 2020. The impact of climatic parameters on the turbidity and natural organic matter content in drinking water in the City of Bor (Eastern Serbia). Environmental Earth Sciences. 79:267. https://doi.org/10.1007/s12665-020-09016-0.

Petković, K. 1976. Geologija Srbije. VIII – 1, Hidrogeologija. Univerzitet u Beogradu. Zavod za regionalnu geologiju i paleontologiju Rudarsko-geološkog fakulteta, Beograd. (in Serbian).

Petrovic, J.V., Alagic, S.C., Milic, S.M., Tosic, S.B., Bugarin, M.M., 2021. Chemometric characterization of heavy metals in soils and shoots of the two pioneer species sampled near the polluted water bodies in the close vicinity of the copper mining and metallurgical complex in Bor (Serbia): Phytoextraction and

biomonitoring contexts. Chemosphere. 262, 127808. https://doi.org/10.1016/j.chemosphere.2020.127808.

Petrović, T., Zlokolica-Mandić, M., Veljković, N., Vidojević, D., 2010. Hydrogeological conditions for the forming and quality of mineral waters in Serbia. Journal of Geochemical Exploration. 107, 373-381. https://doi.org/10.1016/j.gexplo.2010.07.009.

Polomčić, D., Stevanović, Z., Dokmanović, P., Papić, P., Ristić Vukanjac, V., Hajdin, B., Milanović, S., Bajić, D., 2011. Groundwater supply in Serbia-state and perspectives. In: Polomcic, D. & Ristic Vukanjac, V., (Eds.). Our 40 years. University of Belgrade, Faculty of Mining and Geology, Belgrade, Serbia. Pp. 45-75. (in Serbian).

Polomčić, D., Štrbački, J., Bajić, D., 2018. Water supply and groundwater quality in Republic of Serbia. In: Mihajlovic, D. & Dordevic, B. (Eds.). 8th international symposium on natural resources management. Zaječar, Serbia. pp. 205-211. (in Serbian with English abstract).

Popov, P., Berza, T., Grubić, A., Ioane, D., 2002. Late Cretaceous Apuseni-Banat-Timok, Srednogorie (ABTS) Magmatic and Metallogenic belt in the Carpathian-Balkan orogen. Geologica Balcanica. 32(2/4), 145-163.

Popugaeva. D., Kreyman, K., Ray, A.D., 2020. Assessment of Khibiny Alkaline Massif groundwater quality using statistical methods and water quality index. The Canadian Journal of Chemical Engineering. 98, 205-212. https://doi.org/10.1002/cjce.23601.

Rahman, A., Tiwari, K.K., Mondal, N.C., 2020. Assessment of hydrochemical backgrounds and threshold values of groundwater in a part of desert area, Rajasthan, India. Environmental Pollution. 266, 115150. https://doi.org/10.1016/j.envpol.2020.115150.

Reagan, M.T., Moridis, G.J., Keen, N.D., Johnson, J.N., 2015. Numerical simulation of the environmental impact of hydraulic fracturing of tight/shale gas reservoir on

near-surface groundwater: Background, base cases, shallow reservoir, short-term gas, and water transport. Water Resources Research. 51, 2543-2573. https://doi.org/10.1002/2014WR016086.

Reimann, C. and de Caritat, P., 2017. Establishing geochemical background variation and threshold values for 59 elements in Australian surface soil. Science of the Total Environment, 578, 633-648. https://doi.org/10.1016/j.scitotenv.2016.11.010.

Reimann, C., Filzmoser, P., Garrett, R. G., 2005. Background and threshold: critical comparison of methods of determination. Science of the Total Environment. 346, 1-16. https://doi.org/10.1016/j.scitotenv.2004.11.023.

Republic of Serbia, 2011. Meteorological yearbook 1, Climatological data 2010. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2012a. Meteorological yearbook 1, Climatological data 2011. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2012b. Regulation on limit values for pollutants in surface water and groundwater and sediments, and the deadlines for their achievement. Serbian official gazette 50, 1 (in Serbian). Available at: http://www.pravno-informacioni-sistem.rs/SlGlasnikPortal/eli/rep/sgrs/vlada/uredba/2012/50/1/reg. Accessed on: 01 Mar 2019.

Republic of Serbia, 2013. Meteorological yearbook 1, Climatological data 2012. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2014. Meteorological yearbook 1, Climatological data 2013. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2015. Meteorological yearbook 1, Climatological data 2014. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2016. Meteorological yearbook 1, Climatological data 2015. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2017. Meteorological yearbook 1, Climatological data 2016. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2018. Meteorological yearbook 1, Climatological data 2017. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2019a. Meteorological yearbook 1, Climatological data 2018. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Republic of Serbia, 2019b. Official Gazette, no. 42/98 and 44/99 and no. 28/2019 (in Serbian). Available at: https://www.pravno-informacioni-sistem.rs/SlGlasnikPortal/eli/rep/slsrj/ministarstva/pravilnik/1998/42/2/reg. Accessed on: 01 Dec 2020.

Republic of Serbia, 2020. Meteorological yearbook 1, Climatological data 2019. Republic Hydrometeorological Institute. Belgrade: Press Republic Hydrometeorological Institute of the Republic of Serbia (in Serbian).

Rose, A.W., Hawkes, H.E., Webb, J.S., 1979. Geochemistry in Mineral Exploration. London: Academic Press Limited.

Runnells, D.D., Shepherd, T.A., Angino, E.E., 1992. Determining natural background concentrations in mineralized areas. Environmental Science & Technology. 26, 2316-2323.

Saez, R., Pascual, E., Toscano, M., Almodovar, G. R., 1999. The Iberian type of volcano-sedimentary massive sulphide deposits. Mineralium Deposita. 34, 549-570.

Sainz, A., Grande, J. A., de la Torre M. L., 2003. Odiel River, acid mine drainage and current characterization by means of univariate analysis. Environment International. 29, 51-59. https://doi.org/10.1016/s0160-4120(03)00006-0.

Sako, A., Bamba, O., Gordio, A., 2016. Hydrogeochemical processes controlling groundwater around Bombore gold mineralized zone, Central Burkino Faso. Journal of Geochemical Exploration. 140, 58-71. https://dx.doi.org/10.1016/j.gexplo.2016.08.009.

Sánchez España, J., López Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., Barettino, D., 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. Applied Geochemistry. 20, 1320-1356. https://doi.org/10.1016/j.apgeochem.2005.01.011.

Serbula, S. M., Milosavljevic, J. S., Radojevic, A. A., Kalinovic, T. S., 2017. Extreme air pollution with contaminants originating from the mining-metallurgical processes. Science of the Total Environment, 586, 1066-1075. https://doi.org/10.1016/j.scitotenv.2017.02.091.

Serbula, S.M., Milosavljevic, J.S., Kalinovic, J.V., Kalinovic, T.S., Radojevic, A.A., Apostolovski Trujic T.Lj., Tasic, V.M., 2021. Arsenic and SO_2 hotspot in South-Eastern Europe: An overview of the air quality after the implementation of the flash smelting technology for copper production. Science of the Total Environment. 777, 145981. https://doi.org/10.1016/j.scitotenv.2021.145981.

Sinclair, A.J., 1974. Selection of threshold in geochemical data using probability graphs. Journal of Geochemical Exploration. 3, 129-149.

Sinclair, A.J., 1986. Statistical Interpretation of Soil Geochemical Data. In: Robertson, J.R. (Ed.) Exploration Geochemistry: design and interpretation of soil surveys.

Society of Economic Geologists: Reviews in economic geology, Vol. 3, pp 97-115.

Sinclair, A.J., 1991. A fundamental approach to threshold estimation in exploration geochemistry: probability plots revisited. Journal of Geochemical Exploration. 41, 1-22.

Sophocleous, M., 2002. Interactions between groundwater and surface water: the state of the science. Hydrogeology Journal. 10, 52-67. https://doi.org/10.1007/s10040-001-0170-8.

Stevanovic, Z.O., Antonijevic, M.M., Bogdanovic G.D., Trujic V.K., Bugarin, M.M., 2011. Influence of the chemical and mineralogical composition on the acidity of an abandoned copper mine in Bor river valley (eastern Serbia). Chemistry and Ecology. 27(5), 401-414. https://doi.org/10.1080/02757540.2011.575375.

Stevanović, Z., Jemcov, I., Milanović, S., 2007. Management of karst aquifers in Serbia for water supply. Environmental Geology. 51, 743-748. https://doi.org/10.1007/s00254-006-0393-z.

Stevanović, Z., Obradović, Lj., Marković, R., Jonović, R., Avramović, Lj., Bugarin, M., Stevanović, J., 2013. Mine waste water management in the Bor municipality in order to protect the Bor River water. In: Garcia Einschlag FS (Ed.). Water water-treatment technologies and recent analytical developments. InTech. Pp. 41.62. https://dx.doi.org/10.5772/51902.

Šerbula, S. M., Antonijević, M. M., Milošević, N. M., Milić, S. M., Ilić, A. A., 2010. Concentration of particulate matter and arsenic in Bor (Serbia). Journal of Hazardous Materials. 181, 43-51. https://doi.org/10.1016/j.jhazmat.2010.04.065.

Šerbula, S., Ristić, A., Manasijević, S., Dolić, N., 2015. Heavy metal ions in the wastewater of the Majdanpek copper mine, Zaštita materijala, 56, 52-58 (in Serbian with English abstract).

Šerbula, S., Stanković, V., Živković, D., Kamberović, Z., Georgievski, M., Kalinović, T., 2016. Characteristics of wastewater streams within the Bor copper mine and their influence on pollution of the Timok River, Serbia. Mine Water and the Environment. 35, 480-485. https://doi.org/10.1007/s10230-016-0392-6.

Tanasković, I., Golobocanin, D., Miljević, N., 2012. Multivariate statistical analysis of hydrochemical and radiological data of Serbian spa waters. Journal of Geochemical Exploration. 112, 226-234. https://doi.org/10.1016/j.gexplo.2011.08.014.

Tang, D., Warnken, K., Santschi, P.H., 2001. Organic complexation of copper in surface waters of Galveston Bay. Limnology and Oceanography. 46, 321-330. https://doi.org/10.4319/10.2001.46.2.0321.

Vasić, Lj., Živojinović, D., Rajaković-Ognjanović, V., 2020. Hydrochemical changes and groundwater grouping data by multivariate statistical methods within one karst system: recharge-discharge zone (Eastern Serbia case study). Carbonates and Evaporates. 35, 15. https://doi.org/10.1007/s13146-019-00548-6.

Von der Heyden, C.J. and New, M.G., 2004. Groundwater pollution on the Zambian Copperbelt: deciphering the source and the risk. Science of the Total Environment. 327, 17-30. https://doi.org/10.1016/j.scitotenv.2003.08.028.

Von Quadt, A., Peitcheva, I., Cvetkovic, V., Banjesevic, M., Kozelj, D., 2002. Geochronology, geochemistry, and isotope tracing of the Cretaceous magmatism of East Serbia as part of the Apuseni-Timok-Srednogorie metallogenic belt. 17th Congress of Carpathian-Balkan Geological Association, Geologica Carpatica, Special issue, 175-177.

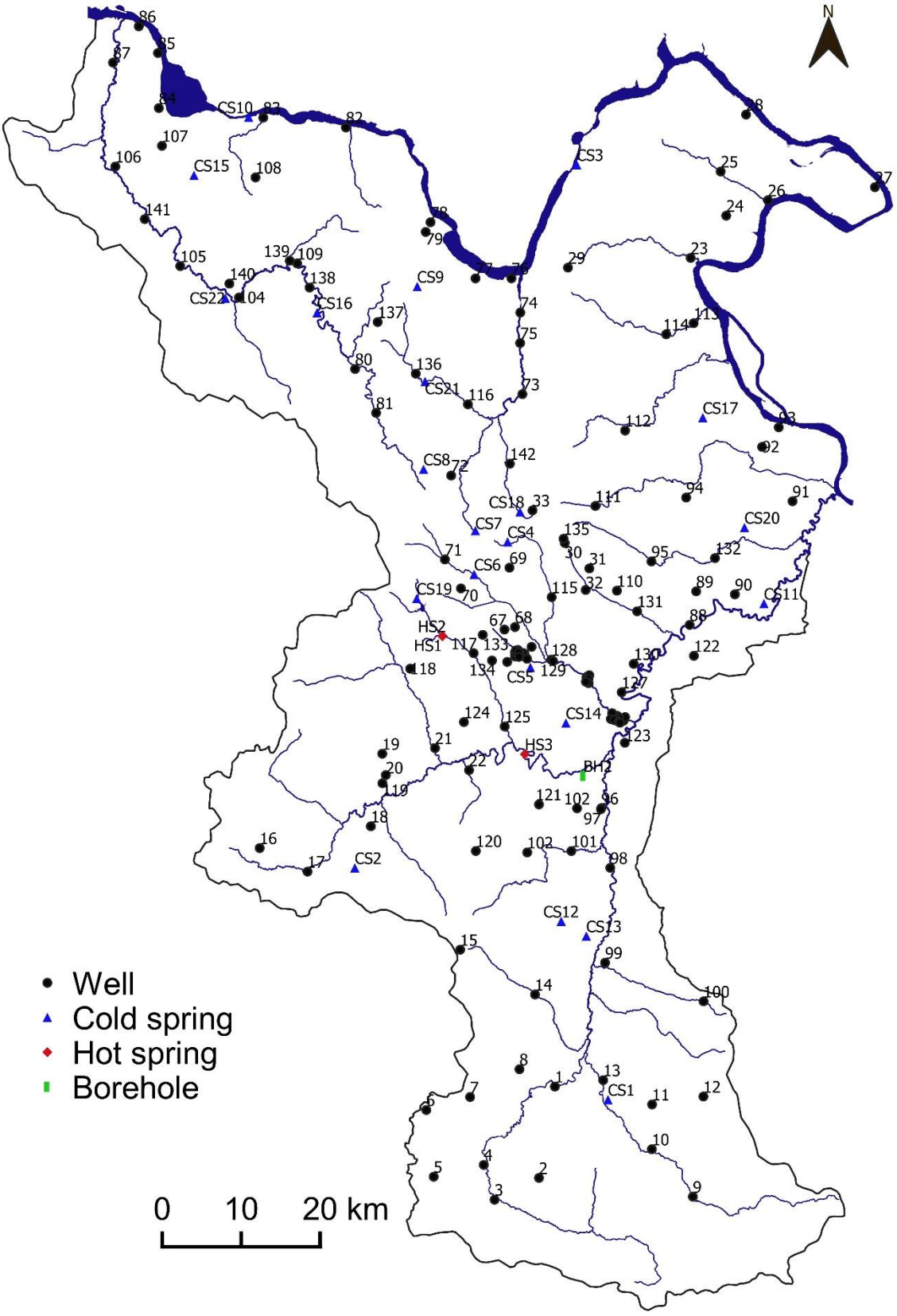
Waeles, M., Tanguy, V., Riso, R.D., 2015. On the control of copper colloidal distribution by humic substances in the Penzé estuary. Chemosphere. 119, 1176-1184. https://doi.org/10.1016/j.chemosphere.2014.09.107.

Živanović, V., Jemcov, I., Dragišić, V., Atanacković, N., Magazinović, S., 2016. Karst groundwater source protection based on the time-dependent vulnerability

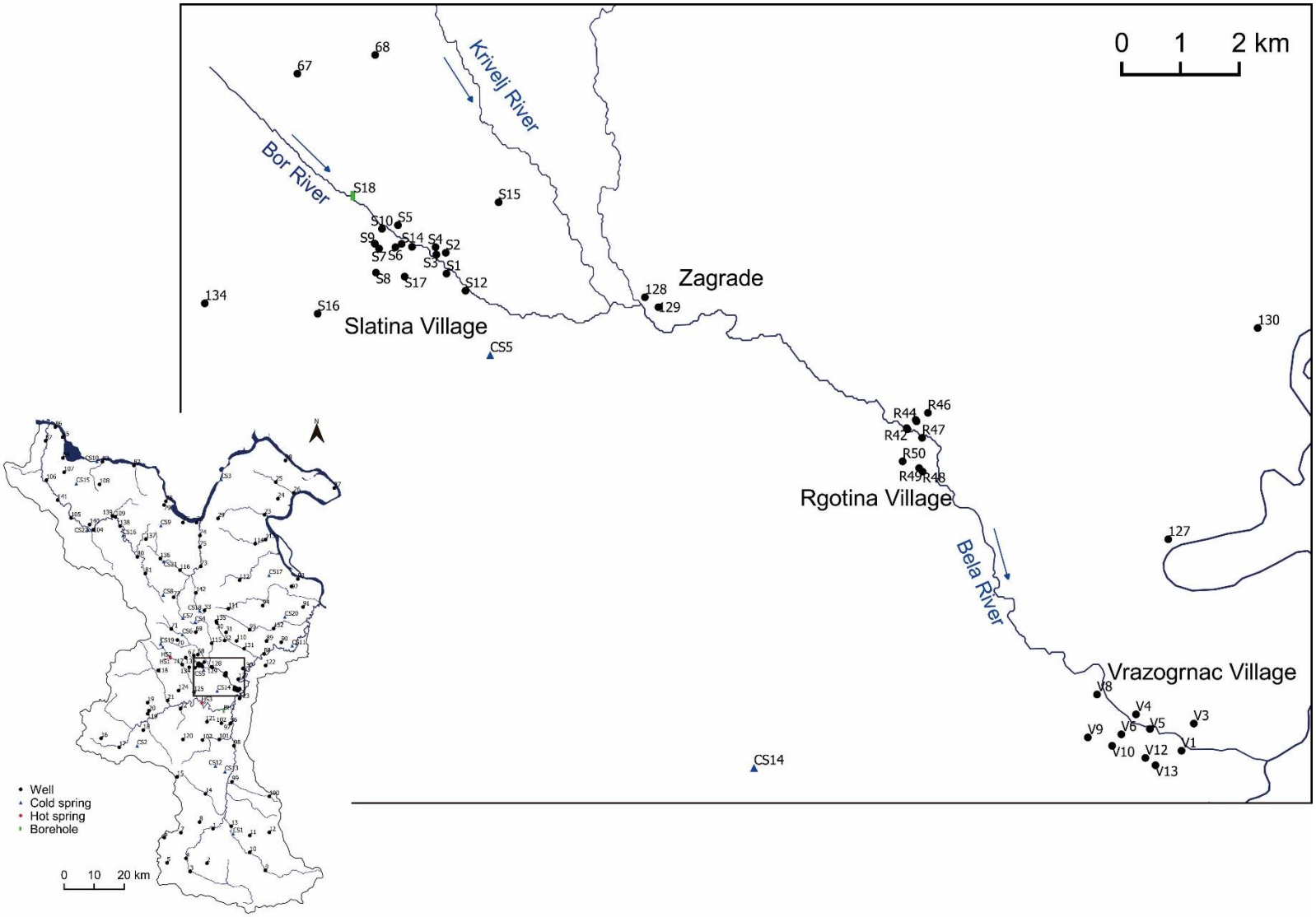
assessment model: Crnica spring study, Eastern Serbia. Environmental Earth Sciences. 75, 1224. https://doi.org/10.1007/s12665-016-6018-2.

Appendices

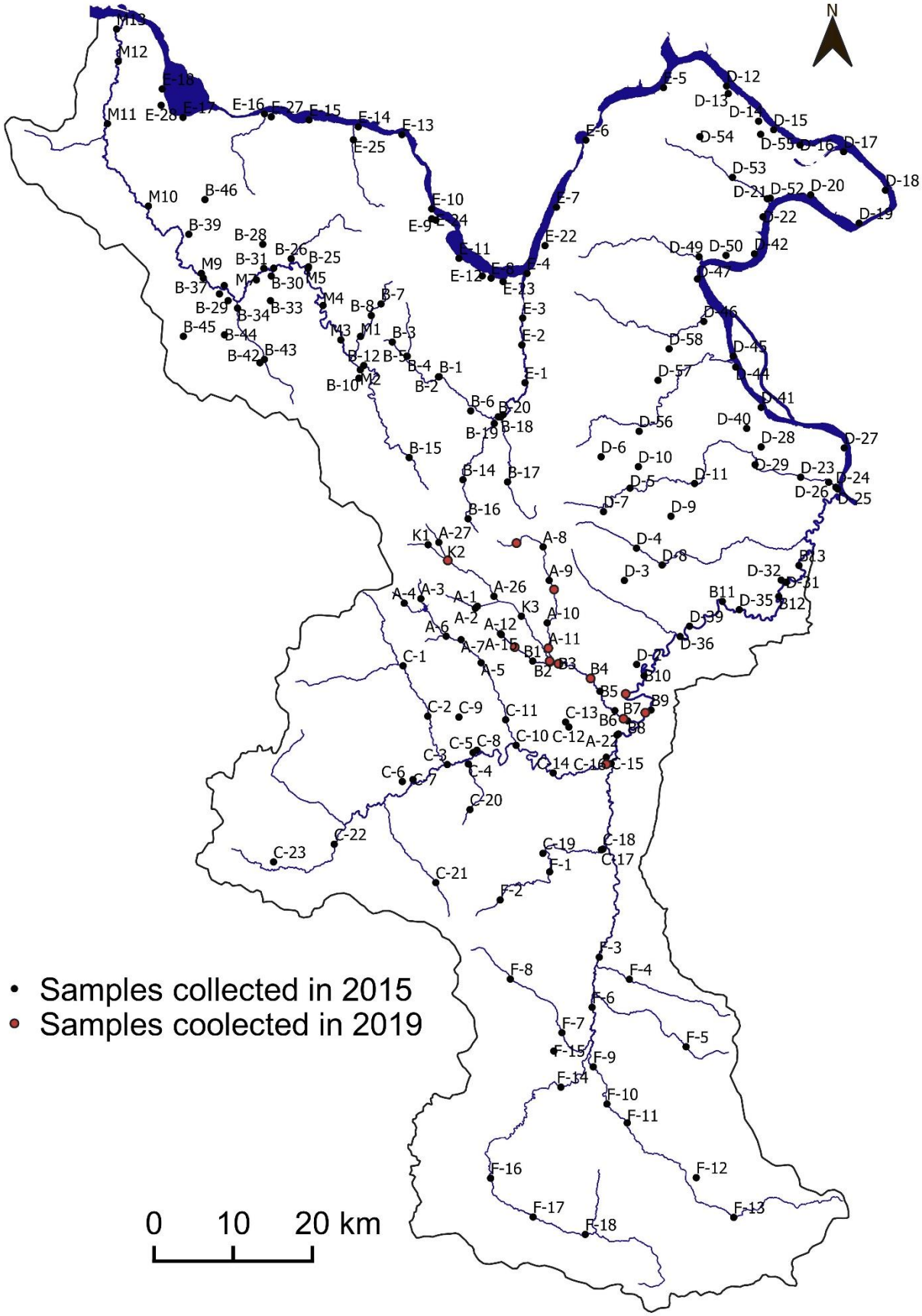
Appendix 1 Map of the study area with labels of the sampling sites of groundwater.



Appendix 2 Map of the Bor mining area with labels of sampling sites of groundwater.



Appendix 3 Map of the Bor mining area with labels of sampling sites of river water.



Appendix 4 Sampling sites, coordinates of sampling sites, water temperature, pH, Eh and concentrations of major cations and anions in groundwater samples collected from wells and boreholes.

Sampling site	Y	X	Depth (m)	t (°C)	pH	Eh (mV)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
Vrazogrnac, Well 1	43.9604	22.32813	2.3	15.1	7.0	466	61.1	51.9	37.5	301.5	62.2	112.9	455.5	615
Vrazogrnac, Well 3	43.96454	22.33084	4.7	13.9	6.8	493	26.8	2.5	30.9	126.2	14.3	110.0	73.1	400
Vrazogrnac, Well 4	43.96609	22.31859	3.0	15.7	7.1	484	36.6	5.2	31.3	232.5	22.3	86.3	324.1	460
Vrazogrnac, Well 5	43.96381	22.3215	1.8	17.4	7.0	433	50.9	11.9	53.1	510.8	38.3	18.6	1110.8	505
Vrazogrnac, Well 6	43.96306	22.31541	2.4	17.5	7.0	466	42.8	26.2	26.9	192.0	46.0	149.2	186.4	460
Vrazogrnac, Well 8	43.96924	22.31039	3.2	16.6	7.1	329	31.0	2.9	22.4	177.4	18.5	2.5	229.2	480
Vrazogrnac, Well 9	43.96267	22.30829	5.5	14.1	7.2	413	40.0	0.8	27.8	124.1	30.0	46.1	110.8	385
Vrazogrnac, Well 10	43.96132	22.31341	5.7	13.9	7.1	486	17.5	1.2	20.3	175.8	21.8	113.7	151.7	385
Vrazogrnac, Well 12	43.95938	22.32043	1.4	19.1	7.1	452	45.5	74.2	32.4	208.7	54.9	49.2	268.1	560
Vrazogrnac, Well 13	43.95823	22.32255	4.0	13.9	7.0	449	41.7	5.7	41.2	218.9	48.2	155.7	269.6	415
Rgotina, Well 42	44.0104	22.27098	4.9	13.1	7.0	279	49.1	174.6	34.6	229.3	41.9	64.4	440.1	570
Rgotina, Well 43	44.01058	22.27083	4.7	13.6	7.2	412	44.4	155.2	22.8	155.4	39.9	46.2	209.5	505
Rgotina, Well 44	44.0116	22.27295	5.0	13.5	7.3	-66	43.4	99.5	45.9	155.5	50.8	0.0	236.9	540
Rgotina, Well 45	44.01182	22.27277	3.3	14.0	7.0	255	49.8	102.5	55.5	164.4	59.8	72.8	355.3	450
Rgotina, Well 46	44.01287	22.2754	2.5	16.1	7.3	292	29.7	19.0	22.5	133.1	22.1	49.5	77.1	440
Rgotina, Well 47	44.00905	22.27407	5.1	15.4	6.9	348	28.2	11.2	36.3	314.3	25.8	14.7	621.1	350
Rgotina, Well 48	44.00386	22.27406	7.1	12.3	6.9	351	64.7	7.3	27.9	263.5	92.3	91.9	309.4	470
Rgotina, Well 49	44.00441	22.27334	4.0	14.2	6.8	362	76.9	18.2	30.4	287.8	90.4	113.5	371.5	530
Rgotina, Well 50	44.00549	22.26986	2.5	17.9	7.4	366	18.9	6.1	10.3	91.2	12.4	38.1	77.4	230
Slatina, Well 1	44.03534	22.17349	1.6	18.4	7.5	343	18.4	3.8	14.4	119.0	4.3	2.4	144.4	270
Slatina, Well 2	44.03854	22.1734	5.6	12.1	6.8	414	50.8	13.5	28.8	177.8	31.0	69.0	222.7	415
Slatina, Well 3	44.03829	22.1714	13.3	13.3	6.6	410	68.7	10.7	28.7	198.8	47.4	127.3	296.9	330
Slatina, Well 4	44.03942	22.17124	3.6	14.2	6.9	387	36.1	36.4	26.6	190.3	37.3	168.7	211.0	350
Slatina, Well 5	44.04288	22.16332	1.8	16.1	6.9	409	95.5	9.9	29.6	163.1	24.7	21.0	255.4	500
Slatina, Well 6	44.0395	22.16272	1.7	14.5	7.1	357	54.3	23.3	33.7	189.0	38.7	56.8	198.5	530
Slatina, Well 7	44.03933	22.15923	4.5	11.8	7.0	368	51.0	1.6	32.8	159.1	26.5	28.2	202.1	450
Slatina, Well 8	44.03564	22.15851	3.2	13.7	7.2	398	39.8	2.1	21.6	192.6	13.0	6.3	297.8	380
Slatina, Well 9	44.04009	22.15834	1.1	18.0	7.3	360	17.1	79.0	11.5	90.0	9.2	53.5	73.5	310
Slatina, Well 10	44.04235	22.15991	4.0	13.5	6.9	394	68.2	0.6	55.0	243.1	52.7	122.7	386.6	555
Slatina, Well 11	44.03952	22.16625	3.9	12.0	6.8	406	48.5	16.9	20.7	211.3	62.5	148.9	208.8	380

Slatina, Well 12	44.03267	22.17748	3.7	13.9	6.9	374	48.3	12.3	21.7	114.1	6.3	9.2	209.5	310
Slatina, Well 14	44.04001	22.16405	2.5	15.4	6.9	373	41.2	23.2	27.7	158.4	38.6	35.0	191.5	385
Slatina, Well 15	44.04618	22.1848	4.1	11.6	7.2	365	60.2	1.9	38.7	128.1	15.8	0.0	172.9	500
Slatina, Well 16	44.02946	22.14598	11.7	11.9	7.2	399	17.1	1.6	17.5	121.3	24.3	144.1	74.0	180
Slatina, Well 17	44.03497	22.16459	1.1	19.8	7.1	387	77.1	2.0	70.0	177.5	10.7	3.0	528.9	420
Slatina, Borehole 18	44.04749	22.15397	5.0	14.5	6.9	297	16.4	7.1	16.6	162.0	18.8	47.7	229.4	270
Rgoste,Well 1	43.54473	22.21153	7.2	15.0	7.4	423	12.3	2.8	15.4	85.8	11.6	22.1	49.0	320
Izvor Reka, Well 2	43.44086	22.18456	1.7	16.0	7.0	308	7.4	8.8	9.7	96.3	11.7	1.9	32.7	490
Svrljig, Well 3	43.41674	22.11469	1.5	16.5	7.0	385	29.3	1.8	38.4	117.7	24.2	47.5	89.4	480
Nisevac, Well 4	43.45656	22.09841	3.7	14.1	7.1	466	22.2	4.6	31.0	121.1	27.8	58.9	69.0	470
Lalinac, Well 5	43.44383	22.01987	3.7	14.3	7.1	482	4.3	2.7	6.8	103.9	7.8	21.2	20.6	460
Galibabinac, Well 6	43.51996	22.00959	1.4	12.7	6.8	464	19.9	2.5	8.4	134.1	26.0	66.1	47.4	500
Beli Potok, Well 7	43.53416	22.07845	3.1	14.9	7.1	457	33.0	46.5	13.2	117.8	30.1	90.0	70.9	555
Vasilj, Well 8	43.56504	22.15637	3.5	13.6	7.1	493	15.6	1.6	19.7	119.4	15.1	31.8	38.9	340
Kalna, Well 9	43.41671	22.42477	8.7	11.1	7.3	289	8.0	1.4	4.8	62.4	10.3	2.0	8.8	210
G. Kamenica, Well 10	43.47157	22.36183	8.3	13.2	7.1	413	8.8	1.2	17.1	90.6	3.5	12.5	35.5	415
Gradiste, Well 11	43.52264	22.36334	5.4	12.9	7.0	435	22.6	11.9	27.8	90.9	10.6	30.3	57.8	380
Aldinac, Well 12	43.53065	22.44395	5.3	12.8	6.8	397	12.1	1.9	28.6	68.5	4.9	6.8	26.0	400
Trgoviste, Well 13	43.55116	22.28737	6.1	13.3	7.0	502	40.3	0.0	29.3	105.5	24.3	68.3	42.6	500
D. Sokolovica, Well 14	43.64995	22.18239	7.2	13.6	6.9	451	55.5	1.3	56.4	166.4	134.7	161.7	124.9	630
Vlasko Polje, Well 15	43.70218	22.06587	4.5	11.1	7.3	454	7.3	1.8	7.1	91.6	5.4	22.2	28.6	270
Krivi Vir, Well 16	43.82051	21.75229	10.5	12.1	7.1	424	7.7	3.9	4.9	148.9	18.0	33.9	40.0	430
Lukovo, Well 17	43.79317	21.82719	3.0	13.7	6.5	463	6.3	2.1	9.9	25.2	1.6	0.5	18.9	190
Mali Izvor, Well 18	43.84404	21.92772	1.3	16.0	7.3	468	10.8	1.2	20.5	85.7	10.8	14.6	27.8	410
Podgorac,Well 19	43.92659	21.94703	3.3	15.5	7.1	469	8.7	0.4	4.0	108.6	12.0	45.0	47.4	360
Bogovina, Well 20	43.90225	21.95215	4.6	14.1	7.1	474	12.7	1.8	11.6	130.3	26.0	41.5	56.3	350
Sumrakovac, Well 21	43.93226	22.03029	2.6	14.7	7.1	427	17.4	12.2	11.0	143.0	12.3	13.8	62.6	500
Osnic, Well 22	43.9067	22.08348	2.9	13.3	6.8	488	27.5	0.6	16.5	75.8	15.2	2.8	56.3	330
Brza Palanka, Well 23	44.48647	22.44708	11.7	13.8	7.5	439	11.4	4.1	16.4	72.8	10.0	44.0	35.4	220
Velika Kamenica, Well 24	44.53389	22.5049	4.1	15.5	6.7	434	27.2	7.0	17.6	78.8	21.6	47.5	56.4	260
Podvrska, Well 25	44.58433	22.49734	2.9	16.0	7.1	433	28.2	37.0	14.3	97.0	23.2	42.3	48.5	380
Milutinovac, Well 26	44.5506	22.57191	1.1	19.2	7.9	427	148.5	18.4	23.7	52.7	88.2	16.4	339.9	110
Rtkovo, Well 27	44.56295	22.7427	16.2	15.5	7.0	314	42.7	1.2	53.0	149.4	62.1	232.3	106.8	225
Novi Sip, Well 28	44.64864	22.53951	7.8	15.6	6.4	429	13.3	0.8	21.3	36.8	9.7	39.8	53.9	135

Miroc, Well 29	44.4777	22.25151	4.0	13.9	7.2	473	29.0	30.4	7.7	101.2	31.0	39.5	41.2	275
Glogovica, M1	44.1781	22.23154	-	17.7	7.2	471	7.6	0.3	20.4	69.0	3.1	2.2	31.5	270
Glogovica, Well 30	44.16406	22.2397	5.5	11.9	7.5	466	33.7	32.5	51.2	143.7	65.9	161.6	141.5	400
Glogovica, Well 31	44.13457	22.27804	6.9	14.1	6.8	431	20.0	0.8	81.1	143.7	73.6	65.8	133.0	605
Dubocane, Well 32	44.11015	22.27171	2.2	15.0	7.1	492	8.0	0.7	19.1	64.7	3.8	23.0	34.4	250
Luka, Well 33	44.20169	22.18948	10.4	13.2	7.0	416	39.0	6.8	25.6	49.3	28.7	82.9	95.4	140
Ostrelj, Well 67	44.06635	22.14238	7.3	12.6	7.2	374	29.6	2.0	13.6	193.5	38.0	44.4	263.2	260
Ostrelj, Well 68	44.06906	22.15898	3.7	12.5	6.9	437	63.3	0.9	20.4	241.8	43.0	182.0	184.9	500
Bucje, Well 69	44.13678	22.15169	8.4	12.9	7.2	394	9.5	3.0	9.0	148.6	20.3	71.1	92.5	400
Brezonik, Well 70	44.1139	22.07446	-	15.0	7.2	358	16.1	0.0	22.2	114.1	8.3	12.6	143.1	275
Cerovo, Well 71	44.14717	22.04959	-	15.0	7.1	283	16.1	3.0	15.4	146.0	14.6	1.1	142.1	370
Gornjane, Well 72	44.24271	22.0613	1.8	13.9	7.1	377	5.2	5.8	14.3	64.6	1.3	4.7	14.9	260
Klokocevac, Well 73	44.3343	22.17605	6.6	18.1	6.8	387	9.9	2.8	13.2	41.2	3.6	0.0	29.5	160
Mosna, Well 75	44.42731	22.17459	2.0	16.4	7.0	354	27.8	9.3	14.6	92.5	23.0	47.7	51.1	280
Topolnica, Well 74	44.39264	22.17366	3.3	15.6	6.9	412	24.7	18.1	25.0	84.0	19.8	40.7	52.4	350
Donji Milanovac, Well 76	44.46652	22.16119	2.0	19.3	8.4	347	28.5	4.3	35.1	75.3	17.4	8.7	57.4	380
Oreskovica, Well 77	44.46701	22.10413	1.2	21.6	6.9	389	16.4	0.9	13.2	49.2	24.8	2.3	35.9	170
Boljetin, Well 78	44.53164	22.03362	2.3	16.6	6.9	443	33.4	6.3	15.5	168.7	80.4	74.0	55.2	435
Boljetin, Well 79	44.52068	22.0258	2.3	17.5	6.9	459	26.0	49.3	21.3	73.7	20.3	74.6	61.9	300
Debeli Lug, Well 80	44.3654	21.91085	3.1	14.7	6.9	377	24.6	90.5	21.4	119.0	35.2	21.0	83.9	470
Leskovo, Well 81	44.31512	21.94342	2.2	16.2	7.0	402	31.4	10.3	14.7	100.3	31.7	43.2	58.6	305
Dobra, Well 82	44.64077	21.90052	1.2	20.3	6.9	394	25.8	12.7	28.8	102.1	38.6	41.6	149.5	250
Brnjica, Well 83	44.65292	21.76872	2.1	17.5	6.6	387	21.4	76.9	10.2	54.1	11.0	53.9	42.0	260
Radosevac, Well 84	44.66485	21.60209	4.1	16.3	7.0	428	21.5	43.2	33.6	98.8	23.4	44.1	41.5	555
Vinci, Well 85	44.72759	21.6014	3.0	17.7	7.5	456	11.7	7.2	16.4	80.2	19.6	6.9	55.7	300
Pozezani, Well 86	44.75821	21.57098	3.5	17.4	7.3	490	2.6	14.8	12.2	83.7	1.4	10.1	13.5	350
Kusice, Well 87	44.71699	21.52939	-	15.0	7.1	380	16.3	4.4	25.7	133.9	13.7	16.3	241.0	260
Tabakovac, Well 88	44.06834	22.43513	2.7	17.1	7.1	315	21.1	13.3	18.9	129.6	18.3	26.9	76.1	520
Brusnik, Well 89	44.10644	22.44644	1.6	17.8	7.2	387	28.8	26.4	12.0	145.5	34.1	42.5	90.3	420
Tamnic, Well 90	44.10227	22.50756	7.2	12.0	6.8	372	23.9	31.1	14.9	172.4	23.2	72.2	98.1	555
Bukovce, Well 91	44.20708	22.60159	10.0	17.2	7.0	438	29.8	20.1	23.0	134.9	23.6	150.7	130.6	335
Samarinovac, Well 92	44.26967	22.55505	11.4	14.6	6.8	468	61.9	2.7	10.9	177.8	36.2	78.7	120.6	530
Prahovo, Well 93	44.29161	22.582	21.4	15.1	7.0	467	21.7	11.1	22.0	104.3	19.8	63.1	68.9	370
Karbulovo, Well 94	44.21351	22.43321	6.1	11.0	7.2	156	2.3	17.5	5.6	60.8	2.8	1.1	9.0	255

Mertis, Well 95	44.14141	22.37642	7.9	12.5	7.1	370	34.4	0.4	46.3	90.3	30.5	77.0	83.0	430
Grljan, Well 96	43.86113	22.29106	10.1	13.7	7.5	41	73.1	6.9	22.5	107.8	54.6	83.8	33.1	650
Grljan, Well 97	43.86004	22.29033	8.9	13.8	7.1	316	38.0	1.0	36.3	122.0	35.3	46.0	115.3	470
Vratarnica, Well 98	43.79303	22.3037	5.9	13.5	6.8	328	44.2	0.7	30.7	165.0	139.9	50.8	73.9	420
Minicevo, Well 99	43.68497	22.29314	8.4	13.3	6.9	378	48.3	5.4	24.5	128.8	37.3	113.2	85.7	410
Novo Korito, Well 100	43.63908	22.44681	8.3	12.3	6.9	398	50.6	2.7	21.7	169.1	80.5	111.1	50.5	605
Grliste, Well 101	43.81283	22.24283	3.0	14.5	7.0	392	18.6	19.0	23.2	145.4	22.1	11.1	118.0	450
Lenovac, Well 102	43.81202	22.17335	5.6	15.2	7.3	407	8.4	1.1	6.8	128.7	35.4	10.8	30.5	385
Sljivar, Well 103	43.86144	22.25284	5.8	13.1	7.2	423	27.4	3.0	21.3	156.1	41.0	11.1	77.9	555
Neresnica, Well 104	44.44813	21.72721	5.3	12.9	7.0	415	130.5	7.2	25.1	133.5	246.6	2.4	54.4	420
Kaona, Well 105	44.4846	21.63431	2.1	15.9	7.8	420	22.0	3.1	16.2	58.4	11.1	42.2	38.9	225
Klenje, Well 106	44.59859	21.53197	5.0	15.3	7.2	431	38.2	13.1	35.9	134.6	13.2	42.6	167.5	460
Malesevo, Well 107	44.62183	21.60664	10.0	13.3	7.0	410	14.2	1.3	13.6	125.8	31.5	38.3	36.6	385
Radenka, Well 108	44.58488	21.75539	10.6	15.6	7.5	332	28.6	3.0	27.6	117.9	31.2	24.6	132.5	290
Brodica, Well 109	44.48644	21.82042	1.6	17.2	7.3	420	17.6	4.0	13.6	57.5	23.3	20.7	43.4	170
Salas, Well 110	44.10872	22.32111	3.8	15.9	7.1	401	21.4	0.0	41.9	110.2	33.2	19.1	81.3	435
Popovica, Well 111	44.20566	22.28919	3.7	13.9	7.6	405	5.5	0.6	3.1	58.8	1.4	1.1	16.0	195
Stubik, Well 112	44.29107	22.3382	3.9	15.0	6.9	430	22.5	30.7	11.9	100.0	59.2	56.9	32.5	335
Ng-Slatina, Well 113	44.41201	22.44987	3.3	19.2	7.0	411	15.2	18.6	16.2	129.8	13.4	33.4	75.8	420
Urovica, Well 114	44.39993	22.40598	6.9	14.2	7.0	445	15.8	5.2	17.7	122.2	16.8	26.6	39.8	440
D.B.Reka, Well 115	44.1025	22.21772	3.9	14.2	7.1	387	10.2	0.7	15.2	82.7	9.5	2.9	64.5	260
Rudna Glava, Well 116	44.32361	22.08932	3.3	16.0	6.7	463	24.8	6.1	32.9	113.4	51.0	84.2	59.5	390
Brestovac, Well 117	44.03991	22.09324	3.0	15.5	7.8	363	244.1	14.1	22.3	191.5	81.1	32.8	214.8	805
Zlot, Well 118	44.02316	21.9926	8.2	12.4	6.9	107	47.2	1.5	25.0	99.5	94.8	0.0	0.5	410
Selo Bogovina, Well 119	43.89297	21.94667	3.6	14.7	7.3	390	29.2	8.7	8.7	148.6	27.4	92.9	56.1	360
Vrbovac, Well 120	43.81446	22.09254	4.2	14.9	7.1	426	25.9	26.5	14.4	130.2	8.1	12.0	66.9	445
Lubnica, Well 121	43.86654	22.19296	5.2	14.4	7.1	402	36.9	10.8	16.6	118.4	13.4	26.5	66.7	400
Mali Jasenovac, Well 122	44.03304	22.44106	5.1	13.8	7.2	394	46.5	0.9	53.3	118.5	75.7	31.8	58.3	580
Veliki Izvor, Well 123	43.9353	22.32978	3.6	15.1	7.1	443	21.9	19.6	15.5	160.4	34.4	72.5	108.9	370
Sarbanovac, Well 124	43.96153	22.07644	5.5	14.4	7.2	436	20.9	0.5	43.9	143.1	39.9	139.7	94.8	370
Metovnica, Well 125	43.95592	22.14061	5.6	15.5	7.4	410	16.2	4.0	13.1	85.4	28.4	9.0	25.5	270
Trnavac, Well 127	43.99289	22.32603	4.4	14.4	7.7	378	69.1	275.0	69.0	81.6	58.5	7.1	256.7	740
Zagradje, Well 128	44.03127	22.21561	2.0	15.4	7.2	407	14.5	4.1	22.0	130.0	15.7	10.6	100.0	380
Zagradje, Well 129	44.02971	22.21844	3.0	14.3	7.3	391	20.1	1.5	13.8	253.7	9.6	10.8	270.4	490

Cokonjar, Well 130	44.02509	22.34577	5.0	13.3	6.9	402	22.6	3.8	14.6	146.7	20.7	23.1	68.9	480
Velika Jasikova, Well 131	44.08491	22.35255	2.0	16.4	7.4	391	13.0	5.5	26.5	76.9	9.3	15.9	50.2	325
Recka, Well 132	44.14392	22.4772	4.4	12.7	7.4	438	14.0	17.7	12.9	64.6	12.2	15.6	22.2	260
Bor, Well 133	44.06064	22.10797	5.0	14.9	7.2	452	0.04	17.3	24.8	75.1	0.0	13.4	121.3	330
Bor, Well 134	44.03129	22.12201	7.3	12.7	7.4	420	0.1	7.8	0.0	16.8	3.8	5.7	55.9	160
Glogovica, Well 135	44.16885	22.23795	7.8	10.9	6.9	96	6.3	0.3	23.6	57.0	2.2	3.1	39.6	260
Glogovica, M2	44.17077	22.23778	-	10.8	7.2	382	6.9	0.1	24.0	72.4	1.7	0.2	34.5	390
Prerast, Well 136	44.35933	22.00718	2.1	16.9	6.8	422	36.7	3.7	18.8	79.8	26.8	1.0	106.9	260
Majdanpek, Well 137	44.41864	21.94756	8.6	11.0	7.3	453	27.1	2.3	11.4	98.6	51.6	27.9	64.7	260
Bosiljkovac, Well 138	44.45883	21.83986	2.2	15.9	7.4	409	40.4	2.4	40.3	139.3	93.3	1.5	115.2	400
Kraku lu Jordan, Well 139	44.48958	21.80878	3.2	15.5	7.4	424	11.6	56.1	17.9	75.5	8.1	6.8	68.6	320
Sevica, Well 140	44.4641	21.71232	10.4	12.5	6.6	420	28.9	2.9	16.1	57.9	42.8	86.9	45.5	120
Ljesnica, Well 141	44.53841	21.57843	5.8	14.2	6.6	430	31.3	1.4	20.8	84.4	76.1	11.1	97.8	190
Tanda, Well 142	44.25525	22.1546	4.3	12.7	7.0	459	8.3	0.8	27.1	45.1	1.5	2.2	22.1	240
Zajecar, Borehole 2	43.89826	22.26371	382	16.5	8.8	142	125.4	0.5	1.3	8.0	11.8	0.7	25.1	300

Appendix 5 Sampling sites, coordinates of sampling sites, water temperature, pH, Eh and concentrations of major cations and anions in groundwater samples collected from cold springs (CS) and hot springs (HS) in the study area.

Sampling site	Y	X	t (°C)	pH	Eh (mV)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
Zukovac, CS 1	43.5288	22.29439	14.9	7.2	442	5.2	12.0	10.6	85.5	4.1	0.8	25.5	490
Mirovo, CS 2	43.79681	21.90171	9.9	7.1	517	0.9	0.4	19.9	81.7	0.9	1.6	12.5	410
Pecka Bara, CS 3	44.59481	22.2679	13.8	7.5	459	5.2	0.8	16.8	66.0	1.7	2.6	31.0	270
Luka, CS 4	44.16624	22.1493	10.9	7.7	432	3.3	1.0	2.9	84.2	1.1	1.9	35.4	320
Slatina, CS 5	44.02274	22.18254	17.8	7.6	390	24.6	0.1	18.8	100.6	3.7	7.0	125.4	290
Krivelj, CS 6	44.12965	22.09565	15.7	7.4	710	1.4	0.3	6.7	93.3	1.2	4.8	15.2	290
Bele vode, CS 7	44.1795	22.09851	11.4	7.6	385	0.9	0.2	0.8	84.2	0.9	2.0	18.3	320
Vlaole, CS 8	44.25018	22.0176	13.5	7.6	225	51.5	1.4	15.2	35.5	1.0	2.0	23.6	340
N.P. Djerdap, CS 9	44.45849	22.01123	15.2	7.5	452	6.6	2.2	8.4	27.9	1.5	20.7	23.2	90
Brnjica, CS 10	44.65353	21.74539	14.7	7.2	418	6.4	2.1	6.2	89.1	3.4	0.0	39.1	340
Rajac, CS 11	44.09106	22.55329	14.7	7.1	379	29.4	3.1	32.3	88.7	6.7	2.9	82.6	570
Marinovac, CS 12	43.73293	22.22524	16.2	7.5	366	5.1	0.2	7.3	82.1	1.1	2.2	25.8	340
Vrbica, CS 13	43.71563	22.26437	18.3	7.3	374	2.5	0.8	17.2	75.0	2.2	6.5	12.8	350
Nikolicevo, CS 14	43.95878	22.2373	14.4	7.0	377	43.2	15.1	19.8	253.2	81.2	253.7	173.1	440
Krivaca, CS 15	44.58787	21.65738	18.1	7.1	398	2.7	1.0	9.1	85.0	1.0	3.3	11.7	370
Blagojev Kamen, CS 16	44.42998	21.85138	11.0	7.8	409	4.1	3.1	10.5	55.6	2.3	1.5	33.3	190
Dupljane, CS 17	44.3042	22.46185	18.1	7.2	412	6.2	3.0	5.6	134.2	5.3	27.2	12.3	460
Luka, CS 18	44.20016	22.16961	12.5	7.3	429	10.4	3.0	22.8	56.1	2.4	11.8	36.6	240
Bor Lake, CS 19	44.10297	22.00429	12.0	7.4	420	18.7	0.2	13.1	67.9	1.4	0.0	78.5	200
Mokranje, CS 20	44.1781	22.52472	14.3	7.2	440	8.0	1.1	12.3	112.9	3.5	11.8	33.3	460
Blizna, CS 21	44.35023	22.02182	13.8	6.9	408	13.4	2.6	12.0	55.7	2.7	2.7	40.7	210
Neresnica, CS 22	44.4475	21.7056	17.9	6.4	448	55.7	5.2	19.5	231.0	15.4	3.2	9.5	930
Brestovacka Banja, HS1	44.05978	22.04388	37.3	8.8	242	142.0	1.7	0.3	81.0	18.3	<0.01	451.6	30
Brestovacka Banja, HS2	44.05988	22.04437	34.0	7.9	362	141.1	1.5	0.3	81.0	18.2	<0.01	451.2	30
Gamzigradska Banja, HS3	43.92394	22.17179	34.4	7.3	270	63.6	3.6	20.1	65.6	79.4	<0.01	39.7	300

Appendix 6 Concentrations of heavy metals, arsenic and aluminum in groundwater samples collected from wells in the study area.

Sampling site	Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Zn (µg/L)	Co (µg/L)	Ni (µg/L)	Cr (µg/L)	V (µg/L)	As (µg/L)	Al (µg/L)
Vrazogrnac, Well 1	5.4	3.3	58.4	10.7	0.17	3.1	0.11	3.7	2.5	2.5
Vrazogrnac, Well 3	3.8	3.0	1.7	9.3	0.07	1.8	0.3	2.6	0.6	2.5
Vrazogrnac, Well 4	2.4	1.3	97.5	3.7	0.12	2.1	0.19	1.2	1.3	2.0
Vrazogrnac, Well 5	5.4	14.1	1481	91.0	5.39	9.9	0.07	0.1	0.2	1.5
Vrazogrnac, Well 6	2.8	1.2	0.3	3.7	0.11	3.0	0.2	4.8	3.3	1.5
Vrazogrnac, Well 8	5.2	19.9	1.4	10.7	0.05	1.6	0.06	1.0	1.1	1.5
Vrazogrnac, Well 9	1.6	2.2	0.4	11.8	0.03	1.1	0.72	1.5	0.4	3.7
Vrazogrnac, Well 10	2.1	1.3	0.2	7.8	0.1	2.4	0.76	0.8	0.3	2.1
Vrazogrnac, Well 12	28.8	2.6	88.9	99.6	0.2	4.6	0.07	13.8	12.4	3.1
Vrazogrnac, Well 13	4.3	62.8	1.0	7.3	0.17	7.8	23.4	3.5	1.3	1.8
Rgotina, Well 42	6.8	69.1	51.9	13.8	0.39	4.3	0.15	7.8	16.0	1.0
Rgotina, Well 43	6.8	1.1	0.8	10.1	0.16	1.8	0.57	10.3	22.4	0.8
Rgotina, Well 44	3.7	608.4	2585	13.1	9.63	11.4	0.72	6.0	5.7	15.5
Rgotina, Well 45	9.5	4.8	1641	4.4	1.37	15.6	0.19	5.8	3.4	4.6
Rgotina, Well 46	4.0	1.9	1.4	6.4	0.08	1.7	0.09	4.3	2.2	1.8
Rgotina, Well 47	2.5	3.4	0.4	13.3	0.07	3.3	0.16	1.3	1.1	2.5
Rgotina, Well 48	3.6	0.8	0.1	1.2	0.1	3.0	0.13	1.9	0.9	0.8
Rgotina, Well 49	5.5	1.1	0.6	1.8	0.12	3.2	0.11	1.8	1.0	1.3
Rgotina, Well 50	7.2	3.4	0.1	5.4	0.07	1.2	0.44	3.9	4.2	1.8
Slatina, Well 1	27.6	4.8	1.1	4.3	0.07	1.4	0.21	3.1	16.6	3.2
Slatina, Well 2	32.6	1.0	0.2	4.4	0.08	2.1	0.05	1.7	2.4	1.0
Slatina, Well 3	11.2	0.4	142.1	8.3	0.16	4.6	0.02	2.9	5.4	0.8
Slatina, Well 4	13.6	0.2	0.0	5.1	0.1	2.6	0.1	4.5	11.4	0.6
Slatina, Well 5	11.3	1.2	2.4	5.2	0.09	1.9	0.02	8.1	5.7	2.0
Slatina, Well 6	5.8	0.8	71.9	4.3	0.1	2.7	0.02	14.4	9.7	0.9
Slatina, Well 7	4.5	3.7	49.7	6.6	0.27	3.0	0.03	4.1	2.7	1.9
Slatina, Well 8	7.4	0.5	0.2	8.6	0.05	1.7	0.39	3.4	9.1	1.0
Slatina, Well 9	9.5	1.8	1.9	11.5	0.08	1.3	0.04	17.6	10.1	2.9
Slatina, Well 10	8.1	1.2	1.2	4.0	0.08	2.4	0.13	2.5	1.7	0.7
Slatina, Well 11	25.0	10.1	3.4	23.2	0.1	2.7	0.03	7.3	8.8	7.7
Slatina, Well 12	11.1	4.9	0.4	1.5	0.05	1.7	0.02	1.1	1.3	2.9
Slatina, Well 14	5.2	3.9	22.8	11.3	0.11	2.5	0.06	22.6	6.7	1.3
Slatina, Well 15	20.1	12.1	30.7	12.9	0.07	1.5	0.06	2.2	6.6	1.2
Slatina, Well 16	84.0	6.8	0.3	9.5	0.11	1.9	0.15	14.5	97.5	4.6
Slatina, Well 17	4.8	0.5	0.6	7.9	0.04	1.8	0.01	0.7	1.2	0.5
Slatina, Borehole 18	50.1	212.6	277.1	10.2	4.64	8.4	0.06	3.5	9.1	11.3
Rgoste,Well 1	3.0	11.3	0.3	3.9	0.05	1.4	0.3	1.8	2.6	7.3
Izvor Reka, Well 2	2.4	57.0	14.3	7.4	0.08	1.6	0.09	0.3	0.2	5.5
Svrljig, Well 3	1.0	12.7	13.0	5.5	0.07	4.6	0.29	1.7	1.0	4.5
Nisevac, Well 4	1.7	8.0	0.4	4.0	0.1	1.8	0.38	0.9	0.4	2.8
Lalinac, Well 5	3.3	7.2	0.2	5.9	0.04	1.4	0.11	0.5	1.0	2.5
Galibabinac, Well 6	1.6	7.5	0.3	1.5	0.09	2.0	0.09	0.2	0.2	3.1
Beli Potok, Well 7	2.0	11.1	0.3	2.7	0.08	2.0	0.25	0.5	0.3	9.0
Vasilj, Well 8	1.7	24.3	0.9	48.0	0.04	1.5	0.24	0.6	0.4	18.3
Kalna, Well 9	0.7	277.0	35.8	12.7	0.06	0.7	0.19	0.4	0.5	3.3
G. Kamenica, Well 10	0.7	6.8	0.2	26.3	0.02	1.1	0.29	0.1	0.1	2.5
Gradiste, Well 11	3.6	16.5	2.5	11.7	0.11	1.4	0.88	5.9	35.6	5.9
Aldinac, Well 12	1.4	40.4	73.7	5.6	0.21	1.0	0.11	0.7	2.0	4.9

Trgoviste, Well 13	6.4	10.6	0.6	4.7	0.08	1.5	0.52	6.0	2.7	8.0
D. Sokolovica, Well 14	1.8	7.1	0.4	8.9	0.05	2.6	0.08	1.0	0.3	1.9
Vlasko Polje, Well 15	7.2	36.7	7.7	30.5	0.12	1.8	0.44	0.5	1.0	44.5
Krivi Vir, Well 16	0.8	12.8	1.9	14.2	0.03	1.6	0.07	0.3	0.6	1.6
Lukovo, Well 17	1.0	12.0	1.1	1.7	0.02	0.9	0.09	0.1	0.2	7.1
Mali Izvor, Well 18	0.9	4.6	0.3	0.8	0.01	1.1	0.04	0.2	0.1	1.9
Podgorac,Well 19	0.7	5.7	0.1	2.2	0.04	1.5	0.16	0.2	0.2	1.9
Bogovina, Well 20	0.8	6.7	0.2	2.0	0.03	1.4	0.12	3.1	0.4	3.0
Sumrakovac, Well 21	1.7	5.5	24.2	1.1	0.07	1.6	0.04	3.1	2.2	3.2
Osnic, Well 22	1.1	4.4	0.2	0.7	0.02	0.8	0.07	6.7	0.9	2.1
Brza Palanka, Well 23	1.3	6.5	0.1	8.4	0.03	1.2	0.21	0.6	0.3	6.4
Velika Kamenica, Well 24	1.4	7.3	1.5	1.7	0.03	1.5	0.53	0.4	0.2	3.6
Podvrska, Well 25	11.8	4.4	2.6	17.5	0.07	2.0	0.35	1.5	0.5	3.3
Milutinovac, Well 26	7.2	20.7	2.2	98.9	0.07	2.7	0.51	1.7	1.2	22.5
Rtkovo,Well 27	1.3	39.3	3.1	28.4	0.13	2.7	3.63	0.5	0.4	3.4
Novi Sip, Well 28	1.0	18.5	1.5	36.6	0.03	1.4	0.5	0.5	0.1	4.0
Miroc, Well 29	2.0	6.6	0.1	11.7	0.06	1.4	0.21	0.3	0.4	2.3
Glogovica, M1	1.8	7.9	10.9	0.8	0.07	1.1	0.22	3.4	3.5	4.0
Glogovica, Well 30	11.5	9.1	5.3	15.5	0.29	5.9	0.39	3.2	3.6	4.6
Glogovica, Well 31	9.0	26.8	54.3	8.6	0.29	2.0	0.09	5.8	1.7	9.3
Dubocane, Well 32	1.2	6.2	0.2	0.6	0.04	0.8	0.53	2.4	20.7	4.4
Luka, Well 33	4.8	28.6	18.7	54.1	0.19	3.3	0.24	0.4	3.3	19.3
Ostrelj, Well 67	22.0	2.2	1.9	6.6	0.05	2.2	0.2	4.2	24.2	1.6
Ostrelj, Well 68	4.0	0.5	0.3	3.2	0.21	3.5	0.16	2.1	1.0	0.8
Bucje, Well 69	9.0	14.4	0.3	61.1	0.05	2.1	0.1	0.9	0.5	2.6
Brezonik, Well 70	3.8	2.6	0.1	5.8	0.02	1.4	<0.01	3.4	0.2	5.4
Cerovo, Well 71	14.5	362.6	1650	262.2	2.17	2.6	<0.01	0.2	0.2	1.2
Gornjane, Well 72	2.8	1.5	0.4	20.9	0.04	0.9	0.03	0.7	0.3	2.3
Klokocevac, Well 73	12.2	22.3	1.6	101.0	0.05	1.4	0.29	1.7	0.3	10.9
Mosna, Well 75	2.2	18.6	193.8	10.7	0.3	4.1	0.08	0.7	0.9	4.9
Topolnica, Well 74	1.8	6.2	38.4	5.6	0.15	1.7	0.21	0.9	1.1	6.7
Donji Milanovac, Well 76	4.0	4.1	0.6	4.1	0.06	1.7	0.31	1.6	2.8	11.7
Oreskovica, Well 77	1.3	3.0	6.2	21.2	0.04	1.5	0.09	1.0	0.5	4.2
Boljetin, Well 78	1.9	6.7	31.3	6.5	0.11	2.5	0.12	0.8	0.7	3.3
Boljetin, Well 79	4.2	4.2	0.3	3.7	0.13	1.7	0.37	3.0	2.7	6.7
Debeli Lug, Well 80	4.3	22.9	453.0	10.2	0.36	2.1	0.21	2.2	3.5	2.0
Leskovo, Well 81	5.2	1.2	1.4	7.7	0.08	1.4	0.05	4.8	1.6	3.7
Dobra, Well 82	3.1	4.9	0.3	11.8	0.07	3.8	0.44	2.1	1.0	7.0
Brnjica, Well 83	4.2	2.1	16.7	10.1	0.11	1.8	0.03	4.2	2.9	4.4
Radosevac, Well 84	1.2	0.5	0.1	8.1	0.05	1.8	0.48	0.7	0.4	1.8
Vinci, Well 85	1.3	3.9	7.6	3.4	0.1	1.4	0.08	1.9	4.9	4.4
Pozezani, Well 86	3.4	0.7	25.7	4.2	0.05	2.4	0.26	6.5	7.1	2.3
Kusice, Well 87	3.4	22.5	2.4	71.2	0.05	1.8	0.05	0.2	0.1	1.3
Tabakovac, Well 88	3.3	38.9	0.5	5.6	0.09	2.5	0.08	1.3	0.6	1.9
Brusnik, Well 89	3.0	0.5	0.0	5.0	0.09	2.5	0.33	2.1	1.1	1.5
Tamnic, Well 90	3.0	8.4	39.1	27.0	0.11	5.0	0.02	1.0	0.9	6.0
Bukovce, Well 91	3.5	8.5	0.6	8.4	0.09	2.6	0.93	0.4	0.2	2.5
Samarinovac, Well 92	2.0	2.0	1.9	23.4	0.05	2.9	0.59	0.7	0.7	2.3
Prahovo, Well 93	17.7	3.9	1.0	106.8	0.05	2.4	1.15	2.4	2.3	3.5
Karbulovo, Well 94	1.3	459.8	1077	5.0	1.23	7.2	0.15	0.8	4.3	4.6
Mertis, Well 95	2.0	13.9	1.0	22.8	0.04	5.1	0.49	1.9	0.3	3.5
Grljan, Well 96	3.2	55.2	694.4	2.6	0.51	4.3	0.05	2.2	18.8	4.2

Grljan, Well 97	2.6	4.1	1.1	1.6	0.03	1.9	0.31	1.2	0.4	2.0
Vratarnica, Well 98	2.5	19.7	12.7	6.4	0.06	2.7	0.04	0.6	0.4	3.5
Minicevo, Well 99	2.8	2.0	3.1	29.2	0.1	2.2	0.07	0.5	0.4	2.5
Novo Korito, Well 100	4.1	11.6	27.8	9.3	0.14	4.4	0.01	0.2	0.3	2.4
Grliste, Well 101	2.2	3.3	1.3	5.4	0.07	10.1	<0.01	0.2	0.6	4.0
Lenovac, Well 102	2.4	0.0	12.0	3.1	0.1	1.6	<0.01	0.3	0.2	2.6
Sljivar, Well 103	1.7	0.0	0.2	4.8	0.03	1.9	1	2.0	0.4	2.8
Neresnica, Well 104	4.4	1.9	12.1	4.8	0.04	2.0	0.04	0.8	0.3	2.7
Kaona, Well 105	1.5	9.3	0.3	4.1	0.03	1.2	0.34	0.7	0.6	5.7
Klenje, Well 106	3.2	1.0	0.8	120.8	0.06	2.3	0.24	1.3	0.9	4.3
Malesevo, Well 107	0.7	0.9	0.4	43.9	0.01	1.4	0.22	1.0	0.3	2.7
Radenka, Well 108	7.0	14.2	15.2	287.0	0.06	8.6	0.09	0.8	0.9	1.6
Brodica, Well 109	9.6	2.6	5.6	22.6	0.11	3.2	0.03	0.9	2.8	4.0
Salas, Well 110	1.8	0.0	0.5	1.6	0.05	2.1	0.41	9.9	0.7	0.6
Popovica, Well 111	1.2	0.0	0.1	3.4	0.02	0.8	0.03	0.3	0.2	3.3
Stubik, Well 112	1.2	0.0	0.2	9.1	0.04	1.3	<0.01	0.6	0.5	1.5
Ng-Slatina, Well 113	1.3	5.2	0.1	12.4	0.03	1.8	0.03	0.2	0.1	1.9
Urovica, Well 114	2.0	148.5	0.6	16.0	0.05	1.9	0.14	0.4	0.2	2.9
D.B.Reka, Well 115	1.6	5.7	4.3	2.0	0.02	1.0	0.02	0.3	0.4	1.2
Rudna Glava, Well 116	2.7	0.0	0.3	5.4	0.07	2.1	0.24	1.5	0.4	1.8
Brestovac, Well 117	151.2	39.2	492.2	14.2	2.52	7.6	0.29	8.1	25.6	14.4
Zlot, Well 118	1.3	6387	1268	1.8	0.41	1.2	<0.01	0.6	1.1	3.7
Selo Bogovina, Well 119	3.4	10.0	1.1	52.1	0.07	2.3	0.13	3.5	10.0	3.3
Vrbovac, Well 120	1.5	3.2	0.9	4.5	0.03	1.6	0.25	0.6	0.2	4.1
Lubnica, Well 121	11.5	8.1	5.2	30.2	0.04	1.6	0.01	7.7	2.9	4.7
Mali Jasenovac, Well 122	2.1	0.0	0.4	11.2	0.01	1.7	0.03	0.9	0.2	2.0
Veliki Izvor, Well 123	1.6	0.0	0.3	2.6	0.05	2.1	0.29	0.6	0.3	4.5
Sarbanovac, Well 124	2.5	0.0	0.3	4.3	0.03	1.8	<0.01	4.2	0.1	2.9
Metovnica, Well 125	4.1	3.0	2.4	9.6	0.02	1.4	0.12	4.9	3.8	5.8
Trnavac, Well 127	19.1	8.3	82.5	18.7	0.15	7.8	0.08	17.8	25.8	4.6
Zagradje, Well 128	9.2	2.5	0.8	4.1	0.06	1.3	0.26	2.8	6.4	3.4
Zagradje, Well 129	6.5	20.3	10.8	2.5	0.16	2.9	0.06	1.0	1.5	1.9
Cokonjar, Well 130	2.5	0.0	3.1	1.9	0.05	2.2	0.14	0.6	0.8	1.6
Velika Jasikova, Well 131	6.8	7.5	0.5	42.3	0.04	1.6	0.2	3.9	1.3	7.8
Recka, Well 132	5.3	0.0	0.2	6.1	0.03	1.4	0.32	3.0	1.9	2.4
Bor, Well 133	2.8	2.7	0.4	5.7	0.04	1.2	0.08	4.3	0.8	4.8
Bor, Well 134	23.0	25.3	74.9	1.6	0.38	1.7	0.08	4.7	5.0	16.6
Glogovica, Well 135	1.1	1.8	1.8	2.1	0.03	0.8	0.43	3.3	0.5	4.6
Glogovica, M2	1.9	9.0	152.9	1.3	0.59	1.4	<0.01	1.0	2.9	1.1
Prerast, Well 136	3.3	1.6	0.2	3.6	0.03	1.2	0.06	0.8	0.6	2.2
Majdanpek, Well 137	2.8	0.9	0.3	8.9	0.03	1.5	0.08	0.6	0.9	1.4
Bosiljkovac, Well 138	4.4	5.7	0.7	35.1	0.05	2.5	0.12	0.5	2.1	6.4
Kraku lu Jordan, Well 139	7.6	3.5	5.8	54.2	0.14	2.0	0.1	10.1	30.7	3.1
Sevica, Well 140	2.2	16.6	1.0	18.7	0.03	1.3	0.16	0.5	0.4	1.2
Ljesnica, Well 141	1.6	16.7	5.7	130.8	0.04	2.8	0.06	0.5	0.3	2.5
Tanda, Well 142	0.6	0.9	0.1	5.1	0.02	0.8	0.43	1.1	0.2	1.8
Zajecar, Borehole 2	3.0	29.4	10.6	2	<0.003	0.01	<0.01	0.1	5.8	7.4

Appendix 7 Concentrations of heavy metals, arsenic and aluminum in groundwater samples collected from cold springs (CS) and hot springs (HS) in the study area.

Sampling site	Cu (μg/L)	Fe (μg/L)	Mn (μg/L)	Zn (μg/L)	Co (μg/L)	Ni (μg/L)	Cr (μg/L)	V (μg/L)	As (μg/L)	Al (μg/L)
Zukovac, CS 1	0.9	20.6	0.5	2	0.03	1.5	0.09	0.2	0.2	6.5
Mirovo, CS 2	0.6	5.5	0.1	1	0.03	1.4	0.15	0.6	0.2	3.2
Pecka Bara, CS 3	0.3	4.3	0.1	1	0.01	0.7	0.12	0.3	0.2	1.6
Luka, CS 4	0.3	6.7	0.2	0	0.02	1.1	0.14	0.7	0.1	3.0
Slatina, CS 5	4.8	6.4	2.0	15	0.03	0.9	0.43	10.8	0.7	5.8
Krivelj, CS 6	4.1	0.1	0	11	0.02	1.0	0.03	0.4	0.5	1.3
Bele vode, CS 7	2.6	0.3	0.8	25	0.04	1.3	0.05	0.3	0.2	1.0
Vlaole, CS 8	1.3	219.6	4.3	3	<0.003	0.4	<0.01	0.0	7.7	1.5
N.P. Djerdap, CS 9	0.9	3.4	0.4	8	0.01	0.5	0.35	1.0	0.1	9.3
Brnjica, CS 10	0.3	3.6	2	4	0.02	1.4	0.00	0.2	0	1.5
Rajac, CS 11	0.9	0.7	1.5	19	0.02	1.7	0.96	0.7	0.3	1.5
Marinovac, CS 12	0.7	1.8	0.3	1	0.02	1.4	0.03	0.1	0.1	3.5
Vrbica, CS 13	1.1	4.7	0.1	2	0.02	1.5	0.05	0.3	0.6	3.3
Nikolicevo, CS 14	2.2	0	0.1	2	0.07	3.3	0.18	1.5	0.8	1.9
Krivaca, CS 15	0.3	0	0.2	2	<0.003	1.7	<0.01	0.1	2.9	2.8
Blagojev Kamen, CS 16	0.5	8.5	0.1	2	<0.03	0.5	1.10	2.1	1.7	4.5
Dupljane, CS 17	3.2	0.9	0.7	7	0.02	1.9	1.09	1.3	0.5	6.3
Luka, CS 18	2.2	3.5	4.4	4	0.01	0.7	0.21	1.8	0.1	6.0
Bor Lake, CS 21	3.0	0	1.9	9	<0.03	0.6	0.00	2.4	3.6	3.1
Mokranje, CS 24	1.9	0	0.3	4	0.01	1.9	0.00	0.4	0.1	2.2
Blizna, CS 25	1.7	5.2	0.5	2	0.01	0.9	0.83	0.4	0.2	7.4
Neresnica, CS 26	2.4	3.3	0.6	3	0.04	3.9	0.07	1.0	2.7	2.8
Brestovacka Banja, HS 1	3.2	0.01	3.0	0.7	<0.003	0.8	<0.01	0.05	4.5	3.5
Brestovacka Banja, HS 2	3.0	0.01	1.9	0.4	<0.003	0.8	<0.01	0.08	4.5	7.3
Gamzigradska Banja, HS 3	2.4	91.1	53.0	2.2	0.08	0.9	<0.01	0.05	11.5	6.2

Appendix 8 Concentrations of Li, B, Rb, Sr, Ba, Ga, Sb, and U in groundwater from wells and boreholes in the study area.

Sampling site	Li (μg/L)	B (μg/L)	Rb (μg/L)	Sr (μg/L)	Ba (μg/L)	Ga (μg/L)	Sb (μg/L)	U (μg/L)
Vrazogrnac, Well 1	2.4	290.6	0.1	1261	25.3	1.9	0.23	2.7
Vrazogrnac, Well 3	1.8	70.8	0.2	534	63.7	3.3	0.1	2.6
Vrazogrnac, Well 4	1.5	137.3	0.3	965	17.3	1.4	0.12	2.8
Vrazogrnac, Well 5	3.4	103.9	1.1	1385	7.4	0.7	0.05	1.7
Vrazogrnac, Well 6	4.2	220.3	0.4	922	34.7	2.6	0.16	3.0
Vrazogrnac, Well 8	1.3	32.1	0.2	646	19.3	1.8	0.12	2.5
Vrazogrnac, Well 9	2.0	13.9	0.2	781	72.3	3.6	0.07	4.8
Vrazogrnac, Well 10	7.4	194.0	0.1	722	7.1	0.6	0.06	11.7
Vrazogrnac, Well 12	2.3	305.1	4.6	916	60.9	2.8	0.43	2.6
Vrazogrnac, Well 13	2.9	126.3	0.2	932	104.9	5.1	0.13	5.9
Rgotina, Well 42	6.3	386.8	2.0	1147	56.4	3.0	0.22	1.0
Rgotina, Well 43	6.7	377.0	5.3	659	34.9	2.7	0.3	0.9
Rgotina, Well 44	4.3	241.6	2.3	698	116.6	5.7	5.02	0.7
Rgotina, Well 45	4.3	187.5	3.2	776	24.0	1.9	0.6	1.2
Rgotina, Well 46	2.0	152.6	0.5	504	77.7	4.0	0.09	0.9
Rgotina, Well 47	2.7	58.0	0.1	1005	10.6	1.6	0.12	1.7
Rgotina, Well 48	5.4	139.7	0.4	1635	68.4	3.2	0.08	4.1
Rgotina, Well 49	7.5	236.9	0.6	1775	61.8	2.9	0.1	4.4
Rgotina, Well 50	2.8	144.1	0.3	583	26.0	2.2	0.59	0.8
Slatina, Well 1	4.4	198.1	0.6	651	19.2	1.7	0.58	1.4
Slatina, Well 2	6.6	177.6	0.7	1504	103.3	5.3	0.11	3.4
Slatina, Well 3	3.7	295.0	0.5	1082	12.1	1.1	0.09	0.5
Slatina, Well 4	5.9	230.6	0.5	1349	76.6	3.9	0.16	0.9
Slatina, Well 5	2.1	30.7	0.5	1644	23.1	2.3	0.12	7.9
Slatina, Well 6	3.0	174.4	0.7	1502	13.1	1.2	0.12	4.2
Slatina, Well 7	2.8	146.5	0.1	1529	14.1	1.2	0.49	7.4
Slatina, Well 8	5.3	13.1	0.3	999	19.8	2.1	0.43	2.0
Slatina, Well 9	0.8	143.3	2.3	700	26.6	2.3	0.27	0.4
Slatina, Well 10	4.9	16.7	0.5	2391	27.1	2.6	0.06	12.4
Slatina, Well 11	3.4	139.7	0.9	1777	88.2	4.5	0.16	1.7
Slatina, Well 12	2.0	95.5	0.5	661	47.7	3.2	0.18	1.3
Slatina, Well 14	6.0	154.4	0.1	1494	95.0	4.9	0.12	1.0
Slatina, Well 15	9.1	25.4	0.5	1102	82.3	4.3	0.23	6.2
Slatina, Well 16	1.7	68.5	0.4	320	8.0	0.4	0.99	0.3
Slatina, Well 17	38.0	109.3	0.6	1529	21.7	2.4	0.05	12.5
Slatina, Borehole 18	5.2	28.3	0.7	434	12.7	0.6	4.8	2.7
Rgoste,Well 1	33.8	28.3	1.2	1105	22.5	1.8	0.15	2.5
Izvor Reka, Well 2	5.0	23.3	0.2	310	24.0	1.8	0.04	0.5
Svrljig, Well 3	36.1	121.6	0.7	1041	127.3	6.4	0.13	5.6
Nisevac, Well 4	32.2	96.4	0.3	1587	158.4	7.8	0.07	3.8
Lalinac, Well 5	4.3	14.0	0.5	293	18.3	1.4	0.05	0.9
Galibabinac, Well 6	4.2	35.8	0.8	612	21.9	1.6	0.03	0.7
Beli Potok, Well 7	4.6	107.7	0.2	400	142.9	6.8	0.03	0.9
Vasilj, Well 8	7.2	16.4	0.4	676	134.3	6.4	0.06	3.8
Kalna, Well 9	0.4	8.0	0.2	177	48.1	2.3	0.07	1.1
G. Kamenica, Well 10	9.3	28.5	0.5	801	20.0	1.0	0.02	1.0
Gradiste, Well 11	0.5	75.6	0.7	152	23.0	1.1	0.59	0.7
Aldinac, Well 12	0.9	12.2	2.7	96	4.2	0.2	0.04	1.6

Trgoviste, Well 13	27.3	111.5	1.0	1371	21.0	1.7	0.14	1.4
D. Sokolovica, Well 14	8.2	24.9	0.4	3231	158.4	6.4	0.03	6.0
Vlasko Polje, Well 15	0.8	25.7	0.5	188	171.7	8.0	11.83	0.6
Krivi Vir, Well 16	2.6	11.5	1.0	136	103.1	4.7	0.21	0.8
Lukovo, Well 17	5.3	12.1	0.4	75	29.6	2.5	0.24	0.0
Mali Izvor, Well 18	5.9	24.4	0.4	551	11.1	0.9	0.02	0.8
Podgorac,Well 19	3.9	10.5	0.1	327	44.1	3.0	0.02	1.3
Bogovina, Well 20	0.5	290.6	0.3	381	8.4	0.4	0.03	2.6
Sumrakovac, Well 21	2.4	34.1	1.0	352	57.4	2.7	0.27	0.9
Osnic, Well 22	3.1	91.0	0.3	211	3.9	0.2	0.04	0.5
Brza Palanka, Well 23	3.4	21.9	0.4	217	21.6	1.8	0.04	0.1
Velika Kamenica, Well 24	2.8	21.7	0.2	377	120.4	3.9	0.03	0.6
Podvrska, Well 25	3.2	142.8	0.6	300	31.1	2.6	0.08	1.4
Milutinovac, Well 26	23.9	26.4	18.7	422	13.1	1.2	0.94	4.1
Rtkovo,Well 27	7.3	213.4	0.6	476	131.6	6.4	0.05	4.8
Novi Sip, Well 28	1.0	19.0	0.2	166	13.8	1.2	0.02	0.1
Miroc, Well 29	2.7	79.8	0.6	329	17.2	1.4	0.1	0.4
Glogovica, M1	0.0	5.7	0.1	61	0.5	0.0	0.07	0.1
Glogovica, Well 30	0.0	166.8	2.0	539	36.9	3.0	0.21	1.0
Glogovica, Well 31	0.1	14.2	0.4	232	5.0	0.3	0.42	1.6
Dubocane, Well 32	0.1	17.9	0.3	67	1.2	0.1	0.06	0.0
Luka, Well 33	9.4	20.3	0.7	208	17.9	1.6	2.19	0.3
Ostrelj, Well 67	12.8	30.1	0.2	743	14.1	0.7	0.59	13.3
Ostrelj, Well 68	13.3	417.5	0.4	1982	57.6	2.8	0.07	1.9
Bucje, Well 69	2.9	36.4	4.5	137	14.9	0.8	0.1	7.5
Brezonik, Well 70	0.3	5.9	0.1	550	1.9	0.1	0.03	1.1
Cerovo, Well 71	0.6	30.1	1.6	535	26.5	1.4	0.12	0.2
Gornjane, Well 72	0.8	24.9	0.1	285	43.1	2.3	0.09	8.4
Klokocevac, Well 73	1.3	6.4	0.5	186	35.6	1.9	0.31	0.8
Mosna, Well 75	10.2	106.4	0.2	262	85.9	7.4	0.11	1.3
Topolnica, Well 74	2.2	101.5	0.4	322	196.8	9.9	0.12	3.1
Donji Milanovac, Well 76	1.8	33.8	1.6	445	61.4	3.1	0.29	4.8
Oreskovica, Well 77	0.9	27.2	0.3	188	48.1	2.5	0.12	0.2
Boljetin, Well 78	10.2	110.2	0.7	565	191.4	9.3	0.1	0.7
Boljetin, Well 79	1.2	199.9	1.9	260	169.3	8.6	0.28	1.4
Debeli Lug, Well 80	0.6	148.5	4.1	629	55.1	2.5	0.14	1.1
Leskovo, Well 81	0.2	149.8	0.8	517	22.9	1.2	0.16	1.5
Dobra, Well 82	1.5	36.9	0.7	205	86.9	4.4	0.17	0.3
Brnjica, Well 83	2.0	195.8	10.2	129	44.9	2.3	0.33	0.1
Radosevac, Well 84	9.2	87.7	0.4	349	124.8	6.2	0.08	3.1
Vinci, Well 85	2.3	23.2	0.9	181	27.3	1.4	0.13	0.6
Pozezani, Well 86	3.5	33.1	1.6	157	41.0	2.1	0.74	0.4
Kusice, Well 87	0.8	22.7	0.1	392	55.5	2.7	0.05	2.2
Tabakovac, Well 88	11.8	90.3	0.3	459	84.1	4.2	0.08	0.7
Brusnik, Well 89	6.6	154.0	0.9	540	61.6	3.1	0.28	0.6
Tamnic, Well 90	5.0	56.8	0.6	873	140.3	6.9	0.14	1.6
Bukovce, Well 91	1.8	123.7	0.2	181	86.2	4.3	0.03	1.5
Samarinovac, Well 92	4.4	131.0	0.3	437	130.0	6.5	0.07	1.8
Prahovo, Well 93	6.9	112.4	2.6	683	71.1	3.6	0.26	4.2
Karbulovo, Well 94	0.2	22.0	1.3	162	55.6	2.9	0.08	0.1
Mertis, Well 95	0.2	11.8	0.4	479	26.7	1.4	0.03	5.7
Grljan, Well 96	3.1	47.1	1.1	476	165.6	8.5	0.12	2.4

Grljan, Well 97	4.5	45.1	0.2	545	124.5	6.4	0.04	5.0
Vratarnica, Well 98	4.0	26.2	0.4	492	156.1	7.7	0.07	3.6
Minicevo, Well 99	3.6	158.4	0.4	369	163.0	8.2	0.04	2.4
Novo Korito, Well 100	23.2	70.3	4.0	800	383.4	22.2	0.11	1.1
Grliste, Well 101	11.1	20.2	3.7	404	80.7	4.1	0.2	5.0
Lenovac, Well 102	8.8	12.1	0.2	373	192.2	9.5	0.05	0.9
Sljivar, Well 103	6.0	16.8	0.2	1122	116.1	5.6	0.04	3.2
Neresnica, Well 104	5.3	18.0	0.4	363	113.8	5.4	0.06	18.1
Kaona, Well 105	3.8	266.7	0.6	276	24.4	1.2	0.14	0.4
Klenje, Well 106	58.2	153.2	3.7	1124	36.2	1.8	0.2	5.7
Malesevo, Well 107	12.1	11.1	0.9	311	51.5	2.5	0.06	1.9
Radenka, Well 108	12.4	57.0	0.6	579	25.8	1.3	0.19	4.7
Brodica, Well 109	0.7	48.6	0.4	167	26.8	1.3	0.25	0.8
Salas, Well 110	0.1	19.9	0.2	180	9.9	0.5	0.05	1.2
Popovica, Well 111	0.4	4.1	0.3	112	6.2	0.3	0.04	0.5
Stubik, Well 112	2.8	130.4	0.6	226	119.0	5.8	0.06	0.2
Ng-Slatina, Well 113	8.5	59.2	0.4	535	82.2	3.9	0.05	1.3
Urovica, Well 114	2.8	58.1	0.2	375	53.1	2.6	0.05	2.2
D.B.Reka, Well 115	0.8	11.6	0.1	258	84.0	4.1	0.21	1.5
Rudna Glava, Well 116	10.6	46.0	2.8	356	51.1	2.4	0.08	20.9
Brestovac, Well 117	2.9	181.0	3.6	724	10.7	0.5	1.27	3.0
Zlot, Well 118	0.2	6.0	1.0	678	27.5	1.3	0.06	0.0
Selo Bogovina, Well 119	12.4	875.5	0.8	432	51.6	2.4	0.66	0.2
Vrbovac, Well 120	12.6	84.6	0.2	1082	148.6	6.5	0.04	1.7
Lubnica, Well 121	6.5	196.9	0.3	1023	27.3	1.3	0.09	1.2
Mali Jasenovac, Well 122	19.6	30.3	0.2	1109	74.7	3.5	0.03	6.1
Veliki Izvor, Well 123	6.7	89.6	0.6	602	160.7	7.1	0.06	1.3
Sarbanovac, Well 124	0.5	19.5	0.7	758	7.2	0.3	0.02	0.8
Metovnica, Well 125	5.3	76.8	0.9	455	43.8	2.1	0.36	0.9
Trnavac, Well 127	12.5	222.0	28.4	845	43.0	2.0	0.59	7.7
Zagradje, Well 128	11.1	50.4	0.4	762	93.3	4.9	0.19	1.3
Zagradje, Well 129	11.8	113.7	0.3	1395	50.9	2.5	0.13	1.3
Cokonjar, Well 130	6.6	40.0	0.2	449	13.3	1.1	0.05	3.6
Velika Jasikova, Well 131	0.5	27.2	0.3	161	10.5	0.9	2.36	0.6
Recka, Well 132	1.1	46.6	1.5	344	37.2	3.1	0.28	0.6
Bor, Well 133	0.7	61.2	0.1	256	3.2	0.2	2.71	0.7
Bor, Well 134	0.4	25.0	0.4	240	10.7	0.6	0.59	0.4
Glogovica, Well 135	0.0	6.3	0.1	121	0.8	0.0	0.57	0.1
Glogovica, M2	0.1	6.9	0.3	80	4.9	0.2	0.08	0.1
Prerast, Well 136	5.5	21.1	2.5	404	32.6	1.5	0.3	4.6
Majdanpek, Well 137	4.7	54.3	1.0	300	51.4	2.3	0.18	2.1
Bosiljkovac, Well 138	1.1	35.1	2.5	567	40.0	1.8	1.89	3.7
Kraku lu Jordan, Well 139	1.0	85.1	2.0	203	31.5	1.4	0.71	0.3
Sevica, Well 140	6.7	11.7	0.2	168	53.1	2.4	0.09	0.2
Ljesnica, Well 141	1.6	23.1	1.3	421	92.9	4.2	0.05	0.1
Tanda, Well 142	1.3	10.1	3.3	96	11.6	0.5	0.02	6.3
Zajecar, Borehole 2	7.0	66.4	0.2	176	22.6	1.2	<0.002	0.04

Appendix 9 Concentrations of Li, B, Rb, Sr, Ba, Ga, Sb, and U in groundwater from cold springs (CS) and hot springs in the study area.

Sampling site	Li (μg/L)	B (μg/L)	Rb (μg/L)	Sr (μg/L)	Ba (μg/L)	Ga (μg/L)	Sb (μg/L)	U (μg/L)
Zukovac, CS 1	3.9	9.3	0.2	285	11.4	0.9	0.02	0.8
Mirovo, CS 2	0.3	4.3	0.3	40	9.0	0.5	0.05	0.3
Pecka Bara, CS 3	4.9	4.7	0.4	281	277.8	9.2	0.03	0.8
Luka, CS 4	0.3	4.6	0.8	48	9.5	0.5	0.03	2.8
Slatina, CS 5	6.0	13.3	0.1	248	2.7	0.2	0.02	4.8
Krivelj, CS 6	0.7	5.0	0.4	97	7.2	0.4	0.02	0.3
Bele vode, CS 7	0.2	3.7	0.2	32	8.0	0.4	0.02	0.2
Vlaole, CS 8	4.0	16.7	0.9	1027	40.6	2.2	0.01	0.1
N.P. Djerdap, CS 9	2.6	5.5	1.1	92	18.9	1.0	0.03	1.2
Brnjica, CS 10	11.5	6.0	0.3	92	68.2	3.5	0.01	7.2
Rajac, CS 11	30.2	29.9	0.6	1207	15.1	0.8	0.02	3.6
Marinovac, CS 12	5.2	11.4	0.3	213	102.4	4.3	0.02	0.8
Vrbica, CS 13	2.1	9.2	0.8	199	18.9	1.0	0.03	1.7
Nikolicevo, CS 14	13.3	65.8	0.9	2188	27.4	1.3	0.03	6.9
Krivaca, CS 15	4.4	10.7	1.2	207	24.1	1.2	0.14	0.3
Blagojev Kamen, CS 16	1.1	4.8	2.0	197	150.8	7.5	0.03	10.8
Dupljane, CS 17	3.1	11.2	0.2	230	75.6	3.7	0.03	1.2
Luka, CS 18	3.9	8.8	1.6	132	18.0	0.9	0.9	33.6
Bor Lake, CS 21	1.4	14.2	0.2	350	2.2	0.1	0.38	0.5
Mokranje, CS 24	8.4	11.9	0.8	1244	39.8	3.2	0.03	1.9
Blizna, CS 25	55.9	10.6	3.3	128	5.2	0.3	0.03	27.1
Neresnica, CS 26	56.7	195.0	11.9	452	152.8	6.0	0.04	1.1
Brestovacka Banja, HS1	14.3	302	3.7	634	2.1	0.3	0.05	0.01
Brestovacka Banja, HS2	14.3	302	3.7	633	2.1	0.3	0.05	0.01
Gamzigradska Banja, HS3	78.5	213	8.9	1215	133.4	5.9	0.21	0.08

Appendix 10 Stable isotope composition of groundwater collected from wells and boreholes in the study area.

Sampling site	δD_{SMOW} (‰)	$\delta^{18}O_{SMOW}$ (‰)	d-excess (‰)
Vrazogrnac, Well 1	-69	-10.0	11
Vrazogrnac, Well 3	-71	-10.5	12
Vrazogrnac, Well 4	-70	-10.3	12
Vrazogrnac, Well 5	-70	-10.1	11
Vrazogrnac, Well 6	-68	-9.9	11
Vrazogrnac, Well 8	-73	-10.6	12
Vrazogrnac, Well 9	-70	-10.1	10
Vrazogrnac, Well 10	-63	-9.5	13
Vrazogrnac, Well 12	-61	-8.8	10
Vrazogrnac, Well 13	-69	-9.9	10
Rgotina, Well 42	-69	-10.1	11
Rgotina, Well 43	-70	-10.2	12
Rgotina, Well 44	-69	-9.9	10
Rgotina, Well 45	-66	-9.4	10
Rgotina, Well 46	-69	-10.1	12
Rgotina, Well 47	-70	-10.1	11
Rgotina, Well 48	-70	-10.0	9
Rgotina, Well 49	-69	-9.9	11
Rgotina, Well 50	-55	-7.9	8
Slatina, Well 1	-66	-9.6	10
Slatina, Well 2	-73	-10.6	12
Slatina, Well 3	-70	-10.4	13
Slatina, Well 4	-69	-9.9	11
Slatina, Well 5	-68	-9.6	9
Slatina, Well 6	-69	-10.0	11
Slatina, Well 7	-71	-10.5	13
Slatina, Well 8	-64	-9.5	12
Slatina, Well 9	-74	-10.8	12
Slatina, Well 10	-67	-10.1	14
Slatina, Well 11	-72	-10.7	14
Slatina, Well 12	-74	-11.0	14
Slatina, Well 14	-70	-10.5	14
Slatina, Well 15	-65	-9.4	10
Slatina, Well 16	-75	-10.7	11
Slatina, Well 17	-63	-9.2	10
Slatina, Borehole 18	-61	-8.8	10
Zagradje, Well 128	-72	-10.2	9
Zagradje, Well 129	-67	-9.8	11
Ostrelj, Well 67	-70	-10.1	10
Ostrelj, Well 68	-67	-9.7	11
Cerovo, Well 71	-72	-10.7	13
Rgoste,Well 1	-59	-8.8	11
Izvor Reka, Well 2	-69	-10.1	12
Svrljig, Well 3	-67	-9.8	11
Nisevac, Well 4	-63	-9.0	9
Lalinac, Well 5	-72	-10.5	12
Galibabinac, Well 6	-68	-10.1	13
Beli Potok, Well 7	-71	-10.4	12
Vasilj, Well 8	-67	-9.6	9
Kalna, Well 9	-72	-10.8	14
G. Kamenica, Well 10	-70	-10.2	12
Gradiste, Well 11	-63	-9.1	9
Aldinac, Well 12	-72	-10.6	13
Trgoviste, Well 13	-59	-8.7	11
D. Sokolovica, Well 14	-67	-9.6	10
Vlasko Polje, Well 15	-71	-10.6	13
Krivi Vir, Well 16	-74	-10.6	11
Lukovo, Well 17	-72	-10.6	13
Mali Izvor, Well 18	-70	-10.4	13

Podgorac,Well 19	-67	-9.9	12
Bogovina, Well 20	-71	-10.5	13
Sumrakovac, Well 21	-65	-9.8	14
Osnic, Well 22	-70	-10.2	11
Brza Palanka, Well 23	-68	-10.0	11
Velika Kamenica, Well 24	-70	-10.2	12
Podvrska, Well 25	-69	-10.0	11
Milutinovac, Well 26	-54	-7.6	7
Rtkovo,Well 27	-64	-9.4	11
Novi Sip, Well 28	-65	-9.6	12
Miroc, Well 29	-72	-10.7	14
Glogovica, M1	-73	-10.8	14
Glogovica, Well 30	-73	-10.5	11
Glogovica, Well 31	-65	-9.8	13
Dubocane, Well 32	-68	-10.1	12
Luka, Well 33	-75	-10.8	11
Bucje, Well 69	-72	-10.3	10
Brezonik, Well 70	-72	-10.5	12
Gornjane, Well 72	-75	-11.0	13
Klokocevac, Well 73	-70	-10.3	12
Mosna, Well 75	-67	-10.1	14
Topolnica, Well 74	-71	-10.3	12
Donji Milanovac, Well 76	-67	-9.9	12
Oreskovica, Well 77	-73	-10.4	11
Boljetin, Well 78	-63	-9.2	11
Boljetin, Well 79	-71	-10.3	11
Debeli Lug, Well 80	-74	-10.1	7
Leskovo, Well 81	-73	-10.1	8
Dobra, Well 82	-66	-9.6	10
Brnjica, Well 83	-68	-10.0	12
Radosevac, Well 84	-66	-9.4	9
Vinci, Well 85	-71	-10.0	9

Pozezani, Well 86	-67	-9.3	7
Kusice, Well 87	-69	-10.0	11
Tabakovac, Well 88	-67	-9.7	11
Brusnik, Well 89	-67	-9.5	8
Tamnic, Well 90	-68	-10.4	15
Bukovce, Well 91	-66	-9.6	11
Samarinovac, Well 92	-70	-9.5	6
Prahovo, Well 93	-61	-9.0	10
Karbulovo, Well 94	-72	-10.6	13
Mertis, Well 95	-67	-10.0	14
Grljan, Well 96	-68	-10.3	14
Grljan, Well 97	-70	-10.3	13
Vratarnica, Well 98	-67	-10.0	13
Minicevo, Well 99	-66	-9.5	10
Novo Korito, Well 100	-68	-9.8	10
Grliste, Well 101	-69	-10.1	11
Lenovac, Well 102	-67	-9.9	12
Sljivar, Well 103	-68	-9.9	11
Neresnica, Well 104	-67	-9.6	11
Kaona, Well 105	-72	-10.1	9
Klenje, Well 106	-72	-10.2	9
Malesevo, Well 107	-70	-9.9	10
Radenka, Well 108	-66	-9.7	12
Brodica, Well 109	-60	-8.6	9
Salas, Well 110	-69	-10.0	12
Popovica, Well 111	-84	-12.4	15
Stubik, Well 112	-73	-10.8	13
Ng-Slatina, Well 113	-68	-10.1	13
Urovica, Well 114	-69	-10.5	15
D.B.Reka, Well 115	-71	-10.5	14
Rudna Glava, Well 116	-71	-10.4	12
Brestovac, Well 117	-71	-10.2	11

Zlot, Well 118	-78	-11.4	13
Selo Bogovina, Well 119	-72	-10.3	11
Vrbovac, Well 120	-73	-10.5	11
Lubnica, Well 121	-68	-10.0	12
Mali Jasenovac, Well 122	-64	-9.5	12
Veliki Izvor, Well 123	-61	-9.0	11
Sarbanovac, Well 124	-69	-9.7	9
Metovnica, Well 125	-67	-9.7	11
Trnavac, Well 127	-77	-11.0	11
Cokonjar, Well 130	-71	-10.5	14
Velika Jasikova, Well 131	-67	-9.6	10
Recka, Well 132	-66	-9.9	13
Bor, Well 133	-66	-9.6	10
Bor, Well 134	-71	-10.4	13
Glogovica, Well 135	-74	-11.0	14
Glogovica, M2	-73	-10.9	14
Prerast, Well 136	-66	-10.1	15
Majdanpek, Well 137	-71	-10.6	15
Bosiljkovac, Well 138	-69	-10.1	12
Kraku lu Jordan, Well 139	-71	-10.4	12
Sevica, Well 140	-65	-9.6	12
Ljesnica, Well 141	-64	-9.5	12
Tanda, Well 142	-71	-10.7	14
Zajecar, Borehole	-98	-14.1	15

Appendix 11 Stable isotope composition of groundwater collected from cold springs (CS) and hot springs (HS) in the study area.

Sampling site	δD_{SMOW} (‰)	$\delta^{18}O_{SMOW}$ (‰)	d-excess (‰)
Zukovac, CS 1	-67	-9.6	10
Mirovo, CS 2	-74	-11.0	14
Pecka Bara, CS 3	-70	-10.5	14
Luka, Spring 4	-72	-10.7	13
Slatina, CS 5	-71	-10.5	13
Krivelj, CS 6	-75	-11.1	14
Bele vode, CS 7	-74	-11.1	14
Vlaole, CS 8	-78	-11.5	14
N.P. Djerdap, CS 9	-71	-10.9	16
Brnjica, CS 10	-68	-10.1	13
Rajac, CS 11	-71	-10.4	12
Marinovac, CS 12	-69	-10.3	13
Vrbica, CS 13	-70	-10.5	13
Nikolicevo, CS 14	-67	-9.9	12
Krivaca, CS 15	-69	-10.3	13
Blagojev Kamen, CS 16	-72	-10.9	15
Dupljane, CS 17	-67	-10.3	15
Luka, CS 18	-70	-10.5	14
Bor Lake, CS 21	-73	-10.9	14
Mokranje, CS 24	-67	-10.2	14
Blizna, CS 25	-72	-10.8	15
Neresnica, CS 26	-69	-10.4	14
Brestovacka Banja, HS 1	-80	-11.8	14
Brestovacka Banja, HS 2	-80	-11.8	14
Gam. Banja, HS 3	-74	-10.9	14

Appendix 12 Stable isotope composition of river water collected in 2019 in the study area.

Sampling site	δD_{SMOW} (‰)	$\delta^{18}O_{SMOW}$ (‰)	d-excess (‰)
Bor River, S1[1]	-69	-9.6	8
Bor River, S2[1]	-66	-9.5	9
Krivelj River, S3[1]	-64	-9.2	10
Bela River, S4[1]	-67	-9.5	9
Ravna River, S5[2]	-73	-10.7	12
Bela River, S6[1]	-67	-9.3	8
Bela River, S7[1]	-68	-9.5	8
Timok River, a.c. S8[1]	-69	-9.8	9
Timok River, b.c. S9[2]	-71	-10.2	11
Ravna River, S10[2]	-75	-10.9	12
Timok River, a.c. S11 [1]	-70	-9.7	8
Ravna River, S12[2]	-74	-11.0	14
Krivelj River, S13[1]	-72	-10.4	11

Appendix 13 Sampling sites, coordinates of sampling sites, pH, Eh and concentrations of major cations and anions in river water samples from the study area collected in 2015.

Sampling site	Y	X	pH	Eh (mV)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	F^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
A-1	44.09366	22.09533	2.8	703	96.6	3.3	258.0	434	3.42	13.0	5240	-
A-2	44.09152	22.0921	7.3	464	21.6	1.3	50.4	161	0.1	8.9	494	190
A-3	44.10308	22.00631	7.4	456	8.3	1.1	11.2	42.5	0.12	6.1	62.5	130
A-4	44.09825	21.97992	7.2	370	9.5	0.9	12.5	58.3	< 0.01	2.8	65.7	185
A-5	44.02939	22.10	7.9	444	11.8	0.9	6.8	35.1	0.11	5.1	86.4	50
A-6	44.06014	22.04536	7.9	471	13.7	1.5	9.9	53.2	0.08	9.3	83.7	115
A-7	44.05592	22.06892	8.3	498	12.0	1.2	24.0	88.8	0.16	7.5	170	195
A-8	44.16017	22.20033	8.1	447	9.5	0.8	20.4	66.0	0.03	7.6	44.2	265
A-9	44.122	22.20914	8.1	467	6.9	1.1	13.7	62.4	0.12	4.7	48.8	225
A-10	44.07375	22.20503	8.3	356	2.9	1.2	2.6	75.2	0.03	3.0	23.2	205
A-11	44.04483	22.20625	8.4	427	6.9	3.1	9.5	82.0	0.05	5.5	42.2	240
A-12	44.06222	22.13099	5.3	389	154.0	2.0	366.0	480	2.2	76.6	3430	-
A-13	44.0621	22.13108	8.6	473	42.0	7.2	20.3	251	0.32	31.5	700	-
A-14	44.06192	22.13154	2.6	689	47.7	8.5	197.0	333	4.63	16.8	4550	-
A-15	44.06103	22.13243	4.1	550	57.6	11.2	75.3	292	1.42	32.6	1400	-
B2	44.02966	22.20814	4.2	492	49.9	7.8	71.8	299	1.02	32.3	1510	-
K4	44.03004	22.20814	4.5	498	89.2	10.9	66.0	461	2.19	41.1	2060	-
B3	44.02717	22.22176	4.5	480	60.6	10.0	68.2	351	1.79	33.1	1590	-
B4	44.00987	22.27157	4.7	478	52.6	7.0	60.0	301	1.03	29.4	1360	-
B8	43.96099	22.3292	4.5	538	53.8	7.3	61.2	304	1.31	30.3	1440	-
B7	43.96415	22.32218	4.5	608	52.1	7.1	57.3	324	1.2	30.8	1430	-
A-21-1	43.96394	22.32223	5.0	656	41.1	6.1	60.4	272	1.86	21.1	1070	-
A-22	43.94612	22.31454	7.3	213	17.7	2.6	10.3	66.3	0.08	17.9	46.7	240
A-23	43.94497	22.31227	7.2	453	21.0	0.4	24.3	115	0.41	18.4	114	305
B9	43.97276	22.3664	6.9	383	23.2	3.5	24.5	118	0.31	19.0	316	110
K3	44.08168	22.16451	6.2	623	72.5	7.3	86.6	397	10.4	28.7	2360	-
A-26	44.10481	22.12164	4.4	509	27.1	3.1	179.0	156	16.8	5.5	2510	-

A-27	44.16692	22.03576	8.0	372	12.6	2.1	24.0	168	0.31	2.4	485	-
K1	44.16441	22.01879	7.7	370	11.7	2.1	12.1	51.2	0.13	2.1	196	-
K2	44.14771	22.04872	8.8	357	16.6	2.0	15.2	82.0	0.16	4.8	254	115
B1	44.03053	22.18136	2.9	657	45.8	6.1	97.3	270	6.91	29.8	2010	-
B5	43.99497	22.28653	5.4	434	41.2	5.3	62.6	248	0.5	18.1	924	-
B6	43.97273	22.30953	5.1	445	38.5	5.2	57.9	238	1.25	18.5	935	-
B-1	44.3553	22.03972	7.7	376	8.0	2.1	16.4	41.1	0.1	4.9	38.1	205
B-2	44.35523	22.03857	7.8	441	10.3	2.3	11.6	51.4	0.12	7.6	74.2	130
B-3	44.39538	21.96597	7.9	344	16.4	1.7	11.3	72.0	0.11	22.8	57.8	220
B-4	44.37903	21.98952	7.7	286	5.6	1.9	7.2	27.0	0.08	2.2	29.1	120
B-5	44.3792	21.98885	7.7	387	10.7	2.1	16.5	74.4	0.17	12.3	154	200
B-6	44.31599	22.08884	8.0	360	13.6	2.4	7.2	63.4	0.15	28.8	30.3	225
B-7	44.43887	21.94881	7.7	431	5.2	1.6	5.6	41.9	0.11	1.0	28	165
B-8	44.42577	21.93316	8.1	398	5.7	1.9	7.4	54.5	0.08	4.4	26	205
M1	44.40217	21.91575	7.3	232	35.0	6.4	134.0	335	0.28	11.7	1630	-
B-10	44.35478	21.9125	8.0	397	4.9	1.4	6.8	58.9	0.05	2.7	28	240
M2	44.36421	21.91478	8.2	358	10.8	2.7	10.4	72.0	0.07	5.0	155	155
B-12	44.36906	21.92039	7.6	363	45.2	18.1	12.1	299	0.13	22.9	863	-
M3	44.39846	21.88445	8.4	364	20.2	5.8	62.1	155	0.09	9.8	680	-
B-14	44.23779	22.07513	8.3	342	7.2	1.7	7.1	62.7	0.09	5.1	25.1	240
B-15	44.2638	21.99058	8.3	338	9.8	1.9	9.8	53.6	0.07	2.9	51	240
B-16	44.19336	22.0824	8.2	348	4.6	1.2	6.4	65.1	0.06	6.8	24.4	240
B-17	44.23459	22.14559	8.3	305	9.1	2.3	13.3	43.5	0.22	7.2	33.8	225
B-18	44.30848	22.1362	8.4	335	9.9	2.6	18.2	46.9	0.19	8.2	38	255
B-19	44.30126	22.12585	8.1	332	16.0	3.0	10.2	61.7	0.43	21.8	53.3	230
B-20	44.30882	22.1323	7.8	394	10.9	2.3	12.8	58.4	0.13	16.0	46.8	235
B-21	44.31109	22.14014	8.2	359	10.3	2.4	15.0	53.2	0.15	12.2	42.9	250
M4	44.43782	21.8568	8.3	360	7.2	6.2	18.6	59.8	< 0.01	11.2	142	120
M5	44.48028	21.83355	8.2	334	5.3	13.4	10.6	35.2	< 0.01	12.5	51	120
B-25	44.4819	21.83444	8.4	357	4.8	11.9	8.4	28.7	< 0.01	10.7	24.5	120
B-26	44.49128	21.80701	8.3	349	4.1	3.2	7.5	28.9	< 0.01	3.2	22.4	110
M6	44.48077	21.77899	8.0	391	6.4	3.8	15.6	51.0	< 0.01	3.8	111	110

B-28	44.50808	21.76205	8.0	350	6.6	2.8	7.4	49.6	< 0.01	3.1	25.4	180
B-29	44.44435	21.70625	7.9	376	5.2	2.1	4.8	40.4	< 0.01	1.9	18.7	150
B-30	44.47193	21.77507	7.7	388	6.8	5.0	10.7	52.0	< 0.01	3.7	27.1	210
B-31	44.48061	21.76343	8.0	344	7.1	2.4	7.7	52.4	< 0.01	3.2	27.8	195
M7	44.46762	21.75149	8.0	361	6.4	4.6	14.9	50.7	< 0.01	4.6	105	115
B-33	44.44388	21.77348	8.2	357	5.5	16.3	7.0	28.5	< 0.01	15.8	24.3	115
B-34	44.43565	21.72101	7.9	392	6.1	1.6	6.2	21.1	< 0.01	1.5	20.3	90
M8	44.45209	21.69258	7.7	427	7.8	2.5	18.7	61.4	< 0.01	3.0	135	150
B-36	44.46153	21.70032	8.0	371	11.6	4.3	10.5	94.1	< 0.01	8.3	31.8	350
B-37	44.4703	21.66709	8.4	333	8.5	3.9	8.3	114	< 0.01	5.2	24	310
M9	44.47559	21.66416	7.9	359	8.9	3.1	21.1	73.1	< 0.01	3.9	153	170
B-39	44.52016	21.64465	8.2	342	3.6	2.4	6.5	90.4	< 0.01	2.9	14.1	330
M10	44.55256	21.5808	7.3	349	8.9	3.0	21.2	72.7	< 0.01	4.3	151	140
M11	44.64663	21.51655	7.9	404	8.6	3.2	19.8	70.2	< 0.01	4.4	140	185
B-42	44.3734	21.7558	7.8	408	6.5	1.3	5.0	13.8	< 0.01	1.4	18.2	60
B-43	44.37714	21.76297	7.8	407	4.8	1.1	6.1	19.8	< 0.01	1.3	20.8	80
B-44	44.40556	21.70005	8.1	414	5.0	2.1	4.6	37.5	< 0.01	1.7	18.6	135
B-45	44.40414	21.63478	8.2	358	2.2	1.4	5.4	89.7	< 0.01	1.8	17.2	325
B-46	44.55946	21.67082	8.2	349	2.3	1.3	4.3	82.6	< 0.01	2.1	15.8	285
C-1	44.02706	21.97697	8.1	527	2.5	0.7	3.8	70.1	0.02	0.9	25.7	245
C-2	43.96948	22.01491	7.9	471	25.1	2.9	11.3	81.3	0.04	5.1	36	270
C-3	43.91415	22.04458	7.6	433	8.2	1.0	6.2	90.1	0.05	12.0	32.4	290
C-4	43.9145	22.07778	7.9	409	25.4	3.0	11.5	82.4	0.22	22.0	67.6	290
C-5	43.92739	22.08544	8.4	359	5.9	1.1	6.1	75.4	0.03	7.1	24.2	250
C-6	43.89547	21.97361	8.0	391	10.3	1.7	9.1	109	0.05	10.4	57.2	370
C-7	43.89758	21.99044	7.9	465	4.8	1.2	6.2	76.6	0.03	6.0	21.7	275
C-8	43.93	22.09156	8.0	450	2.1	0.7	5.4	85.6	0.04	2.3	14.4	280
C-9	43.96792	22.06389	7.5	444	14.9	1.9	20.9	108	0.13	28.7	39.4	425
C-10	43.93497	22.15333	8.1	506	10.2	1.2	8.5	63.7	0.09	9.7	45.7	215
C-11	43.96422	22.13736	8.5	444	13.7	1.5	10.4	56.4	0.07	10.0	88.5	165
C-12	43.95494	22.23666	7.6	170	119.0	4.9	9.7	30.0	4.55	30.4	62.5	30
C-13	43.96062	22.23164	7.1	118	22.3	3.4	20.0	141	0.11	15.9	153	430

C-14	43.903	22.21096	8.5	379	11.1	0.8	8.4	54.0	0.06	11.8	43	190
C-15	43.91259	22.30233	8.3	412	10.3	2.1	10.5	68.5	0.06	13.8	42.2	280
C-16	43.91993	22.29483	7.2	64	31.9	5.0	8.8	48.3	0.11	28.2	55	225
C-17	43.81475	22.28491	7.9	378	6.0	2.7	12.6	72.7	0.07	6.7	26.2	300
C-18	43.81554	22.28737	8.1	387	11.0	2.4	10.9	75.4	0.07	15.0	36.9	285
C-19	43.81169	22.19297	7.9	389	14.9	4.0	14.0	108	0.11	13.9	54.5	365
C-20	43.86261	22.0794	7.3	302	10.9	2.7	9.7	151	0.12	12.2	70	550
C-21	43.78006	22.02432	8.5	352	17.6	8.6	13.6	81.4	0.24	7.5	105	240
C-22	43.82501	21.86553	7.5	388	5.3	12.5	9.0	101	< 0.01	15.6	13.9	390
C-23	43.80555	21.77004	7.8	424	3.8	23.6	8.7	105	< 0.01	23.8	11.4	410
B10	44.01188	22.3565	7.2	335	30.8	4.5	26.5	136	0.23	20.3	348	-
D-2	44.02487	22.34505	8.0	426	24.1	13.2	21.2	82.8	0.14	21.3	53.9	360
D-3	44.1206	22.32775	8.1	376	10.3	0.6	26.4	57.0	0.07	6.6	70.1	270
D-4	44.15709	22.34774	8.0	434	7.1	2.7	25.4	52.8	0.04	6.4	38.7	280
D-5	44.22545	22.33898	8.5	413	6.1	1.0	20.4	43.8	< 0.01	4.3	33.9	190
D-6	44.2616	22.2941	8.5	432	2.1	0.7	5.5	87.0	0.04	2.6	19.5	270
D-7	44.19923	22.29655	8.2	422	3.2	0.4	10.8	18.4	< 0.01	1.9	17.4	100
D-8	44.13748	22.38767	8.0	420	12.0	3.6	33.6	63.7	0.07	17.6	47.5	320
D-9	44.19271	22.40301	8.2	418	14.1	1.0	30.2	66.6	0.13	28.8	69.1	270
D-10	44.24971	22.35279	8.0	397	3.5	1.2	5.9	63.6	0.05	3.4	26.5	200
D-11	44.22946	22.44121	8.4	353	7.6	1.7	14.4	61.0	0.08	8.5	53.1	205
D-12	44.68069	22.5034	8.2	369	11.1	2.2	10.2	41.0	0.12	19.6	27.7	140
D-13	44.67211	22.50587	8.4	315	4.0	1.8	6.9	68.5	0.04	2.0	53.4	180
D-14	44.64001	22.55333	8.5	317	17.9	0.9	12.6	32.1	0.39	9.2	79.1	85
D-15	44.63004	22.57711	8.1	297	115.0	2.9	13.2	142	0.09	334.0	36.6	-
D-16	44.61201	22.61844	8.3	322	11.0	2.2	10.1	40.6	0.15	19.5	27.7	140
D-17	44.60353	22.68761	8.7	344	11.2	2.3	10.0	39.2	0.13	19.4	27.7	135
D-18	44.55869	22.75288	8.2	330	13.0	2.2	10.6	37.4	0.12	19.6	27.5	140
D-19	44.52186	22.70985	8.4	282	13.1	2.5	10.6	43.7	0.09	19.5	27.5	140
D-20	44.55504	22.63378	8.4	308	11.9	1.1	32.1	69.1	0.19	12.3	31.3	300
D-21	44.55172	22.56478	8.3	298	15.5	2.7	8.8	59.6	0.13	12.5	41.7	190
D-22	44.53118	22.55742	8.3	306	13.5	2.3	10.9	42.2	0.11	19.5	27.9	150

D-23	44.23438	22.60913	7.8	400	6.4	1.7	9.3	46.0	0.07	5.0	38.4	145
D-24	44.22218	22.66443	7.4	435	23.6	6.8	17.3	127	0.13	21.3	130	285
D-25	44.22018	22.66736	7.7	393	12.7	3.0	12.3	65.7	0.1	11.1	74.5	235
D-26	44.22802	22.65326	7.6	414	6.4	1.8	8.7	46.0	0.07	5.3	37.2	140
D-27	44.26669	22.679	7.8	434	14.4	2.7	11.9	42.1	1.83	21.7	32.3	125
D-28	44.26965	22.54745	7.9	416	16.2	5.1	11.2	96.9	0.12	13.7	74.1	340
D-29	44.24964	22.53737	7.8	434	6.1	1.5	8.4	45.2	0.04	5.0	35.9	160
B13	44.13409	22.6037	8.0	405	8.3	2.1	9.2	89.0	0.08	6.6	111	200
D-31	44.11525	22.58274	8.1	407	8.3	1.9	8.9	86.1	0.09	6.5	92.6	210
D-32	44.11787	22.57516	8.4	382	12.4	7.4	15.4	127	0.14	9.8	69.2	420
B12	44.09921	22.57089	8.1	406	8.4	1.9	9.0	87.3	0.09	6.8	98.5	205
D-35	44.08511	22.50825	7.5	434	8.4	1.9	9.4	88.3	0.12	6.5	112	200
D-36	44.0558	22.41422	7.9	466	9.4	1.9	10.2	89.8	0.1	7.7	110	210
B11	44.09485	22.4817	7.9	437	9.0	2.0	10.4	89.9	0.11	7.9	118	190
D-39	44.0674	22.42936	7.9	419	8.4	1.8	10.5	91.5	0.07	8.0	110	210
D-40	44.29104	22.52526	8.0	401	13.7	3.8	9.8	119	0.12	12.8	65.9	355
D-41	44.31465	22.54885	8.6	376	9.9	2.2	9.3	47.5	0.12	15.8	22.9	160
D-42	44.48932	22.54273	8.0	414	9.2	2.2	9.0	46.5	0.08	14.8	22.6	160
D-44	44.3611	22.50965	7.4	351	11.2	2.5	9.9	108	< 0.01	10.1	41.7	380
D-45	44.37352	22.50596	7.9	315	11.9	2.0	12.0	53.8	< 0.01	15.8	22.7	210
D-46	44.41357	22.46022	7.8	389	9.0	2.8	11.6	103	< 0.01	6.9	51.8	360
D-47	44.46196	22.45153	7.7	367	8.3	1.5	11.9	48.6	0.41	4.9	47.2	186
D-49	44.48717	22.45456	7.9	353	10.0	1.6	9.2	73.2	< 0.01	13.8	22.8	280
D-50	44.4882	22.49753	7.4	334	148.0	11.7	28.4	98.8	< 0.01	246.0	52.6	470
D-52	44.55225	22.56958	7.7	346	14.2	2.8	9.6	71.1	< 0.01	10.5	32.6	260
D-53	44.57674	22.51006	8.0	331	8.2	3.5	8.5	64.6	< 0.01	5.5	32.1	240
D-54	44.62371	22.45941	7.8	411	5.3	2.0	7.0	72.4	< 0.01	2.7	12.7	290
D-55	44.62502	22.55618	8.1	329	7.7	1.3	9.6	79.9	< 0.01	6.3	29.1	280
D-56	44.2899	22.35496	7.2	231	15.9	4.2	17.5	124	< 0.01	18.1	95.1	385
D-57	44.34753	22.38622	7.7	346	11.3	5.2	12.8	130	< 0.01	10.1	68.2	420
D-58	44.38309	22.40465	8.0	370	5.5	2.2	8.4	103	< 0.01	4.3	36.8	345
E-1	44.34716	22.17544	8.2	331	11.3	2.8	15.0	60.7	0.12	11.3	43.6	180

E-2	44.39012	22.17132	8.0	357	15.2	3.7	26.8	74.0	0.13	8.9	72.3	-
E-3	44.42073	22.17326	8.0	359	11.1	4.3	9.1	38.0	0.12	10.9	44.6	160
E-4	44.47138	22.18097	7.9	331	12.4	2.4	10.2	43.6	0.11	19.8	28.3	120
E-5	44.6802	22.40277	8.3	345	12.8	2.5	10.2	43.6	0.13	20.2	28.2	105
E-6	44.62201	22.27776	7.9	343	12.9	2.5	10.4	45.0	0.12	19.6	28.2	120
E-7	44.5462	22.22934	8.0	319	12.3	3.6	10.2	43.2	0.12	19.6	28.1	115
E-8	44.46661	22.12396	8.1	319	27.2	3.1	31.7	90.3	0.37	14.2	99.9	285
E-9	44.53498	22.03097	9.0	305	9.8	4.9	14.2	46.7	0.14	5.3	49.3	145
E-10	44.54626	22.03114	8.4	348	12.6	2.6	10.4	45.8	0.13	19.8	27.4	115
E-11	44.48968	22.07343	8.3	324	14.1	2.7	10.7	45.3	0.1	20.5	29.6	110
E-12	44.46926	22.11008	8.8	322	14.0	3.8	22.7	52.0	0.18	6.0	57.8	150
E-13	44.63106	21.98523	7.8	480	11.2	2.7	9.9	46.2	0.11	16.5	22.8	160
E-14	44.6406	21.91579	7.4	488	9.4	2.3	9.5	48.3	0.08	15.5	23.9	170
E-15	44.64907	21.83763	7.2	449	9.6	2.8	9.4	48.6	0.08	15.9	24	170
E-16	44.6565	21.76678	7.7	453	9.0	2.5	8.8	46.5	0.07	15.0	22.8	165
E-17	44.65321	21.63703	7.5	465	8.7	2.2	9.4	47.3	0.08	15.2	23.5	165
E-18	44.68564	21.60421	7.8	429	8.9	2.2	9.9	49.0	0.08	15.3	24.8	175
M12	44.7174	21.53432	7.5	421	11.5	3.6	32.7	101	0.1	7.8	265	150
M13	44.75411	21.53215	7.6	388	10.6	3.6	29.7	93.1	0.1	8.1	257	160
E-22	44.50268	22.2103	8.1	390	7.3	2.2	10.9	73.0	< 0.01	4.5	50	265
E-23	44.46251	22.1429	8.4	352	17.8	4.0	43.6	75.2	0.17	9.2	82.7	425
E-24	44.53341	22.03751	8.9	319	9.9	5.1	15.0	46.7	0.11	5.0	37.5	220
E-25	44.62588	21.90786	8.2	360	7.1	1.8	15.7	58.0	< 0.01	2.8	28.8	265
E-27	44.65298	21.77747	8.5	327	11.9	4.8	13.1	45.0	< 0.01	3.4	26.9	220
E-28	44.66708	21.60227	8.2	390	17.1	6.3	19.3	110	< 0.01	13.6	25.9	470
F-1	43.79058	22.20314	8.2	327	4.3	1.8	8.6	94.8	< 0.01	2.8	19.4	490
F-2	43.7594	22.12489	8.2	353	9.7	2.9	16.2	71.3	< 0.01	5.2	32.2	295
F-3	43.69269	22.27897	8.1	351	14.2	8.8	13.7	101	< 0.01	12.7	25.4	290
F-4	43.66698	22.32564	8.5	321	7.4	2.7	7.4	68.1	0.1	3.6	30.9	250
F-5	43.58923	22.41258	8.2	331	4.3	1.4	5.6	24.3	< 0.01	1.2	13.1	100
F-6	43.63583	22.26653	8.1	345	8.8	2.2	10.3	75.6	< 0.02	8.6	24.2	280
F-7	43.6074	22.21877	8.2	346	17.1	3.9	19.5	95.6	< 0.02	9.4	43.4	410

F-8	43.66925	22.13908	8.5	350	9.4	4.4	17.5	90.0	< 0.02	5.8	49.7	340
F-9	43.5681	22.26692	8.0	444	5.0	1.6	6.5	48.0	< 0.01	3.6	15.6	180
F-10	43.52565	22.28742	8.2	327	4.9	1.6	6.8	48.5	< 0.01	3.2	15.1	185
F-11	43.50377	22.31866	8.7	334	4.5	2.9	5.2	43.3	< 0.01	4.5	13.7	160
F-12	43.4402	22.42497	8.3	329	4.6	1.2	6.6	24.3	< 0.01	1.3	15	100
F-13	43.39428	22.48235	7.7	324	3.3	0.7	2.4	13.1	< 0.01	2.4	7.3	50
F-14	43.54556	22.21582	8.2	327	7.6	9.4	10.2	99.9	< 0.01	11.3	19.2	380
F-15	43.58673	22.20558	8.1	329	31.1	5.5	33.2	114	< 0.02	23.2	113	460
F-16	43.44315	22.10409	7.9	392	16.3	4.2	14.8	111	< 0.02	20.1	27.1	430
F-17	43.39839	22.16953	8.1	448	6.7	2.1	9.1	89.2	< 0.01	5.9	16.1	350
F-18	43.37766	22.25052	8.0	448	7.2	1.7	9.7	92.7	< 0.01	4.9	16.5	350

Appendix 14 Total (T) and dissolved (D) concentrations of heavy metals and arsenic in river water samples from the study area collected in 2015.

Sampling	Fe (μg/L)		As (μg/L)		Cu (μg/L)		Mn (μg/L)		Zn (μg/L)		Cd (μg/L)		Pb (μg/L)	
site	T	D	T	D	T	D	T	D	T	D	T	D	T	D
A-1	545000	542000	800	708	121000	127000	22200	22500	4130	5400	30.7	33	8.05	8.11
A-2	740	30	7.4	4.4	85	26.7	682	613	28.2	19.3	0.22	0.08	1.93	0.2
A-3	2010	1020	2.0	0.5	3.5	<0.2	562	543	2.4	<0.5	0.02	<0.01	0.15	0.54
A-4	60	30	4.6	3.6	4.2	<0.2	50.5	45.3	1.6	<0.5	0.01	<0.01	0.18	0.16
A-5	210	<10	5.2	3.6	16.6	3.9	41.6	10.1	3.3	<0.5	0.03	<0.01	0.89	0.21
A-6	170	<10	5.9	4.2	12.2	<0.2	22.6	7.1	5.2	<0.5	0.03	<0.01	0.68	<0.01
A-7	300	<10	13.3	11.9	18.9	1.5	40.6	6.1	6.7	<0.5	0.06	<0.01	1.87	0.05
A-8	110	<10	2.4	1.2	3.3	<0.2	4.9	<0.1	1.2	<0.5	<0.01	<0.01	0.17	0.18
A-9	70	<10	2.4	1.2	2.1	<0.2	4.4	<0.1	1.0	<0.5	<0.01	<0.01	0.11	0.14
A-10	160	<10	0.8	<0.03	3.3	<0.2	6.6	<0.1	1.8	<0.5	<0.01	<0.01	0.28	<0.01
A-11	60	<10	2.7	1.5	2.5	<0.2	6.9	<0.1	2.4	<0.5	<0.01	<0.01	0.16	<0.01
A-12	188000	182000	117	89.9	10000	7320	31600	31300	4960	5390	15.2	15.2	1.53	0.34
A-13	45500	<10	53.2	1.7	2430	<0.2	1790	1510	678	4.9	1.04	0.04	29.2	<0.01
A-14	534000	553000	7000	6830	105000	104000	23000	22800	18000	18000	121	138	150	157
A-15	780000	23600	2770	18.9	66000	21000	7700	5550	14000	3120	32.3	22.4	450	11.4
B2	76000	25100	336	16.9	25000	23000	7400	6330	2380	3040	20.9	21.1	52.3	19.4
K4	43900	11600	57.3	1.3	30000	29000	7100	5600	680	951	5.66	6.08	1.14	0.43
B3	288000	18400	1740	27.2	38000	23000	7800	5730	3010	2870	17.2	14.4	208	8.98
B4	46600	10700	376	7.9	20000	18000	4800	5270	1600	1750	13	12.9	59.8	8.52
B8	45700	2530	503	1.4	>50000	22000	>5000	5030	1690	1680	14.2	14.3	48.2	7.46
B7	43200	230	355	2.3	22000	16400	4770	4400	1470	1920	12.1	13.6	41	7.46
A-21-1	63800	38300	657	82.2	>20000	>20000	4110	4320	2020	1840	51.3	51.9	169	69.9
A-22	60	<10	2.2	2.2	4.3	3.6	36.5	33.2	3.4	10.2	<0.01	<0.01	0.25	1.14
A-23	<10	<10	0.2	<0.03	3.1	14.7	0.4	<0.1	1.6	8.8	<0.01	<0.01	0.06	1.53
B9	510	620	5.2	2.8	586	237	1270	1170	156	249	1.65	1.82	0.29	0.89
K3	97000	26400	98.7	2.9	37000	28400	9700	6540	1550	1770	12.3	14.1	2.71	10.5
A-26	36700	21600	4.8	2.5	121000	118000	21400	12600	1700	1910	16.5	14.9	0.14	1.3

A-27	440	<10	0.5	0.3	210	82.5	696	682	23.2	34.6	0.67	0.73	0.28	0.82
K1	460	<10	1.5	1.0	12	5.4	28	13.4	4.3	66.1	0.14	<0.01	0.26	1.03
K2	360	<10	1.5	1.5	268	165	114	119	45.9	54.9	0.48	0.75	0.16	4.24
B1	248000	209000	2780	1660	>50000	>50000	7800	7560	6640	5840	213	209	298	213
B5	45000	22600	546	24.4	14900	13200	4460	4830	1560	1390	24.3	24.6	61.8	4.73
B6	48500	27300	681	34.3	18800	17100	3990	4540	1560	1600	31.2	30.7	78	14.7
B-1	1040	250	2.4	2.5	7.1	14.7	39.3	46.9	37.2	199	0.29	<0.01	0.45	1.95
B-2	880	<10	2.6	2.0	9.6	4.7	55.7	8.2	39.9	7.7	0.1	<0.01	0.42	1.51
B-3	580	330	4.2	3.2	1.8	6.6	139	113	4.3	46.6	0.01	0.15	0.24	1.08
B-4	700	290	2.3	2.0	2.8	6.5	49.3	39	2.9	40.8	<0.01	0.11	0.45	1.48
B-5	80	<10	0.9	1.2	8.5	9.1	53.5	34	13.1	19.6	0.07	0.12	0.03	16.1
B-6	920	<10	1.2	0.7	1.8	2.6	41	5.1	4.0	7.0	<0.01	<0.01	1.06	0.81
B-7	570	120	1.3	1.0	1.7	<0.2	124	115	3.3	6.1	0.01	<0.01	0.2	0.81
B-8	2490	<10	7.3	3.8	23.1	5.2	176	44.3	15.3	7.9	0.1	<0.01	9.85	3.6
M1	8960	300	4.8	0.3	337	22.3	15100	11400	2260	1790	12.6	10	10.3	2.66
B-10	770	<10	2.2	1.5	4	<0.2	56.2	19.4	5.3	12.9	0.03	<0.01	1.16	0.64
M2	360	<10	1.8	1.3	8.1	4.9	53.6	20.2	7.1	10.1	0.05	<0.01	0.39	4.46
B-12	180	<10	5.4	4.2	5.7	<0.2	415	426	11.6	13.8	0.05	<0.01	0.25	0.36
M3	3460	<10	3.9	1.0	120	12.7	3530	3410	472	192	3.63	2.37	27.2	0.5
B-14	210	<10	1.3	1.1	1.8	<0.2	16.3	4.0	6.8	18.1	<0.01	<0.01	0.16	0.62
B-15	210	<10	1.1	0.9	3.2	2.2	17.5	4.5	2.7	24.7	0.02	<0.01	0.32	0.28
B-16	480	<10	2.0	1.8	2	2.6	30.9	12.5	9.2	30.6	0.02	<0.01	0.5	0.36
B-17	350	<10	3.0	3.1	3.1	3	28.2	7.5	4.1	10.7	0.01	<0.01	0.51	0.75
B-18	40	<10	4.9	5.1	2.7	3.3	8.5	7.0	2.1	6.3	<0.01	<0.01	0.13	0.98
B-19	60	<10	1.3	1.5	1.5	3.2	14.1	11.1	1.6	7.6	<0.01	<0.01	0.08	1.12
B-20	60	<10	3.3	3.2	10	3.9	17.7	15.4	3.1	7.8	0.04	<0.01	0.1	0.83
B-21	60	<10	4.0	3.9	2.5	2.6	15	11.7	2.2	<0.5	<0.01	<0.01	0.16	0.96
M4	7460	160	12.1	1.4	265	30.9	736	497	195	26.6	1.0	0.33	25.3	0.87
M5	2350	80	3.7	1.3	67	12	177	97.1	46.9	8.7	0.23	0.09	5.36	0.33
B-25	1020	110	1.6	1.3	10.1	6.6	39.9	5.6	4.1	8.8	0.02	0.02	0.6	0.44
B-26	1910	110	2.9	1.9	5.6	4.9	67	5.7	5.0	5.6	0.03	0.02	0.96	0.6
M6	6410	110	9.9	1.4	208	17	506	237	164	14.9	0.76	0.19	19.5	0.52

B-28	2670	70	2.2	1.2	5.6	3	83.6	10.7	6.3	1.7	0.03	<0.01	1.13	0.23
B-29	720	60	1.8	1.3	2.4	2	39.3	8.7	3.9	<0.5	0.01	<0.01	0.68	0.08
B-30	4230	30	9.2	5.8	12.1	2.8	266	7.6	13.2	1.8	0.08	<0.01	2.11	0.19
B-31	920	20	2.0	1.8	3.2	3.2	37.2	6.3	2.5	2.1	0.01	<0.01	0.84	0.18
M7	5520	90	10.0	1.4	155	16.4	406	198	133	13.9	0.6	0.18	19.4	0.45
B-33	480	20	1.4	1.3	3.6	2.5	23.5	3.2	2.2	1.9	0.01	0.01	0.36	0.21
B-34	560	40	0.7	0.6	2.3	2.8	39.6	9.7	1.5	2.4	0.01	<0.01	0.53	0.17
M8	1740	40	3.1	1.1	71.1	11.9	298	221	66	14.5	0.38	0.21	5.96	0.47
B-36	470	60	1.8	1.7	2.5	2.3	62.2	39	1.8	<0.5	<0.01	<0.01	0.33	0.15
B-37	400	40	2.9	3.1	2.9	2.5	41.5	18.3	7.3	3.0	0.04	0.02	1.62	0.23
M9	1760	30	3.1	1.2	74.9	10.5	292	201	66.2	14.3	0.39	0.18	7.11	0.3
B-39	190	40	1.1	1.1	1.1	2.4	30.9	23.1	2.3	2.0	<0.01	<0.01	0.26	0.13
M10	1390	30	2.8	1.0	51	8.8	179	84.2	52.1	12	0.31	0.11	4.72	0.36
M11	1560	30	3.0	1.2	50.1	8.8	146	31.3	48	8.8	0.25	0.1	4.58	0.21
B-42	700	60	0.5	0.4	2.2	1.4	61.6	5.2	3.5	2.3	0.02	<0.01	0.86	0.18
B-43	490	30	0.7	0.5	2	1.4	36.7	3.3	2.0	0.6	0.01	<0.01	0.63	0.05
B-44	850	100	2.0	1.6	2.7	5.2	46.4	9.8	2.0	25.1	0.01	<0.01	0.7	0.6
B-45	370	20	1.4	1.0	1.6	1.2	31.3	15.1	3.1	1.9	0.01	<0.01	0.51	0.17
B-46	340	30	1.2	1.1	1.7	1.8	38.8	22.2	2.3	2.1	<0.01	<0.01	0.31	0.14
C-1	50	<10	1.0	0.9	1.6	<0.2	5.2	2.9	1.0	6.7	<0.01	<0.01	0.31	1.38
C-2	150	<10	1.7	1.0	1.9	3.2	18.2	8.6	1.4	23.2	<0.01	<0.01	0.13	0.61
C-3	20	<10	0.7	0.7	1.2	<0.2	9.8	6.9	1.0	9.5	<0.01	<0.01	0.05	0.83
C-4	160	<10	1.7	1.6	1.9	3.6	18.8	9.9	1.1	11.4	<0.01	<0.01	0.12	0.42
C-5	70	<10	1.0	0.9	1.9	<0.2	10.4	6.9	1.5	6.7	<0.01	<0.01	0.16	8.9
C-6	80	<10	0.9	0.8	2.2	2	9.8	3.3	2.3	7.2	<0.01	<0.01	0.17	0.97
C-7	50	<10	0.7	0.6	1.5	2	15.1	9.5	1.4	7.0	<0.01	<0.01	0.13	2.1
C-8	100	<10	0.9	0.9	1.1	<0.2	3.0	1.1	1.2	21.7	<0.01	<0.01	0.3	0.79
C-9	90	120	1.9	1.8	1.3	2.4	521	496	1.1	15.1	<0.01	<0.01	0.08	9.24
C-10	40	<10	2.7	2.5	2.5	2.6	16.6	10.5	1.0	11.8	<0.01	<0.01	0.07	1.56
C-11	150	<10	6.2	6.0	8.1	5.3	14.8	4.3	2.9	<0.5	0.02	<0.01	0.44	0.43
C-12	30	<10	0.6	0.8	0.9	<0.2	1.6	3.3	1.2	5.1	<0.01	<0.01	<0.01	1.45
C-13	490	240	2.2	1.9	1.9	<0.2	900	847	1.3	9.3	<0.01	0.17	0.18	1.18

C-14	<10	<10	2.9	2.5	2.5	2.2	12.3	8.0	1.0	5.5	<0.01	0.1	0.12	1.01
C-15	40	3370	2.0	2.2	30.1	4.4	13.8	24.7	0.9	16.4	<0.01	<0.01	0.16	7.81
C-16	130	<10	3.2	3.2	11.2	7.3	35.1	29.6	20.7	12.2	0.01	<0.01	0.87	1.04
C-17	20	<10	0.6	0.7	2.9	4.5	6.7	6.0	3.3	31.2	<0.01	<0.01	0.15	2.56
C-18	70	<10	2.0	1.9	2.3	3.7	14.2	6.6	3.2	8.0	<0.01	<0.01	0.15	0.78
C-19	290	<10	1.0	0.8	2.7	2	36.9	20.8	3.0	7.8	<0.01	<0.01	0.24	0.84
C-20	340	<10	3.3	2.7	2.5	<0.2	1320	1370	13.5	45.2	<0.01	<0.01	0.15	0.71
C-21	140	<10	1.3	<0.03	3.1	2.2	16	4.8	5.6	<0.5	<0.01	<0.01	0.41	0.62
C-22	50	40	1.0	1.2	2.2	2.5	8.9	7.7	4.5	5.7	<0.01	<0.01	0.11	0.21
C-23	50	30	2.0	2.1	2.5	1.9	5.2	4.7	4.0	5.7	<0.01	<0.01	0.35	0.23
B10	640	<10	6.9	2.7	510	109	1420	1050	121	83.3	1.29	2.37	0.45	0.73
D-2	140	<10	2.7	0.9	4.9	6.3	99.7	87.7	5.9	<0.5	0.02	0.19	0.16	<0.01
D-3	240	<10	2.2	0.8	4	7.4	21.8	3.9	3.3	<0.5	<0.01	<0.01	0.25	0.75
D-4	40	<10	4.4	2.9	2.4	3.9	8.9	4.9	19.2	22.8	<0.01	<0.01	0.03	6.9
D-5	20	<10	1.6	1.2	2.3	3.6	4.7	4.5	2.3	37.8	<0.01	0.26	<0.01	2.75
D-6	20	<10	0.2	0.8	0.9	2.2	2.1	2.8	1.7	95.7	<0.01	2.04	<0.01	2.22
D-7	140	<10	1.1	1.1	3.6	<0.2	22.2	8.2	1.6	16.9	0.06	1.01	0.15	<0.01
D-8	90	<10	3.9	3.7	2.5	2.1	27.2	18.7	1.5	<0.5	<0.01	0.78	0.03	0.26
D-9	90	<10	0.7	0.6	1.6	<0.2	15.9	9	10.2	43	<0.01	<0.01	0.06	0.24
D-10	20	<10	0.4	<0.03	1.4	2	3.2	2	4.5	69.5	<0.01	0.69	<0.01	0.32
D-11	10	<10	0.8	0.7	1.2	<0.2	6.9	4.7	0.9	14.9	<0.01	<0.01	<0.01	<0.01
D-12	70	<10	2.0	1.8	2.5	3.2	10.4	1.8	2.4	<0.5	<0.01	1.09	0.26	0.11
D-13	<10	<10	0.2	<0.03	3	44.5	1.0	1.1	2.7	5.4	<0.01	<0.01	0.13	1.03
D-14	40	<10	0.1	<0.03	0.8	<0.2	1.9	1.2	1.2	<0.5	<0.01	1.36	0.08	16.6
D-15	270	<10	0.8	0.7	1.8	3.7	324	250	2.0	<0.5	<0.01	<0.01	0.17	0.52
D-16	60	<10	2.1	2.0	2.8	2.1	9.5	3.5	3.0	<0.5	<0.01	<0.01	0.44	0.14
D-17	120	<10	2.2	2.0	3.1	2.4	10.9	2.5	2.7	6.5	<0.01	0.43	0.31	<0.01
D-18	50	<10	2.2	1.9	2.5	3.1	8.7	4.3	4.0	21.8	<0.01	0.68	0.17	<0.01
D-19	40	<10	2.2	1.8	2.2	2.3	7.6	3.5	11.8	34.4	<0.01	0.17	0.13	0.29
D-20	2590	<10	1.9	0.5	4.3	33	137	13.3	101	53.8	0.02	0.8	2.83	0.12
D-21	120	<10	1.1	0.9	37.9	33.8	93.8	67.8	65.7	101	<0.01	0.31	0.17	<0.01
D-22	70	<10	2.2	2.0	38.8	32.9	10.3	3.9	2.9	18.2	<0.01	9.9	0.24	<0.01

D-23	700	70	1.0	0.8	44.3	15.1	24	4.7	5.9	7.2	<0.01	<0.01	0.72	0.52
D-24	850	80	1.4	1.1	43.6	40.6	210	102	7.9	7.3	0.05	<0.01	0.77	0.41
D-25	430	60	0.8	1.0	8.6	39.6	49.3	39.9	3.3	5.0	<0.01	0.01	0.34	0.16
D-26	320	70	0.8	0.8	38.4	16.5	10.3	5.6	3.8	7.1	0.04	0.01	0.4	0.2
D-27	4100	20	3.6	2.1	9.9	10.2	239	13.3	26.9	2.0	0.31	0.04	6.11	0.11
D-28	200	30	1.2	1.1	8.5	42.1	10.2	5.9	2.6	7.2	<0.01	<0.01	0.19	0.35
D-29	240	50	0.8	0.7	39.3	4.2	10.9	6.6	2.9	3.4	<0.01	<0.01	0.29	0.1
B13	410	10	6.0	3.3	119	47.3	122	106	19	14.8	0.37	0.29	0.48	0.09
D-31	550	<10	6.7	3.3	151	49.9	156	131	21.1	14.7	0.45	0.25	0.75	0.16
D-32	300	<10	1.2	1.1	10.2	16.5	15.7	5.0	2.4	9.2	<0.01	<0.01	0.33	0.39
B12	630	10	6.9	3.1	176	51.8	195	148	22.8	14.3	0.38	0.28	0.65	0.14
D-35	270	<10	5.0	3.0	150	84.5	226	231	30.2	30.6	0.88	0.82	0.27	0.26
D-36	720	20	4.0	1.0	252	93.3	306	327	28.5	43.7	0.6	0.49	0.32	<0.01
B11	480	40	4.8	1.6	217	111	282	284	34.9	39.9	1.11	1.02	0.3	0.08
D-39	560	20	3.4	1.0	215	97.6	284	285	26.6	31.7	0.56	0.51	0.19	0.09
D-40	160	50	1.0	0.8	9	8.4	81.5	78.4	2.8	7.3	<0.01	<0.01	0.12	<0.01
D-41	290	20	1.7	1.4	2.5	2.5	41.9	23.5	2.8	4.6	<0.01	<0.01	0.45	<0.01
D-42	630	20	1.6	1.3	10.2	2.9	45.3	5.1	6.2	6.1	0.03	<0.01	1.43	0.03
D-44	80	40	0.9	0.9	4	5.7	29.8	31.2	6.6	10	0.04	0.07	0.06	0.22
D-45	80	20	1.7	2.7	1.5	2.7	38.4	53.1	2.1	4.1	0.02	0.02	0.12	0.09
D-46	100	20	0.7	0.8	2.3	3.4	18.4	15.8	2.8	5.9	<0.01	0.02	0.09	0.37
D-47	<10	10	0.3	0.5	0.8	1.9	0.9	1.1	0.7	3.7	<0.01	0.01	<0.01	0.15
D-49	20	10	0.5	0.7	1	3.5	3.3	3.5	2.1	6.2	<0.01	0.02	0.03	0.22
D-50	<10	<10	0.7	0.8	2.1	2	15.5	15.7	10	11.8	<0.01	<0.01	<0.01	<0.01
D-52	90	50	0.9	1.1	1.6	2.2	67.7	57.7	8.6	3.2	<0.01	<0.01	<0.01	0.05
D-53	40	20	0.8	0.8	3	3.4	3.8	2.7	10.1	12.2	<0.01	<0.01	0.03	0.07
D-54	140	70	0.6	0.8	4.3	5.1	74.5	59.1	9.8	4.5	0.03	0.02	0.11	0.14
D-55	60	30	0.6	0.6	1.5	1.8	16.5	13.2	9.7	10.6	<0.01	<0.01	<0.01	0.05
D-56	80	70	0.6	0.7	1.1	1.1	91.1	90.9	3.8	1.1	<0.01	<0.01	<0.01	0.22
D-57	30	130	0.6	0.8	5.5	8.1	20	21.9	4.3	9.1	<0.01	<0.01	0.12	0.93
D-58	70	20	0.5	0.6	1.3	1.1	4.8	4.8	9.5	3.4	<0.01	<0.01	0.05	0.05
E-1	60	<10	3.5	2.9	3.6	5.5	14.3	7.8	3.2	<0.5	<0.01	0.12	0.16	0.41

E-2	120	<10	2.6	0.5	7.6	<0.2	11	1.4	5.5	21.1	<0.01	<0.01	0.16	0.53
E-3	40	<10	1.8	2.0	4.7	2.4	6.6	5.3	4.3	33.5	<0.01	<0.01	0.1	0.33
E-4	50	<10	2.2	2.0	2.7	<0.2	8	1.1	3.5	<0.5	<0.01	<0.01	0.16	<0.01
E-5	70	<10	2.2	1.8	2.4	2.2	9.9	1.5	2.1	<0.5	<0.01	0.15	0.21	<0.01
E-6	70	<10	2.2	2.0	3.6	2.5	8.8	1.7	3.0	<0.5	<0.01	1.35	0.25	0.34
E-7	100	<10	2.2	1.9	3.6	2.6	11.3	2.1	6.5	<0.5	<0.01	<0.01	0.29	<0.01
E-8	370	<10	3.1	2.5	6.6	5.4	299	198	5.2	6.4	<0.01	0.39	0.15	0.2
E-9	20	<10	2.0	1.8	3.1	3.7	5.7	2.6	2.7	7.4	<0.01	0.28	0.09	3.35
E-10	180	<10	2.3	1.7	5.1	2.8	15.2	1.9	5.9	<0.5	0.02	<0.01	0.6	<0.01
E-11	160	<10	2.3	2.0	7.4	4.2	16.8	3.7	7.8	8.3	0.01	2.21	0.58	0.54
E-12	40	<10	4.9	4.3	3.3	3.1	20.3	12	1.6	15.5	<0.01	<0.01	0.09	0.22
E-13	280	30	1.5	1.4	13.1	11.1	13.7	3.2	11	5.5	0.02	0.01	0.92	0.2
E-14	240	30	1.6	1.6	10.6	9.8	20.7	20.3	4.2	4.1	0.01	<0.01	0.65	0.58
E-15	270	30	1.8	1.5	10.2	11.3	37.8	24.4	4.9	2.8	0.03	<0.01	0.77	0.18
E-16	280	30	1.5	1.4	11.3	11.4	15.7	4.6	5.0	3.1	0.02	<0.01	0.76	0.27
E-17	210	30	1.5	1.4	11.1	9.5	10.5	3.0	4.1	2.2	0.01	<0.01	0.57	0.17
E-18	210	30	1.6	1.5	10.1	10.2	16	7.9	3.6	2.3	0.01	<0.01	0.55	0.15
M12	1820	<10	2.9	0.8	58	20	133	56.5	64.8	14.9	0.32	0.14	8.59	0.98
M13	2260	20	3.6	0.8	68	7.1	148	34.9	76	13.2	0.37	0.12	12.2	0.09
E-22	60	<10	0.4	0.4	0.8	0.9	10	3.1	2.8	3.4	<0.01	<0.01	<0.01	<0.01
E-23	330	40	9.0	8.5	1.9	1.9	223	60.3	3.4	3.5	<0.01	<0.01	0.09	<0.01
E-24	20	<10	2.4	2.3	2.1	2.2	7.8	6.0	9.0	3.5	<0.01	<0.01	<0.01	<0.01
E-25	270	30	5.9	4.7	0.8	1.1	57.1	31	3.4	6.9	<0.01	<0.01	<0.01	0.24
E-27	400	60	0.7	0.6	1.1	1.1	45.8	3.5	0.7	<0.5	<0.01	<0.01	0.08	<0.01
E-28	140	50	2.3	2.2	1.4	1.5	30.6	27.4	<0.5	2.7	<0.01	<0.01	<0.01	<0.01
F-1	100	20	0.6	0.6	1.6	1.5	6.9	5.0	1.7	2.7	<0.01	<0.01	0.15	<0.01
F-2	510	<10	1.0	0.9	3	1.8	25.9	5.1	2.5	2	<0.01	<0.01	0.41	<0.01
F-3	120	20	2.2	2.1	3.5	2.5	32.2	20.7	9.9	9.6	0.01	<0.01	0.19	0.16
F-4	100	10	0.5	0.5	9	1.9	7.4	2.9	1	3.2	<0.01	<0.01	0.15	0.13
F-5	90	10	0.7	0.6	1.7	1.4	4.5	2.4	2.2	1.5	<0.01	<0.01	0.1	0.01
F-6	90	20	1.7	1.8	2	1.3	29.7	24.6	3.4	4.9	<0.01	<0.01	0.15	<0.01
F-7	150	<10	1.9	1.8	2	1.6	29	18.5	2	2.9	<0.01	<0.01	0.16	<0.01

F-8	600	30	2.5	2.3	3.6	2.2	60.3	14.3	2.4	5.3	<0.01	<0.01	0.5	<0.01
F-9	90	30	1.8	1.7	1.2	1.1	14	8.8	1.8	2	<0.01	<0.01	0.08	<0.01
F-10	70	30	2.0	1.9	2.7	1.5	11.1	8.1	1.6	1.1	<0.01	<0.01	0.12	0.02
F-11	80	20	1.2	1.2	1	1.2	9.3	6.2	1.6	1.8	<0.01	<0.01	0.16	0.03
F-12	170	40	2.4	2.1	2	1.6	10.4	5.0	3.2	4.2	<0.01	<0.01	0.52	0.05
F-13	190	30	1.1	1.0	0.9	0.7	12.2	3.8	1.7	4.3	<0.01	<0.01	0.12	0.02
F-14	80	20	1.2	1.2	1.3	1.5	16.2	12.9	4.9	2.5	<0.01	0.01	0.12	0.05
F-15	2440	40	3.3	2.7	8	3.6	138	8.7	9.1	90.3	0.03	<0.01	2.09	0.13
F-16	1030	110	1.8	1.2	8	3.8	106	56.4	25.6	18.1	0.03	<0.01	1.51	0.11
F-17	170	30	1.2	1.2	1.4	1.6	31.1	24.2	2.8	2.8	<0.01	< 0.01	0.15	<0.01
F-18	310	30	1.0	1.0	1.5	1.2	47.4	30.7	2.6	2.4	<0.01	<0.01	0.19	<0.01