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TECHNICAL ARTICLE

Characteristics of Wastewater Streams Within the Bor Copper Mine and Their Influence on Pollution of the Timok River, Serbia

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Abstract Wastewaters produced by mining and metallurgical treatment of polymetallic sulfide ores have polluted the Timok River in Serbia for more than 100 years. We have characterized seven different wastewater streams within the RTB Bor facilities, investigating their influence on pollution of the Timok River before its confluence with the Danube River. Their relative contribution was calculated by considering the contaminant load of each wastewater stream and non-conservative transport along their flow paths. Three sampling spots in the Timok River, before and after its confluence with the Borska River, were also monitored.

Keywords Metal pollution · Characterization · Copper · Lead · Zinc

Introduction

Mining, mineral processing, and metallurgy have played a vital role in the history and economy of some western Balkan countries, such as Serbia. The area was an important European source of copper, lead, and zinc, but the disintegration of the Yugoslav common market led to worsening economic conditions in the region and a sharp fall in industrial production (Panias 2006; Stevanović et al. 2013).

Copper mining and metallurgical activities in Serbia date back to prehistoric times, but organized exploitation of copper ore in Bor (Eastern Serbia) began in the early twentieth century. Exploitation of copper sulfide ores was carried out both by underground and open pit mining. Ore processing requires that the low-grade ore is enriched by flotation in order to obtain a copper concentrate, which is then treated by a pyrometallurgical process to obtain anode copper and then electrolytic refining (Stevanović et al. 2013). The present smelter, built during the 1960s, is the biggest source of SO_2, particulate matter, and water pollution in Serbia.

Copper production in Bor has long caused serious environmental problems and the Borska River is one of the most polluted watercourses in Europe. The river is 47 km long, with a river basin of about 364 km^2, and is the greatest tributary of the Timok River, which in turn is the largest river in eastern Serbia (202 km, covering an area of 4547 km^2), and the last tributary of the Danube River in Serbia. The Timok water basin is a branchy system of many shorter rivers; the Timok River (also called the Veliki Timok) is formed by the joining of the Beli Timok and the Crni Timok Rivers, which meet at Zaječar. The last 15 km of the Timok River form the border between Serbia and Bulgaria (Brankov et al. 2012; Živković et al. 2012).

The environmental quality and microbiology of the Timok River and its tributaries, pollution caused by wastewater from human settlements, and the transboundary pollution from metal mining in Serbia and Bulgaria via the Timok River to the Danube River Basin have been previously studied (Bird et al. 2010; Brankov et al. 2012; Ilić et al. 2011; Miljković et al. 2011; Stanković et al. 2011). We investigated the influence of the RTB Bor Company's copper mining and production facilities near Bor, Serbia, on the water quality of the Timok River before its confluence with the Danube River. Seven different wastewater streams within the RTB Bor facilities were characterized

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(origin, flow rate, chemical and physical properties). Their relative contribution was calculated by considering the chemical composition and flow rate (i.e. metal loading) of each stream as well as non-conservative transport along their flow paths.

The Study Area

The study area encompasses the town of Bor and its surroundings in eastern Serbia, covering an area of 856 km^2 and a part of the Danube River Basin. Copper sulphide ore (chalcopyrite, chalcozine, and coveline, whose usual minor constituents are: Fe, As, Cd, Pb, Ni, Zn, Mn, and precious metals) is being exploited in an old underground mine, near the exhausted open pit of the Bor mine, and in two other open pit mines in Krivelj and Cerovo. The ore from the underground mine is transported to an old flotation plant, located near the metallurgical plant in Bor (Panias 2006). The wastes formed in this flotation plant are disposed in an artificial lake close to the metallurgical plant. The ore from the open pit mines is processed in the Krivelj flotation plant where the copper concentrate is produced. The flotation tailings, by-products of the ore processing, are transported directly by gravity to the Krivelj flotation tailings ponds in the Krivelj River valley. The mining and mineral processing causes significant environmental problems; the air, water, and soil have all been polluted in the area around the tailings dams (i.e. about 1300 ha of soil has been degraded) (Panias 2006), and by drainage from ore waste heaps in the open pit.

After flotation, copper concentrate is transported directly to the metallurgical plant at the Bor town border. The copper smelter annually emits about 5–8 kg of Zn, 6–25 kg of Pb, and 5–20 kg of As per inhabitant of the Bor region (Šerbula et al. 2010); most of these air pollutants eventually enter the area's streams, along with secondary pollution caused by burning of fossil fuels (Šerbula et al. 2012). The environmental consequences of copper production at the RTB Bor mine are numerous. The wastewaters should be treated before being discharged to river streams (Korać and Kamberovic 2007), in accordance with European environmental legislation. Before developing suitable treatment technologies, the wastewaters had to be characterized with respect to their origin, flow rates, and chemical composition.

Sampling and Measurement Sites

Characteristics of water samples from ten sampling sites (Fig. 1) are given in this paper. The first eight sites were collected where wastewater within the RTB Bor site enter

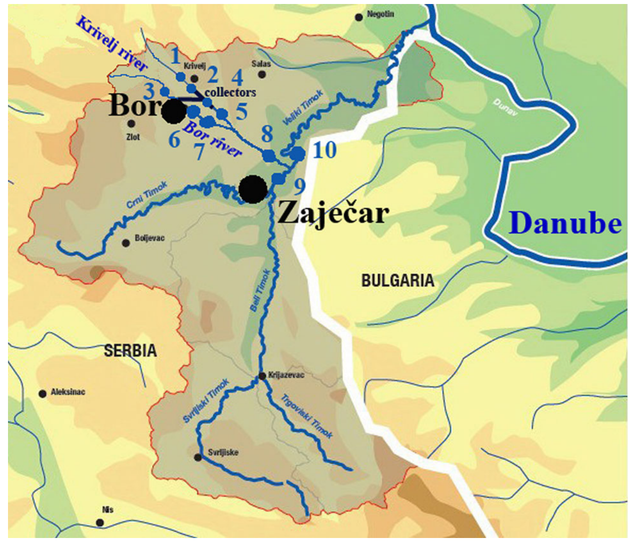


Fig. 1 Ten water-quality sampling sites in the Timok River basin, Eastern Serbia

the Krivelj and Borska Rivers. Samples were also collected at: S9—from the Timok River before it merges with the Borska River, and at S10—from the Timok River downstream of the Borska River confluence, in order to see the influence of the wastewater on the Timok River.

Since wastewater quality is based on physical, chemical, and biological parameters, different methods were used to characterize the wastewaters. The pH measurements and chemical composition for representative samples from sites S1–S10 are presented here. Samples were collected using standard procedures and analyzed using atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and volumetric methods 213.1, 218.1, 220.1, 236.1, 239.1, 243.1, 249.1, and 289.1 (U.S. EPA 1983).

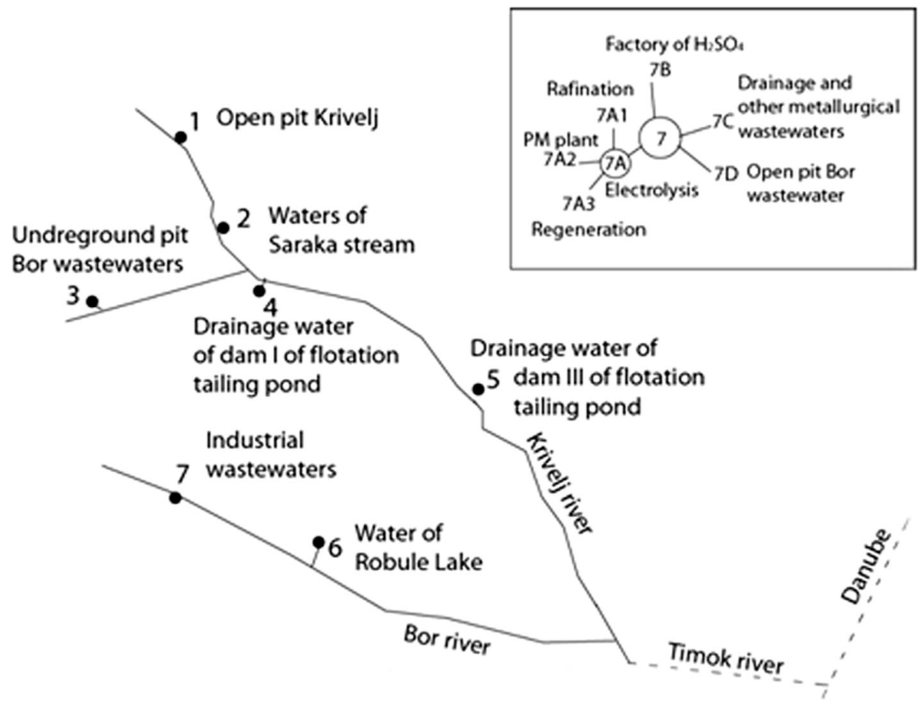
Results and Discussion

The contamination sources as well as the wastewater stream flow sheet and the characteristics of sites S1–S7 are shown in Figs. 2 and 3, respectively.

Wastewater that accumulates in the bottom of the Veliki Krivelj open pit (site S1) includes contaminants from both the atmosphere and groundwater. The wastewater is currently pumped to the Krivelj River at an average flow rate of 2330 m^3/day. Figure 3 (cell 1 in the flowsheet) presents some of the characteristics of this wastewater.

A tailings pond in the Veliki Krivelj open pit drains into the Saraka Stream (site S2—Fig. 3, cell 2 in the flowsheet) and then flow into the Krivelj River at an average flow rate of 3800 m^3/day. Quantities depend significantly on weather conditions.

Fig. 2 Sources of water resources contamination (Korać and Kamberovic 2007; Panias 2006)



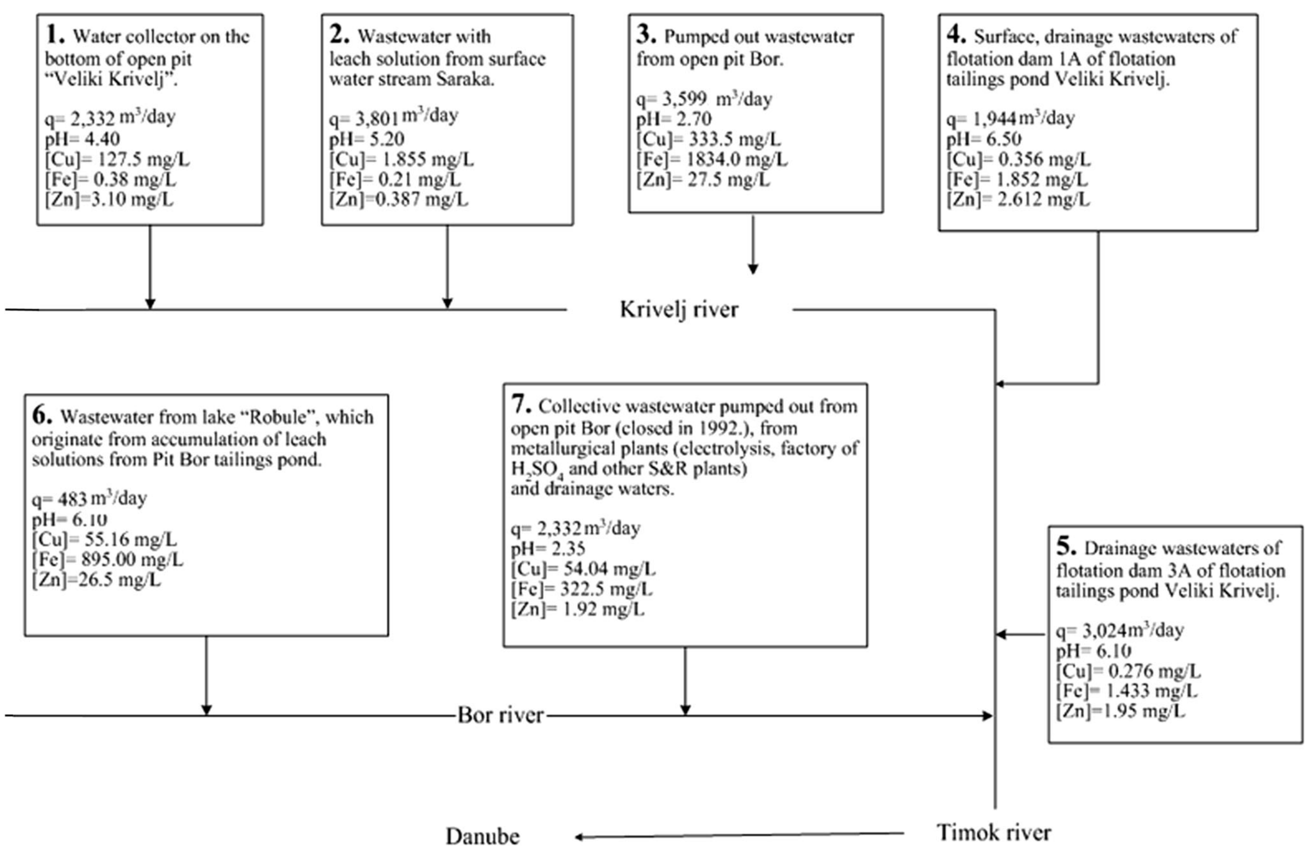


Fig. 3 Flowsheet of wastewater streams from the Bor copper mine and their characteristics (INCO-CT-2003-509167)

Table 1 Average annual amount of metals (kg) discharged into watercourses at sites S1–S7 (Korać and Kamberovic 2007)

Site	Fe	Cr	Cu	Ni	As	Zn	Pb	Cd	Mn
S1	324	0	108,860	65	0	2647	0	0	0
S2	36,356	3	106,691	157	6	1419	12	15	15,987
S3	811,776	4	230,117	203	321	41,270	9	35	13,230
S4	1042	2	143	3	5	221	7	1	450
S5	2313	7	76	5	45	242	10	3	1177
S6	158,491	0	9768	57	0	4693	2	6	22,136
S7	275,352	8	46,140	893	15	1639	1778	192	8222
SUM	1,285,654	24	501,795	1383	392	52,131	1818	252	61,202

Wastewater from the Bor open pit is pumped (site S3) into the Krivelj River, at an average flow rate of 3600 m^3/day. Some of the characteristics of this wastewater are presented in Fig. 3 (cell 3 in the flowsheet).

Wastewater flows from dam 1A (site S4) of the Veliki Krivelj flotation tailings pond into the Krivelj River at an average flow rate of 1940 m^3/day (Fig. 3, cell 4 in the flowsheet). Similarly, water flows from 3A (site S5) of the same flotation tailings pond to the Krivelj River at 3020 m^3/day (Fig. 3, cell 5 in the flowsheet).

Robule Lake (site S6) collects water that leaches from the Bor pit tailings pond. This lake is constant, because it accumulates water from external sources. Average flow rate to the Borska River is 484 m^3/day (Fig. 3, cell 6 in the flowsheet).

Wastewater from the Bor open pit (closed in 1992) and copper smelting and electrolysis, sulphuric acid plant, regeneration and refinery plants (site S7) is pumped to the Borska River at an average flow rate of 2320 m^3/day (Fig. 3, cell 7 in the flowsheet).

Wastewater that flows into the Krivelj and Borska Rivers all flow via the Timok River into the Danube River and ultimately to the Black Sea. The relative contributions of the various locations have varied significantly during the past 5 years, but only some of the nitrite and lead analyses (the Saraka stream and Bor open pit) are questionable. Metals lost through wastewater disposal were calculated (Table 1).

The five-year average pH in the Borska River was 6.2 prior to its flow into the Timok River. Metal ion concentrations are given in Fig. 4. More complete results (complete physico-chemical and microbiological analyses) can be found in Nikolić et al. (2010).

Obviously, most of the considered metal ions from that sampling site (S8) greatly exceed the maximum allowed concentrations (MAC) (Nikolić et al. 2010; Official Gazette of SRS No. 5/68; Stanković et al. 2011). The low pH values are caused by pyrite oxidation and iron hydrolysis (Stanković et al. 2011). Decreasing contaminant concentrations over time is attributed to dilution and increased river flow, due to long rainy periods in the autumn of 2010 when the monitoring was carried out.

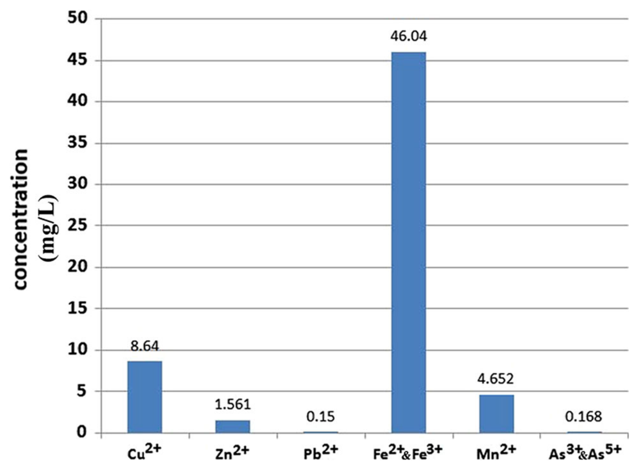


Fig. 4 Five-year average metal ion concentrations in the Borska River prior to its flow into the Timok River, measured in Oct., 2010 (Nikolić et al. 2010; Stanković et al. 2011). *Note* maximum allowed concentration for the mentioned metal ions are: Cu^{2+}—0.1 mg/L; Zn^{2+}—1 mg/L; Pb^{2+}—0.1 mg/L; Fe^{2+} and Fe^{3+}—1 mg/L; Mn^{2+}—not defined; As^{3+} and As^{5+}—0.05 mg/L (according to Serbian legislation: Official Gazette of SRS No. 5/68)

The impact of the Borska River on the Timok River can be seen in Fig. 5. The Borska River is a small river, but is heavily polluted. These polluted waters are naturally diluted after the confluence with the Timok River, but not enough to drop under the MAC, as illustrated in Fig. 5 (Nikolić et al. 2010; Stanković et al. 2011), where the concentration profiles along the Timok River flow path are presented for dissolved Cu and Fe.

There is no Cu in the Timok River sediment at site S9 upstream of the Borska River (M3 in Fig. 5), or at site S10, at the Borska River inflow, where the Cu content in the water is approximately 2 mg/L. Maximum Cu sediment concentrations (almost 5 g/dm^3) was found just a few kilometres downstream of S10.

Mining and metallurgical activities in the RTB Bor have been going on for more than a century and their influence via the Borska River on water quality in the Timok, and

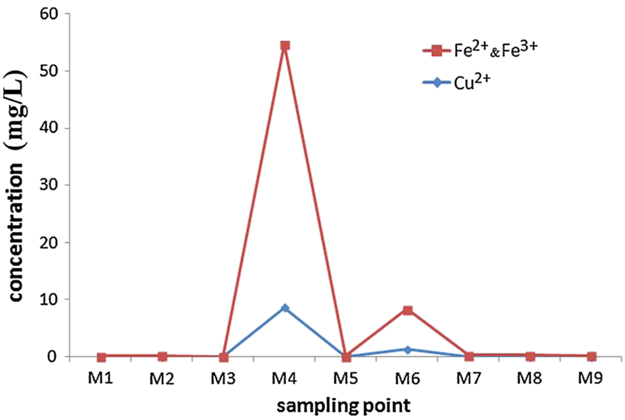


Fig. 5 Distribution of dissolved Cu and Fe along the flow path of the Timok River (Nikolić et al. 2010; Stanković et al. 2011). *Note* sampling points M1–M9 are related to the sites investigated from the City of Zaječar to its confluence with the Danube (Nikolić et al. 2010); *points M3* and *M4* correspond to sites S9 and S10, respectively (Year: 2010)

consequently on the Danube, has presumably gone on for about as long. It is difficult to estimate the damage the site has had on downstream waters and how this pollution affects the aquatic ecosystem in the Timok River and the associated environment, but its influence is long-standing and costly (Nikolić et al. 2010). However, a newly reconstructed sulphuric acid plant and introduction of new smelting technology should help decrease future pollution loads somewhat.

Conclusion

Characterization of the wastewater discharged from the RTB Bor Company facilities represents an important initial step in selecting the best remediation technology because it is clear that the mining, ore processing, and metallurgical activities are causing severe environmental impacts. Increased worldwide concern for the environment, as well as current legislation and stringent restrictions regarding management of wastewaters from industrial applications make wastewater treatment necessary. Continued reductions in discharges from ongoing industrial processes must be a high priority, with additional efforts aimed at reducing the legacy pollution that enters streams and rivers from open pits and tailings ponds.

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