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Importance of Changes in the Copper Production Process through Mining and Metallurgical Activities on the Surface Water Quality in the Bor Area, Serbia

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Abstract: This paper considers the impact of copper mining-influenced water and metallurgical wastewater on the surface water in the Bor area, Serbia. Sampling, realized through the four campaigns (2020–2021), confirmed that both types of water, discharged without appropriate treatment in the Bor River, had a signific impact on the concentration of metal ions, pH and electrical conductivity on the watercourse in the Bor area. The highest concentrations of the following metal ions, Cu—271 mg/L, As—25,991 µg/L, Ni—13,856 µg/L, Cd—2627 µg/L, and Pb—2855 µg/L, were registered in the metallurgical wastewater samples. After changes occurred in the copper production process by stopping the discharge of untreated wastewater into the Bor River, the concentrations of monitored elements were drastically decreased. In the period 2022–2024, the concentration values for Cu, As and Pb ions were below the maximum allowable value, and the concentration values of Ni and Cd ions were also decreased. The values for pH and electrical conductivity were in the maximum allowable range. The return of wastewater to the copper production process would lead to both a reduction in the primary water consumption and reduction in the negative impact on the environment.

Keywords: metal ions; copper production; mining and metallurgy; environment; wastewater; surface water

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1. Introduction

Mining and metallurgy are among the industries that have the biggest impact on the environment [1]. Dust from the open pit, overburden, and flotation tailing dumps, as well as gases from smelters and wastewater from electrolysis plants, are the main sources of air, water, and soil pollution. On the other side, the surface and underground water streams are endangered by mining-influenced water and industrial wastewater from metallurgical facilities.

One of the biggest still-working copper mines—including mines with surface exploitation, underground mines, facilities for mineral processing, and metallurgical plants for copper production—is located near the city of Bor, Serbia (Western Balkan). The Bor copper mine is located in the northeastern part of Serbia, about 11 km west of Bulgaria, and about 70 km south of Romania. The area of the Bor ore field occupies the central part of the Timok eruptive massif. This area is bounded on the west by Crni Vrh (1027 m), on the north by Mali Krš (920 m) and Veliki Krš (1148 m), and on the south side, the terrain is much lower and there is no distinct height. The first mining operations started in 1903 and have been continuously operating for over 120 years. During this period, very large amounts of different kinds of waste were generated. Copper mineralization is predominantly porphyry deposits, with a sulfur mineral associated with pyrites. Contact of pyrite with water and oxygen leads to generating the acid mine drainage (AMD) or acid rock drainage (ARD) forms [2].

It is estimated that about 750 million tons of mining waste, out of about 378 million tons of flotation tailings [3], is deposited near the city of Bor during the exploitation period. This waste contains hazardous and potentially toxic elements such as copper, nickel, arsenic, zinc, antimony, mercury, chromium, bismuth, and other pollutants [4]. Besides polluting the environment, these pollutants are very toxic to human health and can cause a large number of diseases and even death in cases of very high doses when acute poisoning occurs [5–12]. In the Waste Management Strategy of the Republic of Serbia for the period 2022–2031, mining waste from the exploitation of the mineral raw materials is classified into waste group 01 in the waste catalog [13]. During 2020, the ore and stone extraction sector produced 45,709,000 tons of waste, most of which was deposited in landfills [14]. The mining and metallurgy activities in the Bor area are the largest producer of waste.

Problems with mining waste are primarily related to the disposal of a large amount of flotation tailings and overburden. However, since environmental protection was not the focus in the past, these waste materials were not managed properly. The environment in the surroundings of the open pit mines was polluted to the extent that the land, as well as surface and underground water, was not for human consumption or agriculture. Also, the metallurgical facilities, located in the center of the city of Bor, caused a large amount of pollution, especially the gases from the smelter plant that polluted the air, but also other facilities such as wastewater from the electrolysis plant, which is an important source of water pollution. Monitoring of the environment has shown the contamination of air, soil and water with metals, inorganic and organic compounds, PM 10 and PM 2.5, etc. [15,16]. The great negative impact of mining and metallurgy activities on the surface water quality, especially close to the active and abandoned mines, needs some measures for reduction, remediation and elimination of the pollutants [17,18].

The Bor River, Krivelj River, Ravna River, Bela River, and Veliki Timok River are the main rivers of the Bor area watercourse. There are also small creeks and mine-influenced water, along with industrial wastewater from metallurgical processes for copper production flowing into some of the mentioned rivers. As a consequence of the mining and metallurgy activities, some of these rivers have become very polluted mostly by metal ions, such as Pb, Zn, Cd, Ni, Se, As, Fe, etc. The Bor River is one of the most polluted rivers in Europe [19,20]. To find measures and solutions for the reduction, rehabilitation, and elimination of the polluting elements, it is necessary to understand the consequences of more than a century of continuous mining and metallurgical activities in the Bor mining area.

The results for characteristic parameters of the surface water, mine-influenced water, and metallurgical wastewater in the Bor area are presented in this paper. The main objective was to determine the difference in the surface water quality before and after the cessation inflow of the metallurgical wastewater and AMD water from different sources into the Bor River. In case of an inflow of metallurgical wastewater and AMD water into the Bor River, the data were collected during the four sampling campaigns, realized in the period from September 2020 to June 2021. Collecting data of the surface water quality in the Bor area was continued from October 2021 after stopping the metallurgical wastewater and AMD water from inflowing into the Bor River; data are available on the website of the city of Bor. All results were used for a comparative analysis of the surface water quality in the watercourses of the Bor area.

2. Materials and Methods

2.1. Study Area

The study area includes the surface water and water under the influence of the mining and metallurgy activities, and the starting point is the Bor River after merging the untreated municipal wastewater and AMD water from different locations. The other sampling points are located downstream towards the Danube River within a 40 km radius of the city of Bor. This area was chosen because mining and metallurgical activities have been going on for more than 120 years and they are the main sources of pollution [21].

The main sources of water pollution in the Bor area as well as the industrial zone, Krivelj; overburden (near the village of Oštrelj); flotation tailing dumps; metallurgical zone Bor; and open pits are presented in Figure 1.

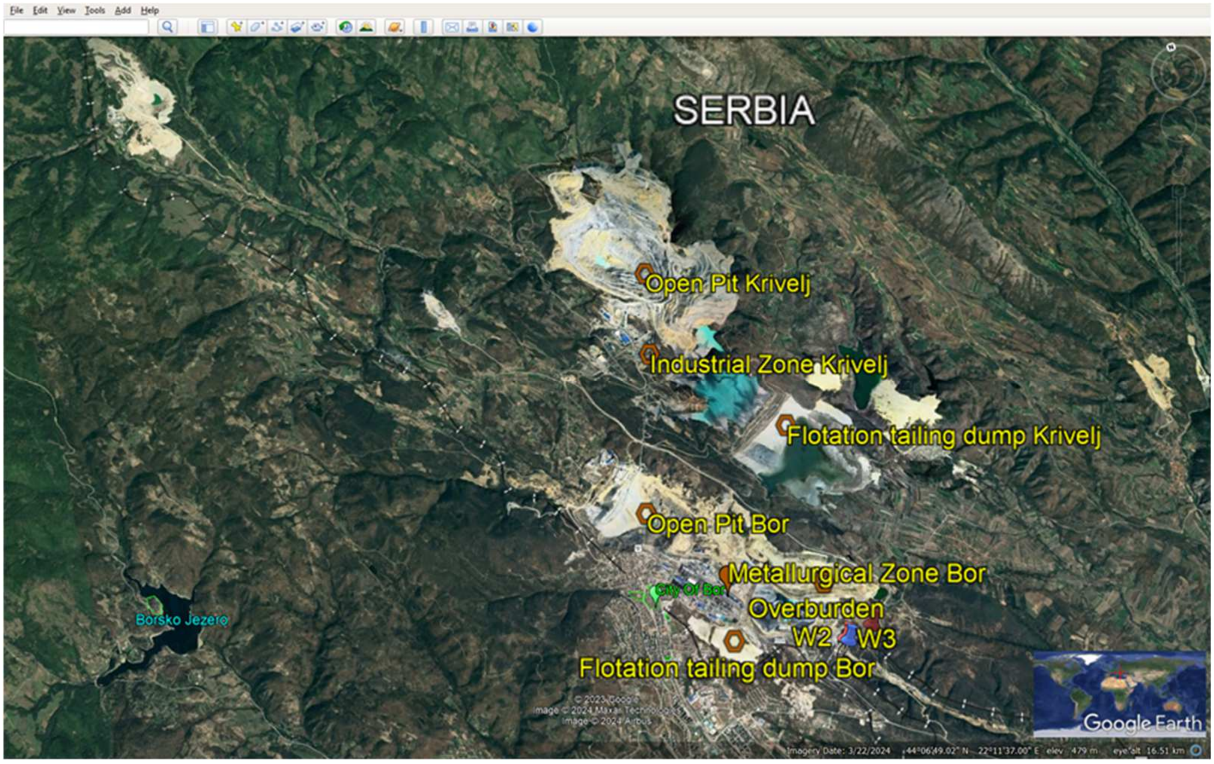

Figure 1. Sources of mining and metallurgical pollution of surface water.

The nine locations chosen to take samples for the physical–chemical characterization aim to define the concentration of Cu, As, Ni, Cd, Pb ions, pH and electrical conductivity (EC) of those samples (Figure 2). The Bor River is formed from the untreated municipal wastewater, AMD water from overburden deposited near the village of Oštrelj (W1), AMD water from flotation tailing dumps which are not in operation (W2) and metallurgical wastewater (W3), also discarded without previous treatment. Sampling of the Bor River (W4) was carried out on the point near the confluence with the Krivelj River (W5). Sampling of the surface water from the Krivelj River was carried out at the place where a significant influence of all wastewater from the study area was (mine, drainage, flotation). The Bela River (W6) was sampled after merging the Bor, Krivelj and Ravna rivers. The Ravna River (W7), which flows relatively far from the area of copper mining and metallurgy activities, was included for an analysis on the basis of literature data about pollution in the earlier exploitation period, realized by the Roman Empire [22].

The Timok River was sampled at two locations: a location marked as W8, out of influence of the mining and metallurgy activities from the study area (near the city of Zaječar), and a location marked as W9, the Veliki Timok River (near the village of Rajac), after inflow of the Bela River into the Timok River. The Veliki Timok River is a last tributary of the Danube River in the Republic of Serbia.

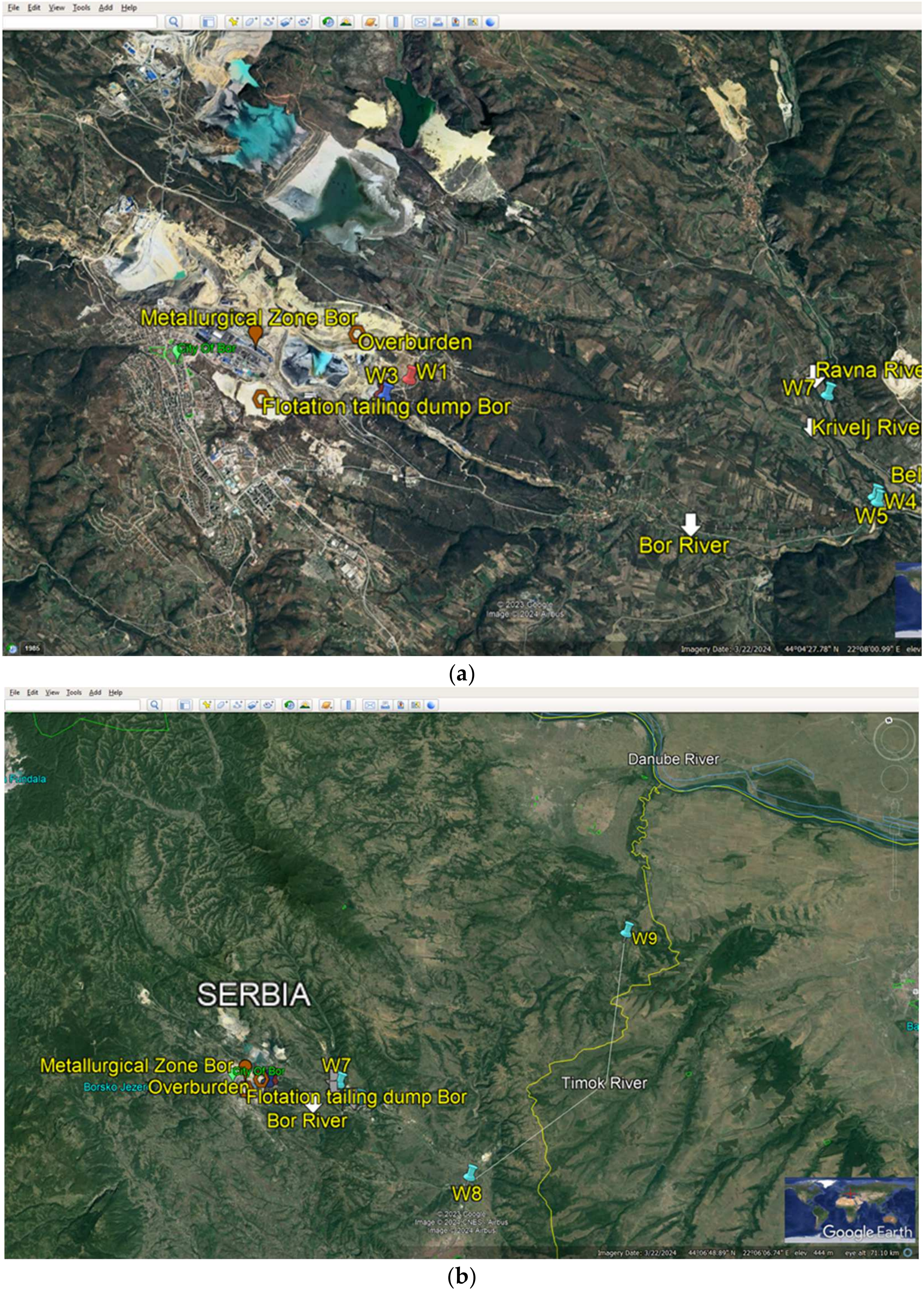

Figure 2. Water sampling locations: (**a**) locations under direct impact of mining and metallurgy activities; (**b**) all sampling locations.

Coordinates of water sampling locations are measured by a GPS device (Global Positioning System) Garmin, eTrex Vista® HCx (Olathe, Kansas City, MO, USA), and presented in Table 1.

Table 1. Coordinates of sampling locations.

Water Sample Mark	Sampling Location	GPS Coordinates	
		Lat. N	Long. E
W1	AMD water from overburden	44°03′46.65″	22°08′11.92″
W2	AMD water from flotation tailing	44°03′47.73″	22°07′51.92″
W3	Metallurgical wastewater	44°03′42.45″	22°07′53.22″
W4	Bor River	44°01′46.81″	22°12′29.46″
W5	Krivelj River	44°01′49.33″	22°12′28.92″
W6	Bela River	44°01′37.65″	22°13′18.56″
W7	Ravna River	44°02′39.69″	22°12′22.24″
W8	Timok River (out of impact the mining and metallurgy activities)	43°56′40.30″	22°18′54.03″
W9	Veliki Timok River (after inflow of the Bela River into the Timok River)	44°05′36.03″	22°34′02.60″

2.2. Sampling Procedure

A crucial factor in water sampling is to collect samples properly with the appropriate equipment so that the analytical results or field measurements will reflect the environmental conditions at the time of sampling. There is a possibility that errors are inadvertently produced during each sampling. This can lead to wrong results and bad conclusions.

Water samples (AMD water, industrial wastewater, and surface water) were sampled by the hand tools according to the standard sampling methods:

- Plastic containers from a high-density polyethylene (volume of 1 L), used for general water sample collection, are rinsed several times in the river or water that will be sampled before filling with a sample.
- An unfiltered water sample is poured into a plastic bottle of 50 mL without prior washing because 2.5 mL of HNO_3 conc. is present there. Exactly 50 mL of the sample is poured into a syringe, and after that, the bottle is sealed and labeled. Before use of a syringe, it should be rinsed three times with a water sample, and contents should be discharged.
- Samples are properly stored in the shipping containers to ensure samples are between 4 and 10 °C, and transported to the laboratories of the Mining and Metallurgy Institute Bor.
- All samples are properly stored from the time they arrive at the laboratory to disposal. Samples are refrigerated at 4 °C before analysis unless the method protocol indicates other storage conditions. In general, the shorter the time that elapses between sample collection and its analysis, the analytical results will be more reliable.
- For certain constituents and physical values, an immediate analysis in the field is required. On a sampling site, part of a water sample from a plastic container was poured into a vessel to measure the pH and electrical conductivity. The vessels for pH and electrical conductivity measuring were also three times rinsed with a water sample before performing the measure.
- All field measurement instruments are calibrated before starting sampling and once again after completing all of the sampling.
- At each sample location, the details relevant to the subsequent analysis and interpretation are entered in the lists for water sample collection and testing. The details in the list include all information necessary to assist in data interpretation and repeatability of sampling. Completion of the list starts in the field, during the sampling activities. The rest of the forms are completed step by step as samples are analyzed; the results will be obtained.

2.3. Physical Chemical Characterization and Statistical Analysis

Relevant international and European standards are used for prescribed appropriate methods for determining the metal ion concentration (Cu, As, Ni, Cd, and Pb), pH, and electrical conductivity.

The Coupled Plasma Optical Emission Spectroscopy analytical technique ICP-AES (model: SPECTRO ARCOS ICP-OES SPECTRO Analytical Instruments GmbH Bosch str. 10, 47533 Kleve, Germany) was used to determine the Cu ions. The Mass Spectrometry with Inductively Coupled Plasma analytical technique ICP-MS (model: Agilent 7700, Agilent Technologies Japan, Ltd. 9-1, Takakura-machi, Tokyo 192-8510, Japan) by the external calibration method was used to determine the As, Ni, Cd, and Pb ions.

The Certified Reference Material (CRM) was used for the quality control of chemical analysis in the laboratory conditions. An analysis of replicate test portions will indicate the repeatability and precisions of measurement.

Electrical conductivity and pH are measured on the field in duration of 10 min. Electrical conductivity is measured with EC1387, CHEMLAND (Stargard, Poland) and pH with WTW 7310, Ino Lab. (Xylem Analytics Germany Sales, GmBH&Co, KG, Weilheim, Germany).

Calculations of the average values and standard deviation of metal ion concentration of samples from the period September 2020–June 2021 were made by the Microsoft Excel 2016 Data Analysis Statistical functions and software package OriginPro 8 [23].

3. Results and Discussion

3.1. Characteristics of Wastewater and Surface Water in the Bor Area (Sampling Period September 2020–June 2021)

The results of more extensive research of the metal ion concentration, pH and electrical conductivity in wastewater, generated from copper mining and metallurgy activities and surface water from rivers, under the influence of mentioned activities, are presented in this paper. Therefore, the observed parameters in eastern Serbia or other areas with copper mining activities can represent a reference point for further research. The water samples, originating from different rivers, mining-influenced water, and metallurgical wastewater streams, are extremely enriched with toxic elements [24]. Sampling was performed during the four campaigns, in the period from September 2020 to June 2021, at defined locations (Table 1). It was aimed at determining the following parameters: pH, electrical conductivity, Cu, As, Ni, Cd, and Pb ion concentration.

According to the Serbian regulation on watercourse categorization, the observed rivers are categorized as the III and IV categories (Table 2). Also, Table 2 presents the maximum allowable values (MAVs) for characteristic parameters.

Table 2. MAVs according to the Serbian legislation for different river categories, adapted from Refs. [25,26].

Parameters	River Category and MAVs	
	III Category (after Inflowing of the Bela River into the Timok River) until the Confluence of the Veliki Timok and Danube Rivers	IV Category (from the City of Bor to the Confluence of the Bela River and Timok River (Out of Impact of the Mining and Metallurgy Activities)
pH	6.5–8.5	6.5–8.5
Electrical conductivity, μS/cm	1500	3000
Cu, mg/L	0.5	1
As, μg/L	50	100
Ni, μg/L	34	34
Cd, μg/L	0.6	0.9
Pb, μg/L	14	14

3.1.1. Concentration of the Cu, As, Ni, Cd and Pb Ions

Figures 3–7 present the obtained values for the concentration of the Cu, As, Ni, Cd and Pb ions during each sampling campaign, in the period from September 2020 to June 2021. Also, all graphs present the MAVs for the corresponding river category.

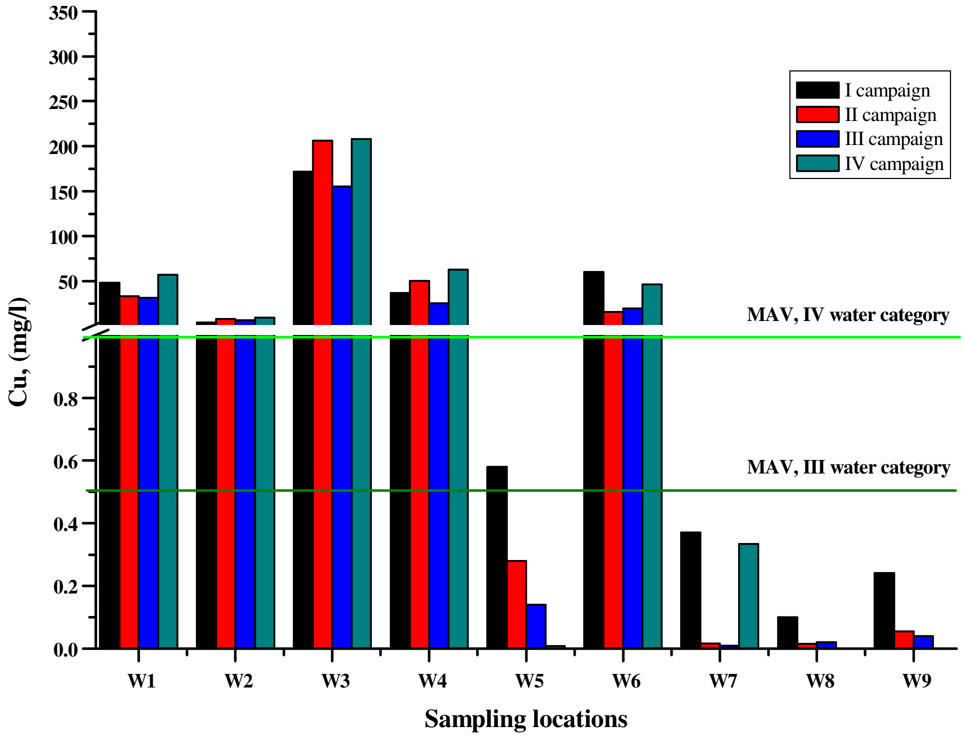

Figure 3. Concentration of Cu ions in the realized sampling campaigns at defined locations.

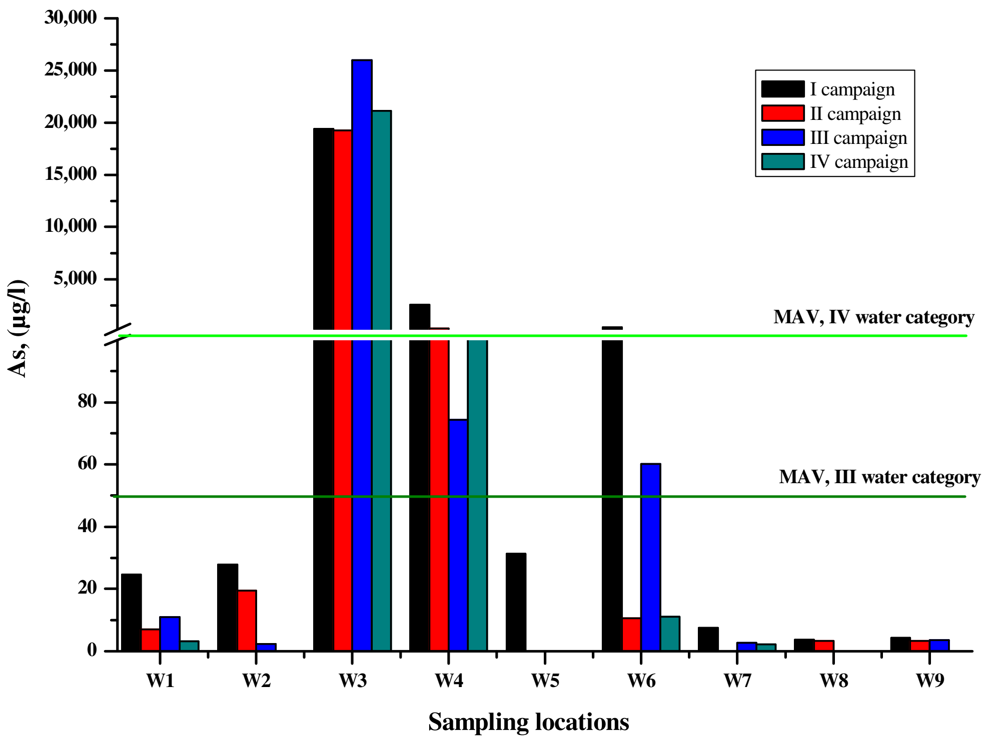

Figure 4. Concentration of As ions in the realized sampling campaigns at defined locations.

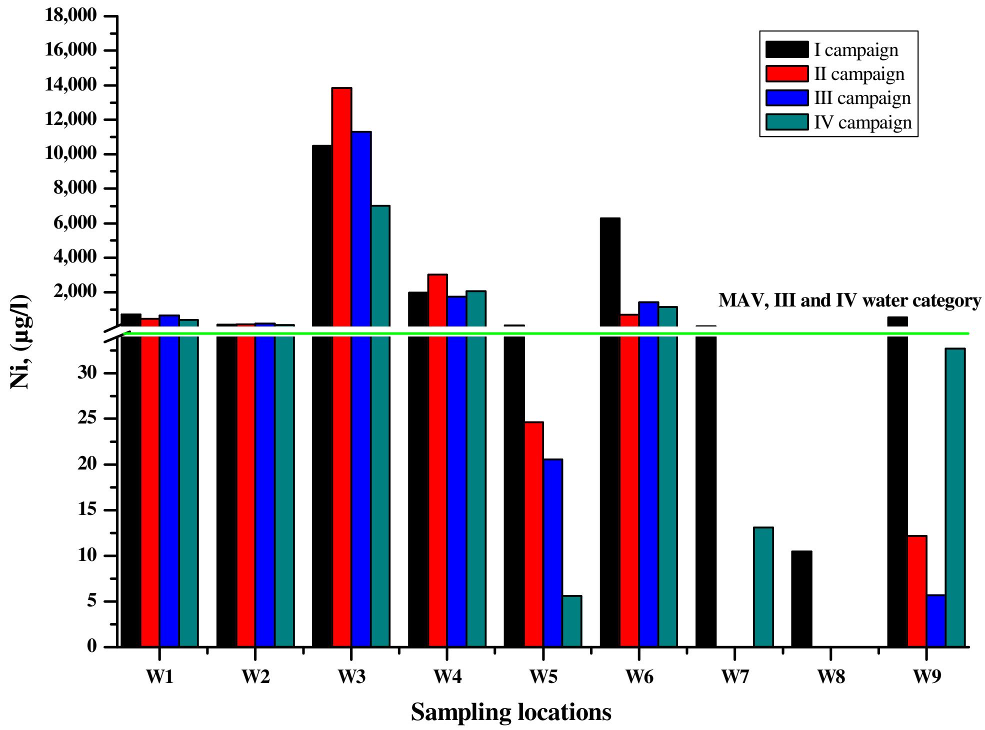

Figure 5. Concentration of Ni ions in the realized sampling campaigns oat defined locations.

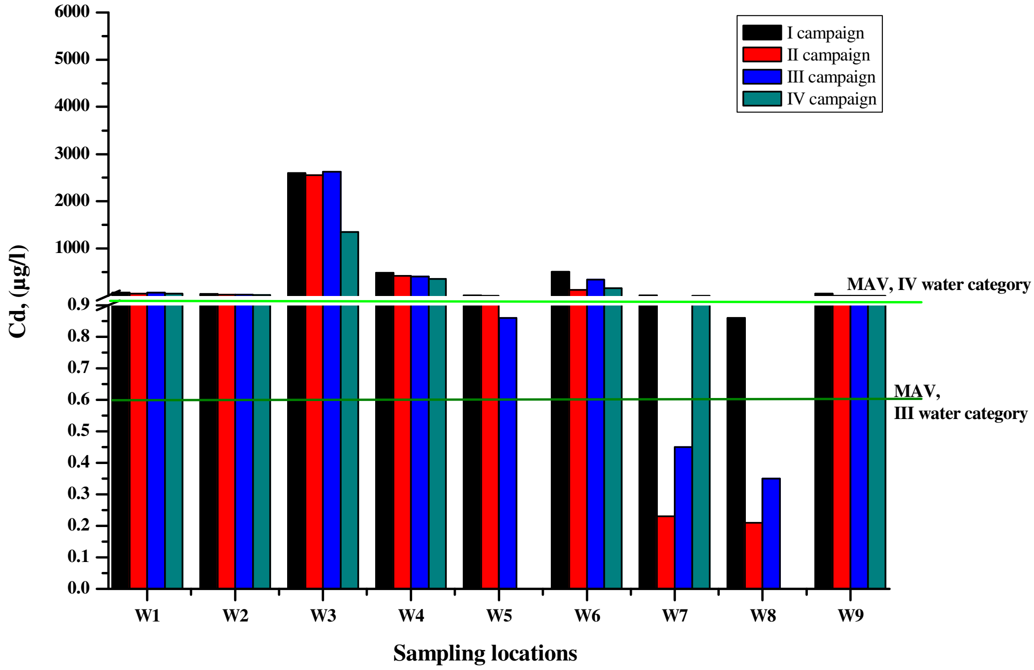

Figure 6. Concentration of Cd ions in the realized sampling campaigns at defined locations.

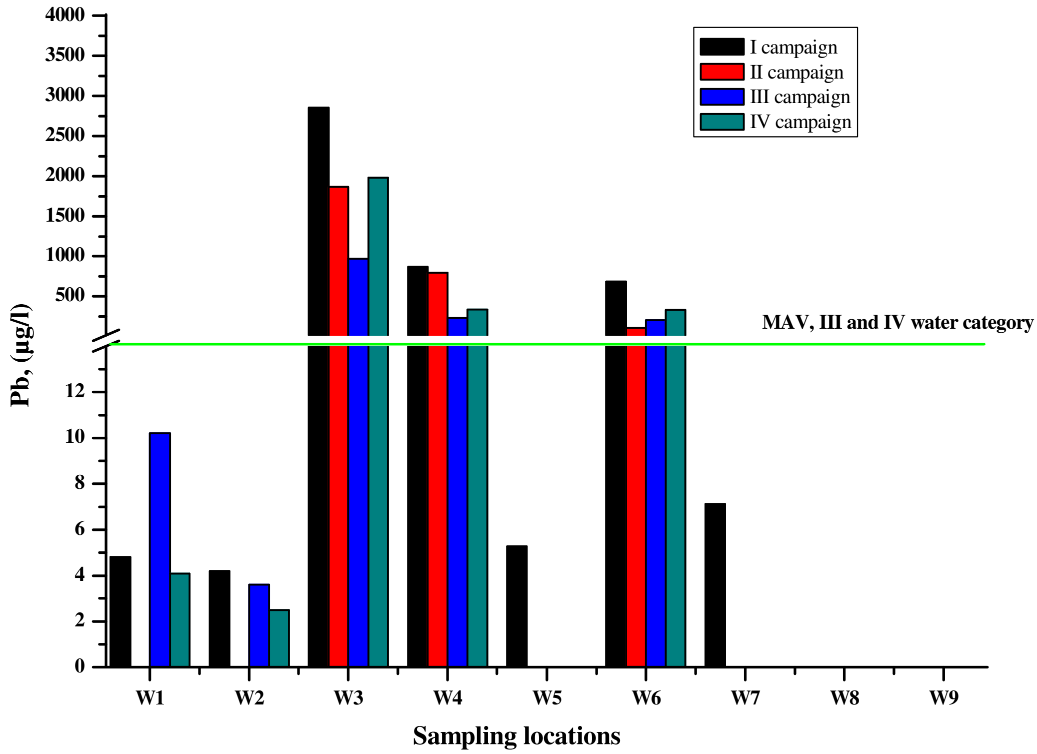

Figure 7. Concentration of Pb ions in the realized sampling campaigns at defined locations.

The calculated average and SD values (plus direction of error bars) for Ni, Cd and Pb are presented in Figure 8.

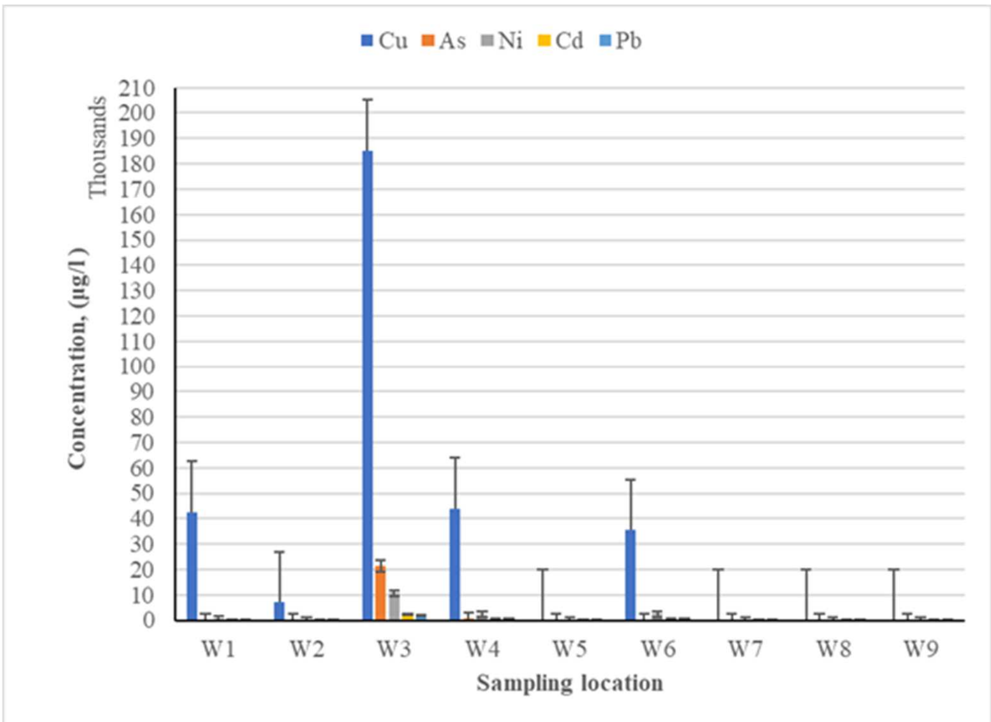

Figure 8. The average and SD values for concentration of Cu, As, Ni, Cd and Pb ions.

During the sampling campaigns, the impact of AMD water from overburden (W1), AMD water from flotation tailings (W2), and metallurgical wastewater (W3) on the surface water of the Bor River (W4) was investigated. The results for the concentration of Cu, As, Ni, Cd, and Pb ions in all three kinds of wastewater that inflow into the Bor River have shown the following: the concentration of Cu ions in water samples, obtained by the natural leaching of overburden (W1), is in the range of 31.6–57.2 mg/L, average ± SD (mg/L) values, 42.68 ± 12.30. The concentration of Cu ions in the AMD water from flotation tailings ranges up to 10 mg/L, average ± SD (mg/L) values, 7.10 ± 2.31, while the concentration of Cu ions in the metallurgical wastewater ranges from 155.27 to 207.9 mg/L, average ± SD (mg/L) values, 185.25 ± 26.05. The obtained results, presented in Figures 3 and 8, have confirmed that the concentration of Cu ions had the highest values in metallurgical wastewater (W3). The literature data have also confirmed that Cu ions are also detected in a similar type of mining-influenced water [24]. The concentration of Cu ions in AMD water at Parys Mountain (Wales) was in the range of 7–44 mg/L. Similar values are registered in the other copper mines in this area [27].

Based on the values for standard deviation, the possibility that the values could be found outside the range is lower for samples from location W1, W2 and W3 (Figure 8) compared to samples from other investigated locations.

The concentration of arsenic ions in the metallurgical wastewater is extremely high (more than 19,000 μg/L) in all samples, average ± SD (μg/L) values, 21,445.97 ± 2725.33. As the metallurgical wastewater inflows into the Bor River, it is clear that a high concentration of As ions in the Bor River is the result of their presence in W3. Also, a high concentration of Ni, Cd, and Pb ions is the result of the presence of those ions in W3, which inflow in W4. The literature data confirm that arsenic is a toxic and harmful impurity in the copper production process. The characteristic of As ions is that they can be found in metallurgical wastewater, and they could have a negative impact on the environment and biodiversity [28,29]. The results have confirmed that metallurgical wastewater (W3) is one of the main pollutants of the Bor River. Based on the results that the concentration of As ions is mostly in the range of SD values, it is real to expect that the concentration of As ions will be in this range in cases of unchanged mining and metallurgy activities (Figure 8).

The results of the concentration of Cu, As, Ni, Cd, and Pb ions in the Bor River (sample location W4), presented in Figures 3–7, have approved that each value is higher than the MAV:

- Cu ions: The highest concentration of Cu ions was registered during the IV sampling campaign, and it was approximately 63 times higher than the MAV. The minimum value was registered during the III sampling campaign, and it was almost 25 times higher than the MAV.
- As ions: The highest concentration of As ions (2552.91 μg/L) was about 26 times higher than the MAV, and was registered during the I sampling campaign. The minimum value (74.4 μg/L) was registered during the III sampling campaign, and it was lower than the MAV.
- Ni ions: The highest concentration of 3020.6 μg/L was registered during the II sampling campaign, and it was about 90 times higher than the MAV. The minimum value (1740.59 μg/L) was registered during the III sampling campaign, and it was 50 times higher than the MAV.
- Cd ions: The highest concentration of 480.15 μg/L was registered during the I sampling campaign, and it was about 533 times higher than the MAV. The minimum value (355.7 μg/L) was registered during the IV sampling campaign, and it was approximately 400 times higher than the MAV.
- Pb ions: The highest concentration of 867.60 μg/L was registered during the I sampling campaign, and it was about 62 times higher than the MAV. The minimum value (231.52 μg/L) was registered during the III sampling campaign, and it was approximately 16 times higher than the MAV.

Generally, the results of samples from the Bor River (W4) have shown that only the concentration of As ions was lower than the MAV in only one sampling campaign. The concentration of all other heavy metal ions was above the MAV, even 533 times higher in the case of Cd ions.

The (W5) concentration of Cu, As, and Pb ions in all cases was lower than the MAV in the Krivelj River. The concentrations during the, I, and II sampling campaign were increased by Cd ions, and the concentration of Ni ions was increased only in the I sampling campaign.

The characteristic of the Ravna River (W7) is that the concentrations of Cu, As, and Pb ions during each sampling campaign had lower values than the MAV, while the concentrations of Ni and Cd ions had higher values than the MAV during the I and IV sampling campaigns. During the I sampling campaign, the concentrations of both elements were increased, and during the IV sampling campaign, only the concentration of Cd ions was increased.

The characteristic of the Bela River (W6), which is formed by merging the Bor, Krivelj, and Ravna rivers, was that the concentrations of Cu, As, Ni, Cd, and Pb ions during each sampling campaign were higher than the MAV. By comparison with the values of appropriate elements in the rivers that form the Bela River, it is clear that the Bor River is a carrier of heavy metal ions that cause an enormous amount of pollution downstream towards the Danube River.

The characteristic of the Timok River (W8), which flows through the area out of impact of the mining and metallurgy activities from the study area, is that the concentration of all monitored element ions is lower than the MAV.

No negative impact of the mining and metallurgical activities on water in the Veliki Timok River (W9) is recorded.

3.1.2. pH Values

The pH values, measured during the realized sampling campaigns, are shown in Figure 9.

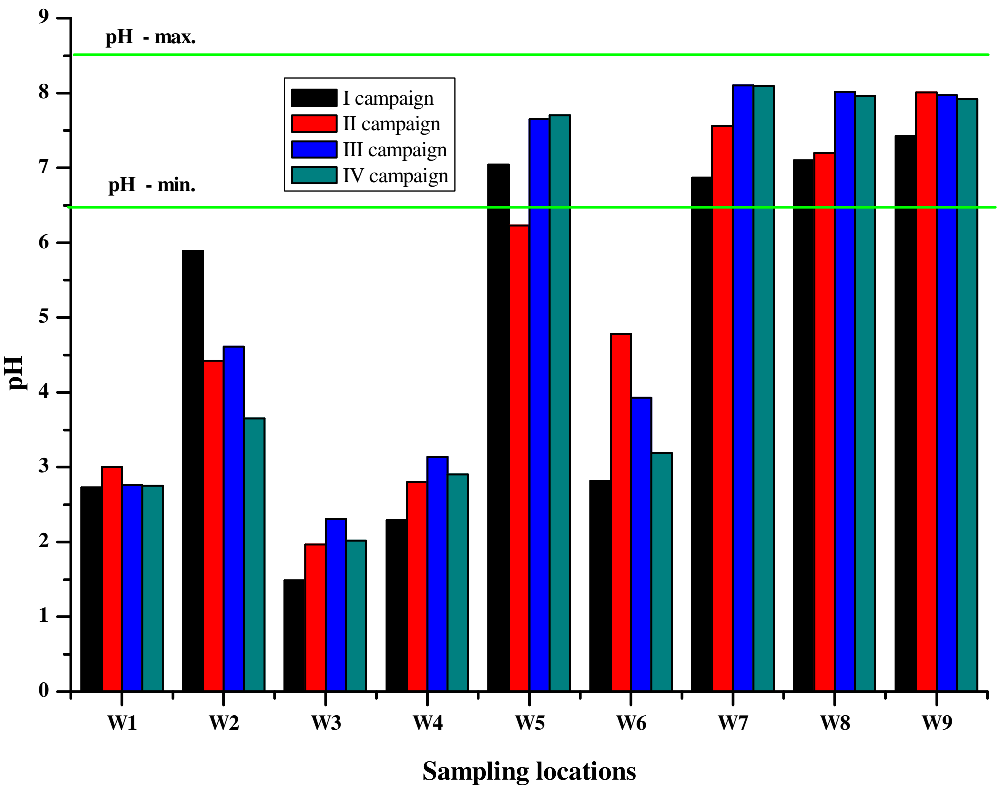

Figure 9. pH values at different sampling locations for each sampling campaign.

It is evident from Figure 9 that mining-affected water (W1 and W2) and metallurgical wastewater (W3) had increased acidity, which was also shown in the literature data for similar water types [30]. Low pH values, also a characteristic of the Bor River, were at the minimum in the I sampling campaign (2.29). In the same campaign, the pH value was the lowest at the W3 location (1.49). The above data have confirmed once again a dominant impact of metallurgical wastewater on the Bor River characteristics, but also that the present impact of mining has affected water.

The Bela River (W6), formed by merging the Bor, Krivelj, and Ravna rivers, is also characterized by low pH values compared to the pH values of surface water from locations W5, W7, W8, and W9. The Krivelj River (W5) is characterized by a pH in the range of 6.23–7.7, but after merging the Bor River with a pH value in the range 2.29–3.14, the pH value of the newly formed river, the Bela River (W6), ranges between 2.82 and 3.78.

The pH values of surface water from location W7, W8 and W9 are within the MAV range (6.5–8.5).

3.1.3. Electrical Conductivity

One of the water properties is its electrical conductivity, i.e., the ability of water to conduct electricity. The electrical conductivity of water shows how many dissolved substances, salts, minerals, and chemicals are present in it. Salts and various chemicals, dissolved in water, consist of positively and negatively charged ions that conduct electricity in water. The increased electrical conductivity of water indicates its possible pollution. The literature data have confirmed the elevated electrical conductivities for the same water types [31]. Figure 10 presents the measured values of electrical conductivity during the realized sampling campaigns.

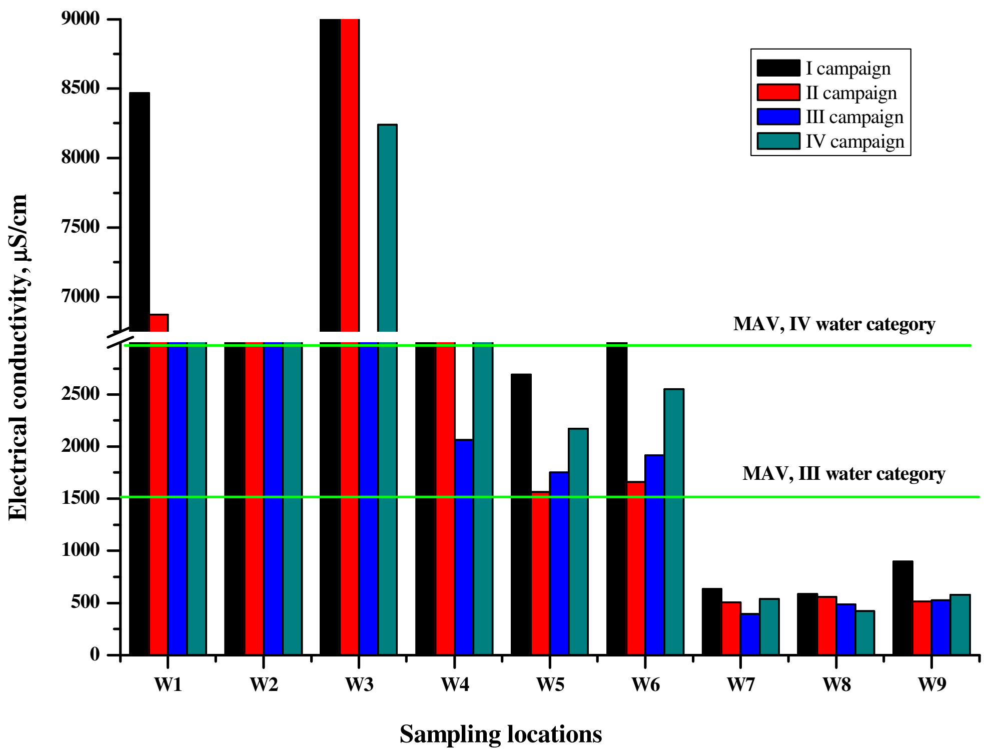

Figure 10. Electrical conductivity at different sampling locations for each sampling campaign.

The electrical conductivity values for wastewater from locations W1, W2, and W3 were very high, ranging from above 3500 µS/cm to 8500 µS/cm, indicating the presence of salts and various chemicals dissolved in water and whose ions enable the conduction of electricity. This confirms the presence of high concentrations of Cu, As, Ni, Cd, and Pb ions in the investigated samples, as shown in Figures 3–7. It was not possible to measure the electrical conductivity of water from the W3 samples in two sampling campaigns (values were above the detection limit of an instrument, 19,990 µS/cm), confirming very high concentrations of metal ions in this water.

The surface water, under a direct impact of mining and metallurgical activities (W4, W5, and W6), is characterized by slightly lower values of electrical conductivity. However, they are still higher than 1500 µS/cm, which is the upper limit for class III water according to the Serbian legislation. The characteristic of surface water from locations W7 and W8 is that the values are below 1500 µS/cm [25,26].

The electrical conductivity of the Veliki Timok River (W9), during certain sampling campaigns, was higher than those values of water samples from locations W7 and W8. This has confirmed the impact of the Bela River (W5) on the electrical conductivity of the Veliki Timok River (W9) after merging the Timok River (W8) and Bela River (W5). A similar situation is registered in the area of the Majdanpek copper mine [32].

3.2. Characteristics of the Bor River and Bela River (Period 2022–2024)

During 2022, the concentrations of Cu, As, Ni, and Pb ions, pH value, and electrical conductivity in the Bor River (W4) were monitored by an authorized institution for the needs of the city of Bor. Also, the monitoring of the Bela River (W6) was started in 2023. The available reports were downloaded from the website of the city of Bor and used for a comparison with the maximum values obtained in four sampling campaigns (September 2020–June 2021). Table 3 presents the data for the pH, electrical conductivity and concentration of Cu ions. Based on the fact that the concentrations of As, Ni, Cd, and Pb ions were expressed in the same measurement units, the results are presented by diagrams in Figure 11.

Table 3. pH values, EC and concentration of Cu ions, adapted from Refs. [33–37].

Parameters	Sampling Location/Date									
	W4/ 20–21	**W6/ 20–21**	**W4/ 07.22**	**W4/ 10.22**	**W4/ 10.23**	**W6/ 10.23**	**W4/ 11.23**	**W6/ 11.23**	**W4/ 03.24**	**W6/ 03.24**
pH	2.29	2.82	8.00	7.90	7.37	7.5	7.26	7.48	7.84	7.91
EC, (µS/cm)	5896	3996	2180	1803	1699	1557	1467	1152	1714	1232
Cu, (mg/L)	62.9	60.45	1.58	0.891	0.031	0.028	0.037	0.012	0.03	0.022

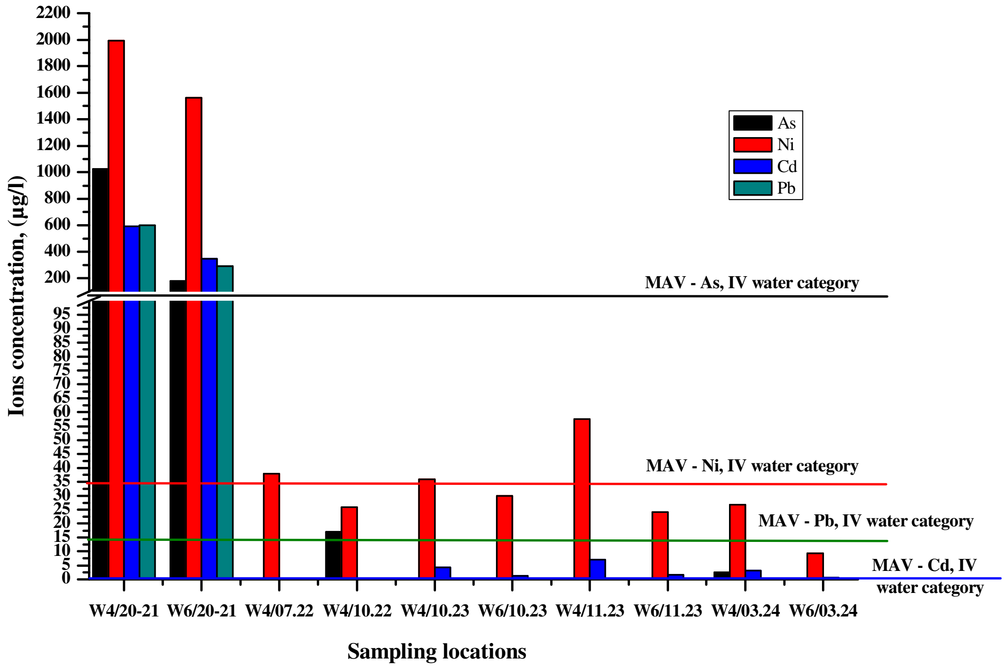

Figure 11. Comparison of concentration of As, Ni, Cd and Pb ions in different periods (2020–2024).

Changes made by the Serbia Zijin Copper d.o.o Bor had a goal to stop the discharge of mining-influenced water (locations W1 and W2) and metallurgy wastewater (locations W3) into the Bor River (W4), reuse this water and reduce the impact on the human and natural environments around the mining area as well as at the other locations [38,39]. The metallurgical wastewater (W3) treatment in a newly built facility, pumped out and neutralized water from location W2, and redirection of the W1 flow into the active flotation tailing dump led to a drastic decrease in the concentrations of Cu, As, Ni and Pb ions in the Bor River (W4) (Table 3). The concentration of Cu ions, determined in July 2022, had a maximum value of 1.58 mg/L, which is almost 40 times less than the maximum concentration of Cu ions determined in the IV sampling campaign (62.9 mg/L, Figure 3). During the last measured time (18 March 2024), the concentration of Cu ions in the Bor River was 0.03 mg/L. It is clear that the concentration of Cu ions in the Bor River in March 2024 is about 50 times lower than the concentration in July 2022.

As a consequence of decreasing the concentration of the Cu ion concentration in the Bor River, the concentration of Cu ions in the Bela River (W6) is also decreased (Table 3). The maximum value for the concentration of Cu ions in the Bela River (60.45 mg/L) is registered in the I sampling campaign (Figure 3), and it is about 2200 times higher than the value registered in October 2023. The same concentration value of Cu ions in the Bela River is registered in March 2024.

The results of the concentration of Cu ions in the Bor River have confirmed that the values are below the MAV for the III water class in the period 2023–2024 (Table 2).

The concentration values of Ni and Cd ions were also decreased in samples from the Bor and Bela rivers, but some values were higher than the MAV.

The concentration of arsenic ions in some cases was below the detection limit of the applied analytical method, and the values were below the MAV for two samples from the Bor River.

The concentration of lead ions was below the detection limit of the applied analytical method for both rivers.

Measurements of the pH value have confirmed that the values were in the MAV range for the IV surface water class according to the data from Table 2. Also, the values of electrical conductivity decreased. It was confirmed that the concentration of metal ions decreased. The values for the pH and electrical conductivity for all samples from the Bor and Bela rivers were in the range of MAVs for the monitored period.

The concentration of 57.5 μg/L for the Ni ions (the highest value in the period 2022–2024) was almost 50 times lower than the highest concentration of 3020.6 μg/L, registered during the II sampling campaign in the period 2020–2021 (Figure 5), but still above the MAV value.

The concentration of Cd ions in the Bor River is still higher than the MAV, but the values in samples from the Bela River are lower than the MAV in two samples (sampling in October 2023 and March 2024).

The characteristics of both rivers (the Bor and Bela rivers), sampled in the period 2022–2024, are much better compared to the characteristics from the period September 2020–June 2021. The study, realized in the earlier period, has confirmed that very serious environmental impacts are detected 30 km along the Bela River. Inflowing of the untreated AMD water from an overburden disposal as well as from flotation tailing dumps will continue to significantly impact the local and regional water resources [40].

4. Conclusions

The obtained values for concentrations of Cu, As, Ni, Cd, and Pb ions in the AMD water from overburden (W1), flotation tailing (W2), and metallurgical wastewater (W3) that flow into the Bor River have confirmed that the concentration of Cu ions has the highest values in the metallurgical wastewater samples. The concentration of arsenic ions in the metallurgical wastewater that inflow into the Bor River was extremely high as well as the concentration of As ions in the Bor River. Also, the high concentration of Ni, Cd, and Pb ions in the Bor River is a consequence of the presence of those ions in the metallurgical wastewater (W3). These results have confirmed that metallurgical wastewater (W3) from on-going mining activity is one of the main pollutants of the Bor River. At the same time, the AMDs that inflow into the Bor River from different locations are the carriers of heavy metal ions and directly affect the quality of the Bor River.

The concentration of Cu, As, and Pb ions in the Krivelj River (W5) was in all cases lower than the MAV.

The characteristic of Ravna River (W7) is that the concentrations of Cu, As, and Pb ions, in each sampling campaign, had lower values than the MAV.

Cd and Ni ions had increased concentrations during some sampling campaigns in the Krivelj (W5) and Ravna rivers (W7).

The concentrations of Cu, As, Ni, Cd, and Pb ions in the Bela River (W6), which is formed by merging the Bor, Krivelj, and Ravna rivers, were higher than the MAV in each sampling campaign.

The characteristic of the Timok River (W8), which flows through the area that is out of impact of the mining and metallurgy activities from the study area, is that the concentration of each monitored element ion is lower than the MAV.

The negative impact of the mining and on-going mining activities on water in the Veliki Timok River (W9) was also recorded.

The pH values during each sampling campaign were low for the AMD water from different locations, metallurgical wastewater, Bor River, and Bela River.

The electrical conductivity of metallurgical wastewater in almost all sampling campaigns had a value which was higher than the instrument detection limit.

The concentration of monitored elements in the Bor River and Bela River after stopping the inflowing of metallurgical wastewater and AMD water from overburden and flotation tailing dumps into the Bor River (detected in the period 2022–2024) confirmed that the quality of the mentioned rivers is better in comparison with the quality of those rivers in the period September 2020–June 2021. All activities realized by a company that manages the mining and on-going mining activities, within the investigated study area, had a positive effect on the environment.

This research can represent a reference point for future studies in eastern Serbia or other areas where the copper overburden and flotation tailings have been deposited, using the observed concentrations of metal ions. Also, further activities, aimed at preventing the inflow of untreated mining-influenced water and industrial wastewater into the surrounding watercourses, will lead to economic and ecological effects.

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