

INFLUENCE OF THE COPPER MINING ACTIVITIES IN MAJDANPEK ON DANUBE RIVER

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1. National Park Đerdap

1.1. Introduction

National Park Đerdap (NP) is located in the north-eastern Serbia on the border with Romania. The National Park includes parts of the Miroč, North Kučaj, and Štrbac mountain massifs. The park spreads on 63,786.48 ha and extends within the municipalities of Kladovo, Majdanpek, and Golubac [1]. The NP Đerdap stretches on the right bank of the Danube for about 100 km from Golubac to Krataš and includes mountain range covered with forest in the width of 2-8 km and rises from 50 to 800 m above sea level. The Đerdap gorge and the natural area along the gorge were placed under protection and declared a National Park in 1974 [2]. The boundaries of the National Park were determined by the law adopted in 1983, while the Law on National Parks confirmed and described the boundaries in detail and established the current management system for the area in 1993.

In addition to the National Park Đerdap, other protected natural resources are:

1. Monument of Nature "Vratna" established in 1957 by the decision of the Institute for Nature Conservation. The approximate area the monument of nature covers is 3 ha (Negotin Municipality) and it includes three stone bridges, i.e. natural limestone arches in the Vratna river canyon;
2. Monument of Nature "Šuplja stena" – "Valja Prerast", which covers approximately 8 ha (Majdanpek Municipality) and includes the stone bridge on the river Valja Prerast, a tributary of Šaška river in the Porečka river basin, established in 1959 by the decision of the Institute for Nature Conservation (outside the National Park); and
3. Nature reserve of strict protection "Konjska glava", which covers the area of 25 ha (Majdanpek Municipality) and includes a stand of Moesian beech, established in 1971 by the decision of the Municipality of Majdanpek, whose status is being reviewed.

The Đerdap is the largest and longest breakthrough type gorge in Europe. In this area the Danube River is the main river and 100 km of its

total length (2,850 km) belongs to the National Park. This part of the Danube River is actually a compound river valley made up of three gorges:

- Golubačka,
- Gospođin Vir, and
- Veliki and Mali Kazan canyon,

and three ravines:

- Ljupkovska,
- Donjomilanovačka, and
- Oršavska.

The Đerdap gorge is the deepest and most beautiful gorge in Europe, which has unpolluted environment, favourable climate, and complex geological and geomorphological characteristics. As such, it represents a unique European reserve of tertiary flora and fauna with a distinctly endemic and relict character.

Furthermore, this area is characterized by rich ornithofauna with as many as 255 reordereed species of birds, which places the NP Đerdap on the list of the important areas for birds – IBA [3].

Due to the favourable living conditions, people were constantly present in this area with numerous archaeological sites from the Neolithic period and various cultural and historical monuments as evidence [3].

Đerdap was the first natural resource registered on the UNESCO global geoparks list. Đerdap geopark covers the coastal belt of the Đerdap gorge in the midstream of the Danube and includes parts of the Miroč and Kučaj massifs [4, 5].

Based on the Law on nature protection, three protection zones (Protection degree I, II, and III) were formed on the territory of the NP Đerdap, as can be seen on Map 1.

Protection degree I zone includes the most preserved parts of the National Park (specimen vegetation found in the Đerdap gorge) with a total area of 5,106.27 ha (14 sites).

Within the Protection degree II zone, there are areas around the natural reserves, monuments of nature, and cultural monuments with a total area of 13,715.39 ha (10 sites). This level of protection provides general protection to the habitats of the rare and endangered plant and animal species, as well as indirect protection degree I.

The remaining part of the National Park, with a total area of 44,964.82 ha, is located in the Protection degree III zone. This zone includes agricultural areas, construction areas in the towns and villages, water, traffic, telecommunications infrastructure, as well as individual facilities involved in forestry, hunting, and fishing.

The area under the Protection degree I covers about 8.01% of the total area, the area under Protection degree II takes 21.50% of the total area, and 70.49% of the total area is covered by the Protection degree III.



Map 1 National Park Đerdap – Protection degree zones (4; 26 November 2020)

Most of the territory of Đerdap is divided into areas with very high environmental quality. The environmental quality differs between the area of the NP and the remaining part outside the protected area. The differences can be found in the degree of pollution, factors that influence

the environmental quality, and the way the pollution problem is being solved.

The lack of intensive economic activities and traffic in the mountain belt of the Đerdap area has a favourable effect on the state of the environment. In the remaining area of Đerdap and outside the National Park, the environment is relatively preserved, except in the area of the municipality of Majdanpek. The exploitation of mineral resources in the mining complex Majdanpek (Serbia Zijin Bor Copper - Copper Mine Majdanpek) contributes to the degradation of the environment. Moreover, the environmental quality is significantly affected by the communal infrastructure (large number of unregulated landfills and wastewater disposals).

The assessment of the ecological status of the river water includes a comparison of the average annual concentrations of the observed physical, chemical, and biological parameters and the maximum allowable concentrations determined in the ecological classification according to national regulations. Standard limit values for all parameters determined for each class of the ecological status are defined for each country, and in Serbia, they are determined at the national level by the Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of groundwater [6], Regulation on emission limit values of polluting substances in surface and groundwater's and deadlines for their achievement [7], and Regulation on emission limit values of priority and priority hazardous substances which pollute surface waters and deadlines for their achievement [8].

1.2. Description of the Pek river basin

The Pek River, whose length is 129 km and basin surface covers 1,236.5 km², is the Danube's tributary, and at the same time the largest river in Eastern Serbia. It originates at the foot of Crni Vrh Mountain and flows into the Danube near Veliko Gradište after flowing for 124 km and it is characterized as a mountain river. The rivers Veliki and Mali Pek merge and form the Pek River. The rivers basin covers the area of 2,230 km². The average water flow is 48.5 m³/s. This area has favourable ecological

conditions for forest vegetation development and a high degree of forest cover. The river is under the significant influence of waste mine waters (especially water washed away from tailings) from Majdanpek in its middle and lower course. The wastewater from the mine and tailings has negative effect on the fish stock in the river [9].

1.3. Mali Pek river basin

Mali Pek River flows through the municipality of Majdanpek (its length is about 15 km), and its river course cuts through the copper mine in Majdanpek. The Mali Pek river basin consists of rivers and streams which emerge from springs (Rajko's Stream which emerges from the Rajko's Cave and Pasko's River that emerges from the Pasko's Cave, as well as several other smaller streams). After a few hundred meters, Mali Pek flows into the Veliki Zaton Lake and then flows through Pemska Street and through Majdanpek. It cuts through the Copper Mine until it reaches the factory that produces copper pipes where it flows into Veliki Pek River, which comes from the direction of Jasikovo, and together they form the Pek River.

1.4. Veliki Pek river basin

The source of the Veliki Pek River is located in the Homolje mountains. The length of Veliki Pek is about 28 km and the rivers Jagnjilo and Boža's River form it. The Jagnjilo River flows from the source located in Jasikovo village, and the source of Boža's River is located in Vlaole village. Near the centre of Jasikovo village, Jagnjilo River and Boža's River form Veliki Pek which further flows through Leskovo village. In the Debeli Lug village, Veliki Pek merges with Mali Pek on an extended area called Čekić at 290 meters above sea level (Majdanpek municipality). When it exits the extended area Čekić, the Pek River enters Volujska canyon which is 25 km long and formed of limestone rocks that are 200-320 m deep. When it exits the Volujska canyon, Pek enters Zvižd and flows for another 31.5 km. The narrowing at Neresnica village forces Pek to divide into two areas, the upper Neresnička plain, which is 7.5 km long and 1-2 km wide, and lower Kučevska plain, which is 6 km long and 1.5 km wide. Pek can flood both plains after heavy rain in a belt that is 100-150 m wide. Downstream from

Kučevo, Pek goes through Kaonska gorge that is 13.5 km long and is formed of limestone rocks that are 250 m deep. Pek exits Kaonska gorge at Lješnica village, and from that point it flows through the fertile Braničevo district for 32.5 km until it reaches the mouth of the river. Here, the riverbed of Pek can be 12-15 m wide in summer and up to 40 m wide in spring. This is the point where new course of the Pek River begins which flows into the Đerdap Lake with a new riverbed, east of Veliko Gradište. When the water levels in Đerdap Lake are high, water from Danube can penetrate about 2.5 km upstream into the Pek riverbed and slow down the water and interfere with sedimentary deposits. The coastal protection is not adequately performed and the embankments are not designed to withstand the high water levels of the Danube, but only the high water levels of the Pek River. Therefore, the river valley of the lower course of the Pek River where the water slows down can be flooded by the water from the Đerdap Lake.

1.5. **The Porečka River**

The Porečka River is about 50 km long and it originates from Šaška and Crnajka Rivers which meet at Miloševa Kula village. It is located in eastern Serbia and it flows into the Danube at its 23rd km near Donji Milanovac. The Porečka river basin and central area of the Đerdap gorge are surrounded by Liškovac and Miroč mountains, and together they form the Poreč area.

2. Pollutants of the **Pek and Poreč Rivers**

The municipality of Majdanpek is located between Kučajske Mountains, Homolje, and Đerdap gorge and is surrounded by the Danube, Pek River, and Porečka River. The municipality covers an area of 1,000 km² [10]. The rivers Veliki and Mali Pek flow through the Majdanpek Municipality and these two rivers form the Pek River in Debeli Lug village. The area of Pek river basin is located in the southwest part of the municipality.

Drinking water in the municipality of Majdanpek, whose population is 18,370 according to the 2011 census, is obtained from the reservoir "Pustinjak" (dam was built in 1973 and it has a volume of 150,000 m³, average depth of 3 m, and its length is 500 m), which is located near the riverbank of Veliki Pek, and the reservoir "Veliki Zaton" on the river Mali Pek. Both reservoirs are alluvial type aquifers.

According to the Local Environmental Action Plan (LEAP 2003) for the Bor District and the Spatial Plan for the municipality of Majdanpek, there are 10 natural resources under protection in this municipality. These are mainly natural reserves and natural treasures spread over an area of 1,046 ha with different species of flora and fauna, five of which belong to the National Park Đerdap and cover an area of 506 ha. The northern part of the municipality of Majdanpek is located in the wider protected zone of the Đerdap National Park (according to the IUCN classification). Due to the mining works, which cover almost 1/3 of the total urban area, the environment is extremely degraded 7-8 km southwest of the NP and west of Majdanpek. The possibility for restoration of natural resources and rich biodiversity represent great potential for permanent development and preservation of this region.

The sewage system in Majdanpek discharges wastewater into Mali Pek River without the prior treatment [11]. The presence of copper, gold, iron, lead, zinc, and pyrite in on the territory of Majdanpek, as well as

agricultural production and use of artificial fertilizers and pesticides, contribute to the deterioration of surface waters quality.

The copper mine in Majdanpek (Serbia Zijin Bor Copper - Copper Mine Majdanpek) is located near the Romanian and Bulgarian borders, at approximately 210 km from Belgrade and about 15 km from the Danube. The mining complex is located in a predominantly hilly area south of Majdanpek at the altitude of 400 to 600 m. Fifty-seven percent of the territory in the municipality has the gradient of the land higher than 20, while only 8% of the territory is flat. The sediment and soil in Majdanpek have been extensively explored for more than three decades. There are two open pits in Majdanpek: South Mining District and North Mining District. The exploitation of copper ore in Majdanpek started back in 1955 and the development plan of the complex included the opening of an open pit, the construction of flotation and other necessary facilities, and construction of an urban settlement as well. Besides to open pits, the mining complex also includes a crushing plant (primary, secondary, and tertiary), flotation, two tailings (Šaški Potok and Valja Fundata), tailings dams in the upper part of the Šaška River, and three main areas for depositing overburden that are located around the open pits.

Mining activities done on the territory of the Majdanpek municipality, the development and application of new technologies for the maximal use of useful components, and constant increase of capacities and usage of space, have had serious consequences for the environment over time. The negative impact is primarily indicated by the production of various types and quantities of industrial waste, pollution of water, air and soil, as well as deterioration of the environmental quality. Industrial waste in Majdanpek includes waste and residue from the mining activities. It is mostly disposed of in the open or in the area with appropriate facilities. The overburden from the open pits is disposed of in the vicinity of the pits without prior preparation of the site or protection of the surrounding settlements. Flotation tailings is mainly deposited in the valleys of the rivers and streams. There are two tailings sites for the disposal of flotation tailings from South and North Mining District. The Šaški Potok tailings operated only from 1989 to 1995. The current tailings Valja Fundata, which

is located southwest of the South Mining District, has been used since 1995. Below the tailings dam, there is a concrete canal used for the collection of drainage water and pump station that pumps back drainage water back to flotation.

The contamination of surface waters in the Majdanpek area can also be caused by heavy rain and snow melting when sudden torrents wash away the material from the sides of the tailings dam. Likewise, the water in the flotation tailings pond and open pits (South Mining District and North Mining District) can cause contamination of groundwater and surface waters. The negative impact of both tailings sites can be noticed in:

- Degradation of large areas and changes in relief due to the deposition of large quantities of flotation tailings,
- Dispersion of dust from the tailings due to air currents or torrents caused by heavy rain, which can wash away solid particles from the sides of the tailings dam, and
- Discharge of chemically polluted water that may contain flotation reagents, dissolved copper ions, zinc, arsenic, mercury, and cadmium, as well as calcium and magnesium ions into the watercourse.

The watercourse is affected by mining works because the drainage of the water from the mines and outflow of the water from the tailings is directed towards the Šaška and Mali Pek Rivers without prior purification. Wastewater generated during the flotation in copper mines (concentrate thickener and other liquids) pollutes the Veliki Pek River, while wastewater from crushing facilities and heavy vehicles workshop pollutes the Mali Pek River. The negative impact caused by the discharge of chemically polluted water in watercourses at Šaški Potok tailings was solved by the construction of a dam and a retention basin of about 180,000m³ for flood wave attenuation. This water is then pumped into a sediment basin at Valja Fundata tailings.

A certain amount of drainage water from Valja Fundata tailings is discharged into the Veliki Pek River. Regardless of the fact that it is mechanically purified water, the presence of the dissolved harmful components, such as flotation reagents and heavy metal salts, causes

pollution of Veliki Pek. The fact that the water from filtration with similar characteristic is occasionally discharged into Veliki Pek should be taken into consideration as well. The mine has a system for the collection of this water, which is again used for the flotation process, and this system eliminates the harmful effect of discharging polluted water into the watercourse [10]. The first tailings seepage occurred in 1963, it lasted for a short period of time and then stopped without any intervention. The second seepage occurred in 1974 and it lasted for several days until all water from the sediment basin flowed into Veliki Pek carrying with it large amounts of sludge. This breach, as well as seepage of large amount of polluted water with flotation sludge, caused great damage to the environment in the downstream part of Veliki Pek [10]. An example that shows how a disaster can endanger a dam on a flotation tailings and the environment occurred in 1996 at the Šaški potok tailings. Due to the lack of mechanization the earth dam that was planned was not upgraded (filter above the drainage collector) which is why the tailings site was not used three years before the breach occurred. In the spring of 1996 snow melted due to the heavy rain. Due to low temperature, a layer of ice formed on the surface of the flotation tailings. The ice prevented atmospheric water and water that was result of snow melting from the surrounding hills to enter the drainage system as seepage water. The water level in the basin rose and water began to overflow the dam. Wet flotation tailings started to move and eroded the dam. The retention basin could not take such amount of tailings, it was filled to the top, and then 70,000 m³ of water and 37,000 m³ of tailings flowed into the stream and the Porečka River. The material that spilled from the tailings flowed into the watercourse and it was deposited along the riverbank, thus polluting its watercourse and other springs along the way.

Based on the fact that drinking water could become a scarce resource in the future, water quality assessment is becoming increasingly relevant. Current problems related to water pollution require ecological classification and identification of the most important parameters that can affect the change in water quality. The assessment of water is often

difficult to interpret when great number of elements of quality is analysed, because each element can indicate different class of quality.

3. Applied legal regulations

3.1. Aim of the study

The impact mining activities in Majdanpek have on the Danube was analysed in this study. It included the analysis of the quality of surface waters and sediments that were in the immediate vicinity of the mine in the area of the municipality of Majdanpek. Moreover, the analysis of the quality of the Pek River at Veliko Gradište and Porečke River at Donji Milanovac, which represented the most remote points covered by the study, was performed as well.

3.2. Limit values of pollutants in surface waters and sediments

According to the Regulation on Determining Water Bodies of Surface and Groundwater [12], the Pek River (measuring points Ujevac and Braničevo) is classified as a Type 2 river – large rivers, medium sediment dominance, except for the rivers in the Pannonian Plain/Type 3 – small and medium watercourses, altitude up to 500m, and dominance of large subsoil.

Limit values for measured parameters are defined in the same Regulation, as well as in the Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of groundwater [6] and the Regulation on emission limit values of polluting substances in surface and groundwater's and deadlines for their achievement [7]. The limit values are given in Table 1.

Table 1 Limit values for parameters analysed in surface waters [6, 7]

Parameter	Unit	Limit value				
		I class*	II class*	III class*	IV class*	V class*
pH		6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	<6.5 or <8.5
Dissolved oxygen (DO)	mgO ₂ /L	8.5	7	5	4	< 4
Suspended matter	mg/L	25	25	-	-	-
Ammonium	mg/L	0.05	0.10	0,8	1,0	>1.0
Nitrates	mg/L	1.5	3.0	6,0	15	>15
Nitrites	mg/L	0.01	0.03	0,12	0,3	>0.3
Total phosphorus	mg/L	0.05	0.2	0,4	1	>1
Orthophosphate	mg/L	0.02	0.1	0,2	0,5	>0.5
Sulphates	mg/L	50	100	200	300	>300
BPK ₅	mgO ₂ /L	1.5(Type 3) 1.8(Type 2)	5(Type 3) 4.5(Type 2)	6(Type 3) 6(Type 2)	20(Type 3) 20(Type 2)	>20(Type 3) >20(Type 2)
HPK (permanganate method)	mgO ₂ /L	5	10	20	50	>50

*I class – The class description corresponds to the high ecological status. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids and salmonids), and they can be used for the following purposes: drinking water supply with prior filtration and disinfection treatments, bathing and recreation, irrigation, and industrial use (process and cooling water).

II class – The class description corresponds to good ecological status. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids) and can be used for the same purposes and under the same conditions as surface waters in class I.

III class – The class description corresponds to moderate ecological status. Based on the limit values of quality elements, surface waters in this class provide living conditions and protection of cyprinids and can be used for the following purposes: drinking water supply with prior coagulation, flocculation, filtration, and disinfection treatment, bathing and recreation, irrigation, and industrial use (process and cooling water).

IV class – The class description corresponds to poor ecological status. Based on the limit values of quality elements, surface waters in this class can be used for the following purposes: drinking water supply with a combination of previously mentioned treatments and advanced treatment methods, irrigation, and industrial use (process and cooling water).

V class – The class description corresponds to bad ecological status. Surface waters in this class cannot be used for any purpose.

Limit values for metals are defined in Regulation on emission limit values of polluting substances in surface and groundwater's and deadlines for their achievement [7] and Regulation on emission limit values of

priority and priority hazardous substances which pollute surface waters and deadlines for their achievement [6] and they are shown in Tables 2 and 3.

Table 2 Limit values of pollutants in surface waters [7]

Parameter	Unit	Limit values ⁽¹⁾				
		Class I ⁽²⁾	Class II ⁽³⁾	Class III ⁽⁴⁾	Class IV ⁽⁵⁾	Class V ⁽⁶⁾
Arsenic	[µg/L]	<5 (or PN)	10	50	100	>100
Copper	[µg/L]	5 (T=10)	5 (T=10)	500	1000	>1000
		22 (T=50)	22 (T=50)			
		40 (T=100)	40 (T=100)			
Zinc	[µg/L]	112 (T=300)	112 (T=300)			
		30 (T=10)	300 (T=10)	2000	5000	>5000
		200 (T=50)	700 (T=50)			
		300	1000			
		(T=100)	(T=100)			
Chromium (total)	[µg/L]	500	2000			
		(T=500)	(T=500)			
		25 (or PN)	50	100	250	>250
Iron (total)	[µg/L]	200	500	1000	2000	>2000
Manganese (total)	[µg/L]	50	100	300	1000	>1000

(1) Unless otherwise stated, values are expressed as total concentrations in the sample

(2) The class description corresponds to the high ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids and salmonids), and they can be used for the following purposes: drinking water supply with prior filtration and disinfection treatments, bathing and recreation, irrigation, and industrial use (process and cooling water).

(3) The class description corresponds to the good ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class provide conditions for the functioning of the ecosystem, existence and protection of fish (cyprinids) and can be used for the same purposes and under the same conditions as surface waters in class I.

(4) The class description corresponds to the moderate ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class provide living conditions and protection of cyprinids and can be used for the following purposes: drinking water supply with prior coagulation, flocculation, filtration, and disinfection treatment, bathing and recreation, irrigation, and industrial use (process and cooling water).

(5) The class description corresponds to the poor ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Based on the limit values of quality elements, surface waters in this class can be used for the following purposes: drinking water supply with a combination of previously mentioned treatments and advanced treatment methods, irrigation, and industrial use (process and cooling water).

(6) The class description corresponds to the bad ecological status based on the classification provided in the Regulation which prescribes parameters for ecological and chemical status of surface waters. Surface waters in this class cannot be used for any purpose.

Table 3 Environmental quality standards for the first and second group of priority substances [8]

Hazardous pollutant	Average annual concentration (µg/l)	Maximal allowed concentration (MAC) (µg/l)
Cadmium and cadmium compounds ¹	<0.08 (class I)	<0.45 (class I)
	0.08 (class II)	0.45 (class II)
	0.09 (class III)	0.6 (class III)
	0.15 (class IV)	0.9 (class IV)
	0.25 (class V)	1.5 (class V)
Mercury and mercury compounds		0.07
Lead and lead compounds	1.2 ³	14
Nickel and nickel compounds	4 ³	34

¹ For cadmium and its compounds, the value of environmental quality standards varies depending on the water hardness, which is categorized into five classes (class 1: <40 mg CaCO₃/l, class 2: 40 to <50 mg CaCO₃/l, class 3: 50 to <100 mg CaCO₃/l, class 4: 100 to <200 mg CaCO₃/l, and class 5: ≥200 mg CaCO₃/l). ³ These values of environmental quality standards indicate the concentrations of the substance that are bioavailable.

Limit values for measured parameters are prescribed by the same Regulation on limit values of pollutants in surface and groundwater and sediment and deadlines for their achievement [7] and are given in Table 4.

Table 4 Limit values for assessment of sediment quality status and trend [7]

Parameter	Unit	Target value	Maximal allowed concentration	Remediation value
Arsenic (As)	mg/kg	29	42	55
Cadmium (Cd)	mg/kg	0.8	6.4	12
Chromium (Cr)	mg/kg	100	240	380
Copper (Cu)	mg/kg	36	110	190
Mercury (Hg)	mg/kg	0.3	1.6	10
Lead (Pb)	mg/kg	85	310	530
Nickel (Ni)	mg/kg	35	44	210
Zink (Zn)	mg/kg	140	430	720
Mineral oils	mg/kg	50	3000	5000
Polycyclic aromatic hydrocarbons (PAH) ⁽¹⁾	mg/kg	1	10	40

Parameter	Unit	Target value	Maximal allowed concentration	Remediation value
Naphthalene	mg/kg	0.001	0.1	
Anthracene	mg/kg	0.001	0.1	
Phenanthrene	mg/kg	0.005	0.5	
Fluoranthenes	mg/kg	0.03	3	
Benzo(a)anthracene	mg/kg	0.003	0.4	
Chrysene	mg/kg	0.1	11	
Benzo(k)fluoranthene	mg/kg	0.02	2	
Benzo(a)pyrene	mg/kg	0.003	3	
Benzo(g,h,i)perilen	mg/kg	0.08	8	
Indeno(1,2,3-cd)pyrene	mg/kg	0.06	6	
Polychlorinated biphenyls (PCB) ⁽²⁾	µg/kg	20	200	1
DDD	µg/kg	0.02	2	
DDE	µg/kg	0.01	1	
DDT	µg/kg	0.09	9	
DDT totla ⁽³⁾	µg/kg	10	-	4000
Aldrin	µg/kg	0.06	6	
Dieldrin	µg/kg	0.5	450	
Endrin	µg/kg	0.04	40	
Cyclodiene pesticides ⁽⁴⁾	µg/kg	5	-	4000
α-HCH	µg/kg	3	20	
β-HCH	µg/kg	9	20	
γ-HCH (lindan)	µg/kg	0.05	20	
HCH total ⁽⁵⁾	µg/kg	10	-	2000
Alfa-endosulfan	µg/kg	0.01	1	4000
Heptachlor	µg/kg	0.7	68	4000
Heptachlor-epoxide	µg/kg	0.0002	0.002	4000

⁽¹⁾ The parameter refers to the sum of the following compounds: naphthalene, anthracene, phenanthrene, fluoranthene, benzo (a) anthracene, chrysene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (g, h, i) perylene, indeno (1, 2, 3-cd) pyrene.

⁽²⁾ The parameter refers to the sum of the following individual compounds: PCB 28, 52, 101, 118, 138, 153, and 180.

⁽³⁾ The parameter refers to the sum of DDT, DDD, and DDE.

⁽⁴⁾ The parameter refers to the sum of aldrin, dieldrin, and endrin.




⁽⁵⁾ The parameter refers to the sum of the four isomers of hexachlorocyclohexane: α-HCH, β-HCH, γ-HCH, and δ-HCH.






4. Materials and methods




4.1. Sampling sites

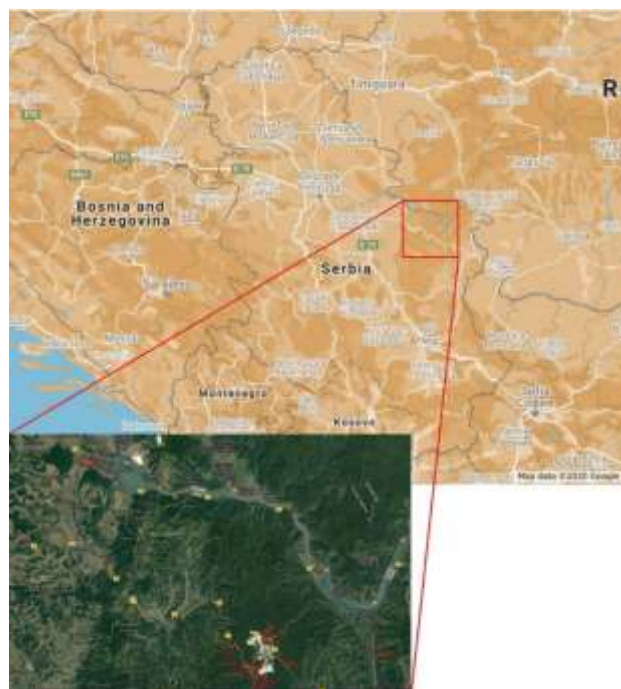
Sampling was performed during three monitoring campaigns (in July, September, and October) at 12 sampling sites located in I, II, and III level of protection areas. Table 5 and Map 2 represent names and coordinates of surface waters and sediments sampling sites.

Table 5 Sampling sites for surface waters and sediments

Sample number	Sampling site name	GPS Coordinates	Sampling site location (taken from https://www.google.com/earth/ 17.11.2020.)
SS 1	Mali Pek at the entrance of the town	N 44°25' 47.59517" E 21°55' 58.72471"	
SS 2	Mali Pek River after the inflow of the city sewage system	N 44°25' 17.97584" E 21°56' 5.24429"	
SS 3	Mali Pek after inflow of drainage water from the North Mining District dump and wastewater from grinding	N 44°22' 46.96202" E 21°54' 7.90727"	

SS 4	Veliki Pek – before surface waters inflow from the cave, below Valja Fundata tailings	N 44°22' 5.78376" E 21°55' 14.96092"	
SS 5	Surface waters from the cave below the Valja Fundata tailings	N 44°21' 51.4925" E 21°54' 43.38354"	
SS 6	Veliki Pek downstream after SS 4 and SS 5 merge	N 44°21' 58.98295" E 21°55' 2.33636"	
SS 7	Veliki Pek after the inflow of wastewater from the filtration and before merging with Mali Pek	N 44°22' 43.70676" E 21°53' 51.45986"	
SS 8	Surface waters after Veliki and Mali Pek merge	N 44°23' 18.36439" E 21°53' 16.30224"	
SS 9	Veliki Pek – tourist site Ujevac (the influence of tailings)	N 44°24' 54.2403" E 21°52' 22.86861"	

SS 10	Pek River (Braničevo) before it flows into Danube	N 44°42' 12.51062" E 21°32' 1.44856"	
SS 11	Šaški potok tailings	N 44°23' 45.15633" E 21°57' 55.24581"	
SS 12	Porečka River	N 44°24' 40.49354" E 22°10' 20.45027"	



Map 2a. Location of the sampling sites ("Serbia and Majdanpek." Map. Google Maps, Google, 07 December 2020. Web. 07 December 2020)



Map 2b. Location of the sampling sites ("Serbia and Majdanpek." Map. Google Maps, Google, 07 December 2020. Web. 07 December 2020)

Photo gallery of water sampling campaigns during three monitoring campaigns, summer – autumn of 2020:



(SS1) Water sampling on Mali Pek at the entrance of the town



(SS2) Water sampling on Mali Pek River after the inflow of the city sewage system



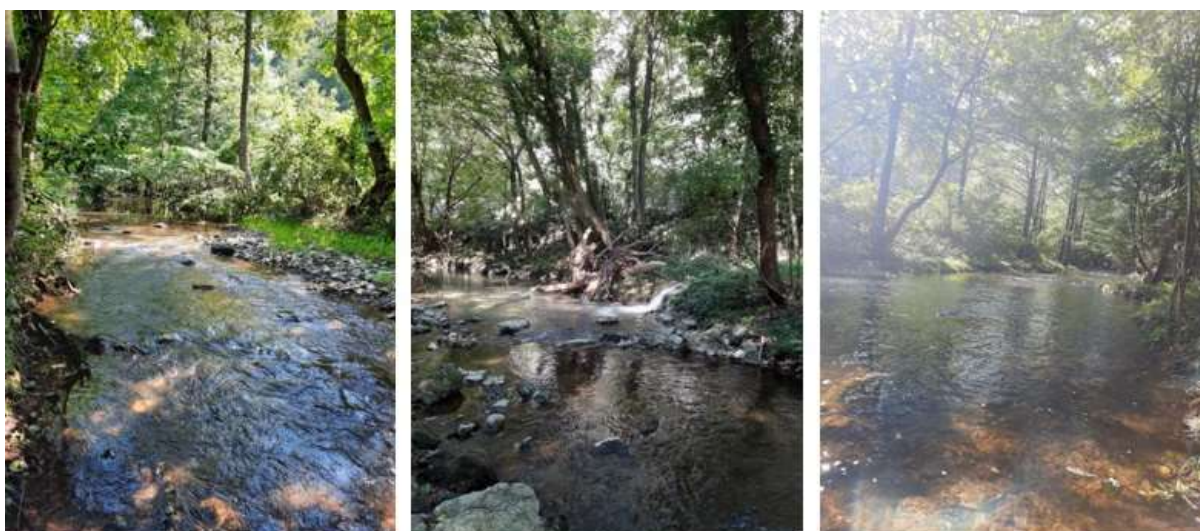
(SS3) Water sampling on Mali Pek after inflow of drainage water from the North Mining District dump and wastewater from grinding



(SS4) Water sampling on Veliki Pek – before surface waters inflow from the cave, below Valja Fundata tailings



(SS5) Water sampling on Surface waters from the cave below the Valja Fundata tailings



(SS6) Water sampling on Veliki Pek downstream after SS 4 and SS 5 merge



(SS7) Water sampling on Veliki Pek after the inflow of wastewater from the filtration and before merging with Mali Pek



(SS8) Water sampling on Surface waters after Veliki and Mali Pek merge



(SS9) Water sampling on Veliki Pek – tourist site Ujevac (the influence of tailings)



(SS10) Water sampling on Pek River (Braničevo) before it flows into Danube



(SS11) Water sampling on Šaški potok tailings



(SS12) Water sampling on Porečka River



View of sediments sampling (selection)

Water sampling was provided by the telescopic sampler with the sampling vessel (Figure 1). Samples were taken at the central part of the watercourse and at 50cm of depth. Air and water temperature, pH, dissolved oxygen (DO), conductivity, and total dissolved solids (TDS) were measured at the site. Samples of river sediment were taken at a depth of 1.5–2 m, depending on the measuring point, and transported in plastic containers to the laboratory, where the analysis of heavy metals and metalloids and granulometric composition were performed. For laboratory analysis water samples were transported to the laboratory in mobile freezers at the temperature of 4°C.



Figure 1. Water and sediment sampling

4.2. Terrain measurements

The multi-parameter handheld instrument (Lovibond® Water Testing Tintometer® Group SensoDirect 150 (Set 1) pH / Con / TDS / Oxi / Temp) was used for the determination of dissolved oxygen, conductivity, total dissolved solid, pH and electroconductivity at the sampling site (Figure 2). In laboratory, the concentration of ammonia, nitrates, nitrites, sulphates, phosphates, chemical oxygen demand (COD), biological oxygen demand (BOD), and heavy metals and metalloids were determined.



Figure 2. Determination of parameters using a multi-parameter measuring instrument

4.3. Laboratory measurements

The laboratory analysis of the ammonia was provided the same day as the sampling. Samples for nitrates, nitrites and phosphates were conserved. Conservation was performed by measuring 125 mL of collected samples in which 0.5 mL of concentrated H_2SO_4 was added. Samples for sulphates were stored at 4°C prior the analysis.

Samples for metals analysis were conserved with nitrous acid (10 mL of sample was weighed and transferred to a 15 mL cuvette and 1 mL of concentrated HNO_3 was added) and kept at the 4°C prior the analysis. However, all the samples were analysed within the 7 days form sampling campaigns. In addition, the concentration of heavy metals and metalloids in the sediments was determined, as well as the granulometric composition of the sediments.

Photo gallery of laboratory analysis:





Methods for parameter analysis are presented in Table 6.

Table 6. Methods for parameter analysis in samples

Parameters	Measurement methods
Temperature of water, pH value, dissolved oxygen, electrical conductivity, total dissolved solids	Handheld instrument (Lovibond® Water Testing Tintometer® Group SensoDirect 150 (Set 1) pH/Con/TDS/Oxi/Temp)
Temperature of air	Thermometer
BOD	Manometric, equipment manufacturer's instructions
COD	Permanganate method/Spectrophotometry
NH ₄ -N [Ammonium ion]	Spectrophotometry, User manual for Photometer HANNA HI 83200 (Adaptation of the ASTM Manual of Water and Environmental Technology, D1426-92, Nessler method)
NO ₃ -N [Nitrates]	Spectrophotometry, User manual for Photometer HANNA HI 83200 (Adaptation of the cadmium reduction method)
NO ₂ -N [Nitrites]	Spectrophotometry, Use manual for Photometer HANNA HI 83200 (Adaptation of the EPA Diazotization method 354.1)
PO ₄ ³⁻ [Phosphates]	Spectrophotometry, Use manual for Photometer HANNA HI 83200 (Adaptation of the Ascorbic acid method)
SO ₄ ²⁻ [Sulphates]	Spectrophotometry, Use manual for Photometer HANNA HI 83200 (Sulphate is precipitated with barium chloride crystals)
Metals and metalloids in water samples	ICP-OES equipment - Perkin Elmer Optima 8300 and version 5.0 WinLab softwer.
Metals and metalloids in sediments	XRF equipment (BRUKER, Germany, S1 TITAN Mod-800)
Granulometric composition of sediments	Laser size analyser (FRITSCH, Germany, ANALYSETTE 22 NanoTec)

Metal and metalloids content measurements were performed on an ICP-OES instrument Perkin Elmer Optima 8300 and version 5.0 of WinLab software. The standards used to prepare calibration standards were Perkin Elmer standards: Interferents A (N9303827) (21215 mg/L Cl, 3000 mg/L Ca,

2500 mg/L Fe, Na, 2000 mg/L C, 1000 mg/L Al, K, Mg, P, S, 20 mg/L Mo, and Ti), and Instrument calibration standard 2 (N9301721) (100 mg/L Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, and Zn). Demineralized water was used to dilute the standards. After obtaining the calibration curves, only those with a linearity greater than 0.9998 were used. To check the long-term stability of the measurements, the quality control standard Perkin Elmer Quality Control Standard 21 (N9303837) (100 mg/L As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, and Zn) was used. The allowed deviation from the quality control standard was $\pm 5\%$. Before the start of the analysis of each batch, the detection limit was calibrated and maintained. Collected and conserved samples were analysed directly without any prior dilution.

Determination of arsenic (As) and mercury (Hg) concentration was performed on the same instrument with sample entry using a Perkin Elmer FIAS 100 device. The injection loop on the device has a volume of 500 μl .

To determine the arsenic content, all samples and standards were prepared in the same way. 5 mL of the sample was weighed and 1 mL of reducing reagent and 5 mL of concentrated HCl were added. The sample was left to stand for 30 min and entered into a FIAS device for analysis. 10% HCl was used as the carrier reagent, and NaBH₄ solution was used to generate the hydride. A solution containing 5% (w/v) KJ and 5% (w/v) ascorbic acid in deionized water was used as the reducing reagent, while the hydride generating reagent contained 0.2% (w/v) NaBH₄ and 0.05 % (m/v) NaOH in deionized water. Before measuring each batch, calibration and determination of the detection limit were performed.

Determination of mercury content was performed without prior sample preparation. Before the analysis, only the preparation of working standards was performed. 3% HCl was used as the carrier reagent in the FIAS device. A solution containing 1.1% (w/v) SnSi₂ and 3% (v/v) HCl in deionized water was used as a reducing agent for the release of elemental mercury. Before measuring each batch, calibration and determination of the detection limit were performed.

5. Results and discussion

5.1. Physicochemical indicators of water quality

The physicochemical parameters of the analysed water samples at twelve defined measuring sites (SS1 - SS12) in the period from July to October 2020 are presented below. Parameters such as dissolved oxygen (DO), nutrient content, total dissolved solids (TDS) then chemical (COD), and biological oxygen demand (BOD) were analysed as physicochemical indicators of water quality. In addition, values of air and water temperature, colour and odour of samples, as well as water flow are shown in Tables 7 and 8.

The values of air and water sample temperatures, as well as the sampling date are summarized in Table 7.

During the sampling period, the air temperature was from 12.8 °C to 35 °C, while the temperature of the water samples was from 11.9 °C to 22.1 °C. The organoleptic parameters (colour and odour) for each sample are also shown in Table 7. All samples during the monitoring period were odourless, except at location 2 in July and September where an unpleasant odour was recorded. Since SS 2 is a sample of water from Mali Pek River after the inflow of the city sewage system, an unpleasant odour was expected. In September, during the sampling period, a smaller flow of water was noticed, which also affected the unpleasant smell of the mentioned sample. The yellow colour of the samples was noticed during July and September in sites 3, 8, and 9. The turbidity of the samples at locations 3, 8, and 9 during September and October was observed, while at locations 2, 5, 7, and 9 it was observed in July. The measured flow values at defined locations are presented in Table 8. In September, during the sampling period, a smaller flow of water was noticed, which also affected the intensity of the unpleasant odour of the sample from the river Mali Pek after the inflow of the city sewage. According to the data in Table 8, it can be noticed that there was a drying up of Šaški potok in September and October.

Table 7. Obtained values of air and water temperatures and organoleptic characteristics of water samples

Code of the sample	Date of sampling			Air temperature (°C)			Water temperature (°C)			Sample colour/turbidity			Sample odour		
SS 1	23 July 2020	9 September 2020	9 October 2020	32.5	35	17.9	20.4	18.7	13.8	without	without	without	without	without	without
SS 2				24.1	28.6	16	22.1	20.6	15	turbidity	without	without	unpleasant	unpleasant	without
SS 3				34.3	34.2	23.3	20.2	18.6	14.2	yellowish	yellow, turbidity	grey, turbidity	without	without	without
SS 4				18.3	16	13.2	17.6	15.1	12.9	without	without	without	without	without	without
SS 5				12.8	15.8	12.9	12	12	11.9	turbidity	without	without	without	without	without
SS 6				20.9	16.5	15.3	17.1	14.6	13.1	without	without	without	without	without	without
SS 7				29.1	33.2	21.4	19.3	17.6	14.3	turbidity	without	without	without	without	without
SS 8				21.3	20.1	14.8	19.7	17.9	14.5	yellowish	yellow, turbidity	turbidity	without	without	without
SS 9				20.3	21.3	19.2	18.7	17.1	13.6	yellowish, turbidity	yellow, turbidity	without, turbidity	without	without	without
SS 10	21 July 2020	11 September 2020	7 October 2020	21.6	26.6	19.5	18.7	17.7	16.7	without	without		without	without	without
SS 11		9 September 2020	9 October 2020	16.8	17.5	17	15.8	16.9	14.3	without	without	without	without	without	without
SS 12		11 September 2020	7 October 2020	21	27.9	22.7	19.1	20.4	17.1	without	without	without, turbidity	without	without	without

Table 8. Water flow (m³/s) at selected sampling sites

Sampling site	July	September	October
SS 1	0.27	0.27	0.27
SS 2	0.2	0.2	0.2
SS 3	0.75	0.12	0.12
SS 4	0.62	0.059	0.72
SS 5	0.073	0.073	0.073
SS 6	0.65	1.04	1.17
SS 7	0.053	0.069	0.069
SS 8	1.04	0.41	0.5
SS 9	1.2	1.4	/
SS 10	8.0	0.9	0.9
SS 11	0.059	0.0	0.0
SS 12	0.66	0.0087	0.18

/ – no data

5.1.1. pH value

The pH value of the analysed samples is shown in Figure 3. In accordance with the Regulation on the parameters of ecological and chemical status of surface and groundwater [6], categories I, II, III and IV have the same limit values of pH. From the graph shown in Figure 3, it can be seen that the value of this parameter depended on the sampling period. Specifically, observing the results recorded in July and October, the pH values ranged from 6.92 to 8.88. However, in the period of September, the pH values of certain measuring points were significantly lower, at locations 3, 8 and 9, where the values were 3.49, 4.64, and 4.64, respectively, while at location 7, in September and October, the pH values were above 8.5 (9.12 and 8.88) and in that period the category of these waters would belong to class V. The lower pH value of the water sample at location 3 was probably a consequence of the inflow of drainage water from the Nort Mining District dump into the river Mali Pek. Also, it is assumed that the water from the filtration affected the pH value of the sample from the river Veliki Pek (SS 7). The pH value of the sample from

measuring point 8, after the merging of Mali and Veliki Pek, also indicated acidity. It is assumed that this was a consequence of the influence of Mali Pek (SS 3), which had a higher flow and lower pH value in the observed period compared to Veliki Pek (SS 7). The influence of tailings can be seen at location 9 (Velik Pek - Ujevac) where the pH value was also lower in September compared to July and October. Based on the presented results and in accordance with the Regulation on water classification [6], the analysed water samples can be classified in I category of surface water quality, except for samples 3, 7, 8, and 9 for a certain period. According to the obtained data, a significant impact of wastewater from the mining complex in Majdanpek can be noticed, especially in September and primarily on the river Mali Pek.

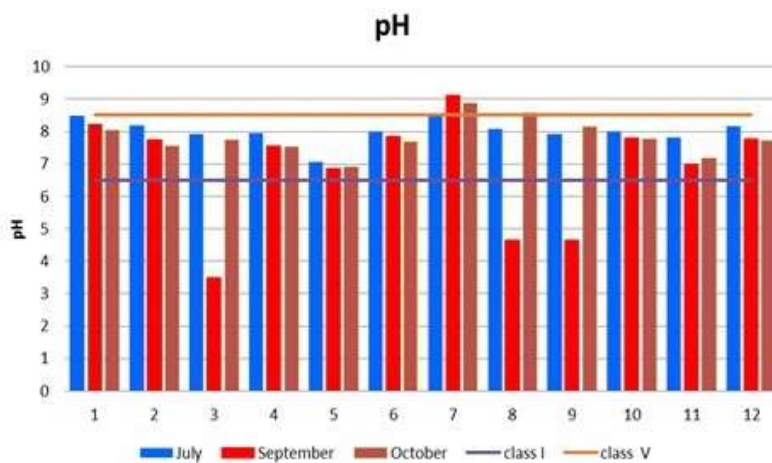


Figure 3 pH values of water samples

5.1.2. Dissolved oxygen

The results of measuring the content of dissolved oxygen are shown in Figure 4. At the analysed locations, the dissolved oxygen values ranged from 1.9 mg/L at measuring point 11 to 6.6 mg/L at measuring point 3. During the monitoring of dissolved oxygen content in July and September, significantly lower values were recorded at locations 2 and 11 compared to other measuring sites in the same period. This could indicate a significant load of these waters with organic matter [13]. In general, according to the Regulation on water classification [6] and based on the value of dissolved oxygen, the quality of these waters belonged to category II. Lower values of

dissolved oxygen in samples from the river Mali Pek (SS 2) were a consequence of the inflow of municipal wastewater.

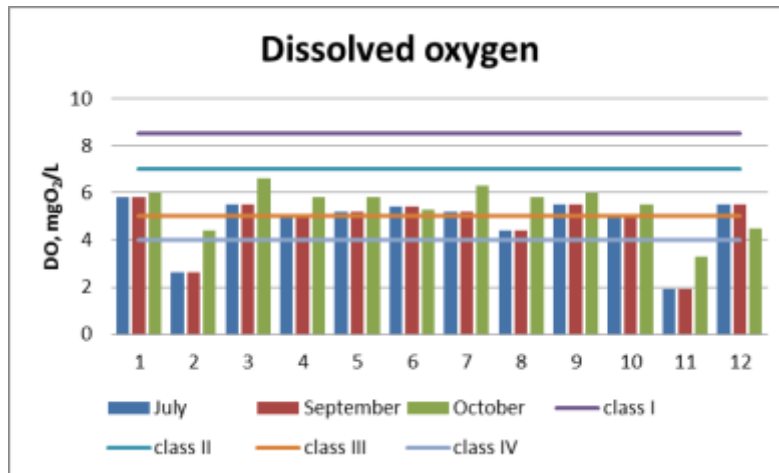


Figure 4 Dissolved oxygen in water samples

5.1.3. Chemical and biological oxygen demand

The chemical oxygen demand (COD) and biological oxygen demand (BOD) are shown in Figures 5 and 6. Obtained COD values ranged from 1.03 mgO₂/L to 10.95 mgO₂/L. Based on the results of COD, an increased value was observed on measuring sites 2 and 3 in comparison to the other sites, while in SS 6, 7, and 8 increases were observed only in a certain period. Based on this parameter, analysed water samples on SS 1, 4, 5, 9, 10, 11, and 12 can be classified in class I, while other samples would belong to class II water.

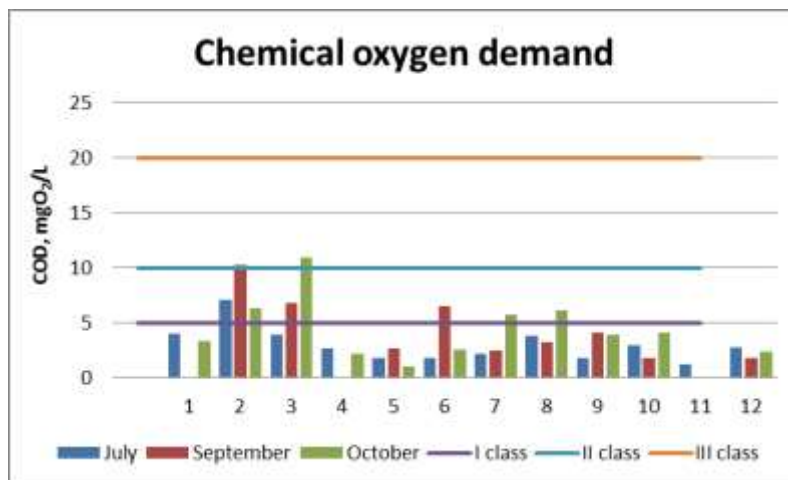


Figure 5 Chemical oxygen demand in water samples

According to the content of organic matter expressed as BOD in water, the values ranged from 0.5mgO₂/L to 42mgO₂/L. In accordance with the presented results and the Regulation on Water Classification [6], the BOD at SS 2, during September and October, exceeded the limit value for water class IV. The increased values of dissolved oxygen content, as well as the parameters of COD and BOD parameters on profile 2 indicated the load of organic matter which was a consequence of the inflow of the city sewage into the river Mali Pek. Also, lower water flow in September was reflected in an increase in BOD. In addition, the values of BOD in SS 3 in July (6.7 mgO₂/L) and SS 7 in September (8.8 mgO₂/L) were higher than the reference value for class III of surface waters, and the quality of these waters would belong to IV class. Other samples can be classified in category II of surface water quality.

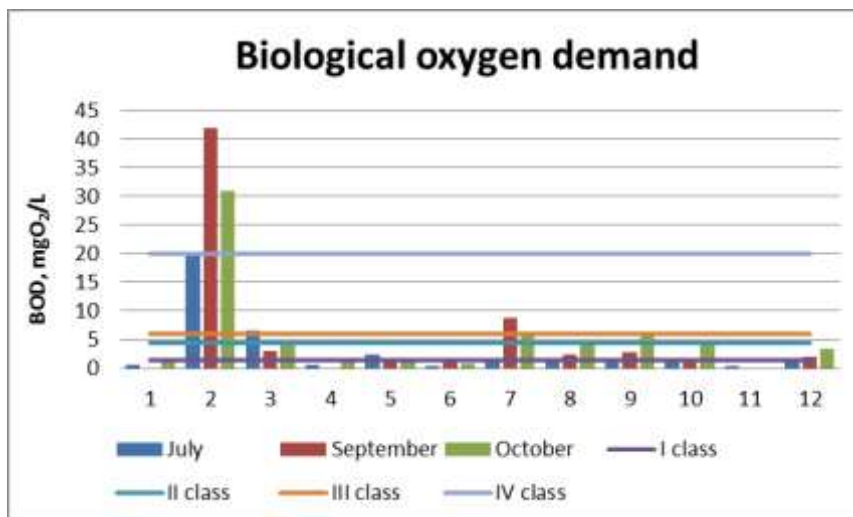


Figure 6 Biological oxygen demand in water samples

5.1.4. Electrical conductivity of water samples

Figure 7 shows the obtained results of electrical conductivity of the analysed samples. Based on the presented data, it can be noticed that higher values of electrical conductivity were recorded during September at all measuring points in regards to July and October due to the lower water flow in September compared to July and October. The highest value

was recorded at measuring point 3 during September (4.020 mS/cm), while the lowest value was detected at measuring point 1 in October (0.304 mS/cm). The water sample from Mali Pek (SS 3), which reflected the impact of the mining complex in Majdanpek, recorded the highest value of electrical conductivity. As noted in Table 8, the lower flow observed in this monitoring period was likely to increase the electrical conductivity. It is assumed that the increased values of electrical conductivity originated from the increased concentration of metallic and non-metallic ions in the specified sample. Also, a lower pH value was recorded at this location, which contributed to the increase in electrical conductivity due to the conductivity of hydrogen ions. Analysing the presented results, the influence of Mali Pek can be noticed at location 8, where the rivers Mali Pek and Veliki Pek merge. The sample taken from the river Veliki Pek (SS 9 – Ujevac) also had increased electrical conductivity in September, which can be related to the increased concentration of sulphate ions. Waters from the tailings of Šaški potok contributed to the increase of electrical conductivity at measuring point 11, while waters from the tailings of Valja Fundata affected the electrical conductivity of surface waters at location 5. Based on the electrical conductivity and according to the Regulation [7], the limit value for electrical conductivity of surface water of the category I is <1000 mS/cm, and based on this parameter the analysed water samples can be classified in the Ist category.

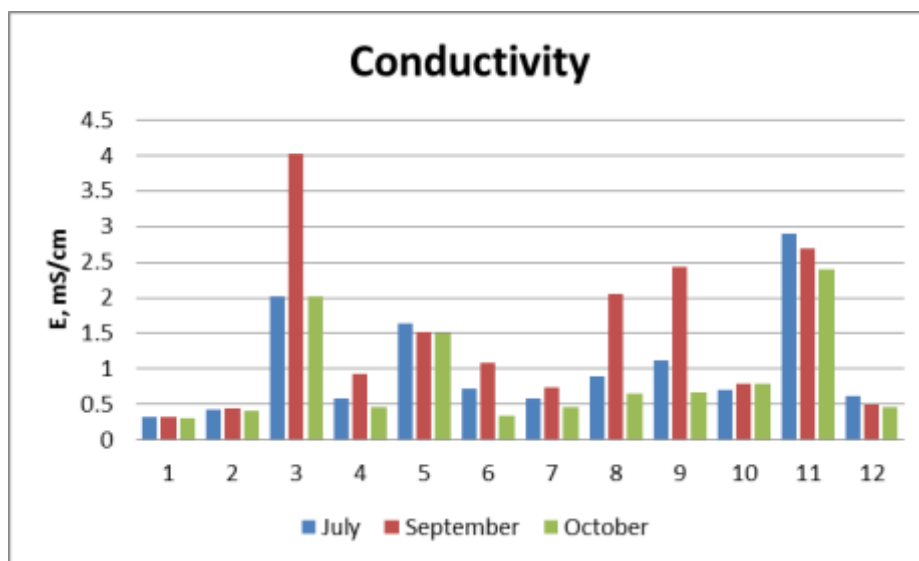


Figure 7 Electrical conductivity of water samples

5.1.5. Total dissolved solids

Figure 8 shows the content of total dissolved solids at measuring points 1–12 during the monitoring period (July–October). The highest content was recorded at location 5, with values 1091 ppm, 1014 ppm, and 982 ppm in July, September, and October, respectively. In addition, increased content was observed at location 3 (1331 ppm) in July.

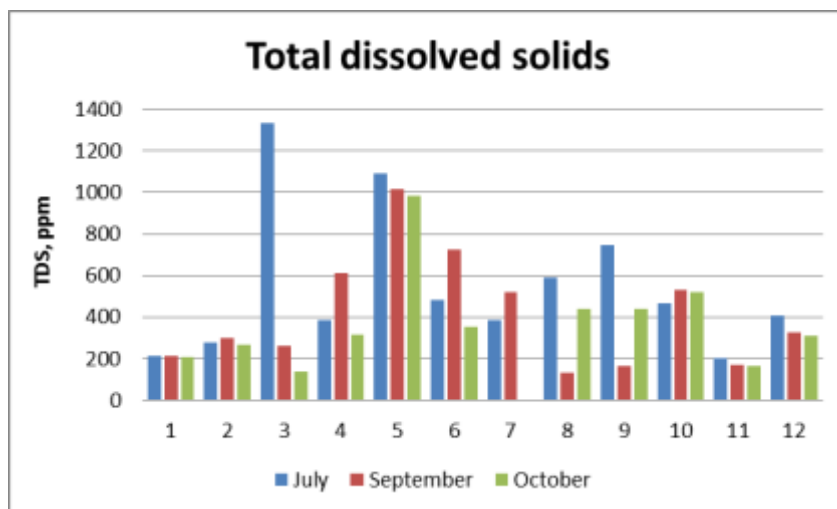


Figure 8 Total dissolved solids in water samples

5.2. Metal and metalloid content in water samples

The results of the metal content in the analysed water samples are presented below.

5.2.1. Arsenic

The presence of arsenic was determined only in September, at locations 3 (113.30 $\mu\text{g/L}$), 8 (39.40 $\mu\text{g/L}$) and 9 (39.64 $\mu\text{g/L}$). During the monitoring period at other sampling sites, arsenic concentrations were below the detection limits of the measuring instrument (0.0041 mg/L). According to the Regulation [7] and the concentration of arsenic, the water quality at sites 8 and 9 belonged to class III, while the sample from site 3 can be classified in category IV.

5.2.2. Cadmium

In the period of monitoring the cadmium concentration at selected locations (1–12), only during the month of September, the presence was detected at places 3 (109.24 $\mu\text{g/L}$), 8 (42.35 $\mu\text{g/L}$), and 9 (33.83 $\mu\text{g/L}$). According to the Regulation on limit values of priority and priority hazardous substances that pollute surface waters and deadlines for their achievement [8] and obtained results, it is observed that the concentration of cadmium in these places is above the maximum allowed value of 1.5 $\mu\text{g/L}$ for class V. At other sampling sites, concentrations of cadmium were below the detection limit of the measuring instrument (0.0019 mg/L).

5.2.3. Copper

The concentration of copper was observed in the analysed water samples at locations 3, 8 and 9, while at locations 2 and 7 the presence of this metal was recorded only in October (Figure 9). At locations 3, 8 and 9, the copper content was above the defined limits for category IV surface water quality. At other measuring points, the copper concentration was below the detection limit of the measuring instrument (0.0041 or 0.0034 mg/L). SS 3 represents a sample of water from Mali Pek and the increased concentration of copper ions in these waters is a consequence of the influence of the mining basin in Majdanpek. It is assumed that the increased content of copper ions is a consequence of the inflow of part of the water from the open pit South Mining District, in addition to the drainage waters from the North Mining District. Sample 9 was taken from the river Veliki Pek (Ujevac) and it is assumed that the tailings had an impact on the increased content of copper ions in these waters. Observing the results on the copper content at the SS 8 site, the influence of the Mali Pek River can be confirmed as already observed on the basis of other parameters (pH value, electrical conductivity). In addition, the increased concentrations of copper ions in September were correlated to the flow and pH value of these waters in the same monitoring period.

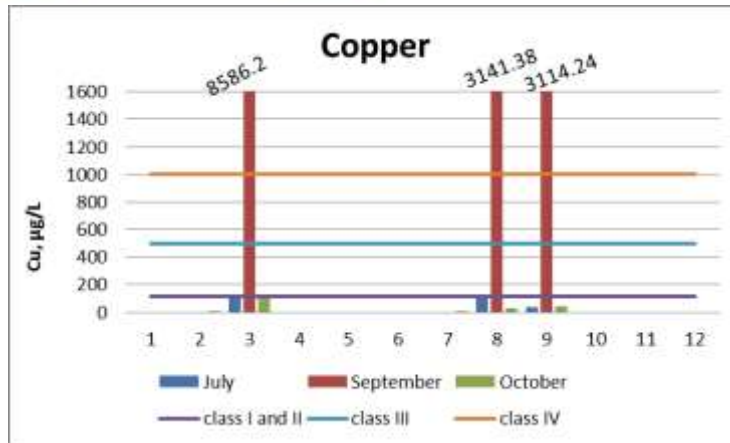


Figure 9 Concentration of copper in water samples

5.2.4. Iron

The concentration of iron in the analysed samples 3, 8, and 9 significantly increased compared to other profiles (Figure 10). Also, higher content at the mentioned locations was noticed in September compared to July and October. Based on the results and in accordance with the Regulation [7], the content of iron ions in these waters exceeded the concentrations for IV category of water quality. The presence of iron in the analysed period was not confirmed in the analysed sample from location 4, while at measurement points 6, 7, 10, and 11 the presence was confirmed only in July. Since ore containing pyrite and various oxide minerals of iron is processed in Majdanpek, this may be the reason for the presence of iron ions at the analysed locations 3, 8, and 9. The increased iron content in September was a consequence of the reduced water flow in this period.

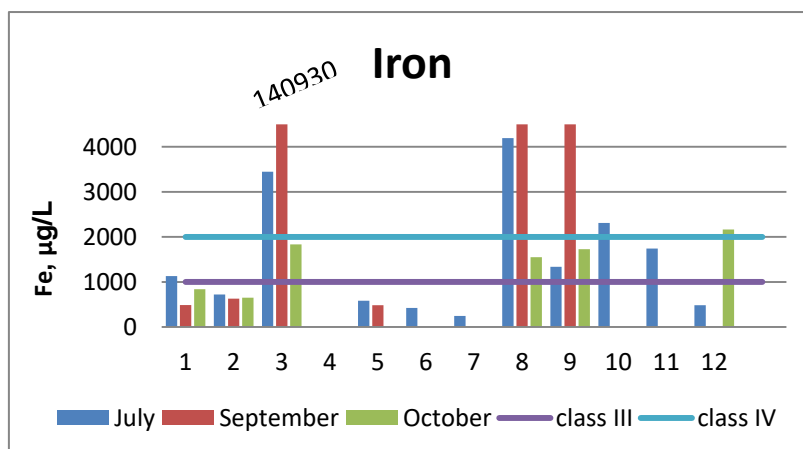


Figure 10 Concentration of iron in water samples

5.2.5. Manganese

The concentration of manganese (Figure 11) at sites 3 (10384.75 µg/L in July; 36919.44 µg/L in September; 12487.74 µg/L in October), 8 (2281.35 µg/L in July; 14715.58 µg/L in September), and 9 (2841.95 µg/L in July; 15408.48 µg/L in September) was higher than the prescribed value for class IV surface water quality [7], especially in the July–September monitoring period. Based on the manganese concentration at location 5 and in accordance with the Regulation [7], the quality of these waters belonged to category IV, while waters from profiles 3, 8, and 9 can be classified in category V. As for other sampling sites, the concentration of manganese was in the range of defined values for I and II category of surface water quality.

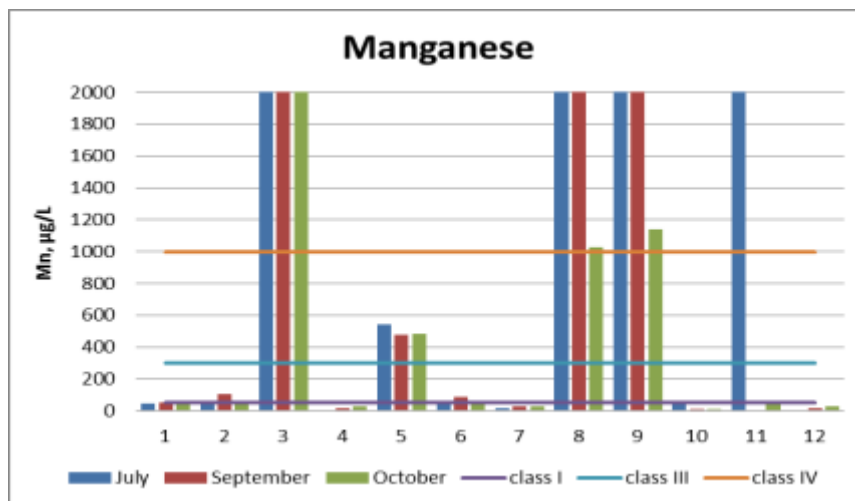


Figure 11 Concentration of manganese in water samples

5.2.6. Nickel

The presence of nickel in surface waters for the monitoring period from July to October was determined at sampling sites 3, 8, and 9, while at location 11 the presence of this metal was confirmed only in July (Figure 12). The lowest concentration of 5.02 µg/L was at SS 11 in July, while the highest value was recorded at location 3 (427.65 µg/L) in September. Based on the Regulation on limit values of priority and priority hazardous substances

that pollute surface waters and deadlines for their achievement [8], the maximum allowable concentration of nickel is 34 µg/L. Accordingly, this value was exceeded at locations 3, 8, and 9, which was especially noticeable in September. Due to the exploitation of copper and polymetallic ores in the mining basin in Majdanpek, and the inflow of wastewater from the mining complex into the Mali Pek River, the presence of metal ions in the samples at the mentioned locations was expected.

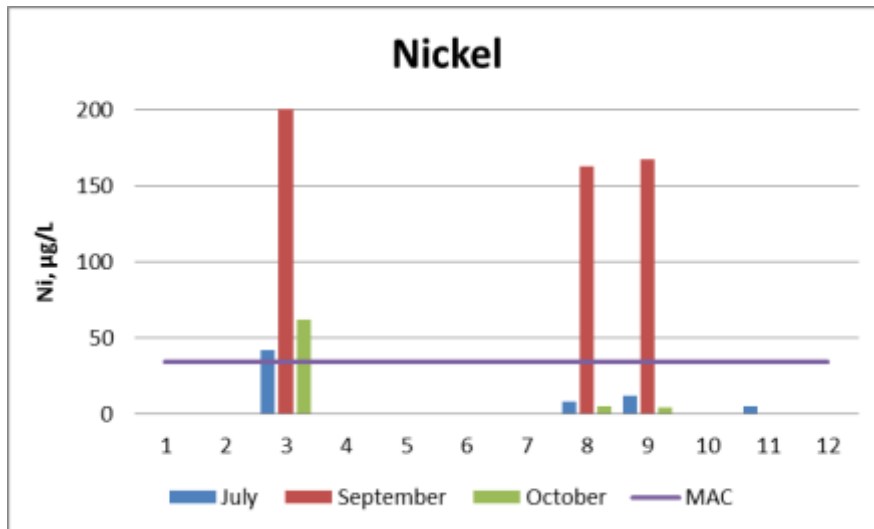


Figure 12 Concentration of nickel in water samples

5.2.7. Lead

The Regulation on limit values of priority and priority hazardous substances that pollute surface waters and deadlines for their achievement [8] prescribes the maximum allowable concentration (MAC) of lead in surface waters is 14 µg/L. According to the Figure 13, at the sampling sites where the presence of lead was detected, the measured concentration was above the MAC.

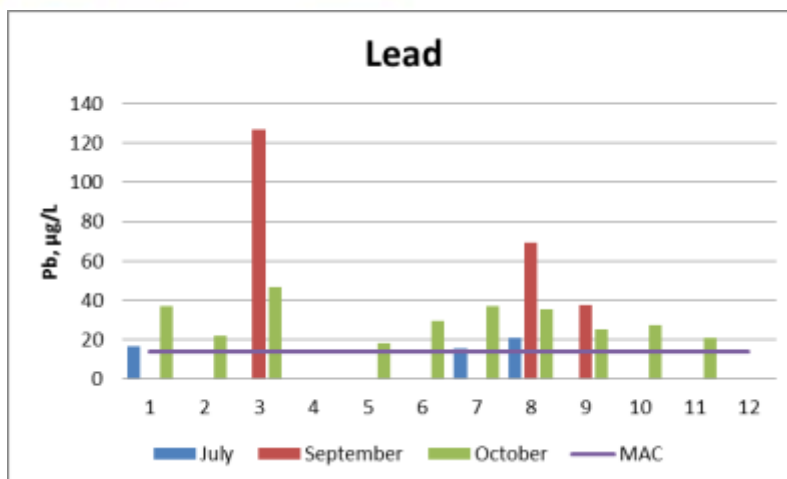


Figure 13 Concentration of lead in water samples

5.2.8. Zinc

The zinc concentration in the samples SS 1–SS 12 is shown in Figure 14. Sampling sites 3, 8, and 9 were also distinguished by the content of this metal ion in relation to other places. Particularly increased content at sites 3, 8, and 9 was observed during September, where concentrations exceeded the values defined by the Regulation on limit values of pollutants in surface and groundwater and sediment and deadlines for reaching them [7] for IV category of surface water quality. As for other samples, based on the zinc content, water quality can be classified in category I.

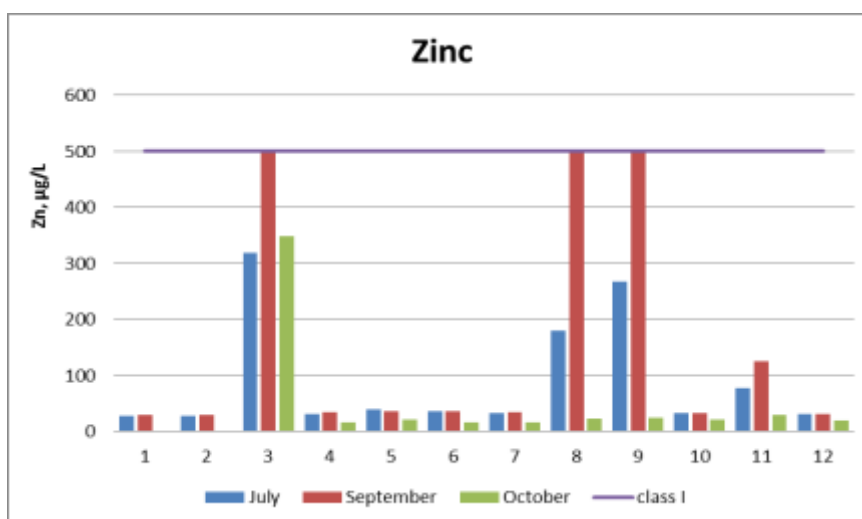


Figure 14 Concentration of zinc in water samples

5.3. Nutrient content in water samples

5.3.1. Ammonia/Ammonium ion

The obtained results on ammonium ion concentrations are presented in Figure 15. The highest concentrations of ammonium ion in the range from 3.97 to 10.43 mg/L were recorded in September at SS 2, 3, 8, and 9. At mentioned locations, based on the ammonium ion content, the quality of these waters belonged to class V. The analysed samples from the remaining sites can be classified in the III category of surface water quality [6].

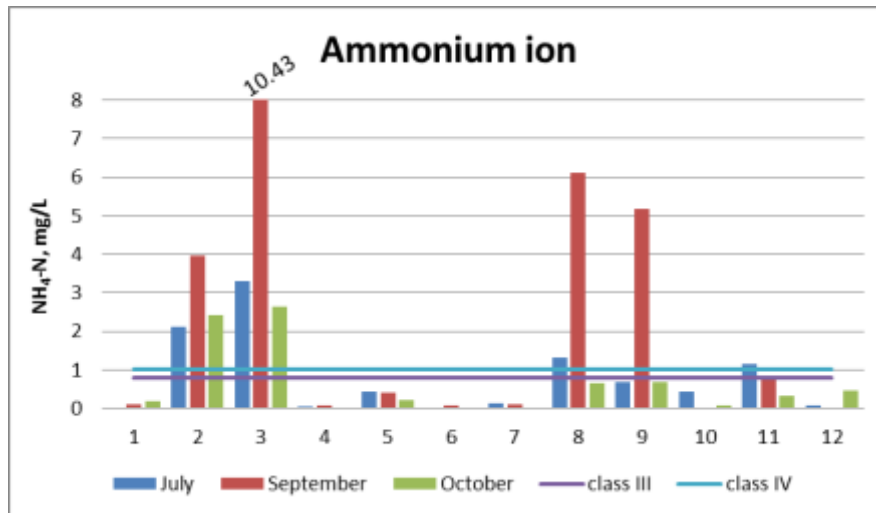


Figure 15 Concentration of ammonium ion in water samples

5.3.2. Nitrates

Figure 16 shows the nitrate concentration in the analysed water samples for the period July – October. The lowest values of nitrate concentration were recorded in July and September, while slightly higher values were recorded in October. In general, based on the results and in accordance with the Regulation [6], surface water quality can be classified in category III, except for locations 3 and 9 in October and location 11 in July, which would be category IV.

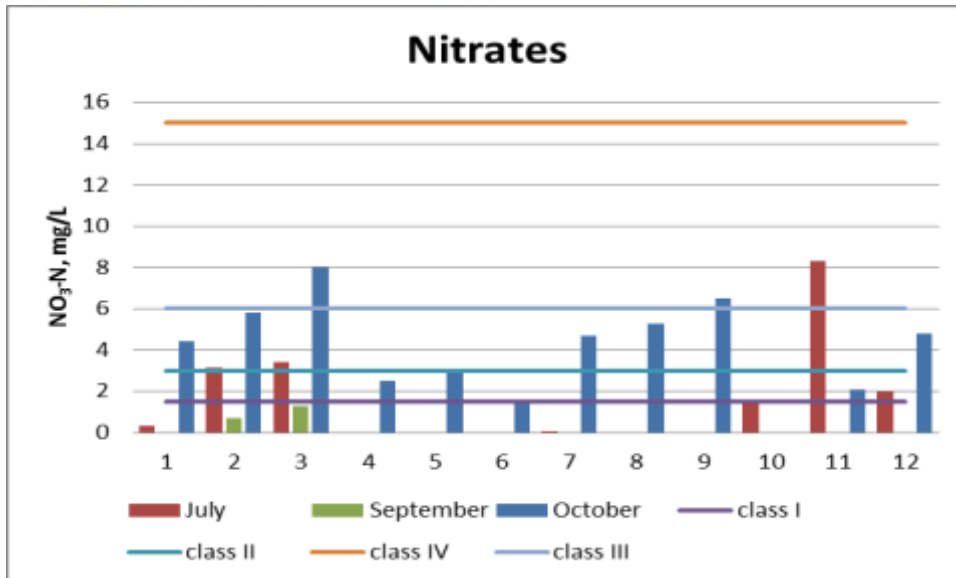


Figure 16 Concentration of nitrates in water samples

5.3.3. Nitrites

Based on the values of nitrite concentration in the analysed samples (Figure 17) and the Regulation [7], water quality can be classified in category III. The highest value of this parameter was recorded at sampling site 12 (0.11 mg/L).

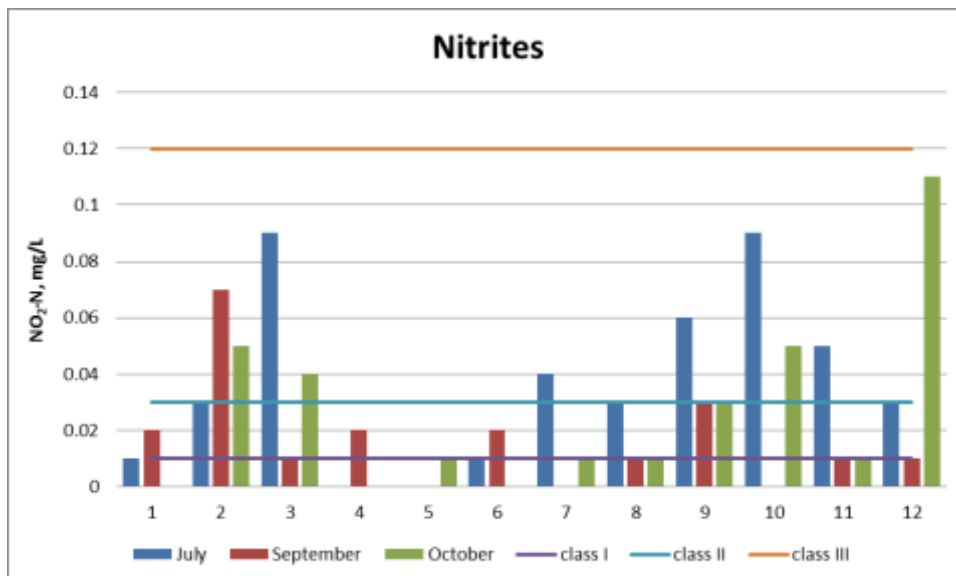


Figure 17 Concentration of nitrites in water samples

5.3.4. Sulphates

The concentration of sulphate ions of the analysed samples differed at the sampling sites, as well as for the sampling periods (Figure 18). At SS 1 and SS 2 during the monitoring period, the concentration of sulphate was the lowest, so the quality of these waters could be classified in category I. However, a particularly pronounced presence of sulphate was observed at locations 3, 5, 8, 9, and 11 where the detected concentrations exceeded the defined value of 300 mg/L for category IV water quality [7]. The increased content of sulphate ions of samples from the river Mali Pek (SS 3) can be assumed as a consequence of the direct influence of copper mines and can be associated with high electrical conductivity and low pH value. At this location, the increased concentration of copper and iron ions was confirmed, as well as the presence of zinc and nickel ions due to the mineral composition of polymetallic ores that are exploited in the mine. The influence of the Valja Fundata tailings can be seen in the sample SS 5, while the tailings Šaški potok affected the sample SS 11 where increased concentrations of sulphate ions were also observed. In the sample from the Veliki Pek river (SS 9 - Ujevac), the presence of sulphate ions can be induced by the overburden sliding from the tailings.

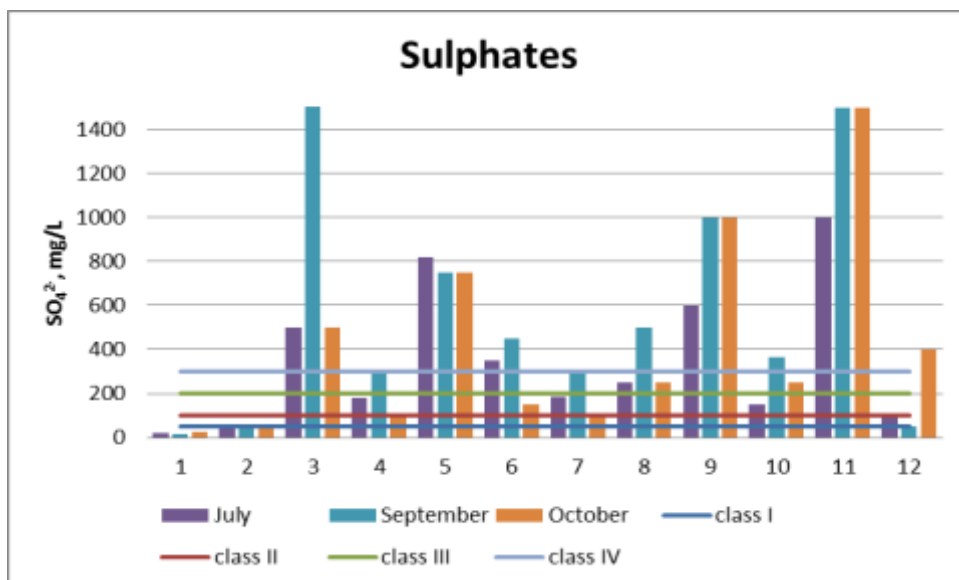


Figure 18 Concentration of sulphates in water samples

5.3.5. Phosphates

The concentration of phosphate ions at sampling sites 1–12 during the period July – October is shown in Figure 19. A slightly higher content of phosphate ions was recorded in July compared to September and October, at SS 2 and 3. On the other hand, at location 9, an increased phosphate content of 0.39 mg/L and 0.35 mg/L was recorded in September and October, respectively, compared to 0.01 mg/L in July. In general, based on the obtained values and in accordance with the Regulation [7], the analysed water samples SS 2, 3, and 9 can be classified in category IV, while the rest would belong to category III.

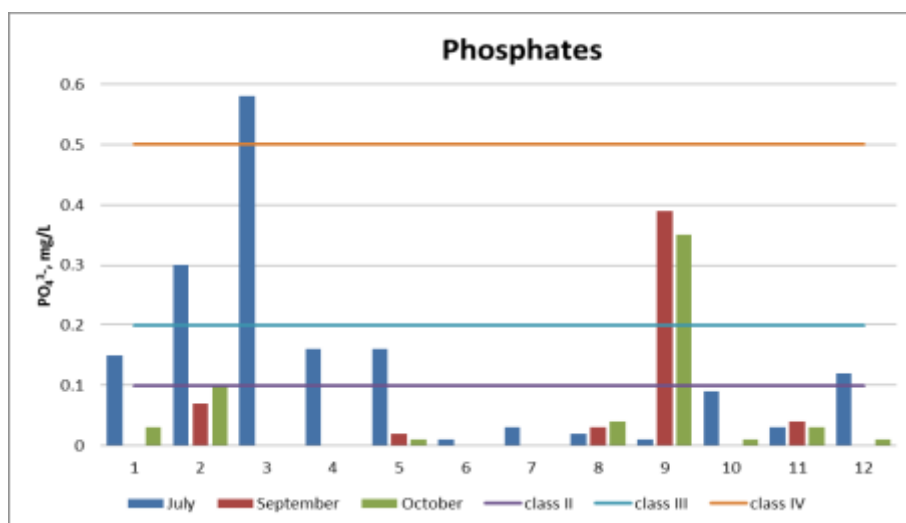


Figure 19 Concentration of phosphates in water samples

5.4. Sediments

Monitoring the concentrations of heavy metals and metalloids in sediment was also the subject of this study. Exploitation of mineral raw materials significantly affected the contamination of the environment. Large amounts of flotation tailings are disposed on soil which thus becomes degraded. Dust particles from tailings led to air pollution, but also to pollution of soil, and surface and groundwater in the wider area.

Hydroxides or carbonates of heavy metals in the form of fine particles are formed due to ion precipitation. Thus, the formed particles could be carried by the water current, whereby aggregation could occur in contact with other suspended particles and deposition at the bottom of the river. The sediment on the bottom, according to its mineral composition, consisted of aluminosilicate particles of micron dimensions, which also contained particles of sulphide minerals, primarily pyrite and copper minerals. In addition, larger particles could be found in the sludge, which were formed due to the decay of biomaterial from the water or from the coast that reached the water. The granulometric composition of sediments is shown in Table 9.

Heavy metals remain in the soil for a longer period of time even after the source of pollution has been removed. Therefore, examination of the concentration of heavy metals in the sediments of the rivers Mali Pek, Veliki Pek, and Pek is of exceptional importance because the content of heavy metals also indicates the quality of the river. Heavy metals are involved in the biochemical processes of element circulation and in the process they undergo various levels of changes, which affect their mobility, binding, and leaching or surface transport in erosive processes. In the long run, they can lead to various health problems in humans, but also in other living beings, because some of them also have carcinogenic properties. The degree of heavy metal sediment load can be low if the concentration of heavy metals in the soil is 5 to 10% of the MAC, medium if the value is 10 to 25% of the MAC, high (25 to 50% of the MAC), and very high if heavy metal concentration is from 50 to 100% of the maximum allowed value of heavy metal concentration in the soil.

Based on the presented data (Table 10), it can be concluded that the concentrations of analysed heavy metals and metalloids in the sediments of the rivers Mali Pek, Veliki Pek, and Pek were below the maximum allowed concentrations according to the Regulation on limit values of pollutants in surface and groundwater and sediment and their deadlines for their achievement [7].

Table 9a. Granulometric composition of sediments

Size class d (µm)	Sample 2A		Sample 2B		Sample 3A		Sample 3B		Sample 5A		Sample 5B	
	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)
-2360.00+1180.00	42.00	100.00	4.00	100.00	0.50	100.00	0.00	100.00	0.05	100.00	0.00	100.00
-1180.00+710.00	24.00	58.00	5.00	96.00	1.00	99.50	0.05	100.00	0.05	99.95	0.05	100.00
-710.00+300.00	16.00	34.00	12.50	91.00	43.50	98.50	10.50	99.95	11.00	99.90	0.40	99.95
-300.00+150.00	2.00	18.00	29.50	78.50	38.00	55.00	32.50	89.45	55.00	88.90	5.00	99.55
-150.00+75.00	1.00	16.00	20.00	49.00	6.50	17.00	24.50	56.95	26.00	33.90	27.50	94.55
-75.00+42.10	0.00	15.00	0.00	29.00	0.00	10.50	0.81	32.45	7.78	7.90	13.21	67.05
-42.10+31.90	0.04	15.00	0.00	29.00	3.65	10.50	1.82	31.64	0.09	0.12	10.19	53.84
-31.90+20.10	1.24	14.96	1.39	29.00	0.50	6.85	5.55	29.82	0.00	0.03	13.07	43.65
-20.10+10.50	3.69	13.72	10.21	27.61	2.09	6.35	8.96	24.27	0.00	0.03	12.81	30.58
-10.50+5.06	3.59	10.03	8.82	17.40	1.83	4.26	6.13	15.31	0.00	0.03	7.04	17.77
-5.06+2.01	3.45	6.44	4.64	8.58	1.29	2.43	4.28	9.18	0.00	0.03	4.49	10.73
-2.01+0.00	2.99	2.99	3.94	3.94	1.14	1.14	4.90	4.90	0.03	0.03	6.24	6.24

SS – sampling site; A – samples were taken from the water (riverbed); B – samples were taken from the riverbank;

Table 9b. Granulometric composition of sediments (continued)

Size class d (µm)	Sample 6A		Sample 6B		Sample 7A		Sample 7B		Sample 8A		Sample 8B	
	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)
-2360.00+1180.00	0.40	100.00	0.35	100.00	33.00	100.00	18.50	100.00	0.85	100.00	1.10	100.00
-1180.00+710.00	1.50	99.60	5.00	99.65	14.50	67.00	19.50	81.50	6.50	99.15	5.00	98.90
-710.00+300.00	38.00	98.10	53.00	94.65	26.00	52.50	30.50	62.00	49.50	92.65	42.50	93.90
-300.00+150.00	45.00	60.10	33.00	41.65	9.00	26.50	20.50	31.50	27.00	43.15	24.50	51.40
-150.00+75.00	9.00	15.10	6.50	8.65	3.50	17.50	7.50	11.00	7.00	16.15	7.00	26.90
-75.00+42.10	2.62	6.10	1.06	2.15	0.56	14.00	1.26	3.50	1.19	9.15	1.91	19.90
-42.10+31.90	0.95	3.48	0.28	1.09	1.39	13.44	0.39	2.24	1.16	7.96	2.17	17.99
-31.90+20.10	0.87	2.53	0.26	0.81	3.44	12.05	0.15	1.85	2.21	6.80	4.12	15.82
-20.10+10.50	0.70	1.66	0.22	0.55	4.14	8.61	0.37	1.70	1.94	4.59	4.49	11.70
-10.50+5.06	0.41	0.96	0.13	0.33	2.56	4.47	0.69	1.33	1.06	2.65	2.79	7.21
-5.06+2.01	0.23	0.55	0.10	0.20	0.97	1.91	0.33	0.64	0.79	1.59	2.17	4.42
-2.01+0.00	0.32	0.32	0.10	0.10	0.94	0.94	0.31	0.31	0.80	0.80	2.25	2.25

Table 9c. Granulometric composition of sediments (continued)

Size class d (µm)	Sample 9A		Sample 9B		Sample 11A		Sample 11B		Sample 12A	
	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)	W (%)	D (%)
-2360.00+1180.00	65.00	100.00	4.50	100.00	4.00	100.00	1.20	100.00	3.00	100.00
-1180.00+710.00	10.50	35.00	3.50	95.50	1.50	96.00	1.00	98.80	4.00	97.00
-710.00+300.00	7.50	24.50	10.00	92.00	10.50	94.50	9.00	97.80	29.50	93.00
-300.00+150.00	9.00	17.00	13.50	82.00	34.50	84.00	40.00	88.80	27.50	63.50
-150.00+75.00	5.00	8.00	30.50	68.50	26.00	49.50	30.00	48.80	15.00	36.00
-75.00+42.10	0.41	3.00	15.81	38.00	7.68	23.50	5.41	18.80	9.01	21.00
-42.10+31.90	0.35	2.59	4.75	22.19	2.75	15.82	1.75	13.39	2.33	11.99
-31.90+20.10	0.46	2.24	5.93	17.44	3.95	13.07	1.90	11.64	3.34	9.66
-20.10+10.50	0.58	1.78	4.75	11.51	3.92	9.12	2.74	9.74	2.94	6.32
-10.50+5.06	0.52	1.20	2.47	6.76	2.45	5.20	2.74	7.00	1.74	3.38
-5.06+2.01	0.30	0.68	1.82	4.29	1.50	2.75	2.11	4.26	0.84	1.64
-2.01+0.00	0.38	0.38	2.47	2.47	1.25	1.25	2.15	2.15	0.80	0.80

Table 10. Concentration of heavy metals and metalloids in sediments

MM	Cr, ppm		Mn, ppm		Fe, ppm		Cu, ppm		Zn, ppm		As, ppm		Pb, ppm		Ni, ppm	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
2A	0.0185		0.1089		5.7723		0.0678		0.047		0.0092		0.0142		0.0033	
2B	0.0117		0.1305		4.3507		0.0568		0.0449		0.0041		0.0132			
3A	0.0091	0.0075	0.1951	0.2132	4.5851	5.104	0.0967	0.1672	0.0868	0.121	0.0045	0.0091	0.0124	0.0165		<LOD
3B	0.0097		0.1299		5.0534		0.1108		0.0624		0.0098		0.0108			
5A	0.0042		0.0742		4.1331		0.103		0.0576		0.0057		0.0039			
5B	0.0092		0.0807		4.2874		0.0571		0.0266		0.0126		0.005			
6A	0.0077		0.0963		3.4743		0.031		0.0236		0.0017					
6B	0.0075		0.0826		3.6037		0.0339		0.0205		0.0009		0.0031			
7A	0.0089	<LOD	0.1088	0.0407	4.597	1.4078	0.0491	0.1248	0.0297	0.0753	0.0026	0.0067	0.0209	0.3851		<LOD
7B	0.0116		0.0816		3.7627		0.0273		0.0134		0.0023		0.0031			
8A	0.0077	0.011	0.1247	0.1199	4.9382	5.8398	0.0984	0.2559	0.0534	0.1594	0.0042	0.0163	0.012	0.0691		<LOD
8B	0.0076		0.1817		5.81		0.1292		0.0832		0.0066		0.0167			
9A	0.0099	0.0144	0.1162	0.1716	2.9549	7.5686	0.0179	0.276	0.0275	0.2585	0.0036	0.0178	0.005	0.0803		<LOD
9B	0.0078		0.1635		3.7384		0.0361		0.0698		0.0066		0.0143			
10A		0.0091		0.1348		2.9164		0.03		0.0316		0.0029		0.0068		<LOD
11A	0.009		1.7975		5.6573		0.1198		0.2114		0.0049		0.0063		0.0067	
11B	0.0104		0.044		4.2799		0.0223		0.0055		0.0028		0.0046			
12A	0.0148		0.0761		3.6194		0.0108		0.0143		0.001		0.0022		0.0041	

I – sampling in July; II – sampling in September; SS – sampling site; A – samples were taken from the water (riverbed); B – samples were taken from the riverbank; LOD – below the detection limit of the measuring instrument

6. Conclusion

National Park Đerdap (NP) is located in the north-eastern Serbia and includes parts of the Miroč, North Kučaj, and Štrbac mountain massifs. The total area of the park is 63,786.48 ha and it covers the territory of the municipalities of Kladovo, Majdanpek, and Golubac. The Djerdap gorge is the deepest and most beautiful gorge in Europe, which is characterized by an unpolluted environment, a favorable climate and complex geological and geomorphological characteristics. As such, it is a unique European reserve of tertiary flora and fauna with a distinctly endemic and relict character. Most of the territory of Djerdap is classified in areas with very high quality environment. The state of the quality of the environment differs between the area of the National Park and the remaining part outside the protected area. The lack of intensive economic activities and traffic in the mountain belt of the Đerdap area has a favourable effect on the state of the environment, except in the area of the municipality of Majdanpek. The exploitation of mineral resources in the mining complex Majdanpek (Serbia Zijin Bor Copper - Copper Mine Majdanpek) contributes to the degradation of the environment. Moreover, the environmental quality is significantly affected by the communal infrastructure (large number of unregulated landfills and wastewater disposals). The negative impact is primarily indicated by the production of various types and quantities of industrial waste, pollution of water, air and soil, as well as deterioration of the environmental quality.

In accordance with the aforementioned, the impact mining activities in Majdanpek have on the Danube was analysed in this study. It included the analysis of the quality of surface waters and sediments that were in the immediate vicinity of the mine in the area of the municipality of Majdanpek. Moreover, the analysis of the quality of the Pek River at Veliko Gradište and Porečke River at Donji Milanovac, which represented the most remote points covered by the study, was performed as well.

The pH value, electrical conductivity, content of total dissolved substances, as well as chemical (COD) and biological (BOD) oxygen demand, content of ammonia, nitrate, nitrite, phosphate, and sulphate were determined in the water samples. Furthermore, concentrations of

metals and metalloids, such as copper, iron, lead, arsenic, zinc, and nickel were determined.

Lower pH values, i.e. water acidity was recorded at several measuring points. This occurrence at the Location 3 can be explained by the inflow of mining waters from the open pit South Mining District and drainage water from the North Mining District into the Mali Pek River. Likewise, it is assumed that the water from the filtration facilities affected the change in the pH value of the sample taken from the Veliki Pek River. The pH value of the sample taken at the point after Mali and Veliki Pek Rivers merged indicated acidity as well. It is assumed that this is a consequence of the Mali Pek inflow, which had higher flow and lower pH value compared to Veliki Pek for the observed period.

Based on the obtained results of the biological oxygen demand analysis, it was determined that Mali Pek had higher content of organic substances that acted as a pollutant. Moreover, it was noticed that the concentration of sulphate ions was very high at locations in the vicinity of the mining complex in Majdanpek, especially in the period when the pH values of these samples were lower compared to the rest of the period. The concentration of sulphate ions at these locations was higher than prescribed value of 300 mg/L for class IV water. The analysis of the metal concentration showed significant increase for copper and iron ions at the locations around the copper mine in Majdanpek, and it increased in the period when lower pH values and lower flow were recorded, showing that the quality of these waters would put them in class V. Lead concentration at multiple locations during the monitoring period was higher than the maximal allowable concentration of 14 µg/L as prescribed in the Regulation on emission limit values of priority and priority hazardous substances which pollute surface waters and deadlines for their achievement ("Official Gazette of the RS", No. 24/2014). The presence of arsenic, manganese, zinc, and nickel was noticed in the analysed water samples as well, which was the result of the different mineral composition of the ore in the mining complex in Majdanpek.

Based on the results, it can be concluded that intensive mining activities in the municipality of Majdanpek, as well as communal infrastructure, affect the quality of surface waters.

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