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Interreg-IPA Cross-border Cooperation Programme Romania-Serbia

Academic Environmental Protection Studies on surface water quality in significant cross-border nature reservations Djerdap / Iron Gate national park and Carska Bara special nature reserve, with population awareness raising workshops

= RORS-462 =

PA2.OI3 Studies in the field of environmental protection and emergency management.

STUDY ON THE INFLUENCE OF THE COPPER MINING ACTIVITIES IN MAJDANPEK ON DANUBE RIVER

AEPS
common history, common future

www.aeps.upt.ro

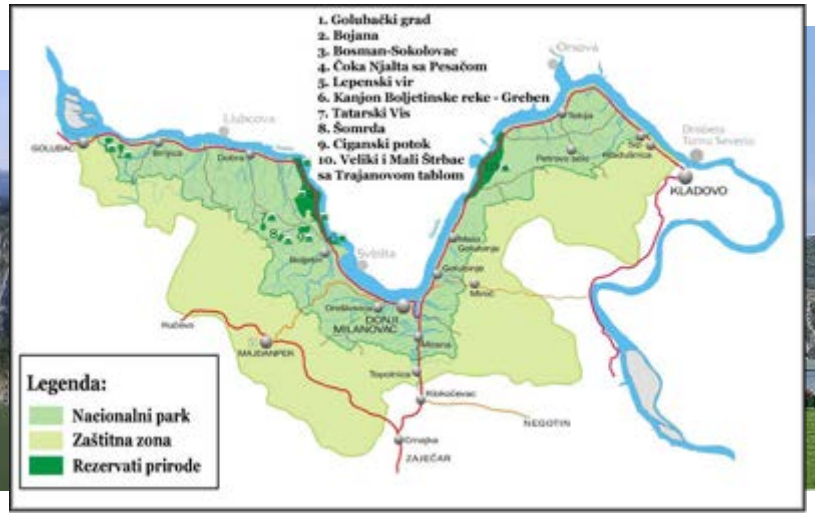
5th – 6th February 2021, Timisoara, Romania

8th – 9th February, Bor, Serbia

AIM OF THE STUDY

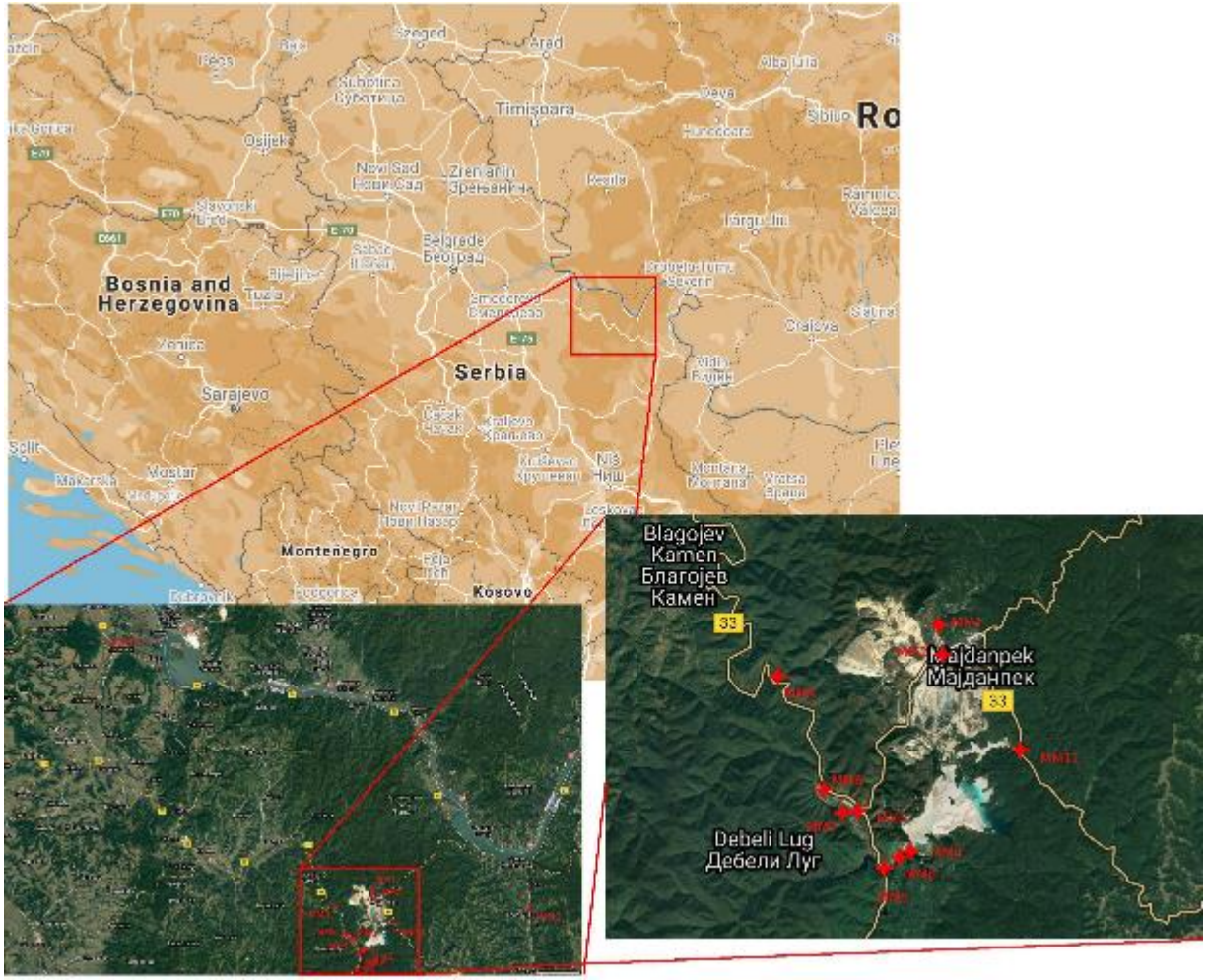
The impact mining activities in Majdanpek have on the Danube was analysed in this study. It included the analysis of the quality of surface waters and sediments that were in the immediate vicinity of the mine in the area of the municipality of Majdanpek. Moreover, the analysis of the quality of the Pek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

NATIONAL PARK ĐERDAP



The total area under first degree protection zone is approximately 8.01%, the second degree protection zone is approximately 21.50%, while the majority of the protected area of 70.49% is in the third degree protection zone

GEOGRAPHICAL LOCATION OF MAJDANPEK, SERBIA



POLLUTANTS OF THE PEK AND POREČ RIVERS
LOCATION OF THE SAMPLING SITES

- The Pek River - length 29 km; basin surface 1,236.5 km^2; flows into the Danube near Veliko Gradište
- 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 source of the Veliki Pek River is located in the Homolje mounatains. The length of Veliki Pek is about 28 km.
- The rivers Veliki and Mali Pek merge and form the Pek 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.

Limit values of pollutants in surface waters and sediments

Applied legal regulations

1. Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of groundwater (“Official Gazette of the RS”, No. 74/2011)

2. Regulation on emission limit values of polluting substances in surface and groundwaters and deadlines for their achievement (“Official Gazette of the RS”, No. 50/12)

3. Regulation on limit values of priority substances and priority hazardous substances that pollute surface waters and deadlines for their achievement (“Official Gazette of the RS”, No. 24/14)

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Sampling sites for surface waters and sediments - MALI PEK

Sample number	SS 1	SS 2	SS 3	Measurement parameters/ Pollutants
Description of sampling site	Mali Pek at the entrance of the town	Mali Pek River after the inflow of the city sewage system	Mali Pek after inflow of drainage water from the North Mining District dump and wastewater from crushing	pH, t, DO, colour, condutivity ammonia, nitrates, nitrites, sulphates, phosphates, chemical oxygen demand (COD), biological oxygen demand (BOD), and heavy metals and metalloids
GPS Coordinates	N 44°25’ 47.59517” E 21°55’ 58.72471”	N 44°25’ 17.97584” E 21°56’ 5.24429’	N 44°22’ 46.96202” E 21°54’ 7.90727”	

Sampling sites for surface waters and sediments - Veliki PEK

Sample number	SS 4	SS 5	SS 6	SS 7	SS 8
Description of sampling site	Veliki Pek – before surface waters inflow from the cave, below Valja Fundata tailings	Surface waters from the cave below the Valja Fundata tailings	Veliki Pek downstream after SS 4 and SS 5 merge	Veliki Pek after the inflow of wastewater from the filtration	Surface waters after Veliki and Mali Pek merge
GPS Coordinates	N 44°22'5.78376" E 21°55'14.96092"	N 44°21' 51.4925" E 21°54'43.38354"	N 44°21'58.98295" E 21°55' 2.33636"	N 44°22' 43.70676" E 21°53' 51.45986"	N 44°23' 18.36439" E 21°53' 16.30224"





Sampling sites for surface waters and sediments - PEK and Porečka River

Sample number	SS 9	SS 10	SS 11	SS 12
Description of sampling site	Pek (Ujevac) -the influence of tailings and ore waste heap	Pek River (Braničevo) before it flows into Danube	Šaški potok tailings	Porečka River
GPS Coordinates	N 44°24′ 54.2403″ E 21°52′ 22.86861″	N 44°42′ 12.51062″ E 21°32′ 1.44856″	N 44°23′ 45.15633″ E 21°57′ 55.24581″	N 44°24′ 40.49354″ E 22°10′ 20.45027″




Materials and methods-Terrain measurements



Lovibond® Water Testing Tintometer®
Group SensoDirect 150 (pH/Con/TDS/Oxi/Temp





MATERIALS AND METHODS-TERRAIN AND LABORATORY MEASUREMENTS

pH, t, dissolved oxygen, conductivity, total dissolved solid, electroconductivity	Temperature of air	BOD	COD	Ammonium ion, Nitrates, Nitrites, Phosphates, Sulphates	Metals and metalloids in water samples	Metals and metalloids in sediments	Granulometric composition of sediments
Lovibond® Water Testing Tintometer® Group SensoDirect 150 (Set 1) pH/Con/TDS/ Oxi/Temp)	Thermometer	Manometric, equipment manufacturer's instructions	Permanganate method/Spectrophotometry	SpectrophotometryPhotometer HANNA HI 83200	ICP-OES equipment - Perkin Elmer Optima 8300 and version 5.0 WinLab softwer	XRF equipment (BRUKER, Germany, S1 TITAN Mod-800	Laser size analyser (FRITSCH, Germany, ANALYSETTE 22 NanoTec)





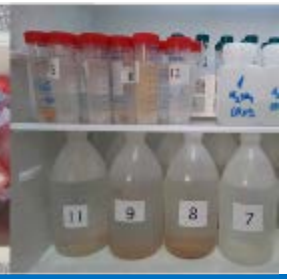

Photo gallery of laboratory analysis















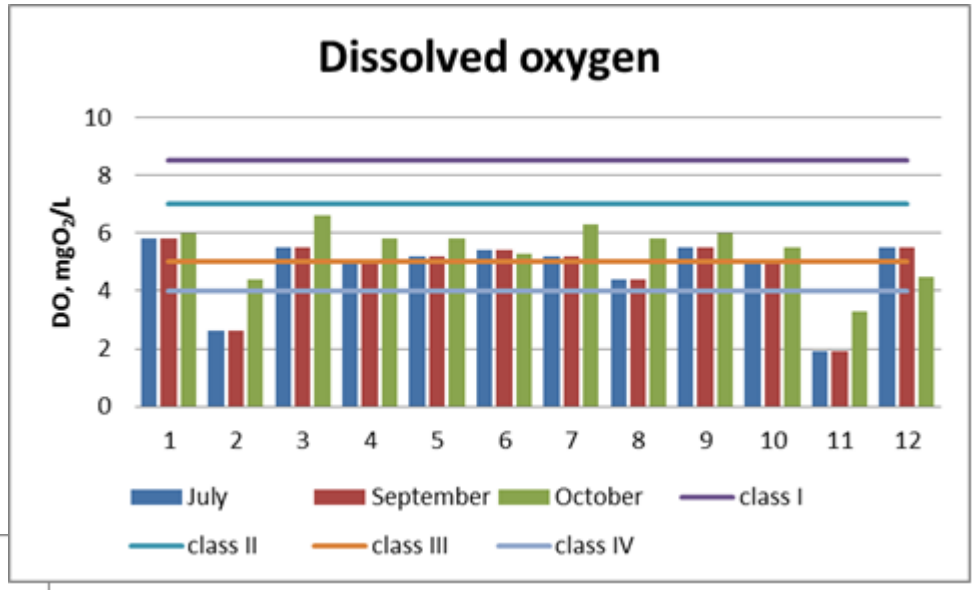

Physicochemical indicators of water quality

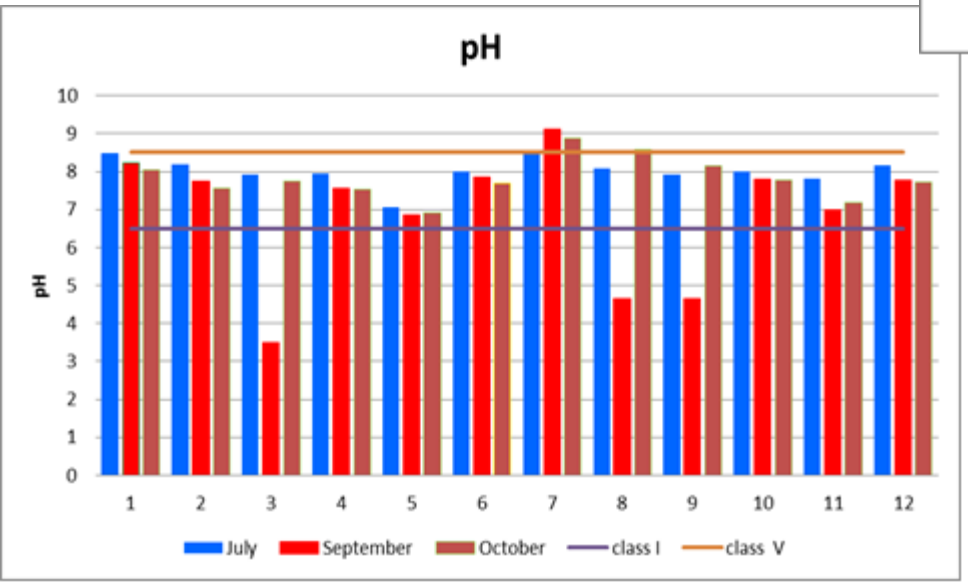
Code of the sample	Air temperature (°C)			Water temperature (°C)			Sample colour/turbidity			Sample odour		
	I	II	III	I	II	III	I	II	III	I	II	I
SS 1	32.5	35	17.9	20.4	18.7	13.8	without	without	without	without	without	witl
SS 2	24.1	28.6	16	22.1	20.6	15	turbidity	without	without	**unpleasant**	**unpleasant**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

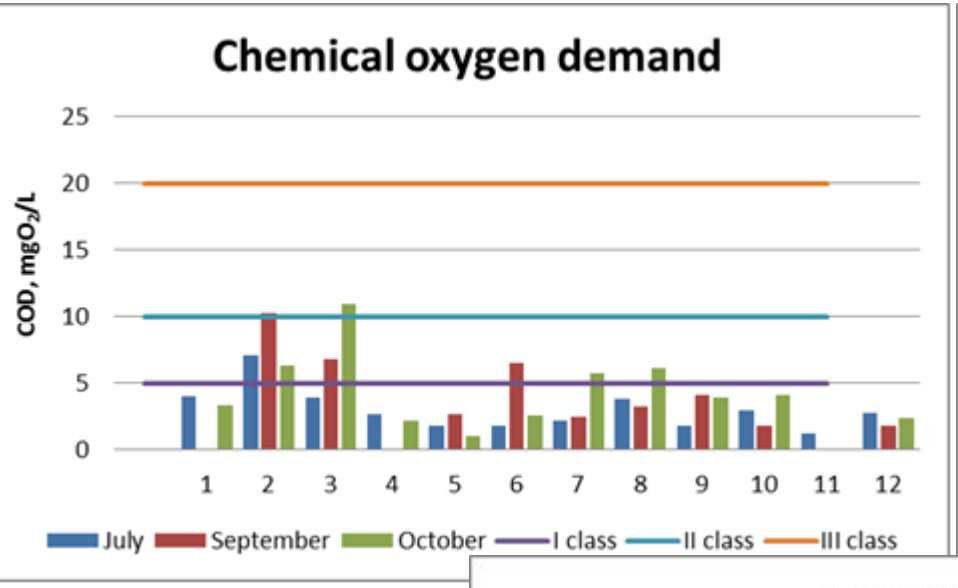
I-July; II-September; III-October

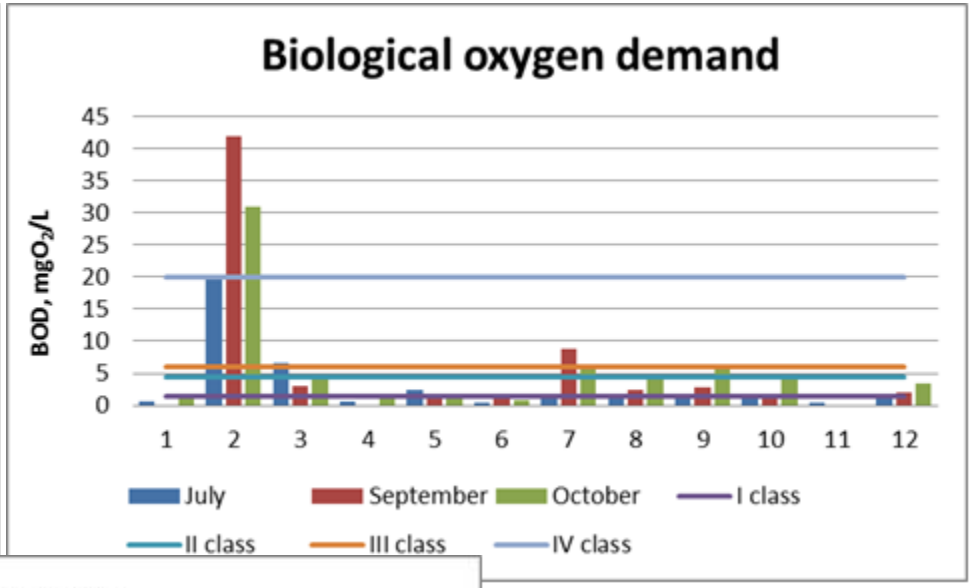
Water flow (m^3/s) at selected sampling sites

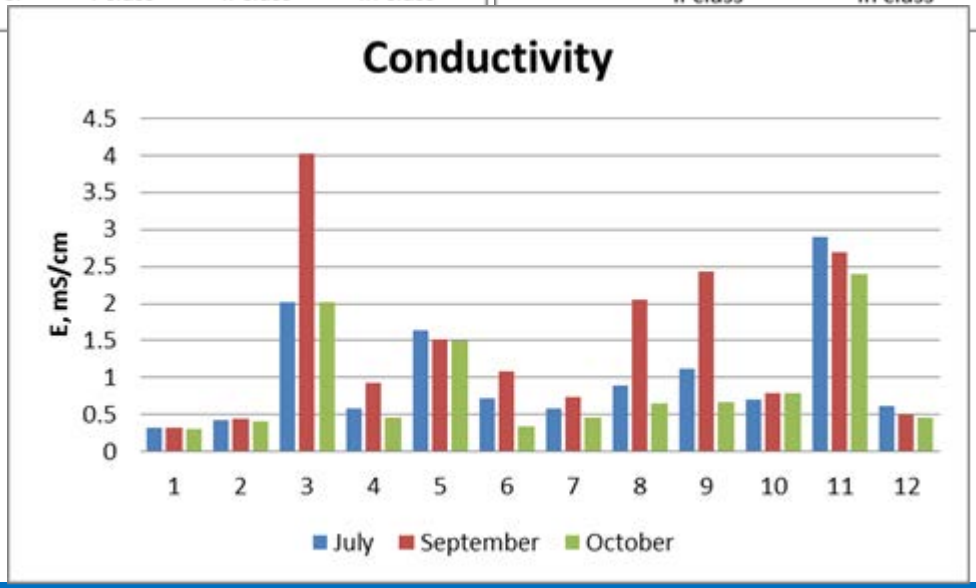
Sampling site	July	September	October
SS 1	0.27	0.27	0.27
SS 2	0.2	0.2	0.2
SS 3	0.75	0.12	0.12
SS 4	0.62	0.059	0.72
SS 5	0.073	0.073	0.073
SS 6	0.65	**1.04**	**1.17**
SS 7	0.053	**0.069**	**0.069**
SS 8	1.04	0.41	0.5
SS 9	1.2	1.4	/
SS 10	8.0	**0.9**	**0.9**
SS 11	0.059	**0.0**	**0.0**
SS 12	0.66	**0.0087**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


Dissolved oxygen
DO, mgO2/L
10
8
6
4
2
0
1
2
3
4
5
6
7
8
9
10
11
12
July
September
October
class I
class II
class III
class IV

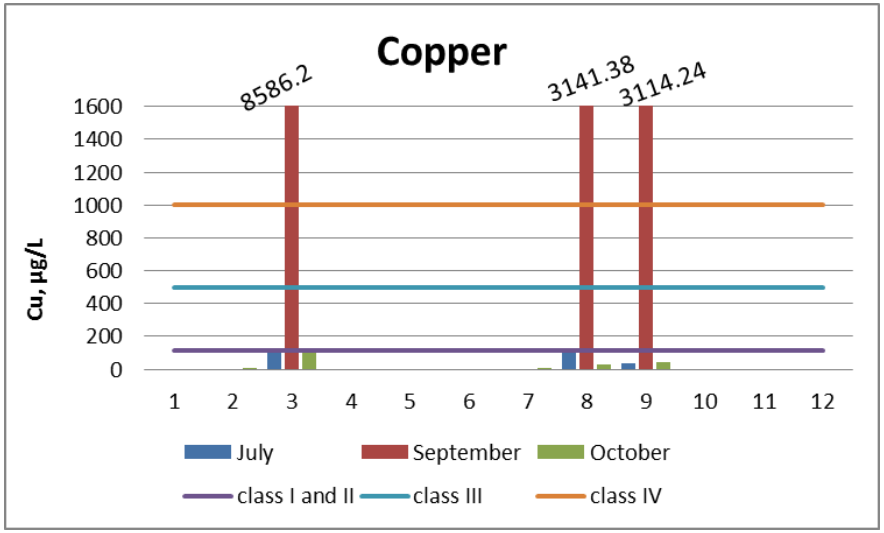

pH
pH
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
9
10
11
12
July
September
October
class I
class V

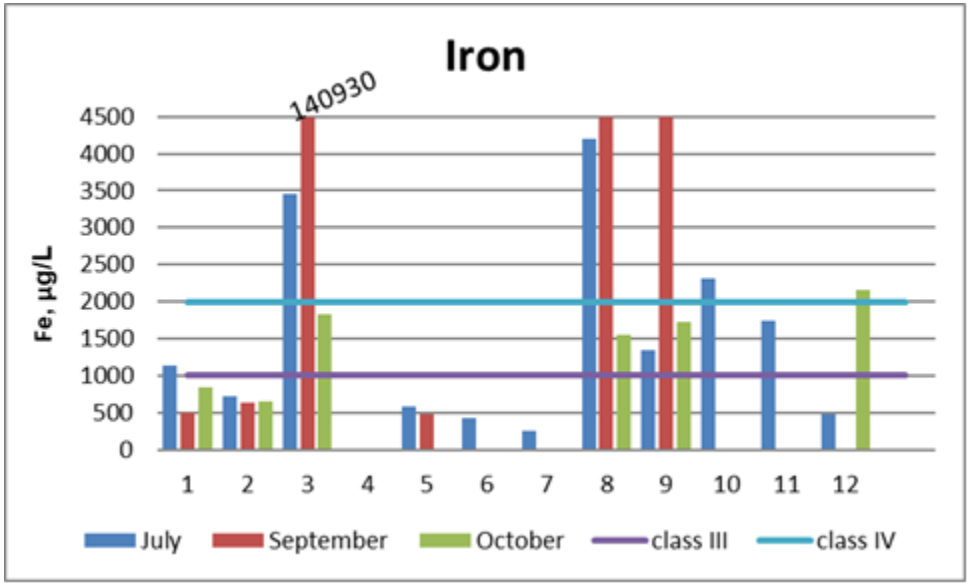

Chemical oxygen demand
COD, mgO2/L
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12
July
September
October
I class
II class
III class

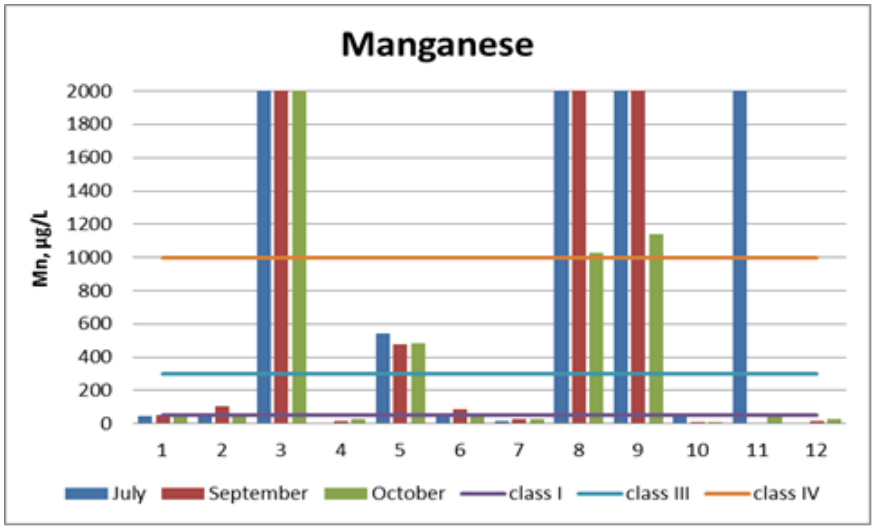

Biological oxygen demand
BOD, mgO2/L
45
40
35
30
25
20
15
10
5
0
1 2 3 4 5 6 7 8 9 10 11 12
July
September
October
I class
II class
III class
IV class


Conductivity
E, mS/cm
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1 2 3 4 5 6 7 8 9 10 11 12
July
September
October

Metal and metalloid content in water samples



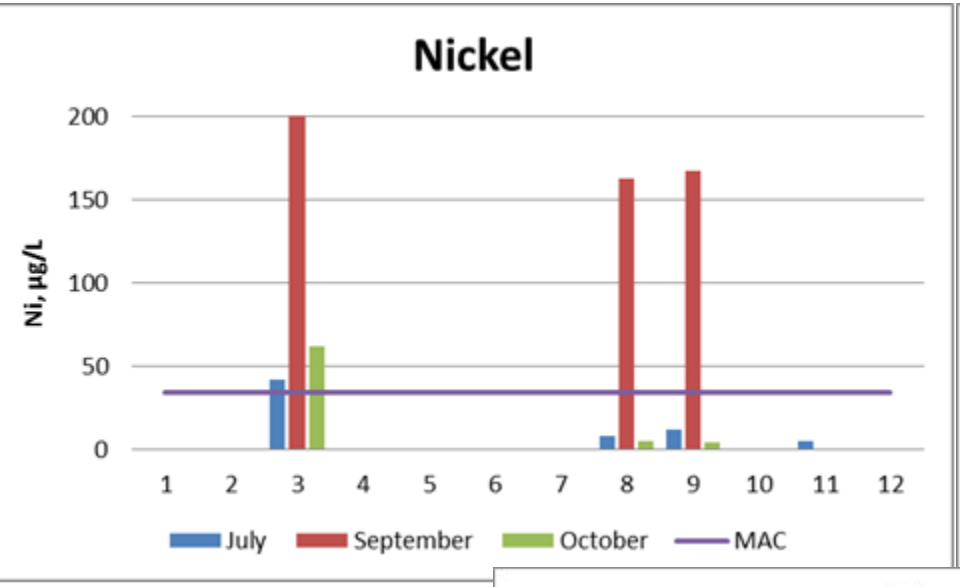


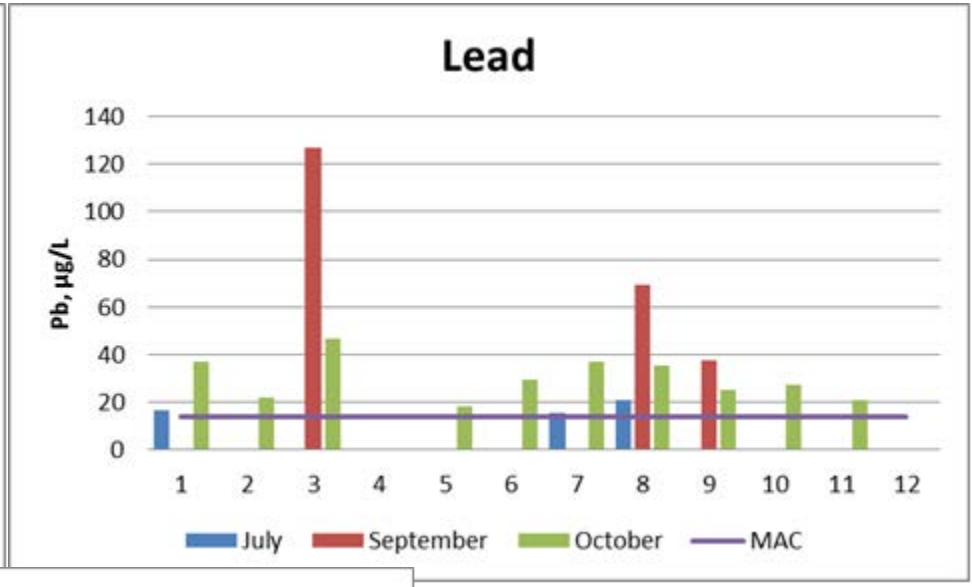


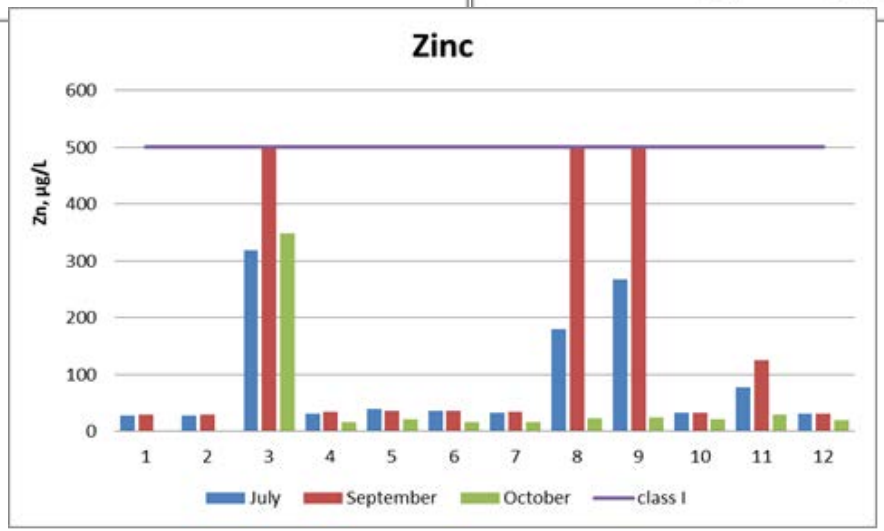
Metal, µg/L	SS 3 Mali Pek	SS8 Pek	SS9 Pek	MAC
As	113.30	39.40	39.64	0.0041 mg/L
Cd	109.24	42.35	33.83	1.5 µg/L (class V)

September;

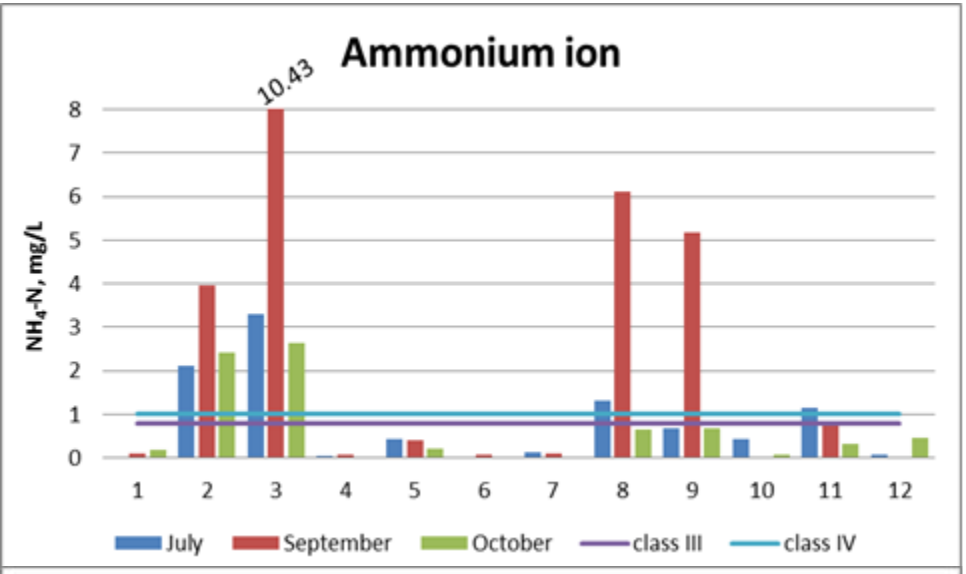
Metal content in water samples

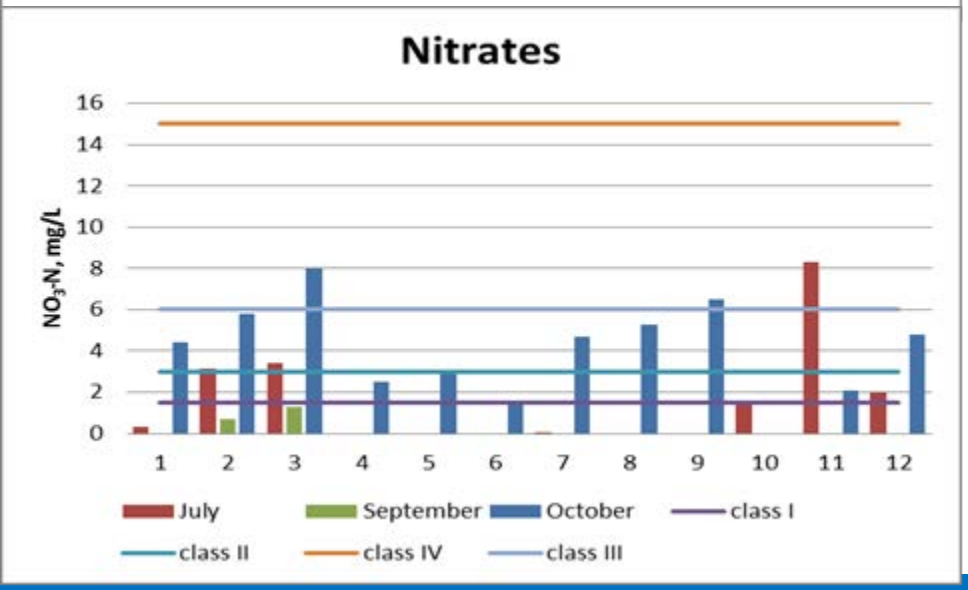






Nutrient content in water samples

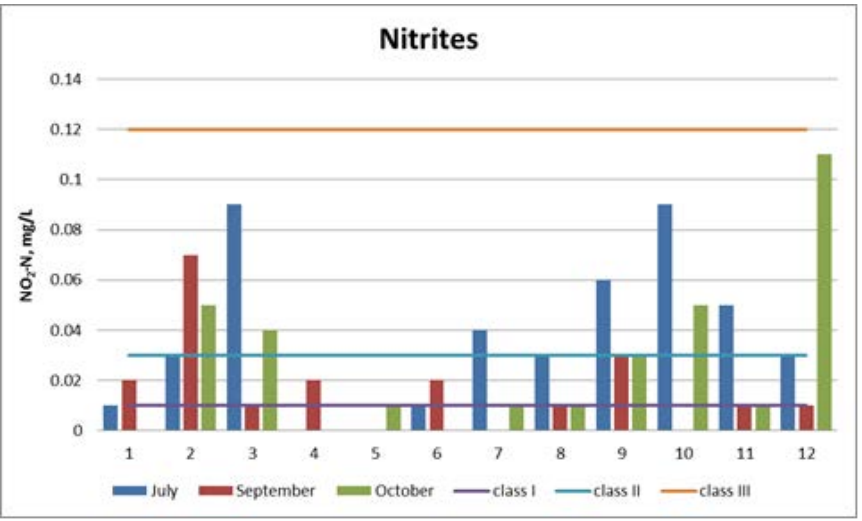


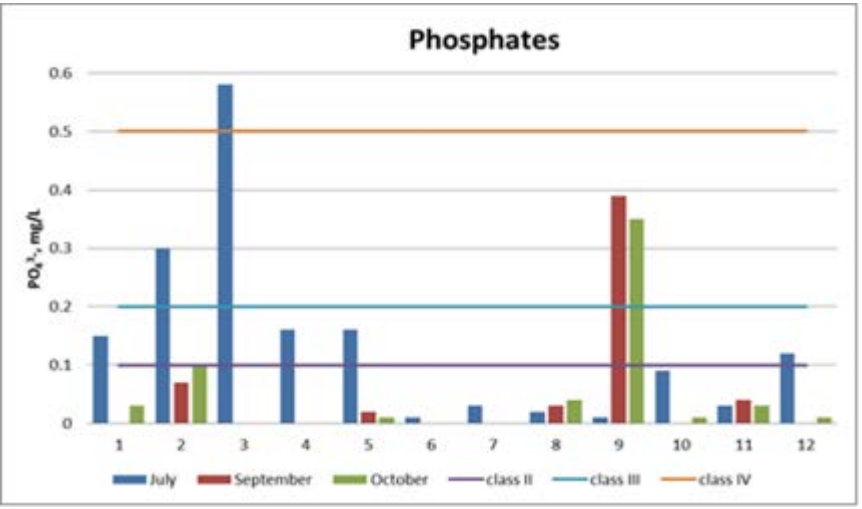


The highest concentrations of ammonium ion in the range from 3.97 to 10.43 mg/L were recorded in September at SS 2, 3, 8, and 9 (class V) The analysed samples from the remaining sites can be classified in the III category of surface water quality

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, 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.



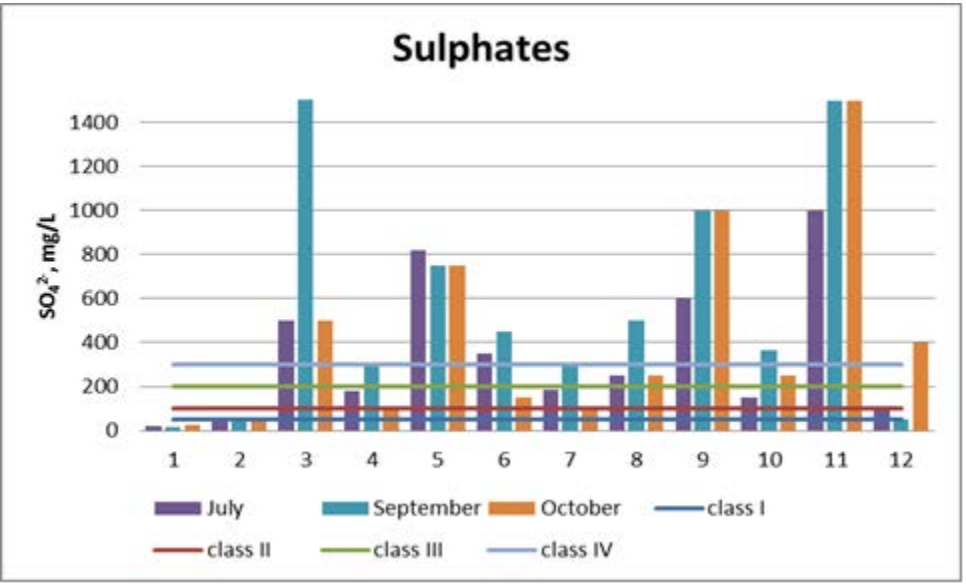


Based on the values of nitrite concentration in the analysed samples water quality can be classified in category III. The highest value of this parameter was recorded at sampling site 12 (0.11 mg/L).

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



The concentration of sulphate ions of the analysed samples differed at the sampling sites, as well as for the sampling periods

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.

At locations 3, 5, 8, 9, and 11 - the detected concentrations exceeded the defined value of 300 mg/L for category IV water quality .

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

Sediments

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		0,10		5,7723		0,0678		0,047		0,0092		0,0142		0,0033	
2B	0,0117		0,13		4,3507		0,0568		0,0449		0,0041		0,0132			
3A	0,0091	0,0075	0,19	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		0,12		5,0534		0,1108		0,0624		0,0098		0,0108			
5A	0,0042		0,07		4,1331		0,103		0,0576		0,0057		0,0039			
5B	0,0092		0,08		4,2874		0,0571		0,0266		0,0126		0,005			
6A	0,0077		0,09		3,4743		0,031		0,0236		0,0017					
6B	0,0075		0,08		3,6037		0,0339		0,0205		0,0009		0,0031			
7A	0,0089	<LOD	0,10	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

CONCLUSION

- 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

- Lower pH values, at the Location 3 (Mali Pek) 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.

- The water from the filtration facilities affected the change in the pH value of the sample taken from the Veliki Pek River

- 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.

CONCLUSION

- 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 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.

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