

To: *Asociation ZA Drinking Fountains*  
Dositejeva 11, Zaječar, Serbia  
Contact: Boban Pogarčić  
Phone: 064/8345-236; E-mail: office@zacesme.rs

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# Laboratory analysis report

## No. 12051609

*Project: ENVIRONMENTAL RESPONSE TO  
MINING EXPANSION IN TIMOČKA KRAJINA*

*Report written by:*

\_\_\_\_\_  
*Aleksandra Onjia Armacki, B.Sc.*

*Laboratory Director:*

\_\_\_\_\_  
*Latinka Slavković Beškoski, M.Sc.*

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## 1. INTRODUCTION

Anahem d.o.o. Laboratory (hereinafter referred to as Anahem) from Belgrade (Serbia) was appointed by Association ZA Drinking Fountains, Zaječar, to carry out the sampling and laboratory analyses of water, sediments and ichthyofauna in the rivers of the Crni Timok, the Veliki Timok, the Borska reka, the Pek, the Dunav at the confluence of the Timok within the Project "ENVIRONMENTAL RESPONSE TO MINING EXPANSION IN TIMOČKA KRAJINA".

The purpose of the study is to investigate existing situation and further monitoring of harmful effects of mining and urban development on the environment in Timočka Krajina. In order to estimate existing situation, samples were taken at ten locations described in the next chapter. Figure 1 shows the map of the area - Timočka Krajina.



Figure 1. Map of Timočka Krajina

Sampling was carried out in the period from 31.08.2022 to 03.09.2022. The analysis of the samples was done in accordance with the scope defined by the offer 12051609, which included:

- Physico-chemical analyzes: 1) Water: color, odor, temperature, electrical conductivity, pH, concentration of dissolved oxygen, as well as concentration of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_3$ , As, Cd, Cu, Fe, Mn, Ni, Pb, Hg, Zn, Co, Sr, S, Ca, Mg, K, Na and Cr; organic and microbiological pollution. 2) Sediment: color and concentration of Mn,

Ni, Co, Sr, As, Cd, Cr, Hg, Cu, Pb and Zn; radioactivity. 3) Ichthio fauna samples: radioactivity and Cd, Pb, As, Cu, Hg, Cr, Co, Ni, Mn, Zn, Fe and Hg concentration.

## 2. LOCATIONS OF SAMPLING POINTS

### 2.1. River Pek

In order to determine the quality of the Pek River, as well as the impact of the mine in Majdanpek, which with flotation and landfills represents a potential source of pollution, sampling was carried out according to the sketch shown in Figure 2. Figure 3 shows a satellite view of the sampling points, and Table 1 lists the GPS coordinates and sample labels.



Figure 2. Sketch of sampling locations



Figure 3. Satellite view of sampling points

Table 1. GPS coordinates of sampling locations and sample IDs

Sample ID		Location	N	E
Water	Sediment			
1205160911	5208300209	Mali Pek before the sewage inlet	44.42810	21.932814
1205160912	5208300210	Mali Pek before the open-pit mine in Majdanpek	44.420611	21.934506
1205160913	5208300211	Mali Pek after the open-pit mine in Majdanpek	44.402428	21.916147
1205160914	5208300212	Veliki Pek downstream from the tailings in Valja Fundata	44.363914	21.913689
1205160915	5208300213		44.363942	21.913892

1205160916	5208300214	Pek after the confluence of the Mali and the Veliki Pek	44.391653	21.888101
1205160917	5208300215		44.397572	21.885186

## 2.2. Borska reka, Brestovačka reka, Timok

Upstream from Bor, the Borska reka is directed into the Kriveljska reka through a tunnel, in order to open a copper surface mine in its valley. Downstream from Bor, communal wastewater, untreated mine water and wastewater from the metallurgy and basic chemistry plants are discharged into the bed of a former watercourse. A large amount of flotation tailings, which flood the banks of this river and the Veliki Timok downstream from its inflow, flows into the river. It flows through the villages of Slatina and Vražognac. The analysis of the samples, sampled based on the sketch (Figure 4), was carried out in order to determine the pollution of the Borska reka and its impact on the quality of the Veliki Timok river.

The water and sediment samples of the Crni Timok river were taken in order to determine the impact of mining and the release of toxic substances on the water quality, but also on the ichthyofauna. This is especially important because of the Timok trout, an autochthonous species, which is particularly threatened by the discharge of wastewater from Čukaru Peki mine. Also, samples of the Brestovačka reka were taken at representative locations in order to determine the pollution caused by the influence of the mine.

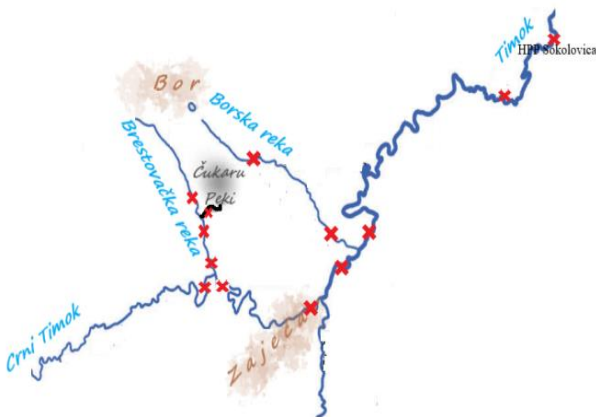


Figure 4. Sketch of sampling locations

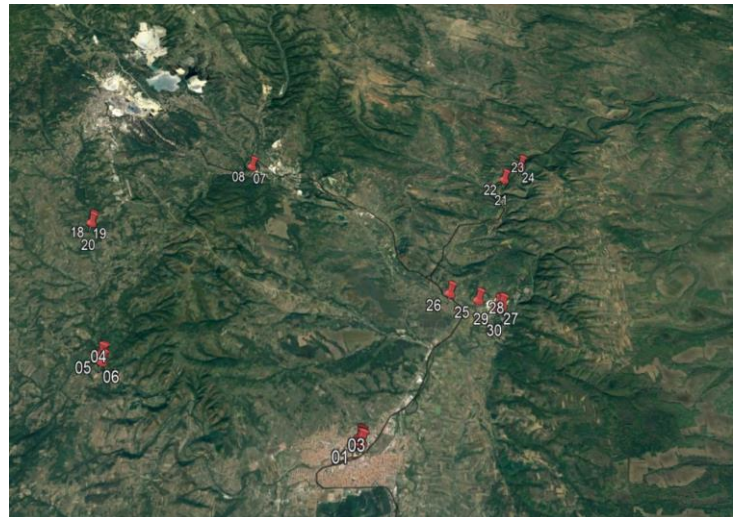


Figure 5. Satellite view of sampling points (Sample ID 12051609xx)

Table 2. GPS coordinates of sampling locations and sample IDs

Sample ID		Location	N	E
Water	Sediment			
1205160901	/	Crni Timok in the part of the course through the City of Zajecar - bathing area of Popova Plaža	43.907989	22.277083
1205160902	/		43.909089	22.277031
1205160903	5208300201	Crni Timok in the part of the course through the City of Zajecar - place of discharge of Zajecar brewery wastewater	43.907753	22.277733
1205160904	5208300202	Brestovačka Reka - before the confluence with Crni Timok	43.938394	22.152508
1205160905	5208300203	Crni Timok before the confluence of the Brestovačka Reka	43.938153	22.15165
1205160906	5208300204	Crni Timok after the confluence with Brestovačka river	43.936880	22.153031
1205160907	5208300205	Borska reka	44.029406	22.208203
1205160908	5208300206		44.029475	22.208353
1205160918	5208300216	The place of discharge of the waste canal from the new Čukaru Peki mine into the Brestovačka reka (the waste canal from the Čukaru Peki mine)	43.99765	22.123969
1205160919	5208300217	Brestovačka reka without the impact of wastewater from the mine	43.996983	22.123689
1205160920	5208300218	Brestovačka reka immediately after the inflow of wastewater from the mine	43.996850	22.123968

1205160921	5208300219	. The Veliki Timok near Hydropower plant Sokolovica (before the reservoir)	44.022472	22.360153
1205160922	5208300220			
1205160923	/	Veliki Timok near HPP Sokolovica (after the reservoir)	44.031078	22.371661
1205160924	/		44.031078	22.371661
1205160925	5208300221	Borska reka before confluence with Veliki Timok	43.961244	22.336511
1205160926	5208300222		43.96415	22.322181
1205160927	5208300223	Veliki Timok after confluence with Borska reka	43.958925	22.34815
1205160928	5208300224		43.958905	22.347376
1205160929	5208300225		43.958407	22.345836

### 2.3. Timok, Dunav

After the confluence of the Borska reka, Veliki Timok flows into the Dunav, where harmful substances and waste water from mines and smelters in Bor end up. Sampling at the locations - the river Timok before its confluence with the Dunav, Dunav after its confluence with the Timok and the Dunav River before its confluence with the Timok determines the pollution and influence of the river Timok on the Dunav.

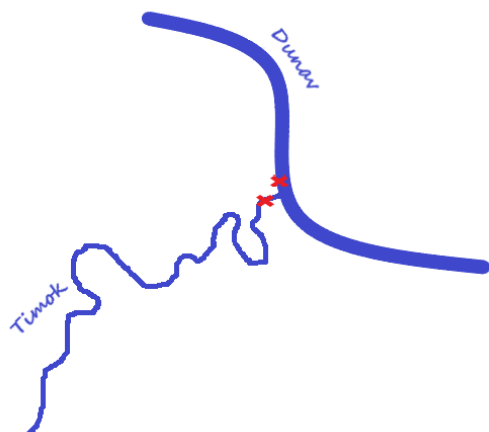


Figure 6. Sketch of sampling locations

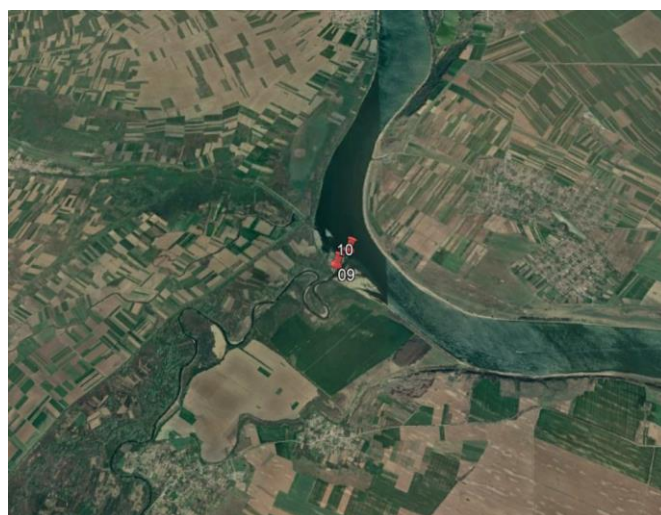


Figure 7. Satellite view of sampling points (Sample ID 12051609xx)

Table 3. GPS coordinates of sampling locations and sample IDs

Sample ID		Location	N	E
Water	Sediment			
1205160909	5208300207	Timok before the confluence with Dunav	44.214375	22.670867
1205160910	5208300208	Dunav before the confluence of the Timok	44.216953	22.672217

In addition to the mentioned samples, the campaign foresees more samples in certain locations where sampling was not carried out for the following reasons:

The sediment sample from the Crni Timok river in the part of the course through the City of Zajecar was not sampled because both the coast and the bottom of the river are paved and there is no sediment. Also, it was not possible to carry out sampling at the place where wastewater from the mine, smelter and sewerage of the city of Bor was discharged into the waste canal of the Borska reka, because the location was inaccessible due to heavy rainfall.

After the confluence of the river Timok, the river Dunav continues its course on the territory of Bulgaria. The field team did not carry out sampling at this location because at that moment they did not have the authorization to move to another country.

The location - Veliki Pek, upstream of the tailings pond in Valja Fundata was also inaccessible, i.e. a ramp has been installed and access was prohibited.

The locations where a fish sample was taken for the purpose of laboratory analysis, on the basis of which the potential pollution of the ichthyofauna can be assessed, are shown in Table 4.



Table 4. Locations and IDs of fish samples\*.

No.	Location	Sample ID
1.	Veliki Timok near HPP Sokolovica (after the reservoir)	4208300101
2.	Crni Timok after the confluence with Brestovačka river	4208300102

\*samples delivered to Anahem

### 3. TECHNIQUES AND METHODS

#### 3.1. Sampling and analysis of water

Sampling and laboratory analysis of surface and groundwater was performed according to standard and validated accredited methods. The following methods for sampling were used: *SRPS EN ISO 5667-1*, *SRPS EN ISO 5667-3*, *SRPS EN ISO 5667-4*, *SRPS EN ISO 5667-6*, and *SRPS EN ISO 19458*. The field analytes were tested at the site. A portable fridge was used to keep samples cold during their transport to the laboratory. Laboratory analyses of water samples were made by using methods given in Table 5.

Table 5. List of methods used for the surface water analysis.

Parameter	METHOD
<b>FIELD MEASUREMENTS</b>	
Water temperature	EPA 170.1
pH Value	EPA 150.1
Conductivity	EPA 120.1
Dissolved Oxygen (O <sub>2</sub> )	EPA 360.1
<b>LABORATORY MEASUREMENTS</b>	
Color	SRPS EN ISO 7887
Odor	DML 2.7
Sulfates (SO <sub>4</sub> <sup>2-</sup> ), Chloride (Cl <sup>-</sup> ), Orthophosphates, Nitrate (NO <sup>3-</sup> ), Nitrite (NO <sup>2-</sup> )	ISO 10304-1
Ammonium ion (NH <sub>4</sub> -N)	SRPS ISO 7150-1
Cadmium (Cd), Nickel (Ni), Lead (Pb), Zinc (Zn), Cobalt (Co)	EPA 200.8
Arsenic (As), Copper (Cu), Chromium (Cr) Total, Iron (Fe), Manganese (Mn), Strontium (Sr), Sulphur	SRPS EN ISO 11885
Magnesium, Potassium, Calcium, Sodium	ISO 14911
Phenols	SRPS ISO 6439
Petroleum hydrocarbons (C10-C40)	ISO 9377-2
Surface active agents (such as lauryl sulfate)	SM 5540C
AOX	DML 2.2
<b>MICROBIOLOGY MEASUREMENTS</b>	
Fecal coliform count in 100 ml MPN Colilert	DML 2.9
Total coliform count in 100 ml MPN Colilert	DML 2.9
Intestinal enterococci	DML 2.10
Aerobic heterotrophic bacteria	SRPS EN ISO 62220

### 3.2. Sampling and analysis of sediment

Accredited methods were used for sediment sampling and analysis. The sediment sampling procedure was performed according to the *SRPS ISO 5667-12* method. Laboratory analyzes of sediment samples were performed using the methods given in Table 4.

Table 4. List of methods used for sediment analysis.

Parameter	METHOD
Metals: Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Nickel (Ni), Zinc (Zn), Manganese (Mn), Cobalt (Co), Strontium (Sr)	EPA 3051A/EPA 6010c
Clay content	ISO 11277
Content of organic matter	EN EN TC WI
Content of radionuclides	SRPS EN ISO 18589-3

### 3.3. Analysis of fish samples

Table 5 shows the methods used for the analysis of fish samples.

Table 5. List of methods used for the analysis of fish samples.

Parameter	METHOD
Cobalt (Co), Nickel (Ni), Manganese (Mn), Chromium (total)	DML 1.1
Cadmium (Cd), Lead (Pb), Arsenic (As), Mercury (Hg), Copper (Cu), Iron (Fe), Zinc (Zn)	SRPS EN 15763
Content of radionuclides	IAEA TRS 295

#### 4. EXPERIMENTAL RESULTS

##### 4.1. Limit values of pollutants in surface waters and criteria for assessing the quality of sediment and permitted methods of handling washed sediment.

Table 6. Regulated limit values of parameters for surface water  
(Official Gazette RS, No 50/2012).

Parameter	Limit values <sup>1</sup>				
	I class	II class	III class	IV class	V class
pH value	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	<6.5 or <8.5
Suspended solids, mg/L	25	25	-	-	-
Dissolved oxygen, mg O <sub>2</sub> /L	8.5	7.0	5	4	<4
Oxygen saturation, %	90-110	70-90	50-70	30-50	<30
BOD <sub>5</sub> , mg O <sub>2</sub> /L	1.8	4.0	7	25	>25
COD (K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ), mg O <sub>2</sub> /L	10	15	30	125	>125
Consumption of KMnO <sub>4</sub> , mg O <sub>2</sub> /L	5	10	20	50	>50
Total organic carbon (TOC), mg/L	2.0	5.0	15	50	>50
<b>Nutrients</b>					
Total nitrogen, mg N/L	1	2	8	15	>15
Nitrate, mg N/L	1.5	3.0	6	15	>15
Nitrite, mg N/L	0.01	0.03	0.12	0.3	>0.3
Ammonia nitrogen, mg N/L	0.10	0.30	0.6	1.5	>1.5
Un-ionized ammonia, mg NH <sub>3</sub> /L	0.005	0.025	-	-	-
Total phosphorus, mg P/L	0.05	0.10	0.4	1	>1
Orthophosphate, mg P/L	0.02	0.10	0.2	0.5	>0.5
<b>Salinity</b>					
Chloride, mg/L	50	100	150	250	>250
Total residual chlorine, mg HOCl/L	0.005	0.005	-	-	-
Sulfates, mg/L	50	100	200	300	>300
Total mineralization, mg/L	<1000	1000	1300	1500	>1500
Conductivity at 20°C, µS/cm	<1000	1000	1500	3000	>3000
<b>Metals, µg/L</b>					
Arsenic	<5	10	50	100	>100
Cadmium	-	-	-	-	-
Copper	5 (T=10) 22 (T=50) 40 (T=100) 112 (T=300)	5 (T=10) 22 (T=50) 40 (T=100) 112 (T=300)	500	1000	>1000
Zinc	30 (T=10) 200 (T=50) 300 (T=100) 500 (T=500)	300 (T=10) 700 (T=50) 1000 (T=100) 2000 (T=500)	2000	5000	>5000
Chromium (total)	25	50	100	250	>250
Chromium III (dissolved)	-	-	-	-	-
Chromium VI (dissolved)	-	-	-	-	-
Iron (total)	200	500	1000	2000	>2000
Boron	300	1000	1000	2500	>2500
Lead (dissolved)	-	-	-	-	-

Manganese (total)	50	100	300	1000	>1000
Mercury	-	-	-	-	-
Nickel (dissolved)	-	-	-	-	-
<i>Organic substances</i>					
Phenol compounds, µg/L	<1	1	20	50	>50
Petroleum hydrocarbons <sup>2</sup>	without	without	without	without	without
Surface active agents, µg/L	100	200	300	500	>500
AOX, µg/L	10	50	100	250	>250
<i>Microbiology</i>					
Fecal coliforms, cfu/100ml	100	1000	10000	100000	>100000
Total coliforms, cfu/100ml	500	10000	100000	1000000	>1000000
Intestinal enterococci, cfu/100ml	200	400	4000	40000	>40000
Aerobic heterotrophic bacteria, cfu/100ml	500	10000	100000	750000	>750000

According to the decree on the categorization of watercourses ("Official Gazette of the RS", no. 5/68), the Pek River belongs to class III from the source to the confluence with the Danube River. Crni Timok from its source to Zaječar and from Zaječar to the confluence of the Bor river belongs to class II, while from the confluence with the Bor river to the confluence with the Danube belongs to class III. The Bor river from its source to Bor belongs to class II, while from Bor to its confluence with Timok it belongs to class IV. The Danube River belongs to class II.

The criteria for assessing the quality of the sediment and the permitted ways of dealing with washed sediment (Official Gazette RS, No 50/2012) are shown in table 7.

Table 7. The criteria for assessing the quality of the sediment and the permitted ways of dealing with washed sediment

Class	Criteria	Ways of handling washed sediment
0	≤ Target value	The concentrations of pollutants in the sediment are at the level of the natural background. Sediments can be dislodged without special protection measures.
1	> Target value and ≤ Limit value	The sediment is slightly polluted. During dislocation, disposal is permitted without special protection measures in a zone up to 20 m wide in the vicinity of watercourses.
2	> Limit value and ≤ Verification limit	
3	> Verification level ≤ Remediation value	The sediment is polluted. It is not allowed to dispose of it without special protective measures. It is necessary to store it in controlled conditions with special protection measures in order to prevent the spread of polluting substances in the environment.

s4	> Remediation value	Extremely polluted sediments. Remediation or storage of ground material in controlled conditions with special protection measures is mandatory to prevent the spread of pollutants into the environment.
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#### 4.2. Analysis of water and sediment

##### 4.2.1. Analysis results - water and sediment quality - River Pek and the impact of the inflow of Mali Pek and Veliki Pek

The results of the analysis of water quality parameters are shown in Table 8

Table 8. The results of the analysis of water quality parameters (Sample ID 12051609xx)

Location:	Mali Pek before the sewage inlet	Mali Pek before the open-pit mine in Majdanpek	Mali Pek after the open-pit mine in Majdanpek	The Veliki Pek downstream from the tailings in Valja Fundata		Pek after the confluence of the Mali and Veliki Pek	
Sample ID:	11	12	13	14	15	16	17
Water temperature, °C	19.8	22	20.1	19.7	19.7	19.6	19.5
Color	Slightly yellow	black	dark yellow	dark yellow	dark yellow	dark yellow	dark yellow
Odor	without	present	present	without	without	without	without
Conductivity $\mu\text{S}/\text{cm}$	451	815	1137	1209	1212	1154	1170
pH	7.5	6.6	7.2	7.4	7.1	7.2	7.1
Dissolved oxygen mg/l	2.5	1.7	1.7	4.1	1.7	1.4	1.7
Sulfates, mg/l	16	115	439	531	471	341	399
Chlorides, mg/l	3.9	17	19	14	20	8.8	9.6
Orthophosphates, mg/l	0.07	0.62	0.81	0.25	0.09	0.89	0.72
Nitrates mgN/l	<0.1	<0.1	2.5	0.11	0.12	0.19	0.24
Nitrites mgN/l	<0.03	<0.03	0.56	0.08	0.04	<0.03	<0.03
Ammonium ion (NH <sub>4</sub> -N) mgN/l	0.45	9.4	11	1.4	1.1	0.11	0.15
Arsenic, mg/l	0.0044	0.016	0.0087	0.0065	0.0053	0.019	0.006
Cadmium, mg/l	<0.001	0.0034	0.0017	<0.001	<0.001	0.0014	<0.001
Copper, mg/l	0.0066	0.34	0.45	0.072	0.058	0.41	0.11

<b>Chromium (total), mg/l</b>	<0.01	0.041	<0.01	<0.01	<0.01	0.028	0.012
<b>Iron, mg/l</b>	0.56	21	13	3.6	2.7	11	7.1
<b>Manganese, mg/l</b>	0.084	1.2	3.5	0.46	0.39	1.5	0.98
<b>Nickel, mg/l</b>	0.0068	0.052	0.024	0.0088	0.0078	0.022	0.01
<b>Lead, mg/l</b>	0.0012	0.062	0.017	0.01	0.0083	0.15	0.079
<b>Zinc, mg/l</b>	0.023	0.44	0.54	0.11	0.067	0.42	0.2
<b>Cobalt, mg/l</b>	<0.001	0.036	0.023	0.0011	<0.001	0.014	0.0041
<b>Strontium, mg/l</b>	0.15	0.25	0.46	1.0	0.99	1.1	1.2
<b>Sulphur, mg/l</b>	5.3	58	149	179	163	187	182
<b>Magnesium, mg/l</b>	8.4	14	38	21	20	25	26
<b>Potassium, mg/l</b>	1.7	5.9	7.1	13	12	11	11
<b>Calcium, mg/l</b>	67	102	141	195	188	189	169
<b>Sodium, mg/l</b>	5.5	18	22	37	36	28	32
<b>Phenol compounds (such as C<sub>2</sub>H<sub>5</sub>OH), µg/L</b>	<1	<1	<1	<1	<1	<1	<1
<b>Petroleum hydrocarbons, mg/L</b>	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
<b>Surface active agents (such as lauryl sulfate), µg/L</b>	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
<b>AOX (adsorbable organic halides), µg/L</b>	<10	<10	<10	<10	<10	<10	<10
<b>Fecal coliforms, MPN/100ml</b>	2400	<10	430	230	230	<10	230
<b>Total coliforms, MPN/100ml</b>	2400	2400	24000	230	230	2400	230
<b>Intestinal enterococci, MPN/100ml</b>	230	24000	24000	230	230	2400	230
<b>Aerobic heterotrophic bacteria, cfu/100ml</b>	9 x 10 <sup>4</sup>	2.8 x 10 <sup>6</sup>	1.2 x 10 <sup>6</sup>	9 x 10 <sup>4</sup>	1.1 x 10 <sup>5</sup>	6.4 x 10 <sup>5</sup>	7 x 10 <sup>4</sup>

The spatial distribution of arsenic (mg/l) and cooper (mg/l) in water samples (Majdanpek area) are shown in Figure 8

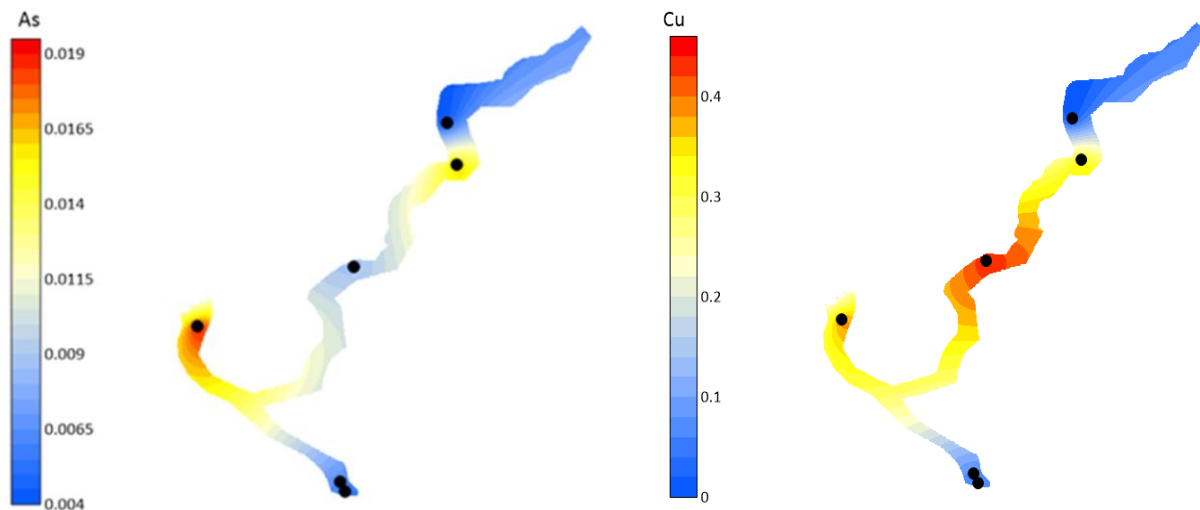


Figure 8. The spatial distribution of arsenic and cooper (mg/l) in water samples (Majdanpek area)

The spatial distribution of sulfates (mg/l) and intestinal enterococci (MPN/100ml) in water samples (Majdanpek area) are shown in Figure 9.

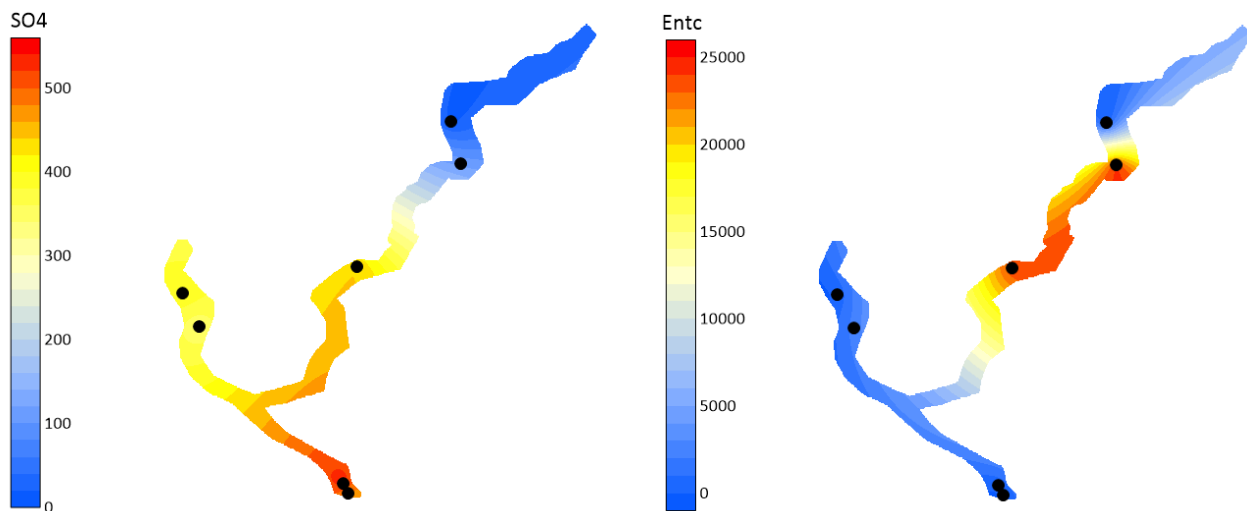


Figure 9. The spatial distribution of sulfates (mg/l) and intestinal enterococci (MPN/100ml) in water samples (Majdanpek area)

The results of the analysis of metal content in sediments in the rivers Mali Pek, Veliki Pek and Pek are shown in the table 9.

Table 9. The results of the analysis of metal content in sediments in the rivers Mali Pek, Veliki Pek and Pek (Sample ID 52083002xx)

Location:	Mali Pek before the sewage inlet	Mali Pek before the open-pit mine in Majdanpek	Mali Pek after the open-pit mine in Majdanpek	The Veliki Pek downstream from the tailings in Valja Fundata		Pek after the confluence of the Mali and Veliki Pek	
Sample ID:	09	10	11	12	13	14	15
Parameter:	Arsenic, mg/kg						
Result:	<b>30</b>	<b>29</b>	<b>51</b>	<b>41</b>	<b>36</b>	<b>32</b>	<b>47</b>
MDK <sup>1</sup>	17.2	21.5	15.5	17.9	19.3	16.3	18.6
MDK <sup>2</sup>	32.6	40.8	29.5	33.9	33.6	31	35.3
MDK <sup>3</sup>	32.6	40.8	29.5	33.9	33.6	31	35.3
MDK <sup>4</sup>	32.6	40.8	29.5	33.9	33.6	31	35.3
Parameter:	Cadmium, mg/kg						
Result:	<b>0.66</b>	<b>2.3</b>	<b>2.5</b>	<b>1.2</b>	<b>1.1</b>	<b>1.5</b>	<b>2.8</b>
MDK <sup>1</sup>	0.5	0.7	0.4	0.5	0.6	0.5	0.6
MDK <sup>2</sup>	1.3	1.7	1.1	1.3	1.4	1.2	1.4
MDK <sup>3</sup>	4.9	6.4	4	4.7	5.4	4.5	5.3
MDK <sup>4</sup>	7.8	10.3	6.4	7.5	8.6	7.1	8.5
Parameter:	Chromium (total), mg/kg						
Result:	<b>7.8</b>	<b>15</b>	<b>5.7</b>	<b>13</b>	<b>6.4</b>	<b>11</b>	<b>9.6</b>
MDK <sup>1</sup>	50.6	59.6	51	58.2	59	50.4	54.4
MDK <sup>2</sup>	192	226	194	221	224	192	207
MDK <sup>3</sup>	192	226	194	221	224	192	207
MDK <sup>4</sup>	192	226	194	221	224	192	207
Parameter:	Copper, mg/kg						
Result:	<b>1596</b>	<b>620</b>	<b>786</b>	<b>557</b>	<b>399</b>	<b>931</b>	<b>1103</b>
MDK <sup>1</sup>	18.3	24.8	15.8	19.3	21.5	17	20.4
MDK <sup>2</sup>	18.3	24.8	15.8	19.3	21.5	17	20.4
MDK <sup>3</sup>	45.7	61.9	39.5	48.3	53.7	42.5	51
MDK <sup>4</sup>	96.4	131	83.4	102	113	89.7	108
Parameter:	Mercury, mg/kg						
Result:	<b>0.055</b>	<b>0.11</b>	<b>0.087</b>	<b>0.053</b>	<b>0.11</b>	<b>0.006</b>	<b>0.1</b>
MDK <sup>1</sup>	0.2	0.2	0.2	0.2	0.2	0.2	0.2
MDK <sup>2</sup>	0.3	0.4	0.3	0.4	0.4	0.3	0.4
MDK <sup>3</sup>	1.1	1.2	1.1	1.2	1.2	1.1	1.2
MDK <sup>4</sup>	6.9	7.8	6.7	7.3	7.5	6.8	7.3
Parameter:	Lead, mg/kg						
Result:	<b>84</b>	<b>79</b>	<b>101</b>	<b>32</b>	<b>17</b>	<b>73</b>	<b>128</b>
MDK <sup>1</sup>	55.5	66.3	51.4	57.2	60.8	53.3	59
MDK <sup>2</sup>	346	413	320	357	379	332	368



MDK <sup>3</sup>	346	413	320	357	379	332	368
MDK <sup>4</sup>	346	413	320	357	379	332	368
Parameter:	Nickel, mg/kg						
Result:	<b>7</b>	<b>13</b>	<b>8.6</b>	<b>12</b>	<b>5.8</b>	<b>7.1</b>	<b>11</b>
MDK <sup>1</sup>	10.3	14.8	10.5	14.1	14.5	10.2	12.2
MDK <sup>2</sup>	10.3	14.8	10.5	14.1	14.5	10.2	12.2
MDK <sup>3</sup>	13.2	19	13.5	18.1	18.6	13.1	15.7
MDK <sup>4</sup>	61.8	88.8	63	84.6	87	61.2	73.2
Parameter:	Zinc, mg/kg						
Result:	<b>65</b>	<b>347</b>	<b>377</b>	<b>176</b>	<b>131</b>	<b>297</b>	<b>529</b>
MDK <sup>1</sup>	58.6	81.6	52.8	67	73	55.3	66.8
MDK <sup>2</sup>	201	278	181	229	250	189	229
MDK <sup>3</sup>	302	420	271	344	375	284	343
MDK <sup>4</sup>	302	420	271	344	375	284	343

MDK<sup>1</sup> – \* Target value

MDK<sup>2</sup> – \* Limit value

MDK<sup>3</sup> - \* Verification Level

MDK<sup>4</sup> - \* Remediation value

\* corrected values related to the content of clay and organic matter, in accordance with the Regulation on limit values of polluting materials in surface and underground waters and sediment and deadlines for their achievement ("Official Gazette of RS", No. 50/12).

The spatial distributions of arsenic (mg/l) and cooper (mg/l) in sediments (Majdanpek area) are shown in Figure 10.

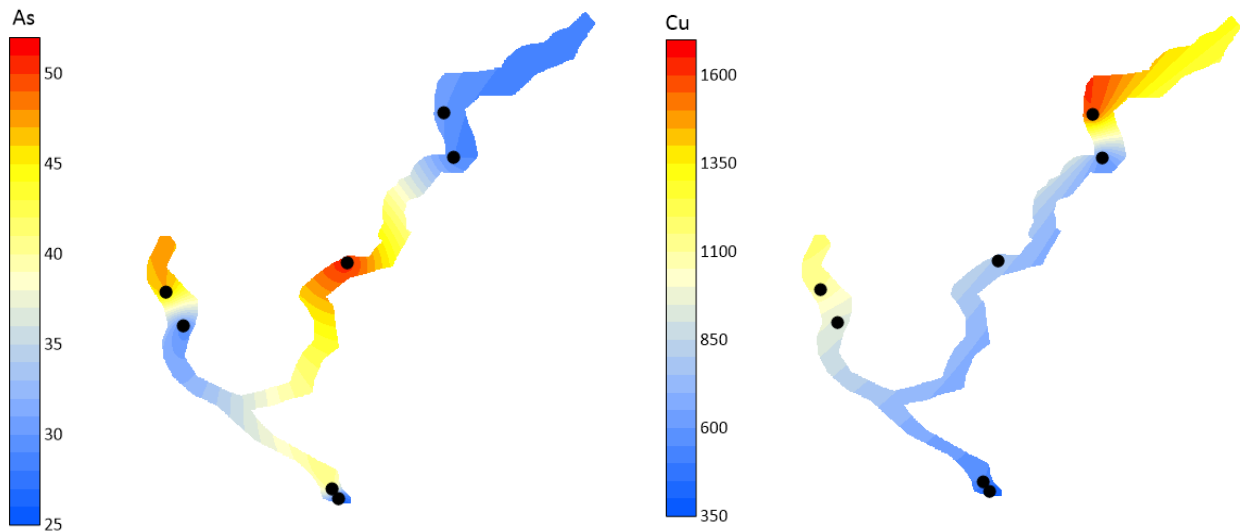


Figure 10. The spatial distribution of arsenic (mg/l) and cooper (mg/l) in sediments (Majdanpek area)

The results of the analysis of the content of radionuclides in sediments in the rivers Mali Pek, Veliki Pek and Pek are shown in the table 10.

Table 10. The results of the analysis of the content of radionuclides in sediments in the rivers Mali Pek, Veliki Pek and Pek

Location:	Mali Pek before the sewage inlet	Mali Pek before the open-pit mine in Majdanpek	Mali Pek after the open-pit mine in Majdanpek	The Veliki Pek downstream from the tailings in Vajja Fundata		Pek after the confluence of the Mali and Veliki Pek	
Sample ID:	09	10	11	12	13	14	15
Parameter:	<sup>137</sup> Cesium, Bq/kg						
Result:	6.1	2.2	<1,0	3.2	6.1	7.1	<1,0
Parameter:	<sup>40</sup> Potassium, Bq/kg						
Result:	93	152	463	330	320	464	253
Parameter:	<sup>232</sup> Thorium, Bq/kg						
Result:	6.1	5.9	13	10	10	16	9.1
Parameter:	<sup>226</sup> Radium, Bq/kg						
Result:	8.1	6.1	15	11	10	18	10
Parameter:	<sup>238</sup> Uranium, Bq/kg						
Result:	<3,0	<3,0	<3,0	<3,0	<3,0	<3,0	<3,0

The spatial distribution of radium-226 in sediments (Majdanpek area) is shown in Figure 11.

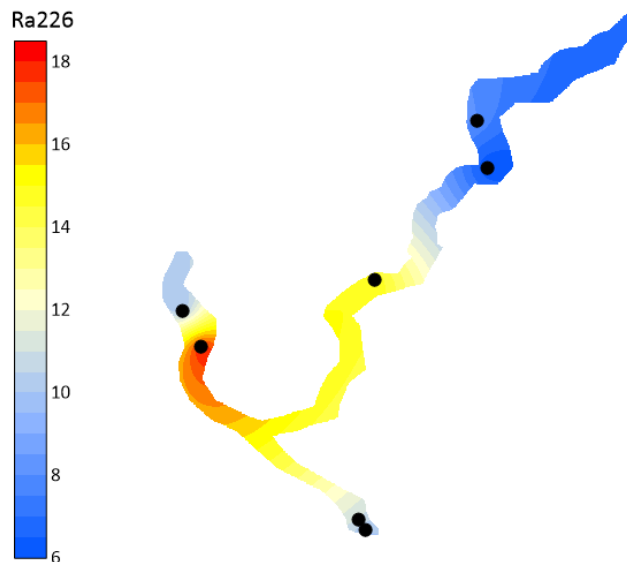


Figure 11. The spatial distribution of radium-226 in sediments (Majdanpek area)

#### 4.1.2. Analysis results - water and sediment quality – Brestovačka reka, Borska reka and their impact on Timok and Dunav

The results of the analysis of water quality parameters are shown in Tables 11, 12 and 13.

Table 11. The results of the analysis of water quality parameters – Brestovačka reka, Crni Timok (Sample ID 12051609xx)

Location:	Brestovačka Reka - before the confluence with Crni Timok	Crni Timok before the confluence of the Brestovačka Reka	Crni Timok after the confluence with Brestovačka river	Waste canal from the Čukaru Peki mine	Brestovačka reka without the impact of wastewater from the mine	Brestovačka reka immediately after the inflow of wastewater from the mine
Sample ID:	04	05	06	18	19	20
Water temperature, °C	19.1	23.4	23.6	19.6	19.1	19.8
Color	Slightly yellow	Slightly yellow	Slightly yellow	Slightly yellow	Slightly yellow	yellow
Odor	without	without	present	without	without	without
Conductivity $\mu\text{S}/\text{cm}$	546	491	495	1039	588	608
pH	7.2	7.6	7.4	7.5	7.1	7.2
Dissolved oxygen mg/l	1.9	3.9	3.3	2	1.4	1.4
Sulfates, mg/l	63	21	31	87	78	84
Chlorides, mg/l	13	5.9	7.4	41	15	16
Orthophosphates, mg/l	0.56	<0.01	0.14	0.21	0.29	0.31
Nitrates mgN/l	0.76	<0.1	<0.1	0.18	0.29	0.34
Nitrites mgN/l	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Ammonium ion ( $\text{NH}_4\text{-N}$ ) mgN/l	0.02	0.07	0.12	0.19	0.13	0.24
Arsenic, mg/l	0.0051	0.0013	0.0026	0.0087	0.014	0.015
Cadmium, mg/l	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Copper, mg/l	0.016	0.0043	0.0038	0.027	0.041	0.036
Chromium (total), mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Iron, mg/l	0.68	0.13	0.21	0.25	1.3	1.2
Manganese, mg/l	0.046	0.016	0.017	0.011	0.070	0.065
Nickel, mg/l	0.0070	0.0063	0.0063	0.0069	0.0067	0.0062
Lead, mg/l	0.0020	<0.001	<0.001	0.0011	0.0047	0.0039
Zinc, mg/l	0.028	0.035	0.037	0.027	0.055	0.048
Cobalt, mg/l	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Strontium, mg/l	0.23	0.13	0.16	0.39	0.27	0.27
Sulphur, mg/l	23	7.2	11	28	28	29
Magnesium, mg/l	9.7	6.0	7.0	18	12	13
Potassium, mg/l	2.7	1.5	1.8	3.1	2.8	2.9
Calcium, mg/l	64	77	75	135	71	72
Sodium, mg/l	20	6.5	9.8	57	19	20

<b>Phenol compounds (such as C<sub>2</sub>H<sub>5</sub>OH), µg/L</b>	<1	<1	<1	<1	<1	<1
<b>Petroleum hydrocarbons, mg/L</b>	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
<b>Surface active agents (such as lauryl sulfate), µg/L</b>	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
<b>AOX (adsorbable organic halides), µg/L</b>	<10	<10	<10	<10	<10	<10
<b>Fecal coliforms, MPN/100ml</b>	230	<10	<10	230	230	230
<b>Total coliforms, MPN/100ml</b>	230	<10	<10	230	2400	2400
<b>Intestinal enterococci, MPN/100ml</b>	<10	<10	<10	40	230	230
<b>Aerobic heterotrophic bacteria, cfu/100ml</b>	1.5 x 10 <sup>4</sup>	2 x 10 <sup>4</sup>	2.5 x 10 <sup>4</sup>	5 x 10 <sup>4</sup>	3.5 x 10 <sup>4</sup>	2 x 10 <sup>4</sup>

Table 12. The results of the analysis of water quality parameters –Crni Timok, Borska reka, Veliki Timok (Sample ID 12051609xx)

Location:	Crni Timok in the part of the course through the City of Zajecar - bathing area of Popova Plaža			Crni Timok - City of Zajecar - place of discharge of Zajecar brewery wastewater		Borska reka		Borska reka before confluence with Veliki Timok		Veliki Timok after confluence with Borska reka		Veliki Timok before confluence with Borska reka	
	01	02	03	07	08	25	26	27	28	29	30		
Sample ID:	01	02	03	07	08	25	26	27	28	29	30		
Water temperature, °C	23.7	23.5	23.8	20.4	20.3	20.6	20.5	20.7	20.6	21.2	21.1		
Color	Slightly yellow	Slightly yellow	Slightly yellow	brown-yellow	brown-yellow	yellow	yellow	yellow	yellow	Slightly yellow	Slightly yellow		
Odor	without	without	without	preset	present	without	without	without	without	without	without		
Conductivity µS/cm	474	467	472	1573	1579	1675	1668	946	947	517	519		
pH	7.5	7.4	7.3	6.7	6.5	6.8	6.8	7.2	7.1	7.3	7.2		
Dissolved oxygen mg/l	4.2	4.9	2.8	1.6	1.9	2.2	1.7	2	1.3	1.6	1.3		
Sulfates, mg/l	22	24	26	813	821	932	973	323	306	29	28		
Chlorides, mg/l	6.3	6.8	7.3	30	32	21	22	18	16	14	12		
Orthophosphates, mg/l	<0.01	<0.01	0.01	0.11	0.28	0.09	0.02	0.17	0.11	0.19	0.35		
Nitrates mgN/l	0.13	0.18	<0.1	2.3	3.8	0.18	0.22	0.25	0.77	<0.1	<0.1		

<b>Nitrites mgN/l</b>	<0.03	<0.03	<0.03	0.76	1.48	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
<b>Ammonium ion (NH<sub>4</sub>-N) mgN/l</b>	0.47	0.29	0.17	7.6	10	0.17	0.39	0.22	<0.01	0.27	<0.01
<b>Arsenic, mg/l</b>	0.0022	0.0022	0.0023	0.11	0.27	0.12	0.11	0.037	0.035	0.0025	0.0025
<b>Cadmium, mg/l</b>	<0.001	<0.001	<0.001	0.0084	0.012	0.0048	0.0052	0.0016	0.0016	<0.001	<0.001
<b>Copper, mg/l</b>	0.0060	0.0036	0.0037	1.2	6.8	3.6	4.2	1.2	1.3	0.0037	0.0036
<b>Chromium (total),mg/l</b>	<0.01	<0.01	<0.01	0.013	0.062	0.04	0.047	0.015	0.014	<0.01	<0.01
<b>Iron, mg/l</b>	0.20	0.13	0.28	88	144	53	65	20	18	0.40	0.34
<b>Manganese, mg/l</b>	0.020	0.018	0.031	4.0	5.1	3.8	3.9	1.4	1.3	0.055	0.052
<b>Nickel, mg/l</b>	0.0074	0.0066	0.15	0.033	0.080	0.046	0.049	0.023	0.022	0.0063	0.0071
<b>Lead, mg/l</b>	0.0034	<0.001	0.0035	0.010	0.15	0.069	0.076	0.022	0.022	0.0011	0.0016
<b>Zinc, mg/l</b>	0.035	0.023	0.029	0.66	2.2	0.68	0.78	0.26	0.25	0.03	0.017
<b>Cobalt, mg/l</b>	<0.001	<0.001	<0.001	0.034	0.081	0.047	0.05	0.019	0.019	<0.001	<0.001
<b>Strontium, mg/l</b>	0.16	0.16	0.16	0.93	1.1	1.2	1.3	0.56	0.54	0.21	0.21
<b>Sulphur, mg/l</b>	9.4	9.3	9.4	279	276	321	326	110	105	9.4	9.3
<b>Magnesium, mg/l</b>	6.3	6.4	6.4	45	46	43	43	20	19	8.4	8.3
<b>Potassium, mg/l</b>	2.3	2.4	2.6	8.4	11	9.3	9.7	5.0	4.8	3.2	3.1
<b>Calcium, mg/l</b>	69	69	69	210	236	277	279	139	136	66	67
<b>Sodium, mg/l</b>	8.6	8.7	8.9	51	45	45	44	23	22	14	15
<b>Phenol compounds (such as C<sub>2</sub>H<sub>5</sub>OH), µg/L</b>	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
<b>Petroleum hydrocarbons, mg/L</b>	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
<b>Surface active agents (such as lauryl sulfate), µg/L</b>	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
<b>AOX (adsorbable organic halides), µg/L</b>	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
<b>Fecal coliforms, MPN/100ml</b>	<10	<10	<10	<10	2400	930	40	230	<10	90	430
<b>Total coliforms, MPN/100ml</b>	<10	<10	<10	230	24000	2400	230	2400	230	230	2400
<b>Intestinal enterococci, MPN/100ml</b>	<10	<10	<10	230	2400	2400	11000	2100	230	40	40
<b>Aerobic heterotrophic bacteria, cfu/100ml</b>	4 x 10 <sup>4</sup>	3 x 10 <sup>4</sup>	1.6 x 10 <sup>5</sup>	1.6 x 10 <sup>6</sup>	1.1 x 10 <sup>7</sup>	6 x 10 <sup>5</sup>	6.2 x 10 <sup>5</sup>	5.4 x 10 <sup>5</sup>	5.7 x 10 <sup>5</sup>	1.4 x 10 <sup>5</sup>	8 x 10 <sup>4</sup>

The spatial distributions of arsenic (mg/l) and copper (mg/l) in water samples (Borska reka-Timok) are shown in Figure 12.

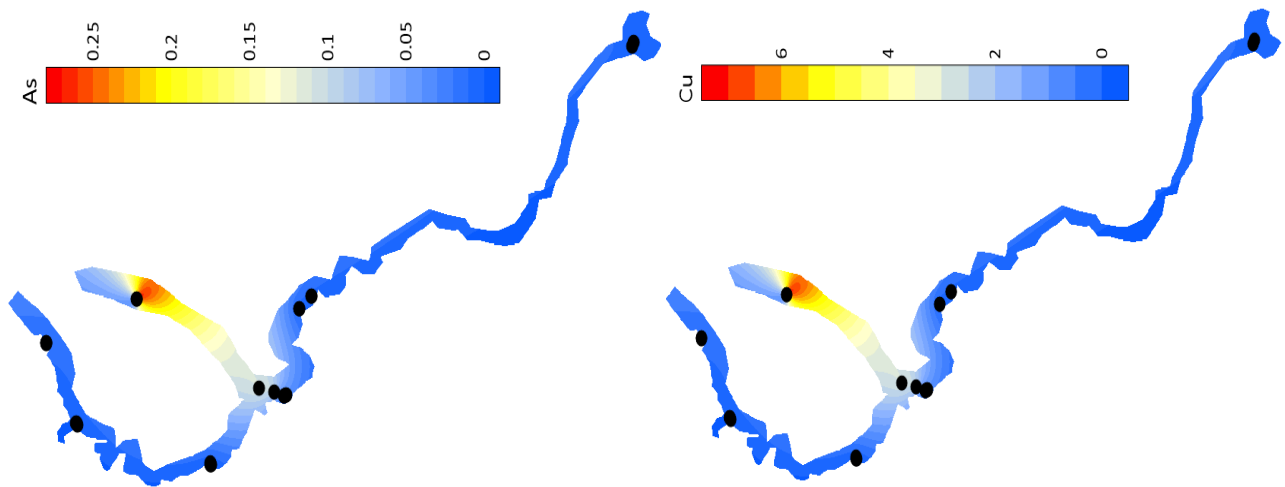


Figure 12. The spatial distributions of arsenic (mg/l) and copper (mg/l) in water samples (Borska reka-Timok)

The spatial distributions of sulfates (mg/l) and Intestinal enterococci (MPN/100ml) in water samples (Borska reka-Timok) are shown in Figure 13.

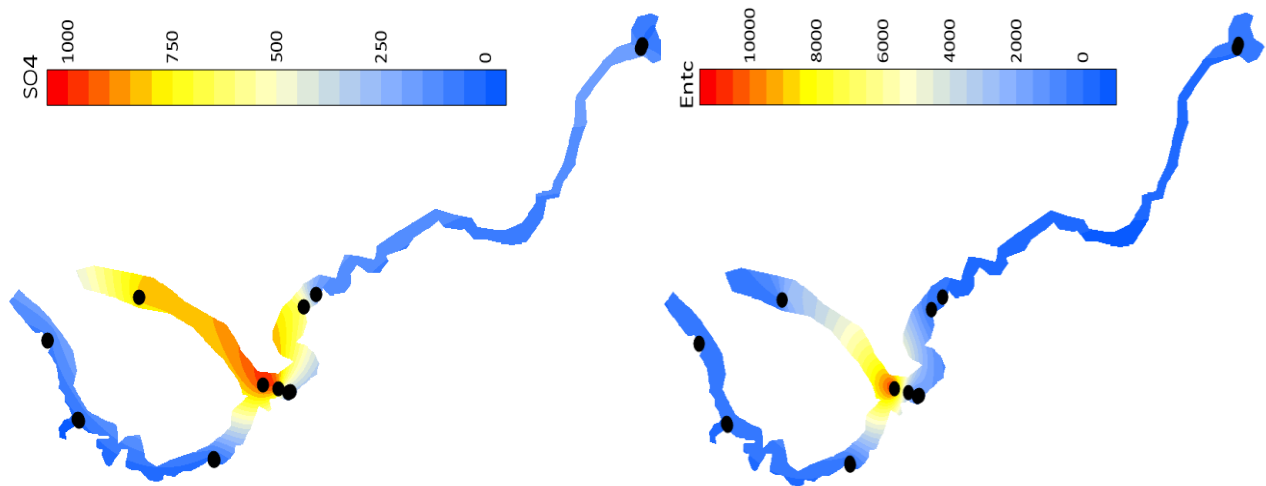


Figure 13. The spatial distributions of sulfates (mg/l) and Intestinal enterococci (MPN/100ml)

Table 13. The results of the analysis of water quality parameters –Timok - Hydropower plant Sokolovica (Sample ID 12051609xx)

Location:	The Veliki Timok near Hydropower plant Sokolovica (before the reservoir)		The Veliki Timok near Hydropower plant Sokolovica (after the reservoir)		Timok before the confluence with Dunav	Dunav before the confluence of the Timok
	21	22	23	24	09	10
Sample ID:	21	22	23	24	09	10
Water temperature, °C	21.8	21.7	21.2	21.3	23.2	23.7
Color	yellow	yellow	slightly yellow	slightly yellow	slightly yellow	slightly yellow
Odor	without	without	without	without	without	without
Conductivity $\mu\text{S}/\text{cm}$	1356	1314	768	752	778	470
pH	6.9	7.2	7.3	7.2	7,7	8,0
Dissolved oxygen mg/l	2.9	2.4	2.1	2.3	4,6	3,8
Sulfates, mg/l	629	632	153	146	201	45
Chlorides, mg/l	13	12	15	17	18	29
Orthophosphates, mg/l	<0.01	<0.01	0.01	<0.01	0,01	0,28
Nitrates mgN/l	<0.1	<0.1	<0.1	<0.1	0,61	0,85
Nitrites mgN/l	<0.03	<0.03	<0.03	<0.03	0,04	<0.03
Ammonium ion (NH <sub>4</sub> -N) mgN/l	0.33	0.21	0.09	0.07	0,36	0,42
Arsenic, mg/l	0.0049	0.0043	0.0066	0.0065	0,0093	0,0034
Cadmium, mg/l	<0.001	<0.001	<0.001	<0.001	<0,001	<0,001
Copper, mg/l	0.031	0.026	0.027	0.026	0,12	0,0086
Chromium (total), mg/l	<0.01	<0.01	<0.01	<0.01	<0,01	<0,01
Iron, mg/l	0.34	0.20	0.31	0.24	2,8	0,38
Manganese, mg/l	0.53	0.48	0.054	0.056	0,098	0,048
Nickel, mg/l	0.0088	0.0090	0.0074	0.007	0,0089	0,0076
Lead, mg/l	<0.001	<0.001	0.0011	<0.001	0,0046	<0,001
Zinc, mg/l	0.048	0.051	0.038	0.052	0,064	0,034
Cobalt, mg/l	<0.001	<0.001	<0.001	<0.001	0,0012	<0,001
Strontium, mg/l	0.7	0.68	0.37	0.35	0,42	0,25
Sulphur, mg/l	225	223	51	49	72	15
Magnesium, mg/l	21	20	15	14	17	11
Potassium, mg/l	5.5	5.2	3.9	3.7	4,1	3,2
Calcium, mg/l	246	228	102	97	98	48
Sodium, mg/l	22	21	21	20	23	18

<b>Phenol compounds (such as C<sub>2</sub>H<sub>5</sub>OH), µg/L</b>	<1	<1	<1	<1	<1	<1
<b>Petroleum hydrocarbons, mg/L</b>	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
<b>Surface active agents (such as lauryl sulfate), µg/L</b>	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
<b>AOX (adsorbable organic halides), µg/L</b>	<10	<10	<10	<10	<10	<10
<b>Fecal coliforms, MPN/100ml</b>	<10	40	230	<10	<10	<10
<b>Total coliforms, MPN/100ml</b>	<10	230	230	<10	<10	230
<b>Intestinal enterococci, MPN/100ml</b>	<10	<10	<10	<10	<10	230
<b>Aerobic heterotrophic bacteria, cfu/100ml</b>	1,6 x 10 <sup>5</sup>	2,6 x 10 <sup>5</sup>	5 x 10 <sup>4</sup>	3 x 10 <sup>5</sup>	9.6 x 10 <sup>5</sup>	1.1 x 10 <sup>5</sup>

Table 14. The results of the analysis of sediments - Brestovačka reka, Crni Timok (Sample ID 52083002xx)

Location:	Brestovačka Reka - before the confluence with Crni Timok	Crni Timok before the confluence of the Brestovačka Reka	Crni Timok after the confluence with Brestovačka river	Waste canal from the Čukaru Peki mine	Brestovačka reka without the impact of wastewater	Brestovačka reka immediately after the inflow of
Sample ID:	02	03	04	16	17	18
Parameter:	Arsenic, mg/kg					
Result:	2.5	3.1	6.9	34	5.6	7.5
MDK <sup>1</sup>	16.6	18.1	23.1	19.3	18.7	21.3
MDK <sup>2</sup>	31.5	34.3	43.8	36.6	35.4	40.3
MDK <sup>3</sup>	31.5	34.3	43.8	36.6	35.4	40.3
MDK <sup>4</sup>	31.5	34.3	43.8	36.6	35.4	40.3
Parameter:	Cadmium, mg/kg					
Result:	0.36	0.43	0.72	0.48	0.55	0.57
MDK <sup>1</sup>	0.5	0.5	0.8	0.6	0.6	0.7
MDK <sup>2</sup>	1.2	1.3	2	1.4	1.5	1.8
MDK <sup>3</sup>	4.5	4.9	7.3	5.4	5.5	6.9
MDK <sup>4</sup>	7.2	7.8	11.8	8.6	8.9	11
Parameter:	Chromium (total), mg/kg					



Result:	0.77	4.9	6.9	9.4	4.4	5.1
MDK <sup>1</sup>	51.6	57.6	58.2	58.8	51.6	51.2
MDK <sup>2</sup>	196	219	221	223	196	195
MDK <sup>3</sup>	196	219	221	223	196	195
MDK <sup>4</sup>	196.1	218.9	221.2	223.4	196.1	194.6
Parameter:	Copper, mg/kg					
Result:	37	37	287	757	129	181
MDK <sup>1</sup>	17.4	19.7	27.2	21.4	20.5	24.4
MDK <sup>2</sup>	17.4	19.7	27.2	21.4	20.5	24.4
MDK <sup>3</sup>	43.6	49.2	67.9	53.6	51.2	61
MDK <sup>4</sup>	92	104	143	113	108	129
Parameter:	Mercury, mg/kg					
Result:	<0.05	<0.05	0.053	0.054	<0.05	<0.05
MDK <sup>1</sup>	0.2	0.2	0.2	0.2	0.2	0.2
MDK <sup>2</sup>	0.3	0.4	0.4	0.4	0.4	0.4
MDK <sup>3</sup>	1.1	1.2	1.3	1.2	1.1	1.2
MDK <sup>4</sup>	6.9	7.3	8	7.5	7.2	7.5
Parameter:	Lead, mg/kg					
Result:	4.3	10	18	10	13	13
MDK <sup>1</sup>	54.1	57.8	70.3	60.7	59.1	65.7
MDK <sup>2</sup>	337	360	438	379	369	409
MDK <sup>3</sup>	337	360	438	379	369	409
MDK <sup>4</sup>	337	360	438	379	369	409
Parameter:	Nickel, mg/kg					
Result:	1.2	6.4	6.6	8.5	3.8	4.2
MDK <sup>1</sup>	10.8	13.8	14.1	14.4	10.8	10.6
MDK <sup>2</sup>	10.8	13.8	14.1	14.4	10.8	10.6
MDK <sup>3</sup>	13.9	17.7	18.1	18.5	13.9	13.6
MDK <sup>4</sup>	64.8	82.8	84.6	86.4	64.8	63.6
Parameter:	Zinc, mg/kg					
Result:	23	19	70	41	49	55
MDK <sup>1</sup>	57.3	67.4	86.6	72.7	64.9	74.4
MDK <sup>2</sup>	196	231	297	249	223	255
MDK <sup>3</sup>	295	346	445	374	334	383
MDK <sup>4</sup>	295	346	445	374	334	383

MDK<sup>1</sup> – \* Target value

MDK<sup>2</sup> – \* Limit value

MDK<sup>3</sup> – \* Verification Level

MDK<sup>4</sup> – \* Remediation value

\* corrected values related to the content of clay and organic matter, in accordance with the Regulation on limit values of polluting materials in surface and underground waters and sediment and deadlines for their achievement ("Official Gazette of RS", No. 50/12).

Table 15. The results of the analysis of the content of radionuclides in sediments- Brestovačka reka, Crni Timok (Sample ID 52083002xx)

Location:	Brestovačka Reka - before the confluence with Crni Timok	Crni Timok before the confluence of the Brestovačka Reka	Crni Timok after the confluence with Brestovačka river	Waste canal from the Čukaru Peki mine	Brestovačka reka without the impact of wastewater from the mine	Brestovačka reka immediately after the inflow of wastewater from the mine
Sample ID:	02	03	04	16	17	18
Parameter:	<sup>137</sup> Cesium, Bq/kg					
Result:	<1.0	<1.0	<1.0	5.9	2	<1.0
Parameter:	<sup>40</sup> Potassium, Bq/kg					
Result:	418	221	125	331	196	105
Parameter:	<sup>232</sup> Thorium, Bq/kg					
Result:	11	9.3	5.4	13	7.2	4.1
Parameter:	<sup>226</sup> Radium, Bq/kg					
Result:	10	12	5.3	12	6.3	5.4
Parameter:	<sup>238</sup> Uranium, Bq/kg					
Result:	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0

Tabele 16. The results of the analysis of sediments - Crni Timok, Borska reka, Veliki Timok (Sample ID 52083002xx)

Location:	Crni Timok - discharge of Zajecar brewery wastewater	Borska reka		Borska reka before confluence with Veliki Timok		Veliki Timok after confluence with Borska reka		Veliki Timok before confluence with Borska reka
Sample ID:	01	05	06	21	22	23	24	25
Parameter:	Arsenic, mg/kg							
Result:	<b>1.8</b>	<b>210</b>	<b>194</b>	<b>109</b>	<b>338</b>	<b>319</b>	<b>157</b>	<b>2.6</b>
MDK <sup>1</sup>	17.8	16.6	16.1	16.5	16.9	27.7	19.7	16
MDK <sup>2</sup>	33.7	31.4	30.4	31.3	32	52.6	37.4	30.3
MDK <sup>3</sup>	33.7	31.4	30.4	31.3	32	52.6	37.4	30.3
MDK <sup>4</sup>	33.7	31.4	30.4	31.3	32	52.6	37.4	30.3
Parameter:	Cadmium, mg/kg							
Result:	<b>0.22</b>	<b>3.4</b>	<b>3.3</b>	<b>1.9</b>	<b>5.1</b>	<b>3.7</b>	<b>2.9</b>	<b>0.27</b>
MDK <sup>1</sup>	0.5	0.5	0.5	0.5	0.5	1.1	0.7	0.5
MDK <sup>2</sup>	1.2	1.2	1.1	1.2	1.3	2.7	1.6	1.1

MDK <sup>3</sup>	4.6	4.6	4.3	4.5	4.7	10.2	6.2	4.2
MDK <sup>4</sup>	7.3	7.3	6.9	7.3	7.5	16.3	9.9	6.8
Parameter:	Chromium (total), mg/kg							
Result:	<b>2.6</b>	<b>6.1</b>	<b>11</b>	<b>9.5</b>	<b>17</b>	<b>17</b>	<b>16</b>	<b>11</b>
MDK <sup>1</sup>	59.6	50.4	50.8	50.4	50.8	50.6	50.6	51
MDK <sup>2</sup>	227	192	193	192	193	192	192	194
MDK <sup>3</sup>	227	192	193	192	193	192	192	194
MDK <sup>4</sup>	227	192	193	192	193	192	192	194
Parameter:	Copper, mg/kg							
Result:	<b>13</b>	<b>4177</b>	<b>3687</b>	<b>1467</b>	<b>4429</b>	<b>2245</b>	<b>1963</b>	<b>10</b>
MDK <sup>1</sup>	19.2	17.4	16.6	17.3	17.8	34.1	22.1	16.5
MDK <sup>2</sup>	19.2	17.4	16.6	17.3	17.8	34.1	22.1	16.5
MDK <sup>3</sup>	47.9	43.4	41.4	43.1	44.6	85.3	55.3	41.1
MDK <sup>4</sup>	101	92	88	91	94	180	117	87
Parameter:	Mercury, mg/kg							
Result:	<b>&lt;0.05</b>	<b>0.11</b>	<b>0.13</b>	<b>0.072</b>	<b>0.085</b>	<b>0.13</b>	<b>0.067</b>	<b>&lt;0.05</b>
MDK <sup>1</sup>	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2
MDK <sup>2</sup>	0.4	0.3	0.3	0.3	0.3	0.4	0.4	0.3
MDK <sup>3</sup>	1.2	1.1	1.1	1.1	1.1	1.3	1.2	1.1
MDK <sup>4</sup>	7.3	6.9	6.8	6.8	6.9	8.4	7.3	6.8
Parameter:	Lead, mg/kg							
Result:	<b>3.3</b>	<b>73</b>	<b>83</b>	<b>65</b>	<b>86</b>	<b>53</b>	<b>39</b>	<b>4</b>
MDK <sup>1</sup>	57	53.9	52.6	53.8	54.7	81.9	61.8	52.4
MDK <sup>2</sup>	355	336	328	335	341	510	386	327
MDK <sup>3</sup>	355	336	328	335	341	510	386	327
MDK <sup>4</sup>	355	336	328	335	341	510	386	327
Parameter:	Nickel, mg/kg							
Result:	<b>2.8</b>	<b>10.9</b>	<b>14</b>	<b>15</b>	<b>25</b>	<b>19</b>	<b>14</b>	<b>8.1</b>
MDK <sup>1</sup>	14.8	10.2	10.4	10.2	10.4	10.3	10.3	10.5
MDK <sup>2</sup>	14.8	10.2	10.4	10.2	10.4	10.3	10.3	10.5
MDK <sup>3</sup>	19	13.1	13.4	13.1	13.4	13.2	13.2	13.5
MDK <sup>4</sup>	88.8	61.2	62.4	61.2	62.4	61.8	61.8	63
Parameter:	Zinc, mg/kg							
Result:	<b>4.7</b>	<b>442</b>	<b>558</b>	<b>184</b>	<b>575</b>	<b>265</b>	<b>206</b>	<b>19</b>
MDK <sup>1</sup>	67.6	56.2	54.5	55.9	57.7	98.2	68.2	54.4
MDK <sup>2</sup>	232	193	187	192	198	337	234	187
MDK <sup>3</sup>	348	289	281	288	297	505	351	279
MDK <sup>4</sup>	348	289	281	288	297	505	351	279

MDK<sup>1</sup> – \* Target value

MDK<sup>2</sup> – \* Limit value

MDK<sup>3</sup> - \* Verification Level

MDK<sup>4</sup> - \* Remediation value

\* corrected values related to the content of clay and organic matter, in accordance with the Regulation on limit values of polluting materials in surface and underground waters and sediment and deadlines for their achievement ("Official Gazette of RS", No. 50/12).

Table 17. The results of the analysis of the content of radionuclides in sediments- Crni Timok, Borska reka, Veliki Timok (Sample ID 52083002xx)

Location:	Crni Timok - discharge of Zajecar brewery wastewater	Borska reka		Borska reka before confluence with Veliki Timok		Veliki Timok after confluence with Borska reka		Veliki Timok before confluence with Borska reka
Sample ID:	01	05	06	21	22	23	24	25
Parameter:	<sup>137</sup> Cesium, Bq/kg							
Result:	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Parameter:	<sup>40</sup> Potassium, Bq/kg							
Result:	253	218	294	358	248	79	110	8.3
Parameter:	<sup>232</sup> Thorium, Bq/kg							
Result:	8.1	6.4	9.2	10	9.1	5.1	8.4	6.1
Parameter:	<sup>226</sup> Radium, Bq/kg							
Result:	11	8.7	10	14	9.6	3.1	5.5	9.2
Parameter:	<sup>238</sup> Uranium, Bq/kg							
Result:	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0

The spatial distributions of arsenic (mg/l) and cooper (mg/l) in sediments (Borska reka-Timok) are shown in Figure 13.

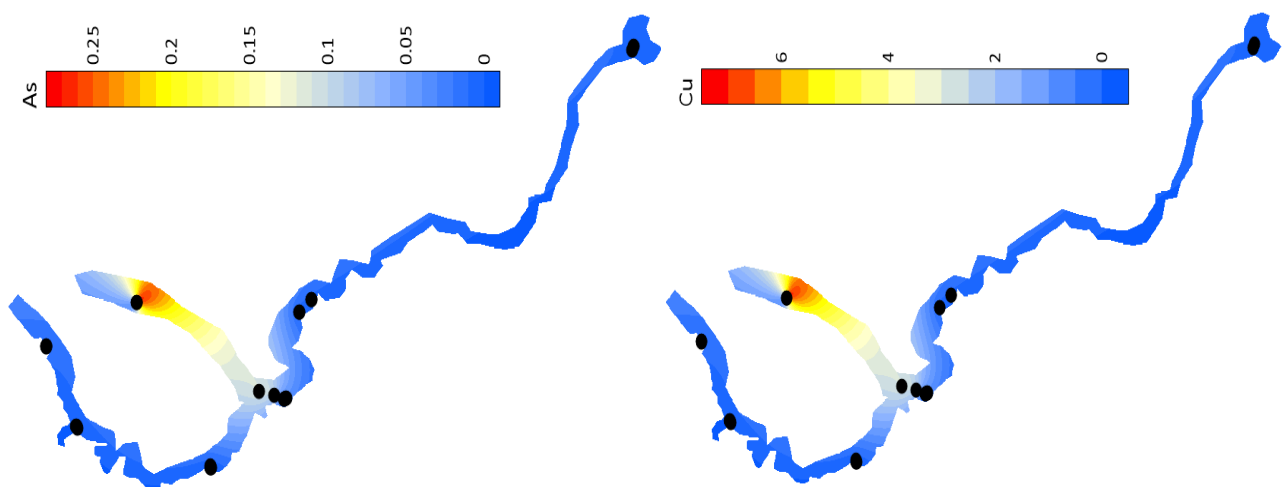


Figure 13. The spatial distributions of arsenic (mg/l) and cooper (mg/l) in sediments (Borska reka-Timok)

The spatial distribution of radium-226 in sediments (Borska reka- Timok) is shown in Figure 13.

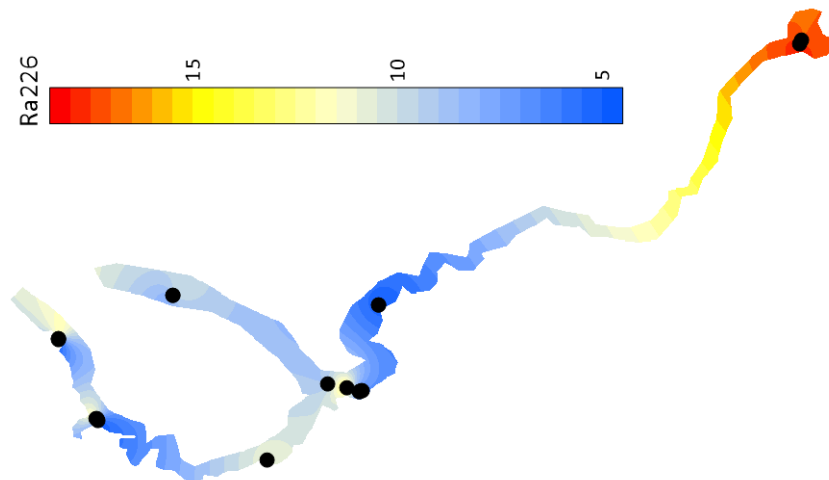


Figure 13. The spatial distribution of radium-226 in sediments (Borska reka-Timok)

Tabele 18. The results of the analysis of sediments – Danube, Timok - Hydropower plant Sokolovica

Location:	The Veliki Timok near Hydropower plant Sokolovica (before the reservoir)	Timok before the confluence with Dunav	Dunav before the confluence of the Timok	
Sample ID:	19	20	07	08
Parameter:	Arsenic, mg/kg			
Result:	<b>625</b>	<b>156</b>	<b>22</b>	<b>26</b>
MDK <sup>1</sup>	26.3	16.2	15.4	15.5
MDK <sup>2</sup>	49.9	30.8	29.2	29.4
MDK <sup>3</sup>	49.9	30.8	29.2	29.4
MDK <sup>4</sup>	49.9	30.8	29.2	29.4
Parameter:	Cadmium, mg/kg			
Result:	<b>41</b>	<b>36</b>	<b>1.5</b>	<b>0.58</b>
MDK <sup>1</sup>	1	0.5	0.4	0.4
MDK <sup>2</sup>	2.5	1.2	1.1	1.1
MDK <sup>3</sup>	9.4	4.4	4	4
MDK <sup>4</sup>	15	7	6.4	6.5
Parameter:	Chromium (total), mg/kg			
Result:	<b>25</b>	<b>13</b>	<b>3.7</b>	<b>8.0</b>
MDK <sup>1</sup>	51.6	50.8	50.4	50.4
MDK <sup>2</sup>	196	193	196	192
MDK <sup>3</sup>	196	193	196	192

MDK <sup>4</sup>	196	193	196	192
Parameter:	Copper, mg/kg			
Result:	<b>9395</b>	<b>4112</b>	<b>253</b>	<b>243</b>
MDK <sup>1</sup>	32	16.8	15.6	15.7
MDK <sup>2</sup>	32	16.8	15.6	15.7
MDK <sup>3</sup>	80	42.1	38.9	39.3
MDK <sup>4</sup>	169	88.9	82.1	83
Parameter:	Mercury, mg/kg			
Result:	<b>0.077</b>	<b>&lt;0.05</b>	<b>&lt;0.05</b>	<b>0.081</b>
MDK <sup>1</sup>	0.2	0.2	0.2	0.2
MDK <sup>2</sup>	0.4	0.3	0.3	0.3
MDK <sup>3</sup>	1.3	1.1	1.1	1.1
MDK <sup>4</sup>	8.3	6.8	6.7	6.7
Parameter:	Lead, mg/kg			
Result:	<b>110</b>	<b>67</b>	<b>9.2</b>	<b>7.4</b>
MDK <sup>1</sup>	78.3	53.1	50.9	51.2
MDK <sup>2</sup>	489	331	318	319
MDK <sup>3</sup>	489	331	318	319
MDK <sup>4</sup>	489	331	318	319
Parameter:	Nickel, mg/kg			
Result:	<b>88</b>	<b>187</b>	<b>15</b>	<b>12</b>
MDK <sup>1</sup>	10.8	10.4	10.2	10.2
MDK <sup>2</sup>	10.8	10.4	10.2	10.2
MDK <sup>3</sup>	13.9	13.4	13.1	13.1
MDK <sup>4</sup>	64.8	62.4	61.2	61.2
Parameter:	Zinc, mg/kg			
Result:	<b>1136</b>	<b>766</b>	<b>53</b>	<b>22</b>
MDK <sup>1</sup>	93.7	55.2	51.7	52.1
MDK <sup>2</sup>	321	189	177	179
MDK <sup>3</sup>	482	284	266	268
MDK <sup>4</sup>	482	284	266	268

MDK<sup>1</sup> – \* Target value

MDK<sup>2</sup> – \* Limit value

MDK<sup>3</sup> – \* Verification Level

MDK<sup>4</sup> – \* Remediation value

\* corrected values related to the content of clay and organic matter, in accordance with the Regulation on limit values of polluting materials in surface and underground waters and sediment and deadlines for their achievement ("Official Gazette of RS", No. 50/12).

Table 19. The results of the analysis of the content of radionuclides in sediments- Danube, Timok - Hydropower plant Sokolovica (Sample ID 52083002xx)

Location:	The Veliki Timok near Hydropower plant Sokolovica (before the reservoir)		Timok before the confluence with Dunav	Dunav before the confluence of the Timok
Sample ID:	19	20	07	08
Parameter:	<sup>137</sup> Cesium, Bq/kg			
Result:	<1.0	<1.0	<1.0	<1.0
Parameter:	<sup>40</sup> Potassium, Bq/kg			
Result:	61	341	399	308
Parameter:	<sup>232</sup> Thorium, Bq/kg			
Result:	4.2	12	12	13
Parameter:	<sup>226</sup> Radium, Bq/kg			
Result:	5.5	11	18	17
Parameter:	<sup>238</sup> Uranium, Bq/kg			
Result:	<3.0	<3.0	<3.0	<3.0

## 4.2.3. Analysis of fish samples

Parameter	Sample ID		MDK
	4208300101	4208300102	
Cadmium, mg/kg	0.27	<0.01	0.050
Lead, mg/kg	0.058	0.041	0.30
Arsenic, mg/kg	0.26	<0.05	-
Copper, mg/kg	5.9	0.71	-
Chromium (total), mg/kg	<0.1	<0.1	-
Cobalt, mg/kg	0.096	<0.03	-
Nickel, mg/kg	0.084	<0.07	-
Iron, mg/kg	20	25	-
Manganese, mg/kg	4.2	3.1	-
Zinc, mg/kg	22	23	-
Mercury, mg/kg	0.098	0.15	0.50

MDK- Rulebook on maximum concentrations of certain contaminants in food, Official Gazette of the RS no. 81/2019, 126/2020, 90/2021 and 118/2021, Annex 1.

## 5. CONCLUSION

Based on the results of laboratory tests, in order to determine the impact of mining on the quality of the rivers - Crni Timok, Veliki Timok, Borska reka, Pek and Danube in accordance with the Regulation on limit values of pollutants in surface and underground waters and sediment and deadlines for their achievement (" Official Gazette of the RS", no. 50/12) and the Decree on the categorization of watercourses ("Official Gazette of the RS", no. 5/68), it can be concluded that there is pollution in the investigated rivers of Timočka Krajina.

The Pek river is formed by the confluence of two rivers - Veliki Pek and Mali Pek. In order to determine the potential pollution of the mentioned river, samples were taken at the points of interest - Mali Pek before the sewage inlet, Mali Pek before and after before the open-pit mine in Majdanpek, Veliki Pek downstream from the tailings pond in Valja Fundat and finally at the target location - after the inlet of both rivers and formation of the river Pek. By laboratory examination of the mentioned samples it can be concluded that:

No contamination was detected in the water sample from the Mali Pek river before the sewage inlet. Further along the river, i.e. In the water sample before the open-pit mine in Majdanpek, the analysis determined an increased content of orthophosphate, ammonium ions, and iron, while after the open-pit mine, in addition to the above parameters, an increased sulfate content was also detected. At both locations, microbiological analysis showed contamination with aerobic mesophilic bacteria and intestinal enterococci. Also, a copper concentration close to the limit value was measured in a water sample of the Mali Pek River at the location after the the open-pit mine in Majdanpek, and this parameter should be monitored.

The analysis showed that in accordance with the above-mentioned Regulations, there is a certain contamination that violates the class of the river Pek, which according to the Regulation falls into class III. Specifically, an increased concentration of sulfate, orthophosphate, iron, manganese and microbiological parameters: aerobic heterotrophic bacteria and intestinal enterococci were detected. As for the examination of sediment samples at the mentioned locations, the analysis showed that in all the analyzed samples the concentration of copper above the remediation value was detected. Also, arsenic concentrations above the remediation value were detected in the sediment samples at the Mali Pek location before the open-pit mine in Majdanpek, Veliki Pek downstream of the tailings in Valja Fundat and in Pek after the confluence of Mali and Veliki Pek. Increased concentrations of zinc were also measured in samples of the Mali Pek River after surface mining and in the Pek River. The assessment of the quality of the sediment is, in accordance with the Ordinance mentioned above, that the sediment is polluted. The content of the analyzed metals is much higher in the sediment samples than in the water samples, which is a consequence of the continuous water flow and the fact that it rained the day before the sampling and at a certain moment during the sampling.

The results of the analysis of water samples of the Brestovačka River after the inflow of the waste channel from the Čukaru Peki mine show that certain values are slightly increased in relation to the values of the parameters at the location before the inflow. The analysis of the Crni Timok river water sample after the Brestovačka river inlet did not show an increase in the concentration of the analyzed parameters, except for the parameter orthophosphates and ammonium ion. Also, the measured dissolved oxygen content is low. These waters need to be monitored further, considering that there was rainfall during the sampling period, which may have an impact on the results of the analysis. The analysis of sediment samples showed that in the sample at the site of the waste channel from the Čukaru Peki mine, as well as in the sample



from the Brestovačka river before and after the waste channel and the sample from the Crni Timok river after the inflow of the Brestovačka river, a high concentration of copper was detected - above the remediation value. Arsenic concentration above the target value was also measured in the waste canal sample.

The further flow of Black Timok, which is categorized as class II, shows increased concentrations of ammonium ions and low content of dissolved oxygen, which impair quality. Microbiological analysis detected an increased content of aerobic mesophilic bacteria at the location of Crni Timok - Town of Zaječar - the place of discharge of wastewater from the Zaječar Brewery.

The surface water of the Bor River, from Bor to its confluence with Crni Timok, is categorized as a river of poor quality and belongs to quality class IV. Analysis of the samples showed an increased concentration of sulfate. The color of the samples of this water is brown-yellow. The analysis of the samples for the content of heavy metals revealed an increased concentration of arsenic, copper, iron and manganese. Based on the examination of water samples taken before and after the confluence of the Bor River into Veliki Timok, it can be concluded that the confluence of the Bor River leads to an increase in the concentration of lead, zinc, nickel, arsenic and calcium. The biggest detected changes are in the concentration of copper, iron and manganese. Regarding the sediment quality test, the analysis showed concentrations of arsenic, copper and zinc higher than the remediation value. Also, the content of lead, cadmium and nickel was detected, which affects the reduction of the quality rating.

The further course of the Veliki Timok river meets the Sokolica Hydroelectric Power Plant. Samples were sampled at the location before and after the tank. The analysis showed that the sample after the reservoir is of better quality in terms of certain parameters - sulfate, manganese, calcium content.

The analysis of sediment samples of the Timok River before its confluence with the Danube River revealed copper content in a concentration higher than the remediation value, arsenic and zinc concentrations above the target value, cadmium above the limit value and nickel above the verification level. In the water sample at the same location, the measured iron content and the number of aerobic heterotrophs exceeded the limit values for class III. The analyzed water sample of the Danube River before the Timok River confluence showed that this water belongs to class II except for the parameters orthophosphates, ammonium ion and the number of aerobic heterotrophs, while in the sediment a concentration of copper exceeding the remediation value was detected, as well as the content of arsenic and cadmium above the target value and nickel above the limit value. The content of the mentioned metals is not negligible and it is necessary to monitor the quality of the water and sediment of the Timok River as well as its tributaries in order to monitor the quality.

6. APPENDIX - Pictures from the field



Mali Pek before the open-pit mine in Majdanpek



Mali Pek after the open-pit mine in Majdanpek



The Veliki Pek downstream from the tailings in Valja Fundata



Pek after the confluence of the Mali and the Veliki Pek



Crni Timok in the part of the course through the City of Zajecar - bathing area of Popova Plaža



Crni Timok in the part of the course through the City of Zajecar - place of discharge of Zajecar brewery wastewater



Brestovačka Reka - before the confluence with Crni Timok



Crni Timok before the confluence of the Brestovačka Reka



Crni Timok after the confluence with Brestovačka river



Borska reka



Waste canal from the Čukaru Peki mine



Brestovačka reka immediately after the inflow of wastewater from the mine



Veliki Timok after confluence with Borska reka



Timok before the confluence with Danube



Danube before the confluence of the Timok