CONTAMINATION IN WATER AND ECOLOGICAL RISK OF HEAVY METALS NEAR A COAL MINE AND A THERMAL POWER PLANT (REPUBLIC OF SRPSKA, BOSNIA AND HERZEGOVINA)

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Abstract. Water samples were collected near the thermal power plant and coal mine (Gacko, Republic of Srpska, Bosnia and Herzegovina) and analyzed to measure the concentration of 33 parameters (pH, temperature, electrical conductivity, alkalinity as $CaCO_3$, total hardness as $CaCO_3$, total solids, total suspended matter, dissolved oxygen, oxygen saturation, biological oxygen demand, chemical oxygen demand with permanganate, ammonia, nitrite, nitrate, P, PAH, PCBs, phenolic index, mineral oils, detergents, content of As, Cd, Cr, Fe, Mn and Pb, sulfates, chlorides, fluorides, aerobic organotrophs, total coliforms, fecal coliforms and fecal streptococci). Determined average mean pH values and EC are within the reference values for class I surface water quality. The surface water in the study area is alkaline, with a mean pH value of 8.01. Depending on the location, other analyzed parameters correspond from I to V water quality classes. The ERI for As, Cd, Cr and Pb is low and for Mn is appreciable. The RI of the surface water in location 1 and 2 were moderate. In other locations, risk coefficients are low.
Keywords: *pollutants, risk, surface water, monitoring, mine, thermal power plant*

Introduction

Water is the most valuable resource for sustaining life on Earth and driving human society's economic growth, and water management is the key to ensuring a quality environment (Dilpazeer et al., 2023; Li et al., 2023 Jat Baloch et al., 2022a; Farooqi et al., 2021;). Surface water is one of the most precious resources in the environment and

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substance present in the most amount. It is also the most widespread natural resource, essential for all living organisms (Jat Baloch et al., 2021; Stojanović Bjelić et al., 2021). The water has been polluted in various ways: physically (waste, suspended particles, heated industrial waters), chemically (heavy metals, various organic and inorganic compounds), biologically (by multiplying bacteria, algae and/or fungi), and radioactively (Bajwa et al., 2023; Ilić and Maksimović, 2021; Jat Baloch et al., 2020; Jat Baloch and Mangi, 2019). Climate change, environmental pollution, fast economic development, population growth, the resulting rapid rise in water use levels, and high water contamination have raised concerns about the unsustainability of present water use (Stojanović Bjelić et al., 2021). The contamination of water resources has become a hot issue these days due to industrial activities and urbanization (Ahsan et al., 2021; Iqbal et al., 2021; Iqbal et al., 2023). Pollutants, including heavy metals are emitted mainly by various anthropogenic sources (Jat Baloch et al., 2022b). Anthropogenic sources of pollution include the release of pollutants into the air during the combustion of fossil fuels and, therefore, into water streams by rain, industrial wastewaters, sewage waters, and other activities (Zhang et al., 2022a). Due to coal combustion, a significant quantity and variety of trace elements and other pollutants, some of them potentially harmful, is transferred to the surrounding environment through different pathways. Literary research indicates that mining and thermal power plants are significant sources of soil toxic metal pollution and directly and indirectly of surface water pollution, with critical sources of heavy metal and other pollutants pollution in surface and groundwater with a significant ecological and health impact (Zhang et al., 2022b; Ilić et al., 2021a, b, 2022; Stojanović Bjelić et al., 2022; Farooqi et al., 2022; Vig et al., 2022; Agrawal et al., 2010; Ahamad et al., 2020). Through the extraction of resources and anthropogenic activities, heavy metals or potentially toxic elements (PTEs) such as cadmium (Cd), arsenic (As), nickel (Ni), chromium (Cr), lead (Pb), and mercury (Hg) have entered the environment. Over-intake of nitrogen (N), phosphorus (P) and other macro and micro nutrients in surface water and excessive phosphorus intake in the surface waters is followed by increased photosynthesis and sedimentation. Intensive process of eutrophication leads to the multiplication of undesirable species of algae, lack of available oxygen and production of various toxic compounds formed by phytoplankton (Tariq, Mumtaz et al. 2022; Jat Baloch 2023a; Jat Baloch 2023b; Tariq, Ali et al. 2023). Areas near mining areas and thermal power plant are high-risk areas for water pollution. Coal combustion in thermopower plants releases various pollutants, which once released into the air reach the land where they are deposited in soil and water (Savic et al., 2018). Various pollutants are usually result from anthropogenic activities, i.e. industrial emissions, incomplete combustion of petroleum, coal, and other fossil fuels. These compounds are widely present in the water, aquatic systems, and soils (Kumar et al., 2022; Zhang et al., 2022a; Jat Baloch et al., 2022c; Ilić et al., 2021a, b, 2022; Stojanović Bjelić et al., 2022). Thermal power plant Gacko 1 was constructed in the southern part of the Mušnica River catchment, near Gacko Town, in 1983, it has become the major source of atmospheric, soil, and water pollution in the study area (Talpur et al., 2020). The main problem is that it is surrounding the city of Gacko is the primary water supply zone of the settlements placed downstream from Gacko and the importance of this area for water supply is immeasurable. Therefore, all possible impacts on the water quality have to be considered, especially to avoid surface and groundwater pollution in this area. Since the field Gatačko is a hydro-ecological collector, where all surface and groundwater flow from the north to the south, exploitation and other similar activities on the surface mine

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can have negative impact, causing pollution in the area downstream from the surface mine. This location is a typical example of the negative impact of coal mines and thermal power plants on the environment. The increase in the amount of the pollutants in the wastewater produced at the surface mine leads to the contamination of the surface and water.

So far, researches are very rarely conducted and are usually related to legal obligations regarding Environmental permit. The research was conducted in the immediate surrounding of the mine and thermal power plant in the municipality Gacko. The aim of this study is to determine the physical characteristics and level of pollutants contamination in surface water and evaluate the ecology risks near Mine and Thermal Power Plant in the municipality of Gacko.

Experimental section

Study region

Gacko is a municipality located in Republic of Srpska, an entity of BiH, in the region of East Herzegovina (*Fig. 1*).

Figure 1. *Locations of surface water sampling measuring points (www.maphill.com/bosnia-and-herzegovina/republika-srpska/gacko/location-maps/shaded-relief-map/free/)*

The Gacko coal mine and thermal power plant (300 MW) are located near the city of Gacko with estimated coal reserves 400 million tons. The coal mine and power plant construction started in 1974 and was completed in February 1983 (https://english.arnika.org/bosnia-and-herzegovina/hot-spots/gacko-tpp). It covers an area of about 40 km² at an altitude of about 940 m, in a typical karst area. The principal sources of surface water in the study area are the Mušnica River, including the Vrba and Klinje reservoirs, and its tributary, the Gračanica River. The Mušnica River catchment is located in the Gacko municipality. The areal extent of the catchment, including the Srđevići hydrological station, is about 208 km^2. Gračanica River is major tributary of the Mušnica River. Rainfall in the Mušnica River catchment region is among the highest in this part of Europe (Talpur et al., 2020). The mean annual precipitation from 1961 to 1990, monitored at eight meteorological stations, was 1,687 mm. The highest rainfall

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occurs between October and March, with a monthly minimum of 141.2 mm (February) and a maximum of 223.7 mm (November). The range of precipitation during the dry season, from April to September, is between 60.3 mm (July) and 145.5 mm (April). The average annual temperatures are 8.2°C at Gacko (951 m a.s.l.) (Talpur et al., 2020).

Sampling and analysis

Surface water testing was performed at six locations (six samples) in the vicinity of the surface mine “Gacko-Centralno polje”: Mušnica after pouring the city sewer (Location 1: 43°09’20.6”N 18°32’01.0”E); The river Mušnica after the gorge Gelja Ljut (Location 2: 43°08’25.5”N 18°30’25.9”E); Gračanica River before the wastewater discharge of TPP Gacko (Location 3: 43°10’31.3”N 18°31’04.4”E); The river Gračanica after the discharge of wastewater from TPP Gacko (Location 4: 43°09’55.3”N 18°30’36.3”E), Srđevića klanac (gorge) (Location 5: 43°10’10.5”N 18°28’42.9”E) and Mušnica after the confluence of the river Gračanica (Location 6: 43°08’07.2”N 18°29’38.7”E) (*Figs. 2* and *3*).

Figure 2. *Locations of wider space sampling measuring points (Photo authors)*

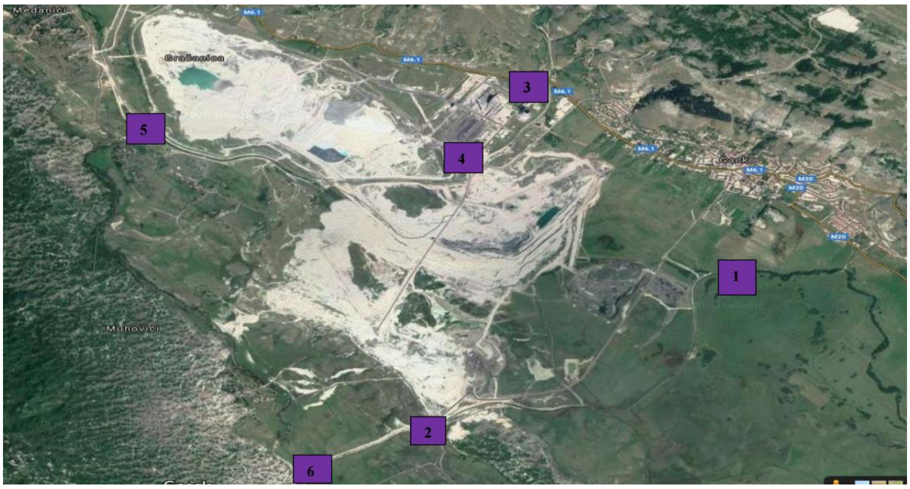

Figure 3. *Locations of surface water sampling measuring points*

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Sampling was performed on 15.01.2020. Sampling programs, sampling techniques, and the handling of water samples was performed in accordance with the standard BAS EN ISO 5667-6:2014 for physical and chemical assessment. For microbiological sampling. Plowing was carried out in accordance with the BAS EN ISO 19458:2009 standard.

Analytical methods of parameter testing in surface water were performed in accordance with Regulation on water classification and categorization of flows (Regulation, 2001). pH values is determined according to EPA 150.1:1982, electrical conductivity (EC) according to EPA 120.1:1982, dissolved oxygen and oxygen saturation are determined according to EPA 360.1:1971 electrochemically, in situ; alkalinity as $CaCO_3$ and total hardness as $CaCO_3$ volumetric, according to EN ISO 9963-1:2007, total solids (TS) and total suspended matter (TSM) gravimetric according to ISO 11465:2002, biological oxygen demand (BOD_5) by the dilution method (internal method), chemical oxygen demand (COD) permanganate by titrimetric method according to EPA 410.4:1993, ammonia, nitrite and nitrate spectrophotometric according to EPA 350.1:1993 and EN ISO 10304-1:2009, N by the Kjeldahl method, P spectrophotometrically with ascorbic acid, PAH and PCBs by gas chromatography. The detector used for PAH analysis is a mass detector coupled to a gas chromatograph (GC/MS). The process of extraction and obtained PAHs and PCBs concentrations were further processed based on the principles described in standard methods with disintegration techniques and analyzed in accordance with accredited standard method EPA 8270D/EPA 3510, EPA 3510:1996, EPA 8082:1996, EPA 3510:1996. Phenolic index is determined spectrophotometric, mineral oils by GC/MS method, according to EN ISO 16703:2013, detergents methylene blue spectrophotometry, As, Cd, Cr, Fe, Mn an Pb atomic absorption spectrometry (AAS), according to Standard methods 3113 (B), Edition APHA-AWWAWEF, 2017, sulfates gravimetry, chlorides and fluorides titrimetric, according to EN ISO 10304-1:2009, aerobic organotrophs, total coliforms, fecal coliforms and fecal streptococci in accordance with the applicable procedures for sanitary-microbiological parameters (Regulation, 2001).

The used analysis devices are: GC/MSD Agilent GC/MSD 5977C, 240FS AA, Photometer PF-12Plus Macherey-Nagel, photometer WTW photoLab S 12, UV-VIS – spectrophotometer UV-1700 Shimatzu, Multimeter Extech DO 700 and other laboratories devices.

Characteristics and pollutants such as COD permanganate, PAHs, PCBs, phenolic index, mineral oils, As, Cd, Cr and Pb were also measured, however, their concentrations were below the detection limit. Accredited quantification detection limit for COD permanganate, PAHs, PCBs, phenolic index, mineral oils, As, Cd, Cr and Pb are <0.5, <0.10, <0.01, <1, <500, <1, <0.5, <4 and <5, respectively. The analyzed parameters for which values less than the detection limit were obtained were not further considered.

Ecological risk assessment

In order to Ecological Risk Assessment, the following criteria were used: Ecological risk assessment (ERI) and Potential Ecological Risk Index (RI).

The method for determination of RI was proposed by Hakanson (1980). This method was used to evaluate the potential ecological risk from a sedimentology perspective to assess the characteristics and environmental behavior of heavy metal contaminants

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(Hakanson, 1980; Jat Baloch et al., 2022a; Long et al., 2021). Ecological risk of toxic metals in the soil can also be accessed by a ERI (*Eq. 1*):

$$ERI = Tr \times CF \quad \text{(Eq.1)}$$

where Tr represents the toxic response factor and CF is concentration factor. Tr for the metals are As = 10, Cd = 30, Cr = 2, Mn = 1 and Pb = 5.

The classification of ecological risk is in five class shown in *Table 1* (Hakanson, 1980; Jat Baloch et al., 2022a; Zheng-Qi et al., 2008; Lu et al., 2015; Ur Rehman et al., 2018; Huang et al., 2019; Imran et al., 2020; Ilić et al., 2022). The RI is given by RI = ∑ERI. Degree of contamination for particular heavy metals for RI shown in *Table 1* (Jat Baloch et al., 2022a).

Table 1. *Classification of ecological risk and potential ecological risk for metals*

Ecological risk	**Low**	**Moderate**	**Appreciable**	**High**	**Extremely high**
Eri	<40	40-80	80-160	160-320	>320
Potential ecological risk	Low	Moderate	Strong		Very strong
RI	<150	150-300	300-600		≥ 600

Statistical analysis

Excel 2016, JASP 0.16.0.0 software were used for statistical data processing. Descriptive statistical operations (mode, median, mean, standard deviation (SD) with coefficient of variation (CV), skewness, kurtosis, Shapiro-Wilk, minimum, maximum) were applied for the analysis of the collected data. Correlations (Pearson's) between parameters in water was applied for getting the qualitative information about the possible source of the toxic metals. A significance level of p-value $p < 0.05$, $p < 0.01$, $p < 0.001$ was used.

Results and discussion

Physical characteristics and pollutants concentrations in surface water

Present study explores the physical characteristics and pollutants concentrations in surface waters originate from human activity in Gacko. According to national legislation, criteria are established and the classification of surface quality is performed, as well as the categorization of watercourses (Regulation, 2001). Classification and categorization is performed to compare the assessment of the degree of anthropogenic pollutants on the quality of surface, and especially to control the effectiveness of protection measures taken to prevent deterioration and gradual improvement and renewal of surface water.

In accordance with national legislation (Regulation, 2001) the investigated watercourses belong to the first category of watercourses, i.e. the first class of watercourses that have a high status of water quality. The biggest problem is that the wastewater of the population and industry is not treated. Wastewater from the majority of the population (close to 90%) is discharged directly into the nearest watercourses or

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underground without treatment. The degree of coverage of the population with the sewerage system in urban areas was 60%.

It can be perceived from *Table 1* that determined average mean pH values and EC are within the reference values according to Regulation (Regulation, 2001) for Class I surface water quality, although there is a high risk of change of pH value at the site, because the Thermal Power Plant in the immediate vicinity discharges excess water, with a typical pH value of 12.4, it is first pumped into a collector inside the mine where it is then diluted with atmospheric water. This mixture is then discharged into the nearby river Gračanica, the main tributary of the river Mušnica (Talpur et al., 2020). The surface water in the study area is alkaline, with a mean pH value of 8.01, corresponding to the carbonate water system, which is in line with previous research (Talpur et al., 2020). The wastewater of the power plant is stored, and the highly alkaline water can be a risk factor. In order to avoid the risk, it is necessary to carry out correct wastewater storage and management and the environmental risk will be low. Otherwise, the consequences of an accident could be catastrophic. Other analyzed parameters correspond from I to V water quality classes.

Descriptive statistics of physical characteristics and pollutants of examined surface water, as well as from all other collected samples, are presented in *Table 2*.

Thermal power plant and mine of coal were the dominant industrial activity that impacted the toxic metal concentrations in soil near Gacko Municipality (Ilić et al., 2022). As the impact on the land has been confirmed, the impact on surface is expected, which has been confirmed in research at other locations (Noli et al., 2016). The mean values for iron in surface water is 354.50 mg/l The manganese content is lower than iron and its mean values is 108.83 mg/l.

The Shapiro-Wilk test was applied to test the data normality (Shapiro and Wilk, 1965), considering that the available sample was small (<50) (Harris, 2008). For data normality testing, the usual significance threshold of $\alpha = 0.05$ was applied. In the research, values higher than 0.05 have temperature, pH, alkalinity, total hardness, TS, TSS, dissolved oxygen, oxygen saturation, ammonia, nitrate, P, Fe, Mn, aerobic organotrophs, total coliforms, fecal coliforms and fecal streptococci.

At last, the null hypothesis was set up: H_0—The sample is from a normal distribution. If $p > \alpha$, the null hypothesis is accepted and assumes that data have a normal distribution, otherwise it is rejected (Savic et al., 2018). It is the in the research p values for EC, BOD_5, nitrite, detergents, sulfates and chlorides less than 0.05 and does not exist normal distribution. In small samples, Skewness test values greater or lesser than 1.96 are sufficient to establish normality of the data (for all toxic metals) (Ghasemi and Zahediasl, 2012). Similarly confirms and Kurtosis test. CV, as an index showing the extent of variability in relation to the mean of the samples for pollutants, can be used to identify the anthropogenic contribution degree for pollution in the environmental studies. If $CV < 0.10$ and >0.90 are mean low and high anthropogenic contributions, respectively (CEPA, 1990). $CV > 0.90$ are for total coliforms, fecal coliforms, sulfates, P, ammonia N, BOD_5, Fe and fecal streptococci. Values are 2.012, 1.996, 1.228, 1.184, 1.036, 0.975, 0.945 and 0.920, respectively. Values for other pollutants were in range from 0.10 to 0.90.

Concentrations of metals detected in the present paper are in the range of values of parameters obtained in previous research, but it is important to note that oxygen saturation (%) was higher in the earlier period (Talpur et al., 2020), which probably indicates the load of these waters with sewage.

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Table 2. *Statistical summary for determined physical and chemical characteristics of the examined surface waters*

Parametes	Mode	Median	Mean	SD	CV	Variance	Skewness	Kurtosis	Shapiro-Wilk	P-value of Shapiro-Wilk	Min	Max	LV [24]
Temperature	2.90	3.50	3.983	1.186	0.298	1.406	0.794	-1.560	0.849	0.155	2.90	5.70	-
pH	7.60	7.99	8.013	0.303	0.038	0.092	0.250	-0.062	0.982	0.961	7.60	8.47	6.80-8.50
EC	299.00	366.50	392.167	98.840	0.252	9769.367	1.990	4.669	0.721	0.010	299.00	586.00	<400
Alkalinity	115.10	183.65	174.700	43.086	0.247	1856.384	-0.408	-1.911	0.908	0.424	115.10	220.60	>175
Total hard.	165.40	215.70	207.317	28.690	0.138	823.122	-0.414	-0.526	0.938	0.644	165.40	245.00	>160
TS	24.00	207.00	222.500	129.479	0.582	16764.700	-0.286	-0.190	0.944	0.691	24.00	380.00	<300
TSS	2.00	13.50	12.567	6.306	0.502	39.767	-0.850	0.837	0.957	0.797	2.00	20.00	<2
Dissolv. O_2	10.70	10.80	10.700	0.807	0.075	0.652	-1.467	3.211	0.859	0.185	9.20	11.60	>7
O_2 satur.	74.00	81.50	81.667	4.676	0.057	21.867	-0.653	0.520	0.939	0.649	74.00	87.00	80-100
BOD5	1.00	1.95	2.733	2.664	0.975	7.099	2.303	5.470	0.649	0.002	1.00	8.10	<2.0
Ammonia	0.01	0.54	0.665	0.689	1.036	0.474	1.001	0.521	0.909	0.430	0.01	1.83	<0.10
Nitrite	0.01	0.02	0.015	0.005	0.365	3.000e-5	7.994e-16	-3.333	0.683	0.004	0.01	0.02	<0.01
Nitrate	0.01	0.26	0.288	0.210	0.728	0.044	0.815	2.110	0.933	0.607	0.01	0.65	<1.0
P	0.01	0.05	0.075	0.089	1.184	0.008	1.458	2.006	0.798	0.056	0.01	0.24	<0.01
Detergents	50.00	50.00	54.667	11.431	0.209	130.667	2.449	6.000	0.496	<.001	50.00	78.00	<100
Fe	50.00	289.50	354.500	335.019	0.945	112237.900	0.262	-2.621	0.821	0.091	50.00	777.00	<100
Mn	50.00	80.50	108.833	76.987	0.707	5926.967	1.166	0.609	0.827	0.101	50.00	241.00	<50
Sulfates	9.00	14.85	43.467	53.387	1.228	2850.175	1.707	2.396	0.726	0.011	9.00	142.50	<50
Chlorides	5.00	5.00	5.583	0.993	0.178	0.986	1.637	1.983	0.696	0.006	5.00	7.40	<20
NO of col. Of aer. Org.	30.000	17.000	18.333	10.405	0.568	108.267	0.187	-2.492	0.859	0.186	7.000	30.000	≤1000
Total col. (MPN)	20.000	22.000	474.400	954.510	2.012	911089.920	2.330	5.493	0.593	<.001	2.400	2400.000	≤50
Fecal col. (MPN)	20.000	22.000	477.333	952.795	1.996	907818.667	2.333	5.504	0.587	<.001	20.000	2400.000	≤20
Fecal str.	160.000	97.000	87.333	80.326	0.920	6452.267	-0.070	-3.150	0.748	0.019	2.000	160.000	≤20

MPN: most probable number

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During the research and analysis of water from water reservoirs and water in surface waters, it was noticed that there was no causal connection with water pollution in terms of the impact of water from water reservoirs. Insight into the location of surface water sampling measuring points confirms the great influence of the city sewage in surface waters, which flows over the northern and northeastern slopes of the surface mine “Gacko-Centralno polje”. The above is the most significant reason why parameter values vary at research locations, depending on the impact of waste water on surface water. The municipality of Gacko has not resolved the issue of city sewerage and sanitary wastewater is discharged at the edge of the mine, and indicators of poor quality of these measuring points are the direct cause of the discharge of this wastewater.

Similar results were obtained in research by other authors in different locations (Farooqi et al., 2022; Vig et al., 2022; Agrawal et al., 2010; Ahamad et al., 2020), with the fact that research is mostly based on the ecological risk of heavy metals. Earlier research indicates that the water quality are deteriorating at an alarming rate. This investigations are relevant for risk management studies of drinkable water. The knowledge from assessment must be considered with maximum priority by national authority considering degrading water quality in the study area. Hence, this research is applicable for designing plans to reduce water resource pollution.

Correlation analysis

The results correlation analysis are shown in *Table 3* and *Figure 4*.

The results of the correlation analysis for P and Mn; detergents and fecal coliforms; detergents and total coliforms; BOD_5 and detergents; BOD_5 and total coliforms are strong positive correlation ($r = 0.991$; 0.989; 0.988; 0.987; 0.983 respectively) for the level of significance $p < 0.001$.

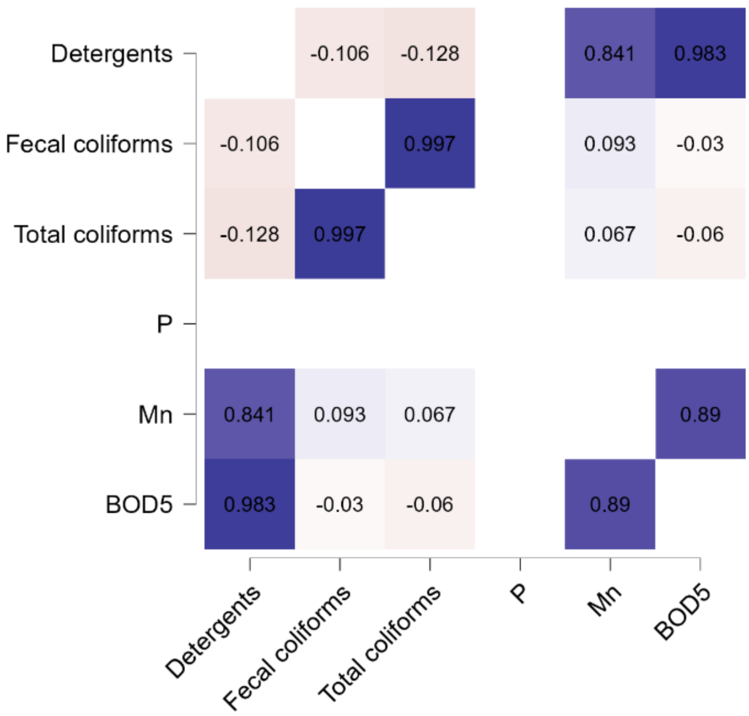

Figure 4. *Correlation analysis for some analyzed parameters in examined surface waters*

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Table 3. *Results of correlation analysis for analyzed parameters in the examined surface waters*

		Pearson's r		p
EC	Nitrate N	0.826	*	0.043
EC	Sulfates	0.896	*	0.016
Alkalinity as $CaCO_3$	P	0.816	*	0.048
Alkalinity as $CaCO_3$	Fe	0.849	*	0.032
Alkalinity as $CaCO_3$	Mn	0.844	*	0.035
Alkalinity as $CaCO_3$	Sulfates	-0.868	*	0.025
Alkalinity as $CaCO_3$	Fecal streptococci	0.922	**	0.009
Total hardness as $CaCO_3$	Nitrate N	0.906	*	0.013
TSM	Dissolved oxygen	-0.830	*	0.041
TSM	Aerobic organotrophs	0.852	*	0.031
Dissolved oxygen	Oxygen saturation	0.922	**	0.009
Dissolved oxygen	BOD5	-0.958	**	0.003
Dissolved oxygen	Ammonia	-0.902	*	0.014
Dissolved oxygen	P	-0.906	*	0.013
Dissolved oxygen	Detergents	-0.910	*	0.012
Dissolved oxygen	Mn	-0.883	*	0.020
Dissolved oxygen	Chlorides	-0.843	*	0.035
Dissolved oxygen	Total coliforms	-0.928	**	0.008
Dissolved oxygen	Fecal coliforms	-0.890	*	0.017
Oxygen saturation	BOD_5	-0.879	*	0.021
Oxygen saturation	Ammonia	-0.958	**	0.003
Oxygen saturation	P	-0.932	**	0.007
Oxygen saturation	Mn	-0.930	**	0.007
Oxygen saturation	Chlorides	-0.824	*	0.044
Oxygen saturation	Aerobic organotrophs	-0.832	*	0.040
Oxygen saturation	Total coliforms	-0.849	*	0.033
BOD_5	Ammonia	0.894	*	0.016
BOD_5	P	0.924	**	0.008
BOD_5	Detergents	0.987	***	<.001
BOD_5	Mn	0.880	*	0.021
BOD_5	Chlorides	0.921	**	0.009
BOD_5	Total coliforms	0.983	***	<.001
BOD_5	Fecal coliforms	0.965	**	0.002
Ammonia	P	0.968	**	0.002
Ammonia	Detergents	0.829	*	0.042
Ammonia	Mn	0.949	**	0.004
Ammonia	Chlorides	0.926	**	0.008
Ammonia	Total coliforms	0.856	*	0.029
Ammonia	Fecal streptococci	0.822	*	0.045
Nitrite	Aerobic organotrophs	0.948	**	0.004
P	Detergents	0.891	*	0.017
P	Mn	0.991	***	<.001
P	Chlorides	0.899	*	0.015
P	Total coliforms	0.931	**	0.007
P	Fecal coliforms	0.853	*	0.031
Detergents	Mn	0.841	*	0.036
Detergents	Chlorides	0.896	*	0.016
Detergents	Total coliforms	0.988	***	<.001
Detergents	Fecal coliforms	0.989	***	<.001
Fe	Fecal streptococci	0.953	**	0.003
Mn	Chlorides	0.836	*	0.038
Mn	Total coliforms	0.900	*	0.014
Mn	Fecal streptococci	0.830	*	0.041
Chlorides	Total coliforms	0.871	*	0.024
Chlorides	Fecal coliforms	0.870	*	0.024
Total coliforms	Fecal coliforms	0.970	**	0.001

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Total coliforms and fecal coliforms is strong positive correlation (r = 0.970) for the level of significance $p < 0.01$. The results for alkalinity as $CaCO_3$ and fecal streptococci; dissolved oxygen and oxygen saturation; dissolved oxygen and BOD_5; dissolved oxygen and total coliforms; oxygen saturation and ammonia; oxygen saturation and P; oxygen saturation and Mn; BOD_5 and fecal coliforms; ammonia and P; ammonia and Mn; ammonia and chlorides; nitrite and aerobic organotrophs; P and total coliforms; Fe and fecal streptococci also have a strong positive correlation, for the level of significance $p < 0.01$, which means that high X variable scores go with high Y variable scores (and vice versa).

Other results for *Table 4* have positive correlation for the level of significance $p < 0.05$, which means there is a tendency for high Pb/Cr/Ni/Cu/Zn variable scores go with high B/Ba/Ba/Ba/B variable scores (and vice versa).

Ecological risk assessment

Table 4 accounts for the ERI and RI of the heavy metals in the surface water at the study area based on Hakanson calculation (Hakanson, 1980). The ERI for As, Cd, Cr and Pb is low and for Mn is appreciable. The RI of the surface water in the location 1 and 2 were moderate. In other locations risk coefficients is low.

Table 4. *ERI and RI of heavy metals*

Sample number	As	Cd	Cr	Mn	Pb	RI	Risk grade
1	<10	<1.5	<8	241	<25	251	Moderate
2	<10	<1.5	<8	151	<25	161	Moderate
3	<10	<1.5	<8	50	<25	60	Low
4	<10	<1.5	<8	50	<25	60	Low
5	<10	<1.5	<8	50	<25	60	Low
6	<10	<1.5	<8	111	<25	121	Low
Average values	<10	<1.5	<8	108.83	<25	118.83	Low
ERI	Low	Low	Low	Appreciable	Low	Appreciable	

Spatial distribution

Spatial distribution of Mn, Fe, Sulfates, Cl, Alkalinity, TSS, TS, EC and Total hard concentration was performed using Surfer 12 software. Surfer includes Kriging method and generates an interpolated grid. The distribution of Mn, Fe, Sulfates, Cl, Alkalinity, TSS, TS, EC and Total hard concentration in selected areas is presented in *Figure 5*. Although spatial distribution is done with a small number of samples, it is useful for informative display, because spatial distribution has never been done in that area. The next research should include a larger number of samples and then the validity of this calculation will be established.

Conclusion

Thermal power plant and coal mine are critical sources of pollutants in surface water with a significant ecology and health impact. The development of mining activities inevitably affects the hydrogeological regime within the mines and cumulatively in the wider environment. Water regime disturbances can have indirect effects on surface

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water regimes, soil fertility and water supply to the population. Infiltration of pollutants from mines and tailings into surface water is possible. Cumulative impacts of thermal power plants and mines in the vicinity are significantly reflected in the pollution of existing watercourses (rivers Mušnica and Gračanica) and accumulation that would directly affect the living world of watercourses, line pollution of related watercourses in the vicinity, loss of fishing and tourist potentials of the area, etc.

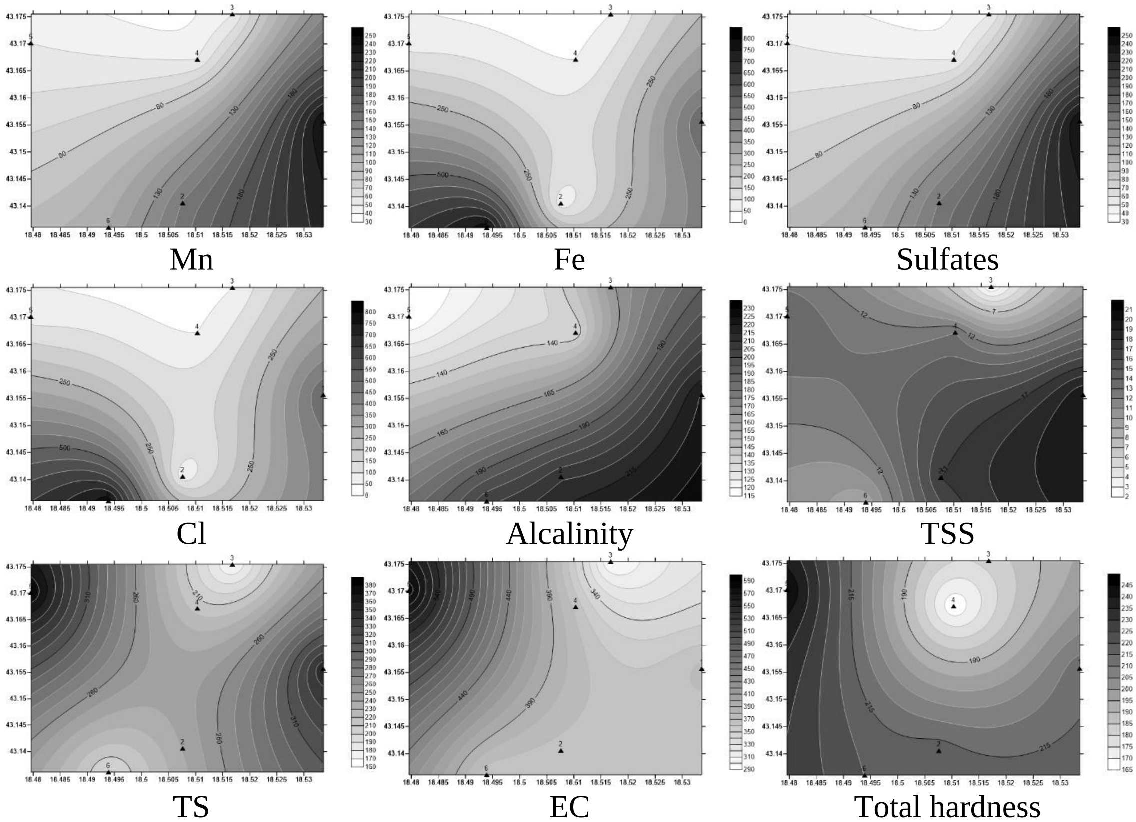

Figure 5. *The distribution of Mn, Fe, sulfates, Cl, alkalinity, TSS, TS, EC and total hard concentration*

Present study explores the physical characteristics and pollutants concentrations in surface waters (temperature, pH, EC, alkalinity as $CaCO_3$, total hardness as $CaCO_3$, TS, TSS, dissolved oxygen, oxygen saturation, BOD_5, ammonia, nitrite, nitrate, P, detergents, Fe, Mn, sulfates, chlorides, aerobic organotrophs, total coliforms, fecal coliforms and fecal streptococci) originate from human activity in Gacko. The impact of wastewater on the environment is manifested, first of all, on the pollution of surface waters used as a recipient and indirectly on the pollution of surface water. Gračanica belongs to the first class of watercourses, and in addition it has a very small flow, so wastewater cannot be discharged into it without prior treatment and cooling. The investigated watercourses belong to the first category of watercourses, i.e. the first class of watercourses that have a high status of water quality. The biggest problem is that the wastewater of the population and industry is not treated. Wastewater from the majority of the population is discharged directly into the nearest watercourses or underground without treatment. The results based on the water samples indicate no serious pollution can be determined but constant monitoring would be necessary.

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The results of the correlation analysis for P and Mn; detergents and fecal coliforms; detergents and total coliforms; BOD_5 and detergents; BOD_5 and total coliforms are strong positive correlation ($r = 0.991$; 0.989; 0.988; 0.987; 0.983 respectively) for the level of significance $p < 0.001$. Total coliforms and fecal coliforms is strong positive correlation ($r = 0.970$) for the level of significance $p < 0.01$. The results for alkalinity as $CaCO_3$ and fecal streptococci; dissolved oxygen and oxygen saturation; dissolved oxygen and BOD_5; dissolved oxygen and total coliforms; oxygen saturation and ammonia; oxygen saturation and P; oxygen saturation and Mn; BOD_5 and fecal coliforms; ammonia and P; ammonia and Mn; ammonia and chlorides; nitrite and aerobic organotrophs; P and total coliforms; Fe and fecal streptococci also have a strong positive correlation, for the level of significance $p < 0.01$.

The ERI for As, Cd, Cr and Pb is low and for Mn is appreciable. The RI of the surface water in the location 1 and 2 were moderate. In other locations risk coefficients is low.

The higher content of pollutants, suggest that it is necessary to provide additional investigation other heavy metals and other potential harmful pollutants and a larger number of samples on location. In regards with these results, it is possible to estimate their influence in the examined area. Since sites are close to the aquatic environment which is used for water supply, sediment and biota samples should be analyzed as well. It is necessary to determine the origin of pollution, to perform the analysis of plant material.

To mitigate possible negative impacts on surface quality, it is necessary to implement appropriate measures to control the surface drainage system, surface wastewater generated and any other spillage of contaminants that may occur. Based on surface water analysis, only constant or still existing pollution could be determined. The sediment is a reservoir of the contaminants; therefore, it is necessary to conduct further sediment research in this area, which could improve the accuracy of the analysis.

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