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AGRO-ECOLOGICAL ASSESSMENT OF SOKOLITSA RIVER WATER AFFECTED BY OPEN COAL MINING ACTIVITY IN THE LARGEST ENERGY COMPLEX IN BULGARIA

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Abstract

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A study of Sokolitsa River was conducted with two monitoring points (MPs) – MP-1, before, and MP-2, after discharge of mining wastewater. The study was carried out during the summer months of the period 2013-2016 by assesing five physicochemical indices, eight heavy metals and metalloids, and three biotic parameters, and the water quality as a natural source and as a source for irrigation. For the sampling of water, living organisms and sample preparation, international ISO and BSS references were used. Sample analyses were made by Multi 340i, spectrophotometric methods and AAS. Based on the obtained analytical results, the following main conclusions were drawn: a) ecological assessment of the river water as a natural source determines water in both monitoring points as water in '*good ecological status*' by pH values and in '*moderate ecological status*' by Dissolved oxygen, Electroconductivity, Ecological Quality Rang, IPS and Biotic index values; b) the priority pollutants levels - Cd, Pb and Ni do not exceed the environmental quality standards and determine the water in '*good chemical status*'; c) the average element concentrations for the study period decreased in the following order Fe>Mn>Zn>Cu>Pb>Ni>Cr>Cd, which are not risky for the hydroecosystem and for irrigated crops; d) assessment of the river water as a source for irrigation determines the water in both monitoring points as appropriate for this purpose by all investigated parameters; e) the wastewater from open coal mining activities, discharged into the river has no significant impact on water quality as a natural source and as a source for irrigation.

Key words: river water, physicochemical and hydrobiological parameters, heavy metals, mining wastewater, water quality

List of abbreviations: BI - Biotic index, DO - Dissolved oxygen, EC - Electroconductivity, EQR - Ecological Quality Rang, GES - Good ecological status, IPS - Diatomic index, MPC - Maximum permissible concentration, MES - Moderate ecological status, MP - Monitoring point, SS - Suspended solids

INTRODUCTION

One of the global environmental problems today is caused by the ubiquitous pollution of water, especially of the surface water. This problem also exists in Bulgaria, despite the application of legal, organizational, technical and practical approaches and solutions. According to the Executive Environment Agency (NRSPEB, 2016), a tendency of improving water quality in the country is observed during the period 1996-2016. Despite this trend, there are still water bodies at risk.

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Surface water bodies in the country have different ecological characteristics due to the formation of different environmental conditions and the degree of anthropogenic pressure. The most vulnerable are rivers where discharged, partially purified or untreated wastewater is accumulated from settlements, industrial enterprises, agriculture and other human activities. Because of water pollution they can not be used, and it also causes significant and often irreparable damage to the environment. Particularly worrying is the situation during the summer months, when the flow of rivers decreases but the quantities of discharged wastewater remains constant and thereby increases the ecological risk for water bodies and the environment (Kostadinova et al., 2006). In 2015 in the Maritsa River basin (East Aegean Region), as well as in previous years, there are many river sections (most of them near to the closed mines) in poor and bad ecological and chemical status, possibly connected with pollution from untreated urban and industrial wastewater (RBMP-EAB, 2015).

Following the changes in EU water legislation, Bulgaria is introducing the new requirements in the national legislation. Some of these key documents are Regulation H-4/2012 for characterization of surface water, Regulation on environmental quality standards for priority substances and certain other pollutants (2010), Regulation No. 18/2009 for quality of irrigation water for agricultural crops and Regulation No. 6/2000 on emission limits for the permissible content of harmful and dangerous substances in the wastewater discharged into water bodies. The effective implementation of the new legal requirements for improvement of the surface water quality is associated with good river water management and water protection, based on study of many aspects - water distribution characteristics, state of the water resources and their complex use, sources of water pollution and their impact on the aquatic ecosystems, self-purifying processes occurring in them after discharging wastewater in water bodies, etc. (Christov, 2012; NRSPEB, 2016).

Some of the recent investigations in the country and abroad reveal different aspects in that issue: hydrobiological monitoring based on composition, abundance of macroinvertebrates and application of some biological water quality indices of watersheds in the East- and West Aegean Sea River Basin Districts in Bulgaria (Vidinova et al., 2008); spatial and temporal distribution of nitrogen compounds in surface water bodies (Georgieva et al., 2013); physicochemical parameters and macrozoobenthos communities as indicators for ecological status assessment of surface water bodies in Tundzha River (Mihaylova et al., 2012; Mihaylova and Kostadinova, 2012); quality assessment of Maritsa and Tundzha Rivers water as a sources for irrigation (Kostadinova et al., 2013, 2017); using the method of Fluctuating Asymmetry in practice in the system of bioindication (populations of gibel carp *C. gibelio*) for initial diagnosis of surface water quality (Zhelev et al., 2015); irrigation with treated low quality water on the heavy metal contents of a soil-crop system in Serbia (Surdyk et al., 2010); seasonal and spatial variations of water quality for irrigation in Büyük Menderes River, Turkey (Yeşilirmak, 2010) and in an agricultural basin in North Greece (Gikas et al., 2013); benthic fauna status as indicator of water quality assessment in Strezhevo accumulation, Macedonia (Nastova et al., 2014); toxicity and ecological impact of heavy metals in surface water of Ganga River around Kolkata, West Bengal (Kar et al., 2008; Aktar et al., 2010); heavy metal contamination status of Erzeni River, Albania (Shehu et al., 2016) and other surface water bodies.

All these studies, for the most part, concern the water quality and assessment (as a natural resource or resource for irrigation) of large rivers. There is no up-to-date scientific information on smaller rivers that have their place and importance to meet water needs for local productions facilities, agriculture and settlements. Some of them are under strong anthropogenic pressure and potential risk of pollution. In these cases it can be affected and the water bodies where these rivers discharged. One of the small rivers is Sokolitsa River, which runs through the territory of the largest energy complex and the largest open coal mine, the ‘Maritsa-East’ complex, situated in the southeastern part of the country. This river deserves attention because the wastewater from mining activities is discharged in it. After that the river water flows into Sazliyka River, which in turn flows into Maritsa River and finaly in Aegean Sea.

The aim of the present study was to investigate and assess the water quality of middle-down course of Sokolitsa River in two monitoring points, before and after discharge of mining wastewater by physicochemical indices, heavy metals, metalloids contents and biotic parameters, as a natural source and as a source for irrigation in accordance with Bulgarian standards.

MATERIAL AND METHODS

Study area

The study was carried out during the summer months for the period 2013 - 2016 in a section of the middle reaches of Sokolitsa River (Code of the water body in this area - BG3-MA200R017), near to Rozov Kladenets dam, Maritsa East-2 Thermal Power Plant (TPP) and an open coal mine (Figure 1). The summer months for exploring river water were selected for two main reasons:

- during summer the water flow (the water quantity) is the lowest and the environmental risk of pollution is the highest;
- the water is used for irrigation in these months.

Sokolitsa River (60.5 km, water catchment area 343 km²) springs from Sakar Mountain (altitude 713 m), Southeastern Bulgaria and flows into Sazliyka River (altitude 86 m), which flows into Maritsa River and Aegean Sea (RBMP-EAB, 2015). The river maximum flow is in January–May and the minimum - in July–October (Figure 2). The river falls into protected area (Code BG0000440) under Habitats Directive (92/43/EEC) and National ecological network ”NATURA-2000”. According to Regulation H-4/2012 for characterization of surface water in the country, the Sokolitsa River type is R13 - small and medium lowland rivers. River water is used for irrigation and industrial water supply. The river passes through an area with a strong anthropogenic impact - large open coal mine and a big TPP. Wastewater from mining activities flows into the river.

Fig. 1. Sokolitsa River basin with monitoring points (MP-1 and MP-2)

Monitoring points

In the study area of Sokolitsa River two monitoring points (MPs) were identified (Figure 1):

- *Monitoring Point 1* (MP-1) – 100 m before the point of discharge of the mine wastewater (N42.08080° E26.01496°);
- *Monitoring Point 2* (MP-2) – 100 m after the point of discharge of the mine wastewater (N42.08063° E26.01401°).

Fig. 2. View of Sokolitsa River
(Source: http://www.zemedelskizemi.com/%D1%)

Sampling and sample preparation

Water samples were collected from both MPs, twice during the summer months of each year of the survey period. For water sampling and sample preparation for analyses, international references (ISO 5667-1, 2, 3; ISO 27828) were used. The samples for physicochemical analysis were collected in dark containers with chemically pure glass beakers (3 L) and for hydrobiological analysis (phytobenthos and macrozoobentos) they were taken in sterile bags. The collected water and biological samples were transported in a cool bag (at 4-6°C) and processed for analysis within 2 hours of collection.

Parameters and methods for analysis

The following 13 parameters characterizing river water quality were defined: *physicochemical parameters* – temperature (^{o}C), pH, dissolved oxygen (DO), mgO_2/dm^3 and electroconductivity (EC), µS/cm - *in situ*, with a Multi-340i meter; suspended solids (SS), mg/dm^3– by BSS EN 872; *heavy metals* (µg/dm^3) - manganese (Mn) and iron (Fe) - by ISO 6333; copper (Cu), zinc (Zn), cobalt (Co), nickel (Ni), cadmium (Cd), lead (Pb) and chromium (Cr) – by ISO 11885 with an AAS "Thermo scientific-3000" at different wavelengths for individual elements; *hydrobiological quality elements* – phytobenthos and macrozoobenthos (composition, variety and abundance) – by ISO 10870.

Water quality assessment

Assessment of Sokolitsa River water quality was carried out in two directions:

- *As a natural resource* - ecologycal assessment of water: physicochemical parameters and heavy metals content – according to Regulation No. H-4/2012 for characterization of surface water and Regulation on EQS for priority substances and certain other pollutants (2010); hydrobiological parameters (at MP-2) – by the metrics Biotic index (BI), Ecological Quality Rang (EQR) and Diatomic index (IPS).
- *As a source for irrigation* - agro-ecologycal assessment of water: physicochemical parameters and heavy metals content – according to Regulation No. 18/2009 for quality of irrigation water of agricultural crops.

Statistical analysis

All data were analyzed by STATISTICA 6.1 (Statistica for Windows, StatSoft. Inc., Tulsa, OK, USA, 1984-2002).

RESULTS AND DISCUSSION

Sokolitsa River water quality as a natural resource

Physicochemical parameters

Temperature (T^{o}C). Sokolitsa River water temperature varied from 28.9^{o}C to 30.2^{o}C at MP-1 and from 27.1^{o}C to 28.7^{o}C at MP-2 (Table 1). Higher temperatures were measured at MP-1 than in MP-2. The differences by years between both MPs ranged from 1.4^{o}C in 2016 to 2.2^{o}C in 2014, average for the period 1.7^{o}C - statistically significant at $P<0.01$. The most likely cause of this fact is the water amount difference between MP-1 and MP-2. The water quantity in MP-1 is less than in MP-2, as mining wastewater, which is discharged after MP-1, increases the water amount in the zone of MP-2. The larger water quantity in MP-2 is warmed more difficult in comparison with the less water quantity in MP-1 at the same conditions (sunshine) - the distance between two monitoring points is only 200 m. Consequently, it can be concluded that the discharged mined wastewater reduces the river water temperature in the order of 1.5-2^{o}C, which could have a positive effect on aquatic organisms. This indicator is not standardized in Regulation H-4 (2012) and for that reason ecological assessment of the water based on its temperature can not be made.

Active reaction (pH). During the monitoring period the pH values varied in a narrow range – from pH 7.74 to pH 8.26 at MP-1 and from pH 7.78 to pH 8.34 at MP-2 (Table 1). Despite the slight fluctuations in the indicator values, an increase of the pH values in MP-2 compared to those in MP-1 is observed - between 1.005 times in 2016 and 1.024 times in 2013, average for the period 1.014 times ($P>0.05$). There is no significant difference in pH values over the years of the controlled period. The active reaction has slightly higher and closer values in 2013 and 2015 compared to 2014 and 2016. Nevertheless, the results obtained characterized the water in both MPs as slightly alkaline. The analogous results are reported by Zhelev et al. (2015) for Sazliyka River - pH 7.97-7.83, 2009-2011 and Kostadinova et al. (2017) for Maritsa River - pH 7.04-7.83, June-August 2014, water bodies which successively accept the Sokolitsa River water. Another large river in the region - Tundzha River, also has a similar water pH values - pH 6.48-8.39, May-August, 2010 (Mihaylova et al., 2012; Kostadinova et al., 2013). These results show that despite the different anthropogenic pressures on the above-mentioned rivers, the pH values characterize them as water bodies with neutral to slightly alkaline reaction.

Ecological assessment determined the quality of Sokolitsa River water in MP-1 and MP-2 as water in '*good ecological status*' as all pH values are within the permissible limits (pH 6.5-8.5, Regulation No. H-4/2012).

Dissolved oxygen (DO). DO values as pH values also varied in a narrow range – from 4.80 to 5.02 mgO_2/dm^3 at MP-1 and from 5.10 to pH 5.57 mgO_2/dm^3 at MP-2 (Table 1). It is observed a negligible increase in the amount of dissolved

Table 1
Concentrations of the physicochemical parameters in Sokolitsa River water by two monitoring points, 2013-2016

No	Parameters	Units	Year	C_x (n=2)		Limit values**	MPC***
				MP-1*	MP-2*		
1.	Temperature	°C	2013	28.9	27.1	Not apply	28
			2014	29.8	27.6		
			2015	30.2	28.7		
			2016	29.5	28.1		
	Mean ± SD, n=8			29.6±0.54	27.9±0.68	P= 0.002399	
2.	pH	pH units	2013	8.14	8.34	6.5-8.5 GES	6-9
			2014	7.78	7.90		
			2015	8.26	8.33		
			2016	7.74	7.78		
	Mean ± SD, n=8			7.98±0.26	8.09±0.29	P=0.054389	
3.	Dissolved oxygen (DO)	mgO_2/dm^3	2013	4.80	5.10	< 6.00 MES	> 2.0
			2014	5.02	5.42		
			2015	4.98	5.38		
			2016	4.88	5.57		
	Mean ± SD, n=8			4.92±0.10	5.37±0.19	P=0.013010	
4.	Electro-conductivity (EC)	µS/cm	2013	1790.4	862.6	> 750 MES	2000
			2014	1778.2	854.8		
			2015	1795.3	849.4		
			2016	1788.2	858.5		
	Mean ± SD, n=8			1788.0±7.19	856.3±5.61	P=0.000000	
5.	Suspended solids (SS)	mg/dm^3	2013	23.4	22.5	Not apply	50
			2014	20.5	25.0		
			2015	5.80	14.4		
			2016	12.7	11.5		
	Mean ± SD, n=8			15.6±7.9	18.4±6.4	P=0.326237	

*MP-1/Mp-2 – Monitoring points - before (1) and after (2) discharging the wastewater in the river water;
** Limit values in accordance with Regulation No. H-4/2012;
***MPC - Maximum permissible concentration in accordance with Regulation No. 18/2009.

oxygen in the water at MP-2 compared to the water at MP-1 – between 1.06 times in 2013 and 1.14 times in 2016 (average for the period 1.09 times) - statistically significant at $P<0.05$. This is probably due to the enrichment of the river water with oxygen during its flowing. The discharge of mining wastewater does not have a negative effect on the dissolved oxygen content of the river water. The established facts give grounds to assume that the wastewater contains similar or even slightly higher amounts of dissolved oxygen compared to the river water. This circumstance should be clarified in future studies. The investigation by years did not reveal significant differences in the indicator values regardless of the monitoring points.

The results obtained are close to the data published by Zhelev et al. (2015) for Sazliyka River (4.73-4.95 mgO_2/dm^3, 2009-2011) and are lower than the results found by

Kostadinova et al. (2017) for Maritsa River (6.21-7.29 mgO$_2$/dm^3, 2014). The date analysis does not prove a negative influence of the Sokolitsa River water on the dissolved oxygen content in the Sazliyka River water, respectively of the Sazliyka River water on the Maritsa River water.

The values of this indicator determined the Sokolitsa River water quality in both monitoring points as water in '*moderate ecological status*' during all years of investigation, because DO was <6.00 mgO$_2$/dm^3 (Regulation No. Н-4/2012).

Electroconductivity (EC). According to the measurement by years EC values were almost the same for both MPs – from 849.4 to 862.6 µS/cm at MP-1 and from 1778.2 to 1795.3 µS/cm at MP-2 (Table 1). Significantly lower was the water electroconductivity at MP-2 compared to that at MP-1 – by 2.07 times in 2013, by 2.08 times in 2014 and 2016, and by 2.11 times in 2015 (average for the period by 2.08 times) - statistically significant at $P<0.001$. This fact can be explained by the dilution of the river water after discharging wastewater from mining activities. It is true that the discharged wastewater contains a large number of minerals, but probably not in the form of ions, which determine the water's electroconductivity. The observed unusual tendency to reduce the electroconductivity of river water after discharge of the mining wastewater, deserves attention and further research.

Results obtained for EC of water at MP-2 are very closed to the data for Sazliyka River water – 654.3-912.2 µS/cm for the period 2009-2011 (Zhelev et al., 2015) and much lower than those for Maritsa River (223-378 µS/cm, 2014), reported by Kostadinova et al., 2017. The EC values in MP-1 are significantly higher than those of the cited authors. These results give grounds to assert that the water of the upper reaches of Sokolitsa River contains more mineral ions than the downstream water. Probably the smaller river water quantity in this area dissolves more minerals and their relative concentration increases.

Analysis of our results and those of other authors shows that along the chain 'Sokolitsa River→Sazliyka River→Maritsa River', the water electroconductivity drastically decreases. Probably, with the increasing water amount in each subsequent water body along the above mention chain, the content of cations (or anions), respectively total salt concentration of water decreases, due to the increasing of its dilution.

On this parameter, the Sokolitsa River water is determined as water in '*moderate ecological status*' (EC >750 µS/cm) for both MPs in all years of the studied period.

Suspended solids (SS). SS values varied considerably – from 5.80 to 23.4 mg/dm^3 in MP-1 and from 11.5 to 25.0 mg/dm^3 in MP-2. It is noticeable that during the two years of the survey period the SS amount decreases at the monitoring point after the wastewater discharge (MP-2) compared to the previous monitoring point (MP-1) – in 2013 with 1.04 times and in 2016 with 1.10 times, respectively. During the remaining two years of the controlled period, the opposite trend is observed - the SS content in MP-2 was higher than in MP-1 - in 2014 with 1.21 times and in 2015 with 2.48 times, respectively. For the study period, the SS content was greater in water from MP-2 than in MP-1, average 1.18 times ($P>0.05$). The reasons for these contradictory trends probably are related to specific natural and climatic conditions (amount of precipitation, respectively the washout of minerals in river water) and the composition of the wastewater, which may also vary over the years. During the first two years of the survey period, the indicator values were significantly higher than the other two years. Therefore, it can be argued that the factor 'year' plays an important role in the formation of SS concentrations in water/wastewater, conditioned by different natural and climatic conditions, respectively different mining activities. The main conclusion that can be drawn is that mining wastewater discharged into Sokolitsa River water has a mixed impact on the content of insoluble substances, as different years create different prerequisites for their formation.

When tracking the amount of SS along the chain 'Sokolitsa River→Sazliyka River→Maritsa River', an uneven increase is observed as follows: Sokolitsa River water (5.80-25.00 mg/dm^3) → Sazliyka River water (29.4-56.5 mg/dm^3) (Zhelev et al., 2015) → Maritsa River water (18.0-140.0 mg/dm^3) (Kostadinova et al., 2017). The results indicate that there is an increase in the SS concentration in each subsequent river that receives the water of the previous river.

Ecological assessment of the Sokolitsa River water on the base of SS content can not be made because this indicator is not included in the standard (Regulation No. Н-4/2012).

Heavy metals and trace elements (Fe, Mn, Cu, Zn, Cr, Cd, Pb, Ni). Investigated elements levels in Sokolitsa River water varied by magnitude (Table 2). The highest concentrations in both MPs was found for Fe (118.2-294.4 µg/dm^3) followed by Mn (22.3-77.6 µg/dm^3), Zn (5.20-22.2 µg/dm^3), Cu (4.22-12.1 µg/dm^3), Pb (1.29-2.80 µg/dm^3), Ni (1.29-2.40 µg/dm^3), Cr (1.00-1.10 µg/dm^3) and Cd (0.49-0.51 µg/dm^3) (Fe>Mn>Zn>Cu>Pb>Ni>Cr>Cd). Kostadinova et al. (2017) established similar values for Maritsa River water, regarding the Fe (68-295 µg/dm^3) and Cd (<1.0 µg/dm^3) content, higher values, regarding the Zn (44-98 µg/dm^3), Cu (15-19 µg/dm^3), Pb (2-7 µg/dm^3), Ni (4-9 µg/dm^3) and Cr (1-4 µg/dm^3) content and lower values, regarding the Mn content (5-18 µg/dm^3). In regards to the downward gradation of the elements concentration differences were also observed between the two rivers. The arrangement of the elements concentrations in the

Maritsa River water (Fe>Zn>Ni>Pb>Cr>Cu>As>Mn>Cd) shows that there is a coincidence with that in the Sokolitsa River, regarding the Fe and Cd content, i.e. for the elements with highest and lowest concentrations, respectively. The remaining elements are ranking in different order, but their concentrations in the Sokolitsa River water are lower than those in the Maritsa River water. The only exception is Mn, which concentration is less in Maritsa River water than the Sokolitsa River water. Probably, in this case, other factors and causes influence the formation of Mn concentrations in the two water bodies. Nevertheless, the accumulation of most of the studied heavy metals in the Maritsa River water is observed. This is logical because the river is the main receiving water body in the region.

When comparing the results between the both monitoring points during all years of the studied period divergent trend of concentrations change in the studied elements is observed. For one group of elements (Fe, Mn and Zn), the content is greater in water at MP-2 than in MP-1: for Fe from 1.04 (2013) to 1.50 (2016) times, for Mn from 1.07 (2013) to 1.22 (2015) times and for Zn from 1.04 (2015) to 1.53 (2016) times. With respect to the mean values for the studied period, differences were statistically significant at $P<0.05$ only for Mn. For the other elements in some years of the investigation the levels were higher in MP-2 than those in MP-1 and vice versa, in other years the levels were lower in MP-2 compared to MP-1. These metals are Cu (increase from 1.01 to 1.31 times, 2013 and 2014; decrease from 1.06 to 1.30 times, 2015 and 2016), Pb (increase from 0 to 1.17 times, 2013 and 2016; decrease from 1.15 to 1.28 times, 2014 and 2015) and Ni (increase from 1.01 to 1.33 times, 2013, 2014 and 2016; decrease with 1.50 times, 2015). In these cases the differences in the mean val-

Table 2
Concentrations of heavy metals and trace elements in Sokolitsa River water by two monitoring points, 2013-2016

No	Parameters	Units	Year	C_x (n=2)		Standards - MPC**		
				MP-1*	MP-2*	Regulation No. H-4/2012	Regulation EQS/2010	Regulation No.18/2009
1.	Fe	µg/dm^3	2013	118.2	123.4	Not apply	Not apply	5000
			2014	120.3	128.5			
			2015	170.6	192.2			
			2016	289.2	294.4			
	Mean ± SD, n=8			174.6±80.1	184.6±79.6	P=0.082677***		
2.	Mn	µg/dm^3	2013	58.3	62.5	Not apply	Not apply	200
			2014	22.3	25.2			
			2015	39.3	48.3			
			2016	69.2	77.6			
	Mean ± SD, n=8			47.28±20.7	53.4±22.3	P=0.027242		
3.	Cu	µg/dm^3	2013	9.22	12.1	Not apply	Not apply	200
			2014	6.12	6.20			
			2015	5.50	4.22			
			2016	11.7	11.0			
	Mean ± SD, n=8			8.14±2.88	8.38±3.77	P=0.807556		
4.	Zn	µg/dm^3	2013	10.2	11.3	Not apply	Not apply	2000
			2014	18.1	22.2			
			2015	5.20	5.41			
			2016	10.2	15.7			
	Mean ± SD, n=8			10.9±5.33	13.7±7.08	P=0.115894		

Table 2 continued

5.	Cr	µg/dm³	2013	1.00	1.00	Cr/III/- 32 Cr/VI/- 8	Not apply	Cr/III/- 500 Cr/VI/ - 50
			2014	1.10	1.10			
			2015	1.00	1.00			
			2016	1.10	1.10			
	Mean ± SD, n=8			1.05±0.06	1.05±0.06		-	
6.	Cd	µg/dm³	2013	0.51	0.51	Not apply	0.45 **** 0.60 *****	10
			2014	0.49	0.50			
			2015	0.50	0.50			
			2016	0.50	0.50			
	Mean ± SD, n=8			0.500±0.008	0.502±0.005		P=0.391002	
7.	Pb	µg/dm³	2013	1.51	1.51	Not apply	14	50
			2014	1.49	1.29			
			2015	1.80	1.40			
			2016	2.80	2.40			
	Mean ± SD, n=8			1.90±0.61	1.65±0.50		P=0.079605	
8.	Ni	µg/dm³	2013	1.50	1.51	Not apply	34	200
			2014	1.49	1.29			
			2015	2.10	1.40			
			2016	1.80	2.40			
	Mean ± SD, n=8			1.72±0.28	1.65±0.50		P=0.805088	

*MP-1/Mp-2 – Monitoring points - before (1) and after (2) discharging the wastewater in the river water;
**MPC - Maximum permissible concentration;
*** P - degree of proof;
****Ist and IInd class (40-50 mg $CaCO_3$/dm^3 in water);
*****IIIrd class (50-100 mg $CaCO_3$/dm^3 in water).

ues between selected monitoring points are not proved. For the third group of elements (Cr and Cd) there is no difference in water concentrations from both monitoring points.

It is noteworthy that the discharged wastewater from open coal mining activities loads the Sokolitsa River water at the MP-2 with heavy metals, which in our case were with the highest concentrations - Fe, Mn, Zn. For elements with intermediate levels (Cu, Pb, Ni) that impact is not unidirectional. For elements with lowest concentrations (Cr, Cd) influence of the wastewater on the river water quality is not observed. The different degree of wastewater impact on the heavy metals content in the Sokolitsa River water at MP-2 can be explained by the assumption that the heavy metal concentrations in wastewater are similar to those in natural river water. Therefore, it can be argued that the way of formation of the studied elements concentrations is similar to the natural river water as well as the open coal mine wastewater.

By years, differences in the studied elements content, regardless of the monitoring point of measurement are also observed. The metal concentrations, averaged for both monitoring points, decreases by years of study as follows: Fe – 2016 > 2015 > 2014 > 2013; Mn – 2016 > 2013 > 2015 > 2014; Cu – 2016 > 2013 > 2014 > 2015; Zn – 2014 > 2016 > 2013 > 2015; Pb – 2016 > 2015 > 2013 > 2014; Ni – 2016 >2015 > 2013 > 2014. There is no difference at Cr and Cd concentrations by years, most likely due to the extremely low levels of those elements in water. Analysis of the data shows that in 2016 the environmental conditions favored the formation of the highest concentrations in most elements (Fe, Mn, Cu, Pb and Ni) in Sokolitsa River water and in mining wastewater. In the rest years of the period, the picture differs both in terms of concentration and by elements. The results give reasons to conclude that environmental conditions in any one year are very important factor for heavy metal formation in natural river water and in open coal mining activities wastewater.

Of all investigated elements in the river water to characterize the surface water quality from the ecological point of view, only Cr/III/, Cr/VI/, Cd, Pb and Ni content based on limit values is regulated in Bulgarian legislation (Table 1). Considering that the results obtained for total Cr content are much lower than the maximum permissible concentrations for Cr/III/ (<32 μg/dm^3) and for Cr/VI/ (<8 μg/dm^3) (Regulation No. H-4/2012), presumably it can be concluded that on this indicator the Sokolitsa River water meets the standard requirements and can be determined as water in '*good chemical status'*.

The assessment of the Sokolitsa River water quality by content of priority substances (in our case Cd, Pb and Ni) according to Regulation for EQS (2010) showed that: Cd content was slightly higher than the MPC for the Ist and IInd classes water (<40 mg $CaCO_3$/L) and in the range of MPC for the IIIrd class water (50-100 mg $CaCO_3$/L); Pb content was much lower than the MPC (14 μg/dm^3) - from 5.0 to 10.9 times; Ni content was also much lower than the MPC (34 μg/dm^3) - from 14.2 to 26.4 times. Consequently, Cd, Cr, Pb and Ni pollution is not a problem for the Sokolitsa River water and for its water receivers - Sazliyka River and Maritsa River.

Biotic parameters. The results for phytobenthos and macrozoobentos metrics values at MP-2 are presented in Table 3. Phytobenthos Ecological Quality Rang (EQR) values ranged from 0.4 to 0.6 and Diatomic index values (IPS) – from 9 to 11. Macrozoobentos Biotic index values and Ecological Quality Rang (EQR) values range between 2.0 and 3.0, and between 0.4 and 0.6, respectively. All these results determined the surface water quality at MP-2, as water in *'moderate ecological status'* (Regulation No. H-4/2012).

Mihaylova and Kostadinova (2012) reported the similar Biotic index values (2.0-3.0), established by macrozoobentos organisms abundance in a section of Tundzha River (MP before Yambol town and MP at Hanovo village) with the same river type (R13) as Sokolitsa River. This similarity in the results suggests that the determining factor for the macrozoobenthos abundance is not so much the size of the river, respectively its flow (Tundzha is much larger than Sokolitsa river), but the river type. It is very likely that the same geology (mixed, silicates) and the dominant bottom substrate (sand, sludge, gravel) characterizing the R13 river type, created similar conditions for macrozoobenthos communities development. This aspect deserves attention and further research.

Sokolitsa River water quality as a source for irrigation

The investigated parameters, characterizing the water quality for irrigation purposes fall into three of the five groups of indices according to Regulation No. 18/2009, as

Table 3
Biotic parameters values of Sokolitsa River water at monitoring point 2, 2015-2016

Parameters	Units	Time determination	Values	Regulation No. H-4/2012, Ecological status
A. Phytobenthos				
EQR*	Points	13.07.2015 15.07.2016	0.5 0.4-0.6	0.43<=EQR<0.64 MES
IPS**	Points	13.07.2015 15.07.2016	9-11 9-10	9<=IPS<13 MES***
B. Macrozoobentos				
BI**** EQR	Points	13.07.2015	2.5 0.5	2.5-3.0 0.5-0.6 MES
BI EQR	Points	15.07.2016	2.0-3.0 0.4-0.6	

*EQR - Ecological Quality Rang;

**IPS - Diatomic index;

****MES - Moderate ecological status;

****BI - Biotic index.

follow: salinity (EC), toxicity (Fe, Mn, Cu, Zn, Cr, Cd, Pb, Ni) and miscellaneous (T°C, pH, DO, SS).

Salinity. Electroconductivity (EC) is the basic parameter, characterizing the water salinity and it is closely correlated with the total salt concentration. Established values were lower than the maximum permissible limit for irrigation water (<2000 µS/cm) - average for the period with 1.12 times at MP-1 and with 2.33 times at MP-2 (Table 1). By this indicator the Sokolitsa River water in both MPs meets the requirements for irrigation of agricultural crops. In this connection Westcot (1997) noted that higher water EC (an indirect indicator for its salinity) increases water infiltration rate in the soil. Therefore, the EC has a direct bearing on the water irrigation quality.

Toxicity. Toxicity of irrigation water is determinated on the basis of the key elements content (Fe, Mn, Cu, Zn, Cr, Cd, Pb, Ni). Assessment of the river water quality as a source for irrigation showed that all measured concentrations of the investigated metals and metalloids were lower than the corresponding limit values according to Regulation No. 18/2009: for Fe - from 17.0 to 42.3 times; for Mn - from 2.57 to 7.93 times; for Cu - from 16.5 to 47.4 times; for Zn - from 90.1 to 384.7 times; for Cr_{total} - from 45.4 (Cr/VI/) to 454.5 (Cr/III/) times; for Cd - from 19.6 to 20.4 times; for Pb - from 17.8 to 38.8 times and for Ni - from 83.3 to 155.0 times. Consequently, the heavy metal content in river water is significantly lower than the permissible limits for irrigation water. Despite this finding, it is worth noting that according to Westcot (1997) during the hot months, the minerals accumulation from the crops is more rapid than in cooler months of the year. In such cases, toxic effect with crop damage and yield reduction may occur (Aktar et al., 2010).

***Miscellaneous*.** The parameters, measured from this group of indices were T°C, pH, DO and SS. The water temperature was higher than the permissible limit (28°C) for irrigation water across all measurements at MP-1 (with 1.8-2.2°C) and in 2016 at MP-2 (with 0.1-0.7°C) (Table 1). It should be borne in mind that biota and some physicochemical processes (oxygen solubility, hydrophobic interactions) are particularly sensitive to temperature changes (Mihaylova et al., 2012). By this indicator the Sokolitsa River water meets the requirements for irrigation only at MP-2 during 2013 and 2014.

All pH, DO and SS values were within the permissible ranges for irrigation water: pH values were between 6 and 9, DO >2.0 mgO_2/dm^3 (higher from 2.40 to 2.55 times) and SS <50 mg/dm^3 (lower from 2.00 to 4.35 times). Consequently, mining wastewater discharged into Sokolitsa River does not have a significant negative impact on the water quality from the point of view of its use for irrigation.

CONCLUSIONS

A study of Sokolitsa River water at two monitoring points (MPs) – MP-1, before, and MP-2, after discharge of mining wastewater, during the summer months of the period 2013-2016, by five physicochemical indices (T°C, pH, EC, DO, SS), eight heavy metals and metalloids (Fe, Mn, Cu, Zn, Cr, Cd, Pb, Ni), and three biotic parameters (EQR, IPS, BI), and assessment of the water quality as a natural source and as a source for irrigation, provides the basis for the following conclusions: a) ecological assessment of the river water as a natural source determines water in both monitoring points as water in '*good ecological status*' by pH values and in '*moderate ecological status*' by Dissolved oxygen, Electroconductivity, Ecological Quality Rang, IPS and Biotic index values; b) the priority pollutants levels – Cd, Pb and Ni do not exceed the environmental quality standards and determined the '*good chemical status*' of the water; c) the average element concentrations for the study period decreased in the following order Fe>Mn>Zn>Cu>Pb>Ni>Cr>Cd, which are not risky for the hydroecosystem and for irrigated crops; d) assessment of the river water as a source for irrigation determines water in both monitoring points as appropriate for this purpose by all investigated parameters; e) the wastewater from open coal mining activities, discharged into the river has no significant impact on water quality as a natural source and as a source for irrigation.

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