Surface Water Pollution with Nutrient Components, Trace Metals and Metalloidsin Agricultural and Mining-affected River Catchments (A Case Study for Three Tributaries of the Maritsa River, Southern Bulgaria)

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Abstract

This work analyses changes in the content of nutrient components and trace metals and metalloids at three tributaries of the Maritsa River flowing in Southern Bulgaria with catchments affected by mining and agricultural activities. Input data includes information about 14 chemical water quality parameters (N-NH$_4$, N-NO$_3$, N-NO$_2$, N-tot, P-tot, P-PO$_4$, Al, As, Fe, Cu, Mn, Ni, Pb, and Zn) obtained from the Executive Environment Agency for the period 2015–2018. Two documented methods were used in this work to determine the pollution status of river waters – Heavy metal pollution index (HPI) and CCME Water Quality Index. The results based on the CCME WQI ranked water quality as "Poor" (WQI values range from 31.2 to 39.9). The HPI ratings achieve scores exceeding the critical pollution value of 100 for some of the metals (Al, Cu, Mn, and Zn), which indicates that water is seriously polluted concerning those variables. Therefore, it can be summarized that the river waters are not appropriate for safe drinking, agriculture, and household use because of significant nutrient and metalloids and trace metalscontamination.

Keywords: water pollution; water quality index; nutrient components; trace metals and metalloids; Bulgaria

Introduction

The surface waterbodies are among the most sensitive sources that areprone to impacts from human activities which may cause degradation of the resource in the future (Roshan et al., 2013; Afkhami et al., 2013). Among the variety of human practices causing deterioration in water quality worldwide, two seem to be particularly troubling – agriculture and mining activities (Novotny, 1999; Reza & Singh al., 2010). The excessive use of chemical agents in agriculture aims to achieve an accelerated yield of crops or to protect the same crops from pests, but it is a major source of diffuse water pollution, which underpins a lot of hydro-ecological issues (Novotny, 1999; Hutchins, 2012; Okumah et al., 2019). The increased levels of nutrients like nitrates and phosphates provoke structural changes in aquatic ecosystems and lead to eutrophication (Khan & Ansari, 2005; OECD, 2012). No less harmful are the effects caused by mining activities.

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The extraction of valuable minerals like ore and coal is often accompanied by unregulated discharges of waste products containing metalloids and heavy metals that are a serious source of water pollution. This problem concerns mining and metallurgical waste dumps, as well as mine tailing dumps (Reza & Singh, 2010). The elevated concentration of trace metalsand metalloids in water bodies is treated as one of the most dangerous and burdensome environmental issues (Kar et al., 2008; Shanbehzadeh et al., 2014; Islam et al., 2015). The health effects of metalloids and trace metalscontamination do not cause immediate symptoms, but manifest themselves after years and still are not fully understood(Lee et al., 2007; Adams et al., 2008; Vinodhini & Narayanan, 2008). The combined effect of nutrient and heavy metaland metalloid pollution results in a decline of ecosystem health and loss of biodiversity (Bourg et al., 1996). In the context of those problems, one of the objectives of the European Union Water Framework Directive (WFD) is to ensure good water quality status in all water bodies (Fritsch et al., 2017).The report of EEA (2018), regarding chemical pollution, concluded that Europe is not on track to minimize the significant adverse effects of chemicals on the environment by 2020. It noted that 62% of the Europe's water bodies are not in good chemical status and the risks from chemical pollution on the environment are "likely to be greatly underestimated" (EEA, 2018). Therefore, regular monitoring of pollutants is necessary in order to assess and limit the potential health risks for humans and aquatic ecosystems from water contamination.

A substantial amount of studies have focused on trace metaland metalloid contamination and nutrient pollution of surface waters all around the world (Nasrabadiet al., 2009; Petrović et al., 2011; Ramos et al., 2012; Dunca, 2018; Chen et al., 2019). Several Bulgarian reports refer to the heavy metal distribution and ecological status of the rivers in the investigated region (Rabadjieva et al., 2009; Velcheva et al., 2012; Georgieva et al., 2014; Varbanov et al., 2015). Most studies performed on the quality of surface waters present the results using differentwater quality indices among them the Heavy metal pollution index (HPI) (Prasad and Kumari, 2008; Reza & Singh,2010; Manoj et al., 2012) and the Canadian Water Quality Index (CCME WQI) (Lumb et al., 2012; Espejo et al., 2012; Mohebbi et al., 2013; Jafarabadi et al., 2016; Venkatramanan et al., 2016). Those indices can provide information in a form that water resources managers and water regulatory agencies can use to evaluate future alternatives and to make effective management decisions (Sutadian et al., 2016).

Both organic pollution and trace metal and metalloids contamination remain unsolved problems facing the water resources management sector in Bulgaria. Thus, the objective of the current work is to analyse the simultaneous impact of two anthropogenic practices influencing the chemical composition and quality status of river waters in mining-affected catchments with agricultural land use through the application of CCME Water Quality Index and Heavy Metal Pollution Index (HPI).

Study area

The investigated region includes the drainage basins of three tributaries of the Maritsa River situated in Southern Bulgaria – the Topolnitsa River, the Luda Yana River, and the Chepelarska River (Figure 1).The Maritsa River is one of the biggest rivers on the Balkan Peninsula. The region is densely populated and highly industrialized with intensive agriculture. The selected rivers have become one of the most seriously polluted streams in Bulgaria over the past few decades due to discharges from agricultural lands, livestock farms, mining and metallurgical industries bearing nutrients and heavy metals into the river systems.
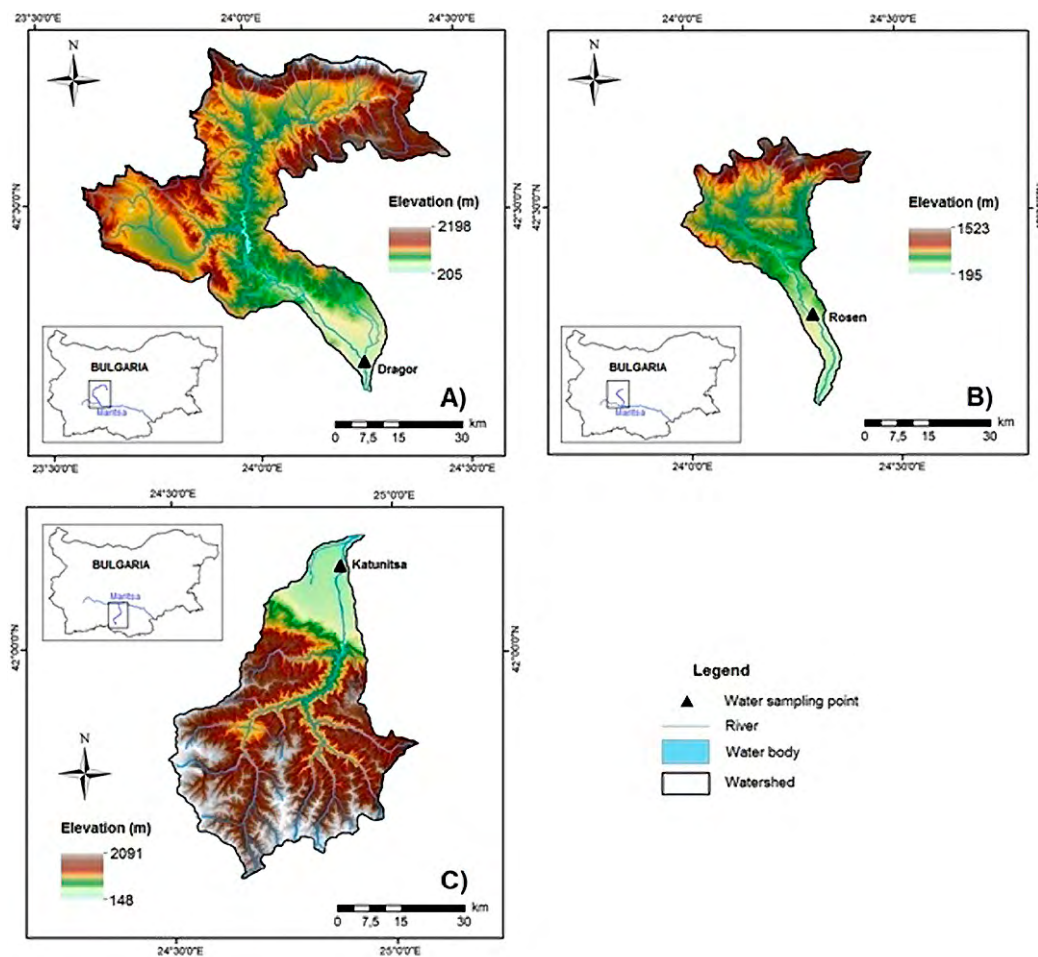
The Topolnitsa River is a left tributary of the Maritsa River with a total length of 154 km. Its catchment covers an area of 1789 km² (Hristova, 2012). The main river body springs from the northeastern slopes of the Bunaya Peak in the Sredna Gora Mountain at an altitude of 1413 m, drains the westernmost part of the Upper Thracian Plain and flows into the Maritsa River

about 2 km west of Pazardzhik (Figure 1A). The mean annual flow is 10 m3/s with maximum discharge values in April and minimum flow volume in August (Hristova, 2012). In the catchment area are located 45 settlements, including the towns of Koprivshtitsa, Zlatitsa, Pirdop, and Ihtiman.

The Luda Yana River, a left tributary of the Maritsa River, flows in length of 74 km and has a drainage area of 685 km2 (Hristova, 2012). The Luda Yana River originates from the western slopes of the Bich Peak in the Sredna Gora Mountain at an altitude of 1449 m. Later it runs through the Upper Thracian Plain and flows into the Maritsa River approximately 8 km east of Pazardzhik (Figure 1B). The mean annual flow is around 4 m³/s with maximum flow volumes in March and April and minimum discharge value in August and September (Hristova, 2012). In the river basin are situated 12 settlements, including the towns of Panagyurishte and Strelcha.

Figure 1. Maps of the relief and the drainage network showing the location of water sampling points: A) Topolnitsa River basin; B) Luda Yana River basin; C) Chepelarska River basin

The Chepelarska River is a right tributary of the Maritsa River with a length of 86 km. Its drainage basin covers an area of 1010 km² (Hristova, 2012). The main river springs from the western slopes of the Rozhen Peak in the Western Rhodope Mountains at an altitude of 1550 m. Upper part flows in a deep and narrow gorge valley, while downstream section runs through a shallow and wide valley in the Upper Thra-cian Plain. The Chepelarska River flows into the Maritsa River about 10 km east of Plovdiv (Figure 1C). The mean annual flow reaches 12 m³/s. The runoff regime is characterized by a high flow phase in April and May and a low flow period in August and September (Hristova, 2012). The catchment area concentrates 22 settlements, including the towns of Chepelare, Laki, Asenovgrad, and Kuklen.

Data and Methods

Research information about the values of 14 chemical water quality parameters has been used. Time-series data include statistical information about the concentration of six nutrient compounds: ammonium nitrogen (N-NH$_4$), nitrate nitrogen (N-NO$_3$), nitrite nitrogen (N-NO$_2$), total nitrogen (N-tot), orthophosphates (P-PO$_4$), total phosphorus (P-tot), and eight metalloid and heavy metal parameters: aluminum (Al), arsenic (As), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn). Between 14 and 16 samples for each variable have been in-situ collected and then processed in an ISO/IEC 17025:2006 Accredited Laboratory following a standardized procedure. The basic measurements were conducted by the Executive Environment Agency at three water sampling sites during the period 2015–2018. The measuring points have been selected so that they are located in downstream river sections in order to present a full picture of surface water pollution within the examined catchment areas (Figure 1, Table 1).

Water quality status in terms of nutrients has been assessed according to the reference values for surface

Table 1. Information about the location of water sampling points

River – Water sampling point	Elevation (m)	Latitude (°)	Longitude (°)
Topolnitsa – Dragor	218	42.2308	24.2918
Luda Yana – Rosen	260	42.3132	24.3624
Chepelarska – Katunitsa	162	42.1033	24.8665

Table 2. Reference threshold values for the concentration of nitrogen and phosphorus compounds in surface water bodies of type R5 as stated in Regulation 4/2012

Surface water body type		Water quality status	Nitrogen and phosphorus concentration (mg/l)					
Code	Description		$N-NH_4$	$N-NO_3$	$N-NO_2$	N-tot	$P-PO_4$	P-tot
R5	Semi-mountain streams in Ecoregion 7 (Eastern Balkans) dominated by a gravel substrate	Excellent	<0.04	<0.5	<0.01	<0.5	<0.02	<0.025
		Good	0.04–0.4	0.5–1.5	0.01–0.03	0.5–1.5	0.02–0.04	0.025–0.075
		Moderate	>0.4	>1.5	>0.03	>1.5	>0.04	>0.075

water body of type R5 stated in the National regulatory standard – Regulation 4 of 14 September 2012 for characterization of the surface waters (Table 2).

The Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) for an overall assessment of nutrient water pollution has been applied. This index is calculated as follows:

$$CCME\ WQI = 100 - \sqrt{\frac{F_1^2 + F_2^2 + F_3^2}{1.732}},$$

where: F_1 – Scope (the percentage of variables whose objectives are not met); F_2 – Frequency (the percentage of samples whose objectives are not met); F_3 – Amplitude (the total amount by which the objectives are not met). The first two components are expressed as a ratio between the number of "failed variables" and "failed tests" to the total number of variables and samples, respectively. The calculation of the third factor requires some additional steps (CCME, 2001).

Water quality parameters are calibrated with a certain limit and then the amount of deviation is determined. In this work the calculations have been conducted according to the maximum permissible limits

for "Good status", stated in Regulation 4/2012 (Table 2).

Denominator 1.732 is chosen to express the result of CCMEWQI as a number between 0 (worst status) to 100 (best status). Table 3 shows a ranking system based on the CCME WQI values.

The CCME WQI is an advantageous approach because its formula allows it to be applied at different scales and locations. In addition, the obtained index ratings can be easily interpreted by using a clearly defined ranking system based on the concept for "desirable levels" (Table 3).

Water quality status with respect to arsenic and trace metals has been assessed following the European guidelines stated in Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on Environmental quality standards for priority substances and some other pollutants (amended in Directive 2013/39/EC), and their equivalent criteria in Bulgaria transposed into Regulation 4/2012 (Table 4). Generally, the Environmental quality standard (EQS) indicates an average annual reference value. Unless otherwise specified, it applies to the total concentration of a given chemical parameter (Directive 2013/39/EC).

Table 3. Ranking system and interpretation of water quality based on CCME WQI (CCME, 2001)

Rating	WQI values	Interpretation
Excellent	95–100	Water quality is protected with a virtual absence of threat or impairment; conditions very closer to natural or pristine levels
Good	80–94	Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels
Fair	65–79	Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels
Marginal	45–64	Water quality is frequently threatened or impaired; conditions usually depart from natural or desirable levels
Poor	0–44	Water quality is almost always threatened or impaired; conditions very often depart from natural or desirable levels

Table 4. Environmental quality standard for priority substances and some other pollutants

Guidelines of Reg. 4/2012and Directive 2013/39/EC	Metalloid and trace metal concentration (µg/l)							
	Al	As	Cu	Fe	Mn	Ni	Pb	Zn
Environmental quality standards (EQS)	15	10	10*	100	50	34**	14**	75*

The reference level has been defined in accordance with the value of calcium carbonate hardness (CaCO3)
**Maximum contaminant level pointed out in Directive 2013/39/EC

In order to evaluate the overall status of waters in terms of arsenic and trace metals, the Heavy metal pollution index (HPI) has been applied. The HPI is a rating method that shows the composite influence of individual metalloid and trace metal parameters on the overall water quality (Mohan et al., 1996). The following formula is usually used to calculate this index:

$$HPI = \frac{\sum_{i=1}^{n} W_i \cdot Q_i}{\sum_{i=1}^{n} W_i},$$

where: n is the number of parameters considered, W_i is the unitweightage of the i-th parameter, and Q_i is the sub-index of the i-th parameter. Q_i is expressed by the equation:

$$QI = \sum_{i=1}^{n} \frac{M_i(-)I_i}{S_i - I_i} \cdot 100,$$

where: M_i, I_i, and S_i are the monitored average value, the ideal value ($I_i = 0$ for each heavy metal), and the standard value of the i-th parameter, respectively. In this formula, the unit weightage (W_i) is computed as a value inversely proportional to the recommended standard (S_i) of individual parameters (Table 4).The obtained ratings of HPI can be classified into three categories: low (less than 100), medium (equal to 100), and high pollution (more than 100). If the HPI rating is more than the critical pollution index value of 100, water cannot be used for drinking and domestic use (Mohan et al., 1996).

Results

Increased levels of nitrogen and phosphorus compounds compared to the reference norms at all measuring sites during the period under review are observed (Figure 2, Table 5). Despite some exceptions, in general terms, nitrate and phosphorus content in surface waters is marked by seasonality – the highest measured values occur in summer and autumn, while the lowest concentrations are detected in winter and spring months. Although runoff data are not used, we can point out that those seasonal changes are inversely related to flow regime.

Excepting the described similarities, based on the analysis of collected samples, some differences from one monitoring point to another are established. For example, with respect to ammonium nitrogen, the most serious exceeding is detected at the Topolnitsa River near Dragor, where the measured maximum concentration is 9.00 times higher than the maximum permissible limit for "Good status" stated in Regulation 4/2012 for characterization of the surface waters and about 56.2% of the recorded samples do not meet the same reference norm. In contrast, the highest observed value of this variable at the Luda Yana River

Table 5. Descriptive statistics of the nitrogen and phosphorus concentration (mg/l) in surface waters

River – water sampling point	Values	Nitrogen and phosphorus concentration (mg/l)					
		N-NH$_4$	N-NO$_3$	N-NO$_2$	N-tot	P-PO$_4$	P-tot
Topolnitsa – Dragor	Minimum	0.033	0.250	0.005	0.600	0.006	0.067
	Average	0.827	0.645	0.018	2.193	0.064	0.229
	Maximum	3.600	1.400	0.069	5.200	0.257	0.466
Luda Yana – Rosen	Minimum	0.010	0.190	0.004	0.500	0.020	0.061
	Average	0.095	0.933	0.023	1.348	0.087	0.195
	Maximum	0.450	1.800	0.084	2.550	0.210	0.340
Chepelarska – Katunitsa	Minimum	0.120	0.280	0.007	0.770	0.012	0.044
	Average	0.368	2.126	0.048	2.875	0.067	0.117
	Maximum	1.040	4.770	0.201	5.300	0.310	0.320
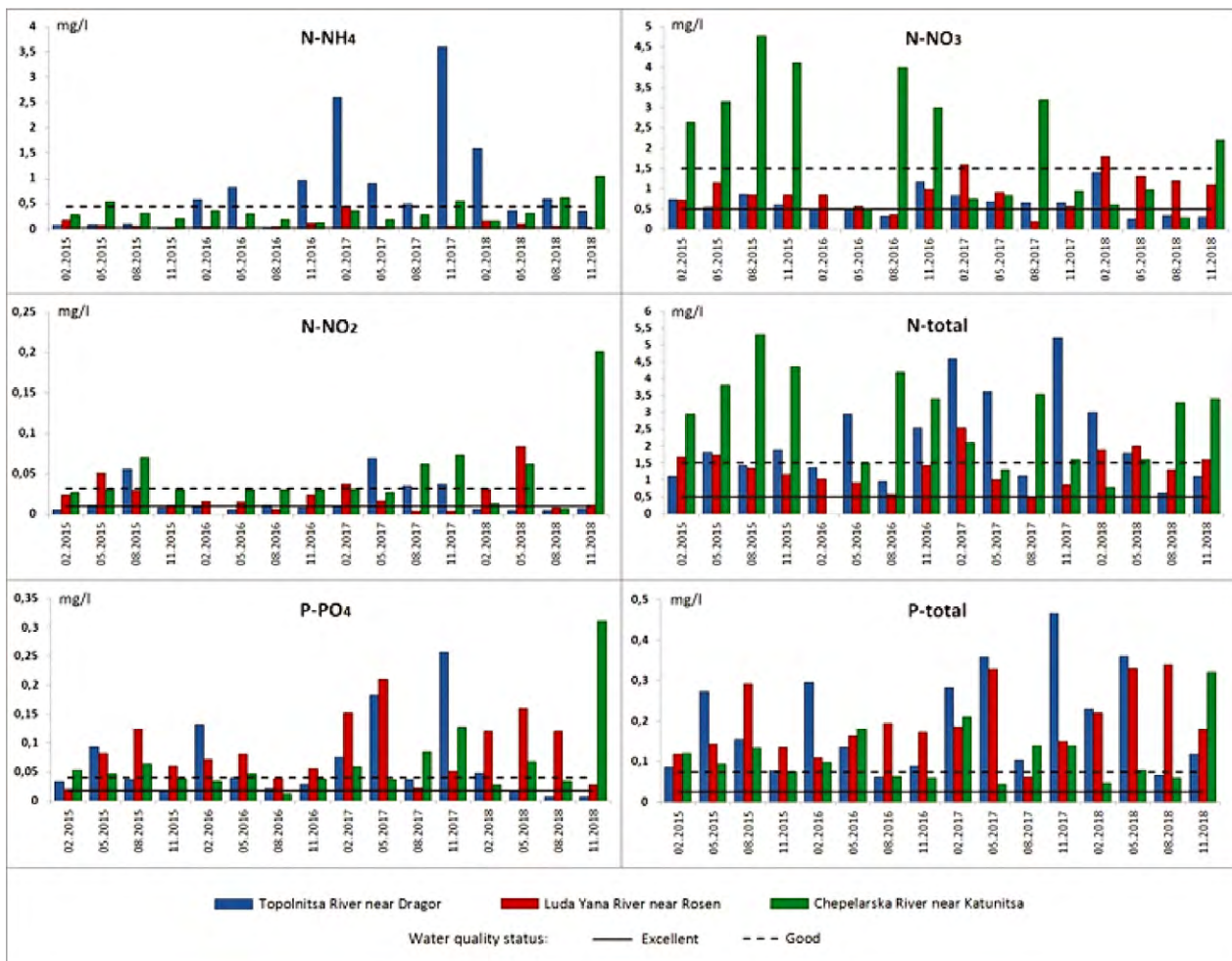
Figure 2. Dynamics in the concentration of nitrogen and phosphorus compounds compared to the maximum permissible limits pointed out in Regulation 4/2012 for characterization of the surface waters

near Rosen slightly exceeds 1.12 times the norm, and it is the only sample not falling within the recommended standard.As regards nitrate nitrogen, most affected appears the Chepelarska River near Katunitsa, where the highest monitored concentration exceeds 3.18 times the maximum permissible limit for "Good status" and about 53.3% of the collected samples remain above the norm. At the same time, values exceeding the critical pollution level of this chemical parameter for the Topolnitsa River near Dragorare not ascertained. Unlike nitrogen compounds whose concentrations show some contrasts from one sampling site to another, analysing the content of total phosphorus and orthophosphates we find that those variables almost constantly exceed the reference norms at all water measuring points. An illustrative example is total phosphorus whose samples with thefollowing frequency do not meet the norm: 81.2%(the Topolnitsa River at Dragor), 93.7% (theLuda Yana River at Rosen), and 62.5% (the Chepelarska River at Katunitsa) (Figure 2, Table 5).

The results based on CCME WQI rank water quality as "Poor" (WQI values range from 31.20 for the

Chepelarska River near Katunitsato 39.91 for the Topolnitsa River near Dragor) (Table 6). The obtained index ratings indicate water quality of the selected rivers is frequently endangered and conditions very often deviate from natural or desirable levels. Water appears critically polluted with nutrient compounds and it is unsuitable for drinking and domestic uses.

Similar assessments were reported from Varbanov et al. (2015). Exploring the human impact on water quality and calculating the CCME WQI ratings of the rivers Topolnitsa and Luda Yana for the period 1981–2010, the authors concluded that water quality is seriously impaired and index values fall in range "Poor" to "Marginal" due to the effect of various anthropogenic pressures. The results from our work show that the water quality is not improving for 2015–2018, which ranks the examined rivers into "highest concern" category about their hydro-ecological status (EEA, 2018).

The analysis of the metalloids and trace metals content reveals that among eight analyzedvariables, five to seven of them at a given point do not meet the EQS (Table 7). In the waters of theTopolnitsa River at Dragor, the largest excess is marked by manga-

Table 6. Obtained ratings of the CCME WQI and basic statistics used in the calculations

River – water sampling site	Total variables	Failed variables	Scope (F₁)	Total tests	Failed tests	Frequency (F₂)	Amount (F₃)	CCME WQI
Topolnitsa – Dragor	6	5	83.3	96	43	44.8	43.4	39.91
Luda Yana – Rosen	6	6	100.0	96	39	40.6	34.6	34.55
Chepelarska – Katunitsa	6	6	100.0	93	48	51.6	39.2	31.20

Table 7. Descriptive statistics of the metalloid and trace metal concentration (µg/l) in surface waters

River – water sampling point	Values	Metalloids and trace metal concentration (µg/l)							
		Al	As	Fe	Cu	Mn	Ni	Pb	Zn
MohanTopolnitsa – Dragor	Minimum	24.0	*<0.5	15.0	1.8	41.0	*<0.5	*<0.4	8.6
	Average	187.1	*~2.1	74.4	56.3	405.4	*~5.2	*~0.6	62.8
	Maximum	386.0	4.1	233.0	462.2	2610.8	21.8	1.0	213.0
Luda Yana – Rosen	Minimum	52.0	*<0.5	30.0	9.9	42.0	*<0.5	*<0.4	3.6
	Average	368.6	*~4.6	79.0	76.7	254.2	*~4.7	*~0.5	28.0
	Maximum	1108.0	12.8	180.0	275.0	950.0	43.2	0.8	120.3
Chepelarska – Katunitsa	Minimum	4.5	*<0.5	20.0	1.8	56.0	*<0.5	*<0.4	32.0
	Average	20.8	*~3.9	31.5	5.2	1210.8	*~1.2	*~5.2	227.0
	Maximum	86.0	14.0	69.0	12.2	13240.0	16.6	55.0	1160.0

The measured minimum levels of arsenic (As), nickel (Ni), and lead (Pb) remain under the detection limit. The obtained average values have been calculated accepting the detection limit as a measured minimum concentration, so those mean numbers should be perceived with some conditionality.

nese and copper whose maximum concentrations remain 52.2 and 46.2 times above the EQS. The Luda Yana River at Rosenappears to be most contaminated with aluminum and copper – up to 73.8 and 27.5 times above the EQS. The contaminants of the Chepelarska River near Katunitsa include manganese and zinc – their maximum values remain 264.8 and 15.4 times higher than the EQS (Table 7). The measured concentrations of copper, lead, and zinc during 2015–2018 fall within or seem to be slightly lower than those recorded in 2004 and 2005 (Bird et al., 2010). The cited authors, exploring the dispersal

of heavy metals in surface water, channel sediment, and floodplain sediment within the investigated area, concluded that those landscape components suffer from significant and widespread enrichment with metalloids and trace metals as a result of mining-related point sources of contamination. Our work confirms past results, shows a partly similar picture for a more contemporary period and assumes that mining activities continue to affect river systems.

The calculated values of the HPI vary from 179.97 (the Chepelarska River at Katunitsa) up to 626.54 (the Luda Yana River at Rosen), which indicates "High

Table 8. Obtained ratings of the HPI and basic statistics used in the calculations

River – water sampling site	Indices	Metalloids and trace metal parameters							
		Al	As	Fe	Cu	Mn	Ni	Pb	Zn
Topolnitsa – Dragor	Wi (1/Si)	0.07	0.10	0.01	0.10	0.02	0.03	0.07	0.01
	Qi (Mi /Si*100)	1247.52	20.63	74.43	563.25	810.89	15.34	4.76	83.73
	Wi .Qi	83.17	2.06	0.74	56.33	16.22	0.45	0.34	1.12
	HPI	390.48							
Luda Yana – Rosen	Wi(1/Si)	0.07	0.10	0.01	0.10	0.02	0.03	0.07	0.01
	Qi(Mi /Si*100)	2457.73	46.40	79.00	767.80	508.33	13.82	3.90	37.34
	Wi.Qi	163.85	4.64	0.79	76.78	10.17	0.41	0.28	0.49
	HPI	626.54							
Chepelarska – Katunitsa	Wi(1/Si)	0.07	0.10	0.01	0.10	0.02	0.03	0.07	0.01
	Qi (Mi /Si*100)	139.21	39.23	31.45	51.76	2421.67	3.64	37.38	302.70
	Wi.Qi	9.28	3.92	0.31	5.18	48.43	0.11	2.67	4.04
	HPI	179.97							

pollution" (Table 8). The results show that the metalloids and trace metals parameters exceeding the critical pollution index level of 100 are arranged as follows: aluminum, manganese, copper (Topolnitsa); aluminum, copper, manganese (Luda Yana); manganese, zinc, aluminum (Chepelarska). Those variables form the largest composite influence and most strongly affect the overall HPI rating, which means that the river waters are seriously contaminated with respect to listed metalloids and trace metals.

Discussion

An important factor, affecting water quality status in a catchment area is a land use/land cover structure. The predominant land cover class in the selected river catchments is "Forest and semi-natural areas", which occupies up to 78.03% of the drainage basins(Figure 3, Table 9). The forest vegetation improves water quality by minimizing erosion, reducing turbidity, maintaining naturally high levels of dissolved oxygen, and absorbing the chemical pollutants (Muscutt et al., 1993). In general terms, the upper river courses are located in mountainous regions with protected natural forest landscapes and relatively low population density.

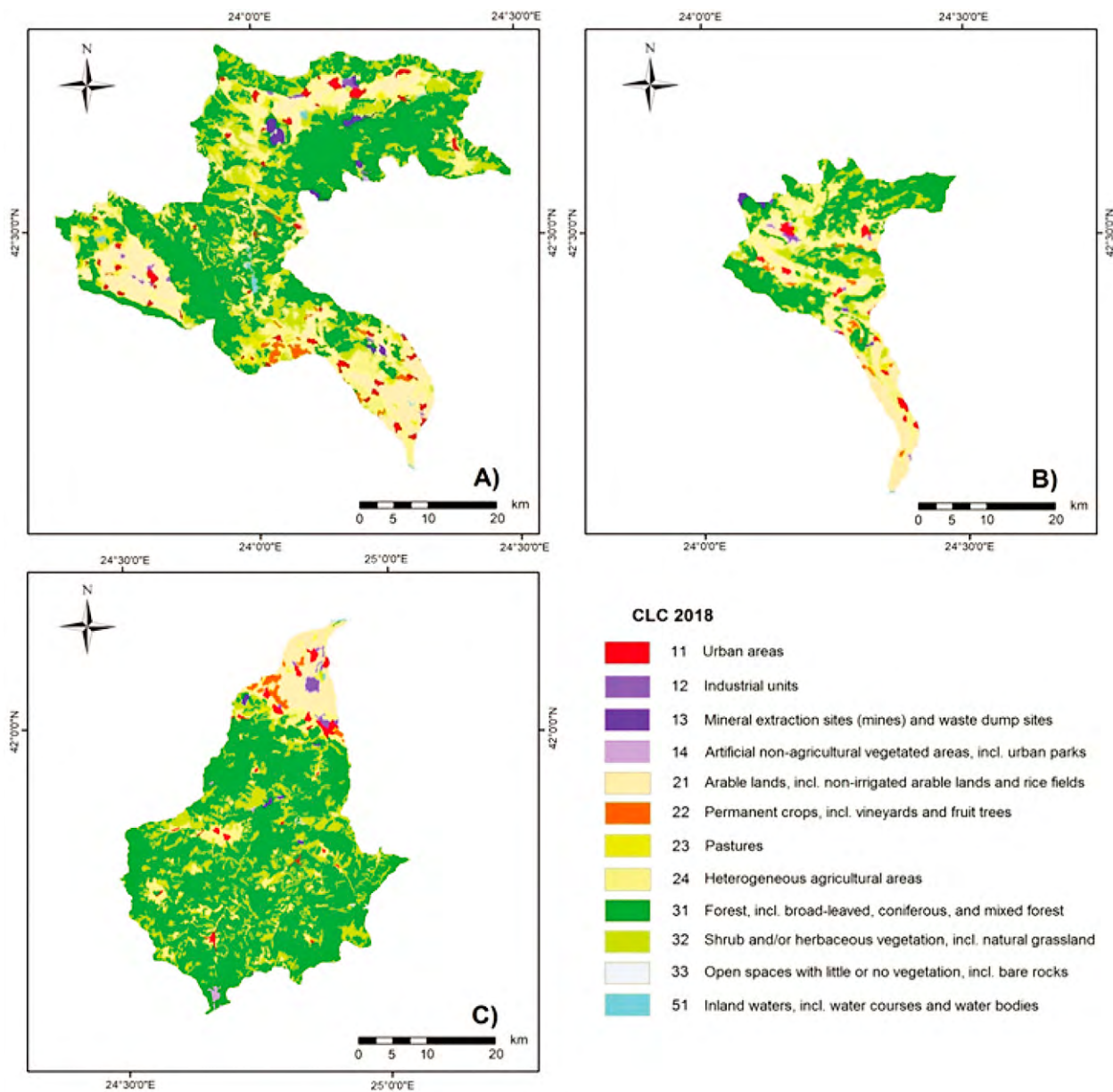However, in this part there are serious sources of heavy metals and metalloidenvironmental pollu-

CLC 2018

🟥	11	Urban areas
🟪	12	Industrial units
🟪	13	Mineral extraction sites (mines) and waste dump sites
🟪	14	Artificial non-agricultural vegetated areas, incl. urban parks
🟨	21	Arable lands, incl. non-irrigated arable lands and rice fields
🟧	22	Permanent crops, incl. vineyards and fruit trees
🟨	23	Pastures
🟨	24	Heterogeneous agricultural areas
🟩	31	Forest, incl. broad-leaved, coniferous, and mixed forest
🟩	32	Shrub and/or herbaceous vegetation, incl. natural grassland
⬜	33	Open spaces with little or no vegetation, incl. bare rocks
🟦	51	Inland waters, incl. water courses and water bodies

Figure 3. Maps ofCORINE Land Cover (2018): A) Topolnitsa River basin; B) Luda Yana River basin; C) Chepelarska River basin

Table 9. Distribution of CORINE Land Cover Classes 2018 (% of catchment areas)

CORINE Land Cover Classes	Catchment areas		
	Topolnitsa	Luda Yana	Chepelarska
1. Artificial surfaces	**3.26**	**2.82**	**3.51**
1.1 Urban areas	2.06	1.80	1.94
1.2 Industrial units	0.45	0.53	0.88
1.3 Mineral extraction sites (mines) and waste dump sites	0.73	0.46	0.34
1.4 Artificial non-agricultural vegetated areas, incl. urban parks	0.02	0.03	0.35
2. Agricultural areas	**29.53**	**38.86**	**18.42**
2.1 Arable lands, incl. non-irrigated arable lands and rice fields	14.22	23.68	8.39
2.2 Permanent crops, incl. vineyards and fruit trees	0.94	0.77	1.45
2.3 Pastures	2.29	0.86	0.62
2.4 Heterogeneous agricultural areas	12.08	13.55	7.96
3. Forest and semi-natural areas	**66.75**	**58.25**	**78.03**
3.1 Forest, incl. broad-leaved, coniferous, and mixed forest	48.74	41.53	63.21
3.2 Shrub and/or herbaceous vegetation, incl. natural grassland	17.85	16.72	14.54
3.3 Open spaces with little or no vegetation, incl. bare rocks	0.16	–	0.28
4. Water bodies	**0.46**	**0.07**	**0.04**
4.1 Inland waters, incl. water courses and water bodies	0.46	0.07	0.04

tion – ore-extraction mines, dressing factories, and metallurgical enterprises that are not connected with mining wastewater treatment plants or if they are connected the effluents appear to be inadequately treated.Such examples in the catchment area of the Topolnitsa River include the copper-extraction mines "Medet", "Elatsite", and "Elshitsa" whose wastewaters enter into the main river through its tributaries. Additionally, the effluents discharging from the ore-processing enterprises near Chelopech ("Dundee Precious Metals") and Pirdop ("Aurubis Bulgaria"), as well as the raw wastewaters flowing out from industrial lagoons and tailing dumps, also influence water quality. It is important to note that the majority of the mining sites are situated before the "Topolnitsa" Reservoir. Although the monitoring point near Dragor is located after the dam, increased values of heavy metals and metalloids in river waters can still be observed. In the catchment area of the Luda Yana River the main source of metalloid and trace metal pollution is "Asarel", a copper mine located before the village of Oborishte, whose wastes get into the main river through its right tributary - the Banska Luda Yana River. The drainage basin of the Chepelarska River is affected by mining as well. The Chepelarska River and its tributaries drain through part of the Rhodope zone with deposits of lead-zinc ore. The produced wastes from the zinc mines "Laki" and "Dzhurkovo" are initially discharged into small gullies and tributaries, which subsequently bear the mining wastewaters into the main river. Additionally, the industrial effluents released from the ore-processing factory "Gorubso –

Laki" and the non-ferrous metals plant "KCM – Plovdiv" also influence water quality of the Chepelarska River. We can summarize that the unregulated discharge of untreated or inadequately treated effluents from ore-extraction mines, dressing factories, tailing dumps, industrial lagoons, and metallurgical dumps explains the elevated concentrations of trace metals and metalloidsin the river waters (Table 7). An implication can be drawn that although the mines occupy less than 1% of the catchment areas, they strongly affect water quality (Figure 3 C, Table 9). Downstream sections of the investigated rivers cover parts of the western half of the Upper Thracian Plain, also known as Pazardzhik-Plovdiv lowland area, which is an important agricultural region. There are situated the most extensive arable lands of Bulgaria with rice paddies, vegetable crops, vineyards and fruit trees, as well as a lot of livestock farms. Agricultural activities are linked to water quality, as discharged effluents help to enrich water bodies with nutrients. In the investigated catchment "Agricultural areas" are the second most characteristic land cover class, constituting up to 38.86% of drainage basins (Figure 3, Table 9). Sources of water pollution by ammonia and ammonium nitrogen include raw wastewaters released from farm complexes as a result of animal husbandry practices. Along the Topolnitsa River are situated livestock farms that are not connected with wastewater treatment plants, which explain the increased values of ammonium nitrogen in the river waters (Figure 2, Table 5). Similarly, water pollution by nitrate nitrogen usually indicates an inflow of soil runoff formed

as a result of flushing from agricultural lands treated with chemical agents like artificial fertilizers or pesticides. The agricultural effluents released from the surrounding arable lands in addition to the produced wastewaters from the vermicomposting enterprise near Asenovgrad explain the elevated values of nitrate nitrogen in the waters of Chepelarska River (Figure 2, Table 5).According to the results phosphor appears to be the most significant pollutant (Figure 2). The main sources of phosphorous pollution are the leaking of urban sewage and septic tanks, usage of phosphorus-rich fertilizers in agriculture, and decomposition of biomass and erosion. The results obtained give us a reason to argue that one of the problems facing the settlements in the region remains the undeveloped public sewerage systems, the uncontrolled deposition of biodegradable wastes into illegal garbage dumps, resulting in poor water quality.

Conclusion

The results show that among the 14 observed chemical parameters, the majority of them do not meet the requirements of Water Quality Standards for Surface Water Environmental Quality. The application of CCME and HPI confirms this result and reveals that river waters are in the "Poor quality" category with respect to nitrogen and phosphorus content and they are "High polluted" with respect to heavy metals (Al, Cu, Mn and Zn). The selected indices prove to be sensitive tools for evaluating water quality depending on given objectives – the index scores indicate water is critically polluted and it is inappropriate for drinking and domestic uses. Adoption of stricter wastewater treatment methods in order to remove the unregulated discharge of raw effluents from mining sites and industrial enterprises, promotion of sustainable agricultural practices, as well as renovation and expansion of sewage systems in the settlements are crucial measures to reduce the impact of various anthropogenic activities on water quality.Furthermore, a comprehensive research of the environmental health status is another step that has to be taken to better control and further protection of river ecosystems. Regular monitoring of pollutants in affected zones and evaluation of pollution effects on human health and aquatic ecosystems are essential steps to abate water contamination in the region.

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