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

Kalina Radeva*, Kalin Seymenov^A
Received: February 10, 2021 | Revised: April 14, 2021 | Accepted: May 21, 2021
doi: 10.5937/gp25-30811

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-NH₄, N-NO₃, N-NO₂, N-tot, P-tot, P-PO₄, 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 metals contamination.

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

Introduction
The surface waterbodies are among the most sensitive sources that are prone 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.
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 metal and metalloid compounds 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 metal contamination 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 metal 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.

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 Nagyurishte and Strelcha.

A substantial amount of studies have focused on trace metal and 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 different water quality indices among them the Heavy metal pollution index (HPI) (Prasad and Kumari, 2008; Reza & Singh, 2010; Mano 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 metalloid 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).
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 Roshen 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 Thracian 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-NH₄), nitrate nitrogen (N-NO₃), nitrite nitrogen (N-NO₂), total nitrogen (N-tot), orthophosphates (P-PO₄), 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...
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:

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

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. Thus, the work has 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 CCME WQI 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 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 |
|-------------------------|----------------------|---------------------------------------------|------|
|                         |                      | N-NH₄ | N-NO₃ | N-NO₂ | N-tot | P-PO₄ | P-tot |
| R5                     | Excellent            | <0.04 | <0.5  | <0.01 | <0.5  | <0.02 | <0.025 |
| R5                     | 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 |
| R5                     | Moderate             | >0.4 | >1.5  | >0.03 | >1.5  | >0.04 | >0.075 |

### 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 |
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 unit weightage of the \( i \)-th parameter, and \( Q_i \) is the sub-index of the \( i \)-th parameter.

\[ Q_i = \frac{M_i - I_i}{S_i - I_i} \times 100, \]

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.

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.

| River – water sampling point | Values | Nitrogen and phosphorus concentration (mg/l) | Metalloid and trace metal concentration (µg/l) |
|-----------------------------|--------|---------------------------------------------|---------------------------------------------|
|                             |        | N-NH₄ | N-NO₃ | N-NO₂ | N-tot | P-PO₄ | P-tot | Al  | As  | Cu  | Fe  | Mn  | Ni  | Pb  | Zn  |
| Topolnitsa – Dragor         | Minimum| 0.033 | 0.250 | 0.005 | 0.600 | 0.006 | 0.067 | 15  | 10  | 10* | 100 | 50  | 34**| 14**| 75* |
|                            | 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 | 12  | 10  | 100 | 50  | 50  | 34**| 14**| 75* |
|                            | 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 |      |     |     |     |     |     |     |     |

*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

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

Table 5. Descriptive statistics of the nitrogen and phosphorus concentration (mg/l) in 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 Katanitsa, 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 Dragor are 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 the following frequency do not meet the norm: 81.2% (the Topolnitsa River at Dragor), 93.7% (the Luda Yana River at Rosen), and 62.5% (the Chepelarska River at Katanitsa) (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 Katanitsa to 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 analyzed variables, five to seven of them at a given point do not meet the EQS (Table 7). In the waters of the Topolnitsa River at Dragor, the largest excess is marked by manga-
Surface Water Pollution with Nutrient Components, Trace Metals and Metalloids in Agricultural and Mining-affected River Catchments (A Case Study for Three Tributaries of the Maritsa River, Southern Bulgaria)

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

| River – water sampling site | Total variables | Failed variables | Scope ($F_v$) | Total tests | Failed tests | Frequency ($F_r$) | Amount ($F_a$) | 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) |
|------------------------------|--------|---------------------------------------------|
|                             | Minimum | As, Fe, Cu, Mn, Ni, Pb, Zn                  |
| MohanTopolnitsa – Dragor     |         |                                             |
| Average                      | 24.0    | *<0.5, 15.0, 1.8, 41.0, *<0.5, *<0.4       |
| Maximum                      | 386.0   | 4.1, 74.4, 56.3, 405.4, *<0.6             |
| Luda Yana – Rosen            | Average | 52.0, *<0.5, 3.0, 9.9, *<0.5, *<0.4       |
| Maximum                      | 368.6   | *<4.6, 79.0, 76.7, 254.2, *<0.5           |
| Chepelarska – Katunitsa      | Average | 1108.0, 12.8, 180.0, 275.0, 950.0         |
| Maximum                      | 386.0   | 4.1, 74.4, 56.3, 405.4, *<0.6             |

* 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.

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

| River – water sampling site | Indices | Metalloids and trace metal parameters |
|-----------------------------|---------|--------------------------------------|
|                             | Wi (1/Si) | 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 metalloid environmental pollu-
Surface Water Pollution with Nutrient Components, Trace Metals and Metalloids in Agricultural and Mining-affected River Catchments (A Case Study for Three Tributaries of the Maritsa River, Southern Bulgaria)

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

| CORINE Land Cover Classes                              | 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        |

...
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 Chepelasarska 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.

References

Adams, R. H., Guzmán Osorio, F. J., & Zavala Cruz, J. (2008). Water repellency in oil contaminated sandy and clayey soils. *International Journal of Environmental Science & Technology* 5(4), 445–454.

Bird, G., Brewer, P., Macklin, M., Nikolova, M., Kotsev, Ts., & Mollov, M. (2010). Dispersal of contaminant metals in the mining-affected Danube and Maritsa drainage basins, Bulgaria, Eastern Europe. *Water, Air, and Soil Pollution* 206, 105–127.

Bourg, A.C., & Bertin, C. (1996). Diurnal variations in the water chemistry of a river contaminated by heavy metals: Natural biological cycling and anthropic influence. *Water, Air, and Soil Pollution* 86, 101–116.

CCME WQI. (2001). Canadian Council of Ministers of the Environment Water Quality Index.

Chen, Xi., Strokal, M., van Vliet, M., Stuiver, H.J., Wang, M., Bai, Z., Ma, Lin & Kroeze, C. (2019). Multi-scale Modeling of Nutrient Pollution in the Rivers of China. *Environmental Science & Technology*, 53(16) 9614-9625.

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 of 12 August 2013).

Dunca, A. (2018). Water Pollution and Water Quality Assessment of Major Transboundary Rivers from Banat (Romania). *Journal of Chemistry* 2018.

Espejo, L., Krestschner, N., Oyarzun, J., Meza, F., Nunez, J., Maturaha, H., Soto, G., Oyarzo, P., Garrido, M., Suckel, F., Amegaza, J., & Oyarzun, R. (2012). Application of water quality indices and analysis of the surface water quality monitoring network in semi-arid North Central, Chile. *Environmental Monitoring and Assessment* 184(9), 5571-5588.

European Environment Agency (EEA). (2018). European waters: Assessment of status and pressures – a specialized report.

Fritsch, O., Adelle, C., & Benson, D. (2017). The EU Water Initiative at 15: Origins, processes and assessment. *Water International* 42(4), 425-442.

Georgieva, G., Uzunova, E., Hubenova, T., & Uzunov, Y. (2014). Ecological Assessment of the Rivers Luda Yana and Banska Luda Yana as Based on Selected Biological Parameters. *Ecologia Balkanica* 5, 89-94.

Hristova, N. (2012). Hydrology of Bulgaria. Sofia: Tip-topress, pp. 830. (in Bulgarian).
Hutchins, M. (2012). What impact might mitigation of diffuse nitrate pollution have on river water quality in a rural catchment? *Journal of environmental management* 109, 19-26.

Islam, M., Ahmed, M. K., Raknuzzaman, M., Habibullah-Al-Mamun, M., & Masunaga, S. (2015). Metal speciation in sediment and their bioaccumulation in fish species of three urban rivers in Bangladesh. *Archives of environmental contamination and toxicology* 68(1), 92-106.

Jafarabadi, R., Masoodi, A., Sharifi, M., & Riya. (2005). Eutrophication: a comparative study of USA and Canadian Water Quality Index Models. *Water Quality, Exposure and Health*, 3, 203-216.

Khan, F. A. and Ansari, A. A. (2005). Eutrophication: an ecological vision. *The Botanical Review* 71(4), 449–482.

Lee, C.-L., Li, X.D., Zhang, G., Li, J., Ding, A. J., & Wang, T. (2007). Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, South China Evidence of the long-range transport of air contaminants. *Atmospheric Environment*, 41(2), 432-447.

Lumb, A., Sharma, T., Bibeault, Jean-François, & Klawunn, P. (2012). A comparative study of USA and Canadian Water Quality Index Models. *Water Quality, Exposure and Health*, 3, 203-216.

Manoj, K., Padhy, PK., & Chaudhury, S. (2012). Study of heavy metal contamination of the river water through index analysis approach and environmental metrics. *Bulletin of Environment, Pharmacology and Life Sciences* 1(10), 7–15.

Mohan, S.V., Nithila, P., & Reddy, S.J. (1996). Estimation of heavy metals in drinking water and development of Heavy Metal Pollution Index. *Journal of Environmental and Public Health* 31(2), 283–289.

Mohebbi, M.R., Saeedi, R., Montazeri, A.A., Vaghefi, K.A., Labbafi, S., Oktaie, S., & Mohagheghian, A. (2013). Assessment of water quality in groundwater resources of Iran using a modified drinking water quality index (DWQI). *Ecological indicators*, 30, 28-34.

Muscutt, A.D., Harris, G.L., Bailey, S.W., & Davies, D.B. (1993). Buffer zones to improve water quality: a review of their potential use in UK agriculture. *Agriculture, ecosystems & environment*, 45(1-2), 59-77.

Nasrabadi, T., Nabi Bidhendi G. R., Karbassi, A. R., Hoveidi, H., Nasrabadi, I., Pezeshk, H., & Rashidinejad, F. (2009). Influence of Sungun copper mine on groundwater quality, NW Iran, *Environmental Geology*, 58, 693–700.

Novotny, V. (1999). Diffuse pollution from agriculture – A worldwide outlook. *Water science and technology*, 39(3), 1-13.

OECD. 2012. *Water Quality and Agriculture: Meeting the Policy Challenge; OECD Studies on Water; Organisation for Economic Co-Operation and Development*: Paris, France.

Okumah, M., Chapman, P. J., Martin-Ortega, J., & Novo, P. (2019). Mitigating agricultural diffuse pollution: uncovering the evidence base of the “Awareness–Behaviour–Water Quality” pathway *Water* 11(1), 29, doi: 10.3390/w11010029.

Petrovic, M., Ginebreda, A., Acunha, V., Batalla, R.J., Elosegui, A., Guasch, H., de Alda, M.L., Marce, R., Munoz, I., Navarro-Ortega, A., Navarro, E., Vericat, D., Sabater, S., & Barceló, D. (2011). Combined scenarios of chemical and ecological quality under water scarcity in Mediterranean rivers. *TrAC Trends in Analytical Chemistry*, 30(8), 1269-1278.

Prasad, B., & Kumari, S. (2008). Heavy metal pollution index of groundwater of an abandoned open cast mine filled with fly ash: A case study. *Mine water and the Environment*, 27(4), 265-267.

Rabadjiwa D., Tepavitcharova S., Todorov, T., Dassanakis, M., Paraskevopoulou, V., & Petrov, M. (2009). Chemical speciation in mining affected waters: the case study of Asarel-Medet mine, *Environmental Monitoring and Assessment* 159, 353-366.

Ramos Ramos, O.E., Cáceres, L.F., Ormachea Muñoz, M.R., Bhattacharya, P., Quino, I., Quintanilla, J., Sracek, O., Thunvik, R., Bundschuh, J., & García, M.E. (2012). Sources and behavior of arsenic and trace elements in groundwater and surface water in the Poopó Lake Basin, Bolivian Altiplano. *Environmental earth sciences* 66(3), 793-807.

Reza, R., & Singh, G. (2010). Heavy metal contamination and its indexing approach for river water. *International journal of environmental science & technology*, 7(4), 785-792.

Regulation No H-4 of 14 September 2012 for characterization of the surface waters.

Shanbehzadeh, S., Dastjerdi, M.V., & Hassanzadeh, A. K. (2014). Heavy metals in water and sediment: A Case Study of Tembi River. *Journal of environmental and public health*, 1–5.

Sutadian, A.D., Muttil, N., Yilmaz, A., & Perera, B. (2016). Development of river water quality indices – a review. *Environmental monitoring and assessment* 188(1), 58.

Varbanov, M., Gartsayanova, K., & Metodieva, G. (2015). Anthropogenic impact on river water quality in the western part of the Pazardzhik-Plowdiv
field. *Problems of Geography* 3(4), 65–72 (in Bulgarian).

Velcheva, I., Petrova, S., Dabeva, V., & Georgiev, D. (2012). Eco-physiological Study on the Influence of Contaminated Waters from the Topolnitza River Catchment Area on Some Crops. *Ecologia Balkanica* 4(2), 33-41.

Vinodhini, R., & Narayanan, M. (2008). Bioaccumulation of heavy metals in organs of fresh water fish *Cyprinus carpio* (Common carp). *International Journal of Environmental Science & Technology* 5(2), 179-182.