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ASSESSMENT OF THE METAL CONCENTRATION IN YANTRA RIVER WITHIN AN AREA WITH ACTIVE ANTHROPOGENIC INFLUENCE

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Abstract

The anthropogenic pollution of the Yantra River was assessed during six year period (2013–2018) in terms of metals in key sites along the river, pointed near to industrial activities, municipal effluents and pollution from tributaries in the catchment area. The assessment of metal concentrations in the water samples was made in accordance with Directive 2000/60/EC – Water Framework Directive and its equivalent criteria transposed into the Water Law in Bulgaria. The results show that the concentrations of metals, such as Hg and Cd, were above the permissible limits of the Bulgarian surface water standard especially in S1 point (the Yantra River near Debeletz). The application of hierarchical cluster analysis for the interpretation of a large and complex dataset obtained during a monitoring program of surface water in the Yantra River is presented in this study. The hierarchical clustering of data shows a correlation between Fe, Mn, Cr, Mg, Ca, Zn, which proves that the increase of Fe concentration could be mainly related to the increased number of the landfills and the unregulated pollution of the catchment area. The overall quality of the Yantra river water corresponds to the descriptive indicator of 'very good' water despite the numerous populated places and industrial activities on the territory of the Yantra River basin. The obtained results would be useful in an in-depth future assessment of the general condition of the Yantra River system.

Key words: metal ions, pollution, statistical treatment, surface water quality.

Introduction

In the European Union (EU), a number of legislative and policy processes have imposed more integrated way of urban rivers management by linking water quality improvements to ecosystem protection (Directive 2000/60/EC; Gunatilaka et al. 2007; Bird et al. 2010a, 2010b; Poórová and Vranayová 2019). The Water Framework Directive (WFD) requires the achievement of good ecological and chemical status for all European surface waters, including rivers. The river water quality depends on a number of interrelated factors like climate, topography, geology, and hydrology (Khatri and Tyagi 2015). The knowledge and understanding of chemical composition of surface water is very important because the accumulation of toxic elements in higher concentration can modify the activity of halophilic microorganisms (i.e. algae, diatomee, *Artemia* sp., *Halobacterium* sp., etc.), which have a vital role in C, N, P and S circuit elements, in order to maintaining the rivers as healthy ecosystems (Radulescu et al. 2014). Surface water plays a very important role in water supply. Rivers provide water for public use, recreation, irrigation, as well as for hydropower production. Many rivers and streams are significantly polluted due to the industry, agriculture and household activity (Aytas et al. 2009). Since ancient times, populated places and industries have been located along the rivers because they provide easy transport and are a convenient place for waste discharge. The industrial effluents contain a variety of pollutants like CN^-, Zn, Pb, Cu, Cd, and Hg, some of them being above permissible limits and may affect different components of the aquatic ecosystem, such as micro- and macro-organisms, as well as the sediments (Demirak et al. 2006; Bird et al. 2010a, 2010b; Karbassi and Pazoki 2015; Vladkova 2016; Vladkova et al. 2018; Hazrat at al. 2019; Yotova et al. 2019). The metals are toxic and may contain carcinogenic metalloids that cause cancer of the skin, lungs and urinary tracts; cardiovascular disease; neurotoxicity; and diabetes (Järup 2003, Björkman et al. 2007, Choong et al. 2007, WHO 2007, Akpor and Muchie 2010, Acosta et al. 2015). It is known that the metals can occur in aquatic environment in various forms like complex compounds, ions adsorbed on the surface of the suspended solids, and as a free ion – the most toxic to living organisms (Manahan 2000, Uyguner and Bekbolet 2005, Koumanova 2006, Singh et al. 2011, Başyiğit and Tekin-Özan 2013, Todorova et al. 2016, Gyosheva et al. 2017). Several physicochemical factors, such as salinity, pH, conductivity, temperature, dissolved oxygen, redox potential, and ionic strength influence the concentrations of metals in river water and sediments (Huang et al. 2017). Many methods for metal ions determination in water samples have been known in the literature (Sanfilippo et al. 2007), e.g. HPLC, electrochemical, spectrochemical methods, but ICP-OES and ICP-MS are methods, allowing multi-element and highly sensitive analyses.

Pollution of water bodies is directly related to the need for continuous monitoring of water on various indicators. In this regard, the present study aims to present an assess of some metal concentration in a short area from Yantra River, Bulgaria, by (i) statistical treatment of data for water quality in the period 2013–2018; (ii) Own monitoring of the surface river waters by collecting samples from ‘hot-points‘ of River Yantra. The obtained information could be useful for making decisions on appropriate management actions from resource managers.

Study Area

This study has been carried out along the Yantra River (Fig. 1), which is one of the main river bodies in the Danube region of Bulgaria and is a right tributary of the Danube River (Gerassimov and Bojilova 2008; RBMP-DR 2010–2015, 2016–2021). It is 285.5 km long and has a wa-

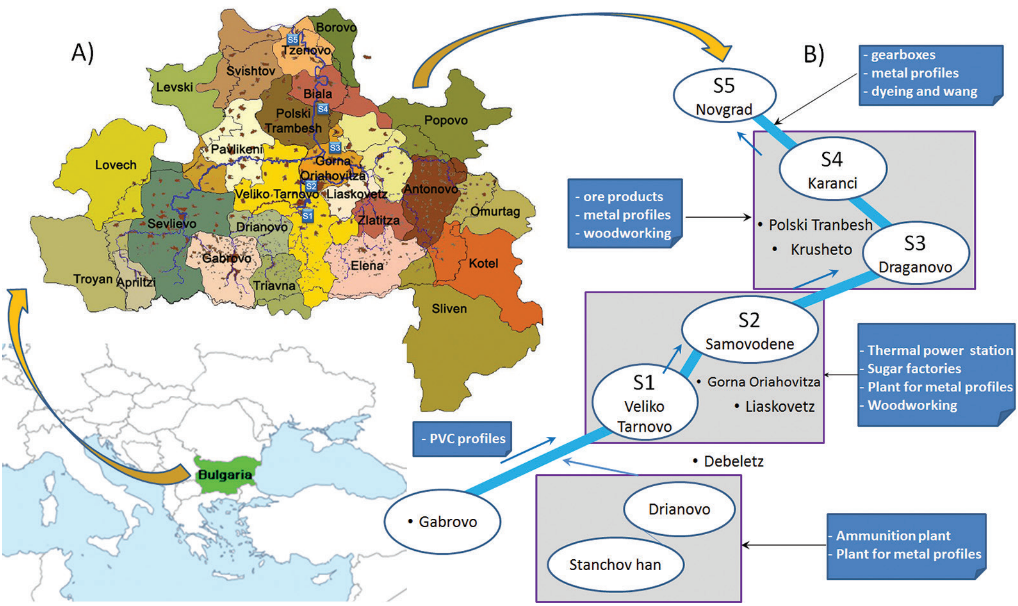

Fig. 1. Study area.

Note: A) The Yantra River basin and the sampling stations; B) Some major pollution zones near the Yantra River Basin.

tershed of 7862 km^2. The river begins from the northern foot of Hadzhi Dimitar peak in Central Stara Planina Mountain, at an altitude of 1340 m and flows into the Danube River near to Svishtov. 783 populated places with approximately 519,000 inhabitants are situated within the Yantra River catchment, representing 6.1 % of the Bulgarian population. Major cities along the river are Gabrovo, Veliko Tarnovo, Gorna Oryahovitsa, Polski Trambesh and Byala. The Yantra River drainage basin is located in one of the economically most important regions of the northern part of Bulgaria. The river water is used for water supply, irrigation and hydropower production. The municipalities are extremely industrialized and negatively influence the ecological state of the environment (Hristov and Ioncheva 2006, Raynova 2015). According to the River Basin Management Plan in the Danube Region (RBMP-DR 2010–2015, 2016–2021), the anthropogenic impact on the Yantra catchment area is complex and it is due to both point and diffuse sources. There are over 100 point sources of water pollution and agriculture is responsible for diffuse pollution. In this way, the contemporary ecological principles of sustainable use of water resources are violated (Namieśnik and Rabajczyk 2010).

Within the Yantra River catchment area the point sources of pollution are different industrial activities like plastic pipes manufacturing, processing of metal surfaces, including galvanizing, wood processing, wastewater treatment plant, thermal power plant, extraction and processing of non-metallic mineral raw materials, industrial laundry and dyeing proposing, which are the main sources of metals in the river basin (RBMP-DR 2010–2015, 2016–2021).

Materials and Methods

Regarding numerous and various anthropogenic activities, this survey takes into consideration the surface water in the Yantra River watershed, considering the spatial and temporal variations in heavy metal content and also evaluated the status of the river water quality with respect to its use for different purposes. The study is based on Ordinance on characterization of surface water (Ordinance No H-4 2012) and Ordinance on environmental quality standards for priority substances and some other pollutant (Ordinance EQSPSSOP 2015).

Sampling and sample locations

In this study, water quality data for certain indicators as metal concentration of Fe, Mn, Mg, Ca, Cd, Hg, As, Cu, Cr, Zn, Pb and Ni, provided by the Executive Environment Agency (ExEA), were used for selected points of the national monitoring network for five year period (2013–2017). On the other hand, during 2018 samples were collected four times per year (once every three months). In order to collect the samples, the basic rules for sampling from water sources were used (DW-GWA 2009). All sampling points selected were situated near suspected sources of industrial, urban or agricultural pollution (Table 1). At least three samples per sampling point were collected. A representative sample (1l plastic bottles, previously washed with HNO_3 solution) from each point was used for analysis. The sampled surface water was put in the acid washed plastic container and acidified with 3 ml nitric acid to avoid unpredictable changes in the water characteristics.

Each of the samples was analyzed for 12 metal ions, such as Fe, Mn, Mg, Ca, Cd, Hg, As, Cu, Cr, Zn, Pb and Ni.

Table 1. The sampling stations of the Yantra River basin.

Sampling station	Location	Water body code	Water catchment area, m^2
S1 (BG1YN00079MS200)	GPS: N 43.06411 E 25.63358 (the Yantra River near to Debeletz)	BG1YN700R1017	330.2
S2 (BG1YN00079MS190)	GPS: N 43.13631 E 25.61356 (the Yantra River near to Samovodene)	BG1YN700R1017	330.2
S3 (BG1YN00059MS130)	GPS: N 43.20484 E 25.74409 (the Yantra River near to Draganovo)	BG1YN307R1127	117.9
S4 (BG1YN00319MS030)	GPS: N 43.38694 E 25.66812 (the Yantra River near to Karanci)	BG1YN130R1029	572.1
S5 (BG1YN00001MS010)	GPS: N 43.61241 E 25.58934 (the Yantra River near to Novgrad)	BG1YN130R1029	572.1

Methods for metals determination

For metal determination, a standard ICP-OES method (Inductively Coupled Plasma Optical Emission Spectroscopy, method: ISO 011885) was used. The main analytic characteristics of the equipment were: Prodigy High Dispersion ICP-OES spectrometer, Teledyne Leeman Labs, USA equipped with a dual view torch, cyclonic spray chamber, and concentric nebulizer with following conditions: coolant gas 18 $L \cdot min^{-1}$, auxiliary gas 0.5 $L \cdot min^{-1}$, nebulizer gas 34 psi, RF power 1.2 kW, pump rate 1.2 $mL \cdot min^{-1}$, sample uptake time 30 s, integration time 40 s. High purity Ar 99.999 % was used to sustain plasma and as a carrier gas (Ilieva et al. 2018, Iacoban et al. 2019). A multi element standard solution ('Ultra scientific', Lot: P00332) was used for calibration (Ilieva et al. 2018). Each solution was scanned at least three times and a mean analytical signal was calculated (Ilieva et al. 2018).

Statistic methods for data analysis

In total, a dataset for water quality of the Yantra River was used for further multivariate analysis. The 56 samples were characterized by 6 variables. Hierarchical cluster analysis was used to reveal similarities between variables and sampling sites. HCA was performed only on the basis of major metal ion concentrations using STATISTICA 8 Software. The Euclidean distance as a similarity measure and Ward's method as a linkage method gave the most efficient results for analysing surface water chemical composition (Retike et al. 2016). Trace elements (here should be listed) were not included in multivariate statistical analysis because complete dataset is required but most of the measurements were made at different times and locations (Surinaidu 2016).

Results and Discussion

The concentrations of analyzed metals in surface water of the Yantra River collected for the period from 2013 to 2018 are presented in Fig. 2. Several so-called 'hot' spots during analyses period were detected. From the results, it has been observed that concentrations of metals such as Fe, As, Mn, Mg, Ca, Cu, Cr and Zn were well below the permissible limits of Bulgarian surface water standard in the last observation period. The mean annual concentrations (mean value from max and min concentration measurement in the each season per year) of Fe, Mn, Mg, Ca, Cd, Hg, As, Cu, Cr, Zn, Pb and Ni are shown on figures 2, 3 and 4 each point of which include total five times sampling for the four seasons of the year (Fig. 2). From the data for the single results by seasons, a tendency increase of the metal concentrations was observed at all points during the summer months.

The values of twelve metals assessed indicated that in sampling station S1, mercury and cadmium detected during 2013–2016 were observed to be higher than the permissible limits for waters with different purpose according to the Bulgarian regulations (Table 2), with mean values of concentrations as follows: 20.10 $\mu g \cdot L^{-1}$, 10.80 $\mu g \cdot L^{-1}$, 15.60 $\mu g \cdot L^{-1}$, 13.00 $\mu g \cdot L^{-1}$ (for Cd) and 71.80 $\mu g \cdot L^{-1}$; 62.70 $\mu g \cdot L^{-1}$; 70.20 $\mu g \cdot L^{-1}$; 67.90 $\mu g \cdot L^{-1}$ (for Hg). In the years of observation (2015–2017), the mercury standards remain relatively high at this sampling point, while those of cadmium are lowered to the required minimum (Fig. 2). A value of cadmium (30.10 $\mu g \cdot L^{-1}$) was

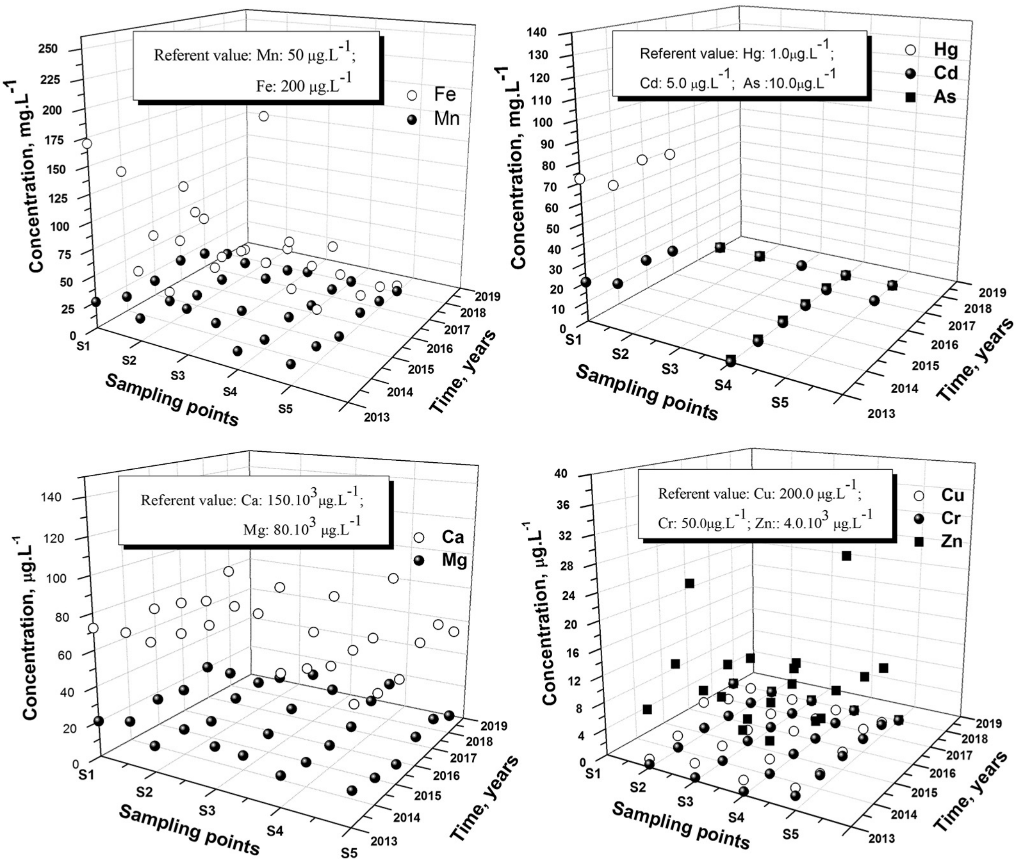

Fig. 2. Distribution of metal content in studied period (2013–2018).

Note: The results are mean value from least three parallel determinations. The referent values according Ordinance No 9 (2001) are given in the boxes of the each graphic plot.

found to be highest during February 2013. The highest concentration (78.80 μg·L^{-1}) that exceeded the maximum permissible concentration of mercury was observed during May 2013. Information on mercury and cadmium content in other samples is scarce. The concentrations of mercury (Hg) and cadmium (Cd) in S1 during almost the whole analysed period are above the permissible limits and this part of the river is determined as the most polluted by heavy toxic metals. Yantra River passes through various urbanized territories, which are local pollutants of the river. One of the major pollutants is the town of Gorna Oryahovitsa, a hot spot of national significance, located between the two main sampling points Draganovo (S3) and Debeletz (S1). The main pollution during this period could be attributed to the existence of factories with poor sewage treatment. The main polluter in this area is the sugar producing plant discharging at the town of Gorna Oryakhovitsa. Basically, water is used as an ingredient, for cleaning and transportation of raw materials, as well as for the cleaning of machines, facilities and work areas. Despite the mentioned

Table 2. The maximum permissible concentration of the investigated metal ions for waters with different purpose according to the Bulgarian regulations.

Bulgarian ordinances	Metal	Ca	Mg	Mn	Fe	Cu	Zn	Pb	Hg	Cd	As	Cr	Ni
		mg·L^{-1}											
No H-4 (2012)		-	-	0.05	0.1	0.001÷ 0.022*	0.008÷ 0.1*	-	-	-	0.025	0.008	-
No 9 (2001)		150	80	0.050	0.200	2.0	4.0	0.010	0.0010	0.005	0.010	0.050	0.02
No 11 (2002)		-	-	-	-	-	-	0.02	0.001	0.005	0.05	0.02	-
No 12 (2002)	Categories A1	-	-	0.05	0.3	0.05	3.0	0.05	0.001	0.005	0.05	0.05	0.02
	Categories A2	-	-	0.1	2.0	0.05	5.0	0.05	0.001	0.005	0.05	0.05	-
	Categories A3	-	-	1.0	1.0	1.0	5	0.05	0.001	0.005	0.1	0.05	-
No 18 (2009)		400	300	0.2	5.0	0.2	2.0	0.05	0.001	0.01	0.1	0.05	0.2
EQSPSSOP (2015)		-	-	-	-	-	-	0.0012	7.10^{-5}	0.0002	-	-	0.0086

Note: * the value depends on the hardness of the water.

above, the analysis of the water samples during 2018 did not show an excess of the permissible limits of the Cd and Hg concentrations.

The concentrations of Mn and Fe were also determinate. Highest mean values of Fe in 2016 and 2017 were observed for S1 (169.50 μg·L^{-1} and 134.70 μg·L^{-1}) (Table 2 and Fig. 2) which are in permissible level of Fe (Table 2). The manganese in the surface water can be found as dissolved Mn^{2+} or as particulate manganese oxides, hyroxides and carbonates. One can see that the total content of manganese in studied water areas is lower than permissible limit. This may be due to the fact that generally, manganese is more prevalent in groundwater than in surface water (Palmucci et al. 2016).

An assessment of the Pb content during the period was also made. Lead is considered to be the most widely used toxic metal due to its widespread use in industry both in the light and heavy industries. A serious increase of the metal norms compared to other sampling points is observed for S5 during 2017 (Fig. 3). However, its content is well below the critical standards for different nature waters (Table 2).

The change in the nickel concentration was also monitored for the period 2013–2018. Nickel was found in some from samples (S4 and S5) (Fig. 4). Despite that the Nickel content is in permission limit it total concentration in all investigated sampling points could be arranged in the following order: S4 (for all period) > S5 (for all period) > S2 (for 2018) > S1 (for 2018) > S3 (for 2018) (Fig. 4). Nickel is biologically important metal

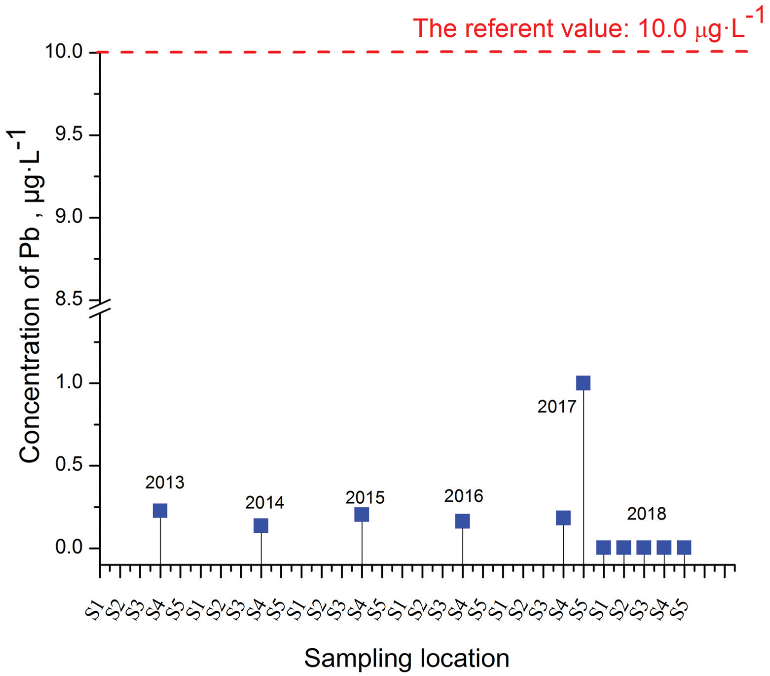

Fig. 3. Concentration of total Pb in studied period.

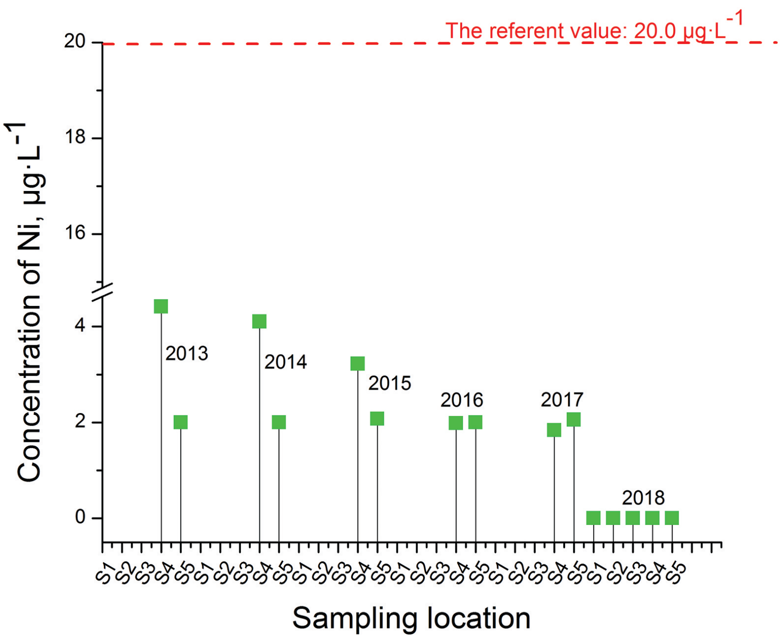

Fig. 4. Concentration of total Ni in studied period.

essential for plants and animals (Poonkothai and Vijayavathi 2012, Zerner 1991). Compared with other transition metals, nickel is a moderately toxic element and its higher concentration can cause a skin disorder known as nickel-eczema (Kristiansen et al. 2000).

In summary, the total content of metals in the samples could be arranged in the following order S1 > S3 > S4 > S2 > S5 (Table 3). The highest portion of metals was observed in S1 showed to be associated with most industrial plants located around the sampling point (Fig. 1).

In order to assess the relationship between individual metals in water, a statistical cluster analysis (CA) was performed using the collected data for six metal ions over the whole study period. A correlation between studied objects and entire data sets was explored using Hierarchical approach, which is the most widely used CA technique (Farmaki et al. 2012). In this study, the cluster analysis was applied for identified Variables' similarities. The dendrogram showed in Figure 5 displaying a significant reduction in dimensionality and complexity of the initial data. Smaller distance between the objects (Euclidean distance) was used because it is preferred for objects similarity interpretation. The data were standardized (mean of 0 and variance of 1) by means of Ward's method, which is the most common way of calculating the distance between two clusters. Thus, one cluster was identified as divided into two subgroups (Fig. 5). The first of them includes Cr, Zn, Mn and

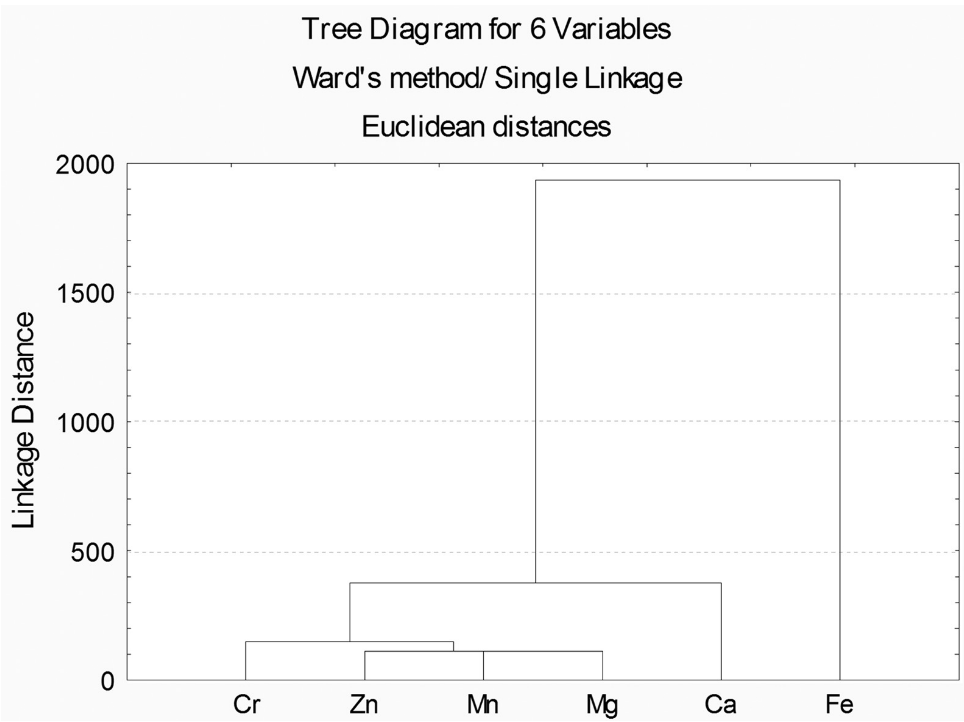

Fig. 5. Dendrograms of the cluster analysis using Ward's method (Euclidean distances) for six variables showing the division of important metals of surface water samples.

Table 3. The mean value for each metal during the period 2013–2018 and total metal content.

Sampling stations / Component, μg·L^{-1}	S1	S2	S3	S4	S5
	***n*/mean ±CI**	***n*/mean ±CI**	***n*/mean ±CI**	***n*/mean ±CI**	***n*/mean ±CI**
Ca, mg·L^{-1}	21/67.12 ±0.03	21/67.29 ±0.01	21/22.60 ±0.02	21/60.345 ±0.002	21/62.6 ±0.1
Mg, mg·L^{-1}	17/15.94 ±0.05	21/14.25 ±0.02	21/17.41 ±0.01	21/15.348 ±0.002	21/15.496 ±0.001
Mn	17/17.72 ±0.08	21/15.675 ±0.007	21/19.97 ±0.03	21/10.354 ±0.003	21/11.678 ±0.003
Fe	17/91.98 ±0.03	21/50.195 ±0.005	21/185.14 ±0.02	21/122.81 ±0.04	21/48.60 ±0.02
Cu	9/0.006 ±0.001	12/2.914 ±0.003	21/2.48 ±0.01	10/2.857 ±0.002	9/2.729 ±0.004
Zn	9/40.01 ±0.01	21/9.13 ±0.02	12/10.13 ±0.02	9/7.24 ±0.07	10/16.41 ±0.04
Pb	5/0.0013 ±0.0002	5/0.003 ±0.001	6/1.20 ±0.02	12/0.182 ±0.002	21/1.00 ±0.001
Hg	17/**68.15 ±0.05**	5/0.07 ±0.02	12/<0.0010	21/0.213 ±0.003	6/0.228 ±0.002
Cd	21/**14.90 ±0.02**	12/0.002 ±0.001	12/0.002 ±0.001	12/0.0224 ±0.0002	12/0.073 ±0.002
As	5/10.0 ±0.2	12/10.1 ±0.6	12/9.62 ±0.04	12/1.016 ±0.001	12/10.40 ±0.08
Cr	10/0.010 ±0.007	21/0.499 ±0.004	21/0.338 ±0.003	21/0.328 ±0.003	17/1.875 ±0.004
Ni	10/4.1 ±0.2	10/4.1 ±0.2	10/3.00 ±0.01	21/3.115 ±0.002	12/2.029 ±0.003
Total heavy metal content, μg·L^{-1}	246.9	92.7	231.88	148.14	95.02

Note: *n* is sampling number; CI is the confidence intervals, calculated by the formula (1); Total heavy metal content is calculated excluding the concentration of calcium and magnesium; the values in bold are above the permissible reference values according the Bulgarian ordinances – No 9 (2001), No 11 (2002), No 12 (2002), No 18 (2009), EQSPSSOP (2015).

$$\Delta\bar{y} = \frac{s \cdot t_{tabl}(P = 95\%; n-1)}{\sqrt{n}}, \tag{1}$$

where: s is standard deviation; $t_{tabl}(P=95\ \%;\ n–1)$ is table value for statistic criteria; n is number of individual results during study period.

Mg, which represent anthropogenic pollutants as discussed above. The second is represented by Ca and Fe. The noted hierarchical cluster analysis of data showed a correlation between some important metal concentrations, which proves that the increase of Fe concentration could be mainly related to the increase of the unregulated industrial pollution in the catchment area.

On the basis of the obtained monitoring data, an ecological and chemical assessment of Yantra River was made (Table 4), (RBMP-DR 2010–2015, 2016–2021; Ordinance No H-4 2012). Despite the variety of the industrial activities along the Yantra river catchment, the river quality is not changed according with previously studied period (1990–2012) (Raynova 2015).

Table. 4. Ecological and chemical assessment of Yantra River.

Water body code	Sampling stations	Ecological	Chemical
BG1YN700R1017	S1 (BG1YN00079MS200) S2 (BG1YN00079MS190)	Moderate	Excellent
BG1YN307R1127	S3 (BG1YN00059MS130)	Excellent	Good
BG1YN130R1029	S4 (BG1YN00319MS030) S5 (BG1YN00001MS010)	Moderate	Excellent

As a whole the river water is assessed as good (Table 4) and may be used for different purposes (Table 2). The set goals for environmental protection of surface water bodies with codes BG1YN700R1017, BG1YN307R1127, and BG1YN130R1029, situated in Danube region, are pollution prevention and keeping good chemical and ecological status.

Conclusions

Heavy metals, even in small doses, possess toxic properties leading to adverse effects on human and ecosystem health. In river water, they are naturally found. The heavy metals are often getting into the environment through dissolution of water-soluble salts, soil erosion, and weathering of rocks but often, their presence in high concentrations is a result of human activities – industrial wastewater discharge and agricultural runoff, as well as illegal landfills. On the basis of this study it could be concluded that the concentrations of heavy metals such as Fe, Mn, Mg, Ca, As, Cu, Cr, Zn, Pb and Ni in the analyzed period are well below the permissible limits of the Bulgarian surface water standard excluding Hg and Cd in some of the sampling points along Yantra river. The data analysis showed that the total metals content was highest in the S1, as the mercury and cadmium content until 2017 were above the permissible limits. It could be associated with the most industrial plants located around the sampling point. In recent years the Bulgarian legislation in the field of environment protection becomes more restrictive, which leads to imposing stricter measures to enterprises, discharging their wastewater into the sewage systems and surface water bodies. This explains the fact that the concentrations of most of the analyzed metals in the waters of the Yantra River over this five-year period are well below the permissible limits, and the concentrations of cadmium and mercury have also decreased over the last two years of the analyzed period. From this point of view, the Yantra River water could be safe for different purposes. The obtained results could be useful for policymakers for water quality management and inclusive monitoring programs should be taken to prevent of further unwanted impact.

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