Assessment of Physical-Chemical Characteristics of Surface Water from Key Sites of the Mesta River: State and Environmental Implications

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Abstract: The anthropogenic source pollution of the Mesta River was assessed during the period 2011 and 2016 in terms of pH, conductivity, chemical oxygen demand (COD), anions and heavy metals in key sites of the Mesta river pointed as: S1 (the Mesta river before the Iztok river); S2 (the Iztok river before the Mesta river); S3 – the river Mesta after the Iztok river; S4 - the river Mesta at Momina Klisura, near Bukovo) and S5 – the river Mesta before the Greece border, after the Matnitsa river. The application of multivariate clustur analysis (CA) for the interpretation of a large and complex data matrix obtained during a monitoring program of surface water in Mesta river is presented in this study. The dataset consists of analytical results from a 6-yrs survey conducted in selected points of the river system. The physical-chemical characterization in the water samples were made in accordance with the Directive 20 00/60/EU–Water Framework Directive (WFD) and its equivalent criteria transposed into the Water Law (WL) in Bulgaria. In water, concentrations (mg L\(^{-1}\)) during 2016 of NO\(_2\)\(^-\) (0.006 to 0.052), NO\(_3\)\(^-\) (0.01 to 1.33) and total contents in µg L\(^{-1}\) of Cu (<0.002), Pb (<0.003), Co(<0.002), Ni(<0.003), S(<0.002) and Zn(<0.02), pH (5.60 to 8.00), and electrical conductivity (0.12 to 48.60 mS.cm\(^{-1}\)) were agreed with environmental standards except cadmium Cd (>0.15 µg L\(^{-1}\)) and PO\(_4\)\(^3\)\(^-\) (0.15 mg L\(^{-1}\)). During analyzed period the cadmium concentration was much higher than recommended limit only. In this sense, it was possible to demonstrate relatively good quality of river water even with numbers of industrial and touristic activities in the analyzed area but also to consider a future concept on cadmium sources and their eliminated.

1. Introduction

Water quality monitoring is a fundamental tool in the management of freshwater resources. Freshwater is very important resource, essential for agriculture, industry and human existence. Without adequate water quality sustainable development will not be possible. Reliable monitoring data and defined the water quality of the river are the indispensable basis for protecting the physic-chemical parameters of the river systems [1].
The main object of this article is the catchment area of river Mesta in southwest part of Bulgaria. The basin of the Mesta river is part of the West Aegean Basin Water Management Area in Bulgaria. It is formed by the merging of the Cherna Mesta and Bella Mesta rivers at an altitude of 941 m. The catchment area in the Bulgarian section of the valley is 2785 km². The Mesta River's basin has the highest average altitude in the country - 1318 m [2]. The river is cross-border and flows into the Aegean Sea on Greek territory Figure 1.

In the Mesta river there are 8 municipalities - Yakoruda, Razlog Bansko, Belitsa, Gotse Delchev, Garmen, Satovcha, Hadjidimovo. The population is the main driving force of economic activities, but at the same time its professional specialization, structure and literacy is closely related to the changes that occur in the environment and in particular with the change of the water quality in the studied region. The largest share in the economy of the surveyed area is the agrarian sector and the services whose activities directly affect the state of the water in terms of their quality characteristics. Once of the main industrial pollutants are the companies that form and distribute in the water bodies or in the urban sewerage networks the substances and the compounds which are from the lists of priority and dangerous substances.

According to the River basin management plan in the West Aegean Region (2010-2015 and 2016-2021) [2] “Magnetic Head Technologies” AD, The Telephone Equipment Factory (ZTA) – Bansko, “Kalida – AD – Gotse Delchev are like that. Other sources of water pollution are identified the factory for low-current relays situated in village of Banya, Razlog, pig farming (in village of Borovo), Gotse Delchev, car-washes and others. In the basin of river Mesta the only one urban wastewater treatment plant (WWTP) is for the town of Razlog (in operation since 2008) and purifies the domestic and industrial waste water of the city. Receiver of purified water is the Iztok River. In the process of designing and building are WWTPs for the towns of Gotse Delchev and Bansko. Towns of Yakoruda, Belitsa, Bansko, Gotse Delchev, Hadzhidimovo, as well as the villages of Dobrinishte, Garmen and Satovcha are larger settlements in the Mesta river basin without built and operating WWTP. These towns and villages have a mixed sewerage system in good condition. Diffused sources of pollution in the catchment area of the analyzed river are: diffuse dirt from settlements without built-in sewer systems or not well-functioning, contaminations from farmland treated with fertilizers and plant protection products, livestock farming and use of organic fertilizer, tailing ponds and the consequences of mining. Another major problem for the Mesta River Basin is the problem of the still widespread practice of dumping solid waste into unregulated landfills, most notably dry gullies, gullies or floodplains of rivers. This practice, prohibited by the law, is the cause of a continuous process of drainage and seepage of contaminated water into the surface water. In fact, there is no information on the number and area of unregulated landfills, as well as the quantity and type of waste. Finally the identification of anthropogenic impacts on the waters of the Mesta River is necessary for the preparation of prevention programs for those river sections that are at risk of contamination.

In connection with the numerous and varied anthropogenic activities in the basin of river Mesta the article aims to identify the changes in water quality in the studied river by chemical analysis of selected physicochemical indicators for the period 2011-2016. As the base information of the study we used the sampling data for over then indicators (as pH, conductivity, chemical oxygen demand (COD), anions (PO₄³⁻, NO₃⁻, NO₂⁻), metals and etc.) reported at the monitoring points of the Mesta river: S1 (the Mesta River before the Iztok river); S2 (the Iztok river before the Mesta River); S3 – the river Mesta after the Iztok river); S4 – the river Mesta at Momina Klisura, near Bukovo) and S5 – the river Mesta before the Greece border, after the Matnitsa River.

The study is based on Directive 2000/60/EU–Water Framework Directive (WFD) [3] Water Law (WL) in Bulgaria [4] and especially on Ordinance N-4/2012 on characterization of surface water (OG. 22 on 03/05/2013) [5] and Ordinance on environmental quality standards for priority substances and some other pollutant (OG. 88 on 09.11.2010) [6]. To achieve the goal of this analysis the following tasks were done:
creating of the database, assessment of the water quality by selected indicators in five sites, identification of the sources of pollution – pointed and diffused.

Figure 1. The Mesta River basin and the analyzed sites.

2. Methods and materials
2.1. Sampling and sample location
The samples were collected from key sites of the Mesta river pointed as follow: S1 (the Mesta River before the Iztok river); S2 (the Iztok river before the Mesta River); S3 – the river Mesta after the Iztok river); S4 – the river Mesta at Momina Klisura, near Bukovo) and S5 – the river Mesta before the Greece border, after the Matnitsa River. Sampling was done in the properly cleaned glass jars, precleaned by washing with non-ionic detergents, rinsed in tap water, in 1:1 hydrochloric acid and finally with deionised water before usage. Immediately after collection, the samples were analyzed for pH, chemical oxygen demand (COD), conductivity, nitrates ($NO_3^-$), nitrites ($NO_2^-$), phosphates ($PO_4^{3-}$), as well metals as Na, K, Ca, Mg, Sr, Ba, Fe, Al, Cr, Co, As, S, U, Mo, Ti, V, Mn, Pb, Cd, Cu, Zn and Ni.

2.2. Methods for determination of metals, pH, conductivity, COD, $NO_3^-$, $NO_2^-$, $PO_4^{3-}$ and $SO_4^{2-}$ in samples
The study is based on the analysis and evaluation of the monitoring data provided by the Executive Environment Agency (ExEA) for the following physicochemical quality parameters: pH, conductivity, nitrates ($NO_3^-$), nitrites ($NO_2^-$), orthophosphates ($PO_4^{3-}$), COD and metals – Cu, Cd, Zn, Pb, Ni, As and Cr.
for period 2011-2015. The data for metal contents as well as pH, conductivity, COD, NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-} and PO\textsubscript{4}\textsuperscript{3-} for 2016 were collected from samples analysis in analytical chemistry laboratory at University of Chemical Technology and Metallurgy using standard methods.

The pH of water was measured with the Janway pH meter immediately after sample collection. pH measurements were carried out with digital pH-meter (Jenway). A CDM92 conductivity meter was used to measure the conductivity values of samples. The concentrations of COD were determinate by permanganate titrimetric method [7]. According to this method the COD determinations (range 0 to 1500 mg L\textsuperscript{-1} COD), 50.0 ml of water sample was added into solution of H\textsubscript{2}SO\textsubscript{4} (15 ml) and 10.00 ml standard solution of KMnO\textsubscript{4}. The solution is boiled for 10 min. Then H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} was added and the solution was titrated with standard solution of KMnO\textsubscript{4}.

Phosphate, nitrate and nitrates were determined using an ion chromatograph (IC-850 Professional model, Metrohm AG, Switzerland) equipped with auto sampler, the samples filtration system with a 0.2 µm membrane, injection valve, high-pressure pump, suppressor module, an eluent degasser and conductivity detector. The separation was performed on Metrosep A Supp 7-250 column (250 x 4 mm, 5 µm particle size), with 3.6 mmol L\textsuperscript{-1} Na\textsubscript{2}CO\textsubscript{3} as eluent in isocratic mode at flow rate of 0.7 ml min\textsuperscript{-1}, temperature 45 °C and injected volume of 20 µl. For adjust the baseline under 0.99 µS cm\textsuperscript{-1} was used 0.1 M sulfuric acid solution and ultrapure water (Milli-Q) were used for automatic chemical suppression. Under the working conditions all anions were separated completely and total analysis time was 33 min. Deionized water from Millipore Milli-Q (18.2MΩcm, equipped with a Millipack 0.22µm filter) was used for the preparation of solutions. Eluent solution was prepared by sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}, Merck) in Milli-Q water. Standard solutions of nitrite, nitrate and phosphate were prepared by appropriate dilution of their anion standard stock solution from Fluka (1000 mg L\textsuperscript{-1}, TraceCERT, Sigma–Aldrich, Buchs, Switzerland) for IC. All solutions were prepared by gravimetrically method on the balance. The preparation of samples are used MF-Millipore membrane filter with pore size 0.45 µm.

Standard ISP-OES method (Inductively Coupled Plasma Optical Emission Spectroscopy) by properly calibrating the equipment with standards for précised results was used for metal determination.

2.3. Statistic methods for data analysis
In total, a dataset for water quality of Mesta river was used for further multivariate analysis. The 98 samples were characterized by 13 variables. Cluster analysis was used in this work for revealing similarities between variables and sampling sites. Surface water hydrochemical groups were defined using hierarchy cluster analysis (HCA). HCA was performed only on the basis of major ion concentrations, pH, conductivity and COD using STATISTICA 8 software. The Euclidean distance as a similarity measure and Ward’s method as a linkage method give the most efficient results for analysis of the surface water chemical composition [8] were used. Trace elements were not included in multivariate statistical analysis because complete data matrix is required but most of the measurements were made at different times and locations [9].

3. Results and discussion
The surface water quality of five sites of the Mesta River is discussed. The results from different physicochemical measurements are shown in Tables 1 and 2. The pH and chemical oxygen demand (COD) data of the executive agencies for the survey period are scarce (Figure 2 and Figure 3). The pH values taken in period 2015-2016 varied between 7.3 and 8.5 (S1, S3, S4 and S5) which is good accordance with Bulgarian target water quality range for pH in surface water [5]. In 2015 a slight increasing of pH at all sites is observed which is even a little over the reference value for S2. (Figure 2). One can see that a significant increase of organic pollution in 2015 is also observed, especially in sites S1, S2, S3 and S4 (Figure 3). The Bulgarian acceptable limit for COD in river waters 6.0 mg L\textsuperscript{-1} [5]. This
limit was not exceeded in the river water samples of all sites and the parameter does not give cause for concern. Influenced concentrations of COD in this period varied between 10.0 mg L\(^{-1}\) and 12 mg L\(^{-1}\) at point S1, 3.7 mg L\(^{-1}\) and 11 mg L\(^{-1}\) for S2, 4.3 mg L\(^{-1}\) to 11.5 for S3, 4.3 mg L\(^{-1}\) to 12 mg L\(^{-1}\) for S4 and it ranged from 4.1 mg L\(^{-1}\) to 8.5 mg L\(^{-1}\) for S5 (Figure 3). During 2016 analysis of the chemical oxygen demand in our laboratory showed much lower concentrations (4.56 mg L\(^{-1}\) for S1; 3.45 for S2, 4.03 for S3, 3.23 for S4 and 4.42 mg L\(^{-1}\) for S5) than required (6.0 mg L\(^{-1}\)). The slight increase in the pH of the water and over the reference rang values of COD could be due to contamination with fecal waste water from the domestic and livestock sectors which is abolished in 2016. Cluster analysis of data (Figure 6) also showed a relationship between pH and COD, which proves that the increase of pH is mainly related to the increase in organic pollution of the river.

The electrical conductivity of water estimates the total amount of solids dissolved in water and is a useful and easy indicator of its salinity or total salt content. The main sources of salts are domestic sewage, municipal storm water drainage and industrial effluent discharges. A very high salt concentration (>1000 mg L\(^{-1}\)) imparts a brackish, salty taste to water and is discouraged because of the potential health hazard. For this reason electrical conductivity can serve as a useful salinity indicator when considered with other factors and when a natural geological origin does not apply in terms of the source of dissolved salts. Electrical conductivity data were evaluated in period 2015-2016 for sites S1, S2, S3, S4 and S5 of Mesta river and the results are presented on Figure 4. The guideline for conductivity according Bulgarian acceptable limit is 750 µS cm\(^{-1}\) [5]. The water conductivity values are within this acceptable limit. Electrical conductivity values for 2016 varied between 125 µS cm\(^{-1}\) at S1 and 270 µS cm\(^{-1}\) at S2 and are within acceptable limit as well.

![Figure 2. Results for pH measurement in all sites (S1, S2, S3, S4, S5) in the period 2011-2016.](image)

The data for nitrates and nitrites are in concentration lower than acceptable limit [5] (Table 1; Figure 5). The analysis of the components shows a light increased nitrite quantities for the samples of S2 (Table 2), which could be attributed to an increased fertilization process of the agricultural areas in the region. Nitrate values were low for both in S1 and in S2 (Table 1, 2). The low values of nitrate in the influent might possibly be due to loss of NO₃\(^{-}\) via denitrification. Thus, nitrate concentration is not considered to pose a problem for the river water. The Bulgarian guideline for phosphate in surface water of rivers is <0.020 mg L\(^{-1}\) PO₄\(^{3-}\) [4]. The levels of phosphate in the river water ranged from 0.007 to 0.12 mg L\(^{-1}\),
PO₄³⁻ as the means value of all sites is around 0.078 (Table 1) which is four times under the norm [4] and could be attended to fecal water pollution and fertilization. Cluster analysis of data (Figure 6) also showed a relationship between anion content, which shows that the increase of NO₂⁻ could be mainly related to the increase NO₃⁻ content and the all increasing of the anion concentration could be attributed to increasing the fertilization process of the agricultural areas in the region. According the data (for S2, S4, S5), the values (the average annual value) [5] for the element Cadmium (Cd) are above the acceptable limits (0.15 µg L⁻¹) [6] for the whole period of time (2011-2016). The maximum values are identified in the years 2011(0.40 µg L⁻¹) and 2012 (0.33 µg L⁻¹). In 2016 analysis shows that the values are over the standard more than 10 times in analyzed sites (Table 2). Cadmium is in the list of priority substances in the field of water policy according the ordinance on environmental quality standards for priority substances and certain other pollutants [6]. The higher concentration of cadmium in drinking water may cause kidney damage [10, 11]. In this sense preventing the reduction of cadmium levels is therefore essential especially if water would be used for drinking and irrigation. The concentrations of metals such as As, Pb, Cu are in the norm for the analyzed period (2011-2016), exception is registered for the components Zn (2011, 2012 - 100 µg L⁻¹) and Ni (2011 – 28 µg L⁻¹ 0,028 mg L⁻¹, 2012 - 5 µg L⁻¹ 0,005 mg L⁻¹) for S2 and S4. For S5 the values of Zn (2011, 2012) are not in the permissible limits. Analysis 2016 for heavy metals shows that for the more of the analyzed elements values are lower than limit of detection of the applied method (Table 2) and are in the standards except Cd and Pb. The higher concentration of cadmium and lead can be due to the potential tailing ponds and the consequences of mining and unregulated landfills in the catchment area (Table 2). Cluster analysis of data (Figure 6) also showed a relationship between cadmium content and anion and some metal (Pb, Ni, As) concentrations, which proves that the increase of Cd could be mainly related to the increase landfills in the unregulated catchment area pollution.

![Figure 3](image-url)  
**Figure 3.** Data for chemical oxygen demand (COD) in all analyzed sites in period 2011-2016.
Figure 4. Data for water conductivity in all analyzed sites in period 2011-2016.

Figure 5. Data for nitrates, nitrites and phosphates in all analyzed sites in period 2011-2016.
Table 1. Nutrients levels in surface water of Mesta River for samples taken in period 2011-2016.

| Sampling sites | Months/Year | Physical-chemical parameters |
|----------------|-------------|-----------------------------|
|                |             | NO₃, mg L⁻¹ | NO₂, mg L⁻¹ | PO₄³⁻, mg L⁻¹ |
| S1             |             |              |              |                |
| 01; 04; 07; 10/2011 | 0.016; 0.007; 0.049; | 0.76; 0.31; 0.70; 0.57; | 0.10; 0.027; 0.094; |
| 01; 04; 07; 10/2012 | 0.053 | 0.90; 0.38; 1.3; 0.37; | 0.15 |
| 01; 04; 07; 10/2013 | 0.017; 0.014; 0.0112 | 0.9; 0.53; 0.18; 0.71; | 0.086; 0.15; 0.043; - |
| 01; 04; 07; 10/2014 | 0.016; 0.015; 0.042; | 0.79; 0.48; 0.72; 0.32; | 0.067; 0.026; 0.057; |
| 01; 04; 07; 10/2015 | 0.022 | 0.72; 0.38; 0.42; 0.33; | 0.046 |
| 07/2016 | 0.010; 0.01; 0.016; 0.006 | 0.31 | 0.05; 0.007; 0.047; |
| Average ± S.D. |             | 0.52 ± 0.19 | 0.57 ± 0.24 | 0.078 ± 0.053 |
| S2             |             |              |              |                |
| 01; 04; 07; 10/2011 | 0.019; 0.016; 0.043; | 0.64; 0.37; 0.56; 0.57; | 0.14; 0.053; 0.12; |
| 01; 04; 07; 10/2012 | 0.022 | 0.82; 0.27; 1.0; 0.52; | 0.033 |
| 01; 04; 07; 10/2013 | 0.020; 0.014; 0.012; | 0.72; 0.47; 0.28; 0.48; | 0.14; 0.032; 0.062; |
| 01; 04; 07; 10/2014 | 0.055 | 0.83; 0.49; 0.47; 0.39; | 0.12 |
| 01; 04; 07; 10/2015 | 0.021; 0.0091; 0.022; | 0.43; 0.35; 0.28; 0.41; | 0.11; 0.22; 0.069; |
| 01; 04; 07; 10/2016 | 0.026 | 0.62 | 0.074 |
| Average ± S.D. |             | 0.52 ± 0.051 | 0.52 ± 0.19 | 0.079 ± 0.053 |
| S3             |             |              |              |                |
| 01; 04; 07; 10/2011 | 0.0085 | 0.88 | 0.018 |
| 01; 04; 07; 10/2012 | 0.026 | 0.85 | 0.092 |
| 01; 04; 07; 10/2013 | 0.0067 | 0.67 | 0.028 |
| 01; 04; 07; 10/2014 | 0.0032 | 0.60 | 0.021 |
| 01; 04; 07; 10/2015 | - | - | - |
| 01; 04; 07; 10/2016 | 0.0029 | 0.65 | 0.036 |
| Average ± S.D. |             | 0.011 ± 0.010 | 0.76 ± 0.12 | 0.044 ± 0.033 |
| S4             |             |              |              |                |
| 01; 04; 07; 10/2011 | 0.011; 0.013; 0.028; | 0.38; 0.32; 0.47; 0.25; | 0.048; 0.021; 0.33; |
| 01; 04; 07; 10/2012 | 0.008 | 0.73; 0.18; 0.44; 0.17; | 0.049; 0.12; 0.034; |
| 01; 04; 07; 10/2013 | 0.012; 0.010; 0.029; | 0.71; 0.35; 0.23; 0.09; | 0.092; 0.046 |
| 01; 04; 07; 10/2014 | 0.012 | 0.70; 0.44; 0.28; 0.47; | 0.061; 0.059; 0.018; |
| 01; 04; 07; 10/2015 | 0.006; 0.0091; 0.014; | 0.6; 0.038; 0.30; 0.26; | 0.051 |
| 01; 04; 07; 10/2016 | 0.022 | 0.30 | 0.070; 0.076; 0.060; |
| 01; 04; 07; 10/2017 | 0.015; 0.017; 0.022; | 0.017 |
| 01; 04; 07; 10/2018 | 0.013 | 0.060; 0.035; 0.021; |
| 01; 04; 07; 10/2019 | 0.011; 0.0082; 0.018; | 0.10; 0.15 |
| Average ± S.D. |             | 0.019 | 0.39 ± 0.20 | 0.072 ± 0.067 |
| S5             |             |              |              |                |
| 01; 04; 07; 10/2011 | 0.010; 0.014; 0.017; | 0.48; 0.35; 0.30; 0.18; | 1.48 |
| 01; 04; 07; 10/2012 | 0.014 | 0.57; 0.16; 0.24; 0.20; | - |
| 01; 04; 07; 10/2013 | 0.018; 0.013; 0.051; | 0.67; 0.33; 0.25; 0.011 | 0.56 |
| 01; 04; 07; 10/2014 | 0.021 | 0.25; 0.56; 0.20; 0.33; | - |
| 01; 04; 07; 10/2016 | 0.018; 0.011; 0.020; | 0.30 | 0.32 |
| 01; 04; 07; 10/2017 | 0.024 | 0.006; 0.011; 0.018; | 0.0098 |
| 01; 04; 07; 10/2018 | 0.10 |
| Average ± S.D. |             | 0.022 ± 0.022 | 0.32 ± 0.17 | 0.79 ± 0.61 |
### Table 2. Metal concentrations of key sites of surface water of the Mesta River determined by ISP-OES method for samples taken in 2016.

| Metal conc. mg L⁻¹ | Sites       | S1     | S2     | S3     | S4     | S5     |
|-------------------|-------------|--------|--------|--------|--------|--------|
| Na                | 6.299±0.017 | 2.955±0.016 | 2.075±0.016 | 2.240±0.015 | 2.191±0.015 |
| K                 | 1.319±0.006 | 0.603±0.004 | 0.663±0.006 | 0.619±0.006 | 0.588±0.006 |
| Ca                | 17.09±0.06  | 16.89±0.07  | 12.28±0.05  | 13.13±0.05  | 14.08±0.05  |
| Mg                | 2.678±0.009 | 4.406±0.028 | 2.632±0.009 | 2.589±0.009 | 3.188±0.009 |
| Sr                | <0.001      | <0.001     | <0.001    | <0.001     | <0.001     |
| Ba                | 0.009±0.000 | 0.003±0.0001 | 0.003±0.0000 | 0.004±0.0000 | 0.003±0.0000 |
| Cu                | <0.002      | <0.002     | <0.002   | <0.002   | <0.002   |
| Fe                | 0.173±0.0007 | 0.069±0.001 | 0.264±0.002 | 0.360±0.001 | 0.227±0.002 |
| Al                | <0.004      | <0.004     | <0.004 | <0.004 | <0.004 |<0.004 |
| Zn                | <0.002      | <0.002     | <0.002 | <0.002 | <0.002 |
| Pb                | <0.003      | <0.003     | <0.003 | <0.003 | <0.003 |
| Cr                | <0.002      | 0.0019±0.0001 | <0.002 | 0.0018±0.0002 | <0.002 |
| Mn                | 0.033±0.000 | 0.012±0.0003 | 0.026±0.0003 | 0.0409±0.0001 | 0.026±0.0002 |
| Ni                | <0.003      | <0.003     | <0.003 | <0.003 | <0.003 |
| Co                | <0.002      | <0.002     | <0.002 | <0.002 | <0.002 |
| Cd                | <0.002      | <0.002     | <0.002 | <0.002 | <0.002 |
| As                | <0.010      | <0.010     | <0.010 | <0.010 | <0.010 |
| S                 | <0.050      | <0.050     | <0.050 | <0.050 | <0.050 |
| U                 | <0.003      | <0.003     | <0.003 | <0.003 | <0.003 |
| Mo                | <0.004      | <0.004     | <0.004 | <0.004 | <0.004 |
| Tl                | <0.010      | <0.010     | <0.010 | <0.010 | <0.010 |
| V                 | <0.003      | <0.003     | <0.003 | <0.003 | <0.003 |

*<value

**Figure 6.** Dendrogram from HCA showing division of important physicochemical parameters of surface water samples.
4. Conclusions
On the basis of this study and the results obtained we can conclude that in the analyzed period the surface waters of the river Mesta are in a good physical-chemical status by the analyzed parameters even with the numerous of anthropogenic activities in the evaluated area. The main contaminants of surface water in the basin of the Mesta River are industrial companies, agricultural farms and settlements - towns and villages with built sewage systems but without built-up sewage treatment plants, solid waste as well. Although the water of the river Mesta is relatively in a good quality the prevention should includes: construction of WWTP and improvement of the sewerage network, construction of sewerage systems in small settlements, where none exist, enhanced control over enterprises – pollutants, removal of unregulated landfills, control over the use of fertilizers and consideration of a future concept on cadmium sources and their eliminated.

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