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Distribution of Heavy Metals (Cr, Cu, Ni, Pb and Zn) in the Sediment of Some Tributaries and the Part of the River Spreča Flow Presented by the Kriging Geostatistical Method

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Almir Šestan[*,1], Edin Hadžimustafić[2], Indira Šestan[3], Aldina Kesić[1], Nadira Ibrišimović Mehmedinović[1], Benjamin Ćatović[1]

[1] - *Department of Chemistry, Faculty of Natural Sciences and Mathematics, University of Tuzla, Bosnia and Herzegovina*

[2] - *Department of geography, Faculty of Natural Sciences and Mathematics, University of Tuzla, Bosnia and Herzegovina*

[3] - *Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, Bosnia and Herzegovina*

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ABSTRACT

Sediment is a solid phase of the water system, consisting of biological, biochemical and chemical deposits, and which by physical and chemical processes binds contaminants present in aquatic systems. Heavy metals are one of the priority toxic pollutants that limit the use of water in households and for industrial needs. In this paper, the analysis of heavy metals concentrations in the river sediment of the examined area was carried out. The analysis of heavy metals (Cr, Cu, Ni, Pb and Zn) in river sediment was carried out on the optical emission spectrophotometer, which operates on the principle of induction coupled plasma - type ICP - OES OPTIMA 2100 DV, manufactured by Perkin - Elmer USA, using standard solutions for examined elements of the same manufacturer. The results for the metal content are calculated on the dry mass of the sediment. In this way, the calculated results are processed by a geostatistical method and presented in the form of geochemical maps. The SURFER 11 software was used to plot a three-dimensional distribution of heavy metals concentration in the sediment (geochemical maps). The values of heavy metals concentrations were compared with the Dutch recommendations and Canadian guidelines for the quality of freshwater sediments, which found that most of the values of heavy metals concentrations are above the "target values" or "theoretical value of possible impact". This approach of analysis and presentation of results would certainly contribute to easier monitoring and better understanding of changes in metal concentrations over time in sediment.

INTRODUCTION

Heavy metals appear as natural constituents of the environment and vary in terms of concentrations across geographical areas. They are one of the most important toxic pollutants that limits the use of water in households and industrial needs.[1] At higher concentrations, they manifest toxic effects and if they engage in a food chain they present a major risk to the health of animals and humans.[2] Rapid technological and industrial development, as well as a low level of environmental protection, have led to more intensive contamination and higher input of heavy metals into the ecosystem as a whole. Conditionally speaking, the soil can be defined as the main reservoir of metals originating from both natural and anthropogenic sources, and aquatic systems are the most important intermediaries in their transport and dispersion. Water is the most widespread substance in nature and is the basic condition for the survival of all living beings on the planet. As the most valuable natural raw material, it is necessary for the survival of all living organisms, but also for the industrial and technological progress of mankind. Water is part of our everyday life and it knows no boundaries. Sediment is an essential, dynamic component of all aquatic systems. Due to the strongly expressed tendency of binding, it represents a reservoir of accumulated, toxic and persistent compounds formed by anthropogenic action. Sediment is a solid phase of the aquatic system, which consists of biological, biochemical and chemical deposits, and which by physical and chemical processes binds contaminants present in aquatic systems. In accordance with the above facts, which are more or less known, and supporting the emphasis on the importance of the sediment as the essential components of the aquatic system, the results obtained have been processed by a geostatistical method and presented in the form of geochemical maps. The Geographic Information System (GIS) of the software (SURFER 11) was used to plot a three-dimensional distribution of heavy metals concentrations in sediment samples taken from the examined area. The Kriging geostatistical method has been applied to the interpolation of data in this paper. The obtained variograms were used for the mathematical expression of variances of observed changes in surface area, based on the distance and direction of separation of two sites. Geochemical maps obtained by previous interpolation are overlapped in the GIS with other geographical characteristics (roads, landscapes, rivers, etc.). These spatial plans reveal the trend of heavy metals distribution in river water and sediment as concentrations in milligrams per liter, and their variation in different locations. The method of presenting the contamination state of sediment as deposits with geochemical methods is considered appropriate.[3] It is important to note that the performed interpolations, regardless of the fact that the map covers the whole research area, are valid only along the stream of rivers in which samples are taken. In this way it would be possible to present the monitoring results of all pollutants, not only heavy metals. The area covered by the research is particularly interesting because it is located after the brown coal mine and before the formation of the Modrac Lake, from which water is used for processing and drinking.

MATERIALS AND METHODS

Watercourses in Tuzla Canton area belong to the catchments of Spreča, Bosna and Tinja, where the Spreča catchment is the most extensive. The hydrographic system of Sprečais located within the Spreča basin of the Dinarides direction of orientation with the main direction southeast-northwest. The river Spreča is one of the longest rivers in our country. It springs below Vela Glava (619 m above sea level) near Zvornik and has a flow length of 115.7 km and the catchment area of 1945 km^2.[4,5] The average flow rate of Modrac is 15 -20 m^3/sec. The highest average monthly water level in February is 160 cm, and the lowest in August is 89 cm, and as such can be classified as a variant of the watercourses of the pluvial regime.[6]In the area covered by the survey, 11 sites were selected for *in situ* measurements, followed by sampling of water and sediment for laboratory analysis. For each of the listed locations, the accurate position and altitude (Table 1) were recorded with the Garmin GPS device (MAGELLAN EXPLORIST 210).

Table 1. ***Recorded positions of locations with the altitudes***

Location	Latitude	Longitude	Altitude
1	44°22'49.86"	18°40'06.34"	309.40 m
2	44°24'59.64"	18°39'46.37"	268.60 m
3	44°27'09.07"	18°38'28.79"	241.90 m
4	44°27'49.63"	18°37'10.79"	253.40 m
5	44°28'09.90"	18°37'53.90"	207.26 m
6	44°24'11.48"	18°33'45.16"	360.70 m
7	44°24'31.87"	18°31'49.50"	352.50 m
8	44°24'44.92"	18°32'26.26"	369.10 m
9	44°25'01.81"	18°33'36.36"	331.60 m
10	44°28'46.19"	18°32'51.99"	193.24 m
11	44°27'58.46"	18°35'32.24"	199.34 m

Sampling from sedimentary deposits (bottom) of rivers and lakes was carried out using a semi-automatic soil sampling tool according to the standard - BAS ISO 10 381-3: 2003.[7] The mass of the testing sample ranged around 500g sample. Sediment samples from the sites were collected in plastic containers and delivered to the laboratory where samples were prepared and analyzed. Determination of the concentration of Cr, Cu, Ni, Pb and Zn in the sediment was carried out on the optical emission spectrophotometer, which operates on the principle of induction coupled plasma - type ICP - OES OPTIMA 2100 DV, manufactured by Perkin - Elmer USA using standard solutions for tested elements of the same manufacturer. The results for the metal content are calculated on the dry mass of the sediment. In this way, the calculated results are processed by a geostatistical method and presented in the form of geochemical maps. SURFER 11 software was used for plotting the three-dimensional distribution of heavy metals concentration in sediment (geochemical maps). Analyzes were carried out continuously for all four seasons, and the results of analyzes for the autumn are in this paper.

RESULTS AND DISCUSSION

Table 2 presents the values of total concentrations of analyzed heavy metals in sediment samples from selected sites calculated on the dry mass of sediment. In this way, the results obtained were used to plot a three-dimensional distribution of heavy metal concentrations in the rivers sediment covered by the research. The Kriging geostatistical method has been applied to the data interpolation in this paper. The obtained variograms are used for mathematical expression of variances of observed changes on the surface, based on the distance and direction of separation of two sites. Geostationary method within the software SURFER 11 was used to plot geochemical maps. The Kriging geostatistical method has been applied to the interpolation of data in this paper. The obtained variograms are used for mathematical expression of variances of observed changes on the surface, based on the distance and direction of separation of two sites. The geochemical maps obtained by the previous interpolation are overlapped in the GIS with other geographical characteristics (roads, landscapes, rivers, etc.).

Table 2. ***Analysis results of total concentration of heavy metals in the sediment for the examined locations***

	Cu	Zn	Cr	Ni	Pb
	[mg/kg]				
1	37.97	234.70	24.93	49.73	27.07
2	40.77	293.40	30.50	116.13	25.87
3	44.67	155.80	36.17	123.63	14.70
4	55.43	209.10	39.20	143.87	16.43
5	12.27	108.90	28.63	77.67	13.13
6	39.33	200.30	74.57	212.60	25.03
7	82.50	463.10	53.63	171.20	71.83
8	47.70	325.50	131.07	290.77	39.30
9	83.77	327.10	35.07	206.73	28.03
10	45.70	187.70	37.73	129.87	16.17
11	31.60	191.00	71.47	217.67	18.90

These spatial plans reveal the trend of heavy metals distribution in river water and sediment as concentrations in milligrams per liter, and their variation in different locations. It is important to note that the performed interpolations, regardless of the fact that the map covers the whole area of research, are valid only along the flows of the rivers in which samples were taken. Figure 1 presents the geochemical map of the spatial distribution of copper in the examined sediment. According to the form of interpolation curves, it is to be found that the highest concentration of copper in the area immediately after the brown coal mine wastewater (83.77mg/kg) and the surface sediment of the river Litva (82.50mg/kg) sediment, all in the autumn period. These values are twice as high as the target value (36mg/kg) according to the Dutch recommendations[8] and above the values recommended for freshwater sediment (35.7mg/kg) according to the Canadian guidelines for sediment quality.[9]

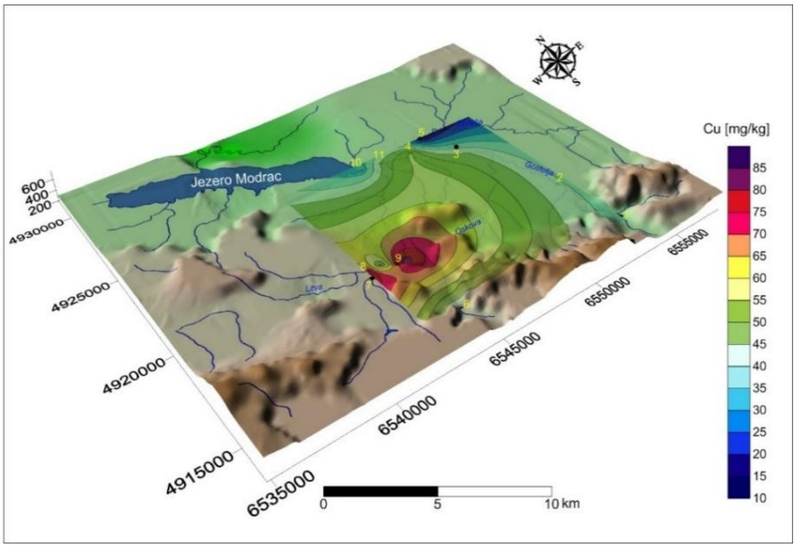

Figure 1. ***Spatial distribution of Cu in the sediment of the examined area***

By plotting the geochemical maps for spatial distribution of zinc (Figure 2), in the area covered by the research, it can be concluded that the highest concentration of zinc is in the sediment of the river Litva at the exit from Banovići (463.10mg/kg).

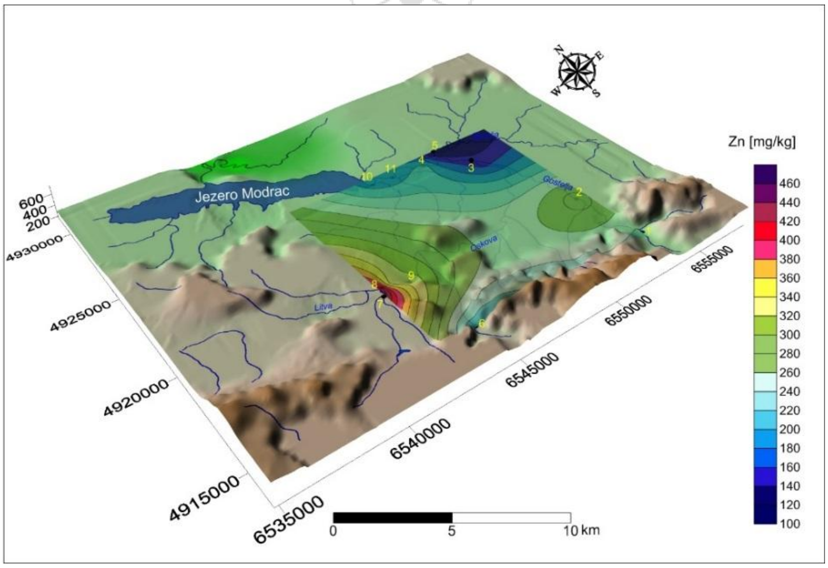

Figure 2. ***Spatial distribution of Znin the sediment of the examined area***

The impact of wastewater from both brown coal mines (greenisolines) on the increase in zinc concentrations in the sediment of the explored watercourses (sites 8 and 9) should certainly not be ignored. These values are higher than the target value (140mg/kg) according to the Dutch rules[8] and above the values recommended for freshwater sediment (315mg/kg) according to the Canadian guidelines for sediment quality.[9] Figure 3 presents the geochemical map of the spatial distribution of chromium in the examined sediment.

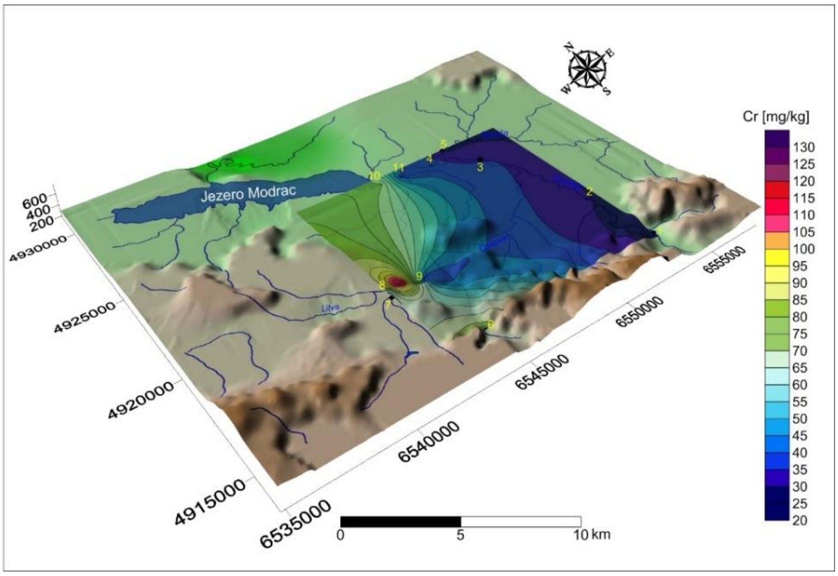

Figure 3. ***Spatial distribution of Crin the sediment of the examined area***

It is clear in the Figure 3 that there is a higher concentration of chromium in the sediment of the river Oskova after the Litva flows into (131.07mg/kg), which is above the value of the possible impact (90.0mg/kg) according to the Canadian guidelines for sediment quality[9] and above the target value (100mg/kg) according to the Dutch rules,[8] all after the wastewater flows into from the brown coal mine.Figure 4 shows the geochemical maps of the spatial distribution of nickel in the examined area. It is clear that the highest concentration of nickel is at the site 8 (290.77mg/kg), which is characteristic due to the proximity of mines and other anthropogenic impacts. The concentration of nickel at this site is above the target value (35mg/kg) and the intervention value (210mg/kg) according to the Dutch recommendations.[8] For nickel, it can be seen that the influence of sewage wastewater (the river Litva at the exit from Banovići-site 8) is significant as well as the impact of wastewater from the mine-site 9 (206.73mg/kg), regardless of the fact that the presence of nickel is characteristic for wastewaters from the mine.

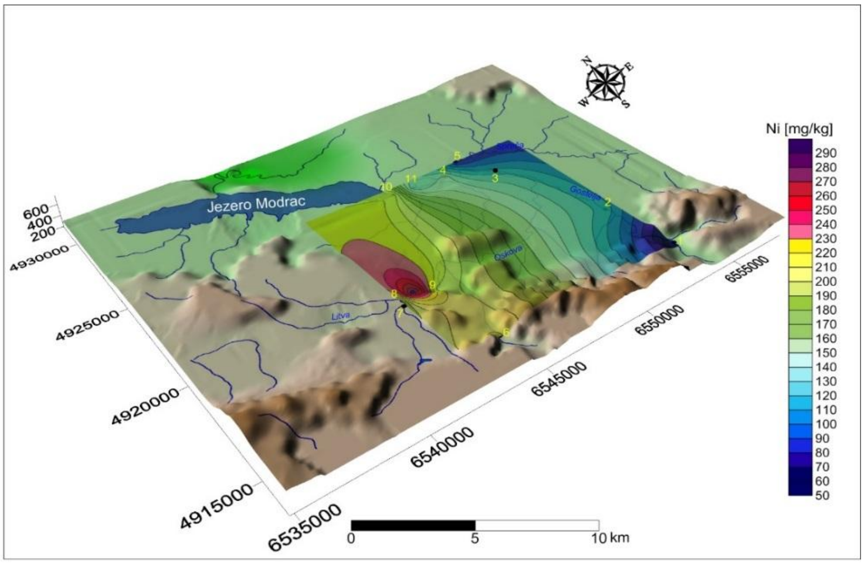

Figure 4 ***Spatial distribution of Niin the sediment of the examined area***

On the geochemical map of spatial distribution of lead for the examined (Figure 5), it can be seen that the highest concentration of lead is in the sediment of the river Litva-site 7 (71.83mg/kg) with the associated wastewaters. It should be noted that the selected sites are located along the motorway where the influence of petrol combustion of gasoline, tire and road wear and their rinsing by precipitation is present, which significantly contributes to the increase in lead concentration. Nevertheless, the lead concentration values are below the target value (85mg/kg) according to the Dutch recommendations[8] and below the value of possible impacts for freshwater sediment (112mg/kg) according to the Canadian guidelines for sediment quality.[9]

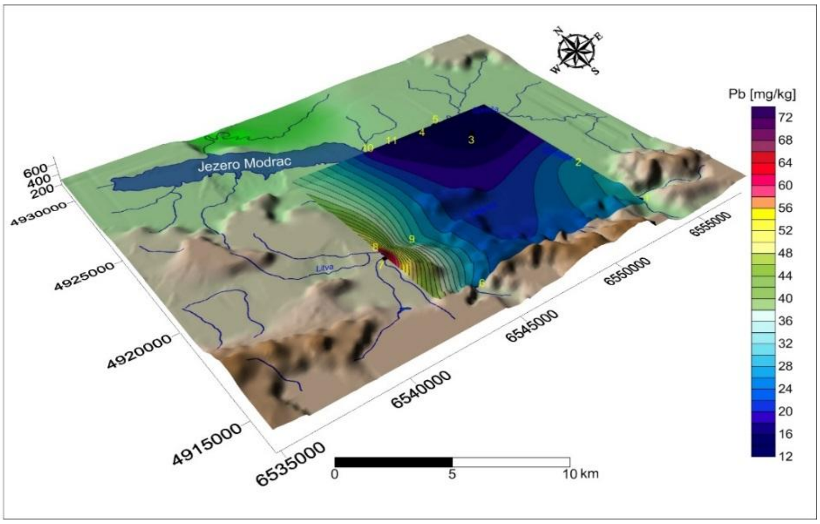

Figure 5. ***Spatial distribution of Pbin the sediment of the examined area***

CONCLUSION

River sediments are examined in many countries for decades through routine monitoring or within specific programs. Rivers have different natural composition of sediment, and therefore there is a tendency for each river catchment to define the natural composition of the sediment from a period in which there was no anthropogenic impact. In this respect, metals are of particular interest because they are present in the sediment, in contrast to the toxic organic substances that appeared only with the development of industry. Therefore, this approach to analysis and presentation of results would certainly contribute to simpler monitoring and better understanding of changes in metal concentrations in sediment over time. This would ultimately facilitate and support the adoption of legislation on the quality of sediment in Bosnia and Herzegovina, which will have to be formed within the application of European standards.

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