SPATIAL DISTRIBUTION OF HEAVY METALS IN THE DANUBE SURFACE SEDIMENTS NEAR THE GALATI CITY

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Abstract: *The aquatic ecosystem pollution by heavy metals is a real problem for the environment biotic components due to their toxic properties. Through the self-cleaning capacity of the Danube water, all heavy metals tend to accumulate in aquatic organisms, in vegetation and especially in surface sediments. The aim of this paper is to analyze the spatial distribution of heavy metals during 2019, in the Danube surface sediments, near the Galați city. The samples were collected from 5 stations, along the Danube river, between Km 160 and Km 117. The following 7 heavy metals were determined and analyzed using the X-ray fluorescence (XRF) technique: Fe, Mn, Cr, Ni, Zn, Cu and Pb. The result showed that the concentrations of Ni, Cr and Cu exceeded the permissible limit imposed by Romanian Order 161/2006, in certain sampling stations.*

Keywords: *heavy metals, Danube River, surface sediments, spatial distribution*

1. Introduction

Heavy metals are defined as metallic elements that have the density of more than 5 g/cm^3. Concentrations of heavy metals that exceed the limit imposed by the legislation are considered a danger to the aquatic environment. Heavy metals have a special behavior, once they arrive in the aquatic ecosystem, they remain in the water column for a short time and then some of the heavy metals are bioaccumulated in aquatic biological organisms [1]. The highest heavy metals content is deposited on the basin bottom, in surface sediments [2]. Periodic monitoring of the sediments quality is necessary because they play an important role in transport of pollutants through river systems to the world's oceans and seas [3].

The Danube river is considered to be a complex aquatic ecosystem and an important source of water used for different purposes, such as: irrigation, drinking water, navigation and other human activities [4]. Moreover, the monitored area represents one of the most important and largest European hydrographic basin due to the two tributaries: Prut and Siret [5]. The main sources of heavy metal pollution of Danube surface sediments are: navigation, extraction and processing industry, chemical industry, agriculture and wastewater [6].

The purpose of the present paper is to analyze the spatial distribution of 7 heavy metals: Fe, Mn, Cr, Ni, Zn, Cu and Pb in the Danube surface sediments, during 2019.

2. Study area

Sediment samples were taken from 5 stations located between km 160 and km 117 of the Danube River.

The sampling stations were named as follows: Priza Dunării – S1, the confluence of the Siret River and Danube River - S2, restaurant Libertatea Galati - S3, Cotul Pisicii- S4 and the confluence of the Prut River and Danube River - S5 (Figure 1).

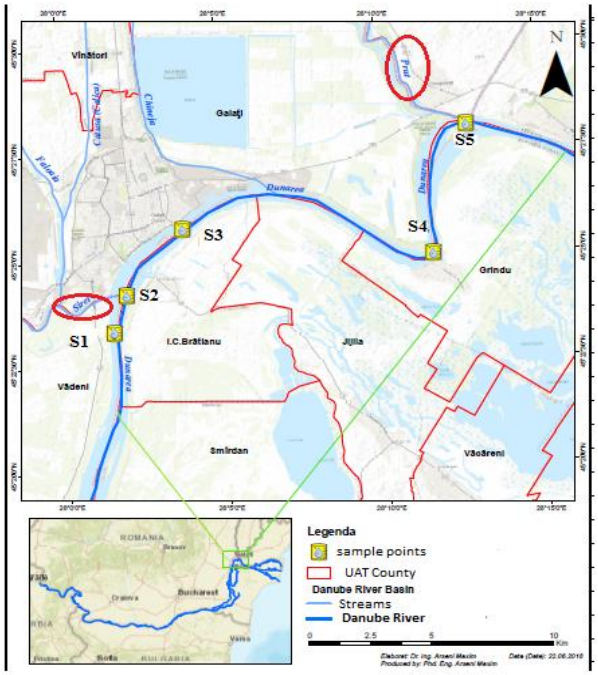

Figure 1: *Study area: Galați City*

3. Materials and methods

From March 2019 to July 2019 were collected 25 surface sediment samples from the Danube River by using a Van Veen grab sampler. After sampling, the sediments were placed in polyethylene recipients and transported in refrigerated boxes at 4 ^{o}C.

The procedure for preparing the sediment samples was as follows: initially the sediments were dried at 105 ^{o}C until they reached a constant weight, then they were sieved using a 125 mm sieve and properly encapsulated.

The X-ray fluorescence technique, *ElvaX Mobile XRF Analyzer from Elvatech*, was used to determine the heavy metals in the sediment samples (Figure 2).

Figure 2: *ElvaX Mobile XRF Analyzer from Elvatech*

4. Results and discussion

Figure 3 shows the statistical distribution of heavy metal concentrations in the sediments of Danube River near the Galați City. For each heavy metal, the results obtained in the 5 months monitored were represented as box plot graphs. Also, the minimum, median and maximum values for all metals analyzed in this study were calculated. All studied heavy metals have a wide variation in their concentrations.

Manganese (Mn) values in the study area ranged from 337 (S5) to 1131 (S3) mg/kg. The median has a decreasing trend from the second sampling station (S2) to the last one (S5). At sampling station S2 a wide range of values is observed for which the median of values is closer to the high values. This fact highlights the influence that the Siret tributary has on the quality of the Danube sediments.

Contamination of the aquatic environment with **Iron (Fe)** influences species abundance such as periphyton, benthic invertebrates and a fish diversity. The main sources of Iron pollution are mining activities [7]. In most of the case, Fe concentrations show some spread in each sampling stations (Fig.3 *b*), this could be explained by the significant influence of anthropogenic sources on the sediments quality. The highest concentrations of Fe and the most outlines were recorded at the S3 sampling station.

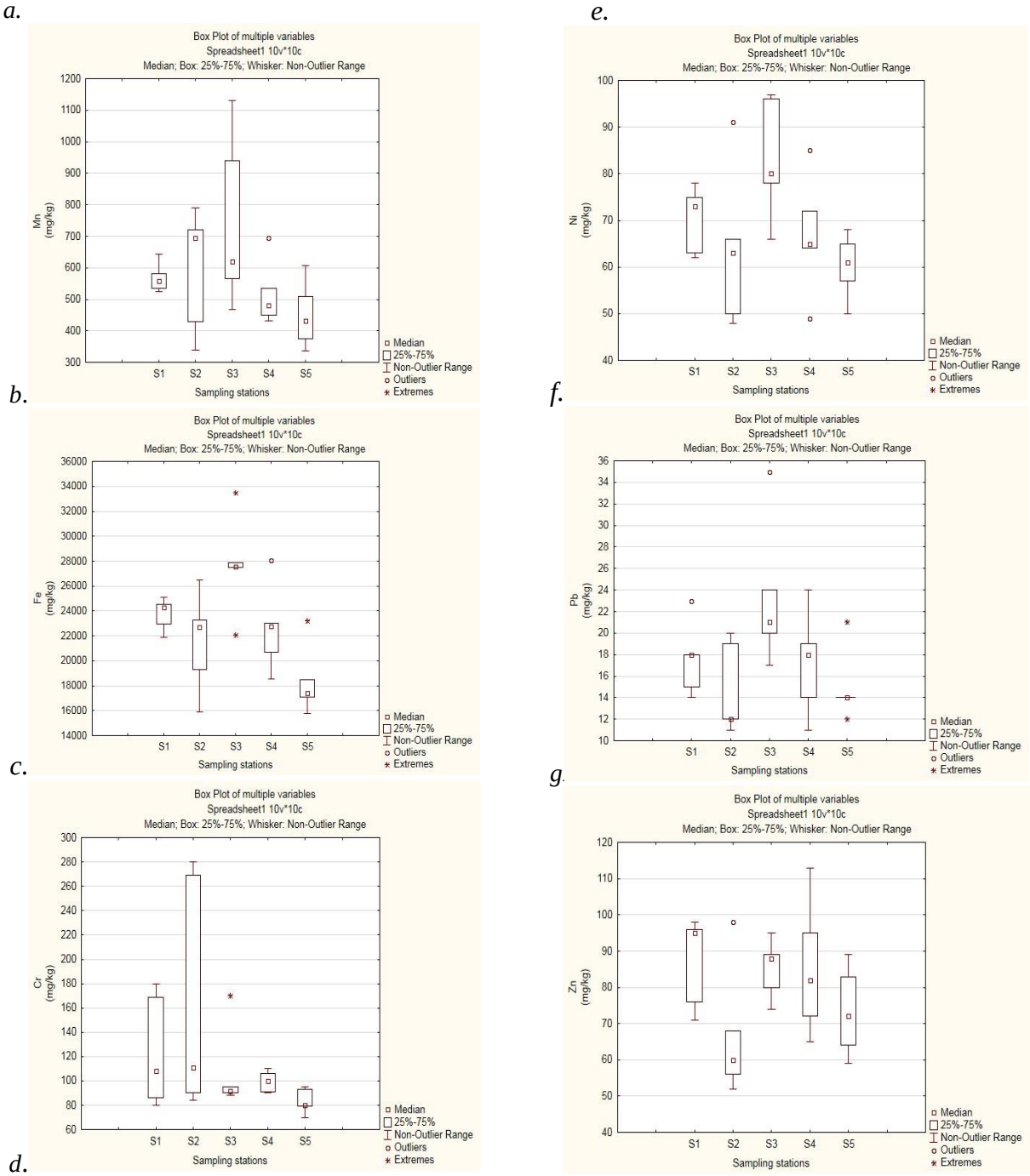

Figure 3: *Spatial distribution of 7 heavy metals concentrations: Mn (a.) Fe (b.), Cr (c.), Cu (d.), Ni (e.), Pb (f.), Zn (g.) in the Danube surface sediments*

Chromium (Cr) compounds are very persistent in surface sediments. They can be encountered in the environment in different states, such as divalents (Cr II), four-valent (Cr IV), five-valent (Cr V) and hexavalent (Cr VI) [7]. Distribution of Cr concentration in the study area ranged from 70 to 280 mg/kg. Cr has a wide variation in his concentrations in

the sampling station S2 and this can be explained by the sediment transport of the Siret tributary. The median has a decreasing trend from the first sampling station to the last one. In the first 4 sampling stations, in certain months, the Cr content exceeds the maximum admissible concentration (100 mg/kg) set by Romanian Order 161/2006 [8]. Chromium is released into the aquatic environment through sewage fertilizers and industrial activities [7].

The BoxPlot representation of **Copper (Cu)** content illustrates also, a spread of Cu concentrations in S2 station (Fig. 3 *d)*. The minimum value of Cu was recorded at the S2 station (25 mg/kg) and the maximum value in S5 (50 mg/kg). In station S1, most concentrations of Cu exceed the maximum allowed limit of 40 mg/kg imposed by the Order 161/2006 [8].

Nickel (Ni) is considered one of the most widespread heavy metal in the environment that comes from natural and anthropic sources. The main sources of the aquatic environment pollution with Ni are: transport, industry, increasing consumption of liquid and solid fuels, as well as municipal and industrial waste [9]. The variation of the Nickel content in surface sediments is similar in all monitored sampling stations (Fig. 3 *e*). The distribution of Ni in the study area ranging from 48 to 97 mg/kg. Throughout the monitored period, in all 5 stations there were recorded of values above the maximum acceptable concentration limits (35 mg/kg).

Lead (Pb) is an extremely toxic metal that in high concentrations can cause ecological disasters. Lead accumulation in aquatic environment is due to mining, manufacturing and fossil fuel burning [7]. Figure 3 *f.* illustrates that the values recorded in station S2 and S4 indicate a relatively high dispersion of Pb concentrations as compared to the other sampling station. However, there

According to Figure 3 *g.*, the **Zinc (Zn)** concentrations were between 52 (S2) - 113 (S4) mg/kg. In all monitored area, the values of Zn have a similar variation in their concentrations. In addition, no value exceeds the maximum allowable concentration of 130 mg/kg.

5. Conclusions

According to the results obtained, the heavy metals content from the Danube surface sediments, near the Galati city, presents certain fluctuations. Furthermore, the present study highlights the contribution that Siret river has on the pollution level of heavy metal in the Danube sediments

The concentrations of heavy metals in Danube surface sediments varied between sampling stations. This is due to the contribution of the natural and anthropogenic factors present in the monitored area.

Some heavy metals concentrations such as: Cr, Ni, Cu exceed the maximum permissible limit imposed by Romanian Order 161/2006 [8].

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Acknowledgments

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