ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
MATHEMATICS, PHYSICS, THEORETICAL MECHANICS
FASCICLE II, YEAR XII (XLIII) 2020, No. 1
DOI: https://doi.org/10.35219/ann-ugal-math-phys-mec.2020.1.09

Preliminary statistical relationship between heavy metals in Lower Danube sediments

Valentina Andreea Calmuc[1,*], Madalina Călmuc[1], Maxim Arseni[1], Catalina Iticescu[1], Lucian P. Georgescu[1]

[1] "Dunarea de Jos" University of Galati, European Center of Excellence for the Environment, Faculty of Sciences and Environment, 111 Domneasca Street, 800201, Galati, Romania, e-mail: valentina.calmuc@ugal.ro*

Abstract
Sediment quality is an important indicator in establishing the ecological status of aquatic ecosystems. Heavy metals are considered toxic and persistent substances that accumulate in the biotic and abiotic components of aquatic ecosystems, especially in sediments. This study presents research on the spatial distribution of 5 heavy metals (Cr, Ni, Cu, Zn, Pb) measured in the Lower Danube surface sediments on the adjacent segment of Tulcea County in the summer of 2019. Moreover, the statistical relationship between the heavy metals mentioned above was studied using preliminary statistical analysis methods, namely Pearson Correlation matrix and Cluster Analysis. Concentrations of the five heavy metals studied were determined using the X-ray fluorescence (XRF) technique. The results of this study indicated the following falling trend of average heavy metal concentrations Cr>Zn>Ni>Cu>Pb. Positive correlations were found between Cu-Ni (r = 0,89), Zn-Ni (r = 0,80), Zn-Cu (r = 0,90), Pb-Ni (r = 0,88), Pb-Cu (r= 0,76), Pb-Zn (r = 0,82) pairs.

Keywords: heavy metals, surface sediments, Lower Danube River, preliminary statistical analysis

1. INTRODUCTION

Sediment is the natural component of aquatic ecosystems that harbors a wide variety of micro-organisms and macro-organisms [1]. Pollution sediments with heavy metals can be a hazard to aquatic organisms due to their toxicity. The presence of heavy metals in aquatic ecosystems is due to both anthropogenic and natural sources [2]. Important natural sources are geological and geographical processes (weathering of parent rock), while the primary anthropogenic sources of heavy metals pollution are industry, the burning of fossil fuels, agriculture (pesticides and fertilizers), atmospheric deposition, municipal wastes, sewage, and urban storm-water run-off [3-4].

In aquatic components, heavy metals can have both different sources of pollution and common sources. The identification of possible sources of heavy metal pollution can be done by performing statistical analysis. Among the preliminary statistical methods used for this purpose are: Pearson Correlation analysis, Cluster Analysis (CA), and Principal Component Analysis (PCA).

The main objectives of this study are to analyse the spatial distribution of heavy metals concentrations quantified in the Lower Danube surface sediments on the adjacent segment of Tulcea County and to study the statistical relationship between heavy metals. For this purpose, Pearson correlations and cluster analysis were performed between the following heavy metals: Cu, Cr, Ni, Pb, and Zn.

2. EXPERIMENTAL

2.1 Study area

Sediment samples were collected from the bottom of the Danube river, specifically on the adjacent sector of Tulcea County. The sampling stations have been strategically chosen to study the impact of anthropogenic activities on the heavy metal pollution level from Lower Danube sediments and to identify potential sources of contamination in the County of Tulcea.

Figure 1 shows on the map the six monitored stations situated near some localities of Tulcea County, as follows:

- S1 - Grindu locality
- S2 - Luncavița locality
- S3 - Somova locality
- S4 - Isaccea locality
- S5 - Shipbuilding Vard Tulcea
- S6 - Tulcea City

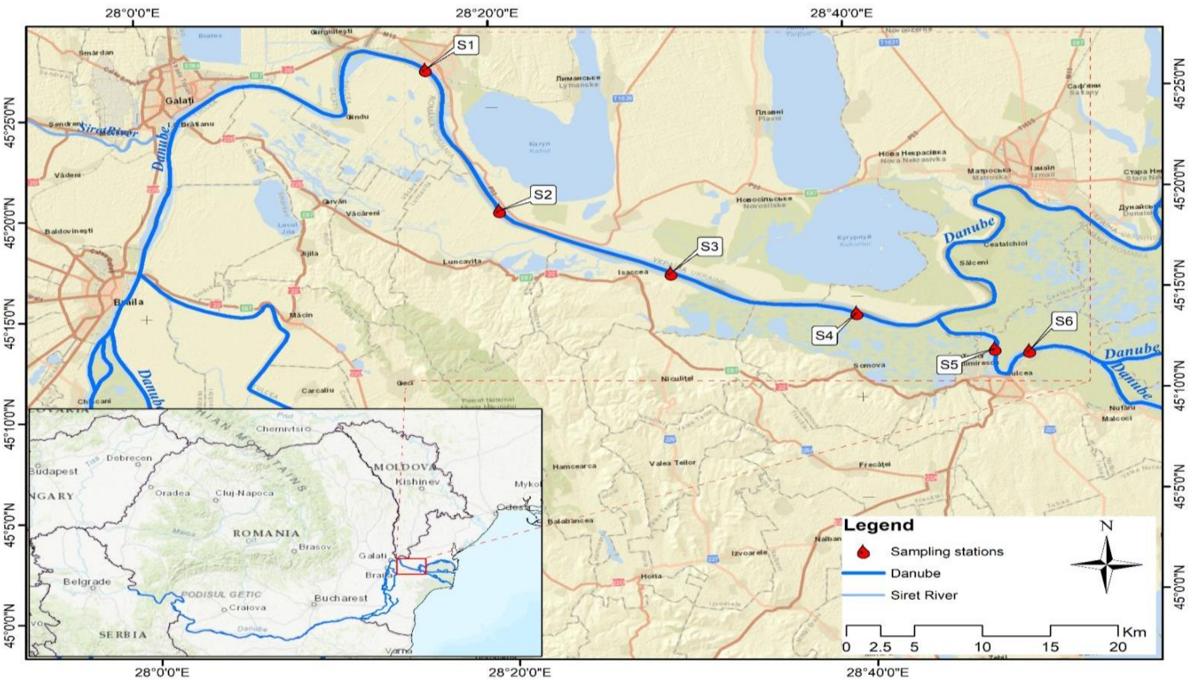

Fig. 1. Sampling Stations along the Lower Danube River

2. 2 Materials and methods

The surface sediment samples were collected using a Van Veen Grab Sampler from within the first 10 cm of sediment surface and deposited in polyethylene recipients. During transportation and temporary storage (1/2 days), the sediment samples were preserved at 4^{o} C. In the preliminary stage, sediment samples were dried at 105^{o} C until they reached a constant weight and were sieved by using a 125 μm sieve.

The heavy metals concentrations were determined by using the XRF (X-ray fluorescence) technique with ElvaX Mobile XRF Analyzer from Elvatech in the Credential Laboratory from the European Centre of Excellence for the Environment.

Fig. 2. Left: surface sediment sampling tool - Van Veen Grab Sampler; middle: preliminary preparation of sediment samples; right: the tool used to measure heavy metals - ElvaX Mobile XRF Analyzer

3. RESULTS AND DISCUSSION

3.1 Analysis of sediment pollution level with heavy metals

Figure 3 shows the spatial distribution of the 5 heavy metals (Cr, Ni, Cu, Zn, Pb) analyzed in the Lower Danube surface sediments on the adjacent segment of Tulcea County.

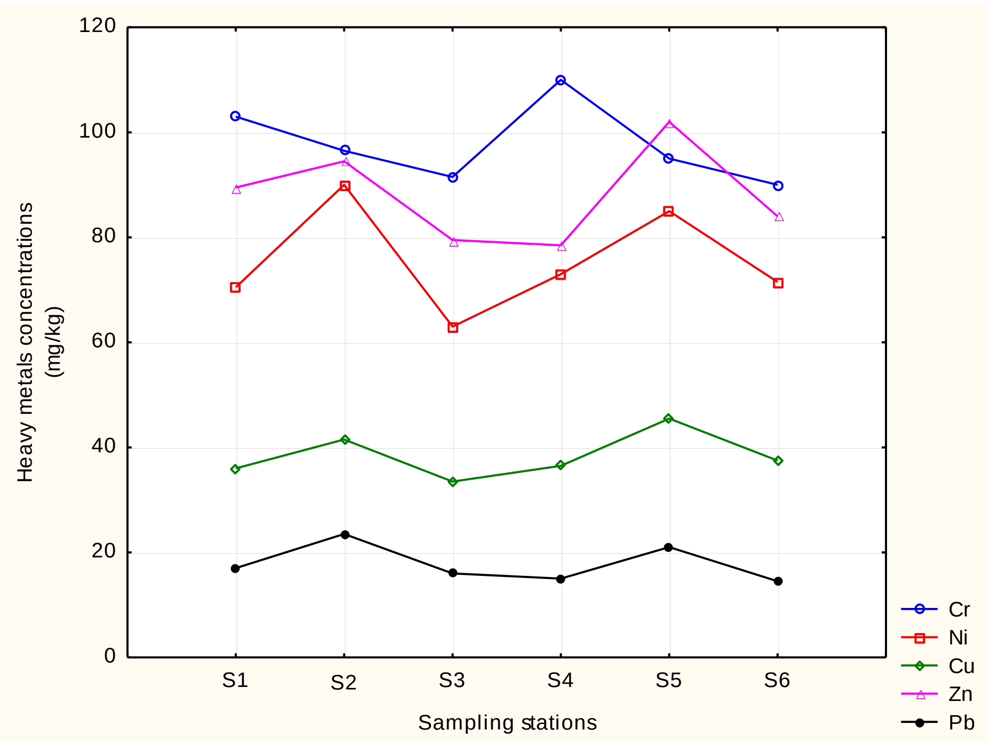

Fig. 3. Spatial distribution of heavy metals concentrations in the Lower Danube surface sediments

The highest concentration was obtained for Cr (110 mg/kg) in the S4 station sampling (Somova locality). According to the Romanian Order 161/2006 [5], this value exceeds the maximum permitted limit of 100 mg/kg. The concentrations of Zn in the surface sediment ranged from 78,5 mg/kg to 120 mg/kg. The values of this metal were below the legal levels admitted, indicating no possible toxic effects for the aquatic organisms.

Regarding Ni, its highest concentration was detected in the S2 sampling station. Furthermore, results showed that the concentrations of Ni at all stations exceeding the maximum accepted levels (35 mg/kg) (Table1). According to Harasim and Filipek (2014), environmental pollution with Ni is caused by industry, transport, municipal and industrial waste, as well as increasing consumption of liquid and solid fuels [6]. The concentrations of Cu range from 33,5 mg/kg (S3) to 45,5 mg/kg (S5), the highest concentration of Cu recorded in surface sediments exceeding the permissible limit of 40 mg/kg (Table 1).

Analysing the results obtained for heavy metal Pb, the lowest concentrations were recorded in the S6 sampling station (14,5 mg/kg), while the highest value was quantified in the S2 sampling station (23,5 mg/kg). All the values of Pb concentrations measured in the Danube surface sediments on the adjacent segment of Tulcea County in the summer of 2019 were within the allowed limits, according to the Romanian Order 161/2006.

Table 1. Standard value of each heavy metal concentration in the sediment according to the Romanian Order 161/2006

Heavy metals	Standard value mg/kg
Pb	85
Cu	40
Cr	100
Zn	150
Ni	35

3.2 Studying the statistical relationships between the heavy metals in Lower Danube sediments

From figure 3 there can be observed that in the case of 4 heavy metals, namely: Pb, Cu, Ni, Zn, the spatial variation of the concentrations are similar. For this reason, the statistical relationship that is established between metals was further studied in this paper, achieving Pearson correlations (Table 2) and Cluster analysis (Fig.4).

Table 2. Pearson Correlation Matrix for heavy metals concentrations in the Lower Danube surface sediments

Element	Cr	Ni	Cu	Zn	Pb
Cr	1.00				
Ni	0.02	1.00			
Cu	-0.13	**0.89**	1.00		
Zn	-0.21	**0.80**	**0.90**	1.00	
Pb	-0.13	**0.88**	**0.76**	**0.82**	1.00

The values of Pearson coefficients obtained for each pair of studied heavy metals are presented in Table 2. Strong positive correlations were observed for Zn-Cu (r=0.90), Cu-Ni (r=0.89), Pb-Ni (r=0.88), Pb-Zn (r=0.82), Zn-Ni (r=0.80) and Pb-Cu (0.79) pairs. These significant correlations obtained between heavy metal pairs indicate that they may have the same pollution source. Moreover, the high correlations indicate that these metals show a similar behavior during their transportation in the aquatic ecosystem [7-12].

Regarding the heavy metal Cr, it is observed that it does not correlate significantly with any of the studied heavy metals. The coefficients of correlation obtained for Cu (r = -0.13), Cr-Zn (r = -0.21) and Cr-Pb (r = -0.13) pairs showed low negative correlations (Table 2). The different behavior of chromium in the sediment may be due to the oxidation-reduction potential [13].

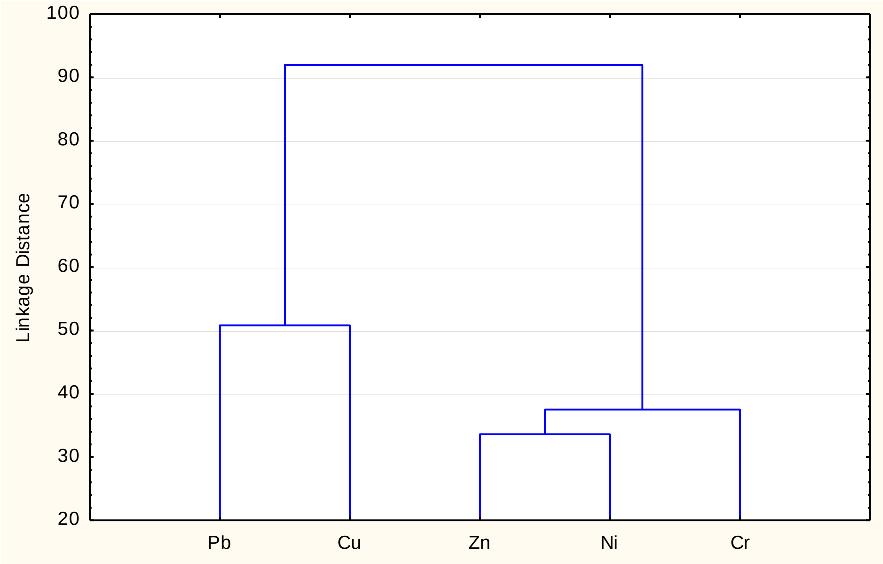

Fig. 4. Dendrogram of the heavy metals concentrations

In order to support the hypothesis of the existence of a common pollution source with different heavy metals, a Cluster Analysis was performed (Fig. 4).

Cluster Analysis is a statistical method that indicates information about the similarity between the studied parameters [14]. The results obtained by applying this method were illustrated by a dendrogram (Fig. 4). Depending on the degree of association between heavy metals, two distinct groups were identified. The first group includes Pb and Cu which support the hypothesis of the existence of a common contamination source. Zn, Ni, and Cr have good similarity and are clustered in the second group.

4. CONCLUSIONS

The statistical methods applied in this study proved to be suitable in analyzing the statistical relationship between the concentrations of heavy metals measured in the Lower Danube surface sediments on the adjacent segment of Tulcea County in the summer of 2019. The spatial distribution of Ni, Cu, Zn, and Pb concentrations indicated a similar variation, for each of these heavy metals - two maximum values were recorded in sampling stations S2 and S5.

The analysis of the preliminary statistical relationship between the heavy metals in the sediments of the Lower Danube indicated the presence of similar behavior between the metals Pb, Cu, Ni, Zn. These results may suggest the existence of common sources of contamination.

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Acknowledgements

Calmuc Valentina Andreea's and Calmuc Madalina's research work was supported by the "Dunarea de Jos" Doctoral Schools, and the work of Maxim Arseni, Catalina Iticescu, and Lucian P. Georgescu was supported by the Romanian Ministry of Research and Innovation, the project Excellence, performance and competitiveness in Innovation, Development, Research at "Dunarea de Jos" University of Galați, EXPERT.