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5. Spatial and seasonal variations of heavy metals in water and sediment samples collected from the Lower Danube River

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Abstract. Surface water pollution with heavy metals represents one of the most relevant environmental issues, with severe outcomes on every other environmental compartment, affecting therefore the human health because of their toxicity, persistence and bioaccumulation tendency. The Danube, one of the most important rivers of Europe considering its course, crossing the continent from west to east, represents the main collector of all pollutants emitted by the ten countries it passes through, prior to discharging into the Black Sea. Given all this, and because of the possible unwanted effects that may occur as a result of recent constructions taking place in the area to improve the navigation conditions, the aim of this study is to evaluate the variation of the global concentration of heavy metals in both water and sediments by calculating the Metal Pollution Index (MPI) on the sector between Calarasi - Braila (km 370 - km 170). Water and sediment samples from Lower Danube were collected between January 2012 and December 2013, from ten different sites. The following heavy metals have been determined: chromium (Cr), copper (Cu), zinc (Zn), lead (Pb) and nickel (Ni). Metal Pollution Index values were used for a seasonal and spatial comparison of the total metal content from the established sites. For a more detailed interpretation of results, Cluster Analysis was performed.
Frequent monitoring of the heavy metal content of Lower Danube has a significant impact on water quality, keeping a low pollution risk and having a long term positive impact on environmental protection of the Black Sea Basin.

Key words*:* Danube River, heavy metals, Metal Pollution Index, Cluster Analysis

INTRODUCTION

Globally, water pollution represents a critical issue, so that the proper management of water resources involves continuous monitoring of its quality ([**9**]; [**10**]). Heavy metals presence in aquatic systems represents a worldwide major threat to environment biodiversity and to human health, becoming a significant concern ([**1**]; [**3**]; [**6**]; [**13**]; [**14**]; [**18**]). These are among the main pollutants to be monitored in order to obtain an overall picture of the aquatic ecosystem health.

Usually, heavy metals are released into environment through water flows, air and waste streams resulting from industrial and socio-economic activities. A special role in the transport of metals in the environment is played by the rivers. After entering the aquatic environment, metals tend to accumulate in sediment and suspended matter and can be taken up by aquatic organisms.

Some heavy metals (Hg, Cd and Pb) are extremely toxic even at very low concentrations, causing many disorders of the nervous system and internal organs, skin diseases, cardiovascular problems and even cancer, while another category of metals in certain limited concentrations (Cu, Fe, Mn, Ni and Zn) play a vital biochemical role essential for vital processes, becoming alarming only at high concentrations ([**6**]; [**7**]; [**9**]; [**10**]; [**14**]).

In Romania, water pollution is the most important environmental issue. Poor water quality is due primarily to low compliance, poor monitoring of industrial effluents and to inadequate wastewater infrastructure.

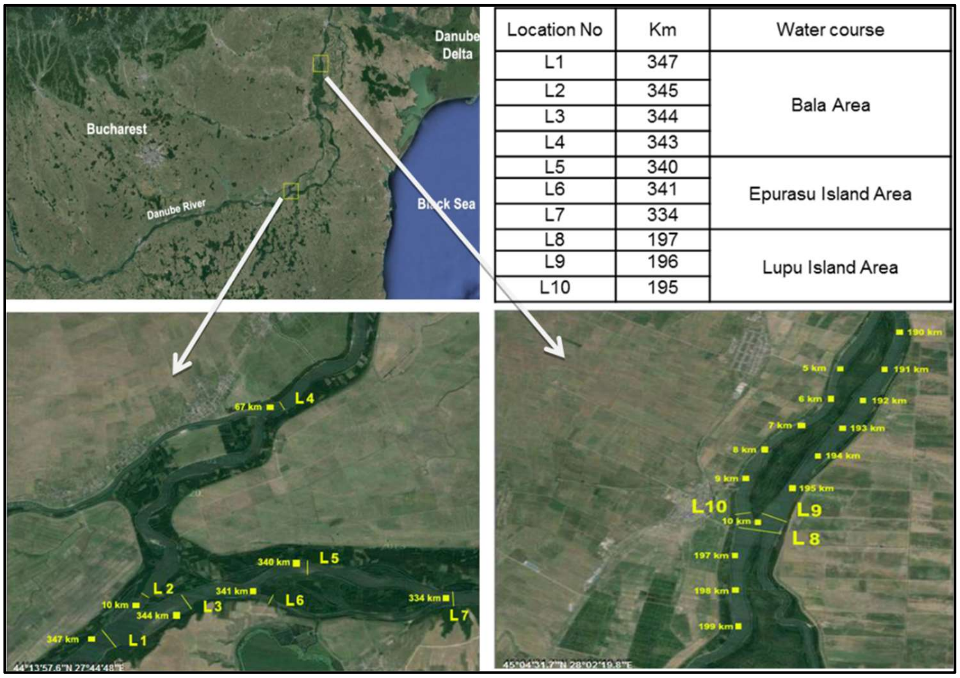
In our country, Danube River is the main source of pollution for the Black Sea, being one of the most important rivers of Europe considering its course, crossing the continent from west to east and representing the main collector of all pollutants emitted by the ten countries it passes through [**13**].

The aim of this study is to evaluate the variation of the global concentration of metals in both water and sediments by calculating the Metal Pollution Index (MPI) on the sector between Calarasi - Braila (km 370 – km 170) considering the possible accumulation of high levels of heavy metals in this part of the river, related to recent construction works taking place in this area for the improvement of navigation conditions. Evaluation of these indices can be a useful tool for monitoring the water and sediment pollution level.

MATERIALS AND METHODS

Study area

The study area is represented by the Lower Danube River. For this purpose, ten sampling locations have been established and marked from L1 to L10 (**Fig. 1**) [**13**].



Location No	Km	Water course
L1	347	Bala Area
L2	345	
L3	344	
L4	343	
L5	340	Epurasu Island Area
L6	341	
L7	334	
L8	197	Lupu Island Area
L9	196	
L10	195	

Fig. 1 Map of study area with the monitoring area sand sampling locations

Sampling and metal analysis

Water samples were monthly collected from January 2012 to December 2013 from the left bank (LB_w) and right bank (RB_w) from a depth of 0.5 m as well as from the center (C_w) of the river from 3 different depths (0.5 m, 1.5 m and 3 m) and sediment samples were taken from left bank (LB_s) and right bank (RB_s). After their transport and conservation, the samples were treated and then the heavy metals (Cu, Cr, Cd, Zn, Pb and Ni) were determined using Atomic Absorption Spectrometry (Solaar M5, Thermo). For the determination of the heavy metals total concentration, the water samples were acidified to prevent hydrolysis of the metals by adding nitric acid (65%). Sediment samples were dried at room temperature, from the fraction < 63 μm, around 0.5 g of sediment has been mineralized with aqua regia, using the microwave digestion.

The quality of the results was ensured by testing a reference material for water (TM - 28.3) and a river sediment standard reference material (LGC 6187). All reagents used in this study were of analytical quality and all glassware used has been previously washed with nitric acid 1.5 mol/L and rinsed in double distilled water and deionized water before use.

Metal Pollution Index

To assess the water quality regarding the level of heavy metal pollution, Metal Pollution Index (MPI) was calculated. Metal Pollution Index is a method of rating that shows the influence of individual parameters on the overall quality of water and sediments, being regarded as a reliable and precise method for metal pollution monitoring. It has a wide application and it is used as the indicator of the quality of river water.

The Metal Pollution Index for water (MIP_w) represents the sum of the ratios of the analyzed parameters to their corresponding maximum allowable concentration for water (1) [**19**]. The Metal Pollution Index for sediments (MPI_s) was obtained by calculating the geometrical mean of concentrations (2) [**20**].

$$MPIw = \sum_{i=1}^{n} \frac{C_i}{(MAC)_i} \quad (1)$$

$$MPIs = (C_{f1} x C_{f2} \dots C_{fn})^{1/n} \quad (2)$$

Where:
MAC - maximum allowable concentration; C_i - mean concentration of each metal; C_{fn} - concentration of the metal "n" in the sample.

For this work the MAC has been used according to MO 161/2006 (Class III of quality) [**12**]. According to Water Quality Classification using MPI, there are six classes of quality, starting from Class I as very pure, to Class VI, as the most affected (**Table 1**) ([**2**]; [**4**]; [**19**]).

Table 1

Water quality classification using MPI

MPI	Characteristics	Class
< 0.3	Very pure	I
0.3 - 1.0	Pure	II
1.0 - 2.0	Slightly affected	III
2.0 - 4.0	Moderately affected	IV
4.0 - 6.0	Strongly affected	V
> 6.0	Seriously affected	VI

Cluster Analysis

Cluster analysis (CA) is the most used statistical technique for the investigation of similarity relationships between datasets leading to dendrograms that provide an overview of the phenomena of grouping data sets [**17**]. Multivariate statistical techniques usage plays an important role in managing reliable water resources, while providing a quick solution for pollution of water bodies used mainly for human consumption.
To establish interdependencies between monitoring indicators and to identify the nature of pollution sources, cluster analysis for both water and sediment samples has been applied.

RESULTS AND DISCUSSIONS

For the calculation of the MPI, the average concentrations of the determined metals have been used (Cu, Cr, Zn, Pb, Ni and Cd). MPI was also calculated separately for each sampling location to compare the pollution load and to assess the water and sediment quality of the selected locations.

In **Fig. 2** the first four locations (L1 - L4) from the Bala area are represented, with Metal Pollution Indexes from water and sediments, represented for Left Bank, Right Bank and Center for entire monitored period.

At the end of the monitoring, the following has been observed:
- complex evolution both for water and sediments;
- similar trend for locations and banks for water;
- maximal values below limits, similar to Class I and Class II of water quality;
- lower values in L4 than L1 - L3 possible due to longer distance from L3 to L4.

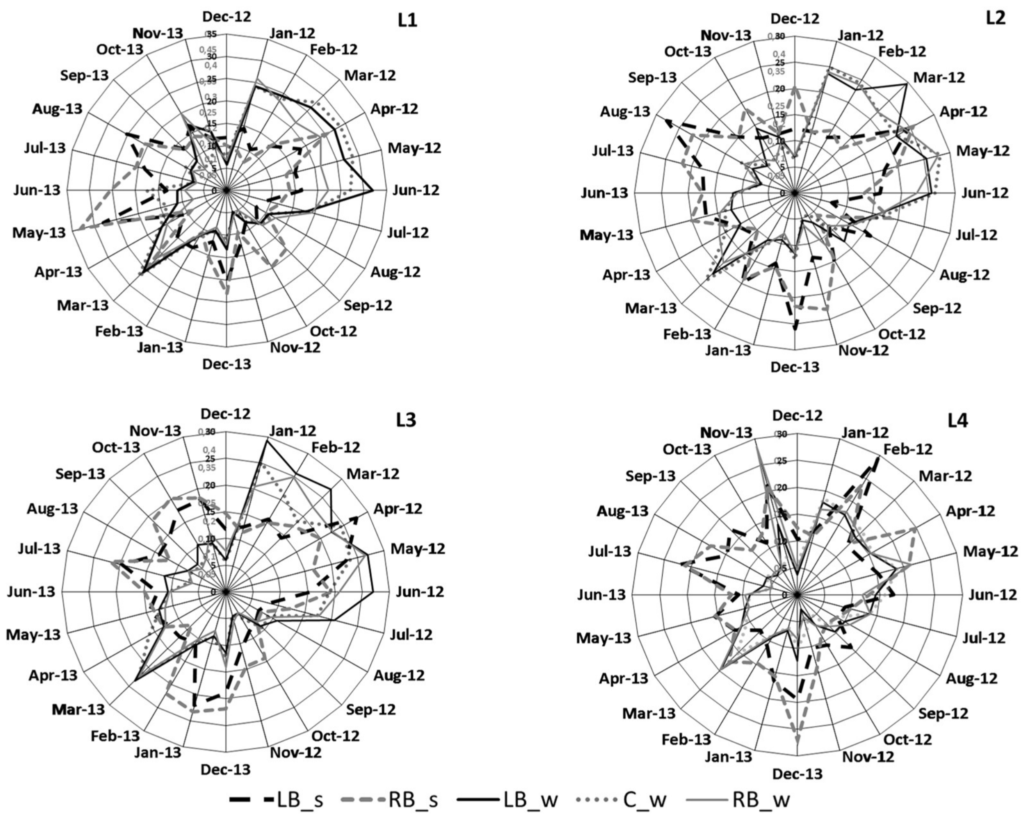


Fig. 2 MPI variation for water and sediment samples in L1 - L4 locations (km 347 - km 343)

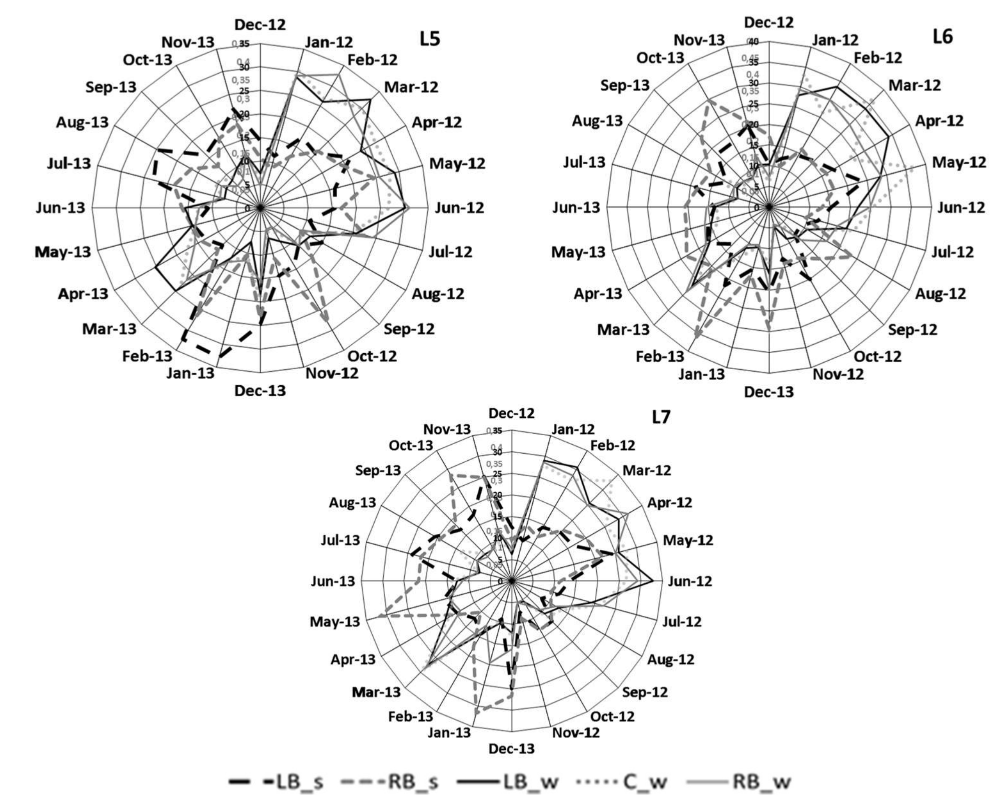


Fig. 3 MPI variation for water and sediment samples in L5 - L7 locations (km 340 - km 341)

For the next three locations (L5 - L7) from the Epurasu Island area (**Fig. 3**), the following has been observed:

- complex evolution both for water and sediments;
- similar variations for water;
- maximal values below limits, similar to Class I and Class II of water quality;
- higher values in L7 than L5 - L6 for sediments.

In the second monitoring area, including location L8 - L10, we concluded the following (**Fig. 4**):

- non-linear evolution for water and sediments;
- similar variations for water, complex evolutions of sediments;
- maximal values below limits, similar to Class I and Class II of water quality;
- higher values in L9 and L10 than L8 for water and sediments.

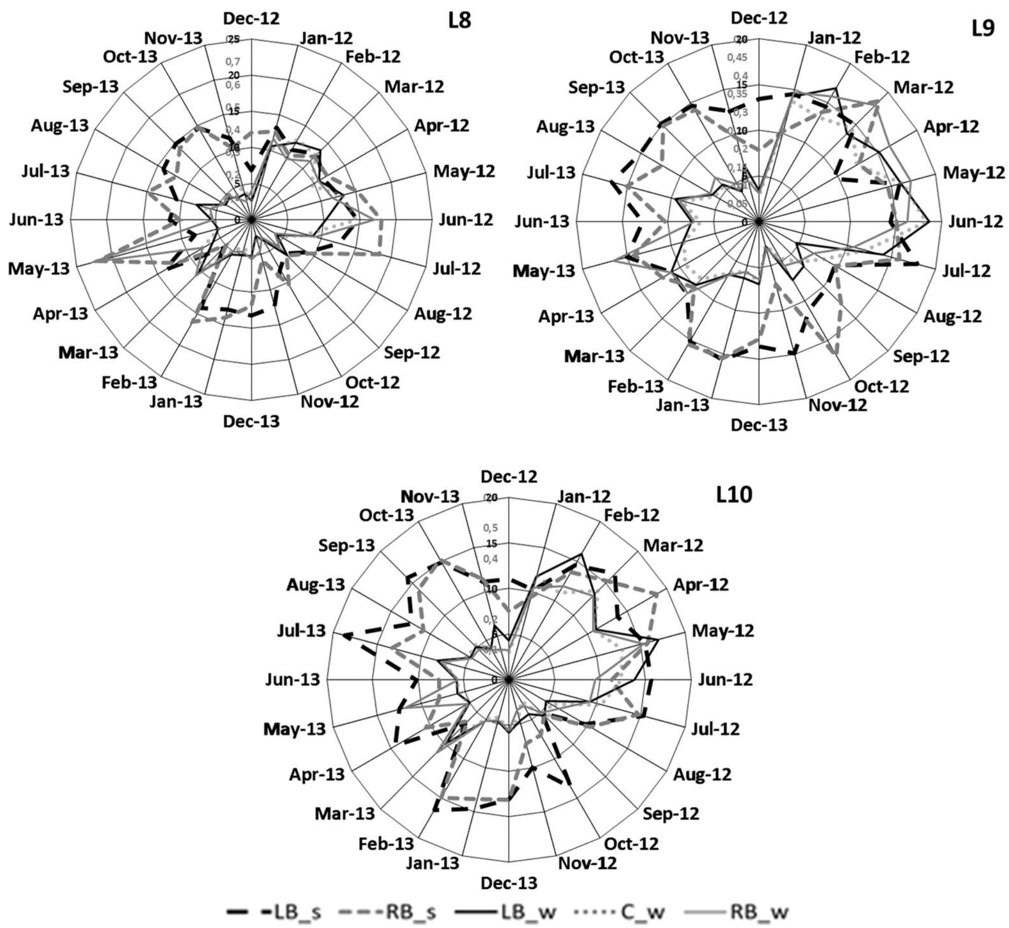
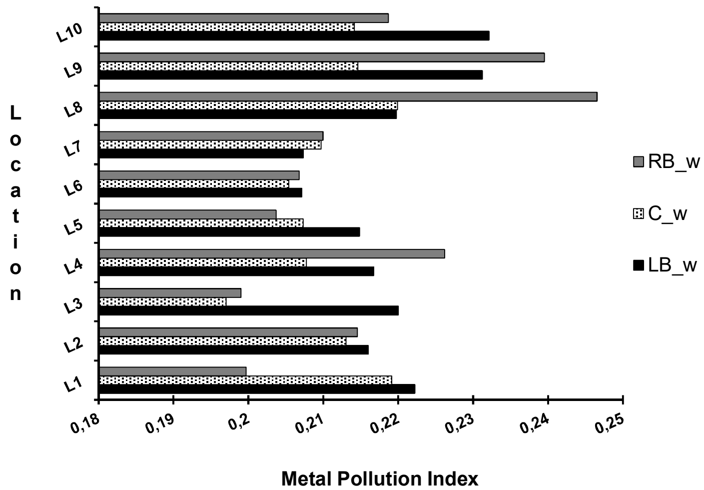


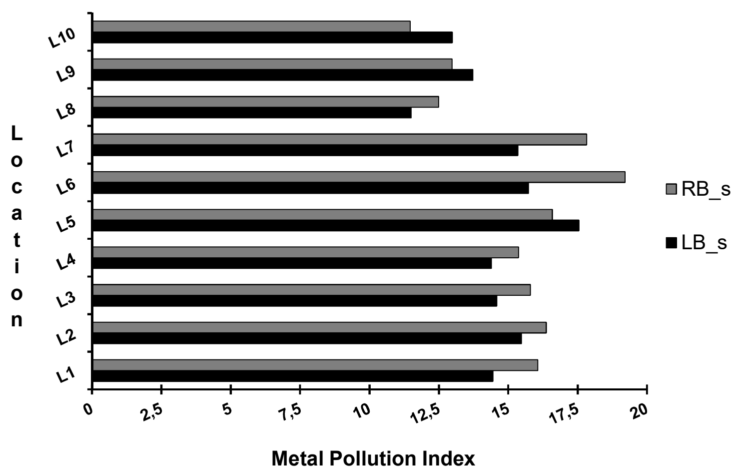
Fig. 4 MPI variation for water and sediment samples in L8 - L10 locations (km 197 - km 195)

Fig 5. a-b illustrates the spatial variation of MPI for water and sediment samples along monitored locations. The spatial analysis for Metal Pollution Index shows:

- same trend for water and sediments for monitored sites;
- different MPI variation between banks;
- maximal MPI values for water in L8 and L9, this being explained due to re-suspending of sediments in water column with flow rise and in L6 and L7 for sediments.



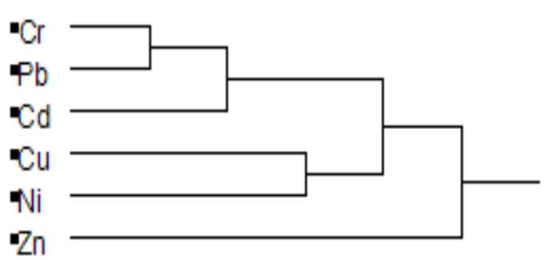
(a)



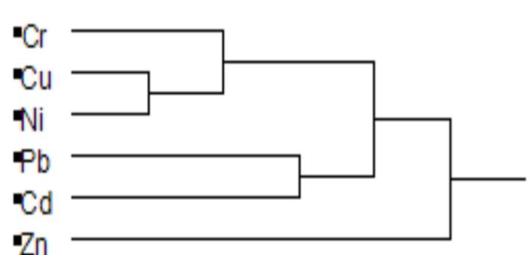
(b)

Fig. 5 MPI variation for water (a) and sediment (b) along monitored locations

For a more detailed evaluation of the trace elements in water and sediment samples, the Cluster Analysis has been performed (**Fig. 6. a-b**). In both cases we obtained five clusters, the most important being clusters one (Cr - Pb for water and Cu - Ni for sediment samples) and two (Cu - Ni for water and Pb - Cd for sediment samples) because they are regarded as an independence of groups and are related to anthropic sources. Clusters three, four and five may be related to both natural and anthropic sources.



(a)



(b)

Fig. 6 Dendrogram of heavy metals in water (a) and sediment (b) samples

CONCLUSIONS

The quality of Lower Danube River has been evaluated using Metal Pollution Index and Cluster Analysis.

- Metal Pollution Index is an effective tool to assess the surface water and sediment pollution and their heavy metal load.
- According to Metal Pollution Index classification, the water quality found for Lower Danube River ranges between classes one to two.
- The two year comparison Metal Pollution Index has proven similar variations to all monitored areas as well as a slight decrease of heavy metal load that may be linked to higher water flows in that period.
- Based on the Cluster Analysis, both sources of pollution (anthropogenic and natural) may be involved, with major importance being assigned to Cu, Ni and Pb.

Greater attention should be given to frequent monitoring of the heavy metal content for a significant impact on water quality of the lower Danube and for a long term positive impact on environmental protection of the final collector, the Black Sea Basin.

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