# Sediments as Indicators of Heavy Metal Contamination in the Lower Danube River

**PETRA IONESCU[1,2]*, VIOLETA-MONICA RADU[1], ELENA DIACU[2]**
[1]National Institute for Research & Development in Environmental Protection, 294 Spl. Independentei, 060042, Bucharest, Romania
[2]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Str., 011061, Bucharest, Romania

*An essential feature for the evaluation of the status of aquatic ecosystems is represented by the sediment quality assessment, as a constitutive part thereof. Sediments reflect all the processes occurring in the hydrographic basin, acting at the same time as a potential source of water pollutants, especially heavy metals. This paper aims to assess the sediment quality of the lower section of the Danube River, in terms of heavy metals content (Cu, Cr, Cd, Pb, Ni and Zn). For this purpose, 10 sampling locations have been assigned and for a period of 12 months (September 2013 - August 2014), sediment samples being monthly collected. To characterize the distribution type and the dynamic variation of heavy metals in the studied section, box plot diagrams have been used, and for the sediment quality evaluation, the obtained values were related to chemical quality standards set out in the Romanian legislation (M.O. 161/2006). For a more detailed assessment of the relationship between metals and for identification of anthropogenic and natural sources, Cluster Analysis (CA) has been used. Following this study, an overview of the sediment quality and the distribution of values obtained on the studied section has been achieved.*

*Keywords: sediment quality, heavy metal, box and whisker plots, Danube River*

Water quality monitoring is a difficult process due to the fact that there is a continuous variation of chemical composition, on the one hand due to climate change that may alter the bioavailability and toxicity of pollutants and on the other hand due to anthropogenic emissions of pollutants resulting from industrial discharges [1, 2]. The chemical composition of sediments reflects long term water quality trends [3, 4]. Sediments are reservoirs for both inorganic pollutants (heavy metals) as well as for persistent organic pollutants [5, 6], while providing information on the historical evolution of anthropic pollution [7, 8]. In the aquatic environment metals are distributed differently between the aqueous phase, sediments and suspended matter [9-11]. Sediments reflect all the processes occurring in the river basin while acting as a potential source of water pollutants, particularly with heavy metals [12, 13]. Due to the high toxicity, persistence and tendency to bioaccumulate in the food chain, heavy metals pose a threat to aquatic ecosystems and to human health, metal concentration in sediments being often related to their concentration found in aquatic creatures [14, 15].

The Danube River is the general collector of all pollutants resulting from discharges from the 10 countries it crosses being at the same time their carrier into the Black Sea, with severe implications on the aquatic ecosystem of the final country, Romania [16, 17].

This study aims to assess the quality of sediments from the lower section of the Danube (Romania) regarding the content of heavy metals considering their increased level of accumulation to the final part of the river, combined with recent construction works in the area for increasing navigation conditions.

## Experimental part

The study area is represented by the lower Danube River. For this purpose, ten sampling locations have been established, marked from L1 to L10 (fig. 1) from which sediment samples were monthly collected from September 2013 to August 2014.

Sediments samples were monthly collected from the left bank and right bank from the established sampling points. Samples were collected using sediment core sampler and stored in PTFE recipients, in the dark and at 4°C until being transported to the laboratory. Prior to analysis, they were dried at room temperature and grinded to ensure a representative sample. From the fraction < 63 $\mu$m, around 0.5 g of sediment have been mineralized with aqua regia, using the microwave digestion. Heavy metal concentrations (Cu, Cd, Cr, Pb, Ni and Zn) have been determined using Atomic Absorption Spectrometry (Solaar M5, Thermo) after complete digestion [18]. Insurance of the quality of the results was performed by testing a river sediment standard reference material (LGC 6187). All reagents used in this study were of analytical grade and all glassware used was washed with nitric acid 1.5 mol/L and rinsed in double distilled water and deionized water before use.

## Results and discussions

In order to obtain information on regarding the central tendency and distribution of each pollutant elements (Cu, Cd, Cr, Pb, Ni and Zn), box and whisker plots were performed, as shown in figure 2 a-f. By representing the data in the Box plot diagrams the center line represents the median, the horizontal edges of the rectangle are the 25th quartiles (bottom) and the 75th (top) and "T"s are

* email: petraionescu2012@yahoo.ro

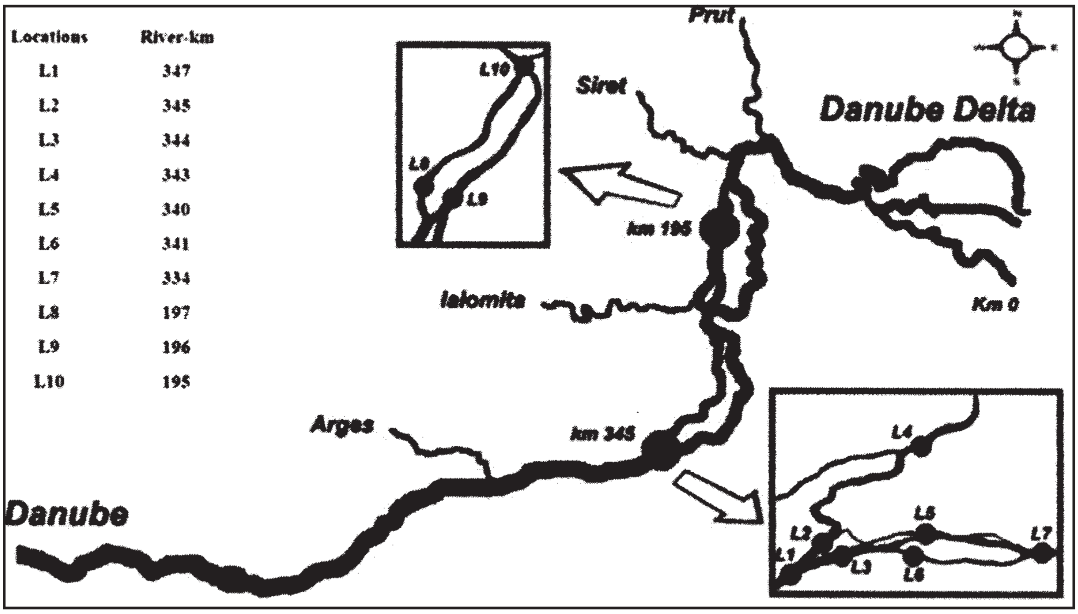


Fig. 1. Map of study area with sampling locations, L1 to L10

the limits. Sediment quality assessment was performed by comparing the values obtained from chemical quality standards set by Ministerial Order 161/2006 [19] (noted as QS and plotted on the secondary axis), order that implements the guidelines of Directive 2000/60/EC of the European Parliament [20].

From figure 2 it is noted that the dynamic analysis and spatial variation of metals in sediments collected from the lower Danube section is about the same for Cd (fig. 2.a), Cu (fig. 2.c) and Pb (fig. 2.d). Also metals Zn (fig. 2.b) and Ni (fig. 2.f) recorded a similar dynamics in the monitored locations. Table 1 shows the distribution type for each studied metal.

For a more detailed assessment of the relationship between metals and for identification of anthropogenic and natural sources, Cluster Analysis (CA) has been used (fig. 3).

The first cluster (Cu and Ni) is the most important, being independent of other groups and indicating the presence of anthropogenic sources. The other four groups indicate sources of both natural and anthropogenic origin.

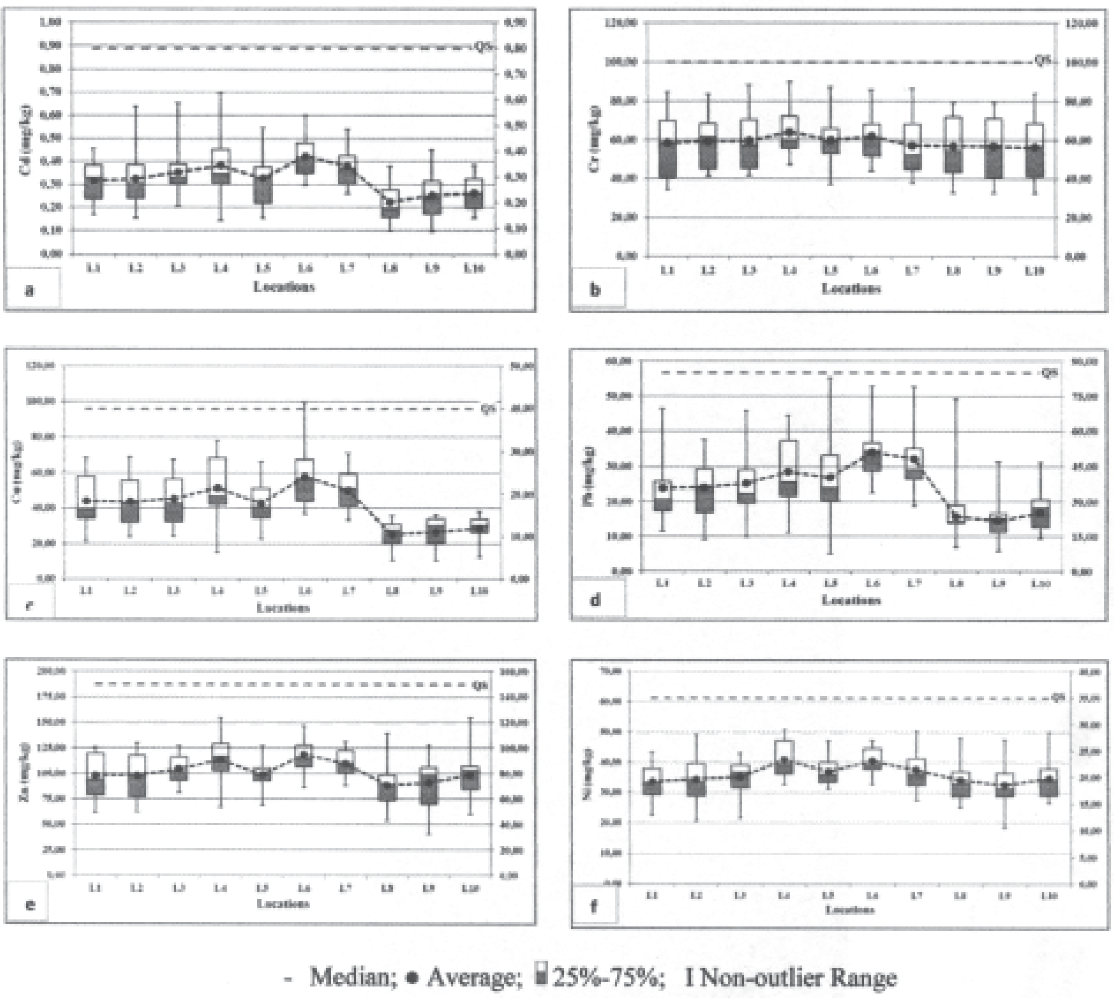


Fig. 2 a-f. Box and whisker plots for heavy metals in sediments

**Table 1**
DISTRIBUTION TYPE FOR HEAVY METALS IN THE MONITORED LOCATIONS

| Heavy metals | Distribution of concentration | | Concentration median | |
|---|---|---|---|---|
| | normal | non-normal | symmetric | asymmetric |
| Cd | L1, L2, L3, L4, L5, L8, L9 and L10 | L6 and L7 | L2, L6, L7, L9 and L10 | L1, L3, L4, L5 and L8 |
| Cr | L5, L6, L7, L8, L9 and L10 | L1, L2, L3 and L4 | L5, L6, L8, L9 and L10 | L1, L2, L3, L4 and L7 |
| Cu | L1, L2, L3, L5 and L7 | L4, L6, L8, L9 and L10 | L2, L3, L6 and L7 | L1, L4, L5, L8, L9 and L10 |
| Pb | L2, L3, L4 and L5 | L1, L6, L7, L8, L9 and L10 | L1 and L2 | L3, L4, L5, L6,L7, L8, L9 and L10 |
| Zn | L2, L3, L4, L5, L6, L7, L8, L9 and L10 | L1 | L1, L2, L4, L5 and L7 | L3, L6, L8, L9 and L10 |
| Ni | L1, L2, L4, L7 and L9 | L3, L5, L6, L8 and L10 | L1, L2, L7 and L8 | L3, L4, L5, L6, L9 and L10 |

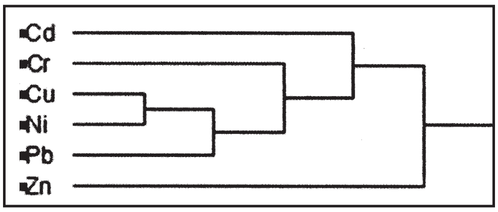

Fig. 3. Cluster Analysis of heavy metals concentration in sediment samples

## Conclusions

Following this study, box and whisker plot diagrams have revealed that heavy metals have a heterogeneous distribution. There have not been recorded any high levels of heavy metal contamination in sediments according to the chemical quality standards from Romanian legislation (M.O. 161/2006). For the elements Cu and Ni, slightly higher values compared to other metals have been recorded, it is assumed that historically contaminated deposits in sediments can be remobilized and transported to upper layers of the sediment or diffused into water. In general, due to different sediment types and levels of inputs there is variable contamination across the entire aquatic ecosystem. Based on the cluster analysis, both sources of pollution (anthropogenic and natural) may be involved, with major importance being assigned to Copper and Nickel. Greater attention should be given to frequent monitoring of the heavy metal content for a significant impact on water and sediment quality of the lower Danube River and for a long term positive impact on environmental protection of the final collector, the Black Sea Basin.

*Acknowledgements: The authors are grateful to the general management and colleagues from INCDPM for their valuable assistance and suggestions. Petra Ionescu's contribution was partially financed by Project SOP HRD – PERFORM 159/1.5/S/138963.*

## References

1.ROBERTS, D.A., BIRCHENOUGH, S.N.R., LEWIS, C., SANDERS, M.B., BOLAM, T., SHEAHAN, D., Global Change Biology, **19**, 2013, p. 340.
2.SHEHU, A., LAZO, P., PJESHKAZINI, L., J. Environ. Prot. Ecol., **10**, no. 2, 2013, p. 386.
3.NGELINKOTO, P., THEVENON, F., DEVARAJAN, N., BIRANE, N., MALIANI, J., BULUKU, A., MUSIBONO, D., MUBEDI, J. I., POTÉ, J, Toxicological and Environmental Chemistry, **96**, no.1, 2014, p. 1.
4.WILLIAMS, M., Phil. Trans. R. Soc. A, **370**, 2012, p. 2093.
5.EVRARD, O., POULENARD, J., NÉMERY, J., AYRAULT, S., GRATIOT, N., DUVERT, C., PRAT, C., LEFČVRE I., BONTÉ, P., ESTEVES, M., Hydrol. Process, **27**, no. 6, 2013, p. 911.
6.LAING, G.D, RINKLEBE J., VANDECASTEELE, B., MEERS, E., TACK F.M.G., Sci. Total Environ, **470**, 2009, p. 3972.
7.SHOMAR, B.H., MÜLLER, G., YAHYA, A., Wetl. Ecol. Manag., **13**, no. 4, 2005, p. 419.
8.HAMAD, S.H., SCHAUER, J.J., SHAFER, M.M., AL-RAHEEM, E.A., SATAR, H., The
Scientific World Journal, **2012**, 2012, p. 1.
9.MWANAMOKI, P.M., DEVARAJAN, N., THEVENON, F., BIRANE, N., DE ALENCASTRO L.F., GRANDJEAN, D., MPIANA, P.T., PRABAKAR, K., MUBEDI, J.I., KABELE, C.G., WILDI, W., POTÉ, J, Chemosphere, **111**, 2014, p. 485.
10.WU, Q., TAM, N.F.Y., LEUNG, J.Y.S., ZHOU, X., FU, J., YAA, B., HUANG, X., XIA L., Ecotox. Environ. Safe, **104**, 2014, p. 143.
11.RADU, V-M, DIACU, E., IONESCU P., DEÁK, Gy., Rev. Chim. (Bucharest), **66**, no. 5, 2015, pp. 601.
12.RADU, V.-M., IONESCU, P., DEÁK, Gy., IVANOV, A.A., DIACU, E., J. Environ. Prot. Ecol., **15**, no. 2, 2014, p. 414.
13.SALEM, D.M.S.A., KHALED, A., EL NEMR, A.E, EL-SIKAILY A., Egyptian Journal of Aquatic Research, **40**, 2014, p. 349.
14.LEPLAND A., ANDERSEN, T.J., LEPLAND A., ARP, H.P.H, ALVE, E., BREEDVELD, G.D., RINDBY, A., Marine Pollution Bulletin, **60**, 2010, p. 1512.
15.***ISO 11047:1999, Soil quality. Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc in aqua regia extracts of soil. Flame and electrothermal atomic absorption spectrometric methods.
16.SYED, J. H, MALIK, R.N., CHAEMFA, J.L.C., ZHANG, G., JONES K.C., Sci. Total Environ, **472**, 2014, p. 204.
17.ZENG, H., WU, J., Int. J. Environ. Res. Public Health, **10**, 2013, p. 793.
18.IONESCU, P., RADU, V.-M, DEÁK, Gy., DIACU, Rev. Chim. (Bucharest), **65**, no. 9, 2014, p. 1092.
19.*** Ministerial Order No 161/2006 for the Approval of the Norm Concerning the Reference Objectives for the Surface Water Quality Classification (Including Quality Standards for Sediments).
20.*** Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy

Manuscript received: 8.06.2015