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ASSESSMENT OF THE TRANSFER PHENOMENA FOR HEAVY METALS IN A FRESHWATER ECOSYSTEM: A FIELD STUDY

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ABSTRACT. Increasingly higher concentrations of heavy metals in aquatic environments pose a major risk to living organisms, as a result of their bioaccumulation and toxicity. For the assessment of the bioaccumulation and trophic transfer, samples of water, sediments, aquatic plants (*Ceratophyllum demersum, Potamogeton crispus* and *Spirogyra algae*), molluscs (*Viviparus viviparus*) and fish (*Ameiurus nebulosus* and *Scardinius erythrophthalmus*) have been collected from Plumbuita Lake, located in a highly urbanized area of Bucharest city (Romania). After bringing the samples in solution, the following heavy metals have been determined using a spectrophotometer with atomic absorption - ContrAA 700 (Analytikjena): copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb) and nickel (Ni). The distribution of heavy metals in the aqueous and solid phase for the collected samples has been assessed using their bioaccumulation factors in relation to water and sediments. For the molluscs species, metal determinations have been performed separately both for the soft tissue and for the shells, revealing that the soft tissue is more effective in accumulation of heavy metals compared to the shell.

Key words: *heavy metals, Plumbuita Lake, bioaccumulation*

INTRODUCTION

The development of technology and industry, along with global population growth has led to a critical problem concerning the fate of the environment as a result of new challenges (Adams, 2014; Resetar-Deac and Diacu, 2015). Deterioration of freshwater habitats occurs much faster than of terrestrial and marine habitats, since the density of the human population is much higher in their proximity and the interdependence of organisms and aquatic environment is much closer for aquatic organisms than for terrestrial (Cieszynska et al., 2012).

One of the strongest threats to the biodiversity of aquatic ecosystems is the metal contamination (Kibria et al., 2016). At the aquatic ecosystem metals are differently distributed among the aqueous phase, suspended matter and sediments through various mechanisms (Islam, 2015; Maria et al., 2013; Radu et al., 2015).

As a result of their toxicity, persistence and tendency to bioaccumulate, heavy metals representd a major environmental health problem (Islam et al., 2015; Li et al., 2016; Radu et al., 2016).

Some metals such as chromium, zinc and copper play an essential role in carrying out all the biochemical and energetic changes with a role in the living tissues, while others such as mercury, cadmium and lead are highly toxic even at very low concentrations, causing numerous health problems (Deák et al., 2015; Mohammadizadeh et al., 2016).

Numerous studies have confirmed that the metals accumulate along the aquatic food chain, reason for which consumption of contaminated fish presents a potential risk to human health, as demonstrated by studies regarding metal concentration in their eatable part (muscle) (Benhamed et al., 2016). In order to obtain an integrated image with respect to the bioavailability of metals, an alternative to physico-chemical measurements for the monitoring of environmental compartments (water/sediment) is the quantification of concentrations of metals in the tissue of the aquatic species (De Jonge et al., 2015). Bioaccumulation of metals in fish and shellfish species may have much higher concentrations compared to their environment (El-Moselhy et al., 2014).

Checking and maintaining contaminants to acceptable levels in terms of toxicity is essential to protect public health. The effects of heavy metal pollution on the human body are extremely serious, in the EU legislation quality standards being set for the content of these metals in the flesh of fish: mercury (0.50 mg/kg), cadmium (0.05 mg/Kg) and lead (0.30 mg/kg) (Commission Regulation (EC) 1881, 2006). Municipality of Bucharest (Romania) is crossed by lakes formed along the Colentina River, one of them being the Plumbuita Lake, in the vicinity of which many constructions with inadequate infrastructure were developed, representing a potential risk to water quality.

The present study was conducted to highlight the levels of heavy metals (Pb, Cd, Cr, Cu, Ni) in water, sediments, aquatic plants (*Ceratophyllum demersum, Potamogeton crispus* and *Spirogyra algae*), molluscs (*Viviparus viviparus*) and fish (*Ameiurus nebulosus* and *Scardinius erythrophthalmus*) from Plumbuita Lake.

MATERIALS AND METHODS

Study area

To characterize the process of transferring heavy metal abiotic compartment to biotic compartment, a sampling campaign for collecting water, sediment, aquatic plants and fish samples from the Plumbuita Lake was organized in June 2015. Water and sediment samples were taken from three locations (L1, L2 and L3) shown in figure 1 (Ionescu et al., 2016).

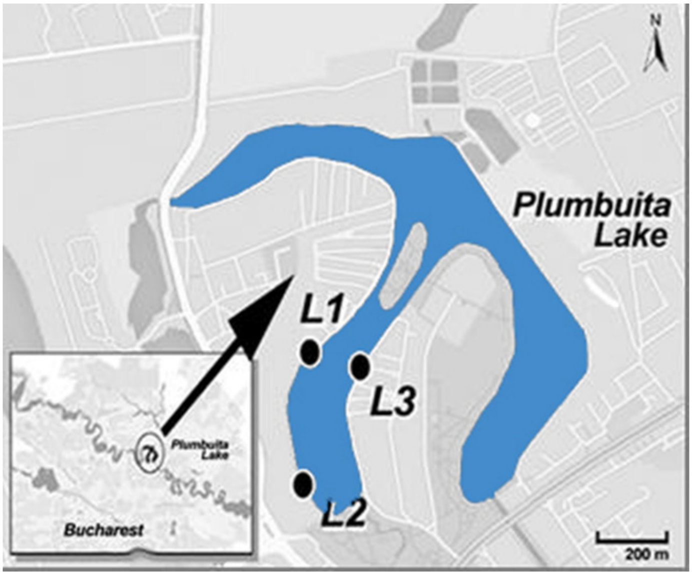


Fig. 1. *Map of study area with sampling locations*

***Sampling and* Sample treatment**

Water samples were collected from about 50 cm below the water surface in polyethylene bottles decontaminated beforehand with nitric acid solution and then rinsed with distilled water (ISO 5667, 2000). To determine the total metal concentration, a volume of 250 mL taken from the test water was acidified to prevent hydrolysis of the metals by adding 0.5 mL of HNO_3 (65%) in it (ISO 8288, 2001).

Sediment samples were collected in polyethylene bottles, washed with detergent and rinsed with distilled water using the core sampler. Approximately 0.5 g of dry sediment sample (fraction <63 μm) was digested with aqua regia (9 mL HCl (37%) and 3 mL HNO_3 (65%)).

Samples of plants (*Ceratophyllum demersum, Potamogeton crispus* and *Spirogyra algae*) were rinsed in double distilled water to remove any traces of powder immediately after being collected, then they were left at room temperature for several days to evaporate the excess of water.

After being collected, the fish samples (*Ameiurus nebulosus* and *Scardinius erythrophthalmus*) and molluscs (*Viviparus viviparus*) were also rinsed in double distilled water to remove impurities, then the fish were dissected carefully removing scales and bones, preserving only the muscle tissue, while for molluscs, the soft tissue was separated from the shells.

Drying of the biota samples to constant weight was carried out by using a laboratory oven set at 80 ^{0}C. After drying, the samples were homogenized by grinding in an agate and kept in sterile vessels in the refrigerator until mineralization.

For digestion, approximately 0.5 g of dry sample were separated, to which 9 mL of 65% nitric acid (Suprapur) was added for the mineralization of samples of aquatic plants and a mixture of 7 mL of 65% nitric acid (Suprapur) and 1 mL of 30% hydrogen peroxide (Suprapur) was added to the samples of fish and molluscs for their mineralization. Microwave digestion system (Ethos 1, Milestone) equipped with a temperature and pressure control was used to digest the samples.

Analysis procedure

After bringing all the samples in solution, for determining the heavy metals (Pb, Cd, Cr, Cu and Ni), a High-Resolution Continuum Source Atomic Absorption Spectrometer - ContrAA 700 was used. All solutions for calibration, samples, and rinsing were prepared using ultrapure water and Suprapur nitric acid (65 %). The stock solutions were prepared using ultrapure water, obtained through a Micropure Ultrapure water system (TKA, Germany).

Bioaccumulation factor (BAF)

The bioaccumulation and trophic transfer assessment was performed by the calculation of the bioaccumulation factor in relation to concentration of water (BAFw) and in relation to the concentration of sediment (BAFs) (Islam et al., 2015; Uysal et al., 2009), as in ecuatin 1.1 and 1.2.

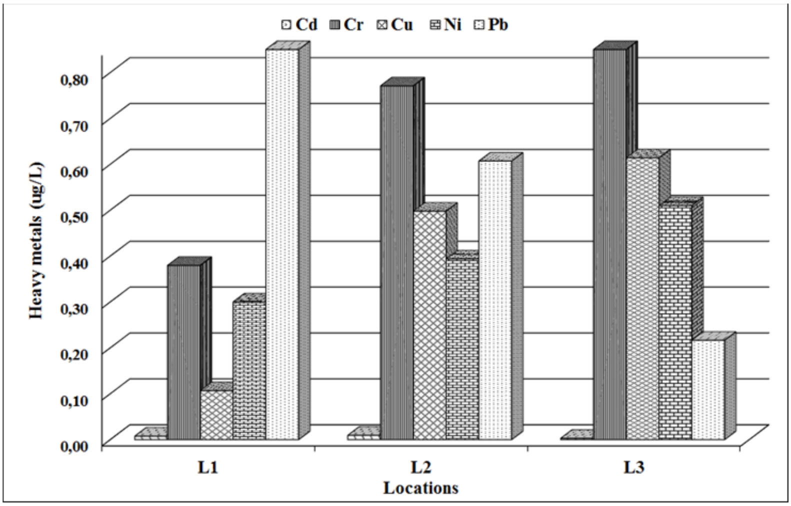
$$BAF_w = \frac{C_{biota\ samples}}{C_w} \tag{1.1}$$

$$BAF_s = \frac{C_{biota\ samples}}{C_s} \tag{1.2}$$

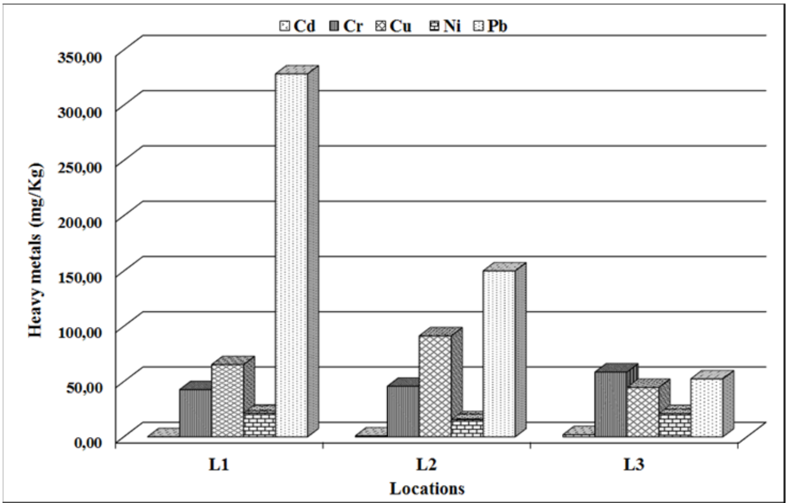
$C_{biota\ samples}$ - the concentration of the heavy metals in biota samples (mg/Kg, dry weight);
C_w - the concentration of the heavy metals in water (mg/L);
C_s - the concentration of the heavy metals in sediment (mg/Kg, dry weight).

RESULTS AND DISCUSSION

Figure 2 presents the variations of metal concentrations in the examined water samples (Fig. 2.a) and in the sediment samples (Fig. 2.b) taken from three selected locations of Plumbuita Lake. After reporting the concentration values determined for heavy metals mentioned in the national legislation (Ministerial Order no. 161, 2006), all recorded values were classified as class I quality for water samples, while sediment samples exceeded the standard of chemical quality for the L2 and L3 sampling locations regarding Cd, for all three sampling locations regarding Cu and for L2 and L3 sampling locations for Pb.



(a)

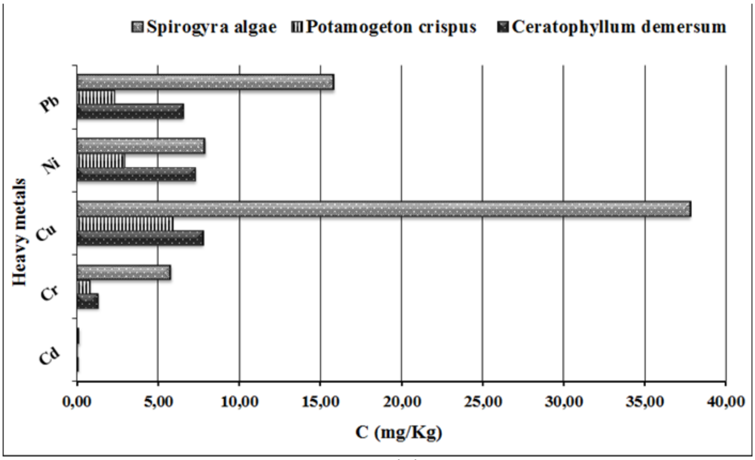


(b)

Fig. 2. *Dinamics of heavy metal variation in water (a) and sediment (b) samples*

Figure 3 show the variations in metal concentrations for three species of aquatic plants (Fig. 3.a) and for two fish species (Fig. 3.b) sampled from Plumbuita Lake. Following the graphics, it was found that the samples *Spirogyra algae* (spirogyra) recorded the highest concentrations of metals and in the case of fish species, *Scardinius erythrophthalmus* (rudd) revealed the highest concentrations of Pb, Ni and Cu, while for *Ameiurus nebulosus* (brown bullhead) higher concentrations were recorded for Pb.

Through a comparative analysis of the determined values for heavy metals in fish fillets, with permissible limits laid down in Regulation EC No 1881/2006, it was observed that the values obtained for Cd do not exceed the limit specified by the Directive, while Pb exceeded the limits.



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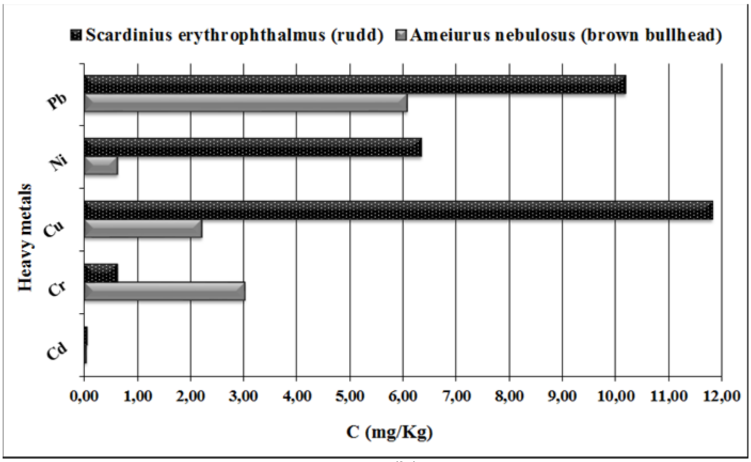


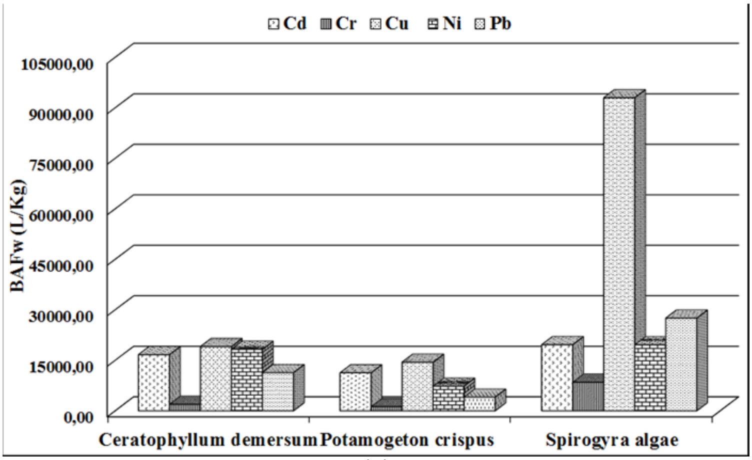
(b)

Fig. 3. *Dinamics of heavy metal variation in the three species of aquatic plants (a) and two fish species (b) analized*

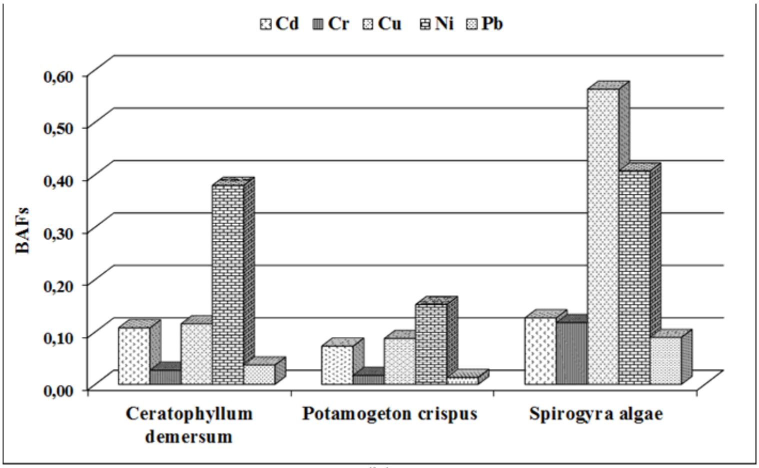
Figure 4 shows the variation of bioaccumulation of heavy metals in plants as compared to water (Fig. 4.a) and to sediments (Fig. 4.b).

From the comparative analysis of the bioaccumulation factor in relation to water (BCF_w) of the three species of aquatic plants, it was found that the species *Spirogyra algae* presents the highest capacity to accumulate heavy metals in the following order: Cu > Pb > Cd > Ni > Cr, followed by the species *Ceratophyllum demersum*: Cu > Ni > Cd > Pb > Cr and finally *Potamogeton crispus* presenting the following accumulation order of heavy metals: Cu > Cd > Ni > Pb > Cr.

In a similar way, for the comparison of heavy metal bioaccumulation factor in relation to the sediments (BCF_s), the order of aquatic plants species to accumulate heavy metals resembles the case of BCF_w, but the heavy metals are absorbed in a different manner by the plants. For *Spirogyra algae* the following order was found: Cu > Ni > Cd > Cr > Pb, for *Ceratophyllum demersum*: Ni > Cu > Cd > Pb > Cr and for *Potamogeton crispus* the bioaccumulation trend was the following: Ni > Cu > Cd > Cr > Pb.



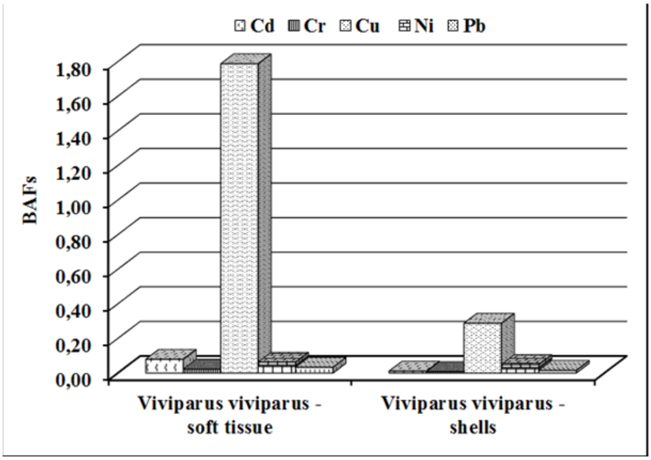
(a)



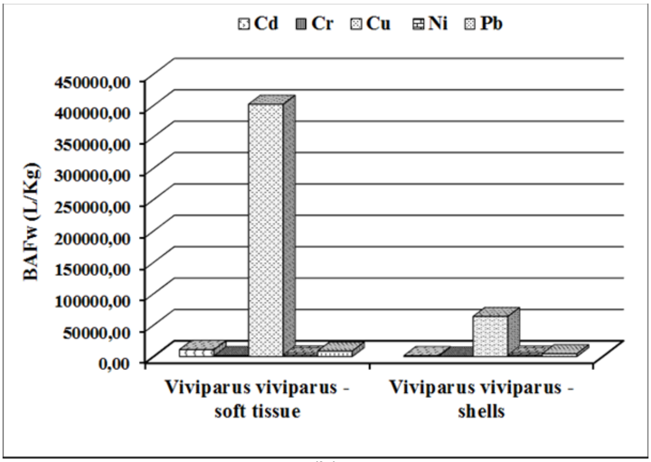
(b)

Fig. 4. *Bioaccumulation factors of heavy metals in plants as compared to water (a) and to sediments (b)*

From the two analysis we concluded that the absorbtion of Cu was higher in the aquatic plants than in the water. In relation to sediments, the aquatic plants have a higher accumulation for Cu and Ni than for the rest of the analyzed heavy metals. Within the analyzed species of molluscs (*Viviparus viviparus*), the recorded values for heavy metals in the soft tissue and shells were higher for both BCF_w and BCF_s in the case of Cu, concluding that this species of molluscs have a tendency to accumulate Cu in the body. Also, after comparing the bioaccumulation factor values it was revealed that soft tissue presents a greater biacumulation rate of the analyzed metals compared to their shell (figure 5).



(a)

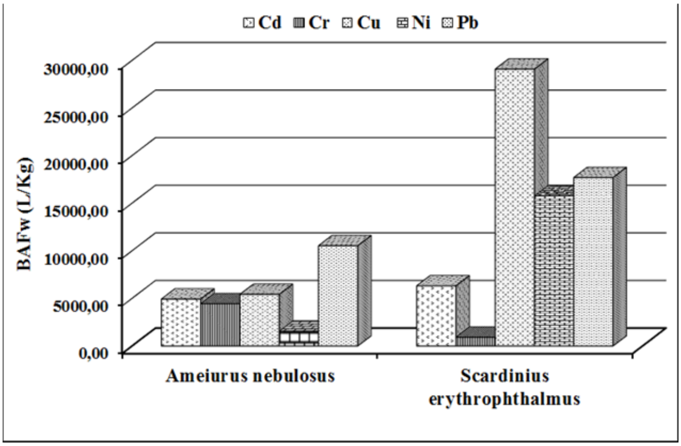


(b)

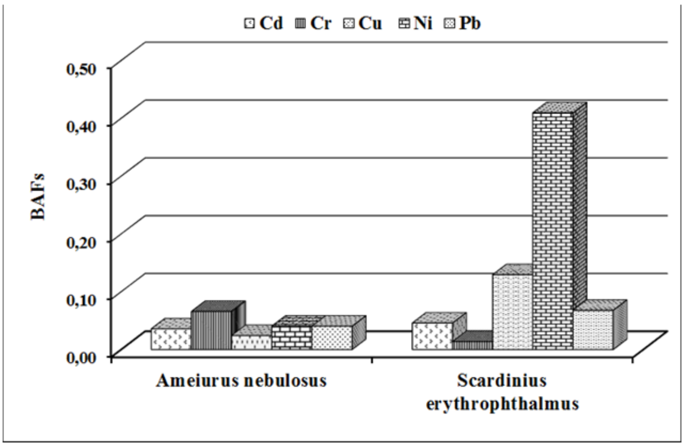
Fig. 5. *Bioaccumulation factors of metals in species Viviparus viviparus for soft tissue and shells as compared to water (a) and to sediments (b)*

Also, for metals analyzed from muscle tissue of both fish species (*Ameiurus nebulosus* and *Scardinius erythrophthalmus*) BCF_w and BCF_s were calculated and the results are shown in figure 6.

By analyzing the graphs obtained for the two fish species (brown bullhead and rudd) it can be concluded that the species of rudd (*Scardinius erythrophthalmus*) has a higher tendency to accumulate Cu and Pb in relation to the concentrations of these metals in water and in comparison to the concentrations of metals in sediments, a higher bioaccumulation rate was found for Ni and Cu. For the species of brown bullhead (*Ameiurus nebulosus*) the values of bioaccumulation factors succeeded in following order: Pb > Cu > Cd > Cr > Ni as compared to the values in the water, as for BCFs the maximum value was recorded for Cr, while the minimum for Cu, and for the metals: Cd, Ni and Pb, roughly equal values were recorded for BCFs.



(a)



(b)

Fig. 6. *Bioaccumulation factors of heavy metals in fish species biota-water (a) and biota-sediments (b)*

CONCLUSIONS

In this paper, concentrations of heavy metals (Pb, Cd, Cu, Ni and Cr) were determined in water, sediments and biota in order to study the phenomenon of transferring them to the freshwater ecosystem.

Metal concentrations determined in water samples taken from the three selected locations on Plumbuita Lake witin the Municipality of Bucharest were low compared to the national legislation (Ministerial Order no. 161, 2006), falling below the first grade of quality, while for sediment samples the recorded values exceeded their chemical quality standards for Cd, Cu and Pb.

For the two species of fish caught in the lake, *Ameiurus nebulosus* (brown bullhead) and *Scardinius erythrophthalmus* (rudd), no exceedances of the limit of 0.05 mg/kg for cadmium required under applicable law (the EC Regulation 1881/2006) were recorded, while the limit of 0.30 mg/kg required for lead was overcome by both analyzed fish species.

From the comparative analysis of the bioaccumulation factor in relation to water (BCF_w) and the bioaccumulation factor in relation to sediments (BCF_s) of the three analyzed species of aquatic plants, it was found that they posess the ability to accumulate metals in the following order: *Spirogyra algae* > *Ceratophyllum demersum* > *Potamogeton crispus*, generally with a higher bioaccumulation affinity for Cu, Cd and Pb from water and Cu and Ni from sediments.

For the analyzed species of molluscs (*Viviparus viviparus)* it was found that the soft tissue presents a higher degree of bioaccumulation of metals compared to the shell.

As a result of the analysis of heavy metals in the muscle tissue of the two species of fish *Ameiurus nebulosus* (brown bullhead) and *Scardinius erythrophthalmus* (rudd) it was found that both species have a higher tendency to bioaccumulate Cu and Ni as compared to other metals.

In conclusion, regardless of the heavy metal analyzed in the plant or animal tissue, when surveyed, BCF values are higher in the water column, indicating that the bioaccumulation of heavy metals (bioconcentration, bioaccumulation) by biota has a higher share on the following trajectory: water - tissue than the corresponding trajectory sediment - tissue.

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REFERENCES

Adams A., 2014, Analysis of Water Pollution in Gumel Local Government Area Jigawa State, Nigeria. *Journal of Environment and Earth Science*, **12**, pp. 7-11.

Benhamed S., Guardiola F.A., Martínez S., Martínez-Sánchez M.J., Pérez-Sirvent C., Mars M., Esteban M.A., 2016, Exposure of the gilthead seabream (Sparus aurata) to sediments contaminated with heavy metals down-regulates the gene expression of stress biomarkers. *Toxicology Reports*, **3**, pp. 364-372.

Cieszynska M., Wesolowski M., Bartoszewicz M., Michalska M., Nowacki J., 2012, Application of physicochemical data for water-quality assessment of watercourses in the Gdansk Municipality (South Baltic coast). *Environmental Monitoring and Assessment*, **4**, pp. 2017-2029.

Deák Gy., Daescu V., Holban E., Marinescu P., Tanase G.S., Csergo R., Daescu A.I., Gaman S., 2015, Health-environment relation: a key issue of romanian environmental protection. *Journal of Environmental Protection and Ecology*, **16**, pp. 304-315.

De Jonge M., Belpaire C., Van Thuyne G., Breine J., Bervoets L., 2015,Temporal distribution of accumulated metal mixtures in two feral fish species and the relation with condition metrics and community structure. *Environmental Pollution*, **197**, pp. 43-54.

El-Moselhy Kh.M., Othman A.I., Abd El-Azem H., El-Metwally M.E.A., 2014, Bioaccumulation of heavy metals in some tissues of fish in the Red Sea. *Egyptian Journal of Basic and Applied Sciences*, **1**, pp. 97-105.

Ionescu P., Deák Gy., Diacu E., Radu V.-M., 2016, Assessment of heavy metal levels in water, sediment and fish from Plumbuita Lake, Romania. *Rev. Chim. (Bucharest)*, *in press*.

Islam M.S., Ahmed M.K., Raknuzzaman M., Habibullah-Al-Mamun, M., Masunaga S., 2015, Metal speciation in sediment and their bioaccumulation in fish species of three urban rivers in Bangladesh. *Archives of environmental contamination and toxicology*, **68**, pp. 92-106.

Kibria G., Hossain M.M., Mallick D., Lau T.C., Wu R., 2016, Trace/heavy metal pollution monitoring in estuary and coastal area of Bay of Bengal, Bangladesh and implicated impacts. *Marine Pollution Bulletin*, **105**, pp. 393-402.

Li M., Yang W., Sun T., Jin Y., 2016, Potential ecological risk of heavy metal contamination in sediments and macrobenthos in coastal wetlands induced by freshwater releases: A case study in the Yellow River Delta, China. *Marine Pollution Bulletin*, **103**, pp. 227-239.

Maria C., Tociu C., Maria G., 2013, Improvement of aquatic pollutant partition coefficient correlations using 1D molecular descriptors – chlorobenzene case study. *Chemical Papers*, **67**, pp. 73-185.

Mohammadizadeh M., Bastami K.D., Ehsanpour M., Afkhami M., Mohammadizadeh F., Esmaeilzadeh M., 2016, Heavy metal accumulation in tissues of two sea cucumbers, Holothuria leucospilota and Holothuria scabra in the northern part of Qeshm Island, Persian Gulf. *Marine Pollution Bulletin*, **103**, pp. 354-359.

Radu V.-M., Raischi S., Szep R., Tănase G.S, Ionescu P., 2015, Evaluation of priority hazardous substances present in the sediments of the Lower Danube section using multivariate statistical analysis. *Water resources, forest, marine and ocean ecosystems, SGEM*, **1**, pp. 277-283.

Radu V.M., Ivanov A.A., Deák Gy., Diacu E., 2016, Assessment of Heavy Metals Content in Water and Sediments from the Lower Danube River Using EcoIndex. *Rev. Chim. (Bucharest)*, **67**, pp. 649-653.

Resetar-Deac A.-M., Diacu E., 2015, Assessment of Aquatic Environment Contamination with Heavy Metals from Abandoned Mines of Northwestern Romania. *Rev. Chim. (Bucharest)*, **66**, pp. 1535-1539.

Uysal K., Köse E., Bülbül M., Dönmez M., Erdogan Y., Koyun M., Ömeroglu C., Özmal F., 2009, The comparison of heavy metal accumulation ratios of some fish species in Enne Dame Lake (Kütahya/Turkey). *Environmental Monitoring and Assessment*, **157**, pp. 355-362.

***Commission Regulation (EC), 2006, 1881, setting maximum levels for certain contaminants in foodstuffs, *Official Journal of the European Union*, Brussels, 24.

***ISO 5667:2000, Water quality. Sampling. Part 4 - Guidance on sampling from lakes, natural and man-made.

***ISO 8288:2001, Water quality. Determination of cobalt, nickel, copper, zinc, cadmium and lead. Flame atomic adsorption spectrometric methods.

***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).