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# TRACE METALS IN WATER AND SEDIMENTS OF THE PRUT RIVER, ROMANIA

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**Abstract**

A 120 kilometers reach of the Prut River, Romania was surveyed and the concentrations of four trace metals (copper, cadmium, lead and zinc) were determined in water and sediments. These elements are the main pollutants expected in the region, as a steel-producing factory in Romania is located in the close neighborhood of an area under protection, the Lower Prut Floodplain Natural Park. Samples were collected in 2010 and 2011 from the water-sediment interface at six locations along the lower sector of the Prut River. Sediments were sampled only once whereas water samples were collected during four campaigns organized at the end of the summer and beginning of the autumn in order to include both high and low flow regimes of the river. Toxic metals (Pb and Cd) were not found to reach notable levels. The resulted concentrations for all trace metals were lower than the values determined in other Romanian rivers (e.g. Danube) and within the values range imposed by the Romanian regulations for water and sediments quality.

*Key words:* trace metals, Prut River, Romania, sediments, water

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## 1. Introduction

The effects of trace metals contaminations of rivers, lakes and seas have been well-documented for different living organisms (Burada et al., 2017; Manahan, 2009; Triebskorn et al., 2008; Zubcov et al., 2012). Therefore, it is of great importance to assess and monitor trace metals in different types of waters. Moreover, sediments analysis can provide useful information regarding mid- and long-term pollution of the aquatic bodies, since they are able to seal and occasionally release important amounts of heavy metals depending on the river regime and extreme situations, such as flooding or severe drought or changes in redox potential (van Gestel, 2008; Verhoeven, 2009). The content of trace metals in water samples collected from Romanian rivers has been investigated so far mostly for the central and western part of the country where traditional metal mining activities led to long-lasting pollution (Bird et al., 2009; Florea et al., 2005; Marin et al., 2010; Paiu et al., 2017; Piştea et al., 2013; Zobrist et al., 2009). However, less investigated is the content of trace metals in rivers sediments (Kraft et al., 2006; Osán et al., 2007; Ponta et al., 2002; Vignati et al., 2013). Trace metals pollution of the rivers crossing the

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southern part of Romania has been also reported (Florea et al., 2005; Matache et al., 2009; Mladin et al., 2010; Stoica et al., 2000a), due to the presence of chemical industries existing in this region, e.g. in or in the vicinity of cities like Târgoviște and Slobozia or Râmnicu Vâlcea and Craiova. In addition, the human and natural impact on the water quality of the Prut River, situated in the eastern part of the country, has also been assessed lately. The ecological status of the Prut hydrological basin was monitored and reported (Bucuresteanu et al., 2008; Corduneanu et al., 2016; David et al., 2012; Lozba-Stirbuleac et al., 2011; Teodosiu et al., 2009; Voiculescu et al., 2011) by evaluation of some biological, chemical and physical indicators as well as some hydro-morphological aspects.

The Prut River is the natural Eastern border between Romania and Moldova. Prior to entering the Lower Prut Floodplain Natural Park (our study area), the Prut River crosses more than 900 km, collecting water from a 27,000 $km^2$ watershed. The potential pollution sources are both agricultural and industrial (Balteanu, 2006). The Lower Prut Floodplain Natural Park is a recently established protected area including the wetlands and lakes from the inferior sector of the Prut River. Wetlands are of great importance for the environment, due to their unique characteristic to make the transition from terrestrial to aquatic ecosystems (Barker and Maltby, 2009). As a result of the fluctuating water levels of rivers (flooding and drought), intense biogeochemical processes occur leading to modifications of the ecosystems evolution (Verhoeven, 2009). The existence of this dynamic ecosystem, which includes both valuable habitats and species, is conditioned by the water quality. Thus, metal contamination of water and sediments can have serious consequences on species perpetuation due to bioaccumulation and biomagnification processes that might appear and subsequently determine physiological changes in species, food contamination etc. (David et al., 2012; Antal et al., 2013).

Due to the ecological importance of the Lower Prut Floodplain Natural Park, two European *Natura 2000* sites overlapping the over 8000 ha park area (Natura 2000 code ROSCI0105 and ROSCI0213) have been declared in order to ensure its conservation.

The park is situated in the vicinity of the most important steel-producing factory in Romania, thus constituting the potential most important pollution source of the river. Therefore, monitoring of trace metals, especially of those with toxic effects on wildlife, is essential for the park conservation. Thus, the aim of this study was to determine the concentration levels of potentially harmful trace metals in water and sediment samples collected from the Lower Prut Floodplain Natural Park.

The obtained data will represent the starting point for the authorities in charge to take the correct measures that will prevent their bioaccumulation and biomagnification in living organisms through the food chain. The reach of the Prut River belonging to the park, of approximately 120 km, was surveyed for the concentration of four trace metals (Cu, Pb, Cd and Zn) in water and sediment samples. The results described herein were obtained for the samples collected from six locations along the lower sector of the Prut River and their concentrations were evaluated during different river regimes (flooding and drought) through a period of two years (2010-2011).

## 2. Experimental

### *2.1. Sample collection*

The monitoring program involved one sampling campaign (September 2010) for sediments and four campaigns for water samples collections (September 2010, October 2010, August 2011, October 2011) during different river regimes (i.e. high and low discharges – Table 1). The analyzed river reach was characterized by samples collected from six sampling locations, determined using a judgmental sampling plan that considered geographical and geological characteristics of the region (river flow rate – Table 1, soils, geology) and main pollution sources that could affect the water quality (David et al., 2012). Fig. 1 shows the locations of the six sites where samples were collected from the Prut River.

From a lithological point of view, the Lower Prut reach is dominated by quaternary sands and clays. The soils within the analyzed Prut River reach belong to mollisols and entisols orders. Mollisol are mainly chernozems, formed in an excess of water, where anoxic alteration determines the formation of humic substances and $H_2S$, which precipitate the iron ions to ferrous sulphide. The entisols are characteristics of the Brates Lake surroundings and are characterized by a lesser amount of humic substances and an increased content of salts (Ioja and Savulescu, 2007).

Sampling point 1 *Cavadineşti* (C on the map) - near the Maţa – Rădeanu fish ponds - is located at the point where the Prut River enters Galați County (northern limit of the Lower Prut Floodplain Natural Park). Sampling point 2 – *Rogojeni* (R) – is located downstream of Pochina and Leahu lakes and village of Rogojeni. Sampling point 3 – *Vlădeşti* (V) – lies downstream of Vlădeşti, Şovârca and Măicaş lakes and villages like Oancea, Slobozia-Oancea and Vlădeşti. Sampling point 4 – *Măstăcani* (M) – is located downstream of Vlăşcuţa lake (Romanian side) and Manta lake (Republic of Moldova) and Brăneşti and Măstăcani villages.

**Table 1.** Water flow values for the Prut River, measured in Oancea during the sampling campaigns*

| ***Month*** | ***August 2010*** | ***September 2010*** | ***October 2010*** | ***August 2011*** | ***September 2011*** | ***October 2011*** |
|---|---|---|---|---|---|---|
| Water flow ($m^3/s$) | 312 | 165 | 123 | 49.2 | 49.7 | 47.3 |

*Official data from the Romanian Water Management Company

Sampling point 5 – *Șivița* (Ș) - is located near the village of Șivița, which is influenced by the Beleu Lake (Moldova) (by an input of higher trace metals concentration during drought periods mainly due to lack of dilution by precipitations and, to a smaller extent, lake water evaporation). Sampling point 6 – *Giurgiuleşti* (G) – lies upstream of Prut River – Danube River junction and is influenced by the Brateş Lake (different sedimentation rate compared with the river, longer contact time of water with sediments) and agricultural fields (through contaminated runoff) in the area. It is the closest point to the city of Galaţi, which hosts the most important Romanian steel factory. Labelled high-density polyethylene bottles were used for collecting the water samples and nitric acid (Merck, 65%) was used as a fixation reagent, in order to prevent analyte losses. Sediments were collected from the upper 10 cm of the alluvial sediments bed. Samples were stored in Teflon boxes and frozen prior to chemical analysis.

*2.2. Sample pre-treatment*

*Water samples:* The samples were digested prior to analysis in order to obtain the real concentration of trace metals that the analyzed water transports. 3 mL concentrated $HNO_3$ and 10 mL concentrated HCl were added to 250 mL water sample, in a Berzelius beaker. The sample was digested on an electric hot plate (90 – 100 ºC). After cooling, the solution was filtered through a 0.45 µm pores filter paper in order to remove the insoluble particles which may clog the nebulizer. The filter was washed three times with ultrapure water to avoid analyte losses. The filtrate was diluted with ultrapure water to a final volume of 25 mL.

*Sediment samples:* 0.5-1.0 g of dry sediment sample (fraction < 63 µm) was finely ground and introduced in a 150 mL Berzelius beaker. A volume between 2.5-5.0 mL concentrated $HNO_3$ and 7.5-15 mL HCl were added preserving a 1:3 ratio between the acids. The vessel was capped with a weighing plate and left to rest for 24 h at room temperature. Then, the sample was concentrated (without bringing to dryness) by heating on a hot electric plate.

The beaker was cooled and 10 mL of ultra-pure water were added. The resulted solution was heated to the boiling point in order to allow salts dissolution and filtered on a filter paper with medium porosity. The filter and the beaker were rinsed with warm water collecting all washing waters in a 50 mL volumetric flask that was brought to constant volume with ultrapure water.

*2.3. Sample analysis*

The concentrations of the trace metals (copper, cadmium, lead and zinc) were determined by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). If not indicated otherwise all reagents used for sediments digestions, water samples conservation and trace metal determination were of analytical reagent grade and purchased from Sigma-Aldrich. Ultrapure water (18.2 MΩ cm) produced with the ULTRA CLEAR system (Siemens, Germany) was used for the preparation of all solutions. Stock solutions of 1,000 mg $L^{-1}$ of each analyzed element were prepared by dissolving the metal samples in $HNO_3$ (1:1) and proper dilution with ultrapure water. Determinations of the trace metals were carried out using a dual view inductively coupled plasma - optical emission spectrometer ICP-OES type Optima 5300 DV Perkin Elmer. Argon (spectral quality) was used for metals determination. The plasma parameters were as follows: nebulizer flow 0.8 L $min^{-1}$; plasma flow 15 L $min^{-1}$; auxiliary flow 0.2 L $min^{-1}$; power 1300 W; axial plasma viewing mode. The wavelengths for metal determination are as follows: 228.802 for Cd; 327.396 for Cu; 220.353 for Pb and 206.200 for Zn, respectively. The calibration curve was made with Multielement Standard Reference Material type Quality Control Standard 21, Perkin Elmer, 100 mg·$L^{-1}$ (Cu, Pb, Cd, Zn). The method of analysis and its parameters for simultaneously determination of metals by ICP-OES were used according to the Romanian standard (ISO, 2007). The limits of detection (LOD) for the method were 0.4 µg $L^{-1}$ (Cd), 1 µg $L^{-1}$ (Cu), 2.0 µg $L^{-1}$ (Pb) and 0.5 µg $L^{-1}$ (Zn).

## 3. Results and discussion

*3.1. Trace metals concentration in water samples*

Trace metals (Cu, Zn, Pb and Cd) concentration levels in water samples collected from the Prut River in 2010 and 2011 (Table 2) were found to be below the maximum admitted concentrations (MAC) established by the Romanian regulations for freshwater bodies, 1$^{st}$ category of quality (MEWM, 2006). Copper and zinc concentrations levels determined in water samples of the Prut River have shown similar trends along the investigated sector (Figs. 2 and 3) with the highest concentration (19.7 µg$L^{-1}$ and 72.0 µg$L^{-1}$ for copper and zinc, respectively) recorded in October 2011 in samples collected from Vlădești (V) (sampling point 3). The concentration of zinc registered in Vlădești was the highest of all points from the surveyed area in three of the four sampling campaigns (the exception is September 2010, when the maximum was recorded in Măstăcani, Fig. 3). These values might be a result of the anthropogenic contamination of the river water (construction works performed at the border-crossing point in Oancea that involved shore consolidation or activities from the urban center in Cahul, Moldova). In the lakes adjacent to the river (e.g. Pochina, Vlășcuța, Vlădești), water is in contact with sediments for longer periods, and during drought periods (such was the case of the summer of 2011) the water level decreases significantly due to lack of precipitation, leading thus to increased concentrations of elements.

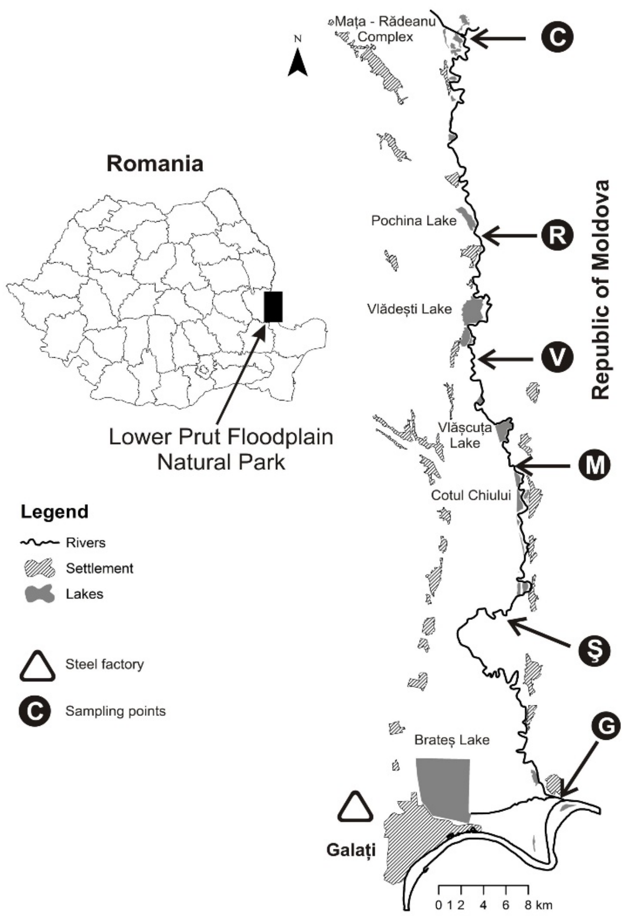


**Fig. 1**. Lower Prut Floodplain Natural Park positioning in Romania. Park area and surroundings. Location of sampling sites

**Table 2.** Ranges of trace metals concentrations in the water samples of the Prut River

| *Sampling point* / *Element* | *Concentration range (μg L[-1])* | | | | | | |
|---|---|---|---|---|---|---|---|
| | *Cavadineşti (C)* | *Rogojeni (R)* | *Vlădeşti (V)* | *Măstacani (M)* | *Şiviţa (Ş)* | *Giurgiuleşti (G)* | *MAC** |
| Cu | 5.4-9.6 | 7.0-8.4 | 4.1-19.7 | 7.1-11.2 | 6.0-11.7 | 4.3-11.1 | 20 |
| Zn | 9.2-16.9 | 8.0-24.1 | 8.0-72.0 | 7.4-25.4 | 7.6-40.4 | 4.0-36.8 | 100 |
| Pb | <LOD-2.1 | <LOD-2.7 | <LOD-9,6 | <LOD-11 | <LOD-4.3 | <LOD-2.5 | 5 |
| Cd | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 0.5 |

*(MEWM, 2006)

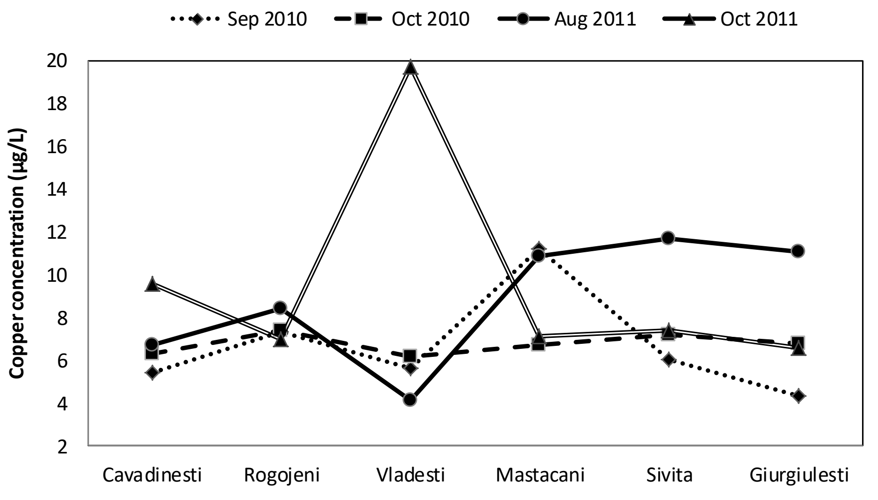


**Fig. 2.** Variation of copper concentrations in water samples collected from the Prut River

Despite the fact that these concentrations are very close to MAC according to Romanian regulations (20 μg $L^{-1}$ and 100 μg $L^{-1}$ for copper and zinc, respectively) for freshwater bodies they still remain under these limits. Thus, concentration levels of these two trace elements in the water of Prut River met the legal requirements in all collected samples (MEWM, 2006). As seen in Fig. 3, zinc concentration appears to increase during 2011 in comparison to 2010. The year 2011 has been characterised by a severe drought compared with 2010 (Table 1), the lack of precipitation determining an increase in metal concentration. As a consequence of the use of lead-containing gasoline for a long time, lead is a frequent contaminant of the Romanian freshwater bodies, and several cases of pollution have been documented, e.g. in the rivers Argeș 0.88 – 42.90 μg $L^{-1}$ (Stoica et al., 2000b), Ialomița 23.9 – 52.1 μg $L^{-1}$ (Matache et al., 2009), Roșia Montană 1.0 – 539.0 μg $L^{-1}$ (Florea et al., 2005) and in Danube River sediments 70.0-347.5 mg $kg^{-1}$ (Matache et al., 2002).

Despite this, to our surprise, lead was detected only in eight of the 24 collected water samples (Table 3) and from these only two samples (collected in 2011) showed lead at concentrations higher than 5.00 μg $L^{-1}$ which is the MAC for lead in freshwater bodies according to the Romanian regulations (MEWM, 2006). These results could be explained by the fact that there is only one national road in close vicinity of the park, which is not hosting important vehicles traffic. Moreover, since lead gasoline was banned from use almost 6 years ago (since January 1st, 2005) any obsolete concentration should come from the sediment bed. No other source of lead was identified within the park area. For all the analyzed samples cadmium concentrations were below the LOD (0.4 μg $L^{-1}$).

*3.2. Trace metals concentrations in sediment samples*

Sediment samples were collected in September 2010 from the six above mentioned sampling points situated along the inferior sector of the Prut River. The concentration levels of all four analyzed elements showed an increasing trend from upstream to the river junction with the Danube River, where the important urban community – Galaţi – and the largest steel factory in Romania are located (Figs. 4-6).

For copper there is a moderate increasing trend (Fig. 5). With the exception of sediment samples collected from sampling points 2 (Rogojeni) and 6 (Giurgiuleşti) copper concentrations remain in the range 30-40 mg $kg^{-1}$, below the MAC for copper of 40 mg $kg^{-1}$ (MEWM, 2006). As observed in Fig. 4-6, all four analyzed trace elements (Pb, Cd, Cu and Zn) showed an intermediate maximum in the samples collected from the second sampling point (Rogojeni).

Several lakes communicating with the river are located upstream Rogojeni. During the summer, the water level decreases significantly (up to completely dry, as it happened in 2011) and the lakes lose communication with the river.

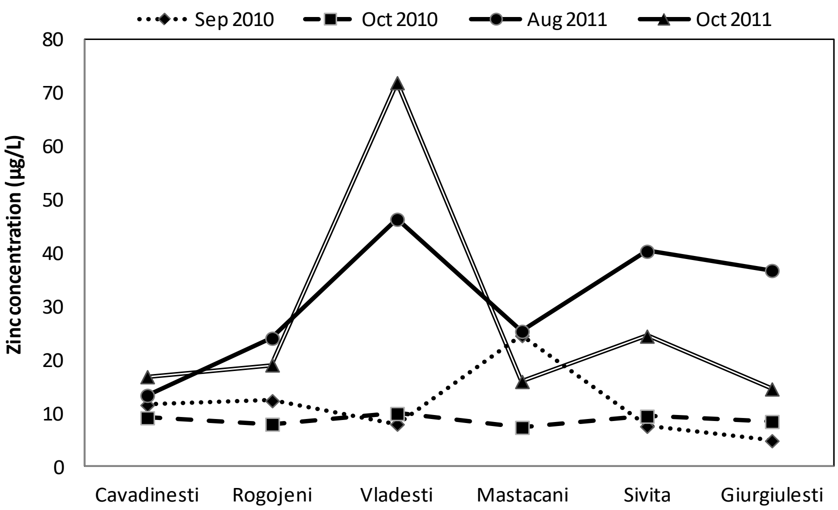


**Fig. 3.** Variation of zinc concentrations in water samples collected from the Prut River

**Table 3.** Lead concentrations in water samples from the Prut River

| ***Sampling point*** / ***Month*** | ***C*±SD (μg L⁻¹)*** | | | |
|---|---|---|---|---|
| | ***September, 2010*** | ***October, 2010*** | ***August, 2011*** | ***October, 2011*** |
| *Cavadineşti (C)* | <LOD | 2.00±0.02 | <LOD | <LOD |
| *Rogojeni (R)* | 2.10±0.03 | 2.70±0,01 | <LOD | <LOD |
| *Vlădeşti (V)* | <LOD | 2.40±0.04 | <LOD | 9.60±0.03 |
| *Măstăcani (M)* | <LOD | <LOD | 11.00±0.06 | <LOD |
| *Şiviţa (Ş)* | <LOD | <LOD | 4.30±0.01 | <LOD |
| *Giurgiuleşti (G)* | <LOD | <LOD | 2.50±0.02 | <LOD |

*C** - mean concentration of three determinations, SD = standard deviation

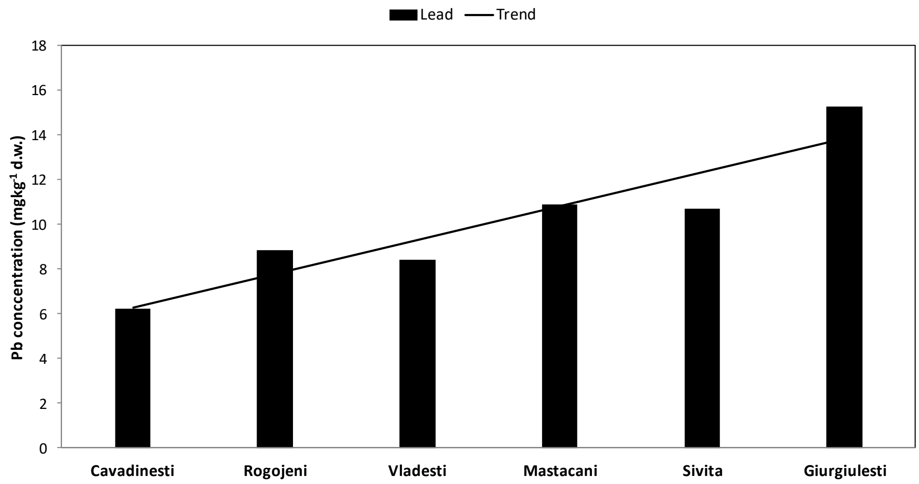


**Fig. 4.** Variation of lead concentrations in sediments collected from the six sampling points located along the Prut River

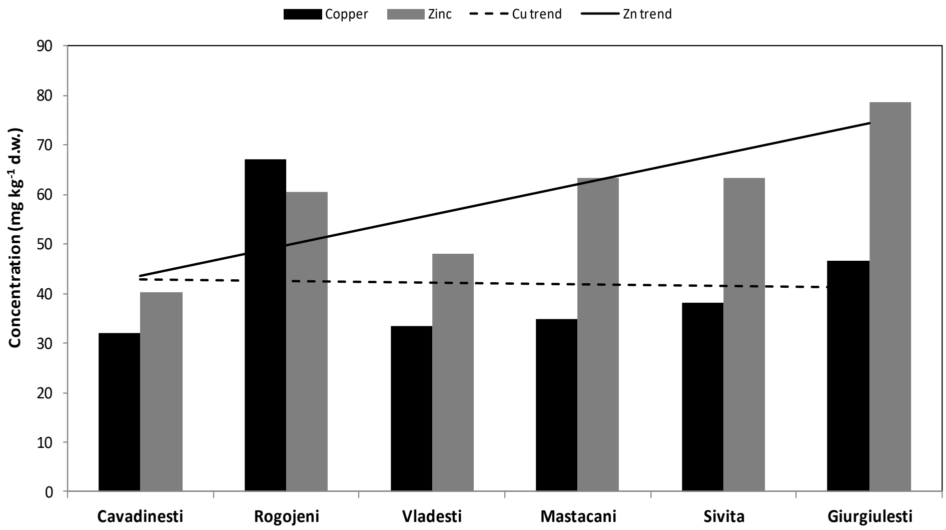


**Fig. 5.** Variation of copper and zinc concentrations in sediments collected from the six sampling points located along the Prut River

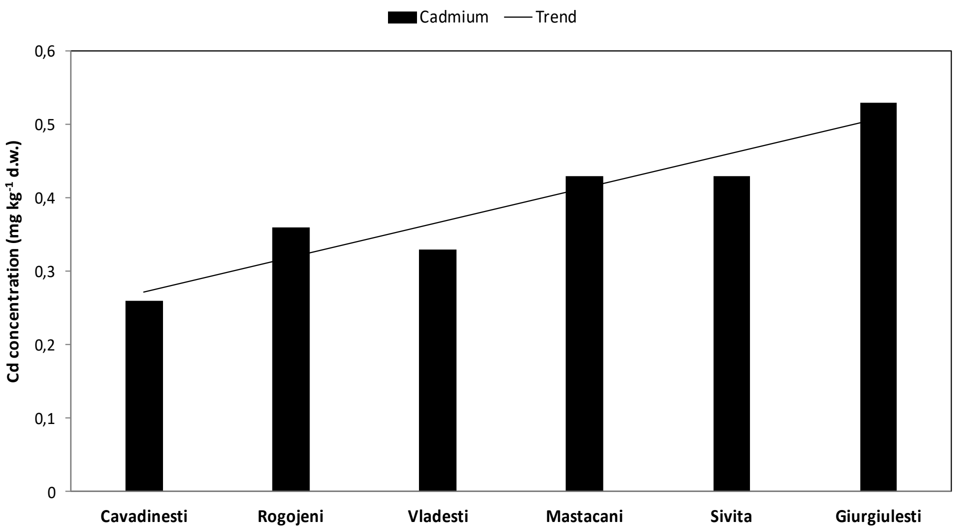


**Fig. 6.** Variation of cadmium concentrations in sediments collected from the six sampling points located along the Prut River

This determines accelerated sedimentation (due to reduced movement of water) and changes in the redox potential (oxygen depletion, increased input of nutrients due to agriculture and subsequently higher content of organic matter due to flora development) and subsequently an increase in trace metals concentration. When the water level increases again, important amounts of metals can be release into the water column. The highest trace metals concentration was found in sediments collected from Giurgiulești (G). As it was already stated, this observation might be explained by the close vicinity of the large city, Galați, hosting the old and huge steel factory, long-distance pollution bringing its contribution to the level of trace metals in the ecosystem. The metals concentrations decreases while distance from the source increases.

Nevertheless, the investigated trace metals concentrations in all collected sediment samples (with the two exceptions observed for copper) remain much below the MAC established for sediments which are 0.8 mg $kg^{-1}$ for cadmium, 85 mg $kg^{-1}$ for lead and 150 mg $kg^{-1}$ for zinc, respectively (MEWM, 2006).

### *3.3. Comparison with similar studies on the Prut River*

We compared the results obtained within our survey with similar studies carried out on the Prut River sediments in the last 10 years (Table 4), in order to assess whether the contamination sources are permanent and remained active or whether an accidental contamination occurred. Two of the studies were performed on the Moldavian shore of the Prut River (Postolachi et al., 2012; Rusu et al., 2004) and one on the Romanian one (Mocanu et al., 2006). All studies considered a wider part of the Prut River, but one identical point – Giurgiulești (G) was identified, and also one very similar point - Oancea, close to the our Rogojeni (R) sampling point. It is important to note that all the studies referred to total concentration of metals in sediments (and not in specific phases) and used methods of analysis of similar performances.

The concentrations of cadmium and zinc are similar in three of the four sets of data, except for the data of Rusu et al. (2004), where the element concentration is ten times lower. For lead, all data are comparable, suggesting that a concentration of lead up to 30.0 mg $kg^{-1}$ (the maximum concentration registered in all studies) represents the natural background level of the element within the sediments of the Prut River. Since the soils constituents do not indicate any natural origin for the element, the differences within this range are generated by anthropogenic input (atmospheric deposition, most-likely due to lead-containing fuels combustion).

Our results showed the highest amount of copper in the sediments samples of all sets and the concentration in both sampling points (i.e. 2 - Rogojeni and 6 - Giurgiulești) must be carefully considered because it exceeds the Romanian standards. Since the other three data sets exhibit similar values, it is possible that an accidental pollution appeared on the Romanian shore of the river. The accidental pollution is supported by the Cu – Zn ratio (Fig. 5), which is higher than 1 only for the sample from Rogojeni. Also relevant is the fact that the highest value appears in Rogojeni, the sampling point which is not included in the previous studies; therefore a bigger difference is expected to a certain extent. For Giurgiulești, the copper concentration level is similar with those recorded by Rusu et al. (2004) and Mocanu et al. (2006).

## 4. Conclusions

The heavy metals (Cu, Zn, Pb and Cd) concentration levels in sediments and water samples collected in 2010 and 2011 from six locations situated along the inferior reach of the Prut River were evaluated and one may conclude that there are minor issues regarding the water and sediment quality of the Prut River. The results obtained for water samples demonstrated that the four investigated trace elements were present at concentration levels below the maximum admitted concentration imposed by the Romanian regulations for freshwater bodies.

Only one exception is recorded for the water samples collected in 2011, where copper and zinc concentrations were higher and very close to the maximum admitted concentration, most likely a consequence of a low flow rate of the Prut River. Moreover, cadmium concentrations in all collected water samples were below the method's detection limit.

**Table 4.** Concentrations of trace metals (in mg $kg^{-1}$) in sediments of the Prut River

| ***Survey*** | ***Cu*** | | ***Cd*** | | ***Pb*** | | ***Zn*** | |
|---|---|---|---|---|---|---|---|---|
| | ***Oancea**** | ***G*** | ***Oancea**** | ***G*** | ***Oancea**** | ***G*** | ***Oancea**** | ***G*** |
| Rusu et al., 2004 | | | | | | | | |
| 2001 | 36.7 | 40.8 | 0.08 | 0.09 | 8.9 | 29.7 | 9.6 | 16.3 |
| Mocanu et al., 2006 | | | | | | | | |
| 2001 | 20.0-30.0 | 30.0-40.0 | 0.25-0.30 | 0.15-0.20 | 10.0-20.0 | 20.0-30.0 | 60.0-80.0 | 80.0-98.0 |
| Postolachi et al., 2012 | | | | | | | | |
| 2009 | 23.0-26.0 | 17.5-20.0 | 0.6-0.7 | 0.5-0.6 | 17.5-20.0 | 12.5-15.0 | 75.0-87.5 | 55.0-70.0 |
| 2010 | 12.5-17.5 | 7.5-10.0 | 0.3-0.4 | 0.2-0.3 | 11.0-13.0 | 9.0-11.0 | 67.5-75.0 | 30.0- 40.0 |
| Our data | | | | | | | | |
| 2010 | 67.0 | 46.7 | 0.36 | 0.53 | 8.85 | 15.3 | 60.5 | 78.6 |

*for our set of data, results from Rogojeni are considered

Thus, toxic metals (Cd and Pb) were not detected to reach notable levels. This may be attributed to the fact that the investigated reach of the Prut River passes through a protected area where anthropogenic activities are limited. The observed increasing trend of trace metals concentrations from upstream to the junction with the Danube River underlines the need for long-term monitoring of trace elements on the investigated Prut River reach.

Finally, the concentrations of the three investigated trace metals (Cd, Pb, Zn) in sediments were in all collected samples much below the MAC established for sediments, indicating a natural occurrence of these elements in sediments of the Prut River. The situation is slightly similar for the copper concentrations also, with the exception of sediment samples from points 2 – Rogojeni (R) and 6 - Giurgiuleşti (G), exceeding Romanian maximum admitted concentration. The results and the change in Cu – Zn ratio indicate an accidental point source. Copper, in particular, requires a continuous evaluation in future studies in order to carefully monitor further contamination and prevent severe consequences on the ecosystem viability.

A general conclusion of the study would be that the general level of pollution on the investigated reach is rather low and thus the immediate threat on the living organisms from the Lower Prut Floodplain Natural Park is limited.

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## References

Aantal L., Halasi-Kovacs B., Nagy S. A. (2013), Changes in fish assemblage in the Hungarian section of River Szamos/Somes after a massive cyanide and heavy metal pollution. *North-Western Journal of Zoology*, **9**, 131-138.

Balteanu D., (2006), *Romania. Space, Society, Environment*, Romanian Academy Publishing House, Bucharest, Romania.

Barker T., Maltby E., (2009), *Introduction – The Dynamics of Wetlands*, In: *The Wetlands Handbook*, Barker T., Maltby E. (Eds.), Wiley-Blackwell, Oxford, 115-119.

Bird G., Macklin M., Brewer P., Zaharia S., Balteanu D., Driga B., Serban M., (2009), Heavy metals in potable groundwater of mining-affected river catchments, North-Western Romania, *Environmental Geochemistry and Health*, **31**, 741-758.

Bucuresteanu M., Rosca B., Grigoras V., (2008), *European Monitoring on the Ecological Status of Water Bodies in the Basin of the Prut River - a River on the EU Eastern Border*, 2nd Int. Conf. on Waste Management, Water Pollution, Air Pollution, Indoor Climate, Mastorakis N. E., Poulos M., Mladenov V., Bojkovic Z., Simian D., Kartalopoulos S. (Eds.), October 26-28, 2008, Corfu, Greece, 106-111.

Burada A., Teodorof L., Despina C., Seceleanu-Odor D., Tudor M., Ibram O., Navodaru I., Murariu G., Topa C.M., Tudor M., (2017), Trace elements in fish tissue with commercial value of the Danube Delta biosphere reserve, *Environmental Engineering and Management Journal*, **16**, 731-738.

Corduneanu F., Vintu V., Balan I., Crenganis L., Bucur D., (2016), Impact of drought on water resources in North - Eastern Romania. Case study - the Prut River, *Environmental Engineering and Management Journal*, **15**, 1213-1222.

David I. G., Matache M. L., Tudorache A., Chisamera G., Rozylowicz L., Radu G. L., (2012), Food chain biomagnification of heavy metals in samples from the Lower Prut Floodplain Natural Park, *Environmental Engineering and Management Journal*, **11,** 69-73.

Florea R.M., Stoica A.I., Baiulescu G.E., Capotă P., (2005), Water pollution in gold mining industry: a case study in Roşia Montană district, Romania, *Environmental Geology*, **48,** 1132-1136.

Ioja C., Savulescu I., (2007), Favorable and restrictive environmental restriction in Lower Prut Floodplain Natural Park, *Geographical Communications* (*Comunicari de Geografie)*, **11**, 541-546.

ISO, (2007), 11885 Water quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES), On line at: http://www.iso.org/iso/catalogue_detail.htm?csnumber=36250

Kraft C., von Tümpling W., Zachmann D. W., (2006), The effects of mining in Northern Romania on the heavy metal distribution in sediments of the rivers Szamos and Tisza (Hungary), *Acta Hydrochimica et Hydrobiologica*, **34**, 257-264.

Lozba-Stirbuleac R. S., Giurma-Handley C. R., Giurma I., (2011), Water quality characterization of the Prut River, *Environmental Engineering and Management Journal*, **10**, 411-419.

Manahan S. E., (2009), *Environmental Chemistry*, CRC Press, Boca Raton.

Marin C., Tudorache A., Moldovan O.T., Povara I., Rajka G., (2010), Assessing the contents of arsenic and of some heavy metals in surface flows and in the hyporheic zone of the Aries stream catchment area, Romania, *Carpathian Journal of Earth and Environmental Sciences*, **5,** 13-24.

Matache M., Pătroescu C., Pătroescu-Klotz I., (2002), Heavy metals concentration in alluvial sediments of Danube on the Bazias - Portile de Fier I sector (1996-1999) (RO), *Revista de Chimie*, **53**, 623-626.

Matache M. L., David I. G., Matache M., Ropota M., (2009), Seasonal variation in trace metals concentrations in the Ialomita River, Romania, *Environmental Monitoring and Assessment*, **153**, 273-279.

MEWM, (2006), Order of the Minister of Environment and Water Management no.161. for the approval of the norms regarding freshwater classification for establishing the ecological status of water bodies, *Romanian Official Monitor*, **511bis,** 2-92.

Mladin C., Preda A., Stefanescu I., Barbu C., (2010), Comparative Study of Heavy Metals from Rivers Around Ramnicu Valcea and Craiova Chemical Platforms from Romania, *Asian Journal of Chemistry*, **22,** 3169-3172.

Mocanu R., Cucu-Man S., Steinnes E., (2006), *Heavy Metals Pollution: An Everlasting Problem*. In: *Environmental Simulation Chambers: Application to Atmospheric Chemical Processes*, Barnes I., Rudzinski K. (Eds.), Springer, The Netherlands.

Osán J., Török S., Alföldy B., Alsecz A., Falkenberg G., Baik S. Y., Van Grieken R., (2007), Comparison of sediment pollution in the rivers of the Hungarian Upper Tisza Region using non-destructive analytical techniques, *Spectrochimica Acta Part B: Atomic Spectroscopy*, **62**, 123-136.

Paiu M., Iancu O.G., Breaban I.G., (2017), Geochemical distribution of trace elements in an abandoned waste mine dump from Giumalau Mountains, Romania, *Environmental Engineering and Management Journal*, **16**, 847-857.

Piștea I., Roșu C., Martonoș I. Ozunu A., (2013), Romanian surface water quality: Tarnava Mare River between Medias and Copsa Mica case study, *Environmental Engineering and Management Journal*, **12,** 283-289.

Ponta M., Frentiu T., Rusu A. M., Cordos E. A., (2002), Traces of Cu, Mn and Zn in aquatic animals and sediments from the Cris river basin West Romania. Part I: Statistical evaluation of data obtained by atomic emission spectrometry with radiofrequency capacitively coupled plasma source and flame atomic absorption spectrometry, *Croatica Chemica Acta,* **75**, 291-306.

Postolachi L., Rusu V., Maftuleac A., Lupașcu T., Mitina T., (2012), *Assessment of Heavy Metals Content in Bottom Sediments and their Interstitial Water of the River Prut (Moldova),* Proc. Conf. on Air and Water – Components of the Environment, March 23rd – 24th, 2012, Presa Universitară Clujeană Publishing House, 141-148.

Rusu V., Lupașcu, T., Revenco, M., Postolachi L., (2004), Dynamics of heavy metals in sediments from River Prut, *Environmental Engineering and Management Journal,* **3,** 305-312.

Stoica A.-I., Capotă P., Baiulescu G.E., (2000a), Determination of Copper, Cadmium, Zinc and Lead in Arges River in Romania during four seasons by Inductively Coupled Plasma Atomic Emission Spectrometry and Anodic Stripping Voltammetry, *Analytical Letters,* **33**, 3025-3035.

Stoica A.I., Baiulescu G.E., Enein H.Y.A., (2000b), Analytical studies on the pollution of Argeş River, *Toxicological and Environmental Chemistry,* **77**, 143-149.

Teodosiu C., Cojocariu C., Musteret C.P., Dascalescu I.G., Caraene I., (2009), Assessment of human and natural impacts over water quality in the Prut River basin, Romania, *Environmental Engineering and Management Journal,* **8,** 1439-1450.

Triebskorn R., Telcean I., Casper H., Farkas A., Sandu C., Stan G., Colărescu O., Dori T., Köhler H.-R., (2008), Monitoring pollution in River Mureş, Romania, part II: Metal accumulation and histopathology in fish, *Environmental Monitoring and Assessment,* **141,** 177-188.

Van Gestel C. A. M., (2008), Physico-chemical and biological parameters determine metal bioavailability in soils, *Science of the Total Environment,* **406,** 385-395.

Verhoeven J. T. A., (2009), *Wetland Biogeochemical Cycles and Their Interactions*, In: *The Wetlands Handbook,* Maltby E., Barker T. (Eds.), Wiley-Blackwell, Oxford, 266-281.

Vignati D.A.L., Secrieru D., Bogatova Y.I., Domnik J., Cereghino R., Berlinsky N.A., Oaie G., Szobotka S., Stanica A., (2013). Trace element contamination in the arms of the Danube Delta (Romania/Ukraine): Current state of knowledge and future needs, *Journal of Environmental Management,* **125**, 169-178.

Voiculescu M., Georgescu L. P., Dragan S., Timofti M., Caldararu A., (2011), Study of the anthropogenic effects on the quality of the lower prut river, *Journal of Environmental Protection and Ecology,* **12,** 16-24.

Zobrist J., Sima M., Dogaru D., Senila M., Yang H., Popescu C., Roman C., Bela A., Frei L., Dold B., Balteanu D., (2009), Environmental and socioeconomic assessment of impacts by mining activities — a case study in the Certej River catchment, Western Carpathians, Romania, *Environmental Science and Pollution Research,* **16,** 14-26.

Zubcov E., Zubcov N., Ene A., Biletchi L., (2012), Assessment of copper and zinc levels in fish from freshwater ecosystems of Moldova, *Environmental Science and Pollution Research,* **19,** 2238-2247.