ASSESSMENT OF HEAVY METALS CONTENT IN BOTTOM SEDIMENTS AND THEIR INTERSTITIAL WATER OF THE RIVER PRUT (MOLDOVA)

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ABSTRACT. – Assessment of heavy metals content in bottom sediments and their interstitial water of the River Prut (Moldova) Composition and quality of natural waters, determined by several factors depending on environmental conditions, is influenced also by the equilibrium of mobilization-immobilization processes of pollutants at the interface of the various phases, in particular, water-particulate materials-bottom sediments system. The peculiarities of spatial, seasonal and multi-annual dynamics of heavy metals content (Cu, Ni, Cr, Zn, Pb, Cd) in aquatic sediments and their interstitial water along the Prut River were established. In order to determinate total content of heavy metals in bottom sediments the procedure recommended by the Geological Agency of USA was used. Obtained results revealed the accumulation of most metals in bottom sediments on the lower course of the Prut River. Maximal content of Zn was recorded on the middle course of the river.

„Keywords”: heavy metals, bottom sediments, interstitial water.

1. INTRODUCTION

Heavy metals are generally considered as serious inorganic pollutants due to their toxic effects, surface enrichment, and slow removal rates. Potentially toxic heavy metals can be inadvertently released from diverse sources into aquatic environments and living habitats by human activity. Once metal contaminants are released into ecosystems, they accumulate in soil, water, sediments, and biota, and accelerate pollution (Jung et al., 2010). Sediments are an important reservoir of heavy metals. They can act as both a source and a sink for such contaminants (Mariani and Pompêo, 2008). According European Union Directive 2006/11/EC, due to its toxic properties, metals and their compounds are included in the list of the main hazardous pollutants for the environment.

The objectives of this paper were (i) to evaluate peculiarities of spatial, seasonal and multi-annual dynamics of heavy metals (Cu, Ni, Cr, Zn, Pb, Cd) level in bottom sediments of the Prut River and (ii) to perform comparative analysis of heavy metals content in interstitial water and bottom sediments.

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2. CASE STUDY

The Prut River, a Danube tributary, is a transboundary river at the centre of Europe. Hydrographical basin has surface about 27 500 km^2 of which on the territory of Ukraine - 9500 km^2, Romania - 9760 km^2 and Moldova - 8240 km^2 (Rusu and Lupascu, 2004). The Prut River has length of 967 km, of which 695 km on territory of Moldova. Samples of bottom sediments were collected during the spring and summer of several years along the Prut River (sites Costesti, Sculeni, Valea Mare, Cahul, Caslita-Prut, Giurgiulesti, Fig. 1).

In order to determine content of heavy metals (Cu, Ni, Cr, Zn, Cd, Pb) in the bottom sediments and their interstitial water, fresh (wet) samples were used. The procedure recommended by USA Geological Survey was used to determine total acid-recoverable content of metals in sediments (***1989). Content of heavy metals in interstitial water was determined after centrifugation of fresh (wet) sediments. After that interstitial water was filtered through 0.45 μm pore diameter filters. Heavy metal analyses were conducted using atomic absorption spectrometer AAS-3. Multi-annual data sampling was performed according with the principle of rotation (rotational approach) (Hirch, 1988).

Fig. 1. ***The River Prut (transboundary river between Moldova and Romania). Sampling sites: Costesti, Sculeni, Valea Mare, Cahul, Caslita-Prut, Giurgiulesti.***

3. RESULTS AND DISCUSSION

3.1 Spatial, seasonal and multi-annual dynamics of heavy metals level in bottom sediments

Spatial dynamics for the most metals (Cu, Cr, Ni, Pb, Cd) during spring and summer of 2009 year had similar trend, being recorded the increasing tendency of the metals amount along the Prut River (Fig. 2). Spatial dynamics established for Zn level was different. To be mentioned, the maximal amount of this metal was registered in bottom sediments of middle sector, namely Valea Mare station. By analyzing of the results performed in the similar period of 2010 year (Fig. 3), a similar spatial dynamics of heavy metals content was established, probability levels (P) of heavy metals in the bottom sediments being 0.75 for Cu and Cd, 0.8 for Cr, 0.85 for Zn and Pb, 0.9 for Ni.

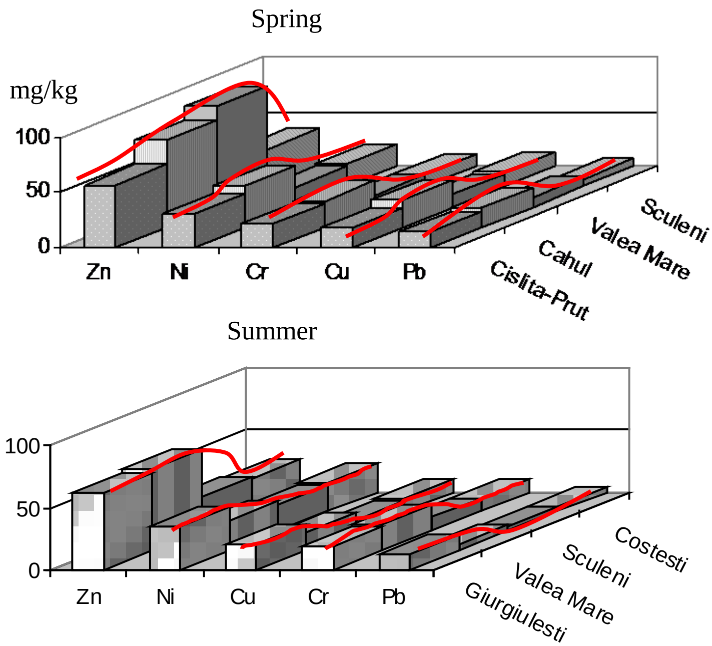

Fig. 2 ***Seasonal dynamics of heavy metals level (mg/kg) in bottom sediments along the Prut River during spring and summer of 2009 year.***

Seasonal dynamics of heavy metals in bottom sediments was less homogeneous than recorded spatial dynamics. Thus, the increasing tendency of Ni level and the decreasing tendency of Pb level from spring to summer of 2009 year were registered. During 2004 year, a similar seasonal dynamics of Ni level was established.

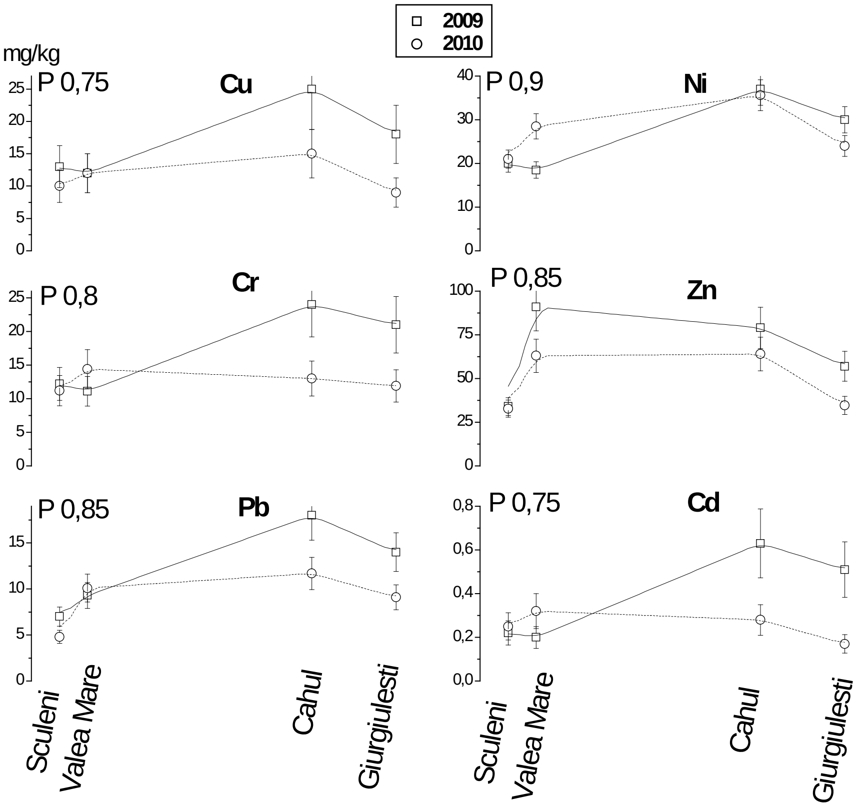

Fig. 3 ***Spatial dynamics of heavy metals content (mg/kg) in bottom sediments along the Prut River during spring of 2009 and 2010 years (P –probability levels).***

Multi-annual dynamics of heavy metals (Zn, Ni, Cu, Cr, Pb) level recorded on lower course of the Prut River (site Giurgiulesti) was as follows: (i) Ni, Cu and Pb content was quite stable during research years (2001-2009), being recorded the higher levels in 2009 year (Fig. 4), (ii) by analyzing of Zn and Cr level, the decreasing tendency during these years was registered, being recorded the highest amounts in 2004. To be mentioned (Fig. 5); on middle course of the Prut River (site Valea Mare) the increasing tendency of Zn level was established. For other metals (Ni, Cr, Cu, Pb) the slight level changes was recorded.

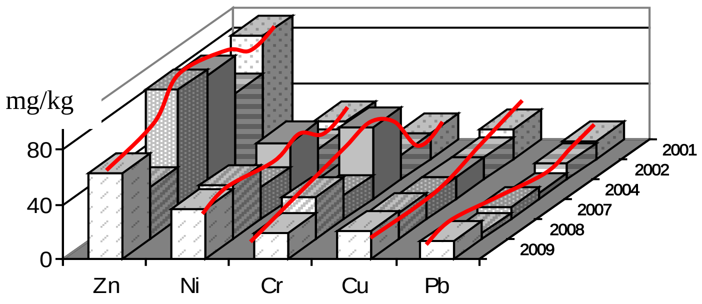

Fig. 4 ***Multi-annual dynamics of heavy metals level (mg/kg) in bottom sediments of the Prut River (site Giurgiulesti) during summer of 2001-2009 years.***

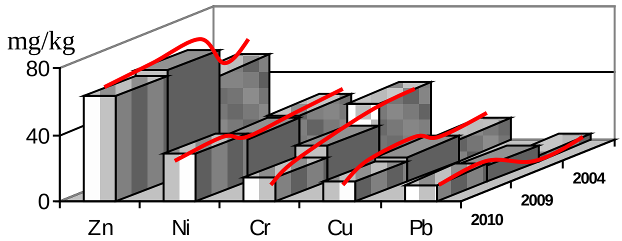

Fig. 5 ***Multi-annual dynamics of heavy metals level (mg/kg) in bottom sediments of the Prut River (site Valea Mare) during spring of 2004, 2009 and 2010 years.***

The ability of bottom sediments for heavy metals binding decreased in the following order: Fe>Mn>Zn>Ni>Cr≥Cu>Pb>Cd, which is similar with sequence for Earth's crust (Yobouet et al., 2010). The order established for bottom sediments of the Prut River, in general, is similar with those presented in specialty literature, namely Fe>Mn>Zn>Ni>Cu≥Cr>Pb>Cd (Lasheen and Ammar, 2009), Fe>Mn>Zn>Co>Ni>Cr>Cu>Pb (Oyewale and Musa, 2006) and Zn>Pb>Cr>Cu>Ni>Co>Mo>Cd (Shuzhen et al., 2002).

3.2 Spatial and seasonal dynamics of heavy metals level in interstitial water of bottom sediments

Mobilization-immobilization processes on the particle surface of sediments occur through/participation interstitial water (Rusu and Lupascu, 2004). During the desorption process from sediments, heavy metals are accumulated in interstitial water, and then can be mobilized in the water horizon overlying the bottom sediments. Reverse process, the immobilization from water in sediments, also occurs through interstitial water. Concentrations of heavy metals in the water horizon overlying the bottom sediments and in interstitial water of bottom sediments can vary greatly, and the direction of mobilization-immobilization processes determines pollution - self-purification processes of water bodies.

Heavy metals (Cu, Zn) content in interstitial water (µg) was computed per volume of interstitial water (IW) extracted from 1 kg of bottom sediments (Fig. 6 and 7). Thus, dynamics of heavy metals level in interstitial water was different to those recorded in bottom sediments. During spring and summer the decreasing tendency of Cu and Zn level in interstitial water along the Prut River was established. There were recorded the higher values of heavy metals on middle sector of the river (Sculeni and Valea Mare stations). Also, during 2009 the increasing tendency of Zn level and the decreasing tendency of Cu level from spring to summer were registered.

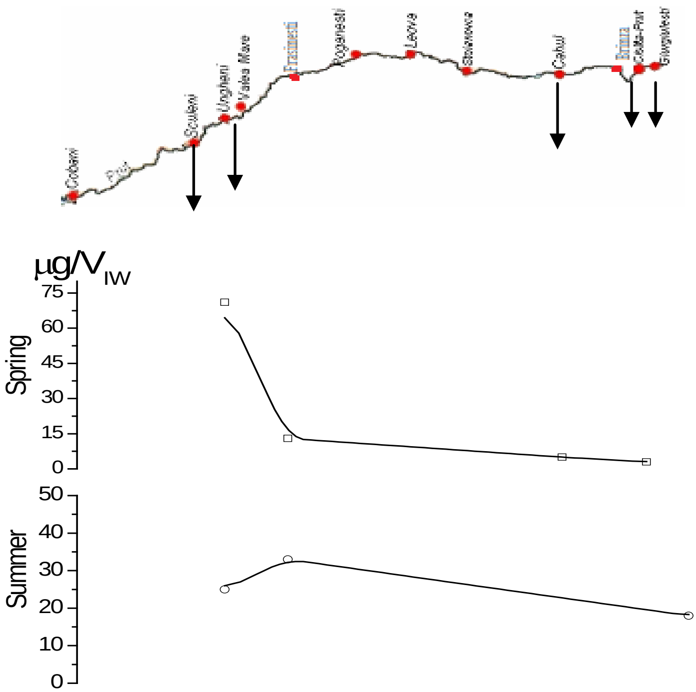

Fig. 6 ***Seasonal dynamics of cooper (Cu) content (µg/V_{IW}) in interstitial water (IW) of bottom sediments along the Prut River during spring and summer of 2009 year. Data are computed per volume of interstitial water (IW) extracted from 1 kg of bottom sediments.***

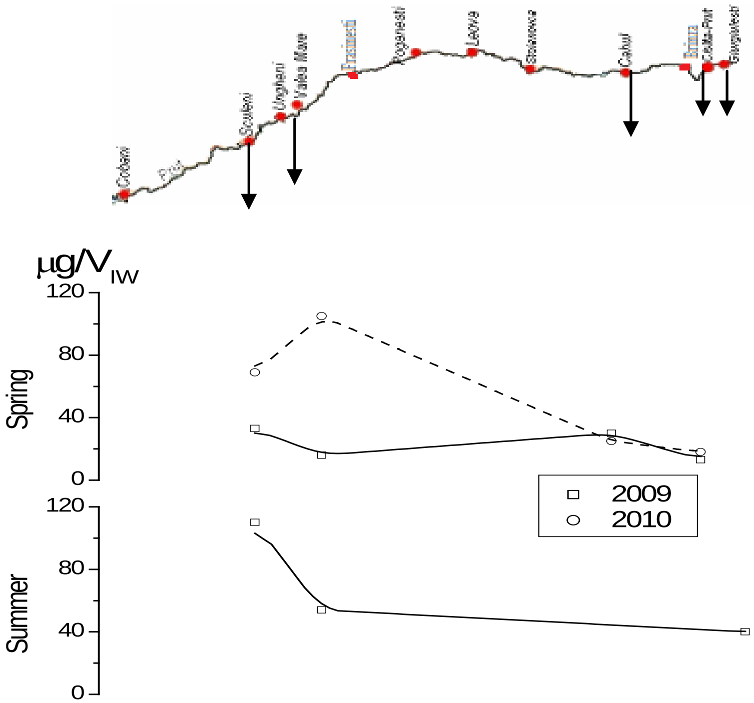

Fig. 7 ***Seasonal dynamics of zinc (Zn) content (µg/V_{IW}) in interstitial water (IW) of bottom sediments along the Prut River during spring and summer of 2009and 2010 years. Data are computed per volume of interstitial water (IW) extracted from 1 kg of bottom sediments.***

3.3 Sediments quality and environmental risk assessment

The establishment of the chemical status of continental aquatic ecosystems, rivers and lakes, natural or artificial, is made on the basis of quality standards for water and sediments of the indicators listed in the Order 161/2006 (Table), heavy metals being introduced in the list of relevant dangerous and priority hazardous substances.

By analyzing of the obtained results, it was established that the level of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in bottom sediments along the Prut River didn't exceed the maximal admissible concentrations (Table).

Table. ***Maximal admissible concentrations (MAC) of heavy metals in bottom sediments of rivers and streams according to Order 161/2006***

Metals	Cd	Cr(total)	Cu	Pb	Zn	Ni
MAC, mg/kg	0.8	100	40	85	150	35

4. CONCLUSIONS

Spatial dynamics for the most metals (Cu, Cr, Ni, Pb, Cd) during 2009 and 2010 years had similar trend, being recorded the increasing tendency of the metals amount along the Prut River. The increasing tendency of Ni level and the decreasing tendency of Pb level from spring to summer of 2009 year were registered. The ability of bottom sediments for heavy metals binding decreases in the following order: Fe>Mn>Zn>Ni>Cr≥Cu>Pb>Cd.

The decreasing tendency of Cu and Zn level in interstitial water of bottom sediments along the Prut River was established. During 2009 year the increasing tendency of Zn level and the decreasing tendency of Cu level from spring to summer were registered.

It was established that level of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in bottom sediments along the Prut River didn't exceed the maximal admissible concentrations, according to Order 161/2006.

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