Migration forms of heavy metals and their impact on water quality in the Hornád river basin

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Formy ťažkých kovov a ich vplyv na kvalitu vody v rieke Hornád
Problém nahromadenia ťažkých kovov v životnom prostredí je jedným z najväčších problémov súčastnosti. Najviac ťažkých kovov pochádzajúcich z antropogénnej činnosti sa hromadí vo vodnom systéme, vďaka tomu sa ťažké kovy dostávajú cez potravinový reťazec do ľudského organizmu, pre ktorý sú vo zvýšených koncentráciách toxické. Z hľadiska toxického pôsobenia na organizmus je dôležité poznať nie len celkové množstvo kovového prvku, ktoré sa nachádza v recipiente, ale aj v akých formách je prvok viazaný. V práci bola navrhnutá metóda postupnej extrakcie, ktorá rozdeľuje jednotlivé formy kovov do 6 frakcií, čo umožňuje ich stanovenie.

Key words: water quality, heavy metals, Hornád river.

Introduction

The acute problem of water pollution has been caused by a continuous growth in the anthropo-genic impact on the natural environment. Heavy metals (HM) occupy one of the first places in the list of the most frequently occuring and toxic contamination. Their compounds are not subject to destruction in the water body i.e. they can only change their migration forms. That is why HM are referred to conservative substances toxic for hydrobionts and man.

Depending on the ambient conditions HM can have different degrees of oxidation or act as various inorganic and organic compounds, or distributed between certain components of aquatic eco-systems and bottom sediments. In this case, HM mobility, toxicity and acceptability for hydrobionts change appreciably, and, correspondingly, their ecological role in the water body changes, too.

The present study, carried out at the Hornad river basin and Ruzin reservoir, are aimed at revealing the impact of HM migration forms on the reservor water quality and mass exchange in the "water column-bottom sediments" systém.

The total content of HM in water and sediments was determined by the DC arc spectrography (Flórián et al., 1992). The forms of the microelement occurence in the solid phase were determined by the method of stage-by-stage extraction (Tessier et al., 1979).The concentration of HM in the obtained solutions was determined by the atomic absorption method with the electrothermic atomization (Sedych et al., 1996).

Materials and methods

The simultaneous sampling of water and sediments was done at choosen sampling sites of the Hornád river (Fig.1). Both types of samples were treated as dry evaporates; the DC Arc spectrography method was developed and optimized for two-sided utilization (Pliešovská et al., 1992). The low detectability of Hg caused the application of a special AAS-based Hg analyzer for both liquid and solid samples with a highly favourable precision and accuracy. The determination of 10 ng of mercury can be carried out with the precision lower than 10% and with the accuracy about 2% (Krakovská, 1986).

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The sequential leaching of river sediments was carried out using a modifed method (Sedych et al., 1996; tab.1).

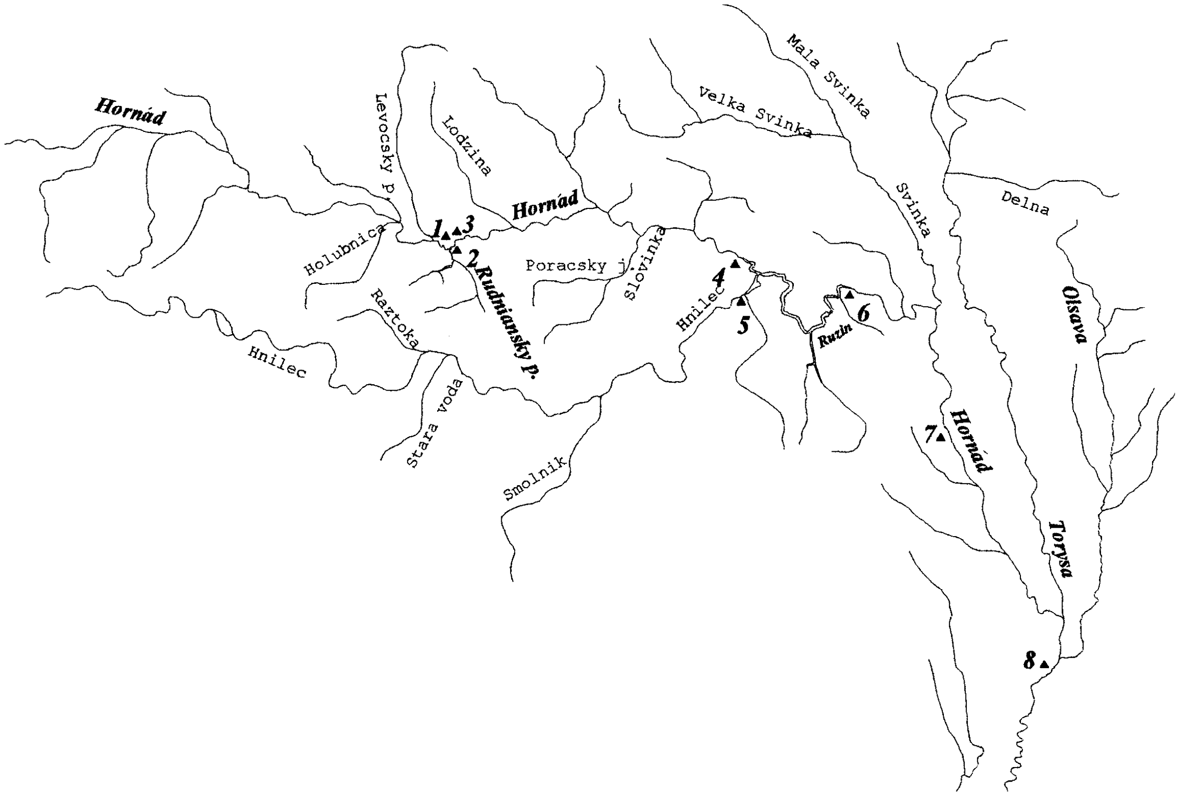


Fig.1. The network of sampling stations of the Hornád river and the water reservoir Ružín. 1-Hornád above Rudňany creek, 2-Rudňany creek under the mine, 3-Hornád under Rudňany creek, 4-Hornád - Richnava, 5-Hnilec - tributary to the Ružín reservoir, 6-Ružín at the dam wall, 7-Hornád - Ťahanovce, 8-Hornád - Ždaňa.

Table 1. List of buffers.

I.	1M sodium acetate
II.	1M sodium acetate and 1M acetic acid
III.	0,1M sodium hydroxide
IV.	1M sodium acetate and 30% hydrogen peroxide
V.	Acetic acid and hydroxylamin hydrochlorid
VI.	10% hydrochloric acid

All reagent solutions were analysed by the AAS spectrometry (the Perkin-Elmer model 603 and 3030 Z with electrothermic atomizators HGA-76 and HGA-600). A complet mineralization of eaching reagents organic parts with hydrogen peroxide and nitric acid was realized by conventional heating, microwave heating and in closed systems (bomb decomposition).

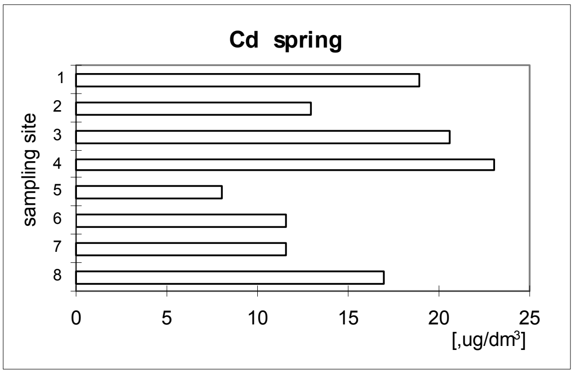
Results and discussion

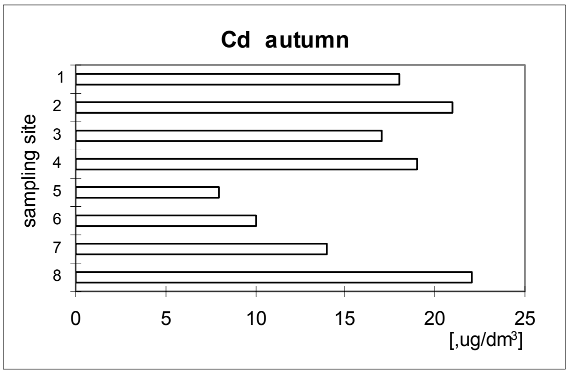
The state standard (STN, 1995) classifying surface water into five quality classes were taken into consideration for the assessment of the water pollution. The study revealed that the gross concentration of HM in water is within the limits, typical for surface fresh water bodies. Cd, Co and Pb were chosen for an illustration (Fig 2 and 3.). Cd is the most toxic element for environment, Pb is toxic too and Co is not so toxic for environment.

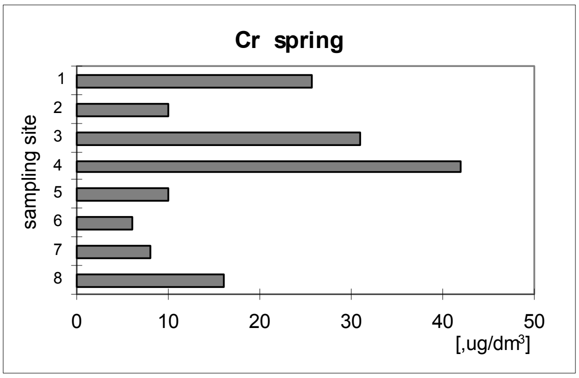
The limits of detection of these elements by AES are sufficient for Co and Pb. The limit of detection for Cd manifests only that Cd is under limits, but this value does not tell anything about in which quality classes this water is.

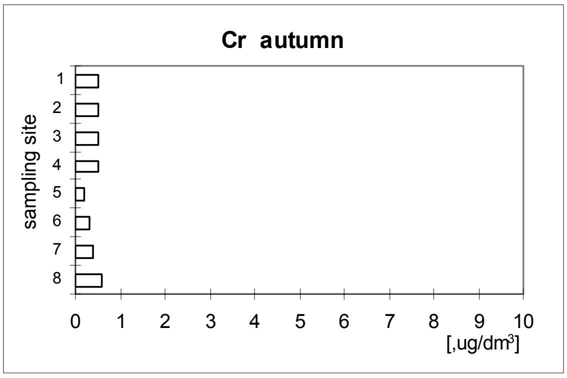
Bottom sediments represent the accumulation environment for HM. Contents of HM in sediments in the Hornád river´s basin are appreciable. Therefore it is very important to know in which forms HM in sediments are found.

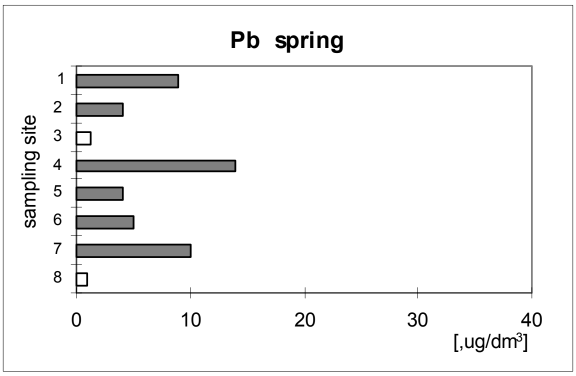
Sampling site	Cd [$\mu g/dm^3$]		Cr [$\mu g/dm^3$]		Pb [$\mu g/dm^3$]	
	spring	autumn	spring	autumn	spring	autumn
1. Hornád above Rudňany creek	<18,9	<18,0	25,6	<0,5	9,0	<1,0
2. Rudňany creek under the mine	<12,9	<21,0	10,0	<0,5	4,0	<1,0
3. Hornád under Rudňany creek	<20,6	<17,0	31,0	<0,5	1,2	<1,0
4. Hornád - Richnava	<23,0	<19,0	42,0	<0,5	14,0	34,0
5. Hnilec - tributary to the Ružín reservoir	<8,0	<8,0	10,0	<0,2	4,0	<0,4
6. Ružín at the dam wall	<11,6	<10,0	6,0	<0,3	5,0	<0,6
7. Hornád - Ťahanovce	<11,6	<14,0	8,0	<0,4	10,0	17,8
8. Hornád - Ždaňa	<17,0	<22,0	16,0	<0,6	1,0	924,0











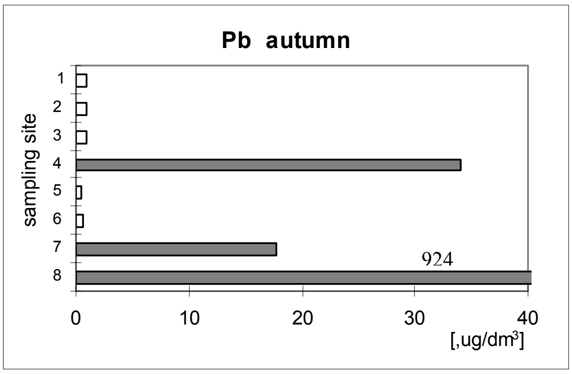


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Fig.2 Contents of the selected heavy metals in water.

Sampling site	Cd [mg/kg] spring	Cd [mg/kg] autumn	Cr [mg/kg] spring	Cr [mg/kg] autumn	Pb [mg/kg] spring	Pb [mg/kg] autumn
1. Hornád above Rudňany creek	<310	<310	121	<1,3	<22	<22
2. Rudňany creek under the mine	<310	<310	210	81	<22	<22
3. Hornád under Rudňany creek	<310	<310	166	49	<22	<22
4. Hornád - Richnava	<310	<310	125	77	<22	<22
5. Hnilec - tributary to the Ružín reservoir	<310	<310	149	<1,3	129	120
6. Ružín at the dam wall	<310	<310	56	<1,3	103	42
7. Hornád - Ťahanovce	<310	<310	340	67	<22	<22
8. Hornád - Ždaňa	<310	<310	146	80	<22	<22

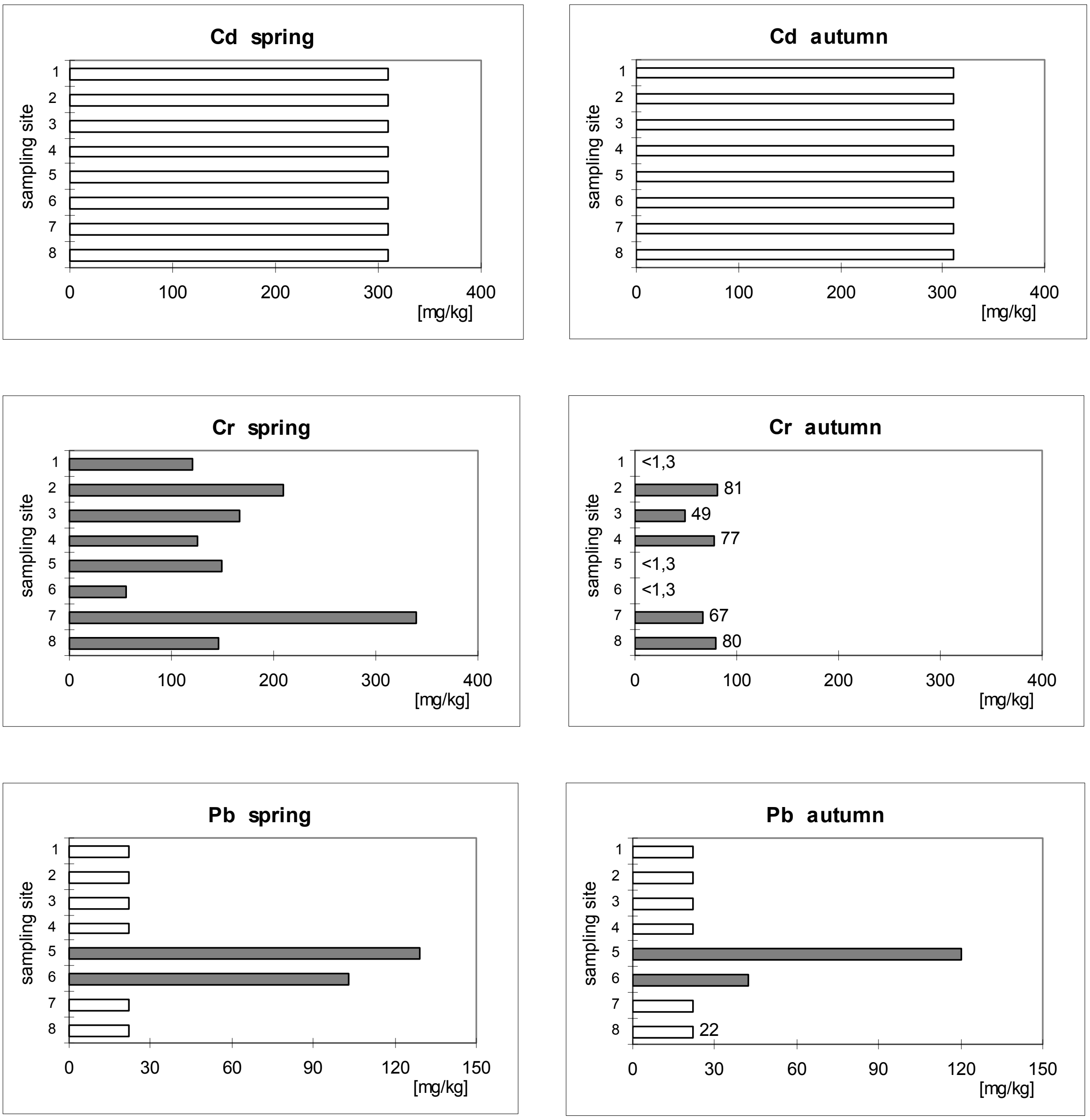

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Fig.3 Contents of the selected heavy metals in sediments.

An average sediment sample was used for initial extraction and contents of HM was analyzed by ETA AAS.

Fraction 1. **Exchangeable Metals**. Concentrations found for exchangeable cadmium. cobalt and lead are: Cd - 23,6%, Co - 14% and Pb - 0,94% from total their contents (Cd - 26 $\mu g.dm^{-3}$, Co - 73 $\mu g.dm^{-3}$, Pb - 127 $\mu g.dm^{-3}$).

Fraction 2. **Metals Bound to Carbonates**. Magnesium and calcium are present with relatively high concentrations. This demonstrates that carbonates fraction of sediment are leaching. The concentrations of Cd, Co and Pb are Cd - 27,55%, Co - 56,0% and Pb - 4,7%.

Fraction 3. **Metals Bound to Humic Matter**. There are Cd - 3,5%, Co - 2,8% and Pb - 7,9% rom total contents of metals in this fraction. The content of Pb is higher in this fraction than in fraction 1 and 2, because Pb bounds to the organic matter better than to the inorganic one .

Fraction 4. **Metals Bound to Organic Matter and Sulfide**. The choice of H_2O_2 represents a compromise between complete oxidation and alteration of silicate material (Tessier et al., 1979). The levels of cadmium, cobalt and lead found in the fraction 4 are Cd 2%, Co - 4%, Pb - 15.7%.

Fraction 5. **Metals Bound to Amorphous Fe-Mn Oxides**. The trace metal levels in the fraction 5 are relatively high and represent a large fraction of the total metal concentrations: Cd - 39,4% Co - 14,1% and Pb - 62,9%. The results illustrate the strong scavenging efficiency of Fe-Mn oxides for trace metals.

Fraction 6. **Metals Bound to Easy Destructive Silicates**. The treatment with HCl results in dissolving metals bound only to easy destructive silicates. The contents of Cd,Co,Pb in this fraction are: Cd - 3,9%,Co- 8,5% and Pb - 7,9%.

Conclusion

The conducted investigations allow to study the transformation processes of different forms of HM taking place on the boundary of the bottom water and the bottom sediment and their influence on the water quality in the basin.

The investigation of the Hornád river basin allowed to study the processes of the HM forms transformation and provided the following conclusions:

More than 80% of Pb are complexes with the organic and the inorganic matter. About 25% Pb is connected with the fulvic and humic acids. It makes them safe for people and hydrobionts.

Co and Cd are mainly in ionic forms, but their concentrations do not exceed the background levels.

No explicit seasonal dynamics was revealed in the HM concentrations. The content of the investigated elements decreases from the spring to the autumn season.

References

Flórián, K., Matherny, M. a Pliešovská, N.: Hladina stopových prvkov v povodí Hornádu. *Vodní Hospod.1992, 42, s.52-54.*

Tessier, A., Campbell, P.G.C. & Bisson M.: Sequential Extraction Procedure for the Speciation of Particulate Trace Metal. *Analytical. Chemistri, 51, 7, 1979, pp. 844-850.*

Sedych, E., Bannych, L., Nosal, S. & Ershova: Influence of Organic and Anorganic Components of Botton Sediments at the Speciacion of Heavy Metals by ETAAS. *Book of Abstract on 2nd European Furnace Symposium, St.Petersburg, 1996, p.90 .*

Pliešovská, N. & Šesták, J.: Examination of Content of Heavy Elements in River Bed Sediments by Optical Emision Spectography. *Transaction of The TU of Košice 1, 1992, pp. 79-84.*

Krakovská, E.: Analytická výkonnosť a využitie ortuťového analyzátora TMA 254. *Zbor. Hydrochémia 86, Bratislava 1986, s. 33-43.*

STN No. 757 221. *Bratislava 1995.*