**Alena Vollmannová*, Michal Kujovsky*, Julius Arvay*, Lubos Harangozo*, Juraj Toth***

# HEAVY METALS IN UPPER NITRA RIVERSIDE

# METALE CIĘŻKIE W TERENACH NADRZECZNYCH GÓRNEJ NITRY

**Key words:** heavy metals, riverside sediments, environment.
**Słowa kluczowe:** metale ciężkie, osady nadrzeczne, środowisko.

*Zlewnia rzeki Nitry jest częścią regionu Górnej Nitry. Rzeka ta ma źródła w środkowej Słowacji na południowych stokach Małej Fatry, płynie przez Nizinę Naddunajską i wpływa do rzeki Wag. Jej długość wynosi 196,7 km. Na jakość wód rzeki Nitry szczególny wpływ ma przemysł. Zakłady Chemiczne Nováky, Kopalnie Górnej Nitry, elektrociepłownia i elektrownia w Zemianskich Kostolanach są najważniejszymi źródłami zanieczyszczeń rzeki Nitry. Wśród zanieczyszczeń stwierdzono obecność metali ciężkich, które charakteryzuje duża toksyczność.*
*Celem prezentowanej pracy jest określenie zawartości metali ciężkich kadmu, ołowiu, niklu, cynku, miedzi, chromu, kobaltu i rtęci w osadach nadbrzeżnych rzeki Nitry. Próbki osadów pobierano w 9 lokalizacjach górnego biegu rzeki na odcinku ok. 50 km, pomiędzy punktami pomiarowymi Opatowce i Topolcany. Zmierzona zawartość była porównana z zawartością dopuszczalną określoną w odnośnym krajowym akcie prawnym (220/2004). Określano także zawartość różnych form metali ciężkich w glebie, stosując w tym celu metodę analizy sekwencyjnej.*
*Do określenia poziomu zawartości metali ciężkich zastosowano metodę płomieniowej spektrometrii absorpcji atomowej. Odczyn pH oznaczony w roztworze KCl wynosił 7,09–7,60, co oznacza, że badane próbki charakteryzował odczyn od obojętnego do zasadowego. Zawartość kadmu i rtęci była kilkakrotnie większa od zawartości tych metali określonej aktem prawnym, wynoszącej w mg·kg$^{-1}$: kadm 2,9–4,7, rtęć 4,4–12,6. W odniesieniu do ołowiu określono frakcję biodostępną, która także przekroczyła dopuszczalną zawartość 1,8–2,5 mg·kg$^{-1}$.*

* ***Prof., RNDr. Alena Vollmannová, PhD., Ing. Michal Kujovský, Ing. Július Árvay, PhD., Ing. Ľuboš Harangozo, PhD., Ing. Juraj Tóth – Dept. of Chemistry, Faculty of Biotechnology and Food Sciences, Slovak University of Agriculture, Tr. A. Hlinku 2, 949 76 Nitra, Slovak Republic; tel.: +421376414374; e-mail: alena.vollmannova@uniag.sk***

*Uzyskane wyniki wskazują na konieczność podjęcia takich działań jak lepsze oczyszczanie ścieków przemysłowych i ścieków z aglomeracji miejskich oraz budowa nowych oczyszczalni.*

## 1. INTRODUCTION

Water with its indispensable economic and ecological importance belongs to basic components of the environment. Groundwater and surface water have important function as the part of the environment and are also very important for ensure of economic and other needs. Due to intensive exploatation it is necessary to save, regulate and regenerate the water sources [Volaufova and Langhammer 2007]. Quality of surface water is influenced by many factors. The most important are geomorphological conditions, atmospheric influences and anthropic activity. In last years especially the influence of human activities on surface water quality is evident. The content of contaminants causes also the unsatisfactory quality of surface water. Nitra river basin is part of Upper Nitra region. The flow stems under Revan (1204.6 m nad m) in Little Fatra, continues into Danube Plain, where drains into Vah river. The length of river flow is 196.7 km. The river basin has several tributaries, which are also contaminated. The river with tributaries forms the environment for the biodiversity of biotops, plant and animal species. The environment is disturbed by human activity. The treatment of the flow and difficult and frequent accidents contribute to decreasing of ecological and environmental quality in river basin [Andreji, Stranai 2007]. The Nitra River is one of most polluted rivers in the Slovak Republic, due to numerous industrial and municipal emissions, and low level of wastewater treatment [Masliev et al. 1994]. The water quality in Nitra river is influenced especially by industrial activity [Liska et al. 1996]. The industrial enterprises epecially chemical factory in Novaky, Upper Nitra Mines (UNM) in Prievidza, Handlova and Novaky, heating plant and power plant in Zemianske Kostolany are the most important sources of Nitra river contamination. Nitra river is during last decades considered as strongly contaminated water flow caused by anthropic activity. The contaminants include also heavy metals with high toxicity.

The aim of the work was to determine the content of Cd, Pb, Ni, Zn, Cu, Cr, Co and Hg in Upper Nitra riverside.

## 2. MATERIAL AND METHODS

The samples of riverside sediments were collected from 9 sites along the upper flow of Nitra river. Distance between the starting site Opatovce upon Nitra and end point site Topolcany was about 50 km. The starting point was chosen because of river Nitra relocation in Opatovce in 2009 into the new riverbed in length 1850 m. The reason to build a new bed is the release of surface for the upcoming a new productive capacity of UNM in Prievidza.

At a depth of over 200 meters the coal seam is located, from which the next few years UNM want to get 7.2 million tons of lignite. Nitra River connects automatically to the original riverbed in Novaky.

The soil samples from these places were taken by valid methods with pedological probe GeoSampler f. Fisher. Pseudototal content of Cd, Pb, Ni, Zn, Cu, Cr and Co including all of the forms besides residual fraction of metals was assessed in solution of *aqua regia* and content of mobile forms of selected heavy metals in soil extract of $NH_4NO_3$ (c = 1 mol·dm$^{-3}$). Gained results were evaluated according to Law 220/2004.

Ecotoxicological studies in soil showed that metal speciation is one of the key factors affecting uptake of metals by plants. Chemical properties of metals in soil and their retention in the solid soil phase is affected by pH, quantity of the metal, cation-exchange capacity, content of organic matter and mineralogy of soil. Changes in chemical properties of soils result in changes in their availability for plants [Vollmannova et al. 2002]. Therefore different metal forms in the investigated riverside sediments were determined by selective sequential extraction (SSE) according Zeien, Brümmer [1989]. This method is based on the extraction of heavy metals bound with the soil components, by the application of different solutions on the same soil sample. The obtained extracts are separated from the solid phase by centrifugation and the residue is subjected to the next step of extraction. SSE is instrumental in the assessment of potential mobility and availability of metals in soils (Tab. 1).

**Table 1.** Metal fractions and extractants according Zeien – Brümmer´s sequential extraction procedure

**Tabela 1.** Frakcje metali i roztwory stosowane do ekstrakcji wg procedury ekstrakcji sekwencyjnej Zeien – Brümmer´s

| Step | Fraction | Specification of binding to soil components | Extractant |
|---|---|---|---|
| I | mobile | water soluble and easily soluble metal forms | 1 M $NH_4NO_3$; 24 h (pH = 7) |
| II | exchangeable | specifically adsorbed metal forms and metal forms bound to carbonates | 1 M $CH_3COONH_4$; 24 h (pH = 6) |
| III | easily reducible | metal forms bound to Mn - oxides | 0.1 M $NH_2OH.HCl$ + 1 M $CH_3COONH_4$; 0.5 h (pH = 6) |
| IV | EDTA extractable | metal forms bound to organic matter | 0.025 M $NH_4$-EDTA; 1.5 h (pH = 4.6) |
| V | moderately reducible | metal forms bound to amorphous Fe - oxides | 0.2 M $NH_4$ – oxalate; 4 h (pH = 3.25) |
| VI | strongly reducible | metal forms bound to crystalline Fe - oxides | 0.1 M Ascorbic acid + 0.2 M $NH_4$ – oxalate; 0.5 h (pH = 3.25) |
| VII | residual | metal forms in silicates | $HNO_3$ + $HClO_4$ |

The flame atomic absorption spectrometry (AAS VarianAASpectrDUO240FS/ 240Z/UltrAA) was the used analytical method for heavy metal levels determination.

In Table 2 the names of localities of sediment sample collection and their position to potential industrial sources of the environmental contamination are presented. The minimal distance from the potential contaminating sources (sample point Novaky) was 2 km from UNM in Novaky (south) and in Prievidza (south-east). The maximal distance (sample point Topolcany) was 42.3 km from UNM in Handlova (north-east-east).

**Table 2.** Localities of sediment sample collection and their position to potential sources of the environmental contamination

**Tabela 2.** Lokalizacja punktów pomiarowych poboru osadów w odniesieniu do potencjalnych źródeł zanieczyszczeń

| Locality of sediment sample collection | Position of locality toward emmission sources | | | |
|---|---|---|---|---|
| | Novaky | Handlova | Prievidza | Zemianske Kostolany |
| Opatovce upon Nitra | SW 6.8 km | SE 14 km | S 5.5 km | SSW 8 km |
| Novaky | S 2 km | SE 14 km | SE 2 km | S 3.20 km |
| Chalmova | NE 6.2 km | NEE 18 km | SE 8 km | SE 4.9 km |
| Male Krstenany | NE 11 km | NEE 23 km | SE 13 km | SE 10 km |
| Partizanske | NE 13.3 km | NEE 25 km | SE 15.5 km | SE 12.3 km |
| Partizanske confluence | NE 16.5 km | NEE 28.5 km | SE 18.8 km | SE 15.5 km |
| Chynorany | NE 21.5 km | NEE 33.5 km | SE 20.6 km | SE 20.7 km |
| Bosany | NE 25.5 km | NEE 37 km | SE 27.5 km | SE 24.5 km |
| Topolcany | NE 30.8 km | NEE 42.3 km | SE 32.8 km | SE 30 km |

## 3. RESULTS AND DISCUSSION

In Table 3 the determined values of active and exchangeable soil reaction and heavy metal contents in soil extract by *aqua regia* are presented. With increasing pH, content of organic mater and clay the solubility of most metals decreases due to their increased adsorption. Of the soil parameters soil pH is one of the parameters that affect significantly the share of bioavailable forms of metals [Takac et al. 2009].

The determined pH/KCl was in interval 7.09 – 7.60, it means the investigated riverside sediments have neutral till alkaline soil reaction. In the sediment samples the humus supply was good till very good (3.03% – 5.81%) due to high content of oxidizable carbon (1.76% – 3.37%).

The soil contamination by Cd and Hg was analytically confirmed. The contents of these risk elements in soil extract by *aqua regia* 2.9 – 4.7 fold (Cd) and 4.4 – 12.6 fold (Hg) exceeded the limit values (0.4 $mg \cdot kg^{-1}$and 0.15 $mg \cdot kg^{-1}$ respectively) given by the legislative.

**Table 3.** Soil reaction and heavy metals content in soil extract by *aqua regia* in mg·kg$^{-1}$

**Tabela 3.** Charakterystyka gleb i zawartość metali ciężkich w ekstrakcie glebowym z zastosowaniem wody królewskiej w mg·kg$^{-1}$

| Locality of sediment sample collection | pH ($H_2O$) | pH (KCl) | *Aqua regia,* mg·kg$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cd | Pb | Ni | Zn | Cu | Cr | Co | Hg |
| Opatovce | 8.40 | 7.28 | 1.48 | 19.80 | 21.80 | 69.00 | 14.00 | 23.40 | 11.00 | 0.06 |
| Novaky | 8.11 | 7.09 | 1.16 | 19.00 | 19.80 | 57.80 | 14.00 | 21.60 | 10.60 | 0.11 |
| Chalmova | 8.43 | 7.60 | 1.22 | 15.60 | 13.80 | 52.20 | 11.20 | 14.60 | 8.40 | 0.66 |
| M. Krstenany | 8.22 | 7.36 | 1.80 | 18.00 | 18.00 | 48.20 | 13.60 | 19.00 | 9.80 | 1.31 |
| Partizanske | 8.32 | 7.22 | 1.40 | 20.20 | 20.20 | 49.00 | 15.00 | 24.00 | 10.40 | 0.66 |
| Partizanske - confluence | 8.19 | 7.41 | 1.36 | 16.80 | 16.40 | 52.00 | 12.40 | 17.60 | 9.00 | 1.07 |
| Chynorany | 8.28 | 7.35 | 1.64 | 20.40 | 21.20 | 58.20 | 17.40 | 23.80 | 10.20 | 1.29 |
| Bosany | 8.14 | 7.31 | 1.88 | 24.40 | 21.00 | 72.20 | 17.80 | 24.20 | 12.00 | 1.89 |
| Topolcany | 8.15 | 7.30 | 1.40 | 21.60 | 22.80 | 70.00 | 18.80 | 35.80 | 11.40 | 1.38 |
| Limit value* | – | – | **0.40** | **25.00** | **40.00** | **100.0** | **30.00** | **50.00** | **15.00** | **0.15** |
| Average | 8.25 | 7.32 | 1.48 | 19.53 | 19.44 | 58.73 | 14.91 | 22.67 | 10.31 | 0.94 |
| Min | 8.11 | 7.09 | 1.16 | 15.60 | 13.80 | 48.20 | 11.20 | 14.60 | 8.40 | 0.06 |
| Max | 8.43 | 7.60 | 1.88 | 24.40 | 22.80 | 72.20 | 18.80 | 35.80 | 12.00 | 1.89 |
| St. dev. | 0.12 | 0.14 | 0.25 | 2.62 | 2.88 | 9.41 | 2.58 | 5.96 | 1.13 | 0.61 |
| Median | 8.22 | 7.31 | 1.40 | 19.80 | 20.20 | 57.80 | 14.00 | 23.40 | 10.40 | 1.06 |

**Note:** *Law 220/2004; – not applicable.

Sin et al. [2001] found more higher concentrations of Cu (1.660 mg·g$^{-1}$), Pb (0.345 mg·g$^{-1}$), Zn (2.200 mg·g$^{-1}$) and Cr (0.066 mg·g$^{-1}$) in surface sediments of the Shing Mun River. The industrial effluents discharged from electroplating, metal works plants, garages and dyeing factories have contributed a significant amount of these metals in sediments. On other hand Cardoso et al. [2001] determined lower contents of Hg and Cu (0.028 mg·kg$^{-1}$ and 14 mg·kg$^{-1}$ respectively) in in the Ribeira Bay sediments. The similarity of the metal concentration in the Ribeira Bay with average shales confirmed that the metal content in the studied area can be explained by natural conditions. The similar results are presented also by Titaeva et al. [2007]. These authors assessed relatively low average concentrations of heavy metals (Pb 16.4; Ni 12.6; Cr 8.8; Co 2.2; Zn 28.6; Cu 10.7 mg·kg$^{-1}$) in upper horizon of riverside soils in Volga River Valley. The alluvial soil in the floodplain differs from the other soil types by its low trace element concentrations. On other hand the flooded soil have higher concentrations of heavy metals as compared to riverside soils. A relatively wide range of soil concentrations of heavy metals in sediments of the River Ravi in Pakistan were determined by Rauf et al. [2009]. Metal concentrations in the sediments ranged from 0.99 to 3.17 for Cd, 4.60 to 57.40 for Cr, 2.22 to 18.53 for Co and 3.38 to 159.79 mg·kg$^{-1}$ for Cu.

From determined soil content of heavy metals only bioavailable forms of Pb determined in soil extract by $NH_4NO_3$ 1.8 – 2.5 fold exceeded the limit value 0.1 mg·kg$^{-1}$.

**Table 4.** Heavy metals content in soil extract by $NH_4NO_3$ and content of $C_{ox}$ and humus in mg·kg$^{-1}$
**Tabela 4.** Zawartość metali ciężkich w ekstrakcie glebowym z zastosowaniem $NH_4NO_3$ oraz zawartość $C_{ox}$ i próchnicy w mg·kg$^{1}$

| Locality of sediment sample collection | $C_{ox.}$, % | Humus, % | 1 mol.dm$^{-3}$ $NH_4NO_3$, mg·kg$^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cd | Pb | Ni | Zn | Cu | Cr | Co |
| Opatovce | 1.76 | 3.03 | 0.05 | 0.20 | 0.13 | 0.08 | 0.09 | 0.04 | 0.13 |
| Novaky | 2.95 | 5.08 | 0.06 | 0.20 | 0.15 | 0.09 | 0.07 | 0.04 | 0.13 |
| Chalmova | 2.32 | 3.99 | 0.05 | 0.19 | 0.12 | 0.08 | 0.06 | 0.02 | 0.11 |
| M. Krstenany | 2.56 | 4.42 | 0.06 | 0.25 | 0.14 | 0.08 | 0.08 | 0.03 | 0.14 |
| Partizanske | 2.88 | 4.96 | 0.06 | 0.23 | 0.15 | 0.60 | 0.09 | 0.03 | 0.14 |
| Partizanske - confluence | 2.18 | 3.75 | 0.05 | 0.18 | 0.17 | 0.10 | 0.09 | 0.04 | 0.13 |
| Chynorany | 2.91 | 5.02 | 0.07 | 0.22 | 0.18 | 0.07 | 0.11 | 0.02 | 0.16 |
| Bosany | 3.12 | 5.39 | 0.07 | 0.23 | 0.19 | 0.10 | 0.10 | 0.03 | 0.17 |
| Topolcany | 3.37 | 5.81 | 0.08 | 0.24 | 0.20 | 0.07 | 0.11 | 0.04 | 0.18 |
| Limit value* | – | – | **0.10** | **0.10** | **1.50** | **2.00** | **1.00** | – | – |
| Average | 2.67 | 4.61 | 0.06 | 0.21 | 0.16 | 0.14 | 0.09 | 0.03 | 0.14 |
| Min | 1.76 | 3.03 | 0.05 | 0.18 | 0.12 | 0.07 | 0.06 | 0.02 | 0.11 |
| Max | 3.37 | 5.81 | 0.08 | 0.25 | 0.20 | 0.62 | 0.11 | 0.04 | 0.18 |
| St. dev. | 0.51 | 0.88 | 0.01 | 0.03 | 0.03 | 0.18 | 0.02 | 0.01 | 0.02 |
| Median | 2.88 | 4.96 | 0.06 | 0.22 | 0.15 | 0.08 | 0.09 | 0.03 | 0.14 |

**Note:** *Law 220/2004; – not applicable.

Because of high soil contents in all investigated sediment samples Cd and Pb belong to the most risky heavy metals in the observed localities. The sequential analysis was applied for diferrent Cd and Pb metal forms determinations. Zeien and Brümmer´s method allows a separation of seven fractions with different activity in the soil environment [Rosada et al. 2007]. It is due to the fact that metals are bound with the soil components, by the different degree. Figure 1 presents different forms of Cd in riverside sediments. Relatively high contents of Cd (52–89%) were determined in IV – VII fractions with a difficult acess for plants.

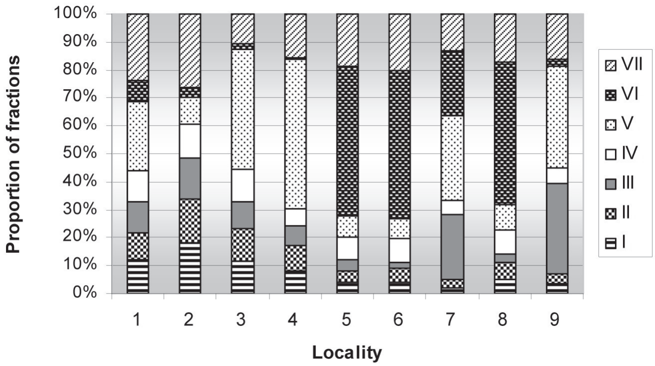


**Fig. 1.** Cadmium content in % in the riverside sediments insulated by SSE

**Rys. 1.** Zawartość kadmu w % w osadach brzegowych izolowanego metodą SSE

On other hand Cd contents in I and II fractions range in interval 5 – 34%. This suggests that Cd in potentially bioavailable in observed riverside sediments because the metals present in the mobile and in the exchangeable fractions are usually thought to be readily available for plant uptake [Xian 1989].

Figure 2 presents different forms of Pb in riverside sediments. In fraction IV – VII higher contents of Pb in relationship to Cd were determined (75 – 80%). Pb is mainly associated with the organic matter (IV. fraction) and with amorphous Fe oxides (V. fraction). The Pb share in these two fractions ranges in interval (16 – 27% and 20 – 41% respectively). Similar results are presented by Jaradat et al. [2006], Miretzki et al. [2011]. Also Ratuzny [2009] confirmed that the grater parts constituted from Pb bound to organic mater and poorly crystalline Fe oxides.

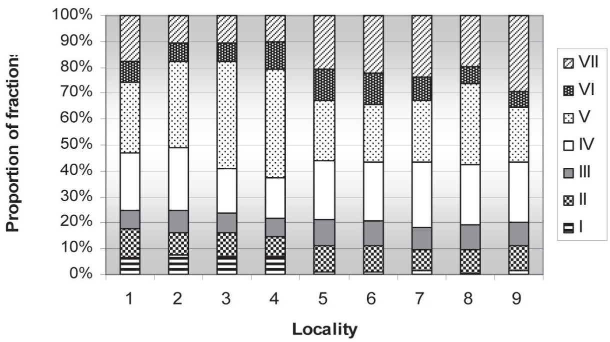


**Fig. 2.** Lead content in % in the riverside sediments insulated by SSE

**Rys. 2.** Zawartość ołowiu w % w osadach brzegowych izolowanego metodą SSE

In 7 from 9 investigated riverside sediment samples also Hg content was exceeded in relation to hygienic limit given by Law 220/2004 for agricultural soils.

## 4. CONCLUSIONS

The polluted river water resulted in pollution of riverside sediments of Nitra river. From obsered heavy metals the most dangerous contaminants are Cd, Pb and Hg. Sequential extraction of Cd and Pb showed that especially Cd is associated with mobile and exchangeable fractions causing also a potential risk for agricultural production in vicinity of Nitra river. The improvement of present situation would be to take effective measures such as better cleaning of waste water from the industrial enterprises and urban agglomeration as well as new waste water treatment plants building.

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