CONTAMINATION OF RIVERSIDE SEDIMENTS AND SOIL IN THE ALLUVIUM OF NITRA RIVER BY CADMIUM, MERCURY AND LEAD AS A RESULT OF PREVIOUS INTENSE INDUSTRIAL ACTIVITY

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ABSTRACT

The Nitra river belongs to the most contaminated rivers in the Slovakia due the previous intensive industrial activity of several enterprises located in its neighborhood. The aim of the study was to estimate the risk of contamination of riverside sediments as well as alluvial soil in vicinity of Nitra river by dangerous heavy metals. Pseudototal content of risk metals (Pb and Cd) including all the forms besides residual metal fraction was assessed in soil extract by *aqua regia* and content of mobile forms of selected heavy metals in soil extract by NH_4NO_3 (c=1mol/L). Used analytical method was flame AAS (AAs Varian AA Spectr DUO 240 FS/240Z/UltrAA). The Hg content was determined using AMA 254 Advanced Mercury Analyzer. Gained results were evaluated according Law No. 220/2004 (valid in the Slovak Republic).The samples of riverside sediments were collected from 28 exactly defined sample points along the Nitra river. The Pollution load index (PLI) has been increasing downstream of Nitra river due to contamination by Cd and Hg. The determined values of total Cd and Hg contents in riverside sediments were in interval 0.74 – 1.88 mg/kg and 0.06 – 5.44 mg/kg, respectively. With exception of two sample points the hygienic limits (0.4 mg Cd/kg and 0.15 mg Hg/kg) were exceeded in all sediment samples. Based on the recommendations of local residents three localities (Male Krstenany, Vycapy–Opatovce and Cernik) along the river Nitra were selected for the research with the requirement that examined site was located in the flood territory and was flooded during the year. In each of the localities the sample points using GPS were assessed. In all studied localities the soil content of mobile Pb forms determined in extract of NH_4NO_3 (c=1mol/L) was higher than the limit value (0.1 mg/kg) given by the legislation. The intervals were 0.10 – 0.24, 0.17 – 0.32 and 0.11 – 0.25 mg Pb/kg of soil in Male Krstenany, Vycapy–Opatovce and Cernik, respectively. The values of total Cd content determined in soil extracts by *aqua regia* were in intervals 0.25 – 0.95, 2.04 – 2.52 and 0.63 – 1.35 and total content of Hg in intervals 0.06 – 1.6, 0.04 – 0.07 and 0.03 – 0.36 mg/kg respectively. The hygienic limits given by the legislation are 0.7 mg Cd/kg and 0.5 mg Hg/kg of soil. It means that cadmium and mercury are the most dangerous metals present in the enhanced amounts in soil of investigated localities. The isoline maps were created for each of determined heavy metal in each locality. The obtained results confirmed the risk of alluvial soils as well as riverside sediment contamination by the Nitra river.

Keywords: riverside sediments, heavy metals, contamination

1. Introduction

Quality of surface water is influenced by many factors. The most important are geomorphological conditions, atmospheric influences and anthropic activity. The Nitra river is 171 km in length and has a mean flow at the mouth of 25 m^3/s (Carmichael and Strzepek, 2000). River Nitra belongs to one of the most contaminated rivers of Slovakia in long-term period. The river basin has several tributaries, which are also contaminated (Slobodnik and Brinkman, 2000; Kordik *et al*., 2012,). The environment is disturbed by human activity. It is an example of area with severe environmental problems in view of the long-standing importance of coal-mining, electricity generation and the chemical industry**.** There is a problem at the chemical plant through the emission of carbide and calcareous dust, chlorine, ethylene/propylene oxides and vinyl chloride (Drgona and Turnock, 2002). The Nitra River is classified as Category V (contamination with As, Cu, Hg and Pb) at Chalmova station (immediately downstream of the Novaky power station and chemical plant). Further pollution in this area arises from lignite - mining (Turnock, 1998). The Nitra River contamination is caused by industrial and municipal emissions, and a low level of wastewater treatment (Masliev *et al*., 1994; Liska *et al*., 1996). The contaminants include also heavy metals with a high ecotoxicity and ability to be acummulated in the biotic and abiotic environmental sphere.

The aim of the study was to estimate the risk of contamination of riverside sediments as well as alluvial soil in vicinity of Nitra river by dangerous heavy metals.

2. Material and methods

2.1. Sampling sites

The samples of riverside sediments were collected in years 2011 and 2012 from 28 exactly defined sample points (using GPS) along the Nitra river. Based on the recommendations of local residents three localities (Male Krstenany, Vycapy–Opatovce and Cernik) along the river Nitra were selected for the research with the requirement that examined site was located in the flood territory and was flooded during the year. In each of the localities the sampling points (in Male Krstenany 17, Vycapy-Opatovce 16 and Cernik 17 sampling points) using GPS were exactly assessed. From each of the points the samples of soil were collected and analysed.

2.2. Soil analysis

In all soil samples agrochemical characteristics were determined. Soil reaction pH/KCl (c (KCl) = 1 mol/dm^3, CentralChem, Slovakia) was determined electrometrically (691 pH Meter Metrohm, Swiss), a content of organic carbon (C_{OX}, %) using volumetric method according to Tjurin (H_2SO_4, $K_2Cr_2O_7$; $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$: Merck, Germany), while a content of humus (Hum, %) was calculated from C_{OX} content. Contents of available nutrients (K, Mg Ca, P) were determined using Mehlich 3 extraction by AAS method (K, Mg Ca) or spectrophometrically (P). Pseudototal content of heavy metals (HMs) (Pb and Cd) including all forms besides residual metal fraction was assessed in soil extract by *aqua regia* (HCl: CentralChem, Slovakia, HNO_3: Merck, Germany) and content of Pb and Cd mobile forms in soil extract by NH_4NO_3 (c = 1 mol/dm^3, Merck, Germany) and determined by AAS method (AAS Varian AA Spectr DUO 240FS/240Z/UltrAA, Varian, Australia). The Hg content was determined using AMA 254 Advanced Mercury Analyzer. Gained results in mg/kg were evaluated according Law No. 220/2004 (valid in the Slovak Republic).

2.3. Statistical evaluation of results

The results were evaluated using the descriptive statistics and regression analysis. To assess the PLI (The Pollution Load Index) of riverside sediments the regression models of PLI dependence from the sample point were used. Regression and correlation analysis (Pearson) was used for the assessment the relationships between HMs. All results obtained from soil sampling of investigated localities were processed into graphic forms of isoline maps using programme ArcView 3.2 (a planar interpolation of observed parameters).

3. Results and discussion

3.1. Contamination of riverside sediments of Nitra river

The samples of river side sediments were collected from 28 exactly defined sample points along the Nitra river. The Pollution load index (PLI) has been increasing downstream of Nitra river due to contamination by Cd and Hg (see Figure 1). The Pollution load index (PLI) (Tomlinson *et al*., 1980) is obtained by calculation from the concentration factor (CF) of each metal, in consideration of its natural background value (Angulo, 1996):

$$CF = \frac{C_{metal}}{C_{background\ value}}$$

where: CF = concentration factor,

n = number of metals,

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times ... \times CF_n}$$

C_{metal} = concentration od metal in sediement,
$C_{background\ value}$ = natural concentration of metal.

If the value of PLI > 1, the sample is contaminated, the value of PLI < 1 indicates that the sample is not contaminated (Harikumar *et al.*, 2009). Natural concentrations of determined elements are (mg/kg): Cd = 0.2; Cr = 82.2; Cu = 18; Hg = 0.06; Ni = 26; Pb = 18; Co = 12 and Zn = 60 (Sefcik *et al.*, 2008)

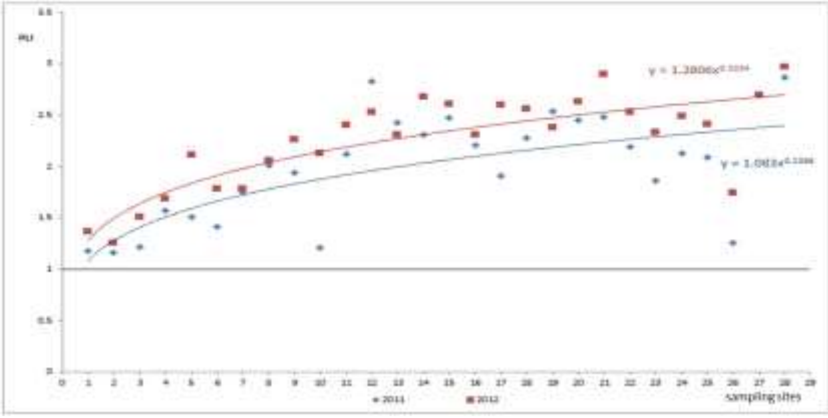


Figure 1: PLI in samples of river side sediments from 28 defined sample points (2010, 2011)

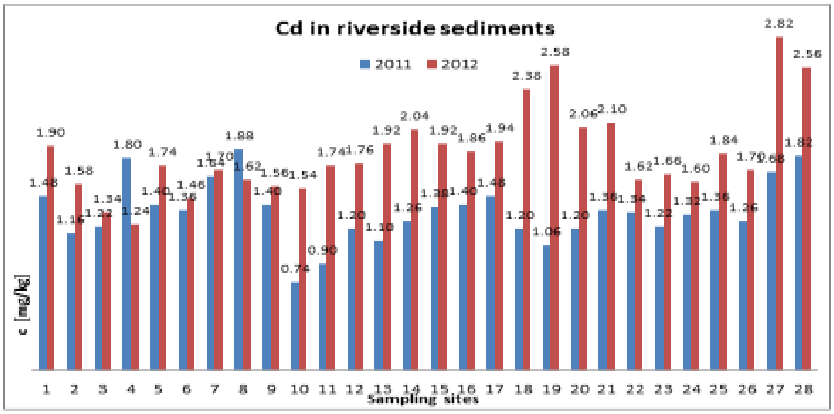


Figure 2: Cd content (mg/kg) in river side sediments along the Nitra river (2010, 2011)

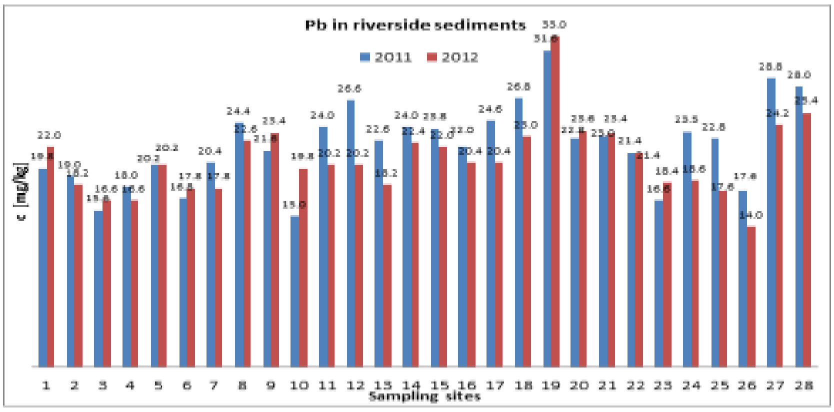


Figure 3: Pb content (mg/kg) in river side sediments along the Nitra river (2010, 2011)

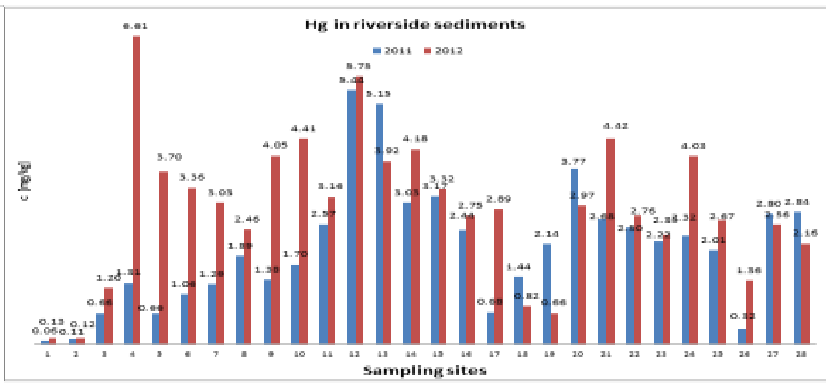


Figure 4: Hg content (mg/kg) in river side sediments along the Nitra river (2010, 2011).

The determined values of total Cd and Hg contents in river side sediments were in interval 0.74-1.88 mg/kg and 0.06-5.44 mg/kg, respectively. In all sample points the hygienic limit for Cd content (0.4 mg Cd/kg) was exceeded (see Figure 2). In 5 sample points the total Pb content in river side sediments was exceeded (see Figure 3). With exception of 2 sample points also the hygienic limit for Hg (0.15 mg Hg/kg) were exceeded in all sediment samples (see Figure 4).

3.2. Contamination of alluvial soil in flood territory of Nitra river

Three localities (Male Krstenany, Vycapy–Opatovce and Cernik) in the flood territory along the river Nitra were investigated. The area of these localities was flooded during the year. Soil in these localities has weakly acid – strongly acid (pH 6.36-9.08) exchangeable soil reaction, humus content 1.09%-4.78% (middle – strongly humic), high Mg (222.30-1856.7), middle till very high K (99.60-463.90) and very low till very high P contents (3.52-241.66 (in mg/kg). In all studied localities the soil content of mobile Pb forms determined in extract of NH_4NO_3 was higher than the limit value given by the legislation. The intervals were 0.10-0.24, 0.17-0.32 and 0.11-0.25 mg Pb/kg of soil in Male Krstenany, Vycapy–Opatovce and Cernik, respectively. The values of total Cd content determined in soil extracts by *aqua regia* were in intervals 0.25-0.95, 2.04-2.52 and 0.63-1.35 and total content of Hg in intervals 0.06-1.6, 0.04-0.07 and 0.03-0.36 mg/kg respectively. It means that cadmium and mercury are the most dangerous HMs present in the enhanced amounts in soil of investigated localities (see Table 1).

Table 1: Determined average values of Cd and Pb mobile forms (MF) contents and pseudototal contents (PC) and Hg total content (TC) in soil from observed localities

Locality	Cd (mg/kg)		Pb (mg/kg)		Hg (mg/kg)
	MF	PC	MF	PC	TC
Male Krstenany (A)	0.059	0.56	0.182	27.65	0.3315
Correlation coefficient R	0.2706		-0.0178		
Vycapy- Opatovce (B)	0.051	2.23	0.235	24.70	0.05882
Correlation coefficient R	0.2683		0.3129		
Cernik (C)	0.06	0.93	0.17	30.86	0.1211
Correlation coefficient R	0.2231		0.4356		
Limit value*	**0.1**	**0.7**	**0.1**	**70**	**0.5**

*Law No. 220/2004

Table 2: The correlation matrix for the determined pseudototal (total) risky HMs

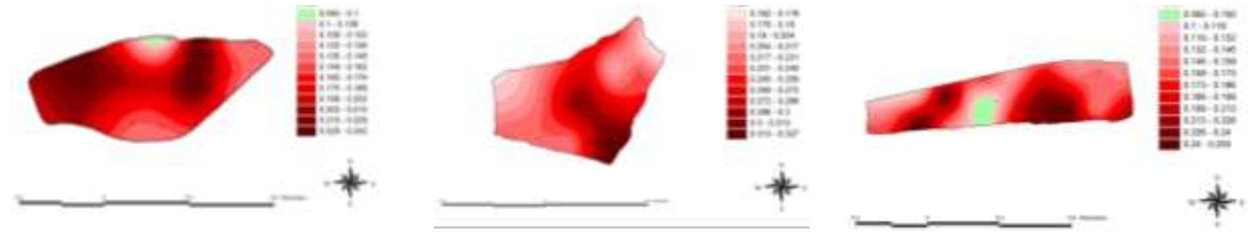
	Cd			Pb			Hg		
	A	B	C	A	B	C	A	B	C
Cd	1	1	1						
Pb	0.374	0.593*	0.502*	1	1	1			
Hg	-0.412	-0.107	0.544*	-0.553*	-0.013	0.286	1	1	1

* Correlation is significant at the $p < 0.05$

Heavy metals can entry into the environment due various human activities and in high concentrations can disrupt the natural terrestrial ecosystem (Yadav *et al*., 2009). In high concentrations all risky HMs have a strong toxic effect and are considered to be dangerous environmental pollutants (Chehregami *et al*., 2005). Cadmium, lead and mercury belong to the most dangerous elements with significant negative effects on all components of the environment as well as on the human health (Zahir *et al*., 2005; Rousseau *et al*., 2007; Cobb, 2008; Bernard, 2008).

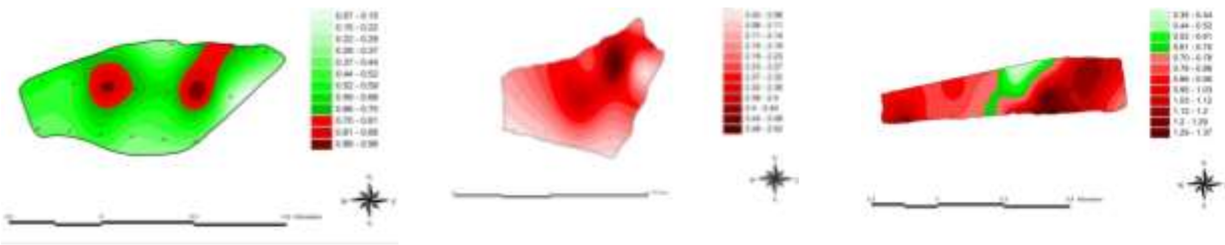
3.3. Isoline maps of the investigated localities

The isoline maps were created for each of determined HMs in each locality (Figures 5-7).



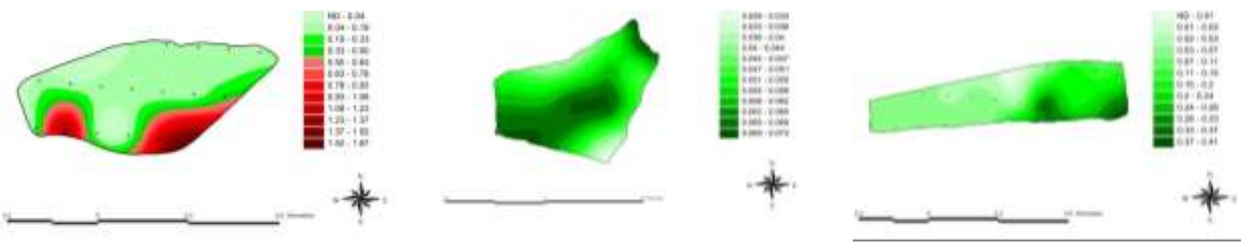
(a) (b) (c)

Figure 5: Content of mobile Pb forms (mg/kg) in Male Krstenany (a), Vycapy-Opatovce (b), Cernik (c).



(a) (b) (c)

Figure 6: Pseudototal Cd content (mg/kg) in Male Krstenany (a), Vycapy-Opatovce (b) and Cernik (c).



(a) (b) (c)

Figure 7: Total Hg content (mg/kg) in Male Krstenany (a), Vycapy-Opatovce (b) and Cernik (c).

4. Conclusions

Based on the obtained results cadmium and mercury could be considered the most dangerous metals present in the enhanced amounts in soil of all three investigated localities. In Cernik also the soil contamination by Co was confirmed, while the determined values of soil content 19.0-25.80 mg Co/kg was by 27-72% higher than the limit value (0.15 mg/kg) given by the legislation. The obtained results confirmed the risk of alluvial soils as well as riverside sediment contamination by the Nitra river.

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