Journal of Microbiology, Biotechnology and Food Sciences

Stanovič et al. 2012 : 1 (February Special issue) 806-812

REGULAR ARTICLE

HEAVY METALS IN MIDDLE NITRA RIVERSIDE

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ABSTRACT

Present state of environment is widely affected by various impacts of man which significantly eliminate negative affecting of its influence on the environment. In the past this fact was not so implemented and thus there was uncontrolled escape of contaminants of organic, but also inorganic origin into various components of environment. The most sensitive component is water ecosystem and its close plates (base sediments, banks sediments and biosphere near the flows).

River Nitra ranks among the most affected water ecosystems in SR that was in 1965 the recipient of sludge, that was by accident in Zemianske Kostoľany uncontrolled spilled into the river with aftermath of long-term contamination of all sub-components in ecosystem, mainly by heavy metals (Hg, As, Pb, etc.).

Soil contamination by Cd and Hg was analytically confirmed. The contents of these risk elements in soil extract of *aqua regia* 1.85 - 3.7 fold (Cd) and 4.57- 36.3 fold (Hg) exceeded the limit values (0.4 $mg.kg^{-1}$ and 0.15 $mg.kg^{-1}$ respectively) given by the legislative. Other metals exceeding limit values were lead (1.064 - 1.072 fold), zinc (1.096 - 1.192 fold) and chromium (1.172 – 1.644 fold).

From assessed soil content of heavy metals only bioavailable forms of Pb determined in soil extract by NH_4NO_3 2.0 - 3.3 fold exceeded the limit value 0.1 $mg.kg^{-1}$.

Keywords: Nitra river, heavy metals, soil contamination, pollution

INTRODUCTION

Water with its indispensable economic and ecological importance belongs to basic components of the environment. Groundwater and surface water have important functions as the part of the environment and are also very important for ensure of economic and other needs. Due to intensive exploitation 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 the 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 above sea level) 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 form the environment for the biodiversity of biotopes, 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 especially 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 objective of the work was to determine the content of Cd, Pb, Ni, Zn, Cu, Cr, Co and Hg in Middle Nitra riverside.

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 Topoľčany 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 Upper Nitra Mines 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 Nováky.

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 of the Slovak Republic.

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**).

The flame atomic absorption spectrometry (AAS Varian AA Spectr. DUO 240 FS/240Z) was the used as the analytical method for heavy metal levels determination.

In Table 1 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 Topoľčany was 30 km from Zemianske Kostoľany (south-west). The maximal distance (sample point Nitra Mlynárce) was 68.5 km from Upper Nitra Mines (UNM) in Handlová (south - west).

Table 1 Localities of sediment sample collection and their position to potential sources of the environmental contamination

No.	Locality of sediment sample collection	Position of locality toward emission sources			
		Nováky	Handlová	Prievidza	Z.Kostoľany
1.	Topoľčany	SW 31 km	SW 46.5 km	SW 40 km	SW 30 km
2.	Topoľčany - bridge	SW 31.5 km	SW 47 km	SW 40.5 km	SW 30.5 km
3.	Kovarce	SW 35.5 km	SW 51 km	SW 44.5 km	SW 34.5 km
4.	Preseľany	SW 41.5 km	SW 57 km	SW 51 km	SW 40.5 km
5.	Koniarovce	SW 43 km	SW 58.5 km	SW 52.5 km	SW 42 km
6.	Výčapy - Opatovce	SW 44.5 km	SW 60 km	SW 54.0 km	SW 43.5 km
7.	Čakajovce	SW 50 km	SW 65.5 km	SW 60 km	SW 49 km
8.	Lužianky	SW 52 km	SW 67.5 km	SW 62 km	SW 51 km
9.	Nitra Mlynárce	SW 53 km	SW 68.5 km	SW 63 km	SW 52 km

Legend: SW – south -west

RESULTS AND DISCUSSION

In Table 2 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 matter 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 **(Takáč 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 (3.12% – 6.24%) due to high content of oxidizable carbon (1.81% – 3.62%).

The soil contamination by Cd and Hg was analytically confirmed. The contents of these risk elements in soil extract by *aqua regia* 1.85 – 3.7 fold (Cd) and 4.57– 36.3 fold (Hg) exceeded the limit values (0.4 $mg.kg^{-1}$ and 0.15 $mg.kg^{-1}$ respectively) given by the legislation. Other metals exceeding limit values were lead (1.064 – 1.072 fold), zinc (1.096 – 1.192 fold) and chromium (1.172 – 1.644 fold).

Table 2 Soil reaction and heavy metals content in soil extract by *aqua regia* ($mg.kg^{-1}$)

No.	Locality of sediment sample collection	pH (H_2O)	pH (KCl)	***Aqua regia*** ($mg.kg^{-1}$)							
				Cd	**Pb**	**Ni**	**Zn**	**Cu**	**Cr**	**Co**	**Hg**
1.	**Topoľčany**	7.72	7.45	**0.74**	15.0	12.2	43.8	9.60	17.6	6.8	**1.703**
2.	**Topoľčany-bridge**	7.86	7.40	**0.90**	24.0	22.2	**109.6**	22.2	31.0	11.4	**2.570**
3.	**Kovarce**	8.21	7.46	**1.20**	**26.6**	25.0	**119.2**	26.0	**73.2**	10.8	**5.444**
4.	**Preseľany**	8.12	7.40	**1.10**	22.6	22.2	**110.0**	22.0	45.4	10.2	**5.152**
5.	**Koniarovce**	8.06	7.51	**1.26**	24.0	21.0	91.6	18.8	**63.2**	10.2	**3.030**
6.	**Výčapy-Opatovce**	8.15	7.46	**1.38**	23.8	23.0	92.0	19.2	**82.2**	10.2	**3.173**
7.	**Čakajovce**	8.04	7.44	**1.40**	22.0	22.8	82.6	17.4	**63.6**	9.4	**2.445**
8.	**Lužianky**	8.00	7.53	**1.48**	24.6	28.0	79.4	20.2	37.8	10.8	**0.685**
9.	**Nitra Mlynárce**	8.12	7.58	**1.20**	**26.8**	30.6	89.4	22.0	**58.6**	11.6	**1.438**
	Limit value*	**-**	-	**0.40**	**25.00**	**40.00**	**100.0**	**30.00**	**50.00**	**15.00**	**0.15**
	Average	8.07	7.47	1.18	23.27	23.00	90.84	19.71	52.51	10.16	2.849
	Min	7.72	7.40	0.74	15.00	12.20	43.80	9.60	17.60	6.80	0.685
	Max	8.45	7.58	1.48	26.80	30.60	119.2	26.00	82.20	11.60	5.444
	St. dev.	0.15	0.06	0.24	3.48	5.11	22.19	4.54	21.01	1.43	1.597
	Median	8.09	7.46	1.20	24.00	22.80	91.60	20.20	58.60	10.20	2.570

Legend: *Law No 220/2004 Z.z. on the protection and use of agricultural land

Sin et al. (2001) found 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 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 reported 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, respectively.

Table 3 Heavy metals content in soil extract by NH_4NO_3 and content of C_{ox} and humus ($mg.kg^{-1}$)

No.	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
1.	Opatovce	1.81	3.12	0.032	**0.200**	0.140	0.110	0.080	0.035	0.105
2.	Novaky	2.90	5.00	0.048	**0.295**	0.220	0.120	0.180	0.040	0.160
3.	Chalmova	3.62	6.24	0.048	**0.285**	0.200	0.105	0.125	0.035	0.160
4.	M. Krstenany	2.85	4.91	0.045	**0.265**	0.200	0.145	0.150	0.040	0.155
5.	Partizanske	3.47	5.98	0.041	**0.225**	0.165	0.105	0.135	0.040	0.120
6.	Partizanske -	2.55	4.40	0.045	**0.265**	0.235	0.150	0.165	0.035	0.125
7.	Chynorany	2.45	4.22	0.048	**0.255**	0.185	0.115	0.140	0.045	0.115
8.	Bosany	2.47	4.26	0.058	**0.330**	0.270	0.115	0.205	0.060	0.165
9.	Topolcany	2.85	4.91	0.046	**0.320**	0.215	0.110	0.175	0.035	0.145
	Limit value*	-	-	**0.10**	**0.10**	**1.50**	**2.00**	**1.00**	-	-
	Average	2.77	4.78	0.05	0.27	0.20	0.12	0.15	0.04	0.14
	Min	1.81	3.12	0.03	0.20	0.14	0.11	0.08	0.04	0.11
	Max	3.62	6.24	0.06	0.33	0.27	0.15	0.21	0.06	0.17
	St. dev.	0.55	0.95	0.01	0.04	0.04	0.02	0.04	0.01	0.02
	Median	2.85	4.91	0.05	0.27	0.20	0.12	0.15	0.04	0.15

Legend: *Law No 220/2004 Z.z. on the protection and use of agricultural land

CONCLUSION

The polluted river water resulted in pollution of riverside sediments of Nitra river. From observed 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.

Acknowledgments: Our work was supported by the project implementation: Centre of excellence for white-green biotechnology, ITMS 26220120054, and by the Research & Development Operational Programme funded by the ERDF.

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