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SHORT COMMUNICATION

YEAR COMPARISON OF CONTENTS OF THE RISK ELEMENTS IN STREAM-SIDE SEDIMENTS IN THE UPPER FLOW OF THE RIVER NITRA

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ABSTRACT

The aim of the work was to compare the content of Cd, Pb, Ni, Zn, Cu, Cr, Co and Hg in Upper Nitra riverside in years 2011 and 2012. 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. Risk metals contents in the soil samples were determined and evaluated according Law 220/2004. The flame atomic absorption spectrometry was the used analytical method for heavy metal levels determination. The average values of pH/KCl were 7,32 (2011) and 7,19 (2012), it means 1,8 % decreased value in comparison to 2011. In 2012 the average Cd sediment content was by 6% higher and the Hg content up to three times higher than those in 2011. 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.

Keywords: heavy metals, riverside sediments, environment

INTRODUCTION

Water is one of the essential elements of the environment with the necessary economic and ecological significance. Groundwater and surface water are a part of the environment and are also important for ensuring economic and other needs. Due to intensive use, it is necessary to save, regenerate and regulate water resources **(Volaufova and Langhammer, 2007)**. Quality of surface water is affected by many factors. The most important are the geomorphological conditions, weather effects, and anthropogenic activity. In recent years, the quality of surface waters is particularly affected by human impact **(Abbas et al. 2007)**. The content of pollutants causes inconvenient quality of surface waters **(Ansari et al. 2009)**. River basin of Nitra is part of the Upper Nitra region. The flow springs in the Malá Fatra mountains and continues into the Danubian Lowland, where it empties into the river Váh. The length of the flow is 196.7 km. The Basin has several water in flower which are also contaminated.

River with its inflous creates an environment for biodiversity of biotopes, vegetable and animal species. This environment is disturbed by the human activity. Heavy and frequent accidents contribute to reducing the ecological environment quality in basin of the river Nitra **(Andrei, Stranai, 2007)**. The river Nitra is one of the most polluted rivers in the Slovak Republic, due to many industrial and communal emissions and low level of procesing the waste water **(Masliev et al., 1994)**.

The quality of water in the river Nitra is particularly influenced by the activity of industrial enterprises, especially Chemical factory in Nováky, mines Upper Nitra in Prievidza and in Handlova, heat station and powerhous in Zemianske Kostoľany **(Liška et al., 1996).** The aim of the contribution was a year comparison of quality of Cd, Pb, Ni, Zn, Cu, Cr, Co and Hg in sediments of the upper flow of the river Nitra.

MATERIAL AND METHODS

The samples of bank sediments along the river Nitra were obtained from nine sites along the upper flow of the river Nitra. The distance between the first point of sample in Opatovce above Nitra and the last sampling point in Topoľčany was 50 km. The starting point was selected because of the relocation of the Nitra River in Opatovce in 2009 to a new river bed in the length of 1850 meters. The reason for building a new bed area for the upcoming release of new production capacity in the mine of Upper Nitra in Prievidza. At a depth of over

200 meters is a coal cave from which it is said to get 7.2 million tons of lignite the next few years. The river is automatically added to the original flow in Novaky.

The samples of bank sediments from these sites were collected by soil probe. Pseudototal content of Cd, Pb, Ni, Zn, Cu, Cr and Co was found in the extract of aqua regia and the content of mobile forms of selected heavy metals in the soil by extraction with NH_4NO_3 (c = 1 mol.dm^{-3}). The results were evaluated according to law 220/2004. As an analytical method for determination of heavy metals was used flame atomic absorption spectrometry (AAS Varian Spectra AA, DUO 240 FS/240Z).

RESULTS AND DISCUSSION

The table 1 lists the names of the sample locations of bank sediments and their consternation from industrial sources polluting the environment. The minimal distance from the source of contamination is Nováky 2 km from the chemical factory Nováky, the maximal distance is Topoľčany 42.3 km from Mine Handlová.

Table 1 Sample points of bank sediments and their distance and orientation of the sources of pollution

Č.	Point of supply	Emission source			
		Nováky	Handlová	Prievidza	Z.Kostoľany
1.	Opatovce ab. Nitra	SSV 6.8 km	SZ 14 km	SZ 5.5 km	SSV 8 km
2.	Nováky	S 2 km	Z 14 km	JZ 2 km	S 3.2 km
3.	Chalmová	JZ 6.2 km	JZ 18 km	JZ 8 km	JZ 4.9 km
4.	Male Kršteňany	JZ 11 km	JZ 23 km	JZ 13 km	JZ 10 km
5.	Partizánske	JZ 13.3 km	JZ 25 km	JZ 15.5 km	JZ 12.3 km
6.	Partizánske - confl.	JZ 16.5 km	JZ 28.5 km	JZ 18.8 km	JZ 15.5 km
7.	Chynorany	JZ 21.5 km	JZ 33.5 km	JZ 20.6 km	JZ 20.7 km
8.	Bošany	JZ 25.5 km	JZ 37 km	JZ 27.5 km	JZ 24.5 km
9.	Topoľčany	JZ 30.8 km	JZ 42.3 km	JZ 32.8 km	JZ 30 km

Table 2 and Table 3 are listed the amounts of the exchangeable soil reaction, humus content and the content of heavy metals in the soil extract in aqua regia in 2011 and 2012. With increasing exchangeable soil reaction, content of organic material and clay, the solubility of many metals degrades due to the increased adsorption and immobilization. One of the parameters that markedly affect the proportion of bioavailable forms of metals is pH **(Takáč et al., 2009)**.

Table 2 Soil reaction and the concentration of heavy metals in bank sediments in the extract of aqua regia (mg.kg^{-1}) in 2011

Č.	Point of supply	pH (KCl)	Cox (%)	*Aqua regia* (mg.kg^{-1})							
				Cd	**Pb**	**Ni**	**Zn**	**Cu**	**Cr**	**Co**	**Hg**
1.	**Opatovce above N.**	7.28	3.03	**1.48**	19.80	21.80	69.00	14.00	23.40	11.00	0.06
2.	**Nováky**	7.09	5.08	**1.16**	19.00	19.80	57.80	14.00	21.60	10.60	0.11
3.	**Chalmová**	7.60	3.99	**1.22**	15.60	13.80	52.20	11.20	14.60	8.40	0.66
4.	**M. Kršteňany**	7.36	4.42	**1.80**	18.00	18.00	48.20	13.60	19.00	9.80	**1.31**
5.	**Partizánske**	7.22	4.96	**1.40**	20.20	20.20	49.00	15.00	24.00	10.40	0.66
6.	**Partizánske-confl.**	7.41	3.75	**1.36**	16.80	16.40	52.00	12.40	17.60	9.00	**1.07**
7.	**Chynorany**	7.35	5.02	**1.64**	20.40	21.20	58.20	17.40	23.80	10.20	**1.29**
8.	**Bošany**	7.31	5.39	**1.88**	24.40	21.00	72.20	17.80	24.20	12.00	**1.89**
9.	**Topoľčany**	7.30	5.81	**1.40**	21.60	22.80	70.00	18.80	35.80	11.40	**1.38**
	Limit value	-	-	**1.00**	**115**	**60.00**	**200**	**70.00**	**90.00**	**20.00**	**0.75**
	Average	7.32	4.61	**1.48**	19.53	19.44	58.73	14.91	22.67	10.31	**0.94**
	Min	7.09	3.03	**1.16**	15.60	13.80	48.20	11.20	14.60	8.40	0.06
	Max	7.60	5.81	**1.88**	24.40	22.80	72.20	18.80	35.80	12.00	**1.89**
	St. dev.	0.14	0.88	0.25	2.62	2.88	9.41	2.58	5.96	1.13	0.61
	Median	7.31	4.96	**1.40**	19.80	20.20	57.80	14.00	23.40	10.40	**1.06**

The amounts of the exchange reaction we found out in 2011 moved in interval 7.09 - 7.60, which defines the spotted sediments as neutral to alkaline. In 2012, amounts of pH / KCl ranged from 6.90 to 7.35, which represents a slight decrease. The average pH / KCl in 2011 was 7.32 and 7.19 in 2012, which represents a 1.8% decrease. In case of the humus content in 2011, the samples can be defined as medium to highly replenished of humus (3.03% - 5.81%). In 2012, the humus content decreased to range between 1.72 to 5.66%.

Contamination of bank sediments by risk elements during the period 2011 and 2012 was confirmed. Cadmium and mercury were the only two elements, in which we observed overrun of limit amounts according to the law 220/2004.

Table 3 Soil reaction and the concentration of heavy metals in bank sediments in extract of aqua regia (mg.kg^{-1}) in 2012

Č.	Point of supply	pH (KCl)	Cox (%)	*Aquq regia* (mg.kg^{-1})							
				Cd	Pb	Ni	Zn	Cu	Cr	Co	Hg
1.	**Opatovce ab. N.**	7.28	2.69	**1.90**	22.0	21.2	83.8	14.6	18.8	11.8	0.13
2.	**Nováky**	7.09	1.72	**1.58**	18.2	21.2	57.8	14.0	22.4	12.4	0.12
3.	**Chalmová**	7.60	4.51	**1.34**	16.6	17.0	68.2	13.2	15.8	10.8	**1.19**
4.	**M. Kršteňany**	7.36	3.48	**1.24**	16.6	14.6	50.6	12.0	16.0	8.8	**6.61**
5.	**Partizánske**	7.22	4.39	**1.74**	20.2	21.8	80.8	16.2	23.2	11.8	**3.70**
6.	**Partizánske-confl.**	7.41	3.72	**1.46**	17.8	19.4	56.0	13.4	18.4	11.4	**3.36**
7.	**Chynorany**	7.35	3.78	**1.70**	17.8	17.4	68.4	14.0	16.8	10.0	**3.03**
8.	**Bošany**	7.31	5.66	**1.32**	22.6	22.0	90.2	18.4	21.8	11.6	**2.46**
9.	**Topoľčany**	7.30	4.75	**1.56**	23.4	22.0	94.0	18.8	27.2	11.4	**4.05**
	Limit value	-	-	**1.00**	**115**	**60.00**	**200**	**70.00**	**90.00**	**20.00**	**0.75**
	Average	7.19	3.86	**1.57**	19.47	19.62	72.20	14.96	20.04	11.11	**2.74**
	Min	6.90	1.72	**1.24**	16.60	14.60	50.60	12.00	15.80	8.80	0.12
	Max	7.35	5.66	**1.90**	23.40	22.00	94.00	18.80	27.20	12.40	**6.61**
	St. dev.	0.14	1.16	0.20	2.64	2.70	15.71	2.36	3.86	1.10	**2.07**
	Median	7.20	3.78	**1.58**	18.20	21.20	68.40	14.00	18.80	11.40	**3.03**

In all locations, the cadmium was in bank sediments above the limit amount. The lowest concentrations of Cd (1.16 mg.kg^{-1}) in 2011 was in Nováky, the highest Cd concentration (1.88 mg.kg^{-1}) was in Bošany site, which represents 16 to 88% of overrun of the limit amounts (1.00 mg.kg^{-1}). The average concentration of cadmium in all areas in 2011 is 1.48 mg.kg^{-1}. It is 48% of the excess of the limit amount.

Also in 2012, the cadmium was in bank sediments at all sites over the limit amount. High concentrations of Cd (1.24 mg.kg^{-1}) in 2012 was in Malé Kršteňany, the highest Cd concentration (1.90 mg.kg^{-1}) was the site Opatovce above Nitra, which represents 24 to 90% exceeded limit amount. The average concentration of cadmium in all sampling sites in 2012 is 1.57 mg.kg^{-1}, which represents 57% exceeded of the limit amounts.

Another risk factor that exceeded the limit amount with his concentration in bank sediments was mercury. In 2011, the excess of the limit was showed in the five sampling sites. The lowest concentration of Hg (0.06 mg.kg^{-1}), which does not exceed the limit amount (0.75 mg.kg^{-1}) was at the point of Opatovce above Nitra. The highest concentration of Hg (1.89 mg.kg^{-1}) was in Bošany. This concentration exceeds 152% of the limit amount. The

average concentration of mercury in all sampling sites in 2011 is 0.94 $mg.kg^{-1}$, which represents 25% of overrun of the limit values.

In 2012, the increased concentration of mercury have resulted in seven sampling sites. The lowest concentration of Hg (0.12 $mg.kg^{-1}$), which does not exceed the limit amount (0.75 $mg.kg^{-1}$) was at the point Nováky. The highest concentration of Hg (6.61 $mg.kg^{-1}$) was in Bošany area that exceeds the limit amount by up to 781%. The average concentration of mercury in all sampling sites in 2012 is 2.74 $mg.kg^{-1}$, which is 487 % of the limit amount.

From all elements we monitored, we did not noticed the overrun of any statutory limit amounts in all sampling sites.

CONCLUSION

From all the risk elements, we observed increases in concentrations only in cadmium and mercury. From other risk elements limits were not exceeded.

A comparison of the average amounts of the concentration of cadmium in the years 2011 and 2012 shows that in 2012 the average cadmium concentration has increased 6%. The average concentration of mercury in 2012 compared the previous year increased three times.

As a result of contamination of bank sediments along the river Nitra can be also polluted water. Improvement of the current situation would be taking an effective measures, such as improvement of cleaning the wastewater from industrial factories and urban areas, as well as construction of new wastewater cleaners.

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