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Assessment of Ecological Risk of Sediment in Rivers of Eastern Slovakia

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The physicochemical processes participating on the heavy metals accumulation in sediment are precipitation, adsorption, chelation, etc. Besides the natural processes, metals may enter into the aquatic system due to anthropogenic factors such as mining operation, disposal of industrial wastes and applications of biocides for pest. The concentration of metals in sediments depends not only on anthropogenic and lithogenic sources but also upon textural characteristics, organic matter contents, mineralogical composition and depositional environment of the sediment. In recent years, numerous sediment heavy metal contamination assessment methods have been developed, including the index method, the dynamic method, the synthesis methods in chemistry, ecology and toxicology, etc.
The aim of this study is to assess the sediment quality in the 22 sampling sites in east of Slovakia using potential ecological risk index for four kind of heavy metals concentrations in the samples taken from different locations of this interest area. The potential ecological risk indices in the following order Cu > Cr > Pb > Zn were found. The results of ecological risk index was from 25.75 to 3798.25, whereas the highest values calculated around areas of mining activities demonstrated extremely strong risk of ecological damage. The potential ecological harms decrease with increasing distance from mining activities.

1. Introduction

Sediment is an essential, integral and dynamic part of river basins. In natural it is derived from the weathering and erosion of minerals, organic material and soils in upstream areas and from the erosion of river banks and other in-stream sources. As surface-water flow rates decline in lowland areas, transported sediment settles along the river bed and banks by sedimentation. Heavy metal pollution in the aquatic environment is one of the critical issues due to the toxic and persistent characters (Zhan et al., 2010, Varol and Sen, 2012). Heavy metals in water reservoir originate from both natural processes and anthropogenic sources. Natural processes like atmospheric inputs and geological weathering of rocks and soil, directly to surface waters, is usually the largest natural source. Comparatively, anthropogenic sources are mainly from industrial processing, urban sewage, mining activity and agricultural run – off (Rezaei and Sayadi, 2015). After being introduced into the aquatic environment, heavy metals from the aqueous phase eventually become deposited to sediment through physical, chemical or biological mechanisms (Yuan et al., 2012; Zhan et al., 2010). Sediments play an important role in elemental cycling in aquatic environment. Sediment can be sensitive indicators for monitoring contaminants in aquatic environments (Sayadi et al. 2010, Sayadi et al., 2008).
Many researchers have used sediment to study the behaviour of metals (Sayadi et al. 2010, Sayadi et al., 2008, Singovszka and Balintova, 2012; Singovszka and Balintova, 2014).
In Slovak republic there are some localities with existing acid mine drainage (AMD) generation conditions. The negative results of AMD activity can be observed mainly in the localities after the mining of sulphide ores and raw materials containing sulphides. At the deposits Roznava and Rudnany the surrounding carbonate system is partly buffering the AMD evolution but the locality Sobov and Smolnik represent the classical mine areas producing AMD with high metal concentrations and low value of the pH (about 3-4) as a result of chemical oxidation of sulphides and other chemical processes (Slesarova et al., 2010). This was the reason for starting a systematic monitoring of geochemical development in acid mine drainage in order to prepare a prognosis in terms of environmental risk and use of these sediment as an atypical source of a wide range of elements

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(Slesarova et al., 2007). It is important to know the migration, transformation behaviour and rules of heavy metals in sediment and make an accurate assessment of contamination level and extent at each site. Till now, researchers have made some achievements on studies of heavy metal pollution. Due to spatial and temporal variations in water and sediment chemistry, a monitoring program that provides a representative and reliable estimation of the quality of surface waters and bottom sediments has become an important necessity (Angelovicova and Fazekasova, 2013). The assessment model on heavy metal pollution in sediment can be useful in environmental protection (Hong-gui et al, 2012).

The overall objective of the present study is to assess the heavy metal contamination in river sediments of some polluted rivers. Specific objective of this study is to assess the level of heavy metal concentrations in the sediment, its spatial distribution and compare it with the USEPA quality guideline, to select different pollution indices of the assessment of heavy metal contamination and to assess the ecological risk resulting from sediment contamination.

2. Materials and methods

2.1 Study area

Eastern Slovakia region (Figure 1) occupies about one third (32%) of an overall area of Slovak Republic, where 29 % of total Slovakian population is situated (1.6 million). Region is bordered with Poland to the north, Ukraine to the east, Hungary to the south and region of Banska Bystrica and Zilina to the west. From an administrative point of view, the region consists of two large territorial units – Presov and Kosice Region. The region of Eastern Slovakia consists of 5 regions: Spis, Saris, Gemer, Abov and Zemplin (Lacika, 2002).

From a geomorphologic point of view, the territory of Eastern Slovakia is rugged and varied. The most important geological formation of Eastern Slovakia is a flysch band, situated in the northern part of the region. Soils in the eastern region have a very diverse representation, because they have developed as a result of geological processes, so they have inherited basic physical and chemical properties of parent rocks.

According to geomorphologic conditions in the Eastern Slovakia, there are 3 climate zones situated here: hot area, slightly warm area and cool area from south to north.

Considering environmental protection, the region of Eastern Slovakia is considered to have the most valuable environment with its fauna and flora. There are several national parks situated in this region: Tatra National Park (TANAP) – which is a biosphere reserve since 1993, National Park of Pieniny (PIENAP), part of this Park is situated in Poland, Poloniny National Park, National Park Slovak Karst, and National Park Slovak Paradise. It is very interesting, that almost all large protected areas have their continuation beyond the state boundary. Typical cross – border national parks include: TANAP, PIENAP (to Poland), POLONINY (Poland, Ukraine) and Slovak Karst (Ukraine) (Nebesky and Wilson, 2001).

Size of total Hornad River Basin in Slovakia is 4 403 km^2. The main districts of river basin are Spiska Nova Ves, Kosice, Kosice-okolie, Gelnica, Presov, Sabinov, Poprad and Bardejov. The Hornad stems in Vikartovce at a height of 1,500 meters above sea level. The most important tributaries of river Hornad include Hnilec, near Jaklovce but folded a water reservoir Ružín. After about 51 km (Kysak) of its water flow and river Svinka the village Nižná Myšľa are in close proximity flows into the river Torysa and Olsava. Hornád River rises on the eastern side of the massif Kráľovej hole. From there flows routed through melaphyre, Paleogene shales, sandstones and conglomerates that also generates river flow in limestone bedrock Slovak Paradise, Galmus, massively Montenegro, which is excreted in quartzite bedrock. The part of assessment river belong to the Bodrog stems (Laborec, Latorica and Ondava). Hornad and its tributaries finally the mouth of the Danube to the Black Sea in Romania (Kupcik, 2013).

2.2 Sediment sampling

Sediments samples were collected from 22 sediment samples in 2015 (Figure 1). The sediment was dried, homogenized and sieved bellow 0,063 mm. Chemical analyses were performed by the XRF method using by SPECTRO iQ II (Ametek, Germany). Results of chemical analyses of the sediment were compared with the limited values according to the Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields and with the USEPA quality guideline.

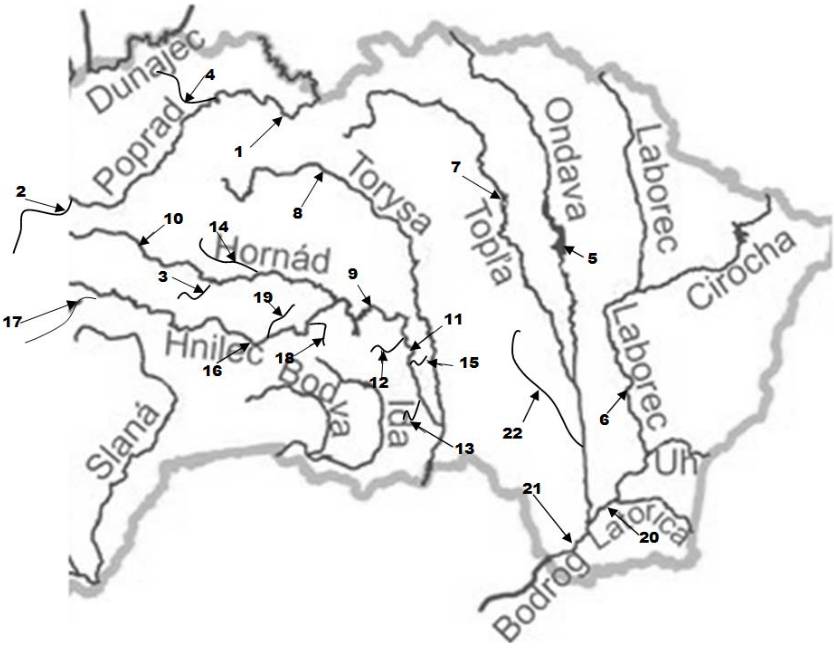

Figure 1: Monitoring area – East Slovakia

2.3 Methods of potential ecological risk assessment

This research employed the Potential Ecological Risk Index (PERI) proposed by Hakanson (1980) to evaluate the potential ecological risk of heavy metals. This method comprehensively considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of heavy metals. (Nabholz, 1991, Singh et al., 2010, Douay et al., 2013). PERI is formed by three basic modules: degree of contamination (C_D), toxic – response factor (T_R) and potential ecological risk factor (E_r). According to this method, the PERI of the single element (E^i_R) and comprehensive PERI can be calculated via the following equations:

$$C_f^i = \frac{C_i}{C_n^i} \quad (1)$$

$$E_r^i = C_f^i x T_r^i \quad (2)$$

$$RI = \sum_{i=1}^{n} E_r^i \quad (3)$$

Where C_i is the mean concentration of an individual metal examined and C^i_n is the background concentration of the individual metal. In this work, as background concentrations the contents of selected elements in sediment unaffected by mining activities in assessment area were used. C_f^i is the single – element index. E_r^i is the potential ecological risk index of an individual metal. RI is a comprehensive potential ecological risk index and T_r^i is the biological toxic factor of a single element, which is determined for Zn =1, Cr = 2, Cu = Pb= 5 (Hakanson, 1980). The criteria for contamination factor its classification shows Table 1. The Table 2 shows Risk grades indexes and grades of potential ecological risk of heavy metal pollution.

Table 1 Criteria for contamination factor and degree of contamination and their classification

Contamination factor	Classification
Cf < 1	Low
1 ≤ Cf < 3	Moderate
3 ≤ Cf < 6	Considerable
Cf ≥ 6	Very high

Table 2 Risk grades indexes and grades of potential ecological risk of heavy metal pollution

E^i_r	Risk grade	RI value	Risk level	Risk degree
$E^i_r < 30$	Slight	$R^i < 40$	A	Slight
$30 \le E^i_r < 60$	Medium	$40 \le R^i < 80$	B	Medium
$60 \le E^i_r < 120$	Strong	$80 \le R^i < 160$	C	Strong
$120 \le E^i_r < 240$	Very strong	$160 \le R^i < 320$	D	Very strong
$E^i_r \ge 240$	Extremely strong	$R^i \ge 320$	E	Extremely strong

3. Results and discussion

The mean total concentrations of 4 heavy metals in sediment of 22 sediments samples are presented in Table 3.
Results of XRF analysis of sediments were compared with the limited values according to the Slovak Act. No. 188/2003 Coll of Laws on the application of treated sludge and bottom sediments to fields (Table 3).
Protection Agency (USEPA) The chemical contaminations in the sediments were evaluated by comparison with the sediment quality guideline proposed by USEPA. These criteria are shown in Table 2, too.
The limits values by US EPA are more strictly like Limits values by Slovak legislation. Limits values for both cases occurred only in concentration of Cu (Slovinky and Turzovsky Creek). Exceedance of limits values may be due to mining activities in the past in this area.

Table 3 The results of chemical analysis of heavy metals concentration in sediment samples

		Place	Cr	Cu	Zn	Pb
1	Main stream	Poprad	<5.0	<1.0	*91.0*	<2.0
2	Tributaries	Beliansky creek	*40.8*	*65.1*	44.3	<2.0
3		Slovinky	*161.5*	***1204***	*462.8*	*61.2*
4		Velicky creek	<5.0	<1.0	*761.4*	<2.0
5	Main stream	Ondava	*60.1*	*29.6*	57.9	<2.0
6		Laborec	*146.9*	<1.0	42.3	<2.0
7		Topla	<5.0	*33.8*	36.0	<2.0
8		Torysa	<20	23.0	32.0	<2.0
9		Hornad	26.5	*97.2*	*273.8*	*57.6*
10		Hornad Betlanovce	<5.0	22.7	66.6	<2.0
11		Hornad Lake	<5.0	*36.4*	46.0	<2.0
12	Tributaries	Cermelsky creek	*504.2*	*90.1*	43.7	<2.0
13		Myslavsky creek	*138.1*	*75.5*	*127.6*	<2.0
14		Novovesky creek	*42.0*	*59.9*	*337.8*	15.7
15		Opatsky creek	<5.0	*125.7*	67.6	<2.0
16	Main stream	Hnilec	*51.7*	*255.0*	*378.4*	*78.2*
17	Tributaries	Herlikov creek	*51.0*	*400.2*	*134.2*	*110.8*
18		Kojsovsky creek	*65.6*	*258.7*	*414.8*	*80.0*
19		Turzovsky creek	*963*	***1925***	*557.8*	*222.8*
20	Main stream	Latorica	<5.0	3.5	26.3	<2.0
21		Bodrog	*131.0*	*30.3*	55.9	<2.0
22	Tributaries	Chlmec	< 5.0	19.7	23.7	<2.0
	Limits	**Slovak legislation**	**-**	**1000**	**2500**	**750**
		US EPA	*40*	*25*	*90*	*25*

In this study, Latorica river is used as a reference element, it has the least impact on the concentration of metals in sediments. The results of potential ecological risk assessment (Table 4) indicated that the potential ecological risk was arranged in the order of E_R^i (Cu) > E_R^i (Cr) > E_R^i (Pb) > E_R^i (Zn). Cu was the key influence factor to cause the risk, an its mean value of E_R^i was up to 61.80. Extremely strong risk demonstrated for Cu in two sampling sites (Slovinky and Turzovsky creek).The range of Ri was 25.75 (Poprad) – 3798.25 (Turzovsky creek), demonstrating that the sediment ecological damage degrees around mining activities were extremely strong risk. The potential ecological harms decrease with increasing distance from mining activities.

Table 4 E^i_r and RI of heavy metals in sediments from waters of Eastern Slovakia

			E_R^i				RI	Risk level
			Cr	**Cu**	**Zn**	**Pb**		
1	Main stream	Poprad	2.00	1.45	17.30	5.00	25.75	A
2	Tributaries	Beliansky creek	16.32	93.00	8.40	5.00	122.72	C
3		Slovinky	64.60	1720	88.00	153.00	2025.6	E
4		Velicky creek	2.00	1.45	144.70	5.00	153.15	C
5	Main stream	Ondava	24.04	42.3.	11.00	5.00	82.34	B
6		Laborec	58.76	1.45	8.05	5.00	73.26	B
7		Topla	2.00	48.3.	6.85	5.00	62.15	B
8		Torysa	8.00	32.85	6.10	5.00	51.95	B
9		Hornad	10.10	138.85	52.05	144.0	345.50	E
10		Hornad Betlanovce	2.00	32.45	12.65	5.00	52.10	B
11		Hornad Lake	2.00	52.00	8.75	5.00	67.75	B
12	Tributaries	Cermelsky creek	201.68	128.70	8.30	5.00	343.68	E
13		Myslavsky creek	55.24	107.85	24.25	5.00	192.34	D
14		Novovesky creek	16.80	85.55	64.20	39.25	205.80	D
15		Opatsky creek	2.00	179.55	12.85	5.00	199.40	D
16	Main stream	Hnilec	20.68	364.30	71.95	195.50	652.43	E
17	Tributaries	Herlikov creek	220.40	571.70	25.50	277.00	1094.60	E
18		Kojšovsky creek	26.24	369.55	88.85	200.00	684.64	E
19		Turzovky creek	385.20	2750	106.05	557.00	3798.25	E
20	Main stream	Latorica	2.00	5.00	5.00	5.00	17.00	S
21	Main stream	Bodrog	52.40	43.30	10.65	5.00	111.35	C
22	Tributaries	Chlmec	2.00	28.15	4.50	5.00	39.65	A

4. Conclusions

The sediment quality in 22 sediment samples of rivers in east Slovakia was evaluated using XRF method. The results were compared with Slovak legislation standard and with US EPA standards.
Based on the comparison of the metals concentration determined in sediments can be said that according to the Slovak legislation mainly bottom sediments from Turzovsky and Slovinky creeks cannot be directly apply into soils. Properly should be used for the evaluation of indicators in the first place our laws and regulations other guidelines should be used only as a supplementary assessment.
The potential ecological risk index for sediments shows extremely strong risk for all tested streams of the Eastern Slovakia. In addition, the research showed that the mining activities in the past and today pollute the sediment in the rivers near the mining area. Appropriate engineering decisions and ecological measures should be taken to control the heavy metals concentration in sediments and it is important to carry out an ecological restoration of the polluted areas.
Ecological risk management provides policy makers and resource managers as well as the public the systematic methods that can affect decision making. The results provide comprehensive sediment contamination status of heavy metals and potential origin of contamination in the creek, giving insight into decision making for water source security.

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Reference

Angelovicova L., Fazekasova D., 2013, The effect of heavy metal contamination to the biological and chemical soil properties in mining region of middle Spis (Slovakia), International Journal of Ecosystems and Ecology Science 3/4, 807-812.

Douay, F., Pelfrêne, A., Planque, J., Fourrier, H., Richard, A., Roussel, H., Girondelot, B., 2013, Assessment of potential health risk for inhabitants living near a former lead smelter, Part 1: metal concentrations in soils, agricultural crops, and homegrown vegetables, Environ. Monit. Assess., 185, 3665–3680, DOI:10.1007/s10661-012-2818-3

Hakanson L., 1980, An ecological risk index for aquatic pollution control, a sedimentological approach. Water Research, 14, 975–1001.

Hong-gui D., Teng – feng G., Ming –Hui L., Deng X., 2012, Comprehensice assessment model on heavy metal pollution in Soil, Int. J. Electrochem. Sci. 7, 5286-5296.

Lacika, J., 2002, Slovakia: Tourist Guide. Bratislava, Priroda, ISBN-80-07-01024-6.

Liao G., Liao D., Li Q., 2008, Heavy metals contamination characteristics in soil of different mining activity zones, Trans. Nonferrous Met. Soc.China, 18, 207-211.

Nabholz, J. V., 1991, Environmental hazard and risk assessment under the United States Toxic Substances Control, Act, Sci. Total Environ., 109 (91), 649–665, DOI:10.1016/0048-9697

Nebesky R. and Wilson N., 2001, Czech and Slovak Republics. London Lonely Planet.

Zhan S., Peng S., Liu C., Chang Q., Xu J., 2010, Spatial and temporal variations of heavy metals in surface sediments in Bohai Bay, North China, Bulletin of Environmental Contamination and Toxicology, 84, 482-487.

Rezaei A., Sayadi M.H., 2015, Long-term evolution of the composition of surface water from the River Gharasoo, Iran: a case study using multivariate statistical techniques, Environmental Geochemistry and Health, 37(2), 251-261.

Sayadi M.H, Sayyed M.R.G., Saptarshi P.G., 2008, An assessment of the Chitgar River sediments for the shortterm accumulation of the heavy metals from Tehran, Iran, Pollution Research, 27, 627-634.

Sayadi M.H., Sayed M.R.G., Suyash K., 2010, Short-term accumulative signatures' of heavy metal in river bed sediments, Tehran Iran, Environmental Monitoring and Assessment, 162, 465-473.

Singh, A., Sharma, R. K., Agrawal, M., Marshall, F. M., 2010, Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India, Food Chem. Toxicol., 48, 611–619, DOI:10.1016/j.fct.2009.11.041

Singovszka E., Balintova M., 2012, Application Factor Analysis for the Evaluation Surface Water and Sediment Quality, Chemical Engineering Transactions, 26, 183-188, DOI: 10.3303/CET1226031

Singovszka E., Balintova M., 2014, Pollution and potential ecological risk assessment of heavy metals in the Smolnik creek (Slovakia), Chemical Engineering Transactions, 39, 1759-1764, DOI:10.3303/CET1439294

Slesarova A., Kusnierova M., Luptakova, A., Zeman J., 2010, An Overview Of Occurrence And Evolution Of Acid Mine Drainage In The Slovak Republic, Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*:* Vol. 12, Article 3. Available at: http://scholarworks.umass.edu/soilsproceedings/vol12/iss1/3

Slesarova A., Zeman J., Kusnierova M., 2007, Geochemical characteristics of acid mine drainage at the Smolník deposit (Slovak republic), IMWA Symposium 2007: Water in Mining Environments, R. Cidu & F. Frau (Eds), Cagliari, Italy, 467-371.

Szabo S., 2013, River Hornad, <http://abov.vucke.sk/trip/abov/abov/priroda/rieka-hornad.html> accessed 16.2.2016 (in Slovak)

Varol M., Sen B., 2012, Assessment of nutrient and heavy metal contamination in surface water and sediments of the Upper Tigris River, Turkey, Catena, 92, 1-10.

Yuan H., Song J., Li X., Li N., Duan L., 2012, Distribution and contamination of heavy metals in surface sediments of the South Yellow Sea, Marine Pollution Bulletin, 64, 2151-2159.