E. Singovszka, M. Balintova
Technical University of Kosice, Slovakia,
Faculty of Civil Engineering, Institute of Environmental Engineering

COMPARISON OF SEDIMENT QUALITY IN RIVER BASINS IN EASTERN SLOVAKIA

The contamination of aquatic and terrestrial ecosystems with heavy metals and other mining chemicals have been major environmental problems in many mining areas of the world. Industrial wastes, geochemical structure and metals mining form a potential source of metal contaminants in the aquatic environment especially in sediment. Monitoring sediment quality is one of the highest priorities in environmental protection policies. For better knowledge about migration, transformation behaviour and rules of heavy metals in sediment, it is necessary to make an accurate assessment of contamination level and extent at each site. The aim of this study is to assess the river sediment quality in the territory of East of Slovakia, representing the water basins of the rivers Hornad, Laborec, Torysa, Ondava and Topla. Sampling points were selected based on the current surface water quality monitoring network. Investigation was focused on heavy metals (Zn, Cu, Pb, Cd, Ni, Hg, As, Fe, Mn). The content of heavy metals reflected the scale of industrial and mining activities in a particular locality. The sediment quality was evaluated using potential ecological risk index for heavy metals concentrations in the samples.

Key words: sediment, heavy metals, potential ecological risk index.

Е. Сінговжка, М. Балінтова
Технічний університет в Кошице, Словаччина,
факультет будівництва, інститут інженерії довкілля

ПОРІВНЯННЯ ЯКОСТІ ВІДКЛАДЕНЬ РІЧКОВИХ БАСЕЙНІВ У СХІДНІЙ СЛОВАЧЧИНІ

Забруднення водних та наземних екосистем з важкими металами та іншими гірничодобувними хімічними речовинами є основними екологічними проблемами в багатьох гірничодобувних районах світу. Промислові відходи, геохімічна структура та видобування металів є потенційним джерелом забруднень металів у водному середовищі, особливо у відкладеннях. Моніторинг якості осадів є одним з найважливіших пріоритетів політики захисту навколишнього середовища. Для кращого знання про міграцію, поведінку трансформації важких металів у відкладах необхідно точно оцінити міру і ступінь забруднення на кожній ділянці. Метою даного дослідження є оцінка якості річкових осадів на території Сходу Словаччини, що представляють водні басейни річок Хорнад, Лаборц, Ториса, Ондава і Топла. Точки відбору проб були відібрані на основі поточної мережі моніторингу якості поверхневих вод. Дослідження було зосереджено на важких металах (Zn, Cu, Pb, Cd, Ni, Hg, As, Fe, Mn). Вміст важких металів відобразив масштаби промислової та гірничодобувної діяльності в певній місцевості. Якість осаду оцінювали з використанням індексу потенційного екологічного ризику концентрації важких металів у зразках.

Ключові слова: відкладення, важкі метали, потенційний екологічний ризик.

Introduction. Sediments accumulate contaminants and serve as sources of pollution to the ecosystems they are connected with. Pathogens, nutrients, metals, and organic chemicals tend to sorb onto both inorganic and organic materials that eventually settle in depositional areas. If the loading of these contaminants into the waterways is large enough, the sediments may accumulate excessive quantities of contaminants that directly and indirectly disrupt the ecosystem, causing significant contamination and loss of desirable species. Many studies have documented the importance of sediment contamination for ecosystem quality and the widespread incidence of sediment contamination [1, 2]. Sediment quality guidelines are very useful to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guideline, provide useful tools for screening sediment chemical data to identify pollutants of concern and prioritise problem sites and relatively good predictors of contaminations. However, these guidelines are chemical specific and do not include biological parameters. Aquatic ecosystems, including sediments, must be assessed in multiple components (biological data, toxicity, physicochemistry) by using integrated approaches in order to establish a complete and comprehensive set of sediment quality guidelines. The overview of existing sediment quality criteria enable us to state the worldwide harmonisation is missing. Such different outcomes assessment occurs because in different countries have been set for individual indicators various occupational exposure and also have different numbers of monitored indicators [3,4].

Pollution of the natural environment by heavy metals is a universal problem because of their undegradability. When permissible concentration levels are exceeded, most of them have toxic effects on the living organisms. Monitoring sediment quality is one of the highest priorities in environmental protection policies. The main objective is to control and minimize the incidence of pollutant – oriented problems, and to provide water of sufficient quality in order to serve various purposes such as irrigation. River sediment quality in the territory of The aim of this study is to assess the sediment quality in the five river basins (Hornad, Laborec, Torysa, Ondava and Topla) in east of Slovakia. Investigation was focused on heavy metals (Zn, Cu, Pb, Cd, Ni, Hg,As, Fe, Mn). The content of heavy metals, evaluated by potential ecological risk index, reflected the scale of industrial and mining activities in a particular locality.

Study area. *River Hornad* belongs to the River basin of Danube. Area of the Hornad river is 4.414 km^2. In the basin is 27.6 % of arable land, 15.7 % of other agricultural land, 47.4 % of forests, 2.7 % shrubs and grasses and 6.6 % is other land. There is 165 surface water bodies while 162 are in the category of the flowing waters/rivers and 2 are in the category of standing waters/reservoirs. Ten groundwater bodies exist in the basin while 1 is in quaternary sediment, 2 is geothermal waters and 7 are in pre-quaternary rocks. The Hornad river has 11 transverse structures without fishpass in operation. From the point of view of environmental loads, there are 11 high-risk localities which have been identified in the river basin. Diffuse pollution is from agriculture and municipalities without sewerage. The upper stretch of the Hornad river to Spišská Nová Ves is in good ecological status which gets worse to poor status or potential by pollution and hydromorphological pressures. From the Ružín Water Reservoir, the Hornad river achieves moderate ecological status. According to chemical status assessment, the Hornád river is in good status. 56 water bodies (34 %) are failing to achieve good ecological status in Hornad river basin. The water body of intergranular ground waters of quaternary alluviums of the Hornad river basin achieves poor chemical status (pollution from the point and diffuse sources) and poor quantitative status identified on the base of long-term decrease of groundwater levels. The water body of pre-quaternary rocks is in good status – quantitative and chemical [3].

River Ondava is a 146.5 km long river in Slovakia, the northern source river of the Bodrog. Its source is in the Low Beskids (Eastern Carpathian Mountains), near the village Nižná Polianka, close to the border with Poland. The Ondava flows south through the towns Svidník, Stropkov and Trhovište, and through the Ondavská Highlands. Near the village Cejkov, the Ondava joins the Latorica and forms the Bodrog river, itself a tributary of the Tisza. The Ondava river is 44 % regulated [3].

River Torysa is a 129 km (80 mi) long river in eastern Slovakia. Its source is in the Levoča Mountains and it flows through the towns of: Lipany, Sabinov, Veľký Šariš, Prešov, and into the Hornád river near Nižná Hutka, southeast of Košice [3].

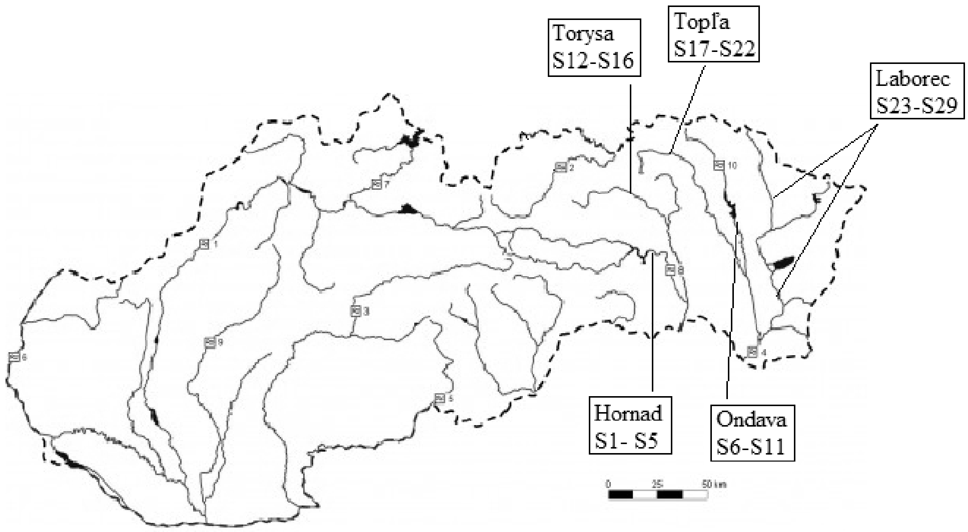
River Topla is a river in eastern Slovakia and right tributary of the Ondava. It is 129.8 km long and its basin covers an area of 1.544 km^2 (596 sq mi).[1]:22 It rises in the Čergov mountains, flows through

Ondava Highlands, Beskidian Piedmont, Eastern Slovak Hills and Eastern Slovak Flat and flows into the Ondava in the cadastral area of Parchovany. It flows through the towns of Bardejov, Giraltovce, Hanušovce nad Topľou and Vranov nad Topľou [3].

River Laborec is a river in eastern Slovakia that flows through the districts of Medzilaborce, Humenné, and Michalovce in the Košice Region, and the Prešov Region. The river drains the Laborec Highlands. Tributaries of the River Laborec include River Uh which joins River Laborec near the city of Drahňov in Michalovce District, and the River Cirocha. River Laborec itself is a tributary, flowing into the River Latorica. Catchment area of Ižkovce hydrometric profile at River Laborec is 4, 364 km^2 and it is situated at 94.36 m a.s.l [3].

Materials and methods

Sample collection. Sediments were collected from 29 sample sites from 5 rivers on eastern Slovakia in 2017 (Figure). The sediment was dried, homogenized and sieved bellow 0,063 mm. Chemical analyses were performed by the XRF method using SPECTRO iQ II (Ametek, Germany). Results of chemical analyses of the sediment were compared with the limited values according with Slovak legislation.



Monitoring area

Method of potential ecological risk assessment. This research employed the Potential Ecological Risk Index (PERI) proposed by Hakanson (1980) [4] 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 [5, 6]. 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 (Ei^R) and comprehensive PERI can be calculated via the following equations:

$$C_f^i = \frac{C_i}{C_n^i} \tag{1}$$

$$E_r^i = C_f^i x T_r^i \tag{2}$$

$$RI = \sum_{i=1}^{n} E_r^i \tag{3}$$

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 [4]. 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

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

RI value	Risk level	Risk degree
RI < 40	A	Slight
40 ≤ RI < 80	B	Medium
80 ≤ RI < 160	C	Strong
160 ≤ RI < 320	D	Very strong
RI ≥ 320	E	Extremely strong

Result and discussion. The mean total concentrations of 8 heavy metals in sediment of 6 rivers on East of Slovakia are presented in Table 2. 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 2). The results of potential ecological risk and its risk grade showed Table 3. The results of potential ecological risk assessment show, that the Topla River is extremely strong contamined by heavy metals and its pollution can be attributed to human activities. The second worst river is Hornad, it dependence by mining activities in the past. The area of Torysa River and Ondava River represent strong pollution by heavy metals.

Table 2

The result of chemical analysis of sediments

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	mg/kg								
Hornád	S1	14,9	< 5,1	35,8	110,3	< 2	59,4	< 2	167
	S2	< 1	< 5,1	24,3	27,4	< 2	24,8	< 2	38,7
	S3	**82,3**	< 5,1	141,2	233	< 2	130,5	37,9	360,4
	S4	< 1	< 5,1	169,9	108,4	< 2	45,2	51,1	177,4
	S5	12,6	< 5,1	189,9	188	< 2	64,6	< 2	202,7
Ondava	S6	< 1	< 5,1	142	46,3	< 2	88	0	55,9
	S7	< 1	< 5,1	110,2	37,8	< 2	69,7	< 2	40,7
	S8	< 1	< 5,1	50,5	27,3	< 2	48,7	< 2	23,6
	S9	< 1	< 5,1	29,1	39,5	< 2	49,7	< 2	26,8
	S10	< 1	< 5,1	125,9	32,8	< 2	60,1	< 2	33,9
	S11	< 1	< 5,1	200,4	41	< 2	55,4	< 2	55,3
Torysa	S12	< 1	< 5,1	94,1	11,9	< 2	32,5	< 2	28
	S13	< 1	< 5,1	73,5	17,3	< 2	34,8	< 2	45,1
	S14	< 1	< 5,1	28,6	21	< 2	38	< 2	36,1
	S15	< 1	< 5,1	70	34,7	< 2	48,6	< 2	53,8
	S16	< 1	< 5,1	141	15,5	< 2	3,4	< 2	1
Topla	S17	< 1	< 5,1	23,7	15,3	< 2	21,8	< 2	25,8
	S18	< 1	< 5,1	144,6	0,3	< 2	21,4	< 2	1
	S19	< 1	< 5,1	81,5	13,1	< 2	26,4	< 2	22,5
	S20	< 1	< 5,1	49,6	27,3	< 2	31,4	< 2	24,7
	S21	< 1	< 5,1	62,7	19,2	< 2	21,9	< 2	30
	S22	< 1	< 5,1	68,2	25,5	< 2	27,3	< 2	30,1
Laborec	S23	< 1	< 5,1	52,6	18,4	< 2	51,7	< 2	36,3
	S24	< 1	< 5,1	21	33,5	< 2	46,2	< 2	31,7
	S25	< 1	< 5,1	28,1	30,1	< 2	66,5	< 2	51,7
	S26	< 1	< 5,1	36,6	35,8	< 2	54	< 2	33,7
	S27	< 1	< 5,1	5	8,7	< 2	31,6	< 2	30,2
	S28	1,3	< 5,1	28	38	< 2	64,6	< 2	61,1
	S29	< 1	< 5,1	19	37,7	< 2	50,1	< 2	40,7
Limits	**SR**	**20**	**10**	**1000**	**1000**	**10**	**300**	**750**	**2500**

Table 3

The result of potential ecological risk

		RI		
Hornád	S1	263,365	Very strong	D
	S3	1077,51	Extremely strong	E
	S4	255,21	Very strong	D
	S5	269,19	Very strong	D
Ondava	S6	120,1	Strong	C
	S7	114,77	Strong	C
	S9	109,19	Strong	C
	S10	113,22	Strong	C
	S11	118,06	Strong	C
Torysa	S12	76,84	Medium	B
	S13	95,68	Strong	C
	S14	87,88	Strong	C
	S16	109,995	Strong	C
Topla	S17	372,85	Extremely strong	E
	S18	108,2	Strong	C
	S19	338,86	Extremely strong	E
	S20	576,33	Extremely strong	E
	S21	445,38	Extremely strong	E
Laborec	S22	169,79	Very strong	D
	S24	101,44	Medium	B
	S25	104,03	Medium	B
	S26	91,25	Medium	B
	S27	106,26	Medium	B
	S28	101,21	Medium	B

Conclusion. Ecological risk assessment were used for the study of the pollution status of sediments contaminated by heavy metals and their relative potential ecological risk indices. Concentration of heavy metals in sediments of East Slovakia followed Torysa<Ondava<Laborec<Hornád<Topla. The results of sediments in samples showed that the area has been moderate to extremely contaminate by heavy metals and its pollution can be attributed to industrial pollution as well as human activities. The contamination assessment was conducted to provide reasonable evidence about the need of sediment remediation and protection of surface water for water management.

Acknowledgements. This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0563/15).

1. Singovszka E., Balintova M., Holub M. (2014). Assesment of heavy metals concentration in sediments by potential ecological risk index. Inzynieria Mineralna. 15(2) , 137-140. 2. Singovszka E., Balintova M., Demcak S. (2015). Heavy Metals as Environmental Risk from Bottom Sediment, In: Seminár UEI 2015, Technicka univerzita Kosice, Stavebná fakulta, 5 p. 3. Burton Jr., G.A. (2002). Sediment quality criteria in use around the world. Limnology, 3(2), 65–75. 4. Iksandar I. K., Keeney, D. R. (1974). Concentration of heavy metals in sediment cores from selected Wisconsin lakes. Environ. Sci. Technol., 8(2), 165–170. 5. Slovak Environmental Agency. "1 Introduction". Pilot Project PiP1: Hornád/Hernád, Integrated Revitalisation of the Hornád/Hernád River Valley. TICAD. p. 5. 6. Håkanson L. (1980). An ecological risk index for aquatic pollution control: A sedimentological approach. Water Res. 14(8), 975–1001. 7. Wu Y. G., Xu Y. N., Zhang J. H., Hu, S. H. (2010). Evaluation of ecological risk and primary empirical research on heavy metals in polluted soil over Xiaoqinling gold mining region, Shaanxi, China. Transactions of Nonferrous Metals Society of China, 20(4), 688–694. 8. Zandbergen P. A. (1998). Urban watershed ecological risk assessment using GIS: a case study of the Brunette River watershed management. J. Hazard Mater. 61(1–3), 163–173. 9. Slovak Act. No. 188/2003 Coll of Laws on the application of treated sludge and bottom sediments to fields.