Eva SINGOVSZKA, Magdalena BALINTOVA

Technical University of Kosice, Faculty of Civil Engineering

Year over year comparison of sediment quality in the rivers of Eastern Slovakia

Introduction

Trace metals entering the river originate from either natural or anthropogenic sources (Bem, Gallorini, Rizzio & Krzemin, 2003; Wong, Li, Zhang, Qi & Peng, 2003; Adaikpoh, Nwejai & Ogala, 2005; Akoto, Bruce & Darko 2008). In unaffected environments, the concentration of most metals is very low and is typically derived from mineralogy and the weathering processes (Karbassi, Monavari, Nabi Bidhendi, Nouri & Nematpour, 2008). The main anthropogenic sources of heavy metal contamination are due to mining, disposal of untreated and partially treated effluents containing toxic metals, as well as metal chelates from different industries and the indiscriminate use of heavy metal – containing fertilizer and pesticides in agriculture fields (Hatje, Bidone & Maddock, 1998; Nouri, Mahvi, Jahed & Babaei, 2008). Metals enter river water from mining areas through various means such as mine discharge, runoff, chemical weathering of rocks and soils, wet and dry fallout of atmospheric particulate matter (Macklin et al., 2003; Bird et al., 2003; Kraft, Tumpling & Zachman, 2006; Singh et al., 2008; Venugopal et al., 2009). The mine water, runoff from abandoned watersheds and associated industrial discharges are the major source of heavy metal contamination, total dissolved solid and low pH of streams in mining area (US EPA, 1998; Mohanty, Misra & Nayak, 2001; Cravotta, 2008; Shahtaheri, Abdollahi, Golbabaei, Rahimi-Froshani & Ghamari, 2008).

The anthropological influences (i.e. urban, industrial and agricultural activities) as well as the natural processes (i.e. changes in precipitation amounts, erosion and weathering of crustal materials) degrade surface water quality and impair its use for drinking, industrial, agricultural, recreational and other purposes. Due to spatial and temporal variations in water chemistry, a monitoring program

that provides a representative and reliable estimation of the quality of surface waters has become an important necessity. Consequently, comprehensive monitoring programs that include frequent water sampling at numerous sites and include a full analysis of a large number of physicochemical parameters designed for the proper management of water quality in surface waters are required.

Potential ecological risk index (PERI), proposed by Hakanson (1980), is used as a quick and practical tool for environmental assessment, obtaining as results the pollution classification of areas and the identification of the toxic substances of interest, supporting actions for pollution control of limnic aquatic systems. Potential ecological risk index provides a fast and simple quantitative value for PER of a given contamination situation. This model, despite being formulated in 1980s and for limnic systems, has an organized structure based on simple algorithms, including the most important environmental parameters for an ecological risk assessment, and also includes the mathematical relationships between them.

Material and methods

Study area

Hornad belongs to Danube river basin. Area of Hornad 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 164 surface water bodies while 162 are in the category of the flowing waters/rivers and two are in the category of standing waters/reservoirs.

Ten groundwater bodies exist in the basin while one is in quaternary sediment, two is geothermal waters and seven are in pre-quaternary rocks. Hornad 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 Hornad to Spišská Nová Ves is in good ecological status while the lower stretch is changed to poor status. From the Ružín Water Reservoir, Hornad achieves moderate ecological status. According to chemical status assessment, Hornad is in good status. Fifty six 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 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 (SEA, 2015).

Poprad is in Vistula river basin district and is the only Slovak river that drains their waters into Baltic Sea. It sources in High Tatras over Popradské Lake. It flows to the southeast direction up to city of Svit. The river mouths into Dunajec from the right side, in Poland, river km 117.00. It drains the area of 1,890 km^2. There are 83 surface water bodies all in the category of the flowing waters/rivers. Five groundwater bodies exist in the basin while one is in quaternary sediment, one is geothermal

waters and three are in pre-quaternary rocks. Poprad has 27 transverse structures without fishpass in operation. Significant industrial and other pollution sources are: Chemosvit Energochem, a.s., Svit, Whirlpool Slovakia, s.r.o., Poprad, screw factory Exim, Stará Ľubovňa, Východoslovenské stavebné hmoty a.s (closed in 2013). From the point of view of environmental loads, there are 17 high-risk localities which have been identified in the river basin. Diffuse pollution is from agriculture and municipalities without sewerage (Ondruš, 1991).

Laborec is a river in Eastern Slovakia that flows through the districts of Medzilaborce, Humenné, and Michalovce in Košice Region, and Prešov Region. The river drains the Laborec Highlands. Tributaries of Laborec include Uh which joins Laborec near the city of Drahňov in Michalovce District, and Cirocha. Laborec itself is a tributary, flowing into Latorica. Catchment area of Ižkovce hydrometric profile at Laborec is 4,364 km^2 and it is situated at 94.36 m a.s.l. (SEA, 2015).

Sampling materials

Sediment was sampled according to standard ISO 5667-6 which outlines the principles and design of sampling programs and manipulation, as well as the preservation of samples. Monitoring was carried out in the 2017–2018. The samples of sediment were air-dried and ground using a planetary mill to a fraction of 0.063 mm. The chemical composition of sediments was determined by means of X-ray fluorescence (XRF) using SPECTRO iQ II (Ametek, Germany, 2000). Sediment samples were prepared as pressed tablets with a diameter of 32 mm by mixing 5 g of sediment and 1 g of dilution material (Hoechs Wax C Micropowder – M-HWC-C38H76N2O2) and compressing them at a pressure of 0.1 MPa·m^{-2}. The mean total concentrations of 8 heavy metals in sediment of sediments samples are presented in Table 1.

Results of XRF analysis of sediments were compared with the limited values according to the Slovak Act 188/2003

FIGURE 1. Situation of three investigation rivers in Eastern Slovakia

TABLE 1. Results of chemical analyses of sediment from the rivers of Eastern Slovakia in 2017–2018

Year	River	Sampling point	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
			mg·kg^{-1}							
2017	Hornád	S1	14.9	< 5.1	35.8	110.3	< 2	59.4	< 2	167.0
		S3	82.3	< 5.1	141.2	233.0	< 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	188.0	< 2	64.6	< 2	202.7
	Laborec	S1	< 1	< 5.1	52.6	18.4	< 2	51.7	< 2	36.3
		S2	< 1	< 5.1	28.1	30.1	< 2	66.5	< 2	51.7
		S3	< 1	< 5.1	36.6	35.8	< 2	54.0	< 2	33.7
		S4	1.3	< 5.1	28.0	38.0	< 2	64.6	< 2	61.1
	Poprad	S1	< 1	< 5.1	124.7	51.6	< 2	65.7	< 2	100.4
		S2	< 1	< 5.1	28.7	24.7	< 2	50.3	< 2	58.1
		S3	< 1	< 5.1	56.9	2.9	< 2	35.5	< 2	118.6
		S4	< 1	< 5.1	38.5	5.6	< 2	20.0	< 2	105.6
2018	Hornád	S1	< 1	< 5.1	122.0	36.2	< 2	39.4	< 2	85.6
		S2	< 1	< 5.1	28.7	29.4	< 2	40.3	2.5	179.7
		S3	< 1	< 5.1	34.1	27.5	< 2	37.4	< 2	55.9
		S4	< 1	< 5.1	50.9	62.9	< 2	33.9	< 2	71.2
	Laborec	S1	< 1	< 5.1	5.0	8.4	< 2	19.7	< 2	< 1
		S2	< 1	< 5.1	5.0	10.1	2.2	17.7	< 2	< 1
		S3	< 1	< 5.1	5.0	1.5	< 2	13.4	< 2	< 1
		S4	< 1	< 5.1	5.0	10.7	< 2	15.5	< 2	< 1
	Poprad	S1	< 1	< 5.1	5.0	8.1	< 2	2.2	< 2	122.7
		S2	< 1	< 5.1	44.7	14.9	< 2	20.9	< 2	39.4
		S3	< 1	< 5.1	5.0	32.7	< 2	34.5	< 2	49.5
		S4	< 1	< 5.1	5.0	11.5	< 2	2.0	< 2	71.0
×			Limits							
			20	10	1 000	1 000	10	300	750	2 500

Coll. of Laws on the application of treated sludge and bottom sediments to fields. It can be stated that limit values comparing with Slovak legislation were not exceeding in all sediment samples in rivers in Eastern Slovakia.

Potential ecological risk index (PERI)

In this research, potential ecological risk index (PERI) proposed by Hakanson (1980) was used 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, Sharma, Agrawal & Marshall, 2010; Ouay et al., 2013). Potential ecological risk index 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 potential ecological risk index of a single element (E^i_R) and comprehensive potential ecological risk index (RI) can be calculated via the following equations:

$$C^i_f = \frac{C_i}{C^i_n} \qquad (1)$$

where C_i is the mean concentration of an individual metal examined and C_n^i is the background concentration of the individual metal. In this work, background concentrations of contents of selected elements in sediments unaffected by mining activities in the assessment area were used (Table 3). Index C_f^i is the single-element one. The sum of contamination factors for all examined metals represents the contamination degree (C_d) of the environment:

$$C_d = \sum_{i=1}^{n} C^i_f \qquad (2)$$

Indicator E_r^i is the potential ecological risk index of an individual metal. It is calculated by

$$E^i_r = C^i_f \cdot T^i_r \qquad (3)$$

where T_r^i is the toxic response factor provided by Hakanson (1980). Indicator

R^i is the potential ecological risk index, which is the sum of E_r^i:

$$R^i = \sum_{i=1}^{n} E^i_r \qquad (4)$$

Hakanson defined five categories of E_r^i and four categories of R^i, as shown in Table 2.

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

E^i_r	Risk grade	R^i	Risk grade
$E^i_r < 40$	low	$R^i < 150$	low
$40 \le E^i_r < 80$	moderate	$150 \le R^i < 300$	moderate
$80 \le E^i_r < 160$	considerable	$300 \le R^i < 600$	considerable
$160 \le E^i_r < 320$	high	$R^i \ge 600$	very high
$E^i_r \ge 320$	very high	$\times$	

Results and discussion

Based on the monitoring data of sediment quality in the study area, a quantitative analysis of heavy-metal pollution in sediment was conducted using the method of PERI. The results based on potential ecological risk index show that the quality of sediment in 2018 is better than 2017. The worst result were obtained for Hornad in 2017. Significant improvement were occurred at the sampling point S2 in Hornad in 2018. The best results were determined for Laborec in 2018.

TABLE 3. Statistical results of potential ecological risk index of a single element (ER) and comprehensive potential ecological risk index (PERI) for rivers of Eastern Slovakia in 2017–2018

Year	River	Sampling point	E_r								R^i	Risk grade
			As	Cd	Cr	Cu	Hg	Ni	Pb	Zn		
2017	Hornad	S1	149	30	2.95	20.13	40	11.98	5	4.32	263.36	moderate
		S2	823	30	11.62	42.52	40	26.31	94.75	9.31	1 077.51	very high
		S3	10	30	13.98	19.79	40	9.11	127.75	4.54	255.21	moderate
		S4	126	30	15.63	34.31	40	13.02	5	5.24	269.19	moderate
	Poprad	S1	10	30	2	255	40	5.05	5	25.8	372.85	considerable
		S2	10	30	6.86	218.35	40	6.15	5	22.5	338.86	considerable
		S3	10	30	4.18	455	40	7.45	5	24.7	576.33	considerable
		S4	10	30	5.28	320	40	5.10	5	30.0	445.38	considerable
	Laborec	S1	10	30	49.88	99.73	40	5	100.4	38.08	497.34	considerable
		S2	10	30	11.48	47.50	40	5	58.1	38.08	325.91	considerable
		S3	10	30	2.0	12.12	40	5	148.2	38.08	335.27	considerable
		S4	10	30	22.76	5.58	40	5	118.6	38.08	301.59	considerable
2018	Hornad	S1	10	30	11.4	20.13	40	11.45	5	3.95	111.8	low
		S2	10	30	9.3	42.52	40	0.64	6.25	8.36	116.06	low
		S3	10	30	8.7	19.79	40	0.54	5	2.6	107.15	low
		S4	10	30	39.8	34.31	80	0.39	10	6.62	196.12	moderate
	Poprad	S1	10	30	0	9.4	40	5	5	9.02	108.92	low
		S2	10	30	0	17.35	40	52.25	5	2.9	147.5	low
		S3	10	30	0	38	40	86.25	5	3.64	212.89	moderate
		S4	10	30	0	13.35	40	5.00	5	5.22	108.57	low
	Laborec	S1	10	30	2	42	40	8.21	5	1	138.21	low
		S2	10	5.8	2	50.5	40	7.375	5	1	121.67	low
		S3	10	30	2	7.5	40	5.585	5	1	101.09	low
		S4	10	30	2	53.5	40	6.46	5	1	147.96	low

Conclusions

Environmental risk in the water catchments are closely related to the quality and quantity of water flows in the catchment and the quality is one of the most important indicators of risk in the river basin. The monitoring and evaluation of water quality have a permanent place in the process of risk management. The possibility of minimizing the negative impact on the environment presents the assessment and management of environmental risks by using different methodologies. Methodology for assessing environmental risks in the basin presents a risk characterization for the particular conditions of water flows. The results represent the basis for risk management in the river basin, whose task is to ensure the sustainability of water bodies.

Different calculation methods on the basis of different algorithms might lead to a discrepancy of the pollution assessment when they are used to assess the quality of sediment. So it is of great importance to select a suitable method to assess sediment quality for decision making and spatial planning. Pollution indices is a powerful tool for processing, analysing, and conveying environmental information to decision makers, managers, technicians and the public. Potential ecological risk index is based exclusively on chemical parameters of sediments because sediment data show mean integrated values in time, with higher stability than water column parameters; sediments are easily sampled at field work; sediment samples are more representative for time and space scales and analytical data are easily obtained, especially because sediments present high concentrations of contaminants, decreasing the possible errors due to detection limits of the applied analytical method. The results show on the basis on potential ecological risk index that the quality of sediment in 2018 is better than 2017.

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Summary

Year over year comparison of sediment quality in the rivers of Eastern Slovakia. Quality is one of the most important

risk indicators in river basins. Therefore, monitoring and evaluating water and sediment quality has a very important role in process of risk management. The aim of the monitoring is provide for the sustainability of water bodies and these results are the basis for the risk management in the river catchment area. Hornad, Laborec and Poprad are the rivers in Eastern Slovakia. Hornad and Laborec belongs to basin of Danube and Poprad belongs to basin of Vistula. Sediment sampling was carried out according to ISO 5667-6. Monitoring was carried out in the spring on 2017–2018. The chemical composition of sediments was determined by means of X-ray fluorescence (XRF) using SPECTRO iQ II (Ametek, Germany, 2000). The results of sediment quality evaluated by method PERI revealed that the quality of sediment in 2018 was better than 2017. Results of XRF analysis of sediments were compared with the limited values according to the Slovak Act 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields. It can be state that limit values comparing with Slovak legislation were not exceeding in all sediment samples in rivers in Eastern Slovakia. Based on the monitoring data of sediment quality in the study area, a quantitative analysis of heavy-metal pollution in sediment was conducted using the method of potential ecological risk index (PERI) which is method for evaluate the potential ecological risk of heavy metals. It is based exclusively on chemical parameters of sediments because sediment data show mean integrated values in time, with higher stability than water column parameters; sediments are easily sampled at field work; sediment samples are more representative for time and space scales and analytical data are easily obtained, especially because sediments present high concentrations of contaminants, decreasing the possible errors due to detection limits of the applied analytical method. This method comprehensively considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of heavy metals. Potential ecological risk index can be obtained using three basic modules: degree of contamination (*CD*), toxic-response factor (*TR*) and potential ecological risk factor (*ER*). The results show on the basis on potential ecological risk index that the quality of sediment in 2018 is better than 2017. The worst result shows Hornad in 2017. Significant improvement occurred at the sampling point S2 in Hornad in 2018. The best results show Laborec in 2018. The results show on the basis on potential ecological risk index that quality of sediment in 2018 is better than 2017.

Authors' address:
Eva Singovszka
Technical University of Kosice
Faculty of Civil Engineering
Institute of Environmental Engineering
Vysokoskolska 4, 042 00, Kosice
Slovakia
e-mail: eva.singovszka@tuke.sk