Assessment of Heavy Metal Pollution of Water Resources in Eastern Slovakia

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Abstract Sediment quality monitoring is amongst the highest priorities of environmental protection policy. Their main objective is to control and minimise the incidence of pollutant-oriented problems and to provide for water of appropriate quality to serve various purposes such as drinking water supply, irrigation water, etc.

The quality of sediments is identified in terms of their physical, chemical and biological parameters. The particular problem regarding sediment quality monitoring is the complexity associated with analysing a large number of measured variables. This research was realised in order to determine and analyse selected heavy metals present in sediment samples from six river basins on East of Slovakia, represented by the rivers Hornád, Laborec, Torysa, Ondava, Topla and Poprad. Sampling points were selected based on the current surface water quality monitoring network. The investigation was focused on heavy metals (Zn, Cu, Pb, Cd, Ni, Hg,

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As, Fe, Mn). The content of heavy metals reflected the scale of industrial and mining activities in a particular locality. The degree of sediment contamination in the rivers has been evaluated using an enrichment factor, pollution load index, geo-accumulation index and potential environmental risk index.

Keywords Heavy metals, Pollution indices, Sediments, Statistic methods

1 Introduction

The analysis of bottom sediment quality is an important yet sensitive issue. 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. Based on spatial and temporal variations in water chemistry, a monitoring programme that provides a representative and reliable estimation of the quality of surface waters has become an important necessity. Heavy metals are usually present at low concentrations in aquatic environments; however, deposits of anthropogenic origin have raised their own concentrations, causing environmental problems in lakes [1, 2]. According to [3] the highest concentrations of heavy metals in sediment may be related to the terrigenous input and anthropogenic influence. The high content of trace metals in the sediments can be a good indication of man-induced pollution, and high levels of heavy metals can often be attributed to terrigenous input and anthropogenic influences, rather than the natural enrichment of the sediment by geological weathering [3]. An associated geochemical process plays an important role in the deposition of trace and heavy elements from the water column to the bottom sediments [1, 4, 5]. Heavy metals are non-biodegradable; they are not removed from the water as a result of self-purification. Once they are discharged into water bodies, they are adsorbed on sediment particles, accumulate in reservoirs and enter the food chain [6]. Consequently, comprehensive monitoring programmes include regular water sampling at numerous places and a whole analysis of a large number of physico-chemical parameters designed for the proper management of water quality in surface waters [7, 8]. Furthermore, they facilitate the identification of the possible factors/sources influencing the system and provide not just a valuable tool for reliable management of water resources but also suitable solutions to pollution problems [9].

In the study of contaminated samples, the determination of the extent or degree of pollution by a given heavy metal requires that the pollutant metal concentration is compared with an unpolluted reference material. Such reference material should be an unpolluted or pristine substance that is comparable with the study samples. In assessing the impact of heavy metal pollution on environments, a number of different reference materials and enrichment calculation methods have been used by various publications [10–12]. There is thus a considerable variation in how the impact of anthropogenic pollution on a given site is quantified.

In the Slovak Republic, there are some localities with existing mining and industrial conditions. Overflows at the rivers in East of Slovakia produce flow with high metal concentrations and low values of pH (about 3–4) as a result of chemical oxidation of sulphides and other chemical processes. This was the reason for initiating the systematic monitoring of the geochemical development to prepare a prognosis in terms of environmental risk [13]. Till now, researchers have made some achievements on studies of heavy metal pollution. The degree of contamination in sediments is determined with the help of three parameters – enrichment factor (EF), pollution load index (PLI) and geo-accumulation index (I_{geo}). A common approach to estimate the degree to which sediment is impacted (naturally and anthropogenically) by heavy metals involves the calculation of the enrichment factor for metal concentrations above uncontaminated background levels [14]. The PLI is aimed at providing a measure of the degree of overall contamination at a sampling site. Sediment geo-accumulation index is the quantitative check of metal pollution in aquatic sediments [15]. Based on spatial and temporal variations in water and sediment chemistry, a monitoring programme which provides a representative and reliable estimation of the quality of surface waters and bottom sediments has become an important necessity [16]. The assessment model of heavy metal pollution in sediments can be used for environmental protection [17].

2 Materials and Methods

2.1 Study Area

Hornád River belongs to the river basin of Danube. Area of the Hornád River is 4,414 km^2. In the basin, 27.6% is arable land, 15.7% is agricultural land, 47.4% is of forests, 2.7% is shrubs and grasses and 6.6% is other lands. There are 165 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 are geothermal waters and seven are in pre-quaternary rocks. The Hornád River has 11 transverse structures without fishpass in operation. Significant industrial and other pollution sources are US Steel Kosice, Rudne bane š. p., Spišská Nová Ves, Kovohuty a.s., Krompachy and Solivary a.s. Prešov. From 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 Hornád River to Spišská Nová Ves is in good ecological status which gets worse to poor status or is potential for pollution and hydromorphological pressures. From the Ružín water reservoir, the Hornád River achieves moderate ecological status. According to chemical status assessment, the Hornád River is in good status. Fifty-six water bodies (34%) are failing to achieve good ecological status in Hornád river basin. The water body of intergranular groundwaters of quaternary alluviums of the Hornád 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 [18].

Poprad River is in the river basin district of Vistula and is the only Slovak river that drains their waters into the Baltic Sea. Its source is in the High Tatras over Popradské Mountain Lake. It flows to the southeast direction up to Svit city. The river mouths into River Dunajec from the right side, in Poland, river km 117.00. It drains an 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 River 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 and Východoslovenské stavebné hmoty a.s. (closed in 2013). From 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 [19].

Ondava is a 146.5-km-long river in Slovakia, the northern source river of the Bodrog. It rises in the Low Beskids (Eastern Carpathian Mountains), next to Nižná Polianka village, close to the border with Poland. The Ondava flows south through the towns Svidník, Stropkov and Trhovište and through the Ondavská Highlands. Next to Cejkov village, the Ondava joins the Latorica and forms the Bodrog River, itself a tributary of the Tisza. The Ondava River is 44% regulated [18].

Torysa is a 129-km (80 mile)-long river in eastern Slovakia. It rises in the Levoča Mountains, and it flows through the towns of Lipany, Sabinov, Veľký Šariš, Prešov and into the Hornád River next to Nižná Hutka village, southeast from Košice [18].

Topla is a river in eastern Slovakia and a right tributary of the Ondava. It is 129.8 km long, and its basin covers an area of 1,544 km^2 (596 mile^2) [1, 22]. It rises in the Čergov mountains, flows through Ondava Highlands, Beskidian Piedmont, Eastern Slovak Hills and Eastern Slovak Flat and joins the Ondava River in the cadastral area of Parchovany. It flows through the towns of Bardejov, Giraltovce, Hanušovce nad Topľou and Vranov nad Topľou [18].

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 Laborec River include River Uh which joins Laborec River near the city of Drahňov in Michalovce District and the River Cirocha. Laborec River itself is a tributary, flowing into the River Latorica. The catchment area of Ižkovce hydrometric profile at Laborec River is 4,364 km^2, and it is situated at 94.36 m a.s.l [18] (Fig. 1).

2.2 Sample and Preparation

Sediment was sampled according to ISO 5667-6 Water Quality, Sampling Part 6: Guidance on Sampling of Rivers and Streams [20]. This standard outlines the

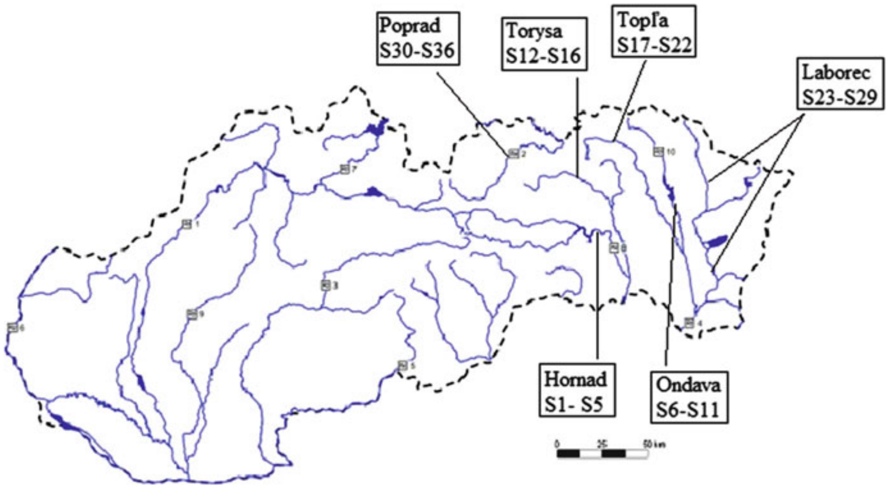

Fig. 1 Location of interested area: East of Slovakia

principles and design of sampling programmes and manipulation, as well as the preservation of samples. 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 using X-ray fluorescence (XRF) SPECTRO iQ II (Ametek, Germany). 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 (Hoechst Wax C Micropowder – M – HWC – $C_{38}H_{76}N_2O_2$) and compressing them at a pressure of 0.1 MPa/m^2.

The mean total concentrations of 8 heavy metals in the sediment of 36 sediments samples are presented in Table 1.

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 [21]; WHO standards (www.who.int); Canadian Sediment Quality Guidelines (CSQG) for protection of aquatic life 1999 [22], with the interim sediment quality values for Hong Kong [23]; Australian and New Zealand Environment and Conservation Council (ANZECC) [24]; and Egyptian drinking water quality standards [25] (Table 1).

The limit values were exceeding for Cu in all rivers excluding Topla River. Nickel and lead are exceeding limit values in all sediment samples according to WHO limit values. Cadmium exceeds the Hong Kong, CSQG, ANZECC and Egyptian limit values, but it is relevant because it depends on the extent of the XRF analysis.

Table 1 Concentration of heavy metals in sediment samples

		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
Poprad	S30	<1	*<5.1*	5	2.6	2.1	2	<2	1
	S31	<1	*<5.1*	*124.7*	51.6	<2	*65.7*	<2	*100.4*
	S32	<1	*<5.1*	28.7	24.7	<2	*50.3*	<2	58.1
	S33	<1	*<5.1*	5	6.3	<2	31.9	<2	*148.2*
	S34	<1	*<5.1*	56.9	2.9	<2	35.5	<2	*118.6*
	S35	<1	*<5.1*	38.5	5.6	<2	20	<2	*105.6*
	S36	<1	*<5.1*	16	1	<2	32.11	2.7	*115.4*
Limits	**SR**	**20**	**10**	**1,000**	**1,000**	**10**	**300**	**750**	**2,500**
	Hong Kong	*12*	*1.5*	–	*65*	–	*40*	*200*	*75*
	WHO		0.01	–	2	–	0.02	0.05	–
	CSQG	33	10	–	110	–	–	250	820
	ANZECC	20	1.2	–	34	–	–	47	200
	Egyptian	–	0.003	–	2	–	0.02	0.01	3

2.3 *Pollution Indices*

2.3.1 Enrichment Factor

Enrichment factor (EF) calculation is a common approach to estimate the anthropogenic impact on sediments [26]. It is mathematically expressed as [27]:

$$\mathrm{EF} = \frac{[M_c/M_r]_s}{[M_c/M_r]_b} \tag{1}$$

where M_c is the content of contamination, M_r is the content of reference elements, s is the sample and b is the background. A reference element is often used as a conservative element [27]. The enrichment factor scale consists of six grades ranging, how indicate the Table 2.

2.3.2 Pollution Load Index

Pollution load index (PLI), for a particular site, has been evaluated using the following method proposed by Tomlinson et al. [28]. This parameter is expressed as:

$$\mathrm{PLI} = (\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \ldots \times \mathrm{CF}_n)^{1/n} \tag{2}$$

where n is the number of the metals (11 in the present study) and CF is the contamination factor. The contamination factor can be calculated from the following relation:

$$\mathrm{CF} = \frac{\text{Metal concentration in the sediment}}{\text{Reference value of the metal}} \tag{3}$$

The contamination factor scale and pollution load index scale are indicated in Tables 3 and 4.

Table 2 The enrichment factor scale

EF $\leq$ 1	Background concentration
EF 1–2	Deficiency to minimal enrichment
EF 2–5	Moderate enrichment
EF 5–20	Significant enrichment
EF 20–40	Very high enrichment
EF > 40	Extremely high enrichment

Table 3 The contamination factor scale

CF < 1	Low contamination
$1 \leq$ CF ≤ 3	Moderate contamination
$3 \leq$ CF ≤ 6	Considerable contamination
CF > 6	Very high contamination

Table 4 The pollution load index scale

PLI < 1	Denote perfection
PLI = 1	Present that only baseline level of pollutants
PLI > 1	Deterioration of site quality

Table 5 Descriptive classes for identifying sediment contamination base on I_{geo} values

I_{geo} values	I_{geo} class	Sediment quality
>5	6	Extremely polluted
4–5	5	Highly polluted
3–4	4	Moderately to highly polluted
2–3	3	Moderately polluted
1–2	2	Unpolluted to moderately polluted
0–1	1	Unpolluted
0	0	Background concentration

2.3.3 Geo-accumulation Index

Geo-accumulation index (I_{geo}), introduced by Muller [12] for determining the extent of metal accumulation in sediments I_{geo}, is mathematically expressed as:

$$I_{geo} = \log_2 \frac{c_n}{1.5B_n} \tag{4}$$

where c_n is the concentration of element n and B_n is the geochemical background value. The factor of 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. The I_{geo} scale consists of six grades ranging (Table 5) from unpolluted to very highly polluted.

2.3.4 Ecological Risk Assessment

For the assessment of sediment pollution, the contamination factor and contamination degree were used. In the version suggested by Hakanson, an assessment of sediment contamination was conducted through references of contaminations in the surface layer of bottom sediments:

$$C_f^i = \frac{C^i}{C_n^i} \tag{5}$$

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, 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. The sum of

Table 6 Criteria for degree of contamination and classification

Contamination factor	Degree of contamination	Classification
$C_f < 1$	$C_d < 1$	Low
$1 \leq C_f < 3$	$1 \leq C_d < 3$	Moderate
$3 \leq C_f < 6$	$3 \leq C_d < 6$	Considerable
$C_f \geq 6$	$C_d \geq 6$	Very high

Table 7 Risk grade indexes and grades of potential ecological risk of heavy metal pollution

E_i^r	Risk grade	Risk level	R^i value	Risk grade
$E_i^r < 40$	Low risk	A	$R^i < 150$	Low risk
$40 \leq E_i^r < 80$	Moderate risk	B	$150 \leq R^i < 300$	Moderate risk
$80 \leq E_i^r < 160$	Considerable risk	C	$300 \leq R^i < 600$	Considerable risk
$160 \leq E_i^r < 320$	High risk	D	$R^i \geq 600$	Very high risk
$E_i^r \geq 320$	Very high risk	E		

contamination factors for all metals examined represents the contamination degree (C_d) of the environment:

$$C_d = \sum_{i=1}^{n} C_f^i \tag{6}$$

E_r^i is the potential ecological risk index of an individual metal. It can be calculated from

$$E_r^i = C_f^i \times T_r^i \tag{7}$$

where T_r^i is the toxic response factor provided by Hakanson (T_r^i for Cr, Cu, Cd, Zn, As, Pb, Ni and Hg are 2, 5, 30, 1, 10, 5, 5 and 40). R^i is the potential ecological risk index, which is the sum of E_r^i:

$$R^i = \sum_{i=1}^{n} E_r^i \tag{8}$$

Hakanson defined four categories of C_f^i, four categories of C_d, five categories of E_r^i and four categories of R^i, as indicated in Tables 6 and 7.

3 Results and Discussion

3.1 Hornád River

The enrichment factor was calculated from the concentrations of heavy metals in bottom sediments of four sampling sites in the study area. The heavy meal

Table 8 Enrichment factor values of heavy metals in Hornád River bed sediment

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S1	0.18	1.00	0.25	0.47	1.00	0.46	0.05	0.46
S3	0.01	1.00	0.17	0.11	1.00	0.19	0.05	0.11
S4	0.01	1.00	1.20	0.47	1.00	0.35	1.35	0.49
S5	0.15	1.00	1.35	0.81	1.00	0.49	0.05	0.56

concentration from sample site S2 was used as background concentration. EF calculation results for sediments are shown in Table 8. The EF values show a depletion trend for As, Cu and Zn (<1). The EF for Cr (S4, S5) and Pb (S4) show minimal enrichment (Fig. 2).

Table 9 shows very high values of PLI (>1) for all sampling sites, which means it is extremely polluted by heavy metals. High values of PLI indicated a deterioration of site quality. The results of the contamination factor for sediment are shown in Table 18. CF for As, Cr, Cu, Pb and Zn show very high contamination.

The calculated I_{geo} values are presented in Table 10. It is evident from the Table that the I_{geo} values for Cd and Hg fall in class "0", indicating that there is no pollution from these metals in the Hornád River sediments. The I_{geo} values for Ni fall within the range 0–2, indicating that it is unpolluted to moderately polluted. Cr and Cu indicated moderately polluted. Highly polluted shows concentration of Pb, which falls to class 5. The extremely polluted for Ondava River is presented by As.

All the values of R^i in the sediments were more than 250, which present moderate to very high risk. The E_r values of all parameters in all sampling locations were from 5 to 823, which reflects a very high ecological risk for the water body posed by these metals (Table 11).

3.2 Ondava River

EF calculation results for sediments are shown in Table 12. The enrichment factor was calculated from the concentrations of heavy metals in bottom sediments of five sampling sites in the study area. The heavy metal concentration from sample site S8 was used as background concentration. The highest enrichment shows chromium and zinc concentration (Fig. 3).

Table 13 shows considerable contamination for Cr and for other elements indicates moderate contamination by heavy metals. High values of PLI indicated a deterioration of site quality (PLI > 1).

The calculated I_{geo} values are presented in Table 14. It is evident from Table 14 that the I_{geo} values for all elements expected Cr fall in class "1", indicating that there is no pollution from these metals in the Ondava River sediments. The I_{geo} values for Cr fall within the range 1–2, indicating that it is unpolluted to moderately polluted.

All the values of R^i in the sediments were less 150 which indicate a low risk for the water body posed by these metals (Table 15).

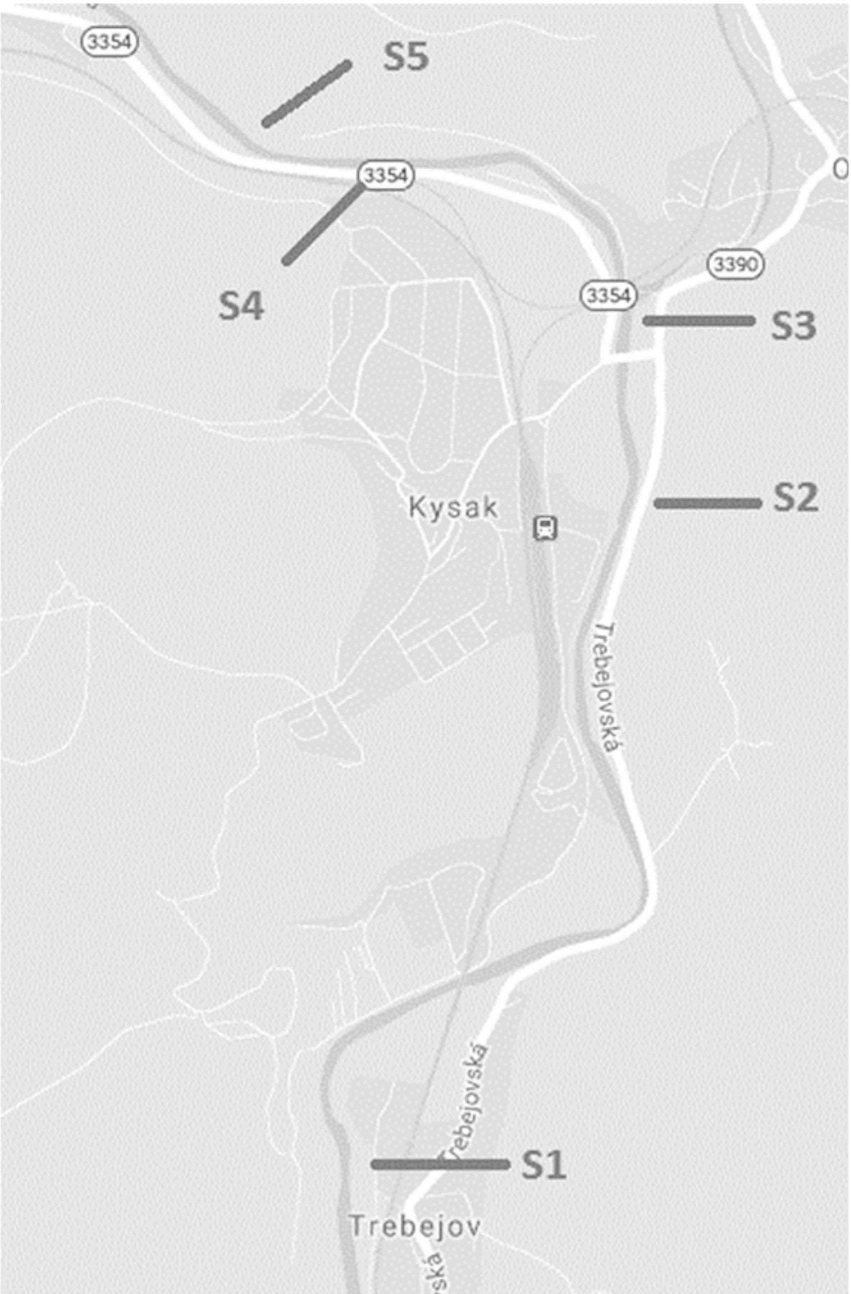

Fig. 2 Location of sediment samples from Hornád River

Table 9 Contamination factor (CF) values and pollution load index of heavy metals in the sediments of Hornád River

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
	CF								PLI
S1	14.90	1.00	1.47	4.03	1.00	2.39	1.00	4.31	2.35
S3	82.30	1.00	5.81	8.503	1.00	5.26	18.95	9.31	6.64
S4	1.00	1.00	6.99	3.96	1.00	1.82	25.55	4.58	2.96
S5	12.60	1.00	7.815	6.861	1.00	2.61	1.00	5.24	3.13

Table 10 Geo-accumulation indexes of heavy metals in Hornád River

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S1	3.31	−0.58	−0.03	1.42	−0.58	0.67	0.58	1.52
S3	5.78	−0.58	1.95	2.50	−0.58	1.81	3.65	2.63
S4	−0.59	−0.58	2.22	1.39	−0.58	0.28	4.09	1.61
S5	3.07	−0.58	2.38	2.19	−0.58	0.79	−0.58	1.80

Table 11 E_r and R^i of heavy metals in sediments from Hornád River

		E_r									
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	R^i	Risk grade
Hornád	S1	149	30	2.95	20.13	40	11.98	5	4.32	263.36	Moderate risk
	S3	823	30	11.62	42.52	40	26.31	94.75	9.31	1,077.51	Very high risk
	S4	10	30	13.98	19.79	40	9.11	127.75	4.54	255.21	Moderate risk
	S5	126	30	15.63	34.31	40	13.02	5	5.24	269.19	Moderate risk

Table 12 Enrichment factor values of heavy metals in Ondava River bed sediment

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S6	1.00	1.00	2.81	1.70	1.00	1.81	1.00	2.37
S7	1.00	1.00	2.18	1.38	1.00	1.43	1.00	1.73
S9	1.00	1.00	0.57	1.45	1.00	1.02	1.00	1.13
S10	1.00	1.00	2.49	1.20	1.00	1.23	1.00	1.43
S11	1.00	1.00	3.96	1.50	1.00	1.14	1.00	2.34

3.3 Torysa River

The results for enrichment factor for Torysa River are shown in Table 16. The highest enrichment indicates zinc concentration. The pattern of the metal concentration at all the stations studied followed Zn > Ni > Cu > As = Cd = Pb = Hg > Cr (Fig. 4).

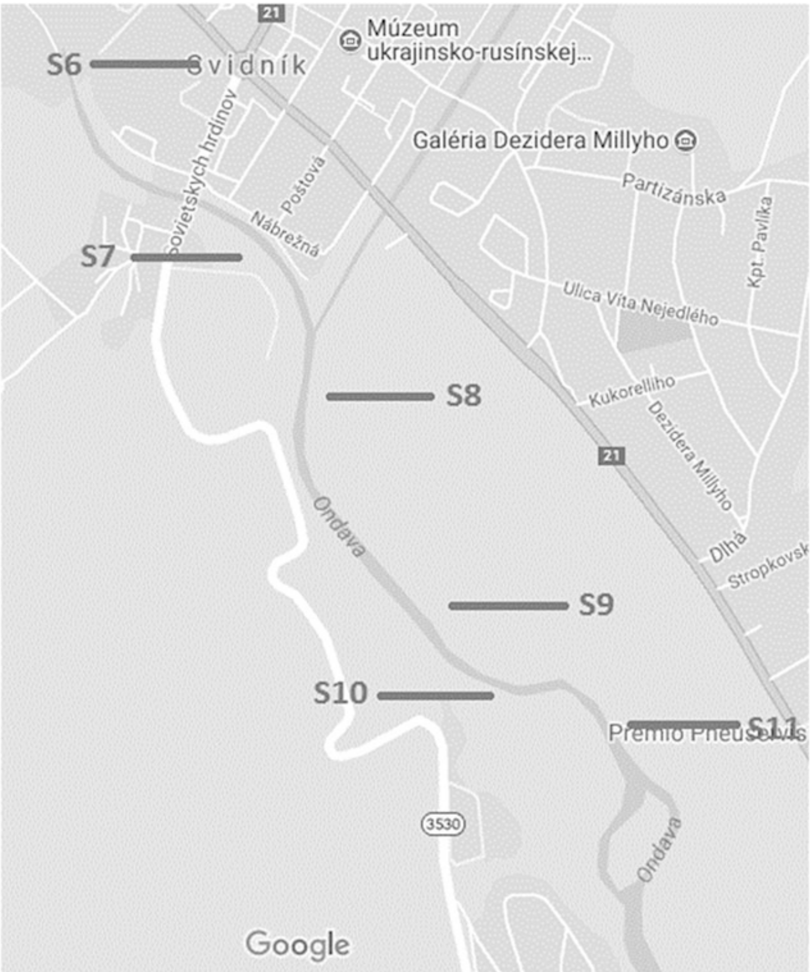

Fig. 3 Location of sediment samples from Ondava River

Table 13 Contamination factor (CF) values and pollution load index of heavy metals in the sediments of Ondava River

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
	CF								PLI
S6	1.96	1.00	2.82	1.70	1.00	1.81	1.00	2.37	1.59
S7	1.96	1.00	2.19	1.38	1.00	1.43	1.00	1.725	1.39
S9	1.96	1.00	0.57	1.44	1.00	1.02	1.00	1.14	1.08
S10	1.96	1.00	2.55	1.20	1.00	1.23	1.00	1.44	1.34
S11	1.96	1.00	3.98	1.50	1.00	1.13	1.00	2.34	1.54

Table 14 Geo-accumulation indexes of heavy metals in Ondava River

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S6	0.39	−0.58	0.91	0.18	−0.58	0.27	−0.58	0.66
S7	0.39	−0.58	0.55	−0.12	−0.58	−0.07	−0.58	0.20
S9	0.39	−0.58	−1.37	−0.05	−0.58	−0.56	−0.58	−0.40
S10	0.39	−0.58	−0.74	−0.32	−0.58	−0.28	−0.58	−0.06
S11	0.39	−0.58	1.41	0.001	−0.58	−0.39	−0.58	0.644

Table 15 E_r and R^i of heavy metals in sediments from Ondava River

	E_r								R^i	Risk grade
	As	Cd	Cr	Cu	Hg	Ni	Pb	Ni		
S6	19.6	30	5.64	8.45	40	9.05	5	2.36	120.1	Low risk
S7	19.6	30	4.38	6.92	40	7.15	5	1.72	114.77	Low risk
S9	19.6	30	1.16	7.20	40	5.1	5	1.15	109.19	Low risk
S10	19.6	30	5.01	6.01	40	6.17	5	1.44	113.22	Low risk
S11	19.6	30	7.96	7.51	40	5.65	5	2.3	118.06	Low risk

Table 16 Enrichment factor values of heavy metals in Torysa River bed sediment

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg
S12	1.00	1.00	0.76	0.67	9.56	1.00	28.00	1.00
S13	1.00	1.00	1.16	0.52	10.23	1.00	45.10	1.00
S14	1.00	1.00	1.35	0.20	11.17	1.00	36.10	1.00
S16	1.00	1.00	2.23	0.49	14.29	1.00	53.80	1.00

Table 17 shows very high contamination for Ni and Zn and for other elements indicates low to moderate contamination by heavy metals. High values of PLI indicated a deterioration of site quality (PLI > 1).

Table 18 presented values of I_{geo}. It is evident from the table that the I_{geo} values for As, Cd, Cu, Pb and Hg belong to class "1", indicating that there is no pollution from these metals in the Torysa River sediments. The I_{geo} values for Cr fall within the range 2–3, indicating that it is moderately polluted. Nickel belongs to class "4" and zinc falls into class "6" which indicates extremely polluted.

All the values of R^i in the sediments belong to range from 150 to 300 which indicate moderate risk for the water body posed by these metals (Table 19).

3.4 Topla River

Table 20 shows the results of enrichment factor for Topla River. As, Cd, Cr, Hg and Pb indicate background concentration. Nickel presents deficiency to minimal

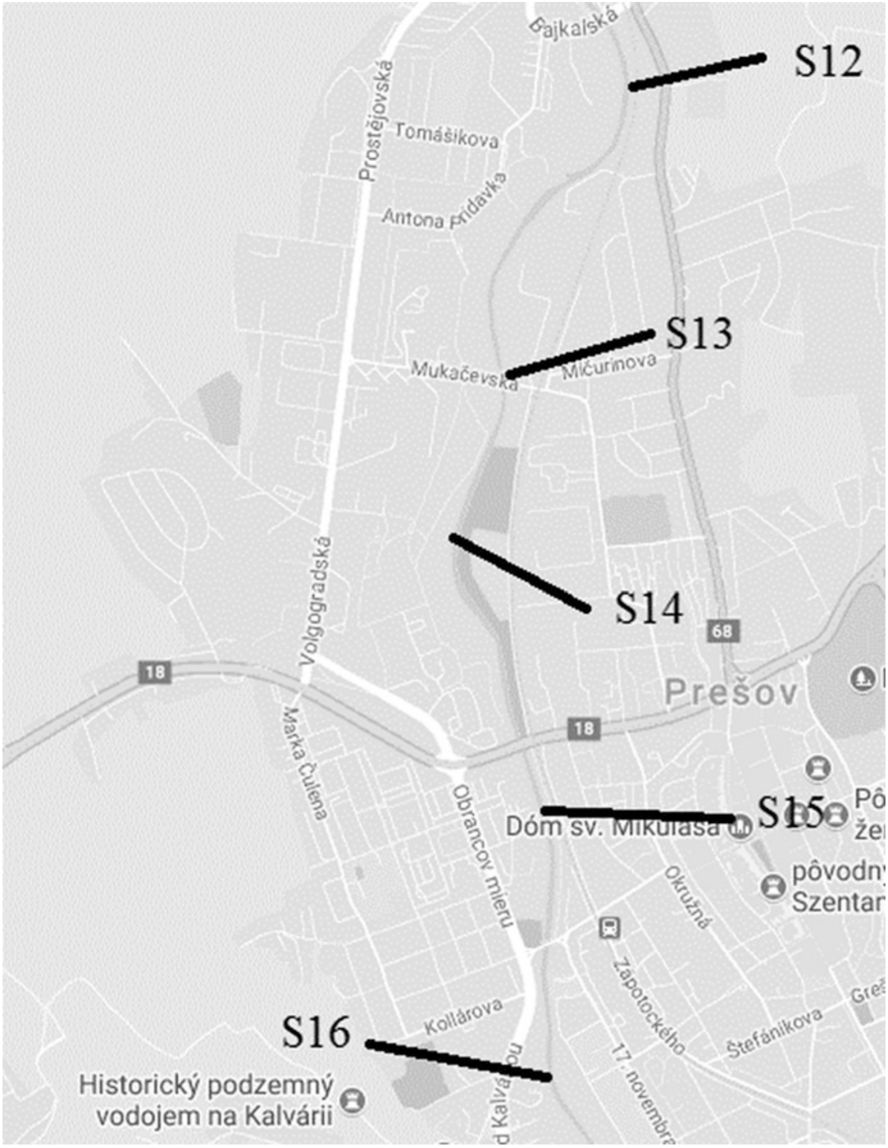

Fig. 4 Location of sediment samples from Torysa River

enrichment, and Zn and Cu indicate very high to extremely high enrichment. The heavy metal concentration from sample site S23 was used as background concentration (Fig. 5).

Table 21 shows very high values of PLI (>1) for all sampling sites, which means it is extremely polluted by heavy metals. High values of PLI indicated a deterioration

Table 17 Contamination factor (CF) values and pollution load index of heavy metals in the sediments of Torysa River

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg	
	CF								PLI
S12	1.00	1.00	0.76	0.67	9.56	1.00	28.00	1.00	1.05
S13	1.00	1.00	1.16	0.52	10.23	1.00	45.10	1.00	1.03
S14	1.00	1.00	1.35	0.20	11.17	1.00	36.10	1.00	1.04
S16	1.00	1.00	2.23	0.49	14.29	1.00	53.80	1.00	1.03

Table 18 Geo-accumulation indexes of heavy metals in Torysa River

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg
S12	−0.585	−0.585	−0.966	−1.168	2.672	−0.585	4.222	−0.585
S13	−0.585	−0.585	−0.426	−1.525	2.771	−0.585	4.91	−0.585
S14	−0.585	−0.585	−0.147	−2.887	2.897	−0.585	4.589	−0.585
S16	−0.585	−0.585	0.578	−1.595	3.252	−0.585	5.165	−0.585

Table 19 E_r and R^i of heavy metals in sediments from Torysa River

	E_r									
	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg	R^i	Risk grade
S12	10.00	30.00	3.80	1.34	47.8	5.00	28.00	40.00	165.94	Moderate risk
S13	10.00	30.00	5.80	1.04	51.15	5.00	45.10	40.00	188.09	Moderate risk
S14	10.00	30.00	6.75	0.40	55.85	5.00	36.10	40.00	184.1	Moderate risk
S16	10.00	30.00	11.15	0.98	71.45	5.00	53.80	40.00	222.38	Moderate risk

Table 20 Enrichment factor values of heavy metals in Topla River bed sediment

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S17	1.00	1.00	0.164	51.00	1.00	1.019	1.00	25.80
S19	1.00	1.00	0.564	43.67	1.00	1.234	1.00	22.50
S20	1.00	1.00	0.343	91.00	1.00	1.467	1.00	24.70
S21	1.00	1.00	0.434	64.00	1.00	1.023	1.00	30.00
S22	1.00	1.00	0.472	85.00	1.00	1.276	1.00	30.10

of site quality. The results of the contamination factor for sediment are shown in Table 18. Contamination factor for Cu, Cr and Zn shows very high contamination by these metals.

The calculated I_{geo} values are presented in Table 22. It is evident from the Table that the I_{geo} values for As, Cd, Hg, Ni and Pb fall in class "1", indicating that there is no pollution from these metals in the Topla River sediments. The I_{geo} values for Cr fall within the range 2–3, indicating that it is moderately polluted. Zinc belongs to class "5" presenting highly polluted. Copper falls to class "6", indicating extremely polluted.

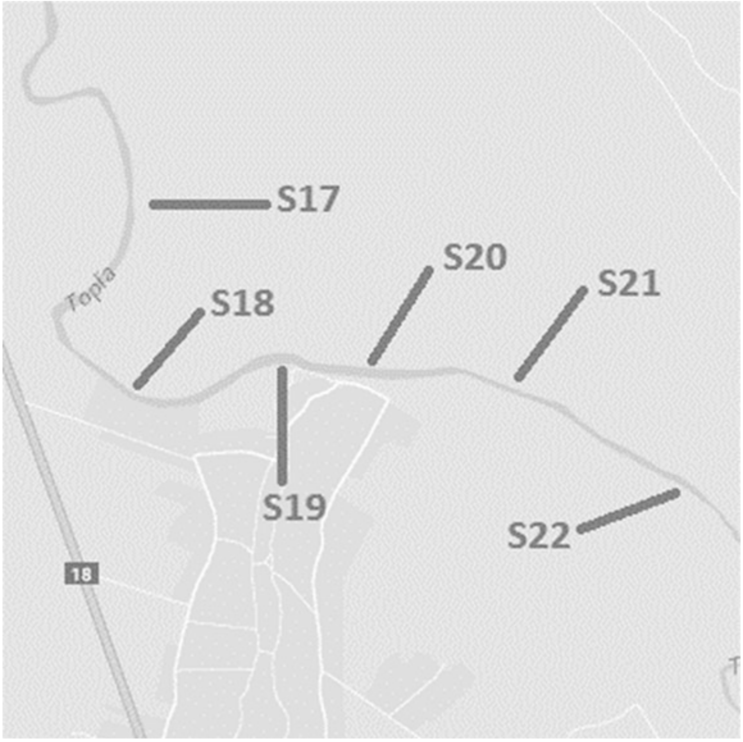

Fig. 5 Location of sediment samples from Topla River

Table 21 Contamination factor (CF) values and pollution load index of heavy metals in the sediments of Topla River

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
	CF								PLI
S17	1.00	1.00	1.00	51.00	1.00	1.02	1.00	25.80	167.60
S19	1.00	1.00	6.1	1.00	1.00	1.00	1.00	1.00	0.77
S20	1.00	1.00	3.44	43.67	1.00	1.23	1.00	22.50	521.37
S21	1.00	1.00	2.09	91.00	1.00	1.47	1.00	24.70	861.44
S22	1.00	1.00	2.65	64.00	1.00	1.02	1.00	30.00	650.63

Table 22 Geo-accumulation indexes of heavy metals in Topla River

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S17	−0.58	−0.58	−0.58	5.09	−0.58	−0.56	−0.58	4.10
S19	−0.58	−0.58	2.02	−0.58	−0.58	−0.58	−0.58	−0.58
S20	−0.58	−0.58	1.19	4.86	−0.58	−0.28	−0.58	3.90
S21	−0.58	−0.58	0.48	5.92	−0.58	−0.03	−0.58	4.04
S22	−0.58	−0.58	0.82	5.42	−0.58	−0.55	−0.58	4.32

The values of R^i in the sediment samples S17, S19, S20 and S21 present a considerable risk. The value for sediment site S22 indicates moderate risk ($R^i = 169.79$). The E_r reflects a very high ecological risk for the water body posed by these metals (Table 23).

3.5 Laborec River

The enrichment factor was calculated from the concentrations of heavy metals in bottom sediments of six sampling sites in the study area. EF calculation results for sediments are shown in Table 24. The EF for Cu indicates moderate enrichment. The EF values show a depletion trend for As, Cd, Cr, Pb and Zn (≤ 1). The heavy metal concentration from sample site S29 was used as background concentration (Fig. 6).

Table 25 shows very high values of PLI (>1) for all sampling sites which means it is extremely polluted by heavy metals. High values of PLI indicated a deterioration of site quality. The results of the contamination factor for sediment are shown in Table 25. Contamination factor for copper shows considerable contamination. CF for other elements indicates low to moderate contamination.

Table 26 shows the results for the geo-accumulation index for Laborec River. As, Cd, Pb, Zn and Hg indicate 0–1 which presents class "1" – unpolluted. Nickel and copper fall to class "2" – unpolluted to moderately polluted. Chromium belongs to class "4" which presents moderately to highly polluted.

On the base of R^i (Table 27) for Laborec River, it can be said that the river presents considerable risk for the water body posed by these metals.

Table 23 E_r and R^i of heavy metals in sediments from Topla River

	E_r									
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	R^i	Risk grade
S17	10	30	2	255	40	5.05	5	25.8	372.85	Considerable risk
S19	10	30	6.86	218.35	40	6.15	5	22.5	338.86	Considerable risk
S20	10	30	4.18	455	40	7.45	5	24.7	576.33	Considerable risk
S21	10	30	5.28	320	40	5.10	5	30.0	445.38	Considerable risk
S22	10	30	5.79	425	40	6.40	5	30.1	169.79	Moderate risk

Table 24 Enrichment factor values of heavy metals in Laborec River bed sediment

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg
S23	1.00	1.00	1.82	0.39	0.89	1.00	0.87	1.00
S24	1.00	1.00	1.63	0.53	1.28	1.00	1.42	1.00
S25	1.00	1.00	1.94	0.69	1.04	1.00	0.92	1.00
S26	1.00	1.00	0.47	0.09	0.61	1.00	0.83	1.00
S27	1.30	1.00	2.06	0.53	1.24	1.00	1.68	1.00
S28	1.00	1.00	2.04	0.36	0.96	1.00	1.12	1.00

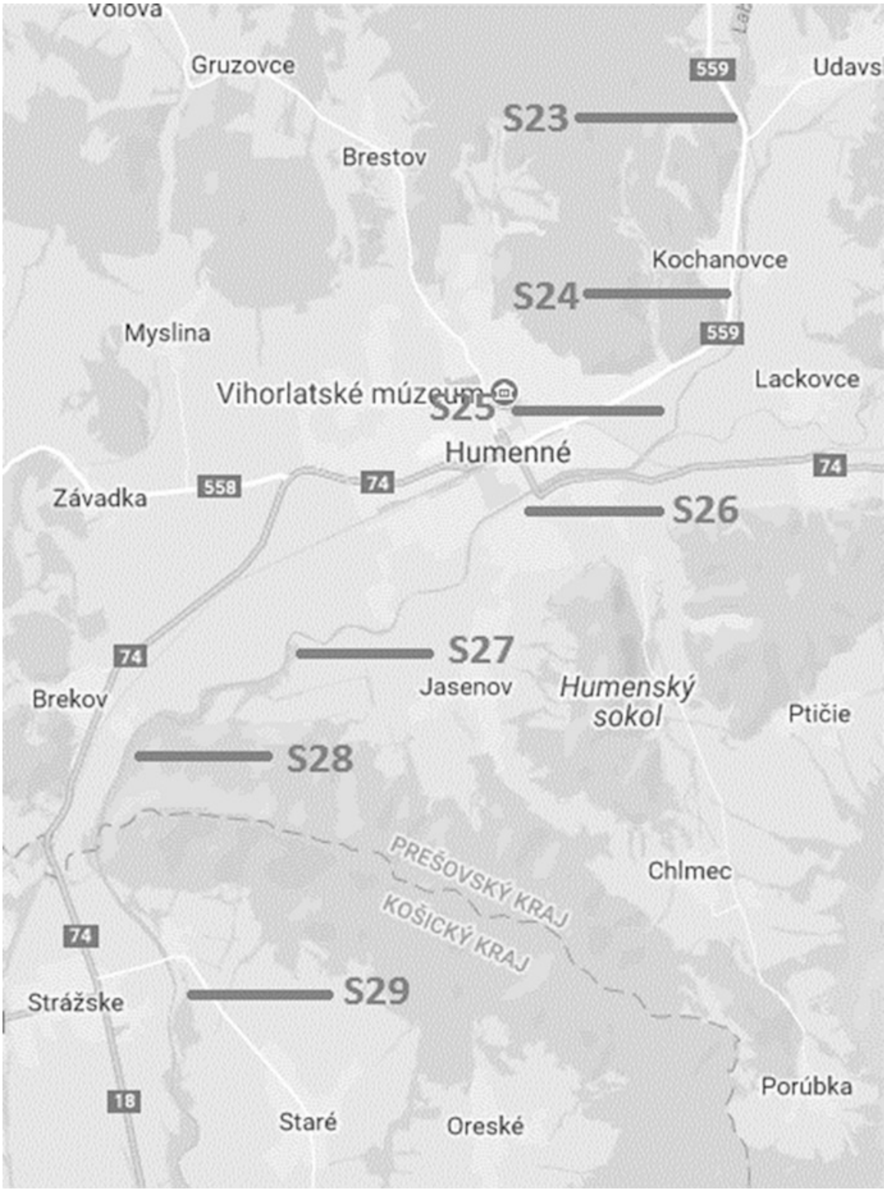

Fig. 6 Location of sediment samples from Laborec River

Table 25 Contamination factor (CF) values and pollution load index of heavy metals in the sediments of Laborec River

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg	
	CF								PLI
S23	1.00	1.00	1.82	0.39	0.89	1.00	0.87	1.00	0.552
S24	1.00	1.00	1.63	0.53	1.28	1.00	1.42	1.00	2.75
S25	1.00	1.00	1.94	0.69	1.04	1.00	0.92	1.00	1.01
S26	1.00	1.00	0.47	0.09	0.61	1.00	0.83	1.00	0.01
S27	1.30	1.00	2.06	0.53	1.24	1.00	1.68	1.00	11.17
S28	1.00	1.00	2.04	0.36	0.96	1.00	1.12	1.00	0.72

Table 26 Geo-accumulation indexes of heavy metals in Laborec River

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg
S23	−0.58	−0.58	0.27	−1.91	−0.74	−0.58	−0.78	−0.58
S24	−0.58	−0.58	0.12	−1.48	−0.22	−0.58	−0.07	−0.58
S25	−0.58	−0.58	0.37	−1.11	−0.52	−0.58	−0.69	−0.58
S26	−0.58	−0.58	−1.66	−3.98	−1.29	−0.58	−0.85	−0.58
S27	−0.58	−0.58	0.46	−1.49	−0.26	−0.44	0.16	−0.58
S28	−0.58	−0.58	0.44	−2.05	−0.63	−0.58	−0.41	−0.58

Table 27 E_r and R^i of heavy metals in sediments from Laborec River

	E_r									
	As	Cd	Cr	Cu	Hg	Ni	Pb	Ni	R^i	Risk grade
S23	10	30	2	255	40	5.05	5	25.8	372.85	Considerable risk
S24	10	30	12.2	5	40	5.00	5	1.00	108.2	Low risk
S25	10	30	6.86	218.35	40	6.15	5	22.5	338.86	Considerable risk
S26	10	30	4.18	455	40	7.45	5	24.7	576.33	Considerable risk
S27	10	30	5.28	320	40	5.10	5	30.0	445.38	Considerable risk
S28	10	30	5.79	425	40	6.40	5	30.1	169.79	Moderate risk

3.6 *Poprad River*

The enrichment factor was calculated from the concentrations of heavy metals in bottom sediments of six sampling sites in the study area. The heavy metal concentration from sample site S1 was used as background concentration. EF calculation results for sediments are shown in Table 28. The EF values show a depletion trend for As, Cu and Hg (≤ 1). The EF for Cr and Ni shows very high enrichment and for Zn indicates extreme enrichment (Fig. 7).

Table 29 shows very high values of PLI (>1) for all sampling sites, which means it is extremely polluted by heavy metals. High values of PLI indicated a deterioration of site quality. The results of the contamination factor for sediment are shown in Table 29. Contamination factor for Cu, Cr, Ni and Zn shows very high contamination.

Table 28 Enrichment factor values of heavy metals in Poprad River bed sediment

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg
S31	1.00	1.00	19.95	24.94	32.85	1.00	100.40	0.95
S32	1.00	1.00	9.50	5.74	25.15	1.00	58.10	0.95
S33	1.00	1.00	2.42	1.00	15.95	1.00	148.20	0.95
S34	1.00	1.00	1.12	11.38	17.75	1.00	118.60	0.95
S35	1.00	1.00	2.15	7.70	10.00	1.00	105.60	0.95
S36	1.00	1.00	0.39	3.20	16.05	1.35	113.40	0.95

Fig. 7 Location of sediment samples from Poprad River

Table 29 Contamination factor (CF) values and pollution load index of heavy metals in the sediments of Poprad River

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg	
	CF								PLI
S31	1.00	1.00	19.95	24.94	32.85	1.00	100.40	0.95	5.55
S32	1.00	1.00	9.50	5.74	25.15	1.00	58.10	0.95	3.94
S33	1.00	1.00	2.42	1.00	15.95	1.00	148.20	0.95	2.95
S34	1.00	1.00	1.12	11.38	17.75	1.00	118.60	0.95	3.51
S35	1.00	1.00	2.15	7.70	10.00	1.00	105.60	0.95	3.26
S36	1.00	1.00	0.39	3.20	16.05	1.35	113.40	0.95	2.70

The calculated I_{geo} values are presented in Table 30. It is evident from the Table that the I_{geo} values for As, Cd, Hg and Pb fall in class "0", indicating that there is no pollution from these metals in the Poprad River sediments. Copper falls to class "4", indicating moderately to highly polluted. The I_{geo} values for Cr and Ni fall within the range 4–5, indicating that it is highly polluted. Zinc belongs to class "5" presenting extremely polluted.

Values of R^i (Table 31) in the sediments were from 150 to 600 which indicate considerable risk for the Poprad River posed by these metals.

Table 30 Geo-accumulation indexes of heavy metals in Poprad River

	As	Cd	Cu	Cr	Ni	Pb	Zn	Hg
S31	−0.59	−0.59	3.73	4.06	4.45	−0.59	6.07	−0.66
S32	−0.59	−0.59	2.66	1.94	4.07	−0.59	5.28	−0.66
S33	−0.59	−0.59	0.69	−0.59	3.41	−0.59	6.63	−0.66
S34	−0.59	−0.59	−0.43	2.92	3.57	−0.59	6.31	−0.66
S35	−0.59	−0.59	0.52	2.36	2.74	−0.59	6.14	−0.66
S36	−0.59	−0.59	−1.96	1.09	3.42	−0.15	6.27	−0.66

Table 31 E_r and R^i of heavy metals in sediments from Poprad River

	E_r									
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	R^i	Risk grade
S31	10.00	30.00	49.88	99.73	164.25	5.00	100.40	38.08	497.34	Considerable risk
S32	10.00	30.00	11.48	47.50	125.75	5.00	58.10	38.08	325.91	Considerable risk
S33	10.00	30.00	2.00	12.12	79.75	5.00	148.20	38.08	335.27	Considerable risk
S34	10.00	30.00	22.76	5.58	88.75	5.00	118.60	38.08	301.59	Considerable risk
S35	10.00	30.00	15.4	10.77	50.00	5.00	105.60	38.08	260.22	Moderate risk
S36	10.00	30.00	6.4	1.93	80.25	5.00	113.40	38.08	282.31	Moderate risk

4 Conclusions

Environmental risk in the water catchments is closely related to the quality and quantity of water flows in the catchment, and 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 minimising 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 characterisation 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 ecological chemistry. So it is of great importance to select a suitable method to assess sediment quality for decision-making and spatial planning. Pollution indices are a powerful tool for processing, analysing and conveying raw environmental information to decision-makers, managers, technicians and the public.

Ecological risk management provides policy makers and resource managers as well as the public with systematic methods that can inform decision-making. The results provide a comprehensive sediment contamination status of heavy metals and potential origin of contamination in the rivers, giving insight into decision-making for water source security.

The above analysis demonstrates the use of pollution index techniques to study the source of chemical parameters in sediments. The heavy metals of sediments were monitored in the six rivers on East of Slovakia. The data obtained in this study has presented consistency in metal pollution indexes of the sediment stations of the study area. This may be due to the continuous dilution of the water body from lower and upper reaches of the river; the similarity of the physical conditions of the sediments, particle composition and organic matter of the sediments may have also played a major role. Hárnad River indicated deficiency to minimal enrichment. The potential ecological risk index indicates moderate to high risk for water basin Hornád. Hornád River on the base of geo-accumulation index belongs to class “5”, which indicates highly polluted.

Ondava River presents minimal to moderate enrichment. The highest enrichment shows chromium and zinc concentration. The I_{geo} values for this water basin fall within the range 1–2, indicating that it is unpolluted to moderately polluted. All the values of R^i in the sediments were less 150 which indicate a low risk for the water body posed by these metals.

The pattern of the metal concentration at all the stations studied in Torysa River followed Zn > Ni > Cu > As = Cd = Pb = Hg > Cr. The I_{geo} values for this water basin belong to class “6”, which indicate extremely polluted. All the values of R^i in the sediments belong to range from 150 to 300 which indicate moderate risk for the Torysa River posed by these metals.

Topla River indicates very high to extremely high enrichment. The I_{geo} values for this water basin fall to class “5”, which indicate extremely polluted. The potential ecological risk index presents a moderate risk.

The EF for Laborec River indicates moderate enrichment (Cu). The EF values show a depletion trend for As, Cd, Cr, Pb and Zn (≤ 1). The I_{geo} values for Laborec fall to class “4”, which indicate moderate to highly polluted. On the base of Ri for Laborec River, it can be said that the river presents considerable risk for the water body posed by these metals.

The EF values show extremely enrichment for Poprad River. The I_{geo} values for this water basin fall to class “5”, presenting extremely polluted. The potential ecological risk index presents considerable risk for the Porpad River posed by these metals.

Pollution load index for all water basins indicates a deterioration of site quality (PLI > 1).

Different calculation methods on the basis of different algorithms might lead to a discrepancy in pollution assessments when they are used to assess the quality of sediment ecological chemistry. Thus it is of great importance to select a suitable method to assess sediment quality for decision-making and spatial planning.

Ecological risk management provides policy makers and resource managers as well as the public with systematic methods that can facilitate informed decision-making. The results provide comprehensive sediment contamination status of heavy metals and potential origin of contamination in the creek, giving insight into decision – ensuring water source security.

5 Recommendations

Environmental risk management provides policy makers and resource managers as well as the public with systematic methods that can facilitate informed decision-making. The results provide comprehensive sediment contamination status of heavy metals and potential origin of contamination in the rivers, giving insight into decision – ensuring water source security.

There have been numerous sediment quality guidelines developed to monitor the sediments. Sediment quality guidelines are very useful to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guidelines, 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 enables us to state the worldwide harmonisation is missing. Such different outcome assessments occur because in different countries have been set for individual indicators various occupational exposure and also have different numbers of monitored indicators. These limit values were influenced by the background values as the concentration of the indicator depends on the geological conditions and so on. It should be properly used for the evaluation of indicators in the first place, and our laws and regulations in foreign countries should be used only as a supplementary assessment.

The present study suggests that these indices are useful tools for the identification of different sources of contamination of the bottom sediment. This paper will hopefully contribute to the development of a water and sediment pollution prevention strategy. The main topics that may need to be investigated are the control of industrial and domestic discharge, regular observation of pollutants, evaluation of the effects of pollutants on the ecosystem over the long term, coordination of the pollution source and prevention of inflow of pollutants to the water and sediment.

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