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Enrichment Factor and Geo-Accumulation Index of Trace Metals in Sediments in the River Hornad, Slovakia

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Abstract. 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.

Numerous sediment quality guidelines have been developed to monitor the sediments. 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. The present study suggests that these indices are useful tools for the identification of different sources of contamination of the bottom sediment. Investigation was focused on heavy metals (Zn, Cu, Pb, Cd, Ni, Hg, As, Fe, Mn). The degree of sediment contamination in the Hornad river has been evaluated using the Enrichment factor and Geo-Accumulation Index. This paper aims to contribute to the development of a 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, and evaluating the effects of pollutants on the ecosystem over the long term, coordinating the pollution source and preventing inflow of pollutants to the sediment.

1. Introduction

Sediments are normally the final pathway of both natural and anthropogenic components produced or derived from the environment. Sediment quality is a good indicator of pollution in the water column, where heavy metals and other organic pollutants tend to concentrate. Metals are introduced in aquatic systems as a result of the weathering of soils and rocks, from volcanic eruptions, and from a variety of human activities involving the mining, processing, or use of metals and/or substances that contain metal pollutants. In natural aquatic ecosystems, metals occurred in low concentrations, normally at nanogram to microgram per liter level. In recent times, however, high contamination levels of heavy metals has become a problem of increasing concern with fear of environmental pollution due to the toxicity of metals and their accumulation in aquatic habitats. Heavy metals, in contrast to most pollutants, are not biodegradable and they undergo a global ecological cycle in which natural waters are the main pathways [1]. The distribution of trace metal concentration in sediments, water and biological materials was of great importance in environmental pollution studies [2]. Extensive studies have been conducted to obtain data on the trace elements in sediments from various environments around the world, including industrialized cities, highway road sides, rural areas in old mining regions,



and agricultural land used for crops or grazing [3–5]. The assessment of metal contamination is very important for human survival. The concentrations of metals in the surface horizons of the sediment alone cannot provide extensive indications about the state of contamination of sediments. This kind of information does not allow the distinction between natural background and anthropogenic enrichment.

There are different indexes generally used to identify metal concentrations of environmental concern, including the metal Enrichment Factor (EF) and Geo-Accumulation indexes (I_{geo}) [6–7]. These indexes numerically identify pollution level sediments. The bio-available metal content in sediment exerts a decisive impact on sediment quality.

The Enrichment Factor (EF) in metals and Geo-Accumulation Index (I_{geo}) are indicators used to assess the presence and intensity of anthropogenic contaminant deposition in surface sediment. [8].

The purpose of this work is to assess the complex phenomenon of pollution of the sediment samples using the Enrichment Factor and Geo-Accumulation Index. This paper describes the consistency in the metal pollution indices among the various stations in the sediment of the contaminated Hornad River.

2. Materials and methods

2.1. Description area

River Hornad belongs to the Danube River basin. The area of the Hornad River basin is 4,414 km². Arable land covers 27.6% of the area; 15.7% is covered by other agricultural land, 47.4% by forests, 2.7% by shrubs and grasses and 6.6% is designated as other land. There are 165 surface water bodies while 162 are in the category of the flowing waters/streams and 2 are in the category of standing waters/reservoirs. Ten groundwater bodies exist in the basin while 1 is situated in quaternary sediment, 2 are geothermal waters and 7 are in pre-quaternary rocks. The Hornad River has 11 transverse structures without fish passes in operation. Significant industrial and other pollution sources include: US Steel Kosice, Rudne bane š. p., Spišská Nová Ves, Kovohuty a.s., Krompachy, Solivary a.s. (Prešov). From the point of view of environmental loads, there are 11 high-risk localities which have been identified in the river basin. Diffuse pollution comes from agriculture and municipalities without sewerage. The upper stretch of the Hornad River to Spišská Nová Ves is in good ecological condition, but gets progressively worse to poor status or potential pollution and hydromorphological pressures. From the Ružín Water Reservoir, the Hornad River is in moderate ecological condition. According to chemical status assessment, the Hornad River is in a good condition, but 56 water bodies (34%) in the Hornad River basin have failed to reach good ecological condition. The water body of intergranular ground waters of quaternary alluviums in the Hornad River basin has poor chemical condition (due to pollution from point and diffuse sources) and poor quantitative condition identified on the basis of long-term decrease of groundwater levels. The water body of pre-quaternary rocks is in a good quantitative and chemical condition [9].

2.2. Sediment samples and preparation

Sediment samples were collected from the Hornad River in the year 2017. The five localities of sediment samples were chosen according to the nearby sources of pollution. Sediment sampling sites are shown in Figure 1. Samples were collected according to ISO 5667-6-2005 “Water quality—Sampling—Part 6: Guidance on sampling of rivers and streams” standard.

The sediment samples were air-dried and sieved to a fraction of 0.063 mm. The chemical composition of sediments was determined by means of the X-ray fluorescence (XRF) method using a SPECTRO iQ II (Ametek, Kleve, Germany). The mean total concentrations of 8 heavy metals in the 5 sediment 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. on the application of treated sludge and bottom sediments to fields [10] and pursuant to WHO standards [11].

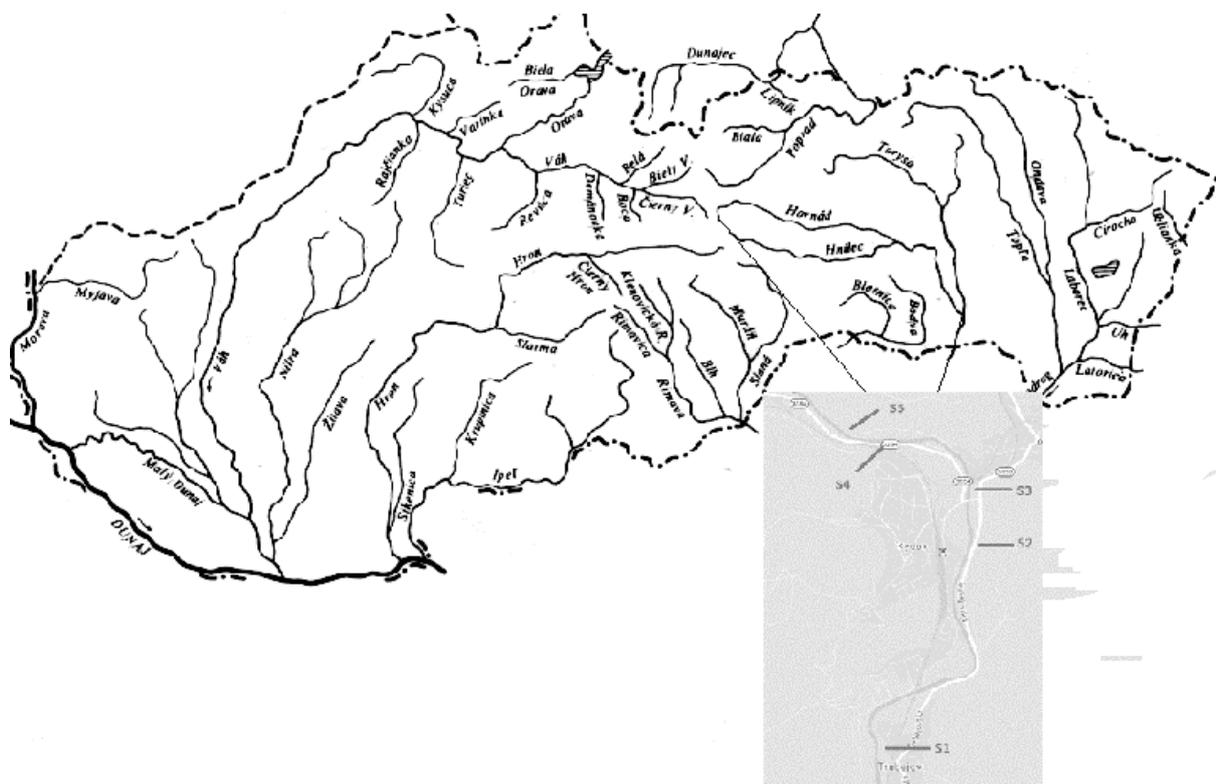


Figure 1. Sediment sampling sites in the Hornad River.

Table 1. Results of chemical analyses of sediment from the Hornad River.

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
		mg/kg							
HORNAD	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
LIMITS	SR	20	10	1000	1000	10	300	750	2500
	<i>WHO</i>		0.01	-	2	-	0.02	0.05	-

2.3. Pollution indices

2.3.1 Enrichment factor

Enrichment factor (EF) calculation is a commonly used approach to estimate the anthropogenic impact on sediments [12]. It is mathematically expressed as [13]:

$$EF = \frac{\left[\frac{M_c}{M_r} \right]_s}{\left[\frac{M_c}{M_r} \right]_b}, \quad (1)$$

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 [13]. The enrichment factor scale consists of six grades ranging, how indicate the Table 2.

Table 2. The enrichment factor scale [13].

EF ≤ 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

2.3.2. Geo-accumulation index

Geo-accumulation Index (I_{geo}), introduced by Muller (1979) [14], is used to determine the extent of metal accumulation in sediments; I_{geo} is mathematically expressed as:

$$I_{geo} = \log_2 \frac{c_n}{1,5B_n} \quad (2)$$

where c_n is the concentration of element “n” and B_n is the geochemical background value. The factor 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 3) from unpolluted to extremely polluted.

Table 3. Descriptive classes for identifying sediment contamination base on I_{geo} values [14].

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

3. Result and discussion

Based on the results in Table 1, we found that the limit value according to Slovak legislation was exceeded only in sediment sample 3 by arsenic. According to the limit values stipulated by the WHO, limits for cadmium, copper, nickel and lead were exceeded in all sediment samples.

The enrichment factor was calculated from the concentrations of heavy metals in bottom sediments of 4 sampling sites in the study area. The heavy metal concentration from sample site S2 was used as background concentration. EF calculation results for sediments are shown in Table 4. The EF values show a depletion trend for As, Cu, Zn (<1). The EF for Cr (S4, S5) and Pb (S4) show minimal enrichment.

Table 4. Enrichment factor values of heavy metals in Hornad 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

The calculated I_{geo} values are presented in Table 5. It is evident from Table 5 that the I_{geo} values for Cd and Hg fall in class “0”, indicating that there is no pollution from these metals in the Hornad 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 moderate pollution. High pollution exists with regard to the concentration of Pb, which falls to class 5. Extreme pollution in the Hornad River is caused by As.

Table 5. Geo- accumulation indices of heavy metals in Hornad 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

4. Conclusion

The data obtained in this study have presented consistency in metal pollution indices of the sediment stations in the study area. This may be due to the continuous dilution of the water body from lower and upper reaches of the river, similarity of the physical conditions of the sediments, and particle composition; organic matter of the sediments may have also played a major role. The River Hornad indicated a deficiency to minimal enrichment. The potential ecological risk index indicates moderate to high risk for the Hornad River basin. On the basis of the Geo-Accumulation Index, the river belongs to class “5”, which indicates high pollution.

The results from this study will become part of baseline data and will also be important to the environmental agency as a policymaker for proper environmental management. This study also provides initial information to the relevant agencies and authorities for preparing preventive plans to control heavy metal and other industrial pollution directly discharged to rivers.

Acknowledgments

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