Assesment of Heavy Metals Concentration in Sediments by Potential Ecological Risk Index

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Summary

Heavy metals contamination has become a serious environmental problem today in both developing and developed countries throughout the world. Heavy metals are of considerable environmental concern due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviour. With the rapid industrialization and economic development in watershed region, the pollution of water body sediment has become very widespread in Slovakia. Depending on hydrodynamics, biogeochemical processes and environmental conditions of rivers, sediments act as an important sink of heavy metals, as well as a potential non-point pollution source which may directly affect overlying waters.

In recent years, numerous methods for assessment of sediments heavy metal contamination have been developed, including the index method, the dynamic method, the synthesis methods in chemistry, ecology and toxicology, etc. Pollution index is a powerful tool for ecological geochemistry assessment. Potential ecological risk index (RI) is a methodology developed by Hakanson to evaluate the ecological risks of heavy metals in sediments.

In this study, the Hakanson potential ecological risk index method was used to assess the risk resulting from concentration of Cu, Zn, As, Cd, and Pb in the sediments taken from the water reservoir Ruzin and its tributaries influenced by mining activity. Results showed that the ecological risk index Eri of five kinds of heavy metals in water reservoir area in eastern Slovakia were classified (average values from three sediment sample sites) in the order Cd (101.4) > As (20.06) > Cu (18.85) > Pb (13.83) > Zn (2.43). The potential ecological risk index Ri of heavy metal was 156.58 (average value from three sediment sample sites), which can be classified as middle ecological risk.

Keywords: heavy metal, sediment, potential ecological risk

Introduction

The rapid industrialization and economic development lead to the heavy metals accumulation in sediment through various ways including fertilization, irrigation, rivers, runoff, atmospheric deposition, and point sources as a metal mining. Sediments are usually regarded as the ultimate sink for heavy metals discharged into environment (Banat et al., 2005), and can be sensitive indicators for monitoring contaminants in aquatic environments (Pekey et al., 2004). Therefore the environmental problem of sediment pollution by heavy metals has received increasing attention in the last few decades in both developing and developed countries through the world (Zhang et al., 2007). Water reservoir Ruzin is located in Eastern Slovakia (situated on the Hornad River) and belongs to one of the most contaminated sites by heavy metals originating from abandoned metallurgical mines producing Acid Mine Drainage (AMD). These acidic waters, which frequently contain high concentrations of heavy metals, often have adverse effect on the quality and ecology of waters receiving the effluent (Singovszka and Balintova, 2009; Holub and Balintova, 2013). Bottom sediments in this reservoir are contaminated mostly by heavy metals, which are alluvial into the reservoir from localities of former mining activities and thus they represent ecological load mainly at the inputs into reservoir. The large share of pollution is coming from the Hnilec catchment where is situated the abandoned mine Smolnik (Jablonovska et al., 2012).

With the development of ecological chemistry survey and data exploration chemistry survey, a great deal of data related to heavy metal concentration in water sediments have been measured which can be used to assess quality of ecological chemistry environment. (Cheng et al., 2007). Different calculation methods on the basis of different algorithms might deal to discrepancy on pollution assessment when they are used to assess 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 (Qingjie et al., 2008).

The aim of this study is to assess the sediment quality in two tributaries (Smolnik creek and Hnilec) and their influence on sediment quality in water reservoir Ruzin in the Eastern Slovakia using potential ecological risk index.

Materials and methods

Sediment sampling localities are shown in Figure 1. Sediment was sampled from three sites – from the Smolnik creek which flows into the river Hnilec (sampling site 2) and third sampling site was the water reservoir Ruzin.

The sediment was dried, homogenized and sieved bellow 0.063mm. Chemical analyses were realized by the XRF method using by SPECTRO iQ II (Ametek, Germany). The sediment samples were prepared as pressed tablets with diameter of 32mm by mixing of 5g of sample and 1g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m^2. 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

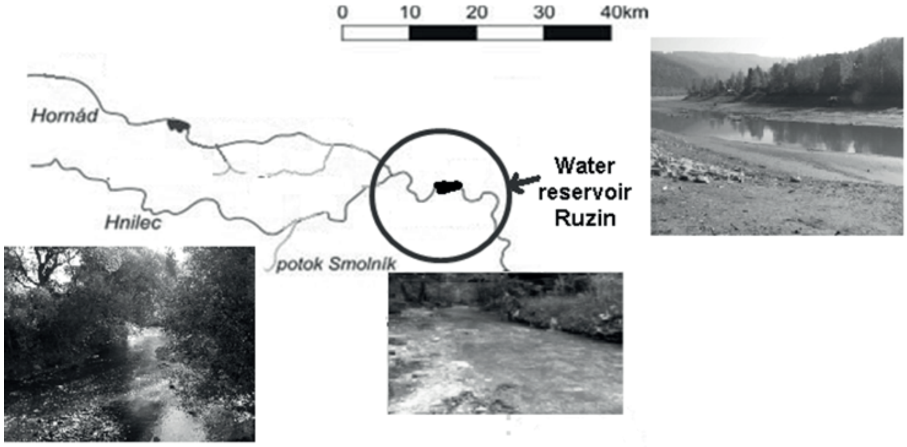

Fig. 1 Sampling sites in the study area – Smolnik creek, Hnilec and water reservoir Ruzin
Rys. 1 Badany obszar – Potok Smolnik, Hnilec i zbiornik wodny Ružín

of treated sludge and bottom sediments to fields.

For assessment of sediment 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:

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

where C_i is the mean concentration of an individual examined metal and C_{in} 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 contamination factors for all examined metals represents the contamination degree (C_d) of the environment:

$$C_d = \sum_{i=1}^{n} C_f^i \quad (2)$$

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

$$E_r^i = C_f^i x T_r^i \quad (3)$$

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

$$R^i = \sum_{i=1}^{n} E_r^i \quad (4)$$

Hakanson defined four categories of C_r^i, four categories of C_d, five categories of E_r^i and four categories of R^i, as shown in Table 1 and 2.

Results and discussion

The mean total concentrations of Cu, Zn, As, Cd and Pb in sediment of Smolnik creek, Hnilec and water reservoir Ruzin are presented in Table 3. The background concentrations were used concentrations of elements without contamination by acid mine waters. 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.

The metal concentrations from three sediment sample localities were evaluated through statistical analysis with SPSS 7 software and with Microsoft Excel. Based on the single-element index (C_f^i) and its grade (Table 3), the sediment in Smolnik creek was classified as considerable for Cu, As and Pb. Zn and Cd can be classified moderate contaminated. Sediment in Hnilec was classified as moderate contaminates excepting Cu, for which was classified as considerable contaminated. Sediments containing heavy metals in reservoir Ruzin were classified as very high for Cd, Cu and Zn represent considerable contamination and for As and Pb moderate contamination. Based on the degree of contamination (C_d) and its grade (Table 4), the sediment in study area was classified as very high contaminated for three sample sites.

The potential ecological risk indices were found in the following order Cd > As > Cu > Pb > Zn (Table 5). The E_r^i – values of all parameters in all sampling locations were less than 40 (low risk), except As in Ruzin, which reflect a high ecological risk for the water body posed by these metals. The values of R^i in the sediments from Smolnik creek and Hnilec represent low ecological risk, but R^i in water reservoir Ruzin was 281.52, which represent moderate ecological risk.

Conclusions

For the study of the pollution status of sediments contaminated by heavy metals the method of potential ecological risk indices was used.

According to this method the concentration of heavy metals in sediments pose low ecological risk to the Smolnik creek and Hnilec, but for reservoir Ruzin is characterized as moderate ecological risk. For the water reservoir Ruzin the potential ecological risk indices were found in the following order Cd > Cu > Pb > Zn > As and R^i in water reservoir Ruzin was 281.52, which represent moderate

Tab. 1 Criteria for contamination factor and degree of contamination and their classification
Tab. 1 Kryteria czynników zanieczyszczenia i stopnia zanieczyszczenia oraz ich klasyfikacji

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

Tab. 2 Risk grades indexes and grades of potential ecological risk of heavy metal pollution
Tab. 2 Indeks stopnia ryzyka i stopień potencjalnego ryzyka ekologicznego zanieczyszczenia metalami ciężkimi

E^i_r	Risk grade	R^i value	Risk grade
$E^i_r < 40$	Low risk	$R^i < 150$	Low risk
$40 \le E^i_r < 80$	Moderate risk	$150 \le R^i < 300$	Moderate risk
$80 \le E^i_r < 160$	Considerable risk	$300 \le R^i < 600$	Considerable risk
$160 \le E^i_r < 320$	High risk	$R^i \ge 600$	Very high risk
$E^i_r \ge 320$	Very high risk		

Tab. 3 Background concentration and mean concentration of heavy metals in sediment samples
Tab. 3 Stężenie tła a średnie stężenie metali ciężkich w osadach

	Cu	Zn	As	Cd	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Background	146.13	158.88	48.63	0.5	46.88
Smolnik	474.57	216.86	167.71	0.5	202.29
Hnilec	235.27	152.03	35.57	5.1	36.03
Water reservoir Ruzin	618.27	693.73	19.93	4.07	72.4
Limits	1000	2500	20	10	750

Tab. 4 Contamination factor and Degree of contamination in sediments from study area
Tab. 4 Czynnik i stopień zanieczyszczenia osadów na badanym obszarze

Sample site / Heavy metal	Cu	Zn	As	Cd	Pb	
			C_f^i			C_d
Smolnik	3.25	1.36	3.45	1	4.32	*13.38*
Hnilec	3.83	1.54	2.17	1	2.45	*11.00*
Ruzin	4.23	4.37	0.41	8.14	1.54	*18.69*

Tab. 5 E_r^i and R^i of heavy metal in sediments from Smolnik creek
Tab. 5 E_r^i i R^i metali ciężkich w osadach z potoku Smolnik

Sample site / Heavy metal	Cu	Zn	As	Cd	Pb	
			E^i_r			R^i
Smolnik	16.25	1.36	34.4	30	21.55	*103.56*
Hnilec	19.15	1.55	21.7	30	12.25	*84.65*
Ruzin	21.15	4.37	4.1	244.2	7.7	*281.52*

ecological risk. The results of sediments quality from three locations showed that the area has been moderate contaminated by heavy metals and its pollution can be attributed to industrial pollution as well as human activities. Contamination assessment provided adequate evidence for the water management about the need of remediation and protection of surface water.

Acknowledgements

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Ocena stężenia metali ciężkich w osadach za pomocą wskaźnika potencjalnego ryzyka ekologicznego

Stężenie metali ciężkich stało się w dzisiejszych czasach poważnym problemem środowiskowym zarówno w krajach rozwiniętych jak i rozwijających się na całym świecie. Metale ciężkie są znaczącym zagrożeniem dla środowiska z powodu ich toksyczności, rozległości źródeł, właściwość nie-biodegradowalności i tendencje do akumulacji. Wraz z szybką industrializacją i rozwojem ekonomicznym w regionie wododziału, zanieczyszczenie wody i osadów stało się rozpowszechnione na Słowacji. W zależności od hydrodynamiki, procesów biogeochemicznych i warunków środowiskowych rzek, osady pełnią funkcję ważnego ujścia dla metali ciężkich, jak i również potencjalnego nie-punktowego źródła zanieczyszczenia, które może bezpośrednio wpływać na opływające je wody.

W poprzednich latach rozwijane były metody numeryczne oceny zawartości metali ciężkich w osadach, włączając metodę wskaźnikową, dynamiczną, metody syntez w chemii, ekologii i toksykologii, itd. Wskaźnik zanieczyszczenia jest ważnym narzędziem oceny geochemii ekologicznej. Wskaźnik potencjalnego ryzyka ekologicznego (RI) jest metodologią opracowaną przez Hakansona w celu oceny ryzyka ekologicznego powodowanego przez metale ciężkie w osadach.

W pracy tej, metoda Hanaksona wskaźnika potencjalnego ryzyka ekologicznego została użyta do oceny ryzyka wynikającego ze stężenia Cu, Zn, As, Cd i Pb w osadach pobranych z wód zbiornika Ruzin i jego dopływów, na które oddziaływała aktywność górnicza. Wyniki wskazują, że indeks ryzyka ekologicznego (ERI) pięciu rodzajów metali ciężkich w obszarze zbiornika wodnego we wschodniej Słowacji były sklasyfikowane (średnie wartości z trzech próbek osadów) w kolejności Cd (101,4) > As (20,06) > Cu (18,85) >Pb (13.,83) > Zn (2,43). Wskaźnik potencjalnego ryzyka ekologicznego (RI) metali ciężkich wyniósł 156,58 (średnie wartości z trzech próbek osadów), co może być sklasyfikowane jako średnie zagrożenie ekologiczne.

Słowa kluczowe: metale ciężkie, osad, potencjalne ryzyko ekologiczne