CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of
AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216 DOI: 10.3303/CET1439294

Pollution and Potential Ecological Risk Assessment of Heavy Metals in the Smolnik Creek (Slovakia)

Eva Singovszka*, Magdalena Balintova

Institute of Environmental Engineering, Faculty of Civil Engineering, Technical University of Kosice, Vysokoskolska 4, 042 00 Kosice, Slovakia,
magdalena.balintova@tuke.sk

Study of heavy metals in sediments is vital in order to understand their impact on water ecosystems. They are usually present at low concentrations in aquatic environments, but deposits of anthropogenic origin have raised their concentrations, causing environmental problems in creeks.
This research was undertaken in order determine and analyse selected heavy metals present in sediment sampled from Smolnik creek, Slovakia, which is a historical Cu, Fe, Ag, Au-mining area that was exploited from the 14-th century to 1990. The Smolnik mine was definitely closed and flooded from 1990 till 1994. Waters from the earth surface penetrated the mine and they were enriched with metals and their pH values decreased. Acidity is caused mainly by the oxidation of sulphide minerals. The whole mine complex produce large amounts of AMD, discharging from the flooded mine (pH = 3-4, Fe 500-400 mg/L; Cu 3-1 mg/L; Zn 13-8 mg/L and Al 110-70 mg/L), that acidified and contaminated the Smolnik creek water and sediments which transported pollution into the Hnilec River catchment.
The mine-system represents partly opened geochemical system into which rain and surface water drain. Potential ecological risk indexes were used to study the pollution status of heavy metals in sediment and assess their potential ecological risk to environment, for the metals Cu, Zn, As, Cd and Pb. The calculated potential ecological risk indices the level of water environment pollution by heavy metals.

1. Introduction

Heavy metals are important environmental pollutants threatening the health of human and natural ecosystems (Cruz – Guzman et al., 2006. Heavy metals are considerable environmental concern due to their toxicity, wide source, non-biodegradable properties and accumulative behaviours (Yu et al., 2008). Depending on hydrodynamics, biogeochemical processes and environmental conditions of rivers, sediments act as an important sink of heavy metals, as well as potential non – point pollution source which may directly affect overlying rivers (Santos et al., 2003). To some extent, heavy metal contents in sediment can reflect the quality of water body. Although sediments act as one of the ultimate sinks for heavy metals input into the aquatic environment, they cannot fix heavy metals permanently (Yu et al., 2008). Taking into account the importance of sediments and the toxicity of heavy metals in them, related researches have been done to understand the effects of heavy metals on ecological systems (Guo et al., 2010). Specifically, opencast mining activities have a serious environmental impact on soils (Bhattacharya et al., 2006) and water streams (Andras et al., 2012), having generated millions of tons of sulphide-rich tailings (Holub and Balintova, 2013). Runoff from mining operations can have negative impacts on the surrounding aquatic environment including heavy loads of suspended solids, decreased pH levels and increased levels of heavy metals. In Slovak republic there are some localities with existing AMD generation conditions. The most critical values were observed in the abandoned deposit Smolnik (Petrilakova and Balintova, 2011). Because sediments are responsible for transporting a significant proportion of many hazardous contaminants, not only research and modelling of erosion phenomena is very acute), but also consideration should be given their quality and their impact on the aquatic environment. The risk assessment of heavy metals would provide a certain theory support for risk management. For an ecological risk assessment associated with pollutant exposure in aquatic systems, several environmental

Please cite this article as: Singovszka E., Balintova M., 2014, Pollution and potential ecological risk assessment of heavy metals in the Smolnik creek (Slovakia), Chemical Engineering Transactions, 39, 1759-1764 DOI:10.3303/CET1439294

factors must be considered, such as chemical physicochemical, biological and ecotoxicological parameters. All these variables must be integrated and some indexes have been applied to do it. (Fiori et al, 2013). A number of studies have applied this method (Ohlson and Serveiss, 2007. Potential ecological risk index (R^i) is a methodology developed by Hakanson to evaluate the ecological risk of heavy metals in sediment (Hakanson, 1980). R^i can be used as a quick and practical tool for environmental assessment, obtaining as results the pollution classification of areas and identification of the toxic substance of interest, supporting actions for pollution control of aquatic systems (Fiori et al., 2013).
The aim of this study is to assess the sediment quality in the Smolnik creek (Slovakia) using potential ecological risk index for heavy metals concentrations in the samples taken from different locations of this creek.

2. Materials and methods

2.1 Study area

The abandoned deposit Smolnik is situated in the south-eastern Slovakia between villages Smolnik and Smolnicka Huta in the valley of Smolnik creek (Figure 1), 11 km south–west of the village Mnisek nad Hnilcom. Geomorphologically, the locality is situated in the area of Slovenske Rudohorie (Slovak Ore Mountains - West Carpathians). It is a historical Cu, Fe, Ag, Au-mining area that was exploited from the 14-th century to 1990 (Spaldon et al., 2006). The mine-system represents partly opened geochemical system into which rain and surface water drain. The Smolnik mine was definitely closed and flooded from 1990 till 1994 (Luptakova et al., 2007). More than 6 Mt of pyrite ores of various qualities have been abandoned in this mine. The analysis of water in the deserted mine and in the broader area surrounding this mine was made after the ecological accident in the Smolnik creek in 1995 (Sottnik et al., 2002). Waters from the earth surface penetrated the mine and they were enriched with metals and their pH values decreased (Singovszka and Balintova, 2012). Acidity is caused mainly by the oxidation of sulphide minerals. The whole mine complex produce large amounts of AMD, discharging from the flooded mine (pH = 3-4, Fe 500-400 mg/L; Cu 3-1 mg/L; Zn 13-8 mg/L and Al 110-70 mg/L) (Luptakova and Kusnierova, 2005), that acidified and contaminated the Smolnik creek water which transported pollution into the Hnilec River catchment (Luptakova et al., 2008).

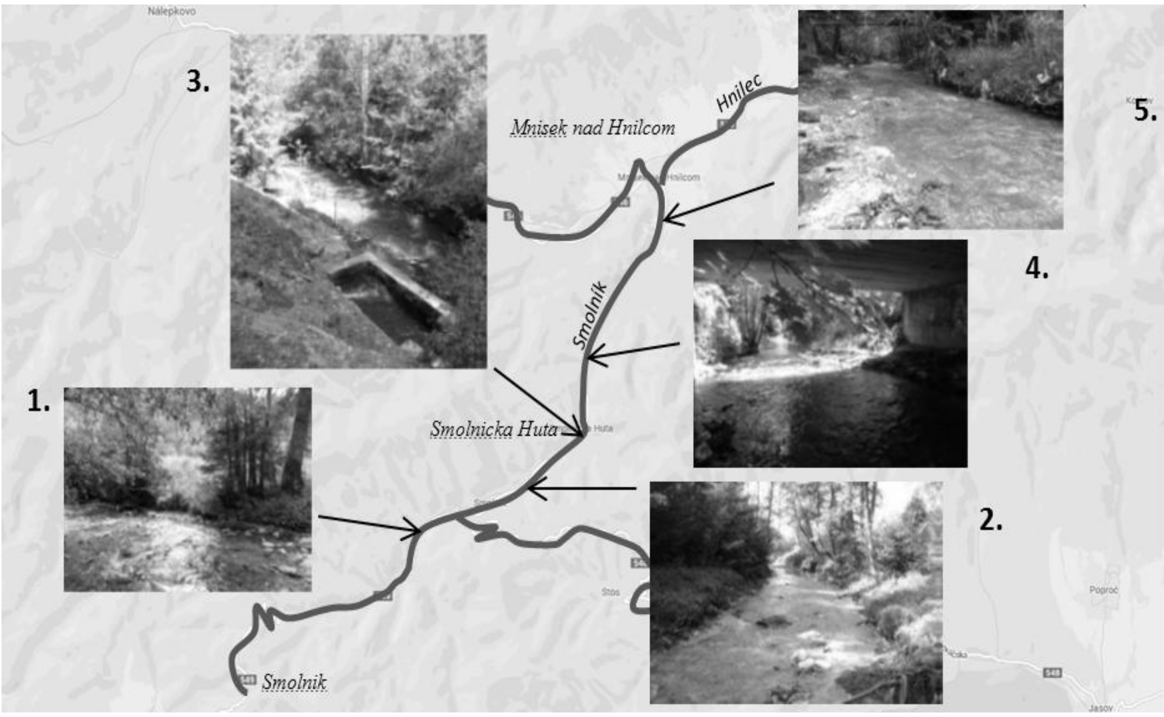

Figure 1: Water sampling location

2.2 Sediment sampling

Sediment sampling localities are shown in Figure 1. Sediment was taken from five sample site during 2006 -2013. Two localities were in the upper part of the Smolnik creek without contamination by acid mine waters from shaft Pech (1 – outside the Smolnik village, 2 - small bridge - crossing to the shaft Pech) and another two sampling localities were located under the shaft (4 – approx. 200 m under the shaft Pech, 5 – inflow to the Hnilec river). The outflow of AMD from shaft Pech (Smolnik mine) has number 3. The chosen physical and chemical parameters were determined by multifunctional equipment METTLER TOLEDO in situ and chemical analyses of water and sediment samples were realized by AAS-ICP (Varian Vista – MPX). 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.

3. Ecological risk assessment

For assessment of sediment contamination the contamination factor and contamination degree were used. In the version suggested by Hakanson (1980), an assessment of sediment contamination was conducted through references of contaminations in the surface layer of bottom sediments:

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

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 (Table 3). C_f^i is the single – element index. The sum of contamination factors for all metals examined represents the contamination degree (C_d) of the environment:

$$C_d = \sum_{i=1}^{n} C_f^i \tag{2}$$

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

$$E_r^i = C_f^i x T_r^i \tag{3}$$

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:

Table 1: Criteria for contamination factor and degree of contamination and their classification

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

Table 2: Risk grades indexes and grades of potential ecological risk of heavy metal pollution

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		

$$R^i = \sum_{i=1}^{n} E_r^i \tag{4}$$

Hakanson (1980) 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 Tables 1 and 2.

4. Results and discussion

The total concentrations of Cu, Zn, As, Cd and Pb in sediment of Smolnik creek are presented in Table 3. The metal concentrations from two sediment sample localities were evaluated through statistical analysis with SPSS 7 software and with Microsoft Excel, and descriptive parameters and probability distributed are obtained and listed in Table 4. It is obvious that higher concentrations of heavy metals were detected at site 4 and site 5 which were located at lower reaches of the Smolnik creek. The contents of As seriously exceeded Slovak Act No. 188/2003 Coll. of Laws on the application of treated sludge and bottom sediments to fields. The concentrations of As in all samples transcended the standard values 2 – 10 times, respectively.

Table 3: Background concentration and concentration of heavy metals in sediment samples

	Cu	Zn	As	Cd	Pb
			(mg/kg)		
background	176	171	50	0,5	50
	103	123	35	0,5	39
	114	140	31	0,5	44
	128	157	52	0,5	43
	111	143	47	0,5	35
	148	179	52	0,5	43
	190	174	56	0,5	60
S4	445	172	154	0,5	172
	903	328	253	0,5	282
	365	214	201	0,5	328
	295	172	161	0,5	198
	281	165	68	0,5	101
	363	191	92	0,5	110
	670	276	245	0,5	225
S5	506	250	97	0,5	111
	661	320	146	0,5	159
	404	193	135	0,5	176
	527	192	83	0,5	106
	836	200	84	0,5	15
	427	242	93	0,5	117
	585	323	102	0,5	119
Limits	1,000	2,500	20	10	750

Table 4: Summary statistics of heavy metals in sediment over the study area

Heavy metal	Minimum concentration (mg/kg)	Maximum concentration (mg/kg)	Mean concentration (mg/kg)	Standard deviation
Cu	281	903	519.14	191.66
Zn	165	328	213.29	59.12
As	68	253	136.71	60.41
Cd	0.4	0.5	0.49	0.03
Pb	15	328	158.50	80.86

Based on the single-element index (C_f^i) and its grade (Table 5), the sediment in Smolnik creek was classified as considerable contaminated for all heavy metals expected Cd and Zn (moderate contaminated) for S4 sample site. The sample site S5 was classified as moderate contaminated excepted Cu, which was classified as considerable contaminated.

Based on the degree of contamination (C_d) and its grade (Table 5), the sediment in study area was classified as very high contaminated for both sample sites (S4 = 13.97, S5 = 11.47).

Table 5: Contamination factor and Degree of contamination in sediments from Smolnik creek (mg/kg)

Sample site	Cu	Zn	As	Cd	Pb	
			C_f^i			C_d
S4	3.42	1.39	3.63	1	4.51	13.97
S5	4.04	1.58	2.29	1	2.56	11.47

The potential ecological risk indices were found in the following order As > Cd > Cu > Pb > Zn (Table 6). All the values of R^i in the sediments were less than 150: S4 – 107.34 and S5 – 87.48. The E_r^i – value of all parameters in all sampling locations were less than 40, which reflects a low ecological risk for the water body posed by these metals.

Table 6: E_r^i and R^i of heavy metal in sediments from Smolnik creek

Sample site	Cu	Zn	As	Cd	Pb	
			E_r^i			R^i
S4	17.10	1.39	36.30	30	22.55	107.34
S5	20.20	1.58	22.90	30	12.80	87.48

5. Conclusion

For the study of the pollution status of sediments contaminated by heavy metals and their potential ecological risk assessment the relative potential ecological risk indices were used.
The heavy metals under investigation in sediments reflected low ecological risk to the Smolnik creek. The results of sediments in samples taken from two locations showed that the creek has been slightly contaminated by heavy metals and its pollution can be attributed to industrial pollution as well as human activities. 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 comprehensive sediment contamination status of heavy metals and potential origin of contamination in the creek, giving insight into decision – making for water source security.

Acknowledgements

This work has been supported by the Slovak Research and Development Agency under the contract No.APVV-0252-10 and by the Slovak Grant Agency for Science (Grant No. 1/0882/11).

References

Andras P., Turisova I., Marino A., Buccheri G., 2012. Environmental hazards associated with heavy metals at Lubietová Cu-deposit (Slovakia), Chemical Engineering Transactions, 28, 259 – 264. DOI:10.3303/CET1228044.

Bálintová M., Petriláková A., 2011. Study of pH Influence on Selective Precipitation of Heavy Metals from Acid Mine Drainage. Chemical Engineering Transactions. 345 - 350. DOI: 10.3303/CET1125058.

Bhattacharya A., Routh J., Jacks G., Bhattacharya P., Mörth M., 2006. Environmental assessment of abandoned mine tailings in Adak, Västerbotten district (Northern Sweden), Appl. Geochem. 21, 1760–1780.

Cruz-Guzman M., Celis R., Hermonsin M.C., Koskinen W.C., Nater E.A., Conejo J., 2006. Heavy metal adsorption by Montmorillonites modified with natural organic cations. Soil Sci.Soc.Am. J. 70 (1), 215 - 221.

Fiori C.S., Rodigues A.P.C, Santelli R.E., Cordeiro R.C., Carvalheira R.G., Araujo P.C., Casthilos Z.C., Bidone E.D., 2013. Ecological risk index for aquatic pollution control: a case study of coastal water bodies from the Rio de Janeiro State, southeaster Brazil. Geochemica Brasiliensis, 27(1), 24-36.

Guo W., Liu X., Liu Z., LI G., 2010. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang harbor, Tianjin. Procedia Environmental Science, 2, 729–736.

Hakanson L., 1980. An ecological risk index for aquatic pollution control, a sedimentological approach. Water Research, 14, 975–1001.

Holub M., Balintova M., Pavlikova P., Palascakova L., 2013. Study of Sorption Properties of Zeolite in Acidic Conditions in Dependence on Particle Size. Chemical Engineering Transactions, 32, 559-564 DOI: 10.3303/CET1332094.

Luptakova A., Kusnierova M., 2005. Bioremediation of Acid Mine Drainage by SRB. Hydrometallurgy, 77, 97-102.
Luptakova A., Macingova E., Apiariova K., 2008. The Selective Precipitation of Metals by Bacterially Produced Hydrogen Sulphide. Acta Metallurgica Slovaca, Special issue 1/2008, 149- 154.
Luptakova A., Spaldon T., Balintova M., 2007. Remediation of acid mine drainage by means of biological and chemical methods. Advanced Materials Research: Biohydrometallurgy: From the Single Cell to the Environment.. 20-21, 283-286.
Ohlson D.W., Serveiss V.B., 2007. The integration of ecological risk assessment and structured decision making into watershed management. Integr. Environ. Assess. Manag., 3(1), 118 -128.
Yu R., Yuan X., Zhao Y., Hu G., Tu X., 2008, Heavy metal pollution in intertidal sediments from Quanzhou Bay, Journal of Environmental Sciences, 20 (6), 664–669.
Santos B.J.C., Beltran R., Gomez A.J.L., 2003. Spatial variations of heavy metals contamination in sediments from Odiel River (Southwest Spain). Environment International, 29, 69–77.
Singovszka E., Balintova M., 2012, Application Factor Analysis for the Evaluation Surface Water and Sediment Quality, Chemical Engineering Transactions, 26, 183-188. DOI: 10.3303/CET1226031.
Sottnik P., Dubikova M., Lintnerova O., Rojkovic I., Sucha V., Uhlik P., 2002, The links between the physico-chemical character of different mining waste in Slovakia and their environmental impacts. Geologica Carpathica. 53, 227-228.
Spaldon T., Brehuv J., Bobro M., Hanculak J., Sestinova O., 2006. Mining development the Spiš-Gemer ore-location. Acta Montanistica Slovaca,.11, 375-379 (in Slovak).