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EVALUATION QUALITY OF SEDIMENTS FOR AQUATIC POLLUTION CONTROL IN SLOVAKIA

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Abstract

Aquatic sediment contaminated with heavy metals is still an unsolved problem in Europe. The problem is serious also in the Slovak water reservoirs. Water reservoir Ruzin located in east Slovakia (situated on the Hornad river) is one of the most contaminated sites by heavy metals coming from abandoned metallurgical mines produced 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. Bottom sediments in this reservoir are contaminated above all 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.

The aim of this paper is assess the quality of sediments along its course from the source (Smolnik creek – Hnilec creek) to the mouth (reservoir Ruzin) based on the requirements of Slovak and EÚ legislation. Use of these tools can provide essential characterizations of key watershed sources, sensitive receptors, natural variation, and both natural and anthropogenic stressors. Only with these multiple tools and an understanding of their interactions can reliable determinations of sediment pollution and longterm consequences be made. Then cost-effective, environmentally protective management decisions can be made about the type, extent, and need for sediment remediation.

Key words

Acid mine drainage; sediment quality; heavy metals; limit values

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1 INTRODUCTION

Sediments accumulate contaminants and serve as sources of pollution to the ecosystems they are connected with. Pathogens, nutrients, metals, and organic chemicals tend to sorb onto both inorganic and organic materials that eventually settle in depositional areas. If the loading of these contaminants into the waterways is large enough, the sediments may accumulate excessive quantities of contaminants that directly and indirectly disrupt the ecosystem, causing significant contamination and loss of desirable species. Many studies have documented the importance of sediment contamination for ecosystem quality and the widespread incidence of sediment contamination [1, 2].

These repositories of contaminants were once ignored when the major problem of pollution was easily identified industrial discharges. As those discharges have improved in quality, diffuse sources of pollution, such as storm water runoff and sediments, are recognized as long-term, widespread sources of pollutants to aquatic systems. Substantial impacts on the ecosystem from sediment-associated contaminant have been found to range from direct effects on benthic communities [3, 4].

Therefore have been numerous sediment quality guidelines (SQGs) developed during the past 20 years to assist regulators in dealing with contaminated sediments. Unfortunately, most of these have been developed in North America. Traditionally, sediment contamination was determined by assessing the bulk chemical concentrations of individual compounds and often comparing them with background or reference values. Since the 1980s, SQGs have attempted to incorporate biological effects in their derivation approach. These approaches can be categorized as empirical, frequency-based approaches to establish the relationship between sediment contamination and toxic response, and theoretically based approaches that attempt to account for differences in bioavailability through equilibrium partitioning (EqP) (i.e., using organic carbon or acid volatile sulphides). Some of these guidelines have been adopted by various regulatory agencies in several countries and are being used as clean up goals in remediation activities and to identify priority polluted sites.

The guidelines are chemical specific and do not establish causality where chemical mixtures occur. Equilibrium-based guidelines do not consider sediment ingestion as an exposure route. The guidelines do not consider spatial and temporal variability, and they may not apply in dynamic or larger-grained sediments. Finally, sediment chemistry and bioavailability are easily altered by sampling and subsequent manipulation processes, and therefore, measured SQGs may not reflect in situ conditions. All the assessment tools provide useful information, but some are prone to misinterpretation without the availability of specific in situ exposure and effects data [5].

Aquatic ecosystems (including sediments) must be assessed in a “holistic” manner in which multiple components are assessed by using integrated approaches.

2 MATERIAL AND METHODS

2.1 Study area

Water reservoir Ruzin is situated in territory, which is well-known by its mining activities for several centuries, such as ore deposit Smolnik [6]. Bottom sediments are contaminated above all by heavy metals, which are alluvial into the reservoir from localities of former activities and thus they represent ecological load mainly at the inputs into reservoir. Enhanced contents of heavy metals hinder in direct application of sediments in agriculture, building and field engineering.

Smolnik is situated in the southeastern Slovakia between villages Smolnik and Smolnicka Huta in the valley of Smolnik creek, 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).

Deposit Smolnik is a historical Cu, Fe, Ag, Au-mining area that was exploited from the 14th century to 1990. 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 [7, 8]. 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 which transported pollution into the Hnilec River catchment [9, 10]. Figure 1 shows sediment location of Smolnik creek, Hnilec and water Reservoir Ruzin on the map of East Slovakia.

Fig. 1: Location of the investigated area on the map of the Slovak Republic

2.2 Sampling preparation

In order to study the interaction between AMD and sediment, nine sampling localities along the Smolnik creek, Hnilec and water reservoir Ruzin were chosen. Sediment sampling localities are shown in Fig. 2.

Sediments samples were collected from Smolnik creek during years 2006-2013, from Hnilec and water reservoir Ruzin in 2012. The chosen physical and chemical parameters were determined by multifunctional equipment METTLER TOLEDO in situ and chemical analyses of sediment samples were realized in accredited laboratory of State Geological Institute of Dionyz Stur, Spisska Nova Ves (sediment from Smolnik creek). The sediment was dried, homogenized and sieved bellow 0,063 mm. 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 32 mm by mixing of 5 g of sample and 1 g of dilution material (M-HWC) and pressed at pressure of 0,1 MPa/m^2 (sediment from Hnilec and water reservoir Ruzin).

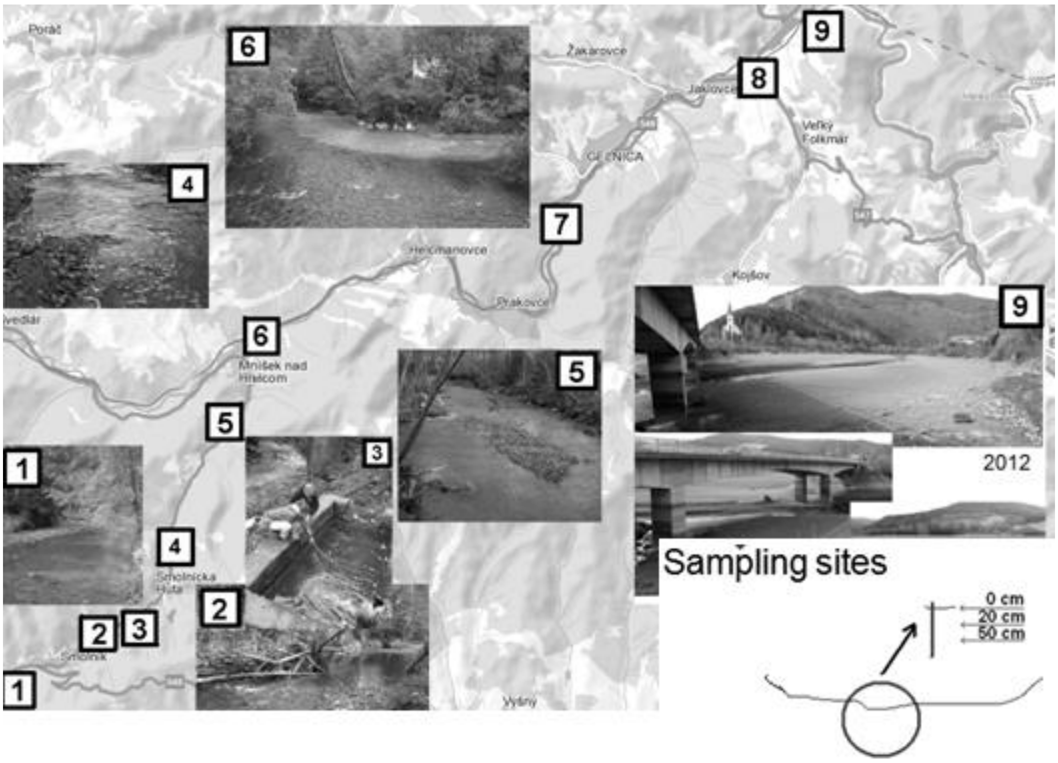

Fig. 2: Sediment samples in investigated area

3 RESULTS AND DISCUSION

Sediment criteria have been developed to deal with many environmental concerns and in response to regulatory programs. These have included determinations of whether sediments are contaminated in the context of restricted disposal of dredged materials, cleanup of industrial and municipal sites, effluent contamination, and spatial extent of contamination in area, ecological or human risk, ranking problem sites, and beneficial use impairments. Traditionally sediment contamination was determined by assessing the bulk chemical concentration of individual compounds and comparing them with background or reference value. The results from chemical analysis of sediment show the Table 1. Results of 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 [11], Regulation 257/2009 Coll. of Laws- Annex 1 - Limit values of risk elements and hazardous substances in the sediment (Czech republic) [12], Sediment quality objective Netherlands Target [13], Honk Kong Interim sediment quality guidelines (Hong Kong ISQG) [14], Flanders reference value [15], Environmental quality standard Human Health Items (Lake Biwa – EQS HHI) [16], Classification of Illinois Stream Sediments [17], Australian and New Zealand environment and Conservation Council (ANZEC) [13], National Oceanic and Atmospheric administration (NOAA) [13], Canadian Sediment Quality Guideline for protection of Aquatic Life 1999 (CDSQG) [18] and with Dutch standard: General environmental a quality standards 2000 (GEQS) [19] (Table 2).

Tab. 1: The result of chemical analysis of sediments

No.	Year	Fe	Mn	Al	Cu	Zn	As	Cd	Pb
		%			[mg/kg]				
S1	2006	3,96	0,108	7,02	176	171	50	<0,5	50
	2007	3,88	0,044	7,14	103	123	35	<0,5	39
	2008 A	3,49	0,062	6,88	114	140	31	<0,5	44
	2008B	4,01	0,116	7,67	128	157	52	<0,5	43
	2009	4,57	0,09	7,68	111	143	47	<0,5	35
	2011	4,92	0,12	8,08	148	179	52	<0,5	43
	2012	4,64	0,1	8,14	190	174	56	<0,5	60
	2013	4,75	0,11	8,02	199	184	66	<0,5	61
S2	2006	6,76	0,040	7,32	234	183	84	<0,5	82
	2007	5,70	0,051	6,76	282	186	88	<0,5	100
	2008 A	4,13	0,073	6,43	252	196	64	<0,5	89
	2008B	7,27	0,051	7,21	237	180	104	<0,5	93
	2009	4,63	0,04	6,63	196	131	65	<0,5	59
	2011	5,83	0,08	6,77	467	273	81	<0,5	147
	2012	6,25	0,06	7,32	368	200	111	<0,5	145
	2013	4,73	0,04	6,75	197	131	56	<0,5	76
S3	2006	23,6	0,096	2,52	448	313	909	<0,5	135
	2007	39,7	0,012	0,46	215	58	1465	<0,5	38
	2008 A	34,6	0,022	4,01	689	150	2206	<0,5	1557
	2008B	26,6	0,024	4,65	663	168	2439	<0,5	2731
	2009	37,4	0,01	0,74	143	45	1500	<0,5	48
	2011	33,0	0,02	2,37	756	128	1975	<0,5	1081
	2012	32,8	<0,01	2,91	603	142	2358	<0,5	225
	2013	38,6	0,01	1,42	495	81	2307	<0,5	215
S4	2006	13,8	0,051	6,09	445	172	154	<0,5	172
	2007	12,3	0,084	6,46	903	328	253	<0,5	282
	2008 A	4,97	0,067	6,16	365	214	201	<0,5	328
	2008B	8,90	0,048	6,84	295	172	161	<0,5	198
	2009	5,07	0,05	6,91	281	165	68	<0,5	101
	2011	5,42	0,06	6,54	363	191	92	<0,5	110
	2012	11,6	0,04	6,63	670	276	245	<0,5	225
	2013	8,81	0,07	6,39	352	169	122	<0,5	133
S5	2006	7,84	0,044	6,55	506	250	97	<0,5	111
	2007	8,82	0,057	6,29	661	320	146	<0,5	159
	2008 A	6,24	0,068	6,39	404	193	135	<0,5	176
	2008B	13,2	0,045	7,26	527	192	83	<0,5	106
	2009	31,7	0,03	2,62	836	200	84	<0,5	15
	2011	5,73	0,07	6,71	427	242	93	<0,5	117
	2012	6,85	0,05	6,55	585	323	102	<0,5	119
	2013	5,58	0,06	6,12	482	225	91	<0,5	112
S6	2012	7,14	0,059	5,162	288,2	97,2	39,6	<5,1	43,3
S7	2012	3,76	0,087	5,142	198,1	139,6	30,1	<5,1	30,9
S8	2012	3,998	0,158	6,17	219,5	219,3	37,0	<5,1	33,9
S9	2012	4,62	0,142	6,645	245,5	321,1	22,9	<5,1	59,4
S9	2012	5,136	0,116	7,226	650,1	853,6	9,8	<5,1	83,9
S9	2012	5,643	0,114	6,97	959,2	906,5	27,1	<2	73,9

Tab.2: Limit values for heavy metals for sediment

GUIDELINE/ELEMENT	Fe	Mn	Al	Cu	Zn	As	Cd	Pb
	%			[mg/kg]				
Slovak Act. No. 188/2003 Coll of Laws	-	-	-	1000	2500	20	10	750
Regulation 257/2009 Coll of Laws (CZ)	-	-	-	100	300	30	1	100
Sediment quality objective Netherlands Target	-	-	-	36	140	2,9	0,8	85
Hong Kong ISQG	-	-	-	65	200	8,2	1,5	75
Flanders reference value	-	-	-	20	168	28	1	0,1
EQS HHI	-	-	-	-	-	0,01	0,01	0,01
Classification of Illinois Stream Sediments	-	-	-	38	80	8	0,5	28
ANZEC	-	-	-	34	200	20	1,2	47
NOAA	-	-	-	18,7	124	8,2	1,2	30,2
CDSQG	-	-	-	110	820	33	10	250
GEQS	-	-	-	15	9,4	25	0,4	11

From Table 2 it can be seen non-harmonisation, which leads to the achievement of different reference values for a same chemical. Data are presented for eight heavy metals (Fe, Mn, Al, Cu, Zn, As, Cd and Pb). For example, the lowest quality criterion (i.e. the most restrictive) for As, Cd and Pb is obtained for the EQS HHI, where all elements exceed the limit values. No regulation does limit values for Fe, Mn and Al.
In this study all heavy metals exceed the limit values in all sediment guidelines except for Slovak Act. No. 188/2003 Coll of Laws. In this case the limit value exceed only As. Limit values for sediment in Slovak Republic are at least stringent for all mentioned regulation.

4 CONCLUSION

The overview of existing sediment quality criteria enable us to state the worldwide harmonisation is missing even if some efforts are being done in Europe. Based on a comparison of content elements identified in sediments can finally say that under current Slovak legislation cannot be tracked bottom sediments directly applied to soils. Such different outcomes assessment occurs 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 depending on the geological conditions and so. Properly should be used for the evaluation of indicators in the first place our laws and regulations in foreign countries should be used only as a supplementary assessment.

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