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Metals in the Surface Sediments of Selected Water Reservoirs, Slovakia

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Abstract Ruzin and Velke Kozmalovce water reservoirs (Slovakia) receive potentially toxic elements through rivers draining catchment areas polluted with the former extensive mining of ore-bearing deposits. In this study, the concentrations and fractionation of metals (antimony, arsenic, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, vanadium and zinc) have been studied in the surface sediments of the two water reservoirs. Comparison of metal concentrations found in the sediments with the mean shale values revealed a significant anthropogenic enrichment mostly with antimony (22.7), copper (8.5), zinc (5.5), cadmium (4.7), mercury (4.7), arsenic (4.5) and lead (3.9), and antimony (9.8), cadmium (8.8), zinc (4.9), lead (3.3) and arsenic (3.1) in the Ruzin and Velke Kozmalovce reservoirs, respectively. The results of fractionation study showed that the major proportion of cadmium (44.9–52.6%), cobalt (35.7–58.3%) and zinc (27.8–48.7%) was found in labile fractions, i.e., water- and acid-soluble fractions, although copper and nickel exhibited also significant labile fractions. When the risk assessment code was applied to the fractionation study, cadmium and cobalt came under high and very high risk category for the environment, and therefore might cause adverse effect to aquatic life.

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Pollution of the natural aquatic environment by metals is receiving still a considerable attention worldwide (Yalcin et al. 2007; Lalah et al. 2008; Liu et al. 2009). Bottom sediments, which act as the important repository of metals in the freshwater environment, are formed by sedimentation of suspended particles from the overlying water column. Dissolved metals adsorb to the suspended sediment depending on many factors such as physicochemical properties of a metal, pH, redox conditions, and mineralogical and chemical composition of suspended material (Jain et al. 2005). However, metals are not always fixed permanently by the sediments. Changing environmental conditions (e.g., pH, redox potential, salinity, temperature…) may cause a significant remobilisation of the accumulated metals. In that way, sediments act as a source of metal contaminants.

It is now well recognized that the role of aquatic sediments as a sink or as a source of metal contaminants cannot be fully assessed by measuring their total concentrations. The toxicity and mobility of a particular metal is strongly dependent on its chemical forms. Therefore, to study the different chemical forms and the possible associations of metals with soil and sediment components, many sequential extraction methods have been developed and used (Rao et al. 2008). Despite the well-known pitfalls of sequential extractions (Nirel and Morel 1990), they are commonly used to assess the mobility and bioavailability of metals in sediments.

Assessment of sediment quality is recognized as a critical step in estimating the environmental risks associated with man-made pollution by metals in aquatic systems.

However, no published data are available on metal pollution of sediments in two important water reservoirs of Slovakia. The main aims of this study were to determine the concentrations and the speciation of metals [arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V) and zinc (Zn)] in the surface sediments from the Ruzin and Velke Kozmalovce water reservoirs.

The Ruzin reservoir with an area of 3.9 km^2 and a water volume of 59 $\times$ 10^6 m^3 lies at the northwest of Kosice in eastern Slovakia (Fig. 1). Ruzin receives waters from the Hornad and Hnilec Rivers. These two rivers drain the Spiš-Gemer Rudohorie Mts., the area with long-time mining activities, ore-treatment and processing industrial activities. Many deposits containing mainly ore minerals of copper, mercury and iron were mined during the last five centuries in the area. Some recent studies have shown that the mining and ore processing activities concentrated along the Hornad and Hnilec Rivers left large amounts of various mining and tailing waste materials that can be considered as a serious problem in relation to environmental pollution (Lintnerová et al. 2006, 2008). Moreover, numerous urban waste discharges drain directly into the rivers. The Velke Kozmalovce reservoir with an area of 0.62 km^2 and a total water volume of 2.7 $\times$ 10^6 m^3 lies on the Hron River near the village of Stary Tekov in western Slovakia (Fig. 1). The Hron River is contaminated by multiple sources of geogenic and anthropogenic origin since wood, petrochemical and mining industries are located in various sites of its catchment area.

The purpose of this study was to determine the concentrations and the speciation of metals (arsenic, cadmium, cobalt, chromium, copper, mercury, molybdenum, nickel, lead, antimony, vanadium and zinc) in the surface sediments from the two above-mentioned water reservoirs and to assess the potential ecological risk of metals based on the examined data.

Materials and Methods

Totally seventeen and six surface sediment samples (0–20 cm) from the Ruzin and the Velke Kozmalovce were collected, respectively, using a stainless-steel corer in June 2005 (Fig. 1). After sampling, sediments were carefully stored into a glass jars and kept frozen at −20°C prior to processing and analysis. In the laboratory, sediment samples were defrosted at room temperature, air-dried and then ground and sieved through a 0.125 mm sieve. For the determination of the total metal concentrations (excepting Hg), sediment samples were digested with a $HF/HNO_3/HClO_4$ acid mixture (1:3:1 v/v). Concentrations of metals (Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn) were determined with atomic absorption spectrometry (AAS, Perkin–Elmer 3030B spectrometer). Mercury concentrations were analyzed directly using AAS on a Mercury Analyzator AMA 254. Antimony and arsenic were measured using AAS equipped with a hydride generation system (Perkin–Elmer 3100 HIAS 100 instrument). The concentrations and possible chemical associations of metals in the selected sediment samples were studied using a modified BCR three-step sequential extraction procedure. All materials and flasks used were previously soaked in 50% (v/v) analytical grade HNO_3 and then extensively rinsed with distilled water. The extraction steps used in this study are described as follows: Step 1—*water-soluble fraction*: 50 mL of distilled water was added to one gram of sediment sample into polypropylene tube and the sample was shaken for 16 h. Step 2—*acid-soluble fraction* (exchangeable and bound to carbonates): 40 mL of 0.11 M acetic acid was added to the

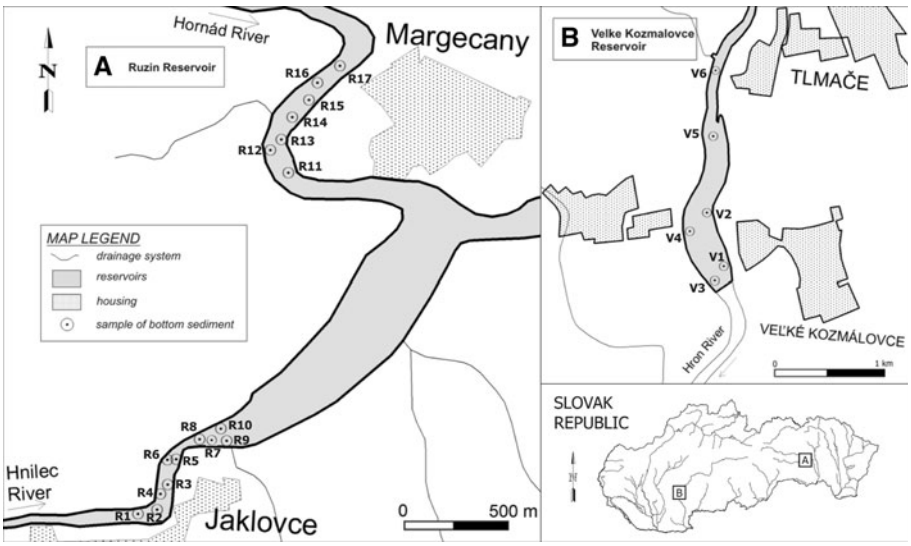

Fig. 1 Sampling locations of the sediments

residue from Step 1. Again, the tube was shaken for 16 h. Step 3—*reducible fraction* (bound to Fe/Mn oxides): the residue from Step 2 was shaken with 40 mL of 0.1 M hydroxylamine hydrochloride acidified to pH of 2 by adding HNO_3. Step 4—*oxidizable fraction* (bound to organic matter and sulphides): the residue from Step 3 was treated twice with 10 mL of 8.8 M H_2O_2 (pH of 2–3) at 85°C followed by extraction with 50 mL of 1 M ammonium acetate adjusted to pH 2 after eliminating the excess of H_2O_2. Step 5—*residual fraction* (incorporated into the crystalline structures of the minerals): the residue from Step 4 was digested with a HF/HNO_3/$HClO_4$ acid mixture. At the end of each extraction step the samples were centrifuged for 20 min at 4000 rpm to separate the sediment. The sediment was washed with distilled water and again centrifuged. The washed water was discarded. Concentrations of metals in the extracts were analyzed by the same methods as described above. The accuracy of the extraction/analytical procedure was controlled by the use of Standard Reference Materials: BCR-320R (channel sediment for total trace elements) and BCR-701 (lake sediment for sequential extractions). Metal recovery varied between 82% and 109% depending on element. Analytical precision of replicates (n = 3) was <10% relative to standard deviation.

Results and Discussion

The concentrations of investigated metals in surface sediments of the two water reservoirs as well as fresh water

Table 1 Concentrations and standard deviation (SD) of individual metals (mg/kg of dry sediment) in the sediment samples

	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	V	Zn
Ruzin												
R1	56.8	1.7	43.2	76.0	847.8	0.67	1.3	46.1	96.2	51.4	91.2	872.4
R2	57.7	1.5	54.2	86.5	523.6	0.66	1.3	56.3	88.1	47.1	99.0	838.2
R3	66.5	1.3	48.0	86.0	516.1	0.59	1.7	55.5	101.3	43.8	101.0	670.9
R4	66.2	1.3	45.9	95.0	438.0	0.59	1.0	57.5	114.2	48.3	106.5	537.7
R5	61.2	1.4	47.3	87.3	517.9	0.46	1.3	54.8	104.3	48.5	102.5	649.0
R6	61.7	1.7	48.7	90.5	537.6	0.55	1.2	56.4	94.6	42.5	112.1	815.8
R7	59.3	1.4	45.8	88.0	421.8	0.63	1.2	53.3	92.3	41.1	111.7	870.9
R8	52.9	1.4	43.9	85.6	447.2	0.57	1.0	51.2	97.3	44.5	80.3	586.0
R9	59.8	1.4	43.8	75.5	458.3	0.58	0.8	48.0	80.6	46.5	88.7	613.1
R10	73.2	1.3	35.4	72.8	463.0	0.75	0.9	52.7	84.1	39.2	78.4	506.9
R11	62.0	1.4	22.1	102.4	213.0	3.35	0.7	79.9	56.1	20.5	93.1	304.6
R12	42.7	1.4	20.6	95.9	151.6	3.70	0.9	66.4	49.2	14.6	104.8	288.6
R13	56.7	1.5	26.0	121.5	197.0	3.43	0.8	100.9	65.7	19.3	109.8	334.5
R14	43.9	1.0	22.1	97.5	155.7	3.41	0.8	65.0	47.0	15.5	110.3	251.5
R15	57.1	1.4	22.0	101.7	188.1	2.80	0.9	74.4	54.2	17.0	102.6	312.3
R16	63.8	1.7	19.1	83.1	241.2	4.45	0.8	68.5	54.2	22.1	72.8	335.0
R17	43.4	1.3	23.3	112.1	178.3	4.98	0.8	87.9	60.1	17.2	118.5	308.5
Mean	57.9	1.4	36.0	91.6	382.0	1.89	1.02	63.2	78.8	34.1	99.0	517.0
SD	8.39	0.17	12.5	12.9	191.0	1.65	0.27	15.0	22.0	14.2	13.1	209.0
Velke Kozmalovce												
V1	44.9	3.0	12.0	37.3	96.6	0.20	1.5	17.2	71.6	15.7	58.3	561.3
V2	36.1	2.7	9.6	35.1	64.2	0.19	1.4	14.4	61.6	15.8	47.9	455.8
V3	29.6	2.1	7.9	29.1	68.9	0.19	1.3	12.1	55.1	13.8	38.4	354.8
V4	44.2	2.6	9.7	31.2	77.6	0.19	1.5	13.8	65.0	15.0	45.4	445.3
V5	39.2	2.5	12.8	33.4	87.6	0.18	1.5	14.9	77.3	15.3	59.6	451.3
V6	47.9	2.9	11.7	34.3	75.7	0.17	1.4	15.2	64.7	12.9	55.2	505.3
Mean	40.3	2.6	10.6	33.4	78.4	0.19	1.43	14.6	65.9	14.8	50.8	462.0
SD	6.74	0.3	1.85	2.91	12.0	0.01	0.08	1.68	7.74	1.16	8.30	68.8
Shale	13.0	0.3	19.0	90.0	45.0	0.40	2.6	68.0	20.0	1.50	130.0	95.0
TEL[a]	5.90	0.60	n.d.[c]	37.3	35.7	0.174	n.d.	18.0	35.0	n.d.	n.d.	123.0
PEL[b]	17.0	3.53	n.d.	90.0	197.0	0.486	n.d.	35.9	91.3	n.d.	n.d.	315.0

[a] *TEL* the threshold effect level (MacDonald et al. 2000); [b] *PEL* the probable effect level (MacDonald et al. 2000); [c] *n.d.* not defined

Table 2 Correlation coefficient between elements in the surface sediments of the Ruzin and the Velke Kozmalovce reservoirs

	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	V	Zn
Ruzin (n = 17)												
As	1.00											
Cd	0.27	1.00										
Co	0.43	0.18	1.00									
Cr	−0.47	−0.21	−0.53[a]	1.00								
Cu	0.46	0.42	0.83[c]	−0.69[b]	1.00							
Hg	−0.54[a]	−0.11	−0.92[c]	0.65[b]	−0.83[c]	1.00						
Mo	0.30	0.18	0.75[c]	−0.39	0.70[b]	−0.66[b]	1.00					
Ni	−0.34	−0.08	−0.71[c]	0.91[c]	−0.75[c]	0.80[c]	−0.54[a]	1.00				
Pb	0.54[a]	0.17	0.92[c]	−0.47	0.82[c]	−0.88[c]	0.70[b]	−0.64[b]	1.00			
Sb	0.54[a]	0.26	0.94[c]	−0.68[b]	0.91[c]	−0.93[c]	0.66[b]	−0.79[c]	0.94[c]	1.00		
V	−0.45	−0.29	0.01	0.64[b]	−0.24	0.15	0.13	0.37	−0.04	−0.22	1.00	
Zn	0.39	0.46	0.91[c]	−0.60[b]	0.94[c]	−0.84[c]	0.76[c]	−0.71[c]	0.81[c]	0.91[c]	−0.10	1.00
Velke Kozmalovce (n = 6)												
As	1.00											
Cd	0.84[a]	1.00										
Co	0.68	0.61	1.00									
Cr	0.57	0.88[a]	0.69	1.00								
Cu	0.53	0.48	0.75	0.51	1.00							
Hg	−0.27	0.07	−0.31	0.14	0.23	1.00						
Mo	0.65	0.59	0.75	0.57	0.67	0.10	1.00					
Ni	0.73	0.90[a]	0.82[a]	0.94[b]	0.76	0.13	0.69	1.00				
Pb	0.52	0.43	0.92[b]	0.56	0.81[a]	−0.09	0.86[a]	0.71	1.00			
Sb	−0.09	0.21	0.18	0.43	0.30	0.68	0.60	0.35	0.43	1.00		
V	0.65	0.66	0.99[c]	0.78	0.74	−0.23	0.72	0.87[a]	0.90[a]	0.23	1.00	
Zn	0.82[a]	0.97[b]	0.75	0.92[b]	0.66	0.07	0.65	0.98[c]	0.60	0.24	0.80	1.00

[a] Correlations are significant at the 0.05 level; [b] Correlations are significant at the 0.01 level; [c] Correlations are significant at the 0.001 level

sediment quality guidelines expressed as threshold effect level (TEL) and probable effect level (PEL) are summarized in Table 1. Based on TEL/PEL comparisons, adverse effects would be expected frequently in most surface sediments of the two water reservoirs because the PELs for various metals are exceeded. Generally, the concentrations of all metals, excepting Cd, Mo, Pb and Zn, were significantly higher in surface sediments of the Ruzin compared with those of the Velke Kozmalovce ($p < 0.05$). The mean metal concentrations in surface sediments from the Ruzin decreased in the order: Zn > Cu > V > Cr > Pb > Ni > As > Co > Sb > Hg > Cd > Mo. Similar metal concentrations were measured by Brehuv (2000) in surface sediments of the Ruzin collected between years 1994 and 1997. Somewhat different order of the metal concentrations was observed in surface sediments of the Velke Kozmalovce: Zn > Cu > Pb > V > As > Cr > Sb > Ni > Co > Cd > Mo > Hg. A comparison of metal concentration in the sediments with the shale standard is generally taken as a quick and practical method of tracing metal enrichment (Förstner and Wittmann 1979). The mean metal concentrations in the sediments of the Ruzin revealed that the concentrations of Mo, Ni and V were lower whereas those of As, Cd, Co, Cu, Hg, Pb, Sb and Zn were higher than the respective mean shale values (Table 1). The concentrations of As, Cd, Cu, Pb, Sb and Zn in the Velke Kozmalovce sediments were also higher than the mean shale values. The enrichment of the metals was found to be significant mainly for Sb (22.7), Cu (8.5), Zn (5.5), Cd and Hg (4.7), As (4.5) and Pb (3.9) in the Ruzin and for Sb (9.8), Cd (8.8), Zn (4.9), Pb (3.3) and As (3.1) in the Velke Kozmalovce. The pollution of the Ruzin reservoir with these metals is due to the long-term mining history in the catchment areas of Hnilec and Hornad Rivers supplying the reservoir with water. There are several abandoned mines with Cu–Hg–Fe sulphide mineralization (Smolnik, Rudnany, etc.) and ore processing plants along the two rivers which continuosly contaminate the whole catchment area with Cu, Hg and associated elements such as As, Cd, Sb, Pb and Zn. For example, Lintnerová et al. (2006, 2008) have reported that waters and suspended solids of the Smolnik Creek, a tributary of the Hnilec

River, contained high concentrations of As, Cd, Cu, Pb and Zn. The Velke Kozmalovce reservoir receives waters and suspended solids of the Hron River, which is contaminated directly by discharges of industrial waste waters. Moreover, the Hron River drains various mountains where huge deposits of Ag–Au–Cu–Pb–Zn–Sb ores were mined over a period of centuries.

Correlation analysis was performed on the concentration data of metals in the sediments to assess possible similar sources and geochemical behaviour of the metals. Correlation coefficients among different metals are shown in Table 2. A correlation matrix shows that the Co, Cu, Pb, Sb and Zn in Ruzin sediments were significantly correlated with each other showing a strong positive association. This indicates that Co, Cu, Pb, Sb and Zn may originate from the same sources and they exhibit a similar behaviour during transport in the river environment. In Velke Kozmalovce sediments, a highly significant positive correlations were found for the following metal pairs: As–Cd and –Zn, Cd–Zn, Co–Pb and Cu–Pb (Table 2).

Sequential extractions were performed on six selected sediment samples and As, Sb, Cd, Co, Cu, Hg, Ni, Pb and Zn were examined. The mean percentages of metals extracted in each step of the sequential extraction procedure are given in Table 3. Similar patterns for the examined metals were observed in both water reservoirs. The order of metals in different fractions according to their percentage contribution is the following: Co > Sb > Ni > Cd ≈ Pb > As > Cu > Zn > Hg in water-soluble forms, Cd > Co ≈ Zn > Cu > Ni > Pb > As > Sb > Hg in acid-soluble forms, Pb > Zn > Cd ≈ Cu > Ni > Co > Sb ≈ As > Hg in reducible fraction, Hg > Cu > Zn > Cd > Ni > Pb > Co > As > Sb in oxidizable fraction and As > Sb > Ni > Co > Cu > Zn > Pb > Hg > Cd in residual fraction. The dominant proportion of Cd (43.6–51.6%) in the sediments was found in acid-soluble fraction, which indicates that Cd is mainly occurred in exchangeable forms and bound to carbonates. This finding agrees well with other studies reporting relatively high Cd mobility (Bird et al. 2003). The significant proportion of Cd, Co, Cu, Ni and Zn extracted in the second step highlights their pollution risk as the metals extracted by acetic acid are considered to be bioavailable. The residual fraction was the most important for As, Sb, Ni and Co. Elements in residual fraction are bonded to the crystal structure of recalcitrant minerals and therefore are unlikely to be released to aqueous phase under environmental conditions (Carral et al. 1995). Mercury and Cu were found mainly in the oxidizable fraction (66.5–99.0% and 26.5–36.4%, respectively), indicating their strong association with organic matter. Mercury and copper can easily form complexes with organic matter due to the high stability constants of organic mercury and copper compounds. This is consistent with the results reported by other investigators (Beldowski and Pempkowiak 2003; Caplat et al. 2005). Most of Pb (75.3–77.4%) was present in the reducible fraction, which coincides with Fe/Mn oxides. The reducible fraction appeared to be important also for Zn, Cd, Cu and Ni. The results are consistent with previous studies, showing that Pb,

Table 3 Mean percentage of metals in each fraction for the selected sediments

	As	Cd	Co	Cu	Hg	Ni	Pb	Sb	Zn
Ruzin-Hnilec (samples R1 and R10)									
Step 1	0.76	1.69	3.69	0.60	0.08	2.30	1.34	3.45	0.18
Step 2	1.75	50.9	54.6	26.6	0.08	17.7	2.80	0.79	36.7
Step 3	2.70	16.1	3.71	27.1	0.51	18.6	76.5	4.22	27.5
Step 4	3.49	22.9	12.2	32.5	91.1	13.0	7.76	0.54	20.8
Step 5	91.3	8.41	25.8	13.2	8.23	48.4	11.6	91.0	15.0
Ruzin-Hornad (samples R12 and R16)									
Step 1	2.08	1.34	6.80	1.10	0.07	1.40	1.85	4.26	0.30
Step 2	2.07	43.6	31.0	18.2	0.01	17.9	1.87	2.13	27.5
Step 3	2.08	32.9	6.80	37.2	0.05	28.1	77.4	2.96	35.8
Step 4	3.47	15.4	6.80	26.5	99.0	11.9	9.81	2.55	16.4
Step 5	90.3	6.76	48.6	17.0	0.87	40.7	9.07	88.1	20.0
Velke Kozmalovce (samples V1 and V6)									
Step 1	2.93	0.78	7.94	1.09	0.45	3.60	1.26	7.14	0.18
Step 2	5.86	51.6	27.8	8.71	0.13	12.2	3.15	2.75	48.5
Step 3	3.49	37.1	7.94	20.5	0.12	15.9	75.3	2.21	30.3
Step 4	3.62	6.64	8.72	36.4	66.5	14.0	7.19	3.30	11.6
Step 5	84.1	3.88	47.6	33.3	32.8	54.3	13.1	84.6	9.42

Zn and Cu are commonly associated with Fe/Mn oxides in sediments (Bird et al. 2003; Liu et al. 2009).

The risk assessment code (RAC) was applied to assess the availability of metals and the risk connected with their presence in aquatic environment. The risk assessment code (RAC) offers an indication of the possible risk by applying a scale to the percentage of metals occurring in water- and acid-soluble fractions. According to RAC, if this fraction is <1% there is no risk for the environment, 1–10% exhibits low risk, 11–30% indicates medium risk, 31–50% high risk and >50% represents very high risk (Jain 2004). The risk assessment code as applied to the present study reveals that 44.9–52.6% of Cd and 35.7–58.3% of Co are present in labile fractions, and therefore come under high and very high risk. Zinc, copper and nickel exhibited also significant labile fractions falling into medium and high risk category.

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