

Study of Environmental Risks at an Old Spoil Dump Field

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Abstract

This environmental case study presents the results of a risk assessment at the deposit in Lubietova, Slovakia. The risks of heavy metals in the studied location are mainly influenced by acid mine drainage (AMD) and natural sorbents presented, i.e. clay minerals (illite, muscovite, smectite, kaolinite, and chlorite), which were identified by x-ray diffraction analysis and create a natural geochemical barrier against their release into ground and surface water. Calculations of the potential for AMD formation show the minimum risks of a dump field to the environment. Seasonal monitoring of ground and surface water contamination by heavy metals and by other inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-}) during March 2008-March 2010 proved the aforementioned facts. Content of Cu in drainage and surface water was increased at the Lubietova-Podlipa deposit. The connection with saturation of natural sorbents with copper also was verified by a study of their sorption properties. Utilization possibilities of natural bentonites and zeolites as sorbents for decreasing Cu content in drainage water were studied as well. Their efficiency was approximately 88-98%. Content of As (As(III):As(V) is 1:5) was not regularly increased in the drainage and surface water in the Lubietova – Svatodusna valley deposit. Nevertheless, it requires regular monitoring.

Keywords: heavy metals, clay minerals, sorption, contamination of natural water, risk assessment

Introduction

Nowadays, the tackling problems with old mining burdens present a hot topic regarding the risks of spoil heaps and the extraction of nonferrous metals and iron. Research of the overcast locations is provided in order to assess the extent of the damage and to design remediation measures [1]. This paper focuses on studying the risks that represent a consequence of the old environmental loads and possibilities of their remediation. The issue is described using the example of the mining location Lubietova, situated in central Slovakia near Banská Bystrica. Lubietova ore field lies in the northeastern part of the Slovenske stredohorie Mts.

that includes the northern part of neovolcanic massif of Polana and the northern part of the Ciertaz Mts. (in Veporske vrchy). In the past, Lubietová belonged to one of the most important copper and iron mining centers. The mining activity continued with breaks until the end of the 19th century in three main deposits – Podlipa (on the eastern end of Lubietova village), and Svatodusna and Kolba at the end of Peklo Valley (approximately 5 km eastwards from the village). Besides Cu and Fe, gold and silver were mined here and the occurrence of Co and Ni was recognized as well. Dump field Podlipa, which directly influences the inhabitants of Lubietova, was studied in detail.

The metal elements, especially heavy metals and metalloids, are extremely toxic, harmful, carcinogenic, mutagenic, teratogenic, and toxic for reproduction even at low

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concentrations. Therefore, today they must be monitored and eliminated to protect human health and the environment. The most toxic properties are characteristic for inorganic metal compounds because they dissociate well and they are easily soluble, so they can easily penetrate through cell membranes and get into internal organs, where they accumulate. Metals and metalloids get into the environment as a result of natural processes (rock decay, soil formation processes, etc.) and anthropogenic contamination (industrial and agricultural activities, as power industry, fertilizers and plant protection products, spoil dumping sites, etc.). The heavy metals from these sources are dispersed in the environment and contaminate soil, water, and air, and through the food chain they get into human and animal bodies [2, 3]

The most dangerous sources of heavy metals contamination are the old spoil dumps. Metals accumulating in the surface soil layer and sediments are mobilized not only by chemically controlled processes of dissolution and leaching, but also as a consequence of contaminated soil layer erosion. They may penetrate into the ground and surface water. Therefore, this problem has been the subject of numerous studies that deal with the sorption properties of different types of soil in relation to heavy metals ions and the risk of their migration.

Decreasing pH and changes of redox potential (Eh) in technogenic sediments of Podlipa dump field on the historical Lubietova Cu-Ag deposit cause the release of heavy metals from hardly soluble minerals or from sorption complex into the ground and surface water. Resistance of the landscape components toward heavy metal contamination is mostly conditioned by the physical and chemical characteristics of soil, i.e. the content of organic mass and clay fraction, mineralogical composition, pH, and others that together form sorption soil properties [4-5].

Mainly clay minerals have a dominant position among natural sorbents [6]. They usually have negative surface charges [7], therefore they are able to fix heavy metals cations on their surface [8]. A dominant process of sorption on clay mineral is ion change between solution and solid phase, and partly also the physical process of adsorption [7]. In the case of most heavy metals, mostly kaolinite is recognized as an excellent sorbent [9].

From the environmental risk point of view, Cu, As, and Sb are the most important heavy metals in the studied location [10].

The main source of copper is minerals such as tetraedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$), chalkopyrite (CuFeS_2), and secondary copper minerals. Copper made parts of solutions during weathering has influence on contamination of the whole hydro-net. The cementation process caused Cu to precipitate on iron oxides (hydrogoethite) and on iron [10]. The sorption of Cu on the surface of clay minerals depends on pH. When carbonates are missing, as in Podlipa, Sun Du et al. [11] describes production of complex compounds $=\text{SOCu}^+$, $=\text{SOCuOH}$, and $=\text{SOCu}_2(\text{OH})_2^+$, as well as $=\text{Cu}(\text{OH})_2$ and $=\text{SOCu}_2(\text{OH})_3$ precipitations during sorption.

Tetraedrite presents a main source of As in Podlipa. Weathering caused the ore minerals with arsenic to easily oxidize, and as a result arsenic moves from a form with lower oxidation numbers to As(V) in the form of arsenic acid compounds. Arsenic acid is soluble in water but only rarely migrates at larger distances because it reacts with heavy metals cations and As is bound in arsenate form. As(III) is in an oxidative zone more mobile than As(V) [12].

The sorption capacity of clay minerals is very high in comparison with As, and it depends on pH, time, and concentration of As in solution and temperature [13]. The most intensive sorption takes place at pH 4 [14, 15]. Among the all clay minerals on the spoil dump field Podlipa, kaolinite is the best As(V) sorbent [16]. Less toxic As(V) are sorbed easier and more quantitatively than As(III). As(III) oxidizes to As(V) in this process [16].

Most Sb has its origins in tetraedrite. Sb(III) and Sb(V) create complex compounds on the surface of hydrogoethite and Sb(III) oxidizes at pH 3-5.9. Sb(III) is sorbed at pH 3-12. Maximal sorption of Sb(V) occurs in pH value below 7. If pH~9, the mobilization and releasing of Sb(V) into solution begins [17, 18].

Experimental Procedures

Sampling – Sediments

Twenty-eight representative samples of technogenic sediments were taken from the spoil dump surface in Lubietova-Podlipa (in 2006-08). The samples were taken from the soil with grain under 1 cm so that they represented the horizon 50 cm deep. After homogenization of 6-10 smaller samples that weighed 3-5 kg, samples were made by subsequent division. Each sample represents an area 20×50 m weighing 30-35 kg. The sample Aref represents a reference area without processed ore outside the spoil dump field. The set of samples was complemented by the sample Ah, i.e. mineral rich in hydrogoethit. Ah sample was prepared by homogenization of 3 samples, with the highest content of hydrogoethit from the studied location.

Sampling – Water

Water sampling was done in 2008-10 according to STN ISO 5667 [19]. Overall, water samples were taken from 17 sampling places 12 times with regard to seasonal influence. The water samples L1-L7 were taken from Lubietova-Podlipa spoil dump field (L1 represents mineral water Lihartovka), and L11-L15 are from Svatodusna Valley dump field. The samples of drinking water (spring ground water), LDW1-LDW4, and surface water L8 from sources directly in Lubietova village were taken as well. These sources are not regularly inspected because the municipality has a public water pipe, in spite of sources LDW1-LDW4 that are used by village inhabitants as drinking water. Surface water source L8 is used for irrigation.

Analysis was done for 25 indicators of water quality and interpreted according to limit values in current national legislation [20, 21] that corresponds to European legislation.

Pre-preparation of water samples for metal determination by AAS was done according to STN ISO 5667 [19]. Samples were preserved by the addition of concentrated nitric acid on pH value < 2 stored at 5°C and analyzed within a month.

Experimental Methodology

Mixed fractions of the clay minerals from collected technogenic sediment samples for X-ray diffraction analysis were obtained according to the method published by Šucha et al. [22]. X-ray diffraction analysis was done at the Geological Institute, Slovak Academy of Sciences (GI SAS), using an X-ray diffractograph PW 1710 Philips Analytical.

Technogenic sediments, prepared from mixed fractions of clay minerals from technogenic sediments, as well as hydrogoethite-rich mineral samples, were analyzed for metal elements (40 elements) by ICP-MS in ACME Analytical Laboratories Vancouver Ltd. Canada (for limits of detection see Table 1). Mixed fractions of clay minerals and hydrogoethite were analyzed for metal elements before and after 14 days maceration in drainage water, to study its free sorption capacity for selected metal elements. Drainage water from a pond in the field depression below Empfängnis gallery, 5 times concentrating by isothermal evaporation, was used.

Total sulfur (S_{tot}), amount of sulfates (S_{SO_4}), and sulfides (S_s) were determined by gravimetric analysis (limit of quantification is 0.01%) in the reference laboratory of the Ministry of the Environment of the Slovak Republic for geology and environment in Dionyz Stur State Geological Institute in Spišská Nova Ves. The results were used for the calculation of potential acid drainage water production according to EPA methodology [23].

Total carbon (C_{tot}), organic carbon (C_{org}), and inorganic carbon (C_{inorg}) were determined in Laboratories of GI SAS in Banská Bystrica using infrared spectroscopy method with a Ströhlein C-MAT 5500 device (limit of detection is 0.05 %). The results were used for the calculation of carbonate content in the location, which determines neutralization of potentially arising acid drainage water.

pH of the sediments was determined in both water solution and KCl solution ($c = 1 \text{ mol.dm}^{-3}$) according to Sobek's et al. [24] methodology. pH and Eh were measured using pH-meter Multi 340i, WTW, Germany.

Water temperature, air temperature, pH and Eh (SenTix 41 probe), dissolved oxygen (Cellox 325 probe) and specific conductivity (Tetra CON 325 probe), were measured directly in place by a Multi 340i portable device (WTW, Germany) with appropriate probes.

The concentrations of chlorides, sulfates, nitrates, nitrites, fluorides, and phosphates were determined by CZE method using an electrophoretic analyzer EA 102

Villa Labeco, Spišská Nova Ves, Slovakia (limits of detection see Tables 4 and 5). Analysis and evaluation were supported by software by Dusan Kaniansky Consulting ACES ver.1.53.

Chemical oxygen demand (COD_{Cr}) was determined by an SQ 118 MERCK photometer. Chemical oxygen demand (COD_{Mn}) was determined by redox titration. Biochemical oxygen demand (BOD_5) was determined by oxygen probe (Cellox 325) using the Multi 340i.

Determinations of Cu, Ni, Pb, Co, Cd, Fe, Zn, and Mn were done with an AAS AVANTA Σ spectrometer by GBC Scientific with flame or electrothermal atomization. PAL 3000 autosampler was used for electrothermal analysis. Analysis and result evaluation were supported by GBC Avanta software ver.2.0 (limits of detection see Tables 4 and 5).

As and Sb were determined by AAS hydride generation technique. Analyses were done in the Regional Authority of Public Health in Banská Bystrica using a PERKIN ELMER 4100ZL device in flow system with Flow Injection Analyzer 100 (limits of detection see Tables 4 and 5).

The sorption properties of prepared mixed fractions of clay minerals from Lubietova were studied in batch experiments according to the methodology by Bhattacharyya et al. [25].

The possibilities of Cu retardation using natural sorbents from Lieskovec and Jelsovy potok deposits and zeolites from Nizny Hrabovec were studied in batch experiments.

Results and Discussion

To assess the risks arising from the content of heavy metals in technogenic sediments and their subsequent release into ground and surface waters, the concentrations of metals were detected in the technogenic sediments, clay fractions from technogenic sediment, and in the samples from ground and surface water.

The potential of clay minerals as natural sorbents capable of capturing metals was determined based on the sorption experiments.

Regarding the possibility of releasing of metals into surface and ground water, the probability of acid mining water formation was evaluated according to EPA methodology. The results were compared with the measured concentrations of metals in the water.

Concentrations of Metal Elements in Technogenic Sediment Samples

The concentration of metal elements in technogenic sediment samples of spoil dump field Lubietova-Podlipa is markedly unequal (Table 1). It is a reflection of original sediment concentrations in single parts of dump field as well as geochemical relations, mainly their migration ability.

Table 1. ICP-MS analysis of technogenic sediments.

		Element							
Content	Unit	Ca	Na	K	Fe	Mg	Al	P	S
Min.	%	0.03	0.03	0.03	0.90	0.34	0.41	0.03	0.03
Max.		4.70	0.82	4.30	3.60	10.00	8.00	0.72	0.50
Average		0.33	0.16	2.90	1.80	1.10	5.90	0.09	0.15
LOD		0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.01
Content	Unit	Cu	Pb	Zn	Cd	Bi	Co	Ni	As
Min.	mg·kg ⁻¹	25	6.5	7	<0.3	<0.3	2.1	5.5	7
Max.		12080	130	211	0.9	103.0	96.0	62.0	397
Average		3143	25	29	0.2	8.9	41.0	31.0	109
LOD		0.1	0.1	1	0.1	0.1	0.1	0.1	0.5
Content	Unit	Au	Ag	Rb	Sr	Hf	V	Ba	Li
Min.	mg·kg ⁻¹	<1.5	<0.3	23	2	<1.5	19	214	4.7
Max.		<1.5	3.4	166	67	<1.5	57	531	53.0
Average		<1.5	0.6	112	29	<1.5	35	333	32.0
LOD		0.5	0.1	0.5	0.5	0.5	2	0.5	0.1
Content	Unit	Mn	Mo	Cr	W	Sb	La	U	Th
Min.	mg·kg ⁻¹	34	<0.3	9	0.6	5.2	15	0.9	4.8
Max.		2755	0.70	38	1.6	98.0	41	3.1	11.0
Average		578	0.30	19	1.2	27.0	25	1.7	7.4
LOD		1	0.1	1	0.1	0.1	0.5	0.1	0.1
Content	Unit	Zr	Ce	Sn	Y	Nb	Ta	Be	Sc
Min.	mg·kg ⁻¹	13	5	<3	3.1	<1.5	<0.3	<3	2.0
Max.		37	77	20	11.0	5.5	2.0	5	7.0
Average		19	45	8	5.5	2.6	0.3	2	3.8
LOD		0.5	0.5	1	0.1	0.5	0.1	1	0.1

LOD – Limit of detection

The concentrations of theoretically extractable elements in spoil dump material varied from 36,000 mg·kg⁻¹ (Fe) to 0.9 mg·kg⁻¹ (Cd). Cu (12,080 mg·kg⁻¹), and As (397 mg·kg⁻¹) concentrations (Table 1) could be considered important. An origin of higher U (3.1 mg·kg⁻¹) and Th (11.0 mg·kg⁻¹) contents in the reference area (Table 1) is connected with Perms rocks.

Weathering processes of high-reactive minerals mobilize metal elements, and that causes the landscape contamination and initiates the production of clay minerals and hydrogoethite. They create a natural geochemical barrier on which the metal precipitation arises into stable bonds.

X-ray diffractive analysis confirmed that predominant natural sorbents are illite – (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)_c(H₂O)], muskovite – KAl₂(AlSi₃O₁₀)(F,OH)₂, and

minerals from the smectite group, and to a lesser extent kaolinite – Al₂Si₂O₅(OH)₄. Hydrogoethite (FeO(OH)·nH₂O) is rather rare.

Heavy Metal Sorption on Clay Minerals and Hydrogoethite

Mixed fractions of clay minerals from 11 representative technogenic sediment samples and hydrogoethite, originated in spoil dump field Lubietova-Podlipa, were studied for heavy metals sorption as well as the existence of free sorption capacity of these natural sorbents.

First, the samples of technogenic sediments were analyzed. Next, clay fractions (prepared from these samples) and clay fractions after 14 days maceration in drainage water were analyzed (Tables 2 and 3).

Table 2. ICP-MS analysis of clay mineral fraction and clay mineral fraction after maceration in drainage water.

Element		Sample									
		Content									
		A-c	A-c	A-c	A-c*	A-c*	A-c*	Aref	Ah	Ah-c	Ah-c*
Unit	Min.	Max.	Average	Min.	Max.	Average	Average	Average	Average	Average	
Fe	%	1.3	3.0	2.8	0.8	5.0	5.3	1.4	1.7	1.5	13.0
Cu	mg·kg ⁻¹	231	8756	2319	176	7654	2151	25	10 000	20 360	23 060
Pb		6.3	64.0	29.0	4.2	229.0	80.0	16.0	8.4	49.0	60.0
Zn		14	40	23	4	176	57	39	59	80	50
Cd		<0.3	<0.3	<0.3	<0.3	0.7	<0.3	<0.3	<0.3	<0.3	<0.3
Bi		0.7	39.0	11.0	0.8	103.0	33.0	<0.3	7.2	6.0	5.0
Co		8.3	98.0	39.0	6.4	105.0	40.0	5.1	73.0	70.0	83.0
Ni		6.3	67.0	35.0	9.7	72.0	48.0	8.5	52.0	43.0	58.0
As		17	258	126	15	628	190	7	289	260	280
Sb		7.1	79.0	34.0	13.0	153.0	56.0	10.0	43.0	40.0	34.0
Mn		64	1322	531	87	1458	582	559	1074	960	1010
V		<6	69	25	<6	77	30	31	15	16	15
Cr		7	39	21	7	67	31	19	7	8	8
Sn		3	13	8	3	29	12	<3	9	4	9
U		1.1	2.5	1.7	1.1	3.3	2.0	2.2	2.3	2.0	1.0
Th	5.3	9.2	6.6	2.2	12.0	6.4	7.7	2.5	2.0	2.0	

Aref – reference sample; Ah – sample of hydrogoethite; Ac, Ah-c – clay mineral fraction; Ac*, Ah-c* – clay mineral fraction after 14 days maceration in drainage water with heavy metals

Clay minerals are able to fix more Pb, Zn, Bi, Sb, V, Cr, Sn, U, and Th in comparison with hydrogoethite. Elements such as Cu, Co, Ni, As, and Mn (Table 2) are preferentially bound in hydrogoethite. Except for the tendency to fix on the clay fraction, heavy metals Fe, Pb, Zn, Bi, As, Sb, Mn, and Cr show free sorption capacity of the clay fraction (Table 2 and Fig. 1). Lower content of heavy metals in clay fraction after macerations (releasing of metals from clay fraction) was shown for Cu (Table 2, Fig. 1) and Th (Table 2).

Sykorova [26] studied in detail the sorption properties of the clay fractions from the Lubietova-Podlipa field specifically technogenic sediment samples with the highest Cu content.

On the basis of obtained results, it could be stated that clay fractions have minimal free sorption capacity (0.3 mg/lg of sorbent) and the change of conditions (e.g. pH, temperature etc.) can cause a reversible process, namely copper releasing into water solution, which is in accordance with reality. This process is considerable mainly in drainage water under the Lubietova-Podlipa dump field, and it is connected with secondary copper mineral production.

The possibilities of Cu retardation by means of natural sorbents were found. Finally for the case study, economically available natural bentonites from Lieskovec and Jelsovy potok deposits and zeolites from Nizny Hrabovec were used. The efficiency of mentioned sorbents in the

process of Cu removal from drainage water from dump field Podlipa was compared. The efficiencies for these sorbents were 88-98%. Without any modifications of pH in real conditions, where natural water pH is approximately 6.4 and sorbent reactions are neutral or alkalic, copper is precipitated as well. This was verified by experiments with clay material from Lubietova, which was, moreover, saturated by Cu and it was able to remove 0.8 mg Cu/1 g of sorbent instead of 0.3 mg Cu/1 g of sorbent. The difference gives us the answer to the precipitated Cu form.

Cd, Co, Ni, and Cr are predominantly bound in sediment. Even if the clay fraction contained lower concentrations, it did not have a distinctive tendency to fix Cd, Co, Ni, and Cr on its surface in the maceration process (Fig. 1). The majority of Cd, Co, Ni, and Cr is bound in solid phase and these metals are hardly released into solution, so autochthonous clay minerals are less saturated by these metals during natural weathering. The same trend was indicated at Co and Ni (also at hydrogoethite), but contents of Cd and Cr were not changed markedly.

The concentration of Th was lower in the clay fraction than in the sediment, and after maceration Th was released from the clay minerals. U is more mobile than Th, and this tendency was reflected at the Lubietova deposit. The content of Th is normally one order of magnitude higher than U content in the soil. However, in plant tissues the rate

Th:U was equal in order of magnitude due to the higher migration ability of U [10].

Total Acid Production and Neutralization Potential

The ability of a sample to create acid products is given by total acid production (TAP) and neutralization potential (NP). TAP (in kg CaCO₃ per 1 ton dump material) value can

be counted as multiples of percentage content of Stot using coefficient 31.25, derived from neutralization equation [24] (CaCO₃ + H₂SO₄ = CaSO₄ + H₂O + CO₂). These data are adequate for acid amount, which can potentially be produced by dump material according to determined S_{tot} content. NP (in kg CaCO₃ per 1 ton dump material) defines the amount of the neutralization substance present in the dump-field that is able to neutralize the acidity produced by dump material. Net neutralization potential (NNP) is equal to the

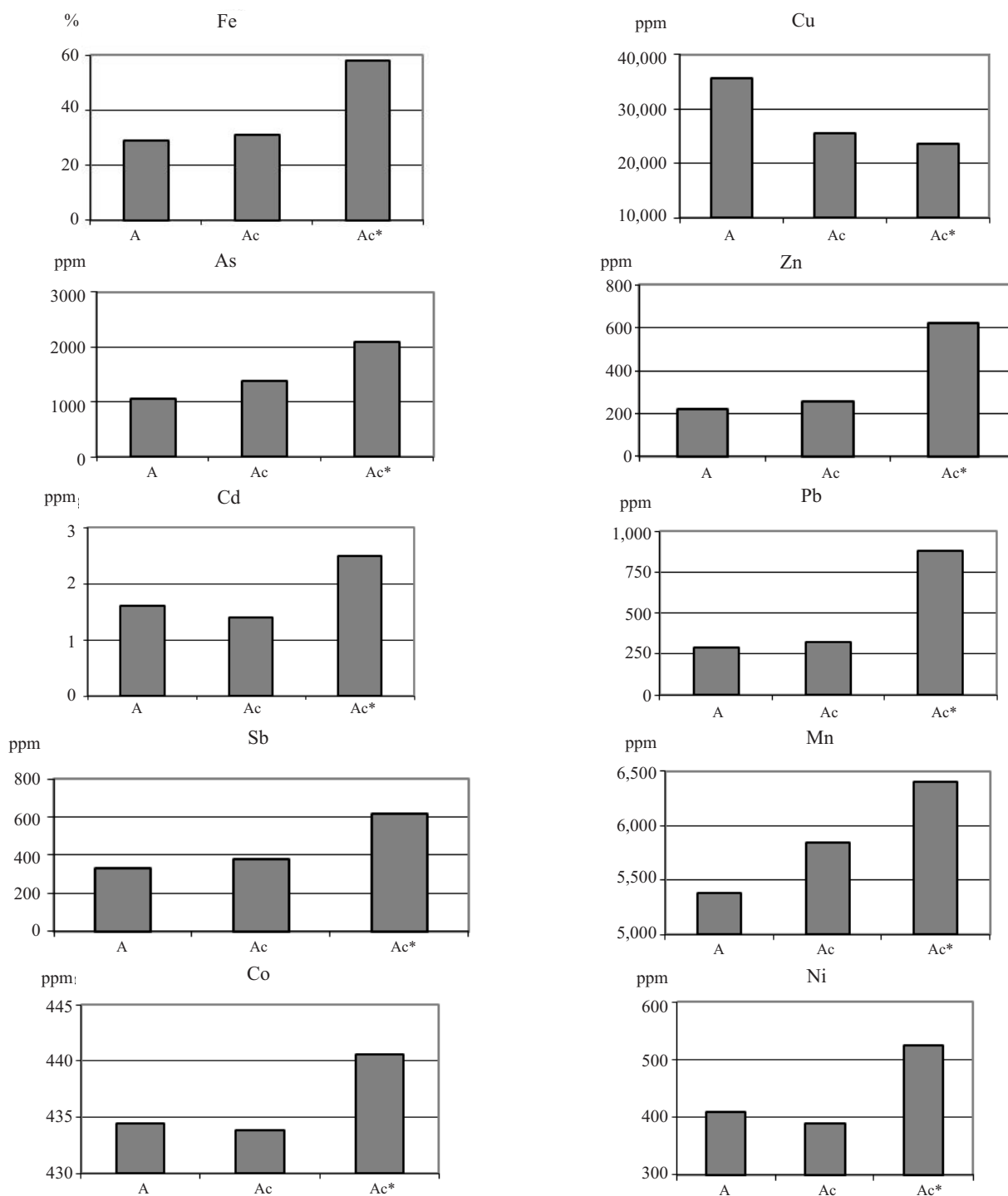


Fig. 1. Total content of Fe, Pb, As, Sb, Zn, Mn, Cu, Co, Cd, Ni (Lubietova – Podlipa)
 a) in technogenous sediments (A)
 b) in clay fraction (Ac),
 c) in clay fraction after 14 days maceration in heavy metal-containing drainage water (Ac*)

Table 3. ICP-MS analysis of drainage water used for 14-day-long maceration of clay fraction.

Element	[$\mu\text{g}\cdot\text{dm}^{-3}$]	Element	[$\mu\text{g}\cdot\text{dm}^{-3}$]	Element	[$\mu\text{g}\cdot\text{dm}^{-3}$]
Fe	486	Cd	0.3	As	14.8
Cu	9864	Bi	2.1	Sb	8.4
Pb	12.4	Co	44.2	Mn	52
Zn	189	Ni	23.1	Cr	8.2

V, Sn, U, and Th concentrations were under detection limits

substance amount (in kg CaCO_3 per 1 ton dump material) necessary for neutralization of the acidity produced by the dump ($\text{NNP} = \text{NP} - \text{TAP}$). Negative values show missing neutralization substances, the positive ones show their presence.

To determine TAP and NP values it is important to know redox potential Eh and pH in both water and KCl solution leachates of the sediments, and also to know the contents of sulfur and carbon. pH value < 5 indicates that the sample contains so-called net acidity, while pH values measured in the presence of carbonates oscillate usually between values pH 8-10. Values of pH above 10 can be considered alkaline [24].

According to our results [10] pH values of technogenic sediments from Podlipa dump field, which were measured in their water and KCl solution leachates, were in the range 4.21-7.93 and 3.47-7.34. Carbon content was low in the sediments: 0.34-4.31% C_{tot} , 0.1-4.18% C_{org} , and 0.08-1.53% C_{inorg} (3 samples were under the detection limit). The sediments contained 0.01-0.42% S_{tot} . In the majority of the samples, the S_s content (0.01-0.27%) was higher than S_{SO_4} (0.01-0.15%), which indicates considerable content of still non-oxidated primary sulfides.

The TAP (0.31-13.12; $\bar{x} = 3.7$) and NP (0-127.1; $\bar{x} = 27.1$) values are different in the individual parts of Podlipa dump field. The average NNP value 23.5 indicates high probability that AMD production will not happen in the future in Podlipa. The NNP values from -20 to 20 kg of CaCO_3 t⁻¹ of dump material can be determined in terms of the potential production of acid substances as uncertainty range. The value NP:TAP 7.4 (or 1.72 after exclusion of the extreme value NP=127.1) points to the low risk of AMD production.

Water Analyses

Quality assessment of surface, ground, and drinking water and Linhartovka mineral water from studied sampling places was done under current legislation [20, 21], which corresponds to the European legislation. Tables 4 and 5 show analyses results of select physical and chemical indicators for studied types of water in 2008-10.

The surface and drainage water from the deposit spoil dump in Lubietova-Svatodusna Valley show irregularly higher As content ($108.2 \mu\text{g}\cdot\text{dm}^{-3}$), and it does not have a negative influence on As contamination in main surface stream – Hutny stream (used for irrigation) as well as

Linhartovka mineral water. Regarding the given reasons, the sorptive properties of the clay fractions from the technogenic sediments from this location have not been studied.

Based on the rate between As(III) and As(V), which was finally 1:5 [27], speciation analysis was done in water samples from Lubietova-Svatodusna valley.

It is possible to state that even one high arsenic concentration requires regular monitoring of the area, which has not been done until now. Arsenic can accumulate in river sediments, it is considerably toxic, it belongs to so-called inhibitors of biochemical oxidations, and its carcinogenic effect has been proven [28].

The surface and drainage water from Podlipa (Table 5) showed higher copper content ($1542\text{-}3816 \mu\text{g}\cdot\text{dm}^{-3}$), which influenced the water quality in Hutny Stream ($24.3 \mu\text{g}\cdot\text{dm}^{-3}$).

Table 4. Comparison of physical and chemical indicator values for mineral water Linhartovka with limits by Government Regulation SR 496/2010 [20].

Indicator	Limit	Unit	Limit of detection	Linhartovka L1
Sb	5	$\mu\text{g}\cdot\text{dm}^{-3}$	0.1	0.4-0.9
As	10	$\mu\text{g}\cdot\text{dm}^{-3}$	0.2	1.4-2.0
Cd	3	$\mu\text{g}\cdot\text{dm}^{-3}$	0.3	UD-1.7
Cu	1.0	$\text{mg}\cdot\text{dm}^{-3}$	0.0005	UD-0.0452
Ni	20	$\mu\text{g}\cdot\text{dm}^{-3}$	1.0	UD-6.9
Pb	10	$\mu\text{g}\cdot\text{dm}^{-3}$	0.3	1.1-6.4
Mn	50	$\mu\text{g}\cdot\text{dm}^{-3}$	0.7	43.0- 81.2
Zn	3.0	$\text{mg}\cdot\text{dm}^{-3}$	0.0001	0.0698-0.1736
Fe	0.2	$\text{mg}\cdot\text{dm}^{-3}$	0.0006	1.4390-1.9700
pH	6.5-8.5		0.05	6.40-6.70
Kappa	125.0	$\text{mS}\cdot\text{m}^{-1}$	0.001	640.0-686.0
COD_{Mn}	3.0	$\text{mg}\cdot\text{dm}^{-3}$	0.17	0.64-1.92
NH_4^+	0.5	$\text{mg}\cdot\text{dm}^{-3}$	0.05	0.32- 2.42
Cl^-	100	$\text{mg}\cdot\text{dm}^{-3}$	0.14	57.00- 224.64
SO_4^{2-}	250	$\text{mg}\cdot\text{dm}^{-3}$	0.17	UD-11.76
NO_3^-	50	$\text{mg}\cdot\text{dm}^{-3}$	0.13	0.60-8.00

UD – undetectable

Table 5. Comparison of surface water indicators in Lubietova region to the limits for surface water by government regulations of SR No. 269/2010 [21].

Indicator	Unit	Limit 1	Limit 2	Limit of detection	Reference sample	Hutný stream	Podlipa	Svatodusna
						L2, L6, L7	L3, L4	L11 – L15
As	$\mu\text{g}\cdot\text{dm}^{-3}$	30	50	0.2	1.2-1.4	1.0-2.1	1.0-3.8	1.7- 108.2
Cd	$\mu\text{g}\cdot\text{dm}^{-3}$	5	5	0.3	UD	UD	UD	< 0.9
Co	$\mu\text{g}\cdot\text{dm}^{-3}$	50	200	1.2	< 3.6	< 3.6	6.3-14.6	< 3.6
Cu	$\mu\text{g}\cdot\text{dm}^{-3}$	20	500	0.5	2.6- 124.1	2.6- 24.3	1542-3816	UD-17.9
Ni	$\mu\text{g}\cdot\text{dm}^{-3}$	20	100	1.0	< 3	< 3	UD-14.40	UD-18.41
Pb	$\mu\text{g}\cdot\text{dm}^{-3}$	20	50	0.3	< 0.9	UD-1.13	< 0.9	UD-2.58
Mn	$\text{mg}\cdot\text{dm}^{-3}$	0.3	3	0.0007	0.005-0.026	0.005-0.055	0.014-0.063	0.005-0.112
Zn	$\text{mg}\cdot\text{dm}^{-3}$	0.1	1	0.0001	0.002-0.017	0.002-0.062	0.006-0.019	0.002-0.027
Fe	$\text{mg}\cdot\text{dm}^{-3}$	2	10	0.0006	0.029-0.190	0.075-1.834	0.014-0.109	0.010-0.281
NO_3^-	$\text{mg}\cdot\text{dm}^{-3}$	22	102	0.13	0.8-7.7	2.5-15.7	2.7-11.0	3.0-15.1
NO_2^-	$\text{mg}\cdot\text{dm}^{-3}$	0.07	undefined	0.17	UD	UD	UD	UD
F^-	$\text{mg}\cdot\text{dm}^{-3}$	1.5	2	0.08	UD	UD	max. 0.85	UD
N-NH_4^+	$\text{mg}\cdot\text{dm}^{-3}$	1	undefined	0.1	UD	UD	UD	UD
BOD_5	$\text{mg}\cdot\text{dm}^{-3}$	7	undefined	0.1	0.9-2.4	0.8-2.4	0.6-1.5	0.5-1.1
COD_{Mn}	$\text{mg}\cdot\text{dm}^{-3}$	15	undefined	0.17	3.2-6.8	2.2-9.6	0.5-2.9	1.0-5.4
COD_{Cr}	$\text{mg}\cdot\text{dm}^{-3}$	35	undefined	0.21	1-18	2-28	1-16.5	1-19
Cl^-	$\text{mg}\cdot\text{dm}^{-3}$	200	300	0.14	0.5-36.6	0.5-34.0	0.3-36.6	0.6-24.5
O_2	$\text{mg}\cdot\text{dm}^{-3}$	>5	undefined	0.1	8.7-11.8	7.5-12.0	8.5-12.1	7.2-12.3
pH		6.5-8.5	5-8.5	0.05	6.55-7.65	7.30-8.40	6.45-7.70	6.90-8.70

Limit 1 – General requirements for surface water quality, Limit 2 – Surface water for irrigation, UD – undetectable

The groundwater from the reference area exceeded Cu limit ($124.1 \mu\text{g}\cdot\text{dm}^{-3}$) as well. The high content of copper in the water confirms the saturation of the clay fractions with this metal element and its release into the water surroundings and consequent formation of the secondary minerals.

In regard to the other studies by Melichova [29] and Mlaka [30], the concentration of heavy metals fluctuates and depends on precipitation in the studied area.

Linhartovka mineral water showed higher values only of those indicators that influenced sensory water properties (conductivity, chlorides, Mn, Fe) connected mostly with geological subsoil. The result is recognition of the concentration of ammonium ions ($2.42 \text{mg}\cdot\text{dm}^{-3}$) and slightly low pH (6.40).

From the heavy metal point of view, the quality of Linhartovka mineral water is appropriate. Higher concentrations of iron and manganese ($\text{Fe } 1.439\text{-}1.970 \text{mg}\cdot\text{dm}^{-3}$ and Mn up to $81.2 \mu\text{g}\cdot\text{dm}^{-3}$) are not harmful to people's health. However, they change color (rusty color) and taste.

According to Lichy et al. [31] guideline values for implementation of measures for the content of natural radionuclides in Linhartovka mineral water are approximately 6-times exceeded in total volume of alpha activity,

according to the Ordinance of Ministry of Health No. 528/2007 Z.z., which sets particulars on the requirement to reduce irradiation from natural radiation [32].

Groundwater that springs directly in the village (LDW1-LDW4) and which is used by inhabitants as a source of drinking water is not regularly inspected because the municipality has a water pipe, and surface water L8 (used for irrigation) did not contain studied metals in concentrations above the limits [26]. Obtained results of heavy metals content in the ground as well as in the surface water are comparable with results published by Lichy et al. [31].

Conclusions

The distribution of heavy metals in rocks and ores of the dump field at Lubietova-Podlipa is irregular and corresponds to the original metal concentration in technogenic sediment as well as to their migration and sorptive properties.

Maximal concentrations of metal elements in dump material were in the range $36,000 \text{mg}\cdot\text{kg}^{-1}$ for Fe to $0.9 \text{mg}\cdot\text{kg}^{-1}$ for Cd. The concentrations of copper ($12,080 \text{mg}\cdot\text{kg}^{-1}$), and arsenic ($397 \text{mg}\cdot\text{kg}^{-1}$) could be considered important.

A large part of metal elements is caught in porous parts, in hydroxides of iron (hydrogoethite), and in clay minerals (mostly V, Cr, Th), which in the case of Fe, Pb, Zn, Bi, As, Sb, Mn, and Cr have considerably free sorption capacity.

X-ray diffractive analyses showed that illite and muscovite predominate in all natural sorbents in the studied area. The occurrence of hydrogoethite is relatively rare.

Oxidation of sulphide minerals in deposit is indicated by the carbonate coating and copper oxides and it is also verified by pH values in leachates from sediments. On the other hand, high concentrations of Stot and Ss give evidence of non-oxidized sulphides occurrence. The average potential of total acidity production TAP = 3.7 corresponds with pure neutralization potential NNP – 23.5 kg of CaCO₃ per 1 ton of dump material.

In spite of a considerable amount of mobilizable metals in dump and certain potential for acidity production, the rate NP:TAP = 7.4 (or 1.72) indicates that it is not imminently dangerous for the surrounding landscape because the production of acid mining drainage water (AMD) is not very presumable in the area of Podlipa.

According to the results of selected heavy metals, as well as other contaminants determination in the water, it is possible to consider the Cu load in drainage water in Lubietova-Podlipa and As load in the drainage and surface water in Svatodusna as the most serious. Regular monitoring of heavy metals content in the surface and ground water in the whole area is necessary because of the dangerous As content in the drinking water.

The quality of other water is influenced to a lesser extent than we expected. According to the results of previous research in the location, the influence of natural geochemical barriers is expected [10]. Cu removal from the drainage water with natural bentonites and zeolites as sorbents was tested. Mentioned natural sorbents showed efficiency of retardation around 88-98%, with a simultaneous adsorption and precipitation process caused by high pH values of the natural water and sorbents. Linhartovka mineral water showed 6-times exceeded total volume alpha activity while the limits for heavy metals content (besides Fe and Mn) were not exceeded.

The natural water that springs directly in the center of the village and is used by inhabitants as drinking water is not harmful to health in terms of heavy metals content.

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