CHARACTERISTICS OF HEAVY METAL DISTRIBUTION AT SPOIL DUMP-FIELDS OF Cu-DEPOSIT ĽUBIETOVÁ (SLOVAKIA)

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Abstract: The mechanism of heavy metal distribution in the Podlipa and Reiner spoil dump-fields of the abandoned Cu-deposit of Ľubietová is influenced by the primary content of ores and individual metals in their substrate, geochemical properties of individual elements, their migration and sorption properties and pH/Eh values. The article presents mapping of Fe, Cu, Pb, Zn, Ni, Co, U, Th, Cd, As, Sb, Ag distribution at the studied dump-fields and study of the reasons and results of their individual migration process. The specific behaviour of individual metals at different localities is selective. These properties are reflected also by correlation relations. While at Podlipa were described correlations only among several few metal couples (Cu/Co, Fe/Ni, Ni/As, Zn/Cd, Zn/Pb, Pb/Cd, U/Th), at Reiner dump-field is the situation substantially different; there were proved several times more metal pairs showing high level of correlation. This result enable suggest that there were different environmental conditions influenced primarily by different rock composition and those also different natural sorbents effecting selective migration mechanism at these two close localities.

Keywords: spoil dump-field, heavy metal distribution, mobility, sorption

1. INTRODUCTION

The area of Ľubietová is situated in the central part of the Western Carpathians. The southern part of the area is there, according to the geomorpho-logical classification of Slovakia in the region of the Slovak Central Mountains, in the Poľana unit (Vysoká Poľana part), the western part in the region of the Slovak Central Mountains in the Zvolen Basin (in the north-western margins of the Bystrica Highlands and the Povrazník Furrow) and the north-eastern part in the region of the Slovak Ore Mountains in the Vepor Hills (Mazúr & Lukniš, 1980).

In the past, the municipality of Ľubietová together with its surroundings was one of the significant copper ore mining regions. Copper mineralisation in the surroundings of the municipality of Ľubietová is developed in three deposits: Podlipa on the eastern edge of the municipality, Svätodušná and Kolba at the end of the Peklo Valley, about 5 km east of the municipality, where cobalt, silver and nickel play, besides copper and iron, an important role. In the area around the municipality of Ľubietová, covering the basin of the Hutný stream and the basin of a stream draining the Peklo Valley east of the municipality, any mining activities have not been performed and only slight prospecting activities have been carried out since the cessation of mining at the end of the 19th century (Ilavský et al., 1994).

While the rock surrounding at Reiner dump-field is formed by arkoses and rauwakes, at Podlipe are these rocks accompanied also by arcose schists (nearby of contact with Permian granitoides). All rocks are intensively influenced by dynamic metamorphism (Bergfest, 1951; Koděra et al., 1990).

Mining and metallurgical activities lasting for centuries formed an extraordinary mining landscape from the landscape around Ľubietová. A lot of remains of former adits, shafts, ore mills and smelting plants, mine roads, water channels and small as well as large spoil dumps put the finishing touches to the variegated, sloping and forested mountain environment. The mining activity changed considerably the original

appearance of part of the municipality and its surroundings (Križáni et al., 2002).

Ore mineralisation is situated in a terrigene crystalline complex of Permian age which consists of greywackes, arcose schists and conglomerates. The probably volcano-sedimentary Cu-(Ag-) mineralisation, genetically connected with the basic, intermediate and acid Permian volcanism, was mobilised by granite intrusion during the Alpine orogeny. The vein mineralisation is characterised by a rather simple paragenesis represented by quartz, siderite, (± calcite and ankerite), chalcopyrite, Ag-bearing tetrahedrite, arsenopyrite, pyrite, barite and rare galena. In the well-developed cementation zone, the main Cu-minerals were cuprite and native copper. The deposit is also famous for the formation of a wide range of rare secondary minerals, such as libethenite, langite, annabergite, aurichalcite, azurite, brochantite, cyanotrichite, erithrine, evansite, euchroite, pharmacosiderite, hemimorphite, chrysocolla, cuprite, limonite, malachite, olivenite, tirolite, pseudomalachite, etc.

There is variation in the mobility of heavy metals carried upwards into surface recipients by groundwater, mine water and leachate from spoil dumps; their substantial contamination is indicated by the abundant occurrence of secondary minerals, considerable part of which are metastable (water soluble), both in subsurface parts of ore bodies and in dumps of waste from the extraction of copper and cobalt-nickel ores. In the points of outflow of dump drainage water to the surface, secondary minerals precipitate (Križáni et al., 2002; Andráš et al., 2009, 2012). Rieuwerts et al., (1998) emphasise the importance of metal mobility to the ability to estimate metal concentrations in soil solution, surface water, drainage water and groundwater. The total concentration of a metal depends on the content of the metal in solution, which again depends on the sorption to natural sorbents (e.g. clay minerals, hydrogoethite, zeolites, etc.) and the release of this metal into soil solution (Sterckeman et al., 2000). Some colloidal components in the soil solution can have, depending on a pH, positive or negative charges, which affects markedly the kinetics of sorption processes in soils, ion-exchange reactions, and thus metal mobility as well (Čurlík et al., 2003).

2. MATERIALS AND METHODS

The sampling of technogenic sediments and soils from the spoil dump material was done in October 2010; samples were taken from individual spoil dumps in 10 x 10 m square grids so that each
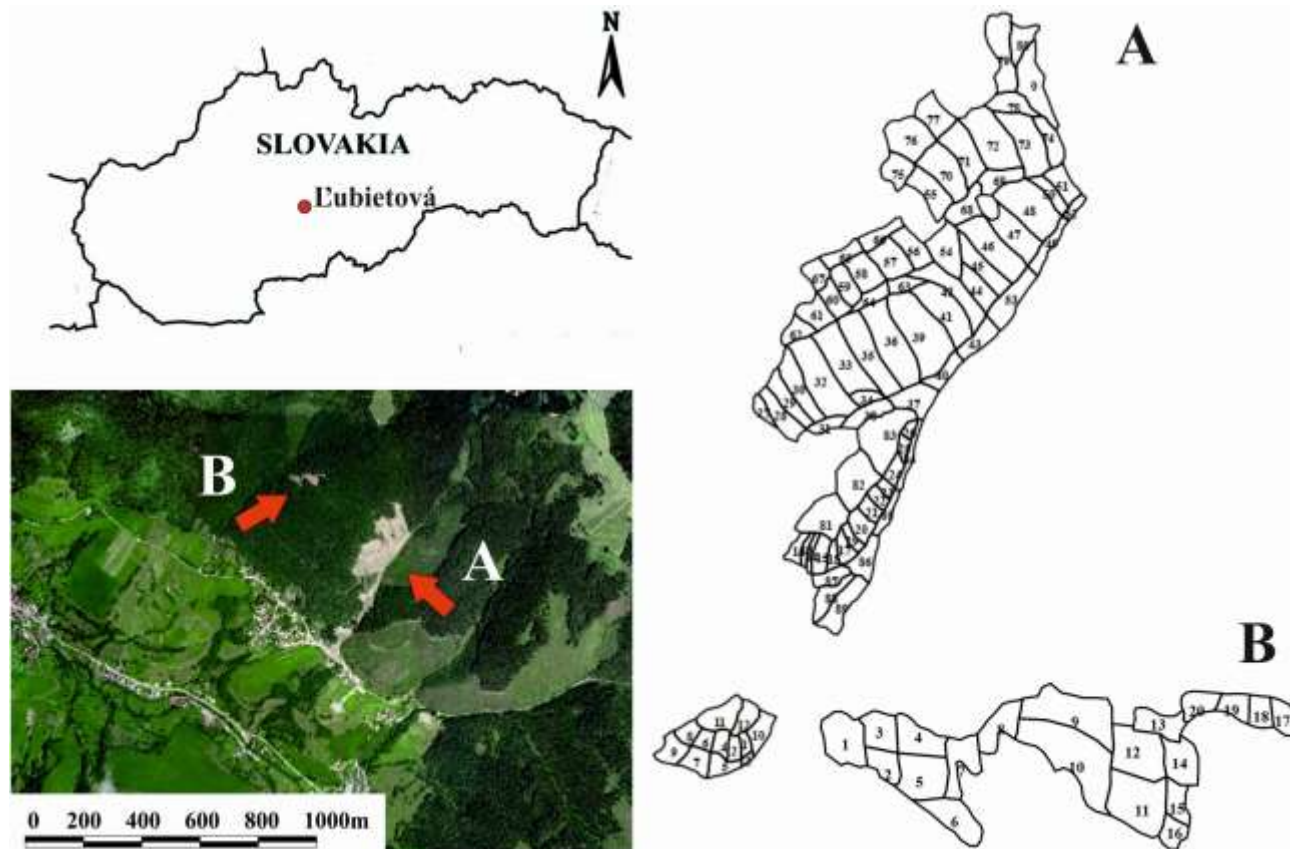

Figure 1. Localisation of technogenous sediment and soil samples at dump-fields A – Podlipa, B - Reiner

sample (of a mass of about 1000 g) might represent a section to the depth of 30 cm in the sampling point Only that part of sediments were taken the grain size of which did not exceed 1.5 cm, because this fine-grained part of sediments represented the most reactive part of them (large fragments of rocks and boulders have small reactive surfaces and, from the point of view of release of heavy metals into the landscape components, do not represent any significant risk). Altogether, 683 incremental samples and 259 incremental samples were taken from Podlipa and Reiner, respectively. The incremental samples were combined to represent one of segments of the spoil dump-field (in the locality of Podlipa 1 - 90 and that of Reiner 1 – 20; Fig. 1). Subsequently, these combined samples were reduced by quartering and homogenized.

The sample material of the technogenic sediments and soils (20 samples from the locality of Reiner and 89 samples from the locality of Podlipa) was dried and sent to be analytically processed to the ACME Analytical Laboratories in Vancouver, Canada. The samples, each having a mass of 0.2 g, were melted by the addition of a lithium metaborate-tetraborate mixture and subsequently dissolved in diluted nitric acid. As and Sb (limit of determination of 0.5 mg.kg^{-1}) and also a whole series of other elements were determined by ICP/MS analysis.

3. RESULTS

The contents of Cu and Ni in the technogenic sediments and soils in the Podlipa spoil dump-field move usually in a range of 425 - >10 000 mg.kg^{-1} for Cu and 10 – 58 mg.kg^{-1} for Ni. The highest contents of both the metals in the spoil dump material were found in the mouths of all three Johan adits (Horná Johan, Stredná Johan, Najnižšia Johan; Fig. 2). Cu and Ni then migrated in the direction of gravitation down the slope of the spoil dump-field and formed Cu- and Ni-contaminated belts as far as the thalweg of the Green Valley. The lowest Cu contents were confirmed in the surroundings of the mouths of Jakob and Maria Empfängnis adits, the lowest Ni concentrations in the surroundings of Andreas adit (Cu concentrations are low here as well; Fig. 2). In contrast to this apparent agreement in the contents and migration pathways between Cu and Ni under supergene conditions, the real, numerically expressed degree of mutual correlation between the mentioned elements is considerably low (correlation coefficient r = 0.176). It is Ni exclusively with As that exhibits the higher degree of correlation (r = 0.724).

In the Reiner spoil dump-field the contents of Cu in the spoil dump material range from 1891 to 8663 mg.kg^{-1} and those of Ni from 25 to 53 mg.kg^{-1}; the highest values were found in the surroundings of Spodná Ladislav and Horná Ladislav adits (Fig. 1, 2). In contrast to the locality of Podlipa, where any correlation between Cu and other heavy metals was not found, in the locality of Reiner the Cu-Ni correlation coefficient is relatively high (r = 0.613). An even higher correlation degree was proved for correlations between Cu and Co (0.870) and Cu and Cd (r = 0.812). In the locality of Reiner, it is the distribution of As (r = 0.8155) and less that of Sb (r = 0.660) that follow the distribution of Cu. In contrast to Podlipa, where Ni correlates only with As, in the Reiner spoil dump-field it exhibits correlations with Ag (r = 0.900), As (r = 0.828) and Sb (r = 0.784) too.

As far as Fe is concerned, the range of values at Podlipa is from 1.14% to 3.48%, and as with copper, the highest intensity of contamination was found in the area of the mouths of the above-mentioned three Johan adits (Fig. 2). The contents of it correlates merely with the contents of Ni (r = 0.635).

In the Reiner area, the highest Fe contents were found on platforms in the uppermost part of the spoil dump-field (1.34% - 3.01%; Fig. 2). The highest correlations are shown between Fe and Sb (r = 0.699), Co (r = 0.692) and Cd (r = 0.688), somewhat lower ones between Fe and As (r = 0.622) and Ni (r = 0.550).

The lead contamination of the sediments and soils at Podlipa was the highest (276 mg.kg^{-1}) on a platform covered by vegetation in the surroundings of Jakob adit. The highest degree of correlation was expected between the contents of Pb and Th; however, a rather significant correlation was only found between Pb and Cd (r = 0.884).

The highest content of Pb in the Reiner locality was recorded in the upper part of the slope of spoil dump-field in the area of the mouth of Horná Ladislav adit (the content varied in range 9 – 39 mg.kg^{-1}). In this spoil dump-field, the Pb-Th correlation is even negative (r = -0.193).

Co and Ni are typical of the Kolba mine field. At Podlipa, the contents of Co are relatively low (6.5 – 124.2 mg.kg^{-1}). A certain low degree of correlation of spatial distribution is exhibited by Co merely in relation with Cu (r = 0.437). Moreover, the Co-Ni correlation is very low (r = 0.437) as well.

The concentrations of Co (46 – 124.2 mg.kg^{-1}) are negligibly higher on an average in the Reiner spoil dump-field (28.24 – 62.53 mg.kg^{-1}). In contrast to the Podlipa spoil dump-field, Co shows high correlations with Cu (r = 0.812), As (r = 0.771) and Fe (r = 0.692). The Co-Ni correlation is unexpectedly comparatively low (r = 0.595).

The contents of Zn are low in both the studied localities: at Podlipa, they range from 9 to 30 mg.kg^{-1} and at Reiner from 18 to 35 mg.kg^{-1}; they exhibit the relatively high closeness of correlation with geochemically related Cd (r = 0.874 and 0.564, respectively). At Podlipa, a correlation between Zn and Pb (r = 0.884) also exists. The contents of Cd are even lower (trace) than the contents of Zn. In both the spoil dump-fields, they vary in a narrow range of values, namely <0.1 – 0.2 mg.kg^{-1}. The highest contents of Zn and Cd were found on the spoil dump platform between the Mária and Jakob adits at Podlipa (Fig. 2, 3). Cd at Podlipa is in correlation with Pb (r = 0.884) and at Reiner with Cu and Sb (r = 0.870 and 0.652, respectively).

In the Permian rocks, in which the Cu-mineralisation is situated, the increased contents of U and Th are typical. The contents of U are lower (1.2 – 3.6 mg.kg^{-1}; the highest values were measured in the mouth of Horná Johan adit) than the contents of Th (5 – 17.5 mg.kg^{-1}; the highest values were determined in the mouth of Francisci adit and on the adjacent slope; Fig. 3). The increased contents were also found below the Najnižšia Johan adit, in the mouth of a caved-in nameless adit (Fig. 3). An inevitable, but comparatively low correlation between Th and U is expressed by the correlation coefficient r = 0.586.

In the locality of Reiner, the highest contents of Th (19.9 mg.kg^{-1}) and U (3 mg.kg^{-1}) were found in the mouth of Reiner adit (Fig. 3). The Th-U correlation is somewhat higher than that at Podlipa (r = 0.734).

To the highest-risk heavy metals from the point of view of toxicity, As and Sb belong. At Podlipa, the contents of them move in ranges of 19 – 504 mg.kg^{-1} (As) and 9 – 132 mg.kg^{-1} (Sb); the highest values were found, as with Cu and Fe, in the surroundings of Spodná Ladislav adit and on the adjacent slopes.
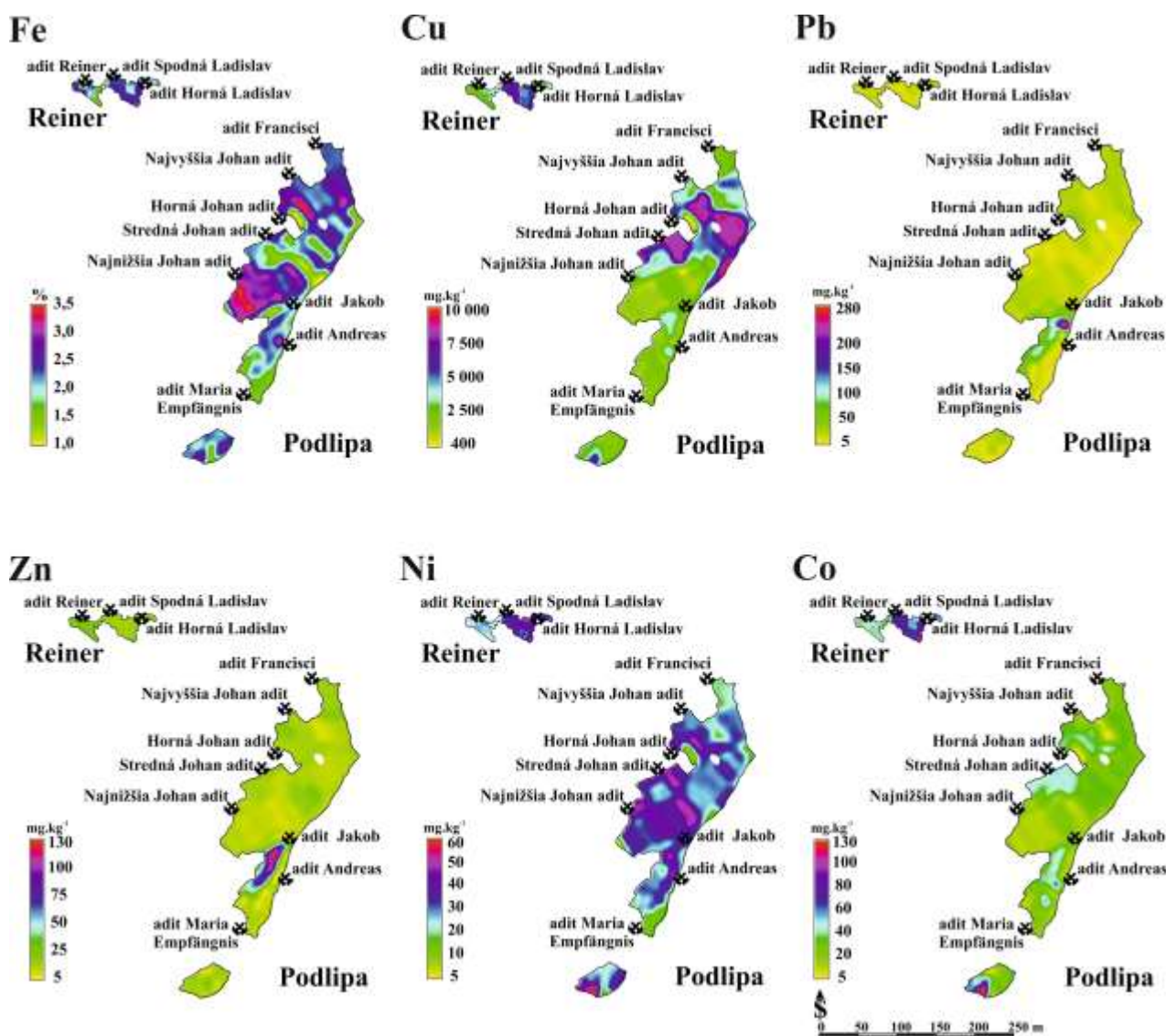

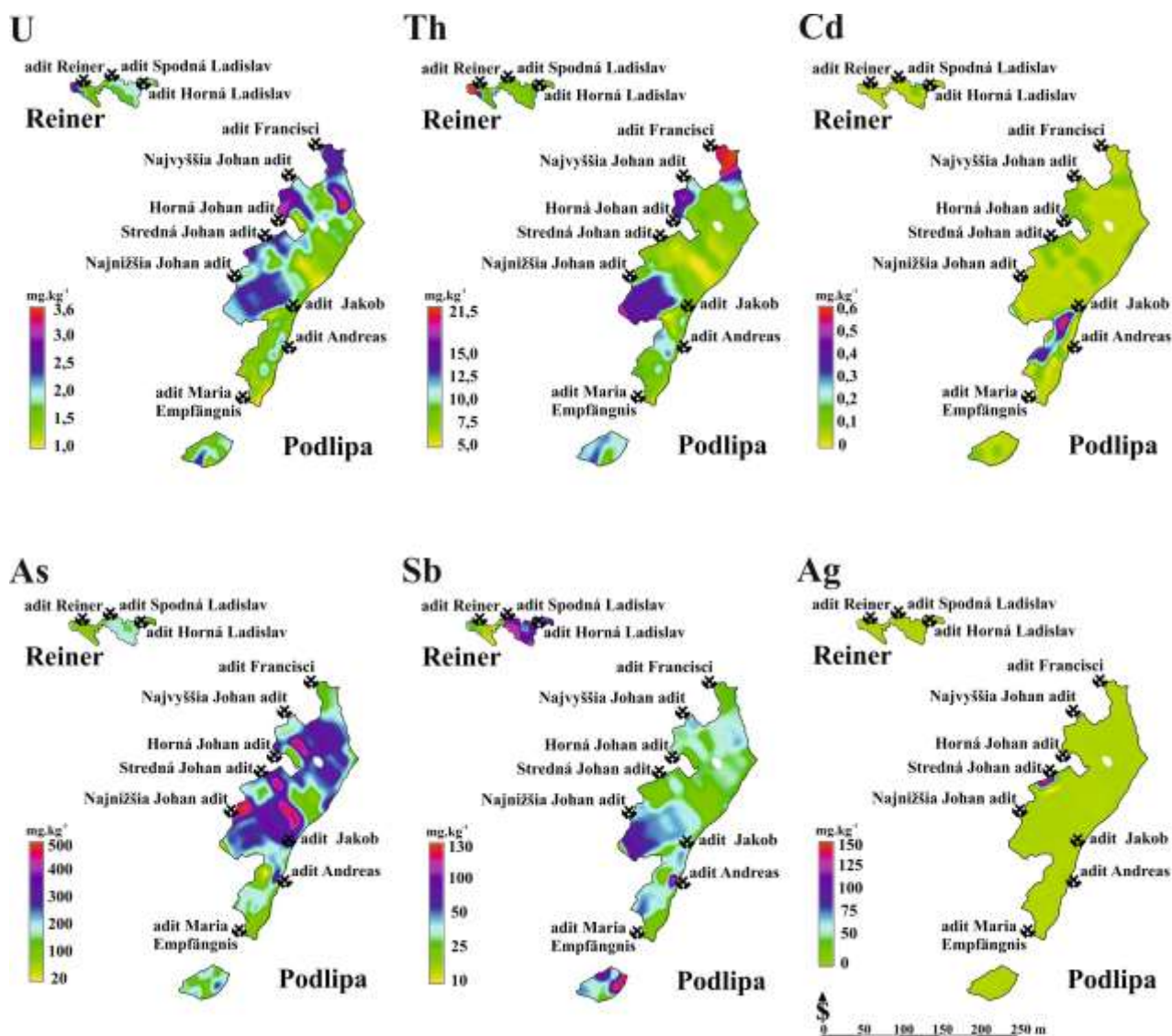Figure 2. Fe, Cu, Pb, Zn, Ni and Co distribution at dump-fields Reiner and Podlipa

Figure 3. U, Th, Cd, As, Sb and Ag distribution at dump-fields Reiner and Podlipa

The highest contents of Sb were confirmed by analytical results along the northern edge of the spoil dump of Maria Empfängnis adit and somewhat lower in the mouth of Najnižšia Johan adit. In the surroundings of the Andreas and Mária Empfängnis adits, the contents of Sb were extraordinarily low. Similarly low are also Sb contents in the area of the mouth of Jakob adit (Fig. 3). The As-Sb spatial distribution correlation (r = 0.304) was not found.

The contents of As and Sb in the Reiner spoil dump-field range from 22 to 192 mg.kg^{-1} and from 6.8 to 36.4 mg.kg^{-1}, respectively. The distribution correlation between As and Sb is high (r = 0.949), and the Sb-Cd correlation (r = 0.652) is comparatively significant as well.

The concentrations of Ag in the technogenic sediments and soil (Fig. 3) are not high in the studied localities: 1 – 6.2 mg.kg^{-1} at Podlipa and 0.8 – 1.6 mg.kg^{-1} at Reiner. In the Reiner spoil dump-

field, silver correlates with Ni (r = 0.900), less with As (r = 0.664). In the Podlipa spoil dump-field any correlation between the content of Ag and that of other elements was not confirmed.

4. DISCUSSION

The highest concentrations of Cu at Podlipa as well as at Reiner in the mouths of Johan and Spodná Ladislav adits (Fig. 2) are natural. From the technogenic sediments and soil, Cu was subsequently leached from primary sulphides (mainly chalcopyrite and tetrahedrite). Soluble cadmium occurs in water as a simple hydrated ion Cd^{2+}, in the form of inorganic complexes $[CdOH]^+$, $[Cd(OH)_2(aq)]^0$, $[Cd(OH)_3]^-$, $[CdCO_3(aq)]^0$, $[Cd(CO_3)_2]^{2-}$, $[CdSO_4]^0$ and in the form of organic complexes with various organic ligands (Smirnov, 1956; Pitter, 1990). It is Cu in surface water with a

pH moving in a range from 6.5 to 8.5 (Polański & Smulikowski, 1978) and Ni at a pH from 6.5 to 7.5 (Zaujec, 1999) that exhibit the highest solubility. The mentioned pH ranges are typical of technogenic sediments and soil in the localities of Podlipa and Reiner (Andráš et al., 2008). Such comparatively good migration abilities of Cu and Ni caused that at Podlipa they migrated together in the direction of gravitation down the slope of the spoil dump-field and formed belts of sediments and soil enriched in Cu and Ni as far as the thalweg of the Green Valley. Nevertheless, the reason why the contents of Cu in the locality of Podlipa correlate with the contents of Ni and in the locality of Reiner with the contents of As and Sb, is not clear.

Copper released into solution has the exceptional ability to form secondary supergene minerals (Polański & Smulikowski, 1978), especially hydroxide carbonates, namely pseudomalachite, malachite $Cu_2CO_3(OH)_2$ and azurite $Cu_3(CO_3)_2(OH)_2$. Of other secondary minerals formed in the deposit, at least brochantite $Cu_4(OH)_6[SO_4]$, olivenite $Cu_2(OH)[AsO_4]$, libethenite $Cu_2(OH)[PO_4]$ and chrysocolla $CuSiO_3.nH_2O$ should be mentioned.

As for Fe, a range of values at Podlipa moves from 1.14% to 3.48%, and similarly to Cu, the highest intensity of contamination was found in the area of the mouths of the above-mentioned three Johan adits (Fig. 2). The contents of Fe correlate merely with the contents of Ni (r = 0.635).

In the area of Reiner, the highest contents of Fe were found on platforms in the uppermost part of the spoil dump-field (1.34% - 3.01%; Fig. 2). The highest correlations are exhibited between Fe and Sb (r = 0.699), Co (r = 0.692) and Cd (r = 0.688); somewhat lower correlations between Fe and As (r = 0.622) and Ni (r = 0.550).

The chemical mobility of Fe in the processes of weathering depends especially on the rate of Fe oxidation and on the possibility to be reduced again from ferric compounds to ferrous compounds, i.e. from Fe^{2+} ions to Fe^{3+} ions and vice versa, and on the hydrolysis of ferric salts. In the process of weathering, Fe is converted to hydroxides (goethite FeO.OH, limonite $2Fe_2O_3.3H_2O$), as the most stable Fe compounds on the earth's surface (Polański & Smulikowski, 1978). As found by Dirner et al., (2012), in the Podlipa and Reiner spoil dump-fields, Fe^{3+} predominates markedly over Fe^{2+}. By contrast, the field measurements of physico-chemical parameters (pH and Eh), Eh calculation and application of the activity diagram of the components in the $Fe^{+3}-SO_4^{-2}-H_2O$ system (according to Sato, 1960a and 1960b) indicated that the main form of occurrence of Fe in sediments and soils of the Podlipa and Reiner spoil dump-fields could be the sulphate form - $FeSO_4$ (Dirner et al., 2012); this is in contrast to data saying that in the material of the spoil dump-fields a considerable occurrence of sulphidic sulphur was confirmed (Andráš et al., 2009). This discrepancy can be explained by the fact that, Fe in the sulphidic form occurs only in unweathered rock fragments that in the course of pH and Eh measurements did not enter into the reaction during analytical procedures with regard to the time factor (60 minutes). The possibility of occurrence of Fe also in the sulphidic form is indicated by calculated values of R^2, which are in contrast to the values obtained based on the field measurements of pH and Eh on the boundary between the stability fields for $FeSO_4$ and FeS_2 (Dirner et al., 2012).

$FeSO_4$ is in neutral and slightly acid solutions, which are typical of the studied Podlipa and Reiner spoil dump-fields, unstable and subjected to hydrolysis to produce the sulphuric acid and alkaline sulphates that at the end are converted to ferric hydroxide – goethite or hydrogoethite, i.e. limonite. Although in such conditions (6.5 – 7.5 pH), Ni is more mobile than Fe (Zaujec, 1999), the high sorption ability of limonite $2Fe_2O_3.3H_2O$ and the ability of Ni^{2+} to precipitate in the form of colloidal hydrosilicates immediately on the weathered substrate explain the possibility of Fe-Ni correlation.

The highest concentrations of Pb were found on the platforms of the spoil dump-fields. Lead is characterised by marked chalcophile properties and in soils is usually in the form of Pb^{2+} (less Pb^{4+}). The majority of its secondary minerals (sulphates and carbonates) are poorly soluble in water (Polański & Smulikowski, 1978; Alloway, 1995), and thus Pb migrated down the slopes only in a very limited degree. Near-neutral pH values in the studied localities (Andráš et al., 2009) decrease the kinetics of pyrite oxidation and for this reason, the potential of spoil dump material to produce acidity (sulphuric acid), which could enable the more intensive migration of Pb, is considerably limited. With reference to the geochemical characteristics of Pb and Th, the mutual causality between these elements could be expected, when the isotope Pb^{208} that is the most abundant isotope in nature is produced by radioactive decay of Th^{232} (Rollinson, 1993). The mutual correlation between these two elements is however extraordinarily low in both the studied localities: at Podlipa, the value of correlation coefficient r = 0.084 and at Reiner, the value of correlation coefficient is even negative, r = -0.193. The correlation between Pb and U was not found either.

Co- and Ni-mineralisation is typical of the near deposit of Kolba, where in addition to Cu ores, Ni-Co mineralisation occurs as well. At Podlipa and Reiner, the contents of Co are comparatively low and correlate rather significantly merely with Cu (Podlipa: r = 0.437; Reiner: r = 0.812), in the locality of Reiner also with As (r = 0.771) and Fe (r = 0.692). Cobalt is immobile in an alkaline environment; in acidic conditions, oxides, hydroxides and carbonates of Co dissolve easily (Čurlík & Šefčík, 1999; Anithamary et al., 2012). The Co-As correlation and Co-Fe correlation are given by related chemical properties of Co and Fe.

The correlation between two metals, Co-Ni, which occur usually together in primary ores, is comparatively low in the zone of hypergenesis (Podlipa: r = 0.437; Reiner: r = 0.595), because in the course of weathering, their geochemical separation takes place. Ni^{2+} is converted to colloidal hydro-silicates and precipitates immediately on the weathered rocks and ores. Cobalt, which accompanies only to a small Ni extent in this process during its accumulation in secondary hydro-silicates, is oxidised more rapidly to Co^{3+}; it is extracted and immobilised in the form of a gel mixture of cobalt oxides and manganese hydroxides farther from the source area (Polański & Smulikowski, 1978; Reimann & Caritat, 1998). As can be seen in figure 2, Co is, in comparison with Ni, more intensively washed out from the spoil dump-fields.

Zn and Cd accumulate mainly on the platform of the spoil dump between the Jakob and the Maria Empfängnis adit near the mouth of the nameless adit in a shallow ground depression in a forest road (Fig. 2, 3). There, in spite of increased acidity (according to Dirner et al., 2012, the platforms of spoil dumps are characterised by increased acidity in relation to the slopes), any marked migration (washing out) of Zn and Cd does not take place probably owing to the isolation of the locality due to underlying clay.

In the process of weathering sulphide ores, Zn and Cd go easily to solution. Of soluble forms of Zn, above all Zn^{2+}, $[Zn(OH)_2(aq)]^0$, $[Zn(OH)_3]^-$, $[Zn(OH)_4]^{2-}$, $[Zn(CO_3)_2]^{2-}$, $[ZnHCO_3]^+$ should be mentioned. In water containing high concentrations of sulphates, an ion associate $[ZnSO_4(aq)]^0$ (Pitter, 1990) may occur as well. It often occurs in association with Fe and Al hydroxides and clay minerals (Kabata-Pendias & Pendias, 2000). In the presence of organic matter, soluble complexes and chelates of Zn are formed and increase its mobility. The complexes $ZnSO_4^0$ and $ZnHPO_4^0$ can significantly contribute to the total content of Zn in solution (Alloway, 1995). In the course of weathering, a cation Cd^{2+} forms complex ions (e.g.

$[CdCl]^+$, $[CdOH]^+$) and organic chelates. In the Podlipa and Reiner spoil dump-fields, conditions for Zn and Cd mobilization have not always been, despite the absence of carbonates which may initiate Cd precipitation (Kabata-Pendias & Pendias, 2000), ideal (pH from 3.47 to 6.48; Andráš et al., 2009; Dirner et al., 2012), because Zn and Cd are the most mobile in acid soils having a pH of 4.5 - 5.5 (Polanski & Smulikowski, 1978; Kabata-Pendias & Pendias, 2000). Surely just these conditions have enabled a correlation between Cd and Pb (r = 0.884) at Podlipa and a correlation between Cu and Sb (r = 0.870 and 0.652) at Reiner.

In supergene conditions, Cd can separate from Zn during migration, because the Cd-sulphide is oxidised more slowly than the Zn-sulphate (that is why Cd is sometimes released from sphalerite in the form of yellow strikes and coatings of greenockite - CdS). In the studied localities, any separation between Zn and Cd did not occur. Zn and Cd were probably as a result of high mobility released from the sediments (and soil) and accumulated in the ground depression on the spoil dump platform between the Mária Empfängnis and the Jakob adit (Fig. 2, 3), from where they could not be washed away any more; thus they still exhibit a considerable degree of mutual correlation between Cd and Zn (Podlipa: r = 0.874; Reiner: r =0.564). Simultaneously, it is necessary to take into account the fact that the exceptionally low contents of Cd make the calculation of correlation coefficient considerably problematic.

Of the rocks of Permian age, in which the Cu-mineralisation in the deposit of Ľubietová is situated, the increased contents of U and Th are typical. The highest concentrations of U and Th were confirmed in the sediments near the mouths of the adits. With reference to the geochemical relationship between U and Th, their mutual correlation is relatively low (Podlipa: r = 0.586; Reiner: r = 0.734). This is caused by different mobilities of U and Th under the supergene conditions. Although in the course of weathering, U^{4+} is relatively immobile, in water characterised by a high oxidation-reduction potential it is however oxidised to U^{6+} and goes to solution (Tölgyessy et al., 2001). Thorium remains in the form of Th^{4+} and is only slightly mobile. Just as a consequence of the higher mobility of U, this obtains considerable predominance in solutions over Th (Polański & Smulikowski, 1978) and is able to migrate over large distance.

The concentrations of As are higher in the Podlipa spoil dump-field and the concentrations of Sb in the Reiner spoil dump-field. This difference indicates different quantitative representations of

minerals of the tetrahedrite–tennantite series in the specific localities and the different spatial distributions of As and Sb following from this.

In the course of weathering, arsenic ore minerals are easily oxidised; As is converted from As^{3+} to As^{5+}, forming compounds of arsenic acid (Lin & Puls, 2000). This is soluble in water, but only seldom can migrate over large distance because it reacts quickly with cations of heavy metals, and As is bound in the form of various arsenates (Gibon, 2003; Selhub et al., 2007). Arsenic forms individual cations neither in sediments, nor in soils, but it is in the form of $[H_2AsO_4]^-$ and partially in the more mobile form of $[H_3A_3O_3]^0$, which is confirmed by results presented by Franková et al., (2012) too. The form of $[H_3AsO_3]^0$ is predominant at low pH and Eh values (O′Neill, 1990).

In water, arsenic is most frequently in the form of $[HAsO_4]^{2-}$, less frequently as $[H_2AsO_4]^-$ and $[HAsO_2]^0$ (Greenwood & Earnshaw, 1990) or complex ions (Fergusson, 1990). In reducing conditions the mobility of As is given by the bond of arsenates and arsenites to the surface of minerals, mainly to Fe-oxyhydroxides, however in sulphide water and in sulphide containing systems, a large part of dissolved As is in the form of As-S compounds that later play a significant role in dissolving As-sulphide minerals in an alkaline environment (Wallschläger & Stadey 2004).

In water, antimony occurs as Sb^{5+} and less as Sb^{3+} or is in the form of complexes with organic acids. Its mobility is controlled by the formation of chelate complexes (Kabata-Pendias & Pendias, 2000). Antimony can be sorbed by clay minerals, active forms of oxides and hydroxides of Fe and Al and by the organic matter. At Reiner, the As-Sb distribution correlation is high (r = 0.949) and As-Fe (r = 0.622) and Sb-Cd (r = 0.652) correlations are also comparatively significant. At Podlipa, merely the As-Fe correlation (r = 0.560) was confirmed.

Antimony and arsenic are important elements determining the composition of minerals of the tetrahedrite-tennantite series; even small differences in a ratio Sb/(Sb+As) affect their characters. It is generally well known that the content of Sb exhibits in them by a negative correlation to As (Johnson et al., 1986; Kharbish et al., 2007).

The concentrations of As and Sb in the studied spoil dump-fields show both positive and no mutual correlations, which may be a result of occurrence of different As- and Sb-minerals (e.g. tetrahedrite, tennantite and many secondary minerals). On the other hand, graphs showing a ratio between As and Sb vs Fe (Fig. 2, 3) reflect a positive mutual correlation of these elements, which

indicates that the concentration of As and Sb does not depend only on the type of present As-Sb minerals, but probably also on the composition of Fe-minerals, occurring in the sediments in the studied spoil dump-fields.

Under hypergene conditions, Ag is oxidised and converted to a soluble sulphate, which similarly to Ni and Cu, reacts with primary sulphides. In the presence of $FeSO_4$ it is precipitated in the form of pure Ag (Polański & Smulikowski, 1978). In the Reiner spoil dump-field, Ag correlates with Ni (r = 0.900), less also with As (r = 0.664). In the Podlipa spoil dump-field, any correlation between the content of Ag and the contents of other elements was not confirmed.

We assume, that the reasons of separate geochemical behaviour of the same elements at the two studied localities is the different rock-surrounding at the mentioned dump-fields Reiner and Podlipa. In more or less homogenous rock-surrounding at Reiner locality consists nearly exclusively of greywakes the released metals migrate alias as within more variable rock-surrounding of Podlipa. Conditions at Podlipa are more complex because of presence of two base rock types. The dump-field is built not only by grauwakes but also by arcose schists, which form different quantity of clay minerals (and hydrogoethite), which are according to Andráš et al., (2009) the most important natural sorbents. The mentioned natural sorbents and their proportion selectively influence the migration ability of metals. Thus, for example, the most intense sorption of As to clay minerals takes place at a pH of 4; to them, less toxic As^{5+} is sorbed much more easily than more toxic As^{3+} (Lin & Puls, 2000). At a pH of 3 – 12, Sb^{3+} is sorbed best, whereas the maximum sorption of Sb^{5+} takes place at a pH < 7 (Leus et al., 2006). The percentage of sorbed Cd^{2+} increases markedly at a pH of 6.5 – 9; to illite it is sorbed more intensely than to kaolinite (Reid & McDuffie, 2005). A comparatively wide range of pH values at Podlipa and Reiner, namely 4.2 – 7.93 (Andráš et al., 2009), enables different sorption intensities in individual polygons of the studied spoil dump-fields. The distribution of elements can be controlled also by formation of various, often metastable, secondary phases of carbonates, oxides or phosphates, which depend on pH and Eh, eventually on ionic radius of elements.

5. CONCLUSIONS

The distribution of individual metals in the studied spoil dump-fields is uneven. It depends on the mineralogical composition of ores, on the

original concentration of the mentioned metals in the technogenic sediments of the spoil dumps, and also on their migration abilities and sorption properties.

The different migration properties of individual metals and the resulting specific mutual correlation relationships in the localities of Podlipa and Reiner can also be explained by their different rock surrounding and consequently by different intensities of sorption on natural sorbents (clay minerals, limonite, etc.), which are formed by weathering of primary rocks. Distribution and bilateral correlation of metals may be influenced by incorporation of elements to various metastable phases and secondary minerals. This process is controlled both by oxidation state and by ionic radius of elements.

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