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Heavy Metal Contamination of the Landscape at the Ľubietová Deposit (Slovakia)

Peter Andráš, Adam Lichý, Jana Rusková, and Lenka Matúšková

***Abstract*—**The heavy metal contamination of the technogenous sediments and soils at the investigated dump-field show irregular planar distribution. Also the heavy metal content in the surface water, drainage water and in the groundwater was studied both in the dry as well as during the rainy periods. The cementation process causes substitution of iron by copper. Natural installation and development of plant species was observed at the old mine waste dumps, specific to the local chemical conditions such as low content of essential nutrients and high content of heavy metals. The individual parts of the plant tissues (roots, branches/stems, leaves/needles, flowers/ fruits) are contaminated by heavy metals and tissues are damaged differently, respectively.

***Keywords*—**Contamination, dump-field, heavy metals, plants, sediment, water.

I. Introduction

THE Ľubietová deposit was in the 15th and 16th centuries one of the most important and most extensively exploited Cu-mines of Europe. Although mining activities were stoped during the 19th century and only a few geological survey activities with negligible effect have been carried out here since [1], the area remains substantially affected.

The main dump-field Podlipa represents about 2 km^2 area. The deposit is situated in the Ľubietová crystalline complex of Permian age which consists of greywackes, arcose schists and conglomerates. The copper content in manually graded ore was about 4 – 10 wt. %. Copper content in dump waste material was 0.9 – 2.4 wt. % [1].

The heavy metals from the ore contaminated the technogenous sediments of the dumps, the soil and the surface water, drainage water as well as the groundwater [2]. The heavy metals can reach plants from the soils due to their higher content in the base rocks or from the sources of different anthropogenic activities. Heavy metals from the air pollutants can reach plants through pores/water or soil solution. Their penetration influences soil-ecological conditions such as soil types, soil pH, concentrations and bonds of heavy metals, humus content in soil, oxidative-reductive conditions around root system connecting with microbial decomposition of inorganic and organic substances, soil moisture, temperature, utilized fertilizes and preparations for the plant protection [2].

Natural installation of mine waste dumps by plants is inhibited due to fine-grained soil flushing from the slopes and fast draining of rain water from the surface into the basal level of dumps or into the impermeable sub-soil by soil-forming substratum. Therefore only several large mine waste dumps provide the possibility to enroot to resistant plants in depressions or at local plains after centuries [2].

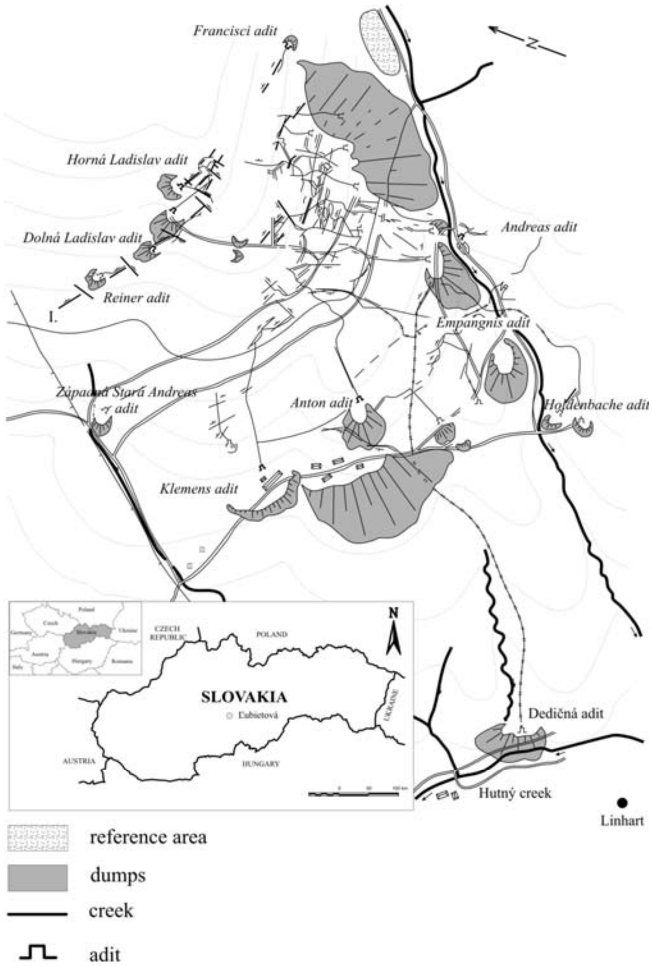

Fig. 1 The dump-field Podlipa in Ľubietová

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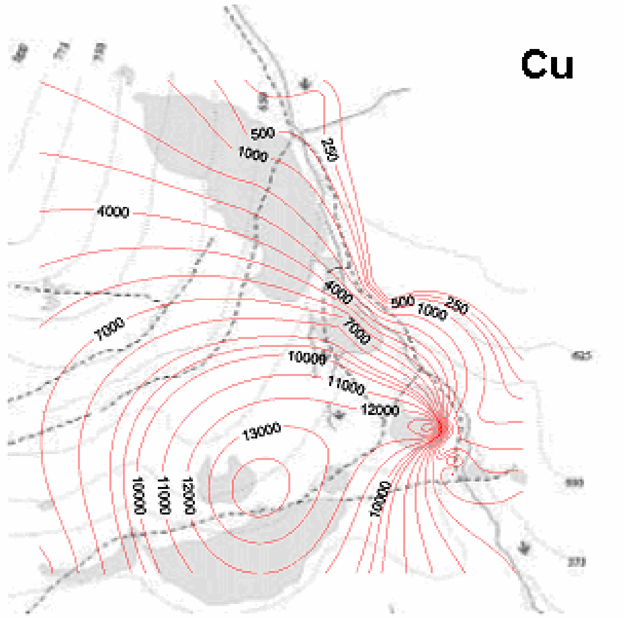
Open Science Index, Geological and Environmental Engineering Vol:2, No:8, 2008 publications.waset.org/9190.pdf

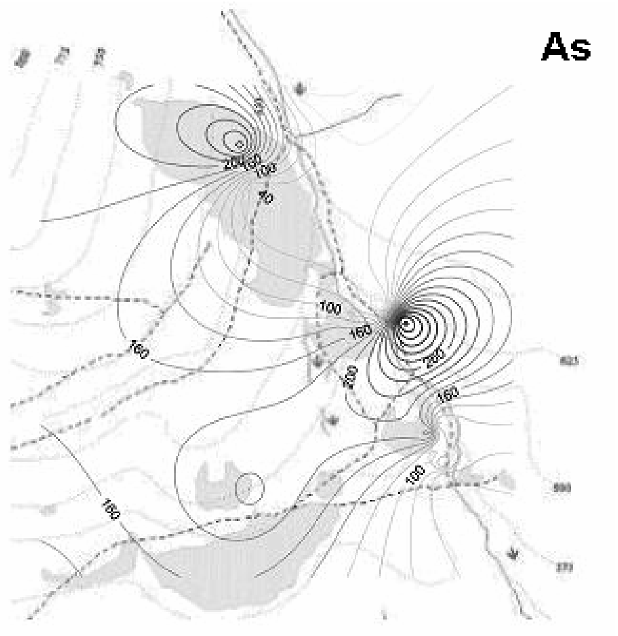
II. Experimental

The samples (of about 10 kg weight) of sediments from the dumps and soils from the 15 – 20 cm depth (the sampling step was 25 m^2), surface water (stream water, drainage water, and groundwater) were collected for the characterization of components of landscape contamination. To the each water samples of 1 000 ml volume was added 10 ml of HCl.

The reference site was selected for comparison of territories loaded by heavy metals and non-contaminated natural environment (Fig. 1). It was situated outside of geochemical anomalies of heavy metals and represent graywakes of Permian age) similar to material at the dump-field. The samples of plant material were collected from the contaminated dumps.

Vegetation creates small isles and is enrooted in few depressions which have enabled limited soil-forming process. The selection of plant species was performed so that it could be possible to compare all identical plant species from the contaminated planes with plants from the reference sites. The samples of hardwood species (*Betula pendula, Quercus petraea, Salix fragilis*), coniferous species (*Pinus sylvestris, Abies alba, Picea abies*) and herbs (*Juncus articulatus, Mentha longifolia*) were studied. At everyone site were sampled 10 individuals of each plant species to get average sample Five coniferous individuals of approximately same age were sampled for branches (in case of *Picea abies* also needles) from the fourth or fifth spike with approximate length of segment from 10 to 15 cm. In the case of *Pinus sylvestris* were analysed two years old needles. Roots of the same length and with 2 - 3 cm diameter were obtained from the surface soil level. Similar mode of sampling was used at hardwood species: 3 – 4 years old branches were sampled from the lower limbs. The samples were dried at laboratory temperature and then homogenized.





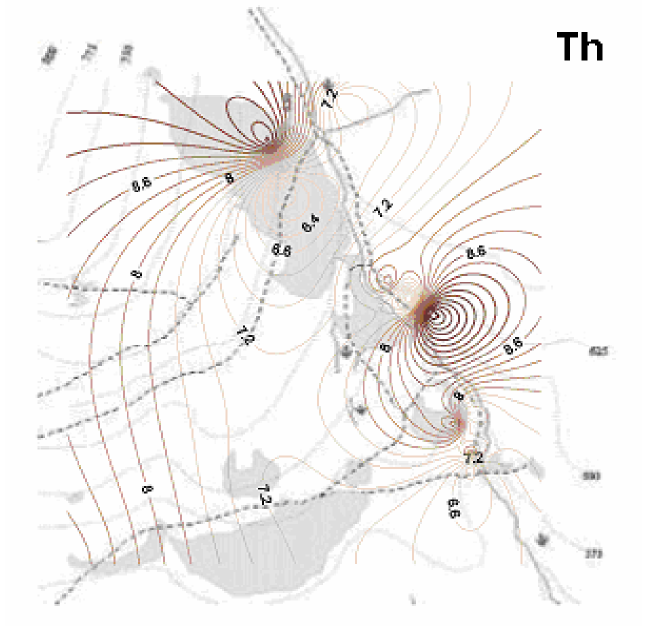


Fig. 2 Distribution of the Cu, As and Th contamination of the dump-field sediments at the Ľubietová deposit. The number indexes on the isolines represent the concentration in ppm

The samples of technogenous sediments from the dumps and soils were dried and 0.25 g of sample was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness. The residue was dissolved in HCl. Solutions were analysed by ICP-MS analyse in the ACME Analytical Laboratories (Vancouver, Canada). Plant samples were divided into roots, branchess/stems, leaves/needles and flowers/fruits. 0.5 g of vegetation sample was after split digestion in HNO_3 and then in Aqua Regia analysed by ICP-MS for ultralow detection limits. The contamination of live and dead parts was

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compared in several plants. Plants were analyzed in the same laboratory as sediments.

The water samples were analyzed using AAS in the National Water Reference Laboratory for Slovakia at the Water Research Institute in Bratislava. The speciation of As was performed on the basis of different reaction rate of As^{3+} and As^{5+} depending on pH.

Microscopical analyses of plant tissues were realized in the laboratories of the Department of Wood Science of the Technical University Zvolen.

III. Contamination of the Landscape Components

A. *Technogenous Sediments and Soil*

The dump-field mining sediments are influenced by heavy metals from the hydrothermal Cu-mineralization. The main contaminants: Cu (up to 20 360 ppm), Fe (up to 2.58 %), As (up to 457 ppm), Sb (up to 80 ppm) and Zn (up to 80 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm). The distribution of the contamination is irregular but in general increase from north to south according to the direction of the slope inclination.

B. *Water*

The surface water in the creek draining the valley along the dump-field is gradually contaminated by heavy metals from leached from the technogenous sediments of the mining dumps. The drainage water contains high Cu (up to 2060 ppm), Fe (up to 584 ppm), Zn (up to 35 ppm) and sometimes also Co (up to 10 ppm) and Pb (up to 5 ppm) concentrations. The highest As concentration is 0.6 ppm.

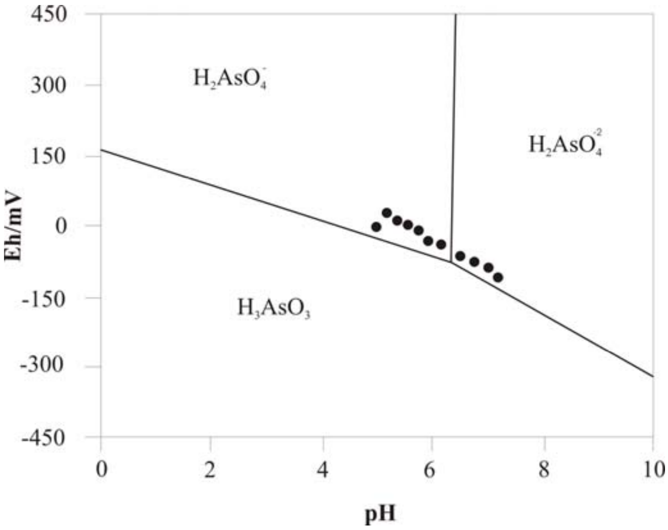

Fig. 3 The pH vs. Eh plot show only the presence of the As^{5+} in the groundwater

The heavy metal content in the water is probably in one third higher during the dry period in comparison with the rainy period. The As content is, both in the surface (and drainage) as well as in the groundwater, not high (0.061 ppm). The speciation of the As proved only the presence of the less toxic As^{5+}. The more toxic inorganic As^{3+} is not present (Fig. 3).

The presence of *Acidithiobacteria* or of sulphate reducing bacteria was not proved. The acidity both of the surface and groundwater is close to neutral pH (6.4 – 7.6) so the formation of acid mine drainage water is not probable.

It was found that the process of the cementation is present but not fast. In spite of the limited kinetics of the process the electron microprobe study proved that the cementation cause on the surface of iron gradual displacement of the Fe^{2+} ions and precipitation of Cu^{2+} ions, both in form of the Cu-oxides, Cu carbonates as well as in form of native copper (Fig. 4). The electron microprobe study show that the cementation copper is of a high fineness. The electron microprobe point analyses proved Cu-contents up to 96.07 $_{wt.}$%.

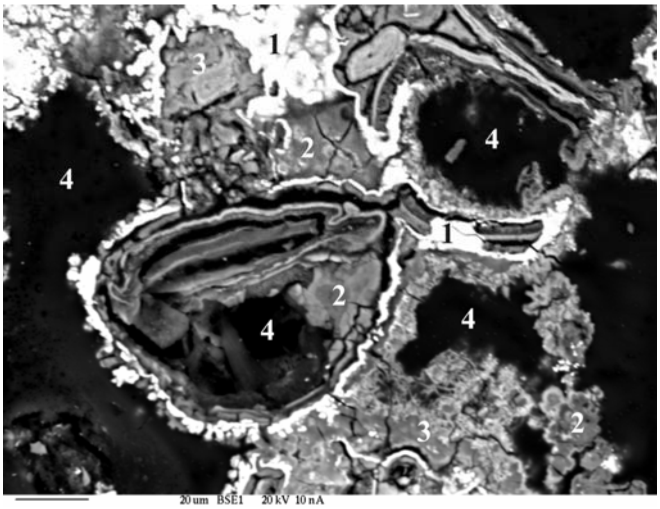

Fig. 4 Native copper (1) of high fineness (up 91,68 % Cu) and the Cu-oxides (2) and carbonates (3) on the oxidized steel surface (4) were precipitated after two months of maceration

The most contaminated is the mineral water from the spring Linhart (Fig. 1). The total radioactivity is 6,498 $Bq.l^{-1}$ and the Fe (381 ppm), Cu (80 ppm), Pb (381 ppm) and Cd (476 ppm) content substantionally exceed the Slovak decrees No. 296/2005 band No 354/2006 Coll.

C. *Plants*

The mineralogical composition of the mine waste dumps at Cu-deposit Ľubietová - Podlipa deposit influence the chemical composition of the products resulted from the specific weathering reactions of the ore and gangue minerals. The geochemistry characteristics of the mine waste dump sediments, soils, surface and drainage water influence the natural installation of the plant species. The chemical analysis of the dump sediments, soils, water and plants from the dump-field show that they are contaminated by heavy metals: Fe, Cu, As, Sb, Cd and others.

The plants adapted to the specific conditions of the different zones of the studied area show different level of the contamination in individual tissues (roots, twigs/stems, leafs/needles or in flowers/fruits). The article presents also results of the plant tissue degradation study in heavy metal contaminated conditions and compares them with those from reference sites.

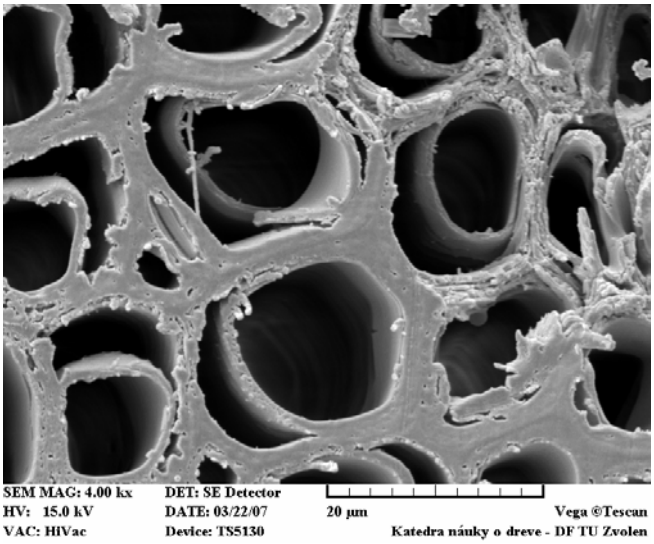

Fig. 4 The living branch of the *Pinus sylvestris;* exfoliation of summer tracheide cell-wall layers

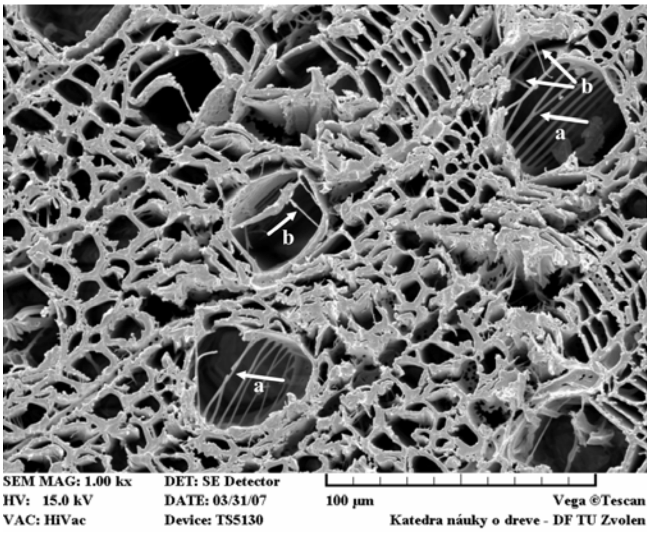

Fig. 5 The branch of the *Betula pendula;* a - scalar perforation in vessels, b - hyphaes

The contents of the heavy metals in plant tissues decrease in the following rank: Fe, Zn, Pb a Cu. In most cases the highest contents of metals were described in roots, than in leaves and stems and less in flowers, semens and fruits. The plant tissues at the dump sites are considerably damaged. Growth of the annual rings is extraordinary tight. Anomalous coarsening of the cell walls, presence of the calluses and of resin canals, as well as of numerous hyfes in vessels (Fig. 5) indicates the defensive plant-reactions.

It was determined that at the Podlipa locality the concentrations of heavy metals decrease in plant tissues in the following order: Fe, Zn, Pb and Cu. The comparison of contamination of individual plant tissues showed that the highest concentrations of heavy metals have roots then leaves and stems. Flowers, seeds and fruits have the lowest concentrations of heavy metals. Plant tissues are considerably damaged at the dump-field and increments of year shoots are extremely narrow. Anomalous cell-wall exfoliation (Fig. 4) and coarsening, occurrence of calluses, resin canals and numerous hyphaes in vessels suggest defense mechanism of plants which are exposed to the stress factors at the dump-field such as contamination by heavy metals, soil and moisture deficiency, movement of incohesive material down to slope.

IV. Conclusion

The results for the irregular contamination of sediments by selected heavy metals are shown at Fig. 2.

The surface water (and drainage water) as well as the groundwater water are substantially contamined predominantly by Cu, Fe and As. Both the As content and its speciation don't pose acute risk (the highest arsenic content is only 0.6 ppm and it is present only in the form of moderately toxic inorganic As^{5+}). The only risk poses the spring of the mineral water Linhart because of the high radioactivity and high Fe, Cu, Cd and Pb contents. For this reason was the spring closed and it is not used for drinking.

The concentrations of the heavy metals in plant tissues decrease seriately in rate: Fe, Zn, Pb and Cu. Comparison of individual types of plant tissues show that the highest concentrations of heavy metals are in roots, than in leafs and stems and the lowest concentrations are in flowers, seeds and in fruits. The plant tissues from the dump-field are heavily damaged and the growth of the current year shoots is extraordinary tight. The results of the research document the plant defense reactions under the influence of stress factors at the dump sites (absence of soil and water, the heavy metal contamination, mobility of the cohesionless slope material).

The ability of the drainage water precipitate cementation copper on the iron surface give possibility to realize Fe-barrier for elimination of heavy metals from the drainage water and contribute to the remediation of the mining country.

Acknowledgment

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