

ASSESSMENT OF Co, Cu, Zn, As AND Cd BIOAVAILABILITY AT SELECTED EUROPEAN Cu-DEPOSITS, COMPARATIVE ENVIRONMENTAL AND GEOCHEMICAL STUDY

Janka ŠEVČÍKOVÁ^{1*}, Pavol MIDULA², Ján SPIŠIAK¹, Jarmila KMEŤOVÁ¹,
Ján TOMAŠKIN¹, Sherif KHARBISH³, Ahmed Mohammed ELDOSOUKY³,
Jana JANŠTOVÁ⁴, & Ingrid TURISOVÁ¹

¹Faculty of Natural Science, Matej Bel University, Tajovského 40, 974 01 Banská Bystrica, Slovakia;
janka.sevcikova@umb.sk; jan.spisiak@umb.sk; jarmila.kmetova@umb.sk; jan.tomaskin@umb.sk;
ingrid.turisoval@umb.sk

²Faculty of Agrobiolgy, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129,165
00 Praha - Suchbátův Újezd, Czechia, midula@af.czu.cz

³Faculty of Science, Suez University, Suez, 43518, Egypt, sherif.kharbish@suezuni.edu.eg;
ahmed.eldosouky@sci.suezuni.edu.eg

⁴Slovak Environment Agency, Tajovského 28, 974 01 Banská Bystrica, Slovakia, jana.janstova@sazp.sk
*Corresponding author:janka.sevcikova@umb.sk

Abstract: The article presents the results of a study of the contamination of heaps with potentially toxic elements, focused on Co, Cu, Zn, As, and Cd, their bioavailability in the area at selected European abandoned Cu-deposits: Špania Dolina (Slovakia), Libiola, Caporciano (Italy), and São Domingos (Portugal). The content of studied metals at selected heaps often exceeds the limits of national and EU legislation. The bioavailability was studied using three-step sequential extraction, using distilled water (step I), ammonium acetate (step II) and citric acid (step III). The best bioavailable elements are Cu, Cd, and Zn. Cobalt and As are less released during the leaching into the solution. The article discusses also the main environmental problems at the individual deposits and suggests possible solutions.

Keywords: contamination, potentially toxic elements, heap, bioavailable fractions

1. INTRODUCTION

Mine waste, which was in equilibrium with the intact rock environment, suddenly found itself on the surface and accumulated in landfills. The left over ores are always present in the tailings. Mining heaps and tailings therefore cause long-term contamination of the surrounding components of the environment (soil, water, air, and biota) with potentially toxic elements (PTEs) (Assabar et al., 2023; Islam et al., 2024).

Environmental risks are conditioned by biochemical processes taking place in the hypergenic zone. These processes cause also the introduction of aerobic microorganisms, yeasts, fungi, molds, algae, and lichens (Andráš et al., 2010). Thus, landfills represent a multi-component abiotic-biotic system with a large reaction interphase surface. The initiator of interphase reactions is rainwater and solutions

created by chemical reactions (Król et al., 2020). Landfills can therefore be understood as biogeochemical reactors. The general reason for the PTEs and other elements migration in the weathering process is the transformation of minerals with a high lattice energy, stable in the conditions of primary formation (endogenous processes) into minerals with a low lattice energy, stable in the subaerial, or underwater environment (exogenous conditions). There is so far only incomplete information on the mobility of the products of interphase reactions taking place in landfills, based on the results of experimental mineralogy. One of the questions is the bioavailability of the PTEs, which may influence the growth and healthy development of biota (Andráš et al., 2010).

The goal of our study is to compare the bioavailability of selected five PTEs (Co, Cu, Zn, As, and Cd) which are present at all studied landfills from

several selected European closed Cu-deposits. Three localities situated in different geological settings were studied. Špania Dolina was an important historical mine, where mining had been carried out since the Bronze Age. The present research was realized at Richtárová heap. The next two studied deposits were the landfills Caporciano in Val di Cecina and Libiola in Italy (Figure 1).



Figure 1. Localization of the studied Cu-deposits (According to: Wikimedia Commons, 2024).

The originally exhalative-sedimentary Cu-mineralization of the siderite formation at Špania Dolina (Central Slovakia, Figure 2) was remobilized during the Carpathian folding. It has been exploited since the Bronze Age. The ores are situated in the rocks of the crystalline, Permian, and Lower Triassic ages, formed by Permian, migmatitic pararules, arkoses, conglomerates, sandstones, and variegated shales. The Triassic is represented by dolomites and quartzites. The main exploited economically important minerals were chalcopryrite and tetrahedrite (Andráš et al. 2013, 2014; Franková et al., 2012).

The chalcopryrite, bornite, and chalcocite ore body at Caporciano mine in Tuscany (Figure 3) is associated with ophiolites of Tuscanian Units, (consisting of diabase, gabbros, and serpentinites) (Dolfini et al., 2020). The medium-temperature hydrothermal ore mineralization is a result of remobilization (Bertolani & Rivalenti, 1973). Massive sulfide ores represented by a mixture of chalcopryrite, bornite, native copper, chalcocite, malachite, and azurite were exploited (Dini & Boschi, 2017; Klemm & Wagner, 1982; Tanelli, 1983; Andráš et al., 2025).

The Libiola in Liguria (Figure 4) belongs to several deposits whose mineralization is genetically connected to Jurassic ophiolites of the northern Apennine. Mineralization is developed in the ophiolite complex. The economically important ores are represented predominantly by pyrite, pyrrotite, and chalcopryrite (Buccheri et al., 2014).

The outcropping São Domingos deposit in the Iberian Pyrite Belt (Figure 5) in the south of Portugal, near the Spanish border belongs to the important world deposits. The exploited ore bodies are situated in the black shales and basic volcanic rocks of the mighty volcano-sedimentary complex. The exploited ore minerals are represented predominantly by massive sulfide and stockwork ores, containing mainly chalcopryrite, pyrite, tetrahedrite, and less also of arsenopyrite and sphalerite (Matos et al., 2020; Vieira et al. 2020).



Figure 2. Heap at Špania Dolina (photo 2023).



Figure 3. The quarry at the top of heap at Libiola (photo 2024).



Figure 4. Great erosion of the heap at Caporciano (photo 2024).



Figure 5. Acid drainage water of the creek in the open pit heap area at São Domingos (photo 2023).

2. MATERIALS AND METHODS

30 samples of technosol were collected from each studied deposit. This set of samples separately from individual deposits was mixed and consequently homogenized to get samples that are representative of the average heap material. After milling, 100 g of this material was pulverized (80 mesh) and dried at 60 °C for 24 hours.

Soil characteristics (active and paste pH_{H_2O}/Eh_{H_2O} ; pH_{KCl}/Eh_{KCl}) are presented in Table 1. They were obtained by measuring using the methodology published by Sobek et al. (1978): the active pH_{H_2O}/Eh_{H_2O} in 10 g of technosol suspension in 20 ml of distilled water and the paste pH_{KCl}/Eh_{KCl} 10 g of technosol in a 20 ml of 1M KCl suspension. After one hour of mixing in an electromagnetic stirrer, the pH/Eh was determined with a WTW Multi 3420 pH meter with a SenTix ORP type redox electrode with a Ag/AgCl reference system (electrolyte 3 M KCl). Obtained values were converted to a standard hydrogen electrode according to Pitter (1990).

Soil samples were homogenized and dried at room temperature and subsequently analyzed for Co, Cu, Zn, As, and Cd by ICP-MS at ACME Laboratory (Vancouver, Canada). 2 g of the sample was moistened with distilled H₂O and subsequently digested to dry vapors in the H₂O-HF-HClO₄-HNO₃ mixture. 10 mL of 50% HCl was added to the samples and the solutions were heated in a water bath, to extract the

total concentration of elements. The well-homogenized and clear solution was refilled with HCl to the exact volume and analyzed by ICP-MS at ACME Laboratories (Vancouver, Canada)

The bioavailability of PTEs was studied by sequential extraction procedure 1 g of sample was in 50 ml falcon tube leached using 2 extraction agents: I. mobile/exchangeable PTEs by shaking with NH₄CH₃CO₂ (ammonium acetate), pH 7 overnight; and II. Acid soluble, shaking with the same solution buffered to pH 5 for 5 hours; These 2 fractions can be considered as bioavailable. The residual fractions were calculated as the difference between the sum of these fractions and the total concentrations accordingly.

3. RESULTS

The pH and Eh (both rinse and paste values) are presented in Table 1. The most acidic heap material is at Libiola (\bar{x} pH_{H_2O} 4.03) and the most close to neutral conditions at Caporciano (\bar{x} pH_{H_2O} 6.56). The Eh shows the most oxidic conditions at São Domingos (\bar{x} Eh_{H_2O} 153.3) and the most reducing conditions.

At all monitored copper deposits, the results show high concentrations of PTEs, first of all of Cu, Zn, and As (Table 1). The heap in Caporciano is primarily typical of the highest Cu contents (\bar{x} 7,295 mg.kg⁻¹), as well as increased Cd contents (\bar{x} 3.4 mg.kg⁻¹; Table 2). The comparison of the substantially higher PTEs contents in heap material with the reference area is presented in Table 3.

The bioavailability of the selected PTEs in heap material from selected deposits is shown in Figure 6. The plot shows that the most leachable metals are Cu, Cd, and Zn. The worst mobile seems to be As.

For the heap in Špania Dolina is the characteristic decrease of the bioavailability heading from Cu to As: Cu > Zn > Cd > Co > As and for heap in Libiola: Cu > Zn > Cd > Co > As. In the Caporciano decreases the mobility, and therefore also bioavailability, in the following order: Cd > Cu > Zn > As > Co. The results obtained from São Domingos waste material show the best bioavailability for As and Co. The bioavailability decreases in the following As > Co > Cu > Cd > Zn (Figure 6).

Table 1. Ranges of a rinse and paste pH and Eh and their average values in the technosol at studied heaps

Heap	$pH_{(H_2O)}$			$Eh_{(H_2O)}$ (mV)			$pH_{(KCl)}$			$Eh_{(KCl)}$ (mV)		
	Range of values		\bar{x}	Range of values		\bar{x}	Range of values		\bar{x}	Range of values		\bar{x}
Š. Dolina	4.72	7.36	5.70	-66	106	36.56	4.20	8.27	5.67	-109	134	39
Libiola	2.76	4.94	4.03	12	146	67.71	3.37	6.47	4.82	32.5	223	129
Caporciano	5.99	7.13	6.56	-12.0	42.01	14.00	5.13	7.01	5.99	-4.0	111	58
S. Domingos	2.74	7.10	4.28	10.7	243.4	153.3	2.70	5.30	3.95	5.6	166	174

Table 2. The average contents of PTEs in the technosol of studied heaps.

Deposit	Co	Cu	mg·kg ⁻¹		
			Zn	As	Cd
Š. Dolina	22	1,511	38	234	0.1
Libiola	89	3,562	364	20	1.5
Caporciano	33	7,299	765	2	3.5
S. Domingos	21	655	971	1,202	0.9

Table 3. The average contents of PTEs in the reference areas.

Deposit	Co	Cu	mg·kg ⁻¹		
			Zn	As	Cd
Š. Dolina	4	45	19	10	0.11
Libiola	4.5	96	14	33	0.0
Caporciano	79	1,003	115	5	0.6
S. Domingos	18	522	176	1.2	2.8

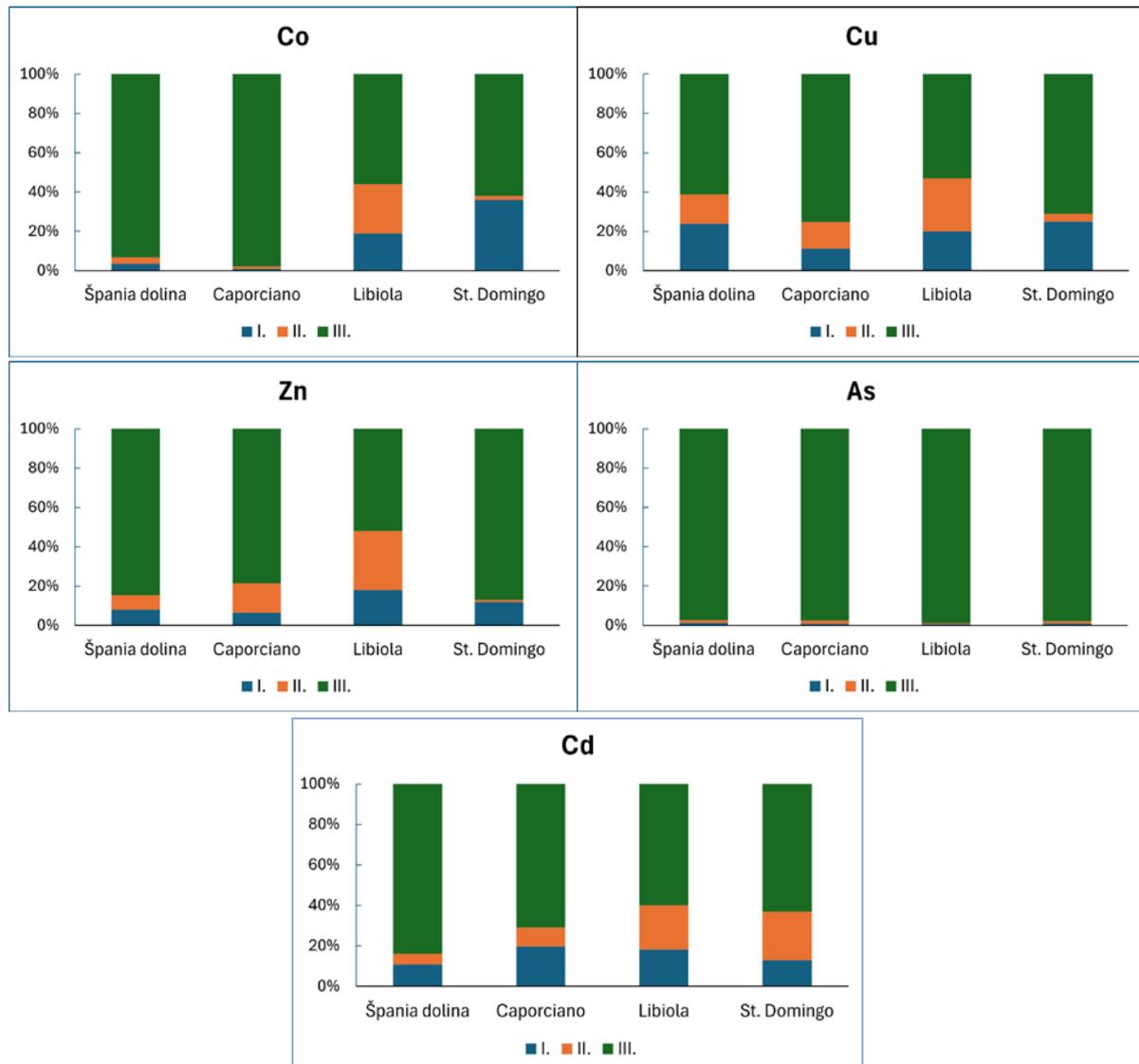


Figure 6. Results of the sequential extraction of PTEs extraction from the technosol from the studied deposits; I. leaching in $\text{NH}_4\text{CH}_3\text{CO}_2$ solution at pH 7; II. leaching in $\text{NH}_4\text{CH}_3\text{CO}_2$ solution at pH 5; III. insoluble rest (the first two fractions can be considered bioavailable).

4. DISCUSSION

The distribution of PTEs content in the heap material on the monitored closed Cu deposits is different (table 2) and irregular within each deposit. The highest Zn, As, and Pb contamination was

reported in the area of the São Domingos mine, while the material from the Libiola heap is rich in Co and the material from the Caporciano heap in Cu and Cd. The highest Sb contamination was found in the heap material from the 40-year closed Špania Dolina deposit.

The specifics of individual terrains remain a certain problem when assessing the bioavailability of the soil (Paller & Knox, 2013). The situation differs for individual deposits because of the physical and chemical heterogeneity of sediments combined with differences in geological characteristics (different characteristics of the rocks/technosol), geochemical conditions pH/Eh and chemical forms and mineralogical bondings of the studied PTEs (e.g. can be expected that As is in oxidic conditions present in less mobile form As⁵⁺; Andráš et al., 2014).

The rocks at all deposits: Libiola, Caporciano, and São Domingos, except Špania Dolina consist of basic to ultrabasic ophiolite or volcano-sedimentary ore-containing rocks. All the studied deposits show the heap material acid conditions, only the technosol at Caporciano has pH values close to neutral values. Caporciano heap seems to be the closest to the neutral conditions (\bar{x} pH_{H₂O} 6.56). The Eh values (both Eh_{H₂O} and Eh_{KCl}) proved the most oxidic conditions at the great open pit São Domingos deposit (\bar{x} Eh_{H₂O} 153.3), whereas the most redox environment was described at Caporciano heap. All these obtained data correspond with a lot of data presented by numerous authors, e.g. Nagyová et al. (2013), Buccheri et al. (2014, 2019), Matos et al. (2020), Dolfini et al. (2020), and others.

Basic data on the studied heap fields in Špania Dolina was published by Andráš et al., (2008; 2009) and Buccheri et al. (2014). At this deposit the content of all PTEs is the lowest. The sandy and gravel sediments in Libiola contain a large amount of material rich in chalcopyrite and pyrite. Secondary Fe-oxides and Fe-oxyhydroxides cause remarkable Fe content, with pyrite being the substantial Co source (Marescotti et al., 2010). During the weathering process, significant amounts of PTEs from primary and secondary mineral phases are released into acid rock drainage, which then contaminates the slightly alkaline Gromolo stream (pH 8) flowing through the valley and inhabited areas (Dinelli et al., 2001; Buccheri et al., 2014). The neutralization of surface water and the massive precipitation of Fe-oxides and Fe-oxyhydroxides causes sorption of PTEs as a result of which the stream water is characterized by acceptable quality in the village area. It is unlikely that there could be a massive mobilization of PTEs (Dinelli et al., 2001). The stabilization of a steep slope under the quarry can be recommended, on which the heap material is deposited either by technical procedures or by suitable pioneer vegetation cover to reduce the penetration of PTEs into surroundings.

The Caporciano heap is primarily characterized by the highest Cu and Cd

contaminations (\bar{x} 7299 mg.kg⁻¹ and 3.5 mg.kg⁻¹, respectively). The main environmental risk in Caporciano is the severe extremely significant erosion of the heap in a deep terrain depression. Poor pioneer plant vegetation (*Pinus* spp. and *Quercus* spp.) is not sufficient to stabilize stabilize the heap material (Buccheri et al., 2014, 2014a). The heap is located high in the mountains, with the nearest populated area approximately 2 km away. As a result, the relatively mobile Cu primarily affects only the vineyards situated downslope. Since there are no creeks in the vicinity, the environmental risk associated with the spread of PTEs through surface water is minimal. The small wetland below the landfill is saturated with sewage from the hotel above the landfill. Adaptation of this marsh to an anaerobic and aerobic wetland system could substantially eliminate the release of Cu into the landscape.

Comprehensive information about the São Domingos deposit was published in a series of articles (Quental et al., 2003; Mateus et al., 2011; Matos et al., 2006, 2020). According to Mateus et al. (2011), the reddish aluminous slag contains up to 1.7% Cu and 0–5% Cu. The current study (Tables 2 and 3) aligns with these findings. The red and brown coloration of the heap material at the São Domingos and Libiola sites suggests oxidic conditions; however, the technogenic sediments in these areas are not sufficiently aerated, and the range of Eh values (-10.7 to 243.4; Table 1) corresponds to those typical of anoxic soils (Alloway, 1992).

The most significant environmental risk in São Domingos is the extensive production of acidic drainage water. The majority of this water accumulates in a flooded surface quarry, while the rest is redirected to a distant stream via canals extending over 14 km. A portion of the water evaporates, while the remainder flows into the stream and eventually dilutes in a nearby lake.

A considerable amount of acidic water is captured by small dams. Enormously extensive mining space does not allow for simple solutions for the remediation of contaminated land. One of the possible procedures to reduce the negative impact of PTEs on environmental components is the phyto-stabilization of metals in the contaminated area using autochthonous and pioneer plant species (Abreu et al., 2010, 2012; Andráš et al., 2021; Midula et al., 2023). Several admixtures are currently being tested that can immobilize PTEs in waste material.

PTEs contents in the studied heap often exceed the limits of national and EU legislation.

Bioavailability is considered as the rate and extent to which PTEs can reach the biota (Adams et al., 2019). Bioavailable are at the selected deposits

from the heap material of all the studied PTEs. Arsenic is at São Domingos extractable even in ammonium acetate at pH 7 (Figure 6). The best extractables are Cu, Cd, and Zn, whereas Co is less bioavailable. These results are comparable with those published by Kim et al. (2015) and Zogai et al. (2014). The Cu and Zn are well soluble also in the second step of sequential extraction using ammonium complexes as described by Davidson, 2012, Helios-Rybicka & Wójcik, 2012). These steps were released to solution the substantial bio-exchangeable parts of the above-mentioned elements. There are some similarities between Špania Dolina and Caporciano deposits. From the heap material of both polygons, the best releasing ability to the solution was detected for Cu and Cd, only the order of these PTEs is different: at Špania Dolina Cu is the best bioavailable, whereas at Caporciano and in Libiola is Cd. The behavior of As is completely different (Figure 6). Our results show the bioavailable As fractions seem to be influenced by pH (the lowest is at São Domingos) and probably by specific bonding in heap material, as mentioned by Singh & Srivastava (2020). Arsenic is more or less bio-inaccessible at three deposits (Špania Dolina, Libiola, and Caporciano), while it is bioavailable in the most acidic conditions at São Domingos even in the first step of sequential extraction using distilled water. The bioaccessibility at this deposit is probably influenced primarily by the differential solubility of the minerals under acidic conditions (Drahota et al., 2025). The obtained data about bioavailability generally corresponds with results published by Lalhruaitluanga (2011).

5. CONCLUSIONS

The highest Zn and As contamination was reported from the mining polygon of São Domingos, while the heap material at Libiola is rich in Co, Ni, and the mine waste at Caporciano in Cu and Cd. The landfill at Špania Dolina is less contaminated with PTEs than the landfills at the remaining four deposits. The PTEs contents in many cases exceed the limits set by EU soil law.

A substantial part of the bioavailable PTEs was generally released from the heap material in the deionized water and less also in 1 M solution of ammonium acetate. At the first three deposits (Špania Dolina, Caporciano in Val di Cecina, and Libiola) it is possible to distinguish generally the two most bioavailable PTEs: Cu and Cd. Less bioavailable are Co and Zn. Except for the heap São Domingos the less immobile metal is As.

Acknowledgments

The article was supported by grant agency VEGA 1/0220/23.

REFERENCES

- Abreu, M., Batista, M. J., Magalhães, M. C. F., & Matos, J., X.** 2010. *Acid Mine Drainage in the Portuguese Iberian Pyrite Belt. Cap. II In Mine Drainage and Related Problems Book, Editor Brock C. Robinson*, Nova Science Publishers, ISBN: 978-1-60741-285-4, New York, USA, 51 p.
- Abreu, M., Magalhaes, M. C., Santos, E. S., & Batista, M. J.,** 2012. *São Domingos Mine Wastes Phytostabilization Using Spontaneous Plant Species, 9th International Symposium on Environmental Geochemistry*. Aveiro, 15th-21th July 2012, 42-49.
- Adams, W., Blust, R., Dwyer, R., Mount, D., Northeim, E., Rodriguez, P. H., & Spry, D.,** 2019. *Environmental toxicology and Chemistry. Metal Bioavailability Modeling: Critical Review*, <https://doi.org/10.1002/etc.4558>, 48-59.
- Alloway, B. J.,** 1992. *Heavy Metals in Soils*. Environmental Pollution, Blackie Academic & Professional, ISBN 978-94-007-4469-1, 368 p.
- Andráš, P., Lichý, A., Krížáni, I., Rusková, J., Ladomerský, J., Jeleň, S., Hroncová, E., & Matúšková, L.,** 2008. *Podlipa heap-field at Lubietová – land contaminated by heavy metals (Slovakia)*. *Carpathian Journal of Earth and Environmental Sciences*, 3, 2, ISSN 1842-4090, 5-18.
- Andráš, P., Lichý, A., Krížáni, I., & Rusková, J.,** 2009. *The heavy metal sorption on clay minerals and risk of the AMD formation at the Reiner and Podlipa heap-fields at Lubietová deposit (Slovakia)*. *Carpathian Journal of Earth and Environmental Sciences*, 2009, 4, 2, ISSN-1842-4090, 133-147.
- Andráš, P., & Krížáni, I.,** 2010. *The impact of mineral extraction on the environment*. *Životné prostredie*: 41, 1, ISSN 0044-4863, 20-23 (in Slovak)
- Andráš, P., Jeleň, S., & Ferenc, Š.,** 2013. *Geologicko-ložisková charakteristika Cu-ložísk Špania Dolina, Staré Hory, Lubietová a Poniky*. In: Andráš, P., Dirner, V., Turisová, I., Vojtková, H. *Remnants of old activity at abandoned Cu-deposits*. Mendelej, Ostrava, 123-141, ISBN 978-80-86832-75-3.
- Andráš, P., Dirner, V., Turisová, I., & Vojtková, H.,** 2014. *Remnants of old activity at abandoned Cu-deposits*. *Ekomonitor*, Ostrava, ISBN 978-80-86832-75-3, 440 p. (in Slovak).
- Andráš, P., Krnáč, J., & Dadová, J.,** 2014. *Environmental problems at ore field of Cu-Ag mine Špania Dolina*. Technical University in Košice, 978-80-553-1798-4, 103 p.
- Andráš, P., Midula, P., Matos, J.X., Buccheri, G., Drímal, M., Dirner, V., Melichová, Z., & Turisová, I.,** 2021. *Comparison of soil contamination at the selected European copper mines*. *Carpathian Journal of Earth and*

- Environmental Sciences, 16, 1, 163-174. ISSN-1842-4090.
- Andráš, P., Midula, P., Kmeťová, J., Ševčíková, J., Tomaškin, J., Drímal, M., Janštová, J., Masný, M., & Kharbish, S., 2025.** *Pedochemical fractionation of potentially toxic elements within the context of soil-plant interactions at abandoned heap-field of Caporciano (Italy)*. Plant & Soil, <https://doi.org/10.1007/s11104-025-07294-w> (early acces),
- Assabar, N., Lahmidi, I., & Jabrane, R., 2023.** *Assesment of heavy metals contamination in spoil heaps of Ain Aouda mine (Taza Morocco)*. Journal of Ecological Engineering, 24, 3, 224-231.
- Bertolani M., & Rivalenti G., 1973.** *Le mineralizzazioni metallifere della miniera di Montecatini in Val di Cecina (Pisa)*. Italian Journal of Geosciences; 92, 3, 635–648.
- Buccheri, G., Andráš, P., Astolfi, M.L., Canepari, S., Ciucci, M., & Marino, A., 2014.** *Heavy metal contamination in water at Libiola abandoned copper mine, Italy*. Romanian Journal of Mineral, 87 (1), 65-70.
- Buccheri, G., Andráš, P., Andráš, P. Jr., Dadová, J., & Kupka, J., 2014a.** *Heavy metal contamination and its impact on plants at Caporciano Cu-mine (Montecatini Val di Cecina, Italy)*. Carpathian Journal of Earth and Environmental Sciences, ISSN-1842-4090, 9, 4, 73 – 81
- Buccheri, G., Andráš, P., Vajda, E., Midula, P., & Dirner, V., 2019.** *Soil contamination by heavy metals at Libiola abandoned copper mine, Italy*, Acta Montanistica Slovaca, 23, 1, ISSN 1335-1788, 337-345.
- Davidson, C. M. 2012.** *Methods for the Determination of Heavy Metals and Metalloids in Soils*. Heavy Metals in Soils, ISBN: 978-94-007-4470-7, 97-140.
- Dinelli, E., Lucchini, F., Fabbri, M., & Cortecchi, G., 2001.** *Metal distribution and environmental problems related to sulfide oxidation in the Libiola copper mine area (Ligurian Apennines, Italy)*. Journal of Geochemical Exploration, 74, 1-3, 141-152.
- Dini, A., & Boschi, C., 2017.** *I giacimenti cupriferi delle ofioliti toscane. Geologia e ipotesi genetiche*. Rivista Mineralogica Italiana. 2, 83, 84–101.
- Dolfini, A., Angelini, I., & Artioli, G., 2020.** *Copper to Tuscany - Coals to Newcastle? The dynamics of metalwork exchange in early Italy*. PLoS ONE, 15, 1, 1-35.
- Drahota, P., Etter, V., & Košek, F., 2025.** *Arsenic bioaccessibility in environmentally important arsenic minerals*. Journal of Hazardous Materials, 485, 136838.
- Franková, H., Čmielová, L., Klimko, T., Lacková, E., Andráš, P., 2012.** *Comparative study of Cu, As and Sb toxicity between dump-fields of anandoned Cu-deposits Lubietová and Špania Dolina (Central Slovakia)*. Carpathian Journal of Earth and Environmental Sciences, 7, 4, ISSN 1842-4090, 79-88
- Helios-Rybicka E., & Wójcik R., 2012.** *Competitive sorption/ desorption of Zn, Cd, Pb, Ni, Cu, and Cr by clay-bearing mining wastes*. Appl Clay Sci 65–66:6–13. <https://doi.org/10.1016/j.clay.2012.06.006>
- Islam, S., Shreejana, K. C., Anjum, N., Poudel, A., & Suchi, S. A., 2024.** *Sources, effects and present perspectives of heavy metals contamination: Soil, plants and human food chain*.
- Kim, R.Y., Yoon, J.K., Kim, T.S., Yang, J.E., Owens, G., & Kim, K.R., 2015.** *Bioavailability of heavy metals in soils: definitions and practical implementation - a critical review*. Environmental Geochemistry and Health, 37, 2015, 1041-1061.
- Klemm, D. D., & Wagner, J., 1982.** *Copper deposit in ophiolites of southern Tuscany*. Ofioliti. 7, 331–336.
- Król, A., Mizerna, K., & Bozym, M., 2020.** *As assessment of pH-dependent release and mobility of heavy metals from metallurgical slag*. Journal of Hazardous Materials, 384, 121502, 1-9.
- Lalhruaitluanga, H., Prasad M.N.V., & Radha, K., 2011.** *Potential of chemically activated and raw charcoals of Melocanna baccifera for removal of Ni(II) and Zn(II) from aqueous solutions*. Desalination, 271 (1-3), 301-308.
- Marescotti, P., Bullet, E., Bullet, A., Servida, D., Carbone, C., Grieco, G., De, L., Bullet, C., & Lucchetti, G., 2010.** *Mineralogical and geochemical spatial analyses of a waste-rock dump at the Libiola Fe–Cu sulphide mine (Eastern Liguria, Italy)*. Environmental Earth Sciences, 61, DOI: 10.1007/s12665-009-0335-7, 187-199.
- Mateus, A., Pinto, A., Alves, L. C., Matos, J. X., Figueiras, J., & Neng, N., 2011.** *Roman and modern slag at S. Domingos mine (IPB, Portugal): compositional features and implications for their long-term stability and potential re-use*. International Journal of Environment and Waste Management Inderscience Publishers Ltd, Vol. 8, n1/2, 39 p.
- Matos, J., Pereira, Z., Oliveiraa, V., & Oliveira, J., 2006.** *The geological setting of the São Domingos pyrite orebody, Iberian Pyrite Belt*. Proceedings of the VII National Geology Congress, Estremoz, 283-286.
- Matos, J.X., Oliveira, D.P.S., Batista, M.J., Pereira, Z., Albardeiro, L., Morais, I., Mendes, M., Marques, F., Solá, R., Salgueiro, R., Carvalho, J., Conçalves, P., & Oliveira, J.T., 2020.** *Iberian Pyrite Belt Exploration*. Comunicações Geológicas, 107, p.150.
- Midula, P., Andráš, P., Ševčíková, J., & Wiche, O., 2023.** *Phytoaccumulation of mercury into vascular plants at area of abandoned Hg-ore deposit Malachov (Central Slovakia)*. Carpathian Journal of Earth and Environmental Sciences 18, 1, 225 – 229, DOI:10.26471/cjees/2023/018/253
- Nagyová, I., Melichová, Z., Komadelová, T., Boháč, P., & Andráš, P., 2013.** *Environmental assessment of impacts by old copper mining activities – a case study at Špania Dolina Starohorské Mts., Slovakia*. Carpathian Journal of Earth and Environmental Sciences, 8, 4, 101 – 108.
- Paller, M. H. & A., S. Knox, A. S., 2013.** *Bioavailability of metals in contaminated sediments*. E3S Web of Conferences 1, /201 02001, 3010200 1, DOI: 10.1051/e3sconf./20130102001, 1-4.

- Pitter, P.**, 1990. *Hydrochemistry*. STNL, Praha, 568 p. (in Slovak).
- Quental, L., Brito, M., Sousa, A.J., Abreu, M., Batista, M., Oliveira, V., Vairinho, M., & Tavares, M.T.**, 2003. *Utilização de imagens hiperespectrais na avaliação da contaminação mineira em S. Domingos, Faixa Piritosa, Alentejo*. Portugal: Ciências da Terra (UNL) M33-M36.
- Singh, S. B., & Srivastava, P. K.**, 2020. *Bioavailability of arsenic in agricultural soils under the influence of different soil properties*. SN Applied Sciences Aim. 1-16.
- Sobek, A. A., Schuller, W. A., Freeman, J. R., & Smith, R., M.** 1978. *Field and laboratory methods applicable to overburden and minesoils*, EPA 600/2-78-054, 203 p.
- Tanelli G.**, 1983. *Mineralizzazioni metallifere e minerogenesi della Toscana*. Memorie della Società Geologica Italiana, 25, 91–109.
- Vieira, A., Matos, J.X., Lopes, L., & Martins, R.**, 2020. *Evaluation of the mining potential of the São Domingos mine waste, Iberian Pyrite Belt, Portugal*. Comunicações Geológicas, 107, 91-100.
- Zogai, M., Pacarizi, M. & Duering, R. A.**, 2014. *Spatial distribution of heavy metals and assessment of their bioavailability in agricultural soils of Kosovo*. Carpathian Journal of Earth and Environmental Sciences, 9, 1, 221-230.

Received:09.02.2025
 Revised:20.03. 2025
 Accepted:24.03.2025
 Published: 25.03.2025