Determination of Risk Elements in Mine Waste Dump Soil Sample Using Sequential BCR Extraction

Barbora VALOVÁ1), Iva KOTALOVÁ2), Silvie HEVIÁNKOVÁ3)

1) VSB- Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava – Poruba, Czech Republic; email: barbora.val@seznam.cz

2) VSB- Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava – Poruba, Czech Republic; email: iva.kotalova@vsb.cz

3) VSB- Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, 708 33 Ostrava – Poruba, Czech Republic; email: silvie.heviankova@vsb.cz

http://doi.org/10.29227/IM-2020-01-69

Submission date: 28-12-2019 | Review date: 028-01-2020

Abstract

The article deals with the determination of mobility of selected risk elements in soil samples of thermally active dump resulting from mining activities in the Ostrava region. The samples were taken from Hedvika dump during 2017 to 2018. Extraction of soil samples was performed using three-step sequential extraction of BCR (Bureau Community of Reference). Sequential extraction can provide information about the processes that normally take place in the environment. The solid soil component is gradually leached in the various extraction agents from the weakest to the strongest. This provides information on the total amount of risk elements potentially available under specific environmental conditions. Selected risk elements (Cr, Cu, Ni, Zn) were determined by ICP - MS method (Inductively coupled plasma mass spectrometry) and AAS (Atomic absorption spectrometry) (Zn). Nitric acid leaching was performed to supplement the total BCR extraction analysis.

Keywords: *BCR sequence analysis, dump, ICP – MS, mobility, mining waste, risk elements, soil*

Introduction

Soil is an important component of the environment and forms the basis for human life on Earth.

The current problem of the soil environment is the strong civilization pressure behind many of the degradations. One of the forms is also chemical degradation of soil, which is caused by pollution, which also includes toxic metals. These are included in the list of global environmental issues.

The most important soil properties influencing the bioavailability and mobility of metals in soils include soil acidity (pH), oxidation and reduction processes as well as sorption properties of soils.

Potentially toxic metals are considered to be a significant source of environmental pollution, especially in urban areas where industry and mining are cumulative. Intensive deep mining of hard coal in the Ostrava-Karviná district (OKR) left behind a large amount of mining waste, mainly in heaps and dumps. The negative impact of dumps on the environment, besides land occupation and changes in landscape character, is primarily their thermal activity. This is often caused by unprofessional intervention, for example due to poor sorting of waste. Spontaneous combustion can then occur primarily by aeration with carbon-rich carbon. Oxygen and water vapour are therefore critical factors for this process. The greatest amount of heat is released by the oxidation of unsaturated organic substances and is exothermic. [1] This is related to the release of toxic substances, the formation and spread of fine dust to the environment, the formation of burned-out cavities inside the dump, the risk of fire on the surface of the dump, the emergence and escape of large amounts of thermal energy, the death of vegetation on the surface of the dump, sinks and dips, smoke, burns, etc. [2, 3]

However, the total content of metals, not just those at risk, in the ecosystem components is not entirely relevant information. In particular, in order to be harmful, the substance must be available for plants and animals. Therefore, bioavailability is being investigated. This is to what extent hazardous metals will be mobile in other environmental compartments and to what extent they are dangerous to the environment.

As part of the project, the thermally active dump of Hedvika was monitored. It is located on the eastern edge of the cadastral part of Radvanice and Michálkovice (Ostrava) in the cadastral districts of Chotěbuz and Zaryje. It lies on the border of the former districts of Ostrava and Karviná. The eastern part of Karviná is part of the Petřvald cadastre near Karviná. The exact date of foundation of the dump is unknown. The first mention dates back to 1903, from excavation and opening works. Probably the material from the digging of the pit and the opening of the Hedvika mine (the original name of the Albrecht Mine) was stored here. The surface was expanded from the original area of its own area Hedvika to the surroundings, especially in the northwest direction, directly to Michálkovice. At the turn of the 1960s and 1970s, a period of intense expansion of the dump into today's form occurred. Storage of tailings ended in 1998. [3, 4]

Hedvika dump forms a massive and flat-sprawling formation of about 32 ha. On the northern and western sides, it forms the border with the former J. Fučík Mine. It is then bordered by the Michalkovice-Petřvald road in the northeast. In the southwest it is adjacent to a mining site. At present, the dump consists of a massive surface formation of gangue with an area of approximately 40.6 ha and an average height of disposed material in the range of 12–15 m. The mass is thus destined to produce smoke and endogenous fires. [4]

Thermal processes have been recorded in various parts of the dump since the 1950s. However, according to the preserved documentation, they were locally eliminated, mainly by firefighters, covering with an insulating layer or by extraction. However, these interventions could not completely prevent the massive development of thermal activity. The temperature at the focal point exceeds 500°C. The last experimental remediation of thermal activity in 2006 by flooding the outbreak of existing vapours with liquid clay suspension was not entirely effective. Thus, since 2010, temperature monitoring and thermal activity observation have been carried out on the dump by means of thermometric probes. [4, 5]

Materials and Methods

Sampling and sampling methodology

Samples were taken from the entire Hedvika area. Samples were taken from a depth of at least 10 cm. If the topsoil was present, it was removed with a spade. Subsequently, these samples were mixed to give a representative and mixed sample. Soil sampling was carried out according to ČSN ISO 10381-6 (836151) Soil Quality – Sampling – Part 6: Guidance for sampling, handling and storage of soil samples under aerobic conditions for the study of microbial processes, biomass and diversity in the laboratory. Subsequently, the samples were treated according to the ČSN ISO 11464 (836160) Soil Quality - Sample Preparation for Physico-chemical Analyses. Grain size was adjusted using Retsch stainless steel sieves with a grain size of 2 mm.

The treated samples were dried to constant weight in a MEMMERT oven at 105 ± 2 °C for 2 hours. Samples were stored in a desiccator to prevent moisture sorption.

Method to determine physical parameters of soil samples

Soil analyses were carried out as follows: dry matter and water content in the sample according to ČSN 11465 (836635) Soil quality – Determination of dry weight and soil moisture content – Gravimetric method; conductivity according to ČSN EN 13038 (836211) Soil quality were monitored in the soil analysis. Auxiliary Soil Substances and Substrates – Determination of Electrical Conductivity Using a WtW inoLab Cond.; pH value according to ČSN ISO 10390 (836221) Soil quality – Determination of pH and exchange capacity according to ČSN E ISO 14254 (836223). Soil Quality – Determination of exchange acidity in extracts with barium chloride, laboratory pH meter inoLab® pH 7110. Oxidation reduction potential (ORP) was measured using an MP-6 Hach Lange multimeter in mVH units. Hydrolytic soil reaction (Ha), exchange of basic cations (S), and maximum sorption capacity of exchangeable base cations (T) were calculated.

BCR sequential extraction method

Sequential extraction can provide information about the processes that normally take place in the environment. Extraction of soil samples was performed by three-steps sequential BCR (Bureau Community of Reference) extraction. A modified version of the sequential extraction method was used according to the procedure of Pueyo et al. [6] The procedure in the individual steps is given in Table 1.

Methodology of risk metals analysis

For the analysis of the contents of hazardous metals, individual extracts of samples from the three-step sequential BCR extraction and extraction of samples from nitric acid (2.0 mol^{-1}) were used. Selected risk elements (Cr, Cu, Ni, Zn) were determined by mass spectrometry AAS (Zn) and inductively coupled plasma ICP - MS (Inductively coupled plasma mass spectrometers, X Series II, Thermo Scientific, Germany). The values were always measured 3 times, so the final values are the arithmetic means. The total metal content was determined by XRF method.

Result and Discussion

Results of physical parameters

The oxidation reduction potential ranged from +155 mV to +278 mV. The average ORP was around + 203 mV. Thus, it is the case of reduction conditions. The measured values did not have negative values, so it can be concluded that there will be no significant anaerobic processes in the soil. According to Blueberry [7], the soil environment can be evaluated as hypoxic, so it can be assumed that there will be a reduction of $FeOH_3$ and NO_3-. A characteristic feature will also be the slow decomposition of organic matter. If the ORP is increased, there may be significant oxygen loss and denitrification (nitrate reduction begins in the ORP range between +300 mV to +400 mV).

Conductivity values ranged from 741 μS cm^{-1} to 1395 μS cm^{-1}. The average value was about 1,048 μS cm^{-1}. The values exceeded the limit value for soil with a higher salt content (120 μS cm^{-1}), so we classify the soil on the Hedvika as heavily salted. As a result, there should be unfavourable conditions for plant growth and subsequent reclamation.

Soil reaction values ranged from 4.2 to 5.3. The mean value of the active soil reaction was around 5. This parameter is relatively constant in the period under review and there are no fluctuations. According to the classification of Blueberries [7] it is a strongly acidic active soil reaction. pH values from 4.2 to 5.0 may cause processes in the soil in which cation exchange capacity and basic cations from the sorption complex occur.

For the soil exchange reaction, the values varied between 4.0 and 4.8. The average soil reaction exchange rate was 4.5, a strongly acidic soil reaction. In general, the measured values of the soil exchange reaction are lower by 0.2 to 1.0 than the soil reaction. This phenomenon occurs because hydrogen protons bound in the sorption complex are also determined together with protons from the soil solution.

Potentially hydrolytic Ha soil reaction values ranged from 35.8 mmol 100 g^{-1} to 157.2 mmol 100 g^{-1}. The average value was about 72 mmol 100 g^{-1}. All Ha values are very high and outweigh the Borůvka criteria [7]. It is therefore a very strong soil reaction.

The instantaneous exchangeable base cation contents ranged from 54.7 mmol 100 g^{-1} to 66.3 mmol 100 g^{-1}. The average value was about 60.3 mmol 100 g^{-1}. These values also exceeded the table values, so this parameter can be classified as very strong.

Tab. 1. BCR sequence extraction in 1 g soil sample
Tab. 1. Ekstrakcja sekwencyjna BCR w próbce 1 g gleby

Step	**Isolated fraction**	**Reagent used**	**Volume [ml]**	**Temperature [°C]**	**Extraction time**
1	Exchange fraction and fractions bound to carbonates	0.11 M CH_3COOH	40	22 (± 5)	Shaking for 16 h
2	Fractions bound to oxides and hydroxides of Fe / Mn - reducible fraction	0.1 M $NH_2OH \cdot HCl$ acidified 2M HNO_3	40	22 (± 5)	Shaking for 16 h
3	Fractions bound to organic matter and sulfides - oxidizable fraction	8.8 M H_2O_2, pH = 2	10	22 (± 5)	Extraction 1 h
				85 (± 5)	Extraction 1 h
		1 M NH_4OAc, pH= 2	50	22 (± 5)	Shaking for 16 h

The saturation levels of the sorption complex were calculated from 78 to 94%. The average value was about 89%, and thus it is a fully saturated sample.

The maximum sorption capacity of the exchangeable basic cations was calculated as the sum of the degree of saturation of the sorption complex and the hydrolytic acidity. These values were between 63.7 mmol 100 g^{-1} and 70.4 mmol 100 g^{-1}. Due to high input values, exceeding the table values, this is a very high maximum sorption capacity.

Chemical parameters

The total chromium content was 104 mg kg^{-1} of dry matter. The nitric acid leachate was 0.47 mg kg-1 of dry matter. In the first BCR extraction step, the value was 2.07 mg kg^{-1} of dry matter, in the second step the lowest measured value was 0.25 mg kg^{-1} of dry matter. The highest value (7.27 mg kg^{-1} of dry matter) was measured in the third step analysis step. Thus, a significant amount of chromium was released from the oxidizable fraction. Under anaerobic conditions, CrIV is reduced to CrIII. Metal mobility, toxicity, binding to organic matter, or low-solubility precipitates are also reduced.

The total copper value was 32.3 mg kg^{-1} of dry matter. The highest measured value for the extract was 6.73 mg kg^{-1} of dry matter. The lowest copper content was measured for the BCR analysis fraction of 0.66 mg kg^{-1} of dry matter. In the second step, the value was 1.97 mg k^{-1} of dry matter. In the third step, the oxidizable fraction, the copper content was 3.53 mg kg^{-1} of dry matter. Due to the high leachate values and low values found in the BCR analysis, it can be assumed that copper has low mobility. This metal is not released from the soil under normal conditions. From the third step, it is apparent that copper is strongly sorbed to clay materials.

Total nickel content in soil 25.5 mg kg^{-1} of dry matter. The nitric acid extract was 2.13 mg kg^{-1}. In the first step of the sequence analysis, the nickel content was 2.23 mg kg^{-1} of dry matter, in the second step it increased to 3.00 mg kg^{-1} of dry matter. In the third step, the oxidizable fraction, the highest measured value was 3.59 mg kg^{-1} of dry matter. In acidic soil, the mobility of nickel is more pronounced, but with increasing pH, a strong affinity for organic matter is manifested. This leads to the formation of solid complexes. This corresponds to the values of the third extraction step.

The values measured for the zinc content of the individual soil fractions ranged from 4 mg kg^{-1} dry weight to 21 mg kg^{-1} dry weight. The highest measured value (21 mg kg^{-1} of dry matter) was from the leachate in nitric acid. The lowest value of 4 mg kg^{-1} of dry matter was for the sample from the first step of the sequence analysis. In the second step, the zinc value was 12 mg kg^{-1} of dry matter and in the third step 7 mg kg^{-1} of dry matter was measured. The total zinc content of the soil was 94 mg kg^{-1} of dry matter. In contrast to the other metals to be determined, zinc is likely to be reluctant in forming complexes with organic compounds.

Conclusion

It is true that soil reaction affects sorption and affects the availability and mobility of both nutrients and hazardous metals. It follows from the measured values that the soil at the back of Hedvika is acidic, and it can be assumed that the most accessible elements will be Fe, Mn, Cu and Zn. The activity of microorganisms and earthworms may slow down, resulting in deterioration of the soil structure. Furthermore, the content of bioavailable Cd, Zn and Pb will increase. In conclusion, however, it can be stated that none of the determined risk metals in the total concentration exceeded the values of the indicators from the methodological guideline of the Ministry of the Environment. However, it should be noted that these are areas with high loading with salts, which may have negative effects on vegetation growth.

Acknowledgements

This article is written as part of the projects no. CZ.11. 4.120/0.0/0.0/15_006/0000074 TERDUMP Spolupráce VŠB-TUO/GIG Katowice na průzkumu hořících hald na obou stranách společné hranice. [8]

Literatura – References

1. TRÁVNÍČKOVÁ, J. Transport kovů v systému půda/rostlina. Porovnání mody aktivního a pasivního vzorkování (technika difúzního gradientu v tenkých filmech). Brno, 2008. Dizertační práce. Vysoké učení technické v Brně, Fakulta chemická, Ústav chemie a technologie ochrany životního prostředí. Vedoucí práce Hana Dočekalová.
2. PERTILE E., SUROVKA D. a BOŽOŇ A. The study of occurrences of selected PAHs adsorbed on PM 10 particles in coal mine waste dumps Heřmanice and Hrabůvka (Czech Republic). International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM[online]. 2016, 3(BOOK 4), 161-168 [cit. 2019-03-25]. Dostupné z: https://www.scopus.com/inward/record.uri?eid=2-s2.085034781162&partnerID=40&md5=bb79daf1a214eb09cf9def3a7338d4a7
3. PERTILE E., SUROVKA D., SARČÁKOVÁ E., BOŽOŇ A. Monitoring of pollutants in an active mining Dump Ema, Czech Republic. Inzynieria Mineralna [online]. 2017, (1), 45-50 [cit. 2019-04-02]. DOI 10.29227/IM-2017-01-09. ISSN 16404920.
4. SUROVKA D., PERTILE E., DOMBEK V., VASTYL M., a LEHER V. Monitoring of Thermal and Gas Activities in Mining Dump Hedvika, Czech Republic. IOP Conference Series: Earth and Environmental Science [online]. 2017, 92 [cit. 2019-03-26]. DOI: 10.1088/1755-1315/92/1/012060. ISSN 1755-1307.
5. HÁJOVSKÝ, Radovan. Monitoring hald [online]. Ostrava: VŠB-TU Ostrava, © 2015 [cit. 2019-03-015]. Dostupné z: http://www.monitoring-hald.com/.
6. PUEYO, M., G. RAURET, D. LÜCK, M. YLI-HALLA, H. MUNTAU, Ph. QUEVAUVILLER a J. F. LÓPEZ-SÁNCHEZ. Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. Journal of Environmental Monitoring [online]. 3(2), 243-250 [cit. 2019-03-26]. DOI: 10.1039/b010235k. ISSN 14640325.
7. BORŮVKA, Luboš. Pedogeochemie. V Praze: Česká zemědělská univerzita, 2005. ISBN 80-213-1309-9.
8. TERDUMP: Spolupráce VŠB-TUO/GIG Katowice na průzkumu hořících hald na obou stranách společné hranice [online]. © 2019 [cit. 2019-03-23]. Dostupné z: https://t4.gig.eu/node/27.

Określenie składowych ryzyka na podstawie próbki gleby ze składowiska górniczego przy zastosowaniu sekwencyjnej ekstrakcji BCR

Przedmiotem artykułu jest określenie mobilności pierwiastków ryzyka w próbkach gleby termicznie aktywnego składowiska, będącego efektem działalności górniczych w regionie Ostrawy. Próbki zostały pobrane ze składowiska Hedvika w okresie 2017–2018. Ekstrakcja prób gleby została wykonana za pomocą trzystopniowej ekstrakcji sekwencyjnej BCR (Bureau Community of Reference). Ekstrakcja sekwencyjna daje informacje na temat procesów, które normalnie mają miejsce w środowisku. Składnik stały gleby jest stopniowo wypłukiwany w różnych odczynnikach ekstrakcyjnych, począwszy od najsłabszego aż do najsilniejszego. To dostarcza danych na temat ogólnej ilości pierwiastków ryzyka obecnych w określonych warunkach środowiskowych. Wybrane pierwiastki ryzyka (Cr, Cu, Ni, Zn) zostały określone za pomocą metody ICP – MS (Inductively plasma mass spectrometry) oraz AAS (atomic absorption spectrometry) (Zn). Wypłukiwanie kwasu azotowego zostało zastosowane aby uzupełnić ogólną analizę ekstrakcji BCR.

Słowa kluczowe: *analiza sekwencyjna BCR, składowisko, ICP – MS, mobilność, odpady górnicze, pierwiastki ryzyka, gleba*