Original Scientific paper
10.7251/AGRENG2301046D
UDC 504.05/06:622(437.6)

CONTENT OF RISK ELEMENTS IN TECHNOSOLS AND THEIR INFLUENCE ON SELECTED SOIL PARAMETERS

Lenka DEMKOVÁ*, Lenka BOBUĽSKÁ

Department of ecology, Faculty of humanities and natural sciences, University of Prešov, 17. novembra 1, 081 16, Prešov, Slovakia
*Corresponding author: lenka.demkova@unipo.sk

ABSTRACT

Mining bodies as remains of mining activities are a source of risk elements that contaminate individual components of the environment and may seriously danger human health. The mining area of Dubnik opal mines (Eastern Slovakia) is known for mining gold, silver, and antimony, but above all, it is a world-famous opal deposit. The study aims to determine the content of risk elements (As, Cd, Cu, Fe, Hg) in soils taken from mining bodies (6 heaps of mining material, 6 open mining pits) and to evaluate their impact on the activity of soil enzymes (urease, acid, and alkaline phosphatase, fluorescein diacetate, and β-glucosidase), nutrient content (Na, K, Mg, Ca) and soil reaction (pH). The aim of the research was also to compare the state of pollution between two types of mining bodies and the influence of pollution on selected soil characteristics. The content of hazardous substances in the soils reached extremely high and above the limit values, especially on the heaps of mining material. Urease was evaluated as the most sensitive soil enzyme while ß-glucosidase showed the highest resistance to contamination. The content of Na, K, and Mg was significantly higher on the heaps of mining material compared to open mining pits.

Keywords: *Opal mines, Soil enzymes, Former mining area, Slovakia.*

INTRODUCTION

Current and former mining activities in Slovakia focused on ore processing, have significantly affected the quality of the environment. In Slovakia, a total of 68 probable and 310 confirmed environmental loads are registered, of which 21 are sludge ponds and 78 localities are affected due to mining or processing activities. Polluted localities affect all components of the environment and the health of living organisms, including humans. Risk elements from mining activities have been shown several times to cause carcinogenic, mutagenic, and respiratory diseases (Agyemang and Duah, 2016). The spread of dust particles from heaps of the waste material, the leaching of acid mine waters and emissions from ore processing plants contribute to the reduced quality of the soil, which is nevertheless economically exploited by the population. Such contaminated soil loses its quality, which is reflected in its reduced fertility (Kelepertzis, 2014), and is also a source of

hazardous substances that enter agricultural products and are stored in the bodies of consumers (Kowalska *et al.*, 2018). Soil enzyme activity is an important indicator of soil quality because it can respond very quickly to environmental stress. Several studies have shown that increasing content of risk elements in the soil, has a negative effect on the activity of soil enzymes (Wyszkowska, 2010). For this reason, enzymes are often used as bioindicators of soil quality (Demková *et al.*, 2015). Soil enzymes are also heavily involved in the nutrient cycle in the soil and their subsequent transformation to be acceptable to plants (Li *et al.*, 2016). The nutrient content in the soil is changing very rapidly depending on external factors (Alghobar and Suresha, 2017). The object of the study was the former mining area Dubnicke opal mines. The area is characterised by a number of open mining pits and heaps of waste material.
The aim of the study was to determine the content of risk elements in soils in the Dubnicke opal mines area and their impact on the activity of soil enzymes, the content of nutrients in the soil, and the soil reaction.

MATERIAL AND METHODS

The research was realized during the summer of 2020 in the area of Dubnik opal mines (East Slovakia). Soil samples (5-15 cm) were taken from 6 heaps of waste material and 6 open mining pits. Approximately 500g of soil was taken at each sampling point, which was transported to the laboratory in plastic bags. A part of soil was frozen and then used fresh to determine soil enzyme activity. The second part of the soil was dried at room temperature and sieved through a sieve with a mesh size of 2 mm. The pH of the soil in 0.01 M $CaCl_2$ solution was determined using a pH meter inoLab pH 720 WTW. Soil urease activity (URE) was determined according to Khaziev (1976). Acid (ACF) and alkaline phosphatase (ALF) activity were determined according to Grejtovský *et al*., (1991). Fluorescein diacetate (FDA) activity was determined according to Green *et al*. (2006). *B*-glucosidase (BG) activity was determined according to Eivazi and Tabatabai (1988). The content of risk elements (As, Cd, Cu, Hg, Fe) as well as the content of nutrients (Ca, Na, Mg, K) was determined using an ICP-OES Agilent 720 instrument (Agilent Technologies, Germany). All statistical operations were performed using the R studio program (R studio Team, 2016). The data were logarithmically transformed before analysis. The Spearman's correlation coefficient was used to determine the relationship between risk elements, soil enzyme activity, nutrients, and soil reaction. Mann-Whitney U test was used to determine the differences in soil characteristics between two types of sampling sites.

RESULTS AND DISCUSSION

The content of risk elements determined at sampling localities together with the limit values (Act no. 220/2004 Coll. of Laws) is given in Table 1. The limit value of Cd, Fe, and Hg was exceeded at all sampling sites, both open mining pits and heaps of waste material. High contents of As, but also Ni were found in 2007 in the sediments of the water reservoir located in the west direction of the evaluated area (Brehuv, 2007). Pyrite (iron ore, Fe_2S) is one of the main iron ores in the area and is usually separated from precious metals as unnecessary (waste) material and is deposited on heaps of waste mining material (Willis, 2006). Salomon and Foster (1984) stated in their study that the release of Fe into the soil environment contributes to the low pH that was found on all heaps of mining material (Table 2). Arsenic is very often released from sludge, but also from dust particles that enter the air during the smelting of ores containing Cu, Zn, Pb, Au, or Ag (Molnár *et al.*, 2010).

Table 1. Descriptive statistics expressing the content of the risk elements determined at two types of mining bodies.

	Open mining pits (min-max(average±st.dev)	**Heaps of waste material** (min-max(average±st.dev)	**Limit value***
As	6.35-27.3(13.4±9.42)	5.10-464(213±189)	25
Cd	2.08-12.9(5.75±4.34)	5.31-17.2(10.9±4.82)	0.7
Cu	5.91-21.7(12.8±6.11)	6.59-38.3(22.7±12.9)	60
Fe	6708-32039(15505±10384)	15558-38737(27103±9453)	550
Hg	13.4-27.4(21.6±5.05)	32-91.2(55.1±25.7)	0.7

*Act no. 220/2004 Coll of Laws.

The soil reaction in open mining pits ranged between 3.60 to 7.42 and on the heaps between 3.20-3.40 (Table 2). According to the classification by Čurlík and Šefčík (1999), the soil in the mining pits can be characterized as extremely acidic to alkaline, while the soil on the heaps of waste material was in all cases extremely acidic. Soil enzymes showed lower activity on the heaps compared to mining pits, which is closely related to the higher content of risk elements on the heaps (Table 2.). Hinojosa *et al.* (2004) confirmed that the impact of soil pollution has a significant effect on decreasing enzyme activity. Gao *et al.* (2010) found that compared to other enzymes, soil URE and phosphatase activity responds more significantly to the presence of risk elements in the soil system.

Table 2. Descriptive statistics expressing the values of soil properties determined at mining bodies.

	Open mining pits (min-max(average±st.dev)	**Heaps of waste material** (min-max(average±st.dev)
Ca	344-3605(1543±1464)	308-2365(1272±844)
Na	211-409(303±85.1)	260-736(529±199)
K	1012-2327(1766±540)	2065-9534(5015±3244)
Mg	631-1081(879±199)	1464-4191(2614±1153)
URE	0.37-0.73(0.59±0.15)	0.07-0.22(0.13±0.06)
ACP	42.8-241(107.2±69.8)	29.1-105(74.7±32.8)
ALP	28.0-169(62.9±47.9)	32.8-96.6(63.5±26.1)
FDA	8.90-57.4(17.3±17.9)	0.00-2.44(0.81±1.15)
BG	11.7-158(101±63.8)	38.7-86.6(61.5±19.6)
pH	3.6-7.42(5.25±1.55)	3.20-3.40(3.34±0.04)

According to the results of the nonparametric Mann-Whitney U test (Table 3.), the content of Hg was significantly higher on the heaps of waste material. Other risk elements reached higher values at heaps compared to mining pits, but the differences were not significant. URE and FDA reached significantly higher values at open mining pits comparing heaps. Soil URE is closely related to the presence of plants, and both types of mining bodies are characterized by a very rare occurrence of vegetation (Polacco, 1977). The contents of other risk elements reached higher values at heaps of mining material compared to mining pits, but the differences were not significant. Heaps of mining material are highly likely to contain risk elements that pollute and threaten the surrounding environment (Rasemann, 2015), while pollution in open mining pits is often associated with water pollution - in terms of acid mine drainage waters (Singovszka *et al.*, 2016). Han *et al.* (2018), who studied the content of the soil in areas polluted by rail transport found increased content of Ca and Mg in the most polluted localities. Alghobar and Suresca (2017), who monitored soil properties under the influence of different amounts of sludge, also confirmed that while the content of K and Na did not change significantly, the content of Ca and Mg increased with increasing sludge content. In our case, the more polluted heaps of waste material showed significantly higher values of N, K and Mg comparing open mining pits.

Table 3. The results of Mann-Whitney U test expressing the differences in the risk element contents, activity of soil enzymes, soil nutrients and soil pH between two types of mining bodies.

Soil characteristics		**U**	**Z**	**p**	**Soil characteristics**		**U**	**Z**	**p**
As	Between mining bodies	12.0	-0.88	0.37	Mg	Between mining bodies	0.00	-2.72	0.001**
Cd		8.00	-1.56	0.12	URE		0.00	2.80	0.003**
Cu		8.00	-1.53	0.14	ACP		12.0	0.88	0.37
Fe		8.00	-1.52	0.12	ALP		14.0	-0.56	0.54
Hg		0.00	-2.80	0.004*	FDA		0.00	2.80	0.001**
Ca		16.0	0.24	0.80	BG		12.0	0.88	0.37
Na		6.00	-1.84	0.05*	pH		0.00	2.80	0.002**
K		4.00	-2.16	0.03*	BG		12.0	0.88	0.37

*$p<0.05$; **$p<0.01$

Correlation relationships between soil characteristics are listed in Figure 1. Risk elements correlated significantly positively between themselves (Hg correlated significantly only with As). As in the study by Árvay *et al.* (2017), also in our case, it was confirmed that the high content of risk elements has an inhibitory effect on the soil reaction. Soil pH gave a negative correlation with all evaluated heavy metals. FDA and BG correlated positively with soil pH, even URE gave a significant positive correlation with pH. ACP, ALP gave with pH negative correlation. Nutrients correlated with pH differently, while Mg, K, and Na gave with pH negative correlation, Ca correlated with pH positively. A significant positive correlation was found between nutrients and risk elements. In the case of Na, K the correlation with risk elements was significant. Between soil enzymes and risk elements, almost in all cases negative correlation was found. Additionally, URE was found the most sensitive to environmental stress. In line with our findings, Wyszkowska *et al.* (2010) have found that soil urease responded most sensitively to the presence of risk elements in the soil system. Martinez-Toledo *et al.* (2017) noted a strong correlation between the FDA, and URE, as well as between KF, AF, and BG. In our case, significant positive correlation between FDA – URE, and ACP-ALP was determined. The correlations between the other enzymes (themselves) were not significant.

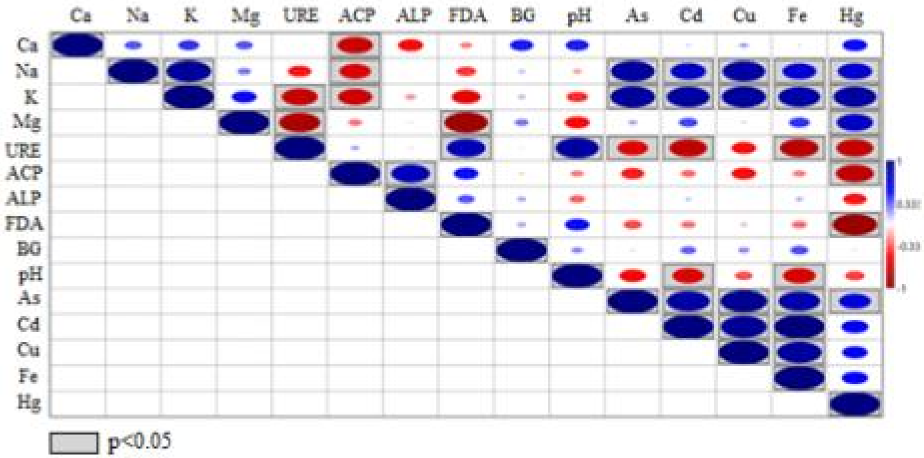

Figure 1. Correlation relationship between evaluated risk elements, nutrients, soil pH and soil enzymes (regardless the type of mining body).

CONCLUSION

The high content of risk elements in the soil environment is a serious environmental problem not only in former mining areas but also in the vicinity of industrial plants or major transport hubs. Poor soil quality has a negative effect on the quality of agricultural production, toxic substances enter the food chain and endanger human health. Among the evaluated elements, Cd, Hg, and Fe exceeded the limit values on all sampling sites. Soil enzyme activity decreased with the increasing content of risk elements in the soil, which was confirmed by the negative correlation between individual enzymes and risk elements. Soil reaction values ranged from extremely acidic to alkaline, with the lowest (most acidic) values were recorded at the most polluted heaps of waste material. The individual nutrients reacted differently to the content of hazardous substances in the soil, while the content of K and Na did not change significantly due to the influence of hazardous substances, the content of Ca and Mg reached the highest values at the most polluted sampling sites.

ACKNOWLEDGEMENT

The research was supported by the project VEGA 1/0213/22.

REFERENCES

Act no. 220/2004 Coll. Act on the protection and use of agricultural land and amending Act no. 245/2003 Coll. on Integrated Pollution Prevention and Control and on the amendment of certain laws

Agyemang-Duah, W., Yeboah, J. Y., Gyasi, R. M., Mensah, Ch. M., Arthur-Holmes, F. (2019). Mining and Public Health Implications: Evidence from the Newmont Ghana Gold Limited Enclaves. Research Journal of Applied Sciences, Engineering and Technology, Vol. (12), pages (272-281).

Alghobar, M. A., Suresha, S. (2017). Evaluation of metal accumulation in soil and tomatoes irrigated with sewage water from Mysore city, Karnataka, India. Journal of the Saudi Society of Agricultural Sciences, Vol. (16), pages 49-59.

Alghobar, M. A., Suresha, S. (2017). Evaluation of metal accumulation in soil and tomatoes irrigated with sewage water from Mysore city, Karnataka, India. Journal of the Saudi Society of Agricultural Sciences, Vol. (16), pages 49-59.

Árvay, J., Demková, L., Hauptvogl, M., Michalko, M., Bajčan, D., Stanovič, R., Tomáša, J., Hrstková, M., Trebichalský, P. (2017). Assessment of environmental and health risks in former polymetallic ore mining and smelting area, Slovakia. Spatial distribution and accumulation of mercury in four different ecosystems. Ecotoxicology and Environmental Safety, Vol. (144), pages 236–244.

Brehuv, J., Špaldon, T., Šestinová, O., Slančo, P., Hančulák, J., Bobro, M. (2007). Contamination of the Water and Sediment Load from the Drainage Basin of the Slaná River by Influence of Former and Present Mining Activities. Acta Facultatis Ecologicae, Vol. (16), pages 91–100.

Čurlík, J. Šefčík, P. (eds.) (1999). Geochemical atlas of the Slovak Republic. Part V: Soils. Soil Science and Conservation Research Institute, Bratislava, 99 pp.

Demková, L., Árvay, J., Bobuľská, L., Hauptvogl, M., Michalko, M. (2019). Activity of the soil enzymes and moss and lichen biomonitoring method used for the evaluation of soil and air pollution from tailing pond in Nižná Slaná (Slovakia). Journal of Environmental Science and Health, Part A, Vol. (54), pages 485–497.

Eivazi, F., Tabatabai, M. A. (1988). Glucosidases and Galactosidases in Soils. Soil Biology and Biochemistry, Vol. (20), pages 601–606.

Gao, Y., Zhou, P., Mao, L., Zhi, Y., Shi, W. (2010). Assessment of effects of heavy metals combined pollution on soil enzyme activities and microbial community structure: modified ecological dose-response model and PCR-RAPD. Environmental Earth Sciences, Vol. (60), pages 603–612.

Green, V. S., Stott, D. E., Diack, M. (2006). Assay for Fluorescein Diacetate Hydrolytic Activity: Optimization for Soil Samples. Soil Biology and Biochemistry, Vol. (38), pages 693–701.

Han, I., Wee, G. N., No, J. H., Lee, T. K. (2018). Pollution level and reusability of the waste soil generated from demolition of a rural railway. Environmental pollution, Vol. (240), pages 867-874.

Hinojosa, M.B., Carreira, J.A., Garcia-Ruiz, R. (2004). Soil moisture pretreatment effects on enzyme activities as indicators of heavy metal-contaminated and reclaimed soils. Soil Biology and Biochemistry, Vol. (36), pages 1599-1568.

Kelepertzis, E. (2014). Accumulation of Heavy Metals in Agricultural Soils of Mediterranean: Insights from Argolida Basin, Peloponnese, Greece. Geoderma, Vol. (221–222), pages (82–90).

Khaziev, F. K., (ed.), (1976). Soil Enzyme Activity. Moscow: Nauka.

Kowalska, J. B., Mazurek, R., Gasiorek, M., Zaleski, T. (2018). Pollution Indices as Useful Tools for the Comprehensive Evaluation of the Degree of Soil Contamination–A Review. Environmental Geochemistry and Health, Vol. (40), pages (2395–2420).

Li, J., Yang, H., Shi, X., Fan, M., Li, L. (2016). Correlations between enzymes and nutrients in soils from the Rosa sterilis S.D Shi planting bases located in karst areas if Giuzhou. Advances in Energy, Environment and materials Science, Wang and Zhao (Eds). London: Taylor & Francis Group, pages 91-96.

Martinez-Toledo, A., Montes-Rocha, A., González-Mille, D.J., Espinosa-Reyes, G., Torres-Dosal, A., Mejia, J., Ilizaliturri-Hernándze, C.A. (2017). Evaluation of enzyme activities in long-term polluted soils with mine tailing deposits of San Luis Potosi, Mexico. Journal of Soils and Sediments, Vol. (17), pages 1-12.

Molnár, F., Nagymarosy, A., Jeleň, S., Bačo, P. (2010). Minerals and wines: Tokaj Mts., Hungary and Slanské vrchy Mts., Slovakia. Acta Mineral-Petrograph Field Guide Series, Vol. (15), pages 1–40.

Polacco, J.C. (1977). Nitrogen Metabolism in Soybean Tissue Culture: II. Urea Utilization and Urease Synthesis Require NI^{2+}. *Plant Physiology*, Vol. (59), pages 827–830.

R Core Team (2016). A language and environment for statistical computing. R Foundation for Statistical Computing Vienna, Austria

Rasemann, W. (2015). Industrial wastes and waste dumps, sampling, and analysis. Encyclopaedia of Analytical Chemistry. John Wiley & Sons, Ltd.

Salomon, S.W., Forstner, U. (1984). Metals in hydrocycle. Belin: Springer-Verlag.

Willis, B.A. (2006). Mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery. Elsevier: Butterworth Heinemann, London.

Wyszkowska, J., Kucharski, J., Waldowska, E. (2002). The Influence of Diesel Contamination on Soil Enzyme Activity. Rostlinná Výroba, Vol. (48), pages 58–62.

Wyszkowska, J., Kucharski, M., Kucharski, J. (2010). Activity of beta-glucosidase, arylsulphatase and phosphatases in soil contaminated with copper. Journal of Elementology, Vol. (15), pages 213–226.