Ekológia (Bratislava) - Journal of the Institute of Landscape Ecology, Slovak Academy of Sciences Vol. 41, No. 3, p. 201–211, 2022
DOI:10.2478/eko-2022-0020

ASSESSMENT OF HEAVY METALS CONCENTRATION IN INITIAL SOILS OF POST-MINING LANDSCAPES IN KRYVYI RIH DISTRICT (UKRAINE)

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Received: 22 February 2022 / **Accepted:** 18 April 2022

Abstract

Savosko V.M., Bielyk Y.V., Lykholat Y.V., Heilmeier H.: Assesment of heavy metals concentration in initial soils of post-mining landscapes in Kryvyi Rih District (Ukraine). Ekológia (Bratislava), Vol. 41, No. 3, p. 201–211, 2022.

Assessment of heavy metals content in the initial soils of the post-mining landscapes plays an important role in pollution control, ecological protection, and safe-guarding human health. In this study, the site-specific pedogeochemical background contents of several metals in soils in Kryvyi Rih Iron Ore Mining & Metallurgical District (central part of Ukraine) were determined. The metal concentrations in the soils of Petrovsky waste rock dump were also quantified and were also assessed using indices of pollution. The field sampling was carried out at a depth of 0-10 cm in five plots in dump area and in one plot in control site. The 43 soil samples were collected. The results showed that local background concentrations of heavy metals in soils of studied area decreased in the following order (mg×kg^{-1}): Fe (42 510) > Mn (761.7) > Cr (94.48) > Zn (90.51) > > As (31.85) > Cu (28.10) > Pb (18.73) > Co (16.21) > Sn (4.64) > Mo (0.28) > Cd (0.16). In the initial soils of devastated lands at Petrovsky waste rock dumps the predominance of increased Cd, Co, Fe, Mm, Mo and Sn content and the predominance of decreased As, Cr and Pb content were observed. Based on the mean values of the individual indices of pollution (Pollution index, Geoaccumulation index, Enrichment factor, Contamination factor) can be assumed that in these soils As, Cd, Fe, Mo, Pb and Sn are mostly coming from industrial activities. Co, Cr, Cu, Mn and Zn are mostly related to their natural occurrence in devastated lands. The values of integrated indices of pollution (Nemerow pollution index, Pollution load index, Degree of contaminated, Modified degree of contamination) indicated that the initial soils of post-mining landscapes can be evaluated as no polluted – and extremely heavy polluted.

Key words: landscape ecology, environmental chemistry, devastated lands, indices of pollution, iron ore mining area, waste rock dumps.

Introduction

Historically, the iron mining operations produce several types of the waste materials, such as a low grade ore, waste rock and overburden. This material is commonly drilled, blasted and hauled to a permanent storage location of in the dumps named as 'the waste rock dumps'. Generally, these man-made landforms are large and represent complex geotechnical structures and are usually the most visually obvious post-mining landscapes left after open pit (Demkova et al., 2017; Izakovicova, Petrovic, 2018; Savosko et al., 2018; van der Sluis et al., 2019). Numerous researchers have convincingly proven that waste rock dumps have a strong and negative impact on the environment. Moreover, in many countries, especially in developing countries, environmental, social and stabilization issues have not been considered as an integral part in mining (Fazekas et al., 2018; Savosko et al., 2020b, 2021; Sediva, Izakovicova, 2015; Urminska et al., 2019).

According to interpretation of satellite images results (by applying the automated geospatial and geometric operations and approximating the geographical coordinates of more than 600 active mining sites in the word), across the globe mining area, post-mining landscapes and waste rock dumps add up to (10^9 ha) 5.73. 8.25 and 3.21, respectively (Maus et al., 2020). *I*n Europe the largest waste rock dumps areas are in Germany, Poland, Greece, the Czech Republic and Romania, spanning an area (10^3 ha) of 27.8, 14.4, 10.9, 8.8, and 8.7, respectively *(August et al., 2021; Maus et al., 2020). Based on an interpretation of satellite images results and our calculation results (according to environmental passports of all regions)* in Ukraine, the waste rock dumps covers an area of 43.48*10^3 ha, account for 1.38% of the worlds' dump area *(Zhukov et al., 2021; Zverkovskyy et al., 2018).*

In Kryvyi Rih Iron Ore Mining & Metallurgical District (central part of Ukraine) the waste rock dumps spread over an area of 7.10*10^3 ha (accounts for 15.96 % of the Ukraine dumps area). Finally, the waste rock dumps cause a wide range of environmental social and problems around the world in Ukraine and in Kryvyi Rih District (Bielyk et al., 2020; Gryshko et al., 2012; Savosko, 2016; Savosko, Tovstolyak, 2017; Savosko et al., 2020a). Therefore, it is essential., to carry out and adopt an effective system for stabilization of the waste rock dumps area and better environmental protection of the surrounding areas.

Different approaches to stabilization of waste rock dumps areas have been tested, including remediation, restoration, rehabilitation and reclamation. At this time, many authors *noted* that remediation, restoration and rehabilitation are all aspects of reclamation (de San Miguel et al., 2019; Savosko et al., 2020a; Zhukov et al., 2021; Zverkovskyy et al., 2018). We also need to emphasize that the reclamation of the dumps is very costly and often ecologically insufficient in the post-mining landscapes where natural revegetation had been started. Thereforeit is necessary to look for new technologies to stabilization of waste rock dumps.

Numerous studies confirmed that revegetation is the most efficient, effective and widely accepted way to environmental stabilization of waste rock dumps in post-mining areas. The scholars and experts indicated that a sustainable vegetation cover can cause many positive on the dumps (de Lima, Mendanha, 2019; Zverkovskyy et al., 2018; Zhukov et al., 2021; Urminska et al., 2019). But, the practical application of revegetation techniques is very difficult for the following reasons: (i) high cost of the implementation; (ii) long-term preparation and (iii) potential limitations of material availability (Lacy, 2019; Raizada, Dhyani, 2020; Stanturf et al., 2021; Vriens et al., 2020). That is the reason the direct planting of a tolerant plant species becomes more important.

Previous research has shown that, most young post-mining landscapes have a moderately favourable physical structure and little favourable chemical composition as a result of the high content of toxic elements (such as As, Cd, Cr, Pb and Sn) and a short time of weathering work. The natural restoration of plant and an initial soil formation occur on post-mining activity areas (Angst et al., 2018; Mhlongo et al., 2019; Savosko, Alekseeva, 2007). In post-mining landscapes, the speed of soil-forming processes depends both on properties of the pattern materials/the type of vegetation and have very little value from 1.5 to 3.5 mm*year^{-1} (Angst et al., 2018; Gwenzi, 2021; Savosko, 2010). Finally, properties of initial soils as well as heavy metal concentrations are often adverse and pose constraints for revegetation establishment (Savosko et al., 2010, 2018; Sinnett et al., 2020). Therefore, it is necessary to assess the the heavy metals content in the initials of the devastated land in waste rock dumps.

In recent years, the quality of the soil polluted by heavy metals can be evaluated by several criteria such as absolute content of metals tests, ecotoxicological tests or bioindicators and statistical practice. However, the methods do not provide comprehensive information on the degree of soil pollution. Moreover, there is no generally accepted algorithm to identify the degree of soil pollution. One of the perspective methods for comprehensive evaluation of the degree of heavy metals content in initial soils of the devastated land at waste rock dumps is the use of indices of pollution. At present, the the most commonly used indices are Pollution index, Geoaccumulation Index, Enrichment factor, Contamination factor, Nemerow pollution index, Pollution load index, Degree of Contamination and Modified degree of contamination. These indices can also help to determine the heavy metal contents in initial soils due to the result of anthropogenic activities or due to natural processes (Holtra, Zamorska-Wojdyla, 2020; Kowalska et al., 2018; Mazurek et al., 2017).

According to previous studies, knowledge on the heavy metal content and assessment in initial soils in post-mining landscapes play a important role in pollution control, ecological protection and safe-guarding human health (Baghaie, Aghili, 2019; Demkova et al., 2017; Gryshko et al., 2012). In the past several decades, the main pattern of heavy metals in soils in mining areas is well understood. However, only very few publications have considered heavy metals concentrations and assessment in initial soils of the devastated lands in waste rocke dumps. That is the reason it is essential to evaluate the contamination with heavy metals of the initial soils, and consequently, a new paper of these main asesments is clearly needed. Therefore, the objectives of this study were (i) to determine the site-specific pedogeochemical background contents of As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb and Sn in soils in the Kryvyi Rih District, central part of Ukraine; (ii) to quantify the heavy metals contents in the initial soil of waste rock dumps in the study area; (iii) to assess the heavy metals concentration in the initial soil of waste rock dumps in the study area using individual and integrated indices of pollution.

Material and methods

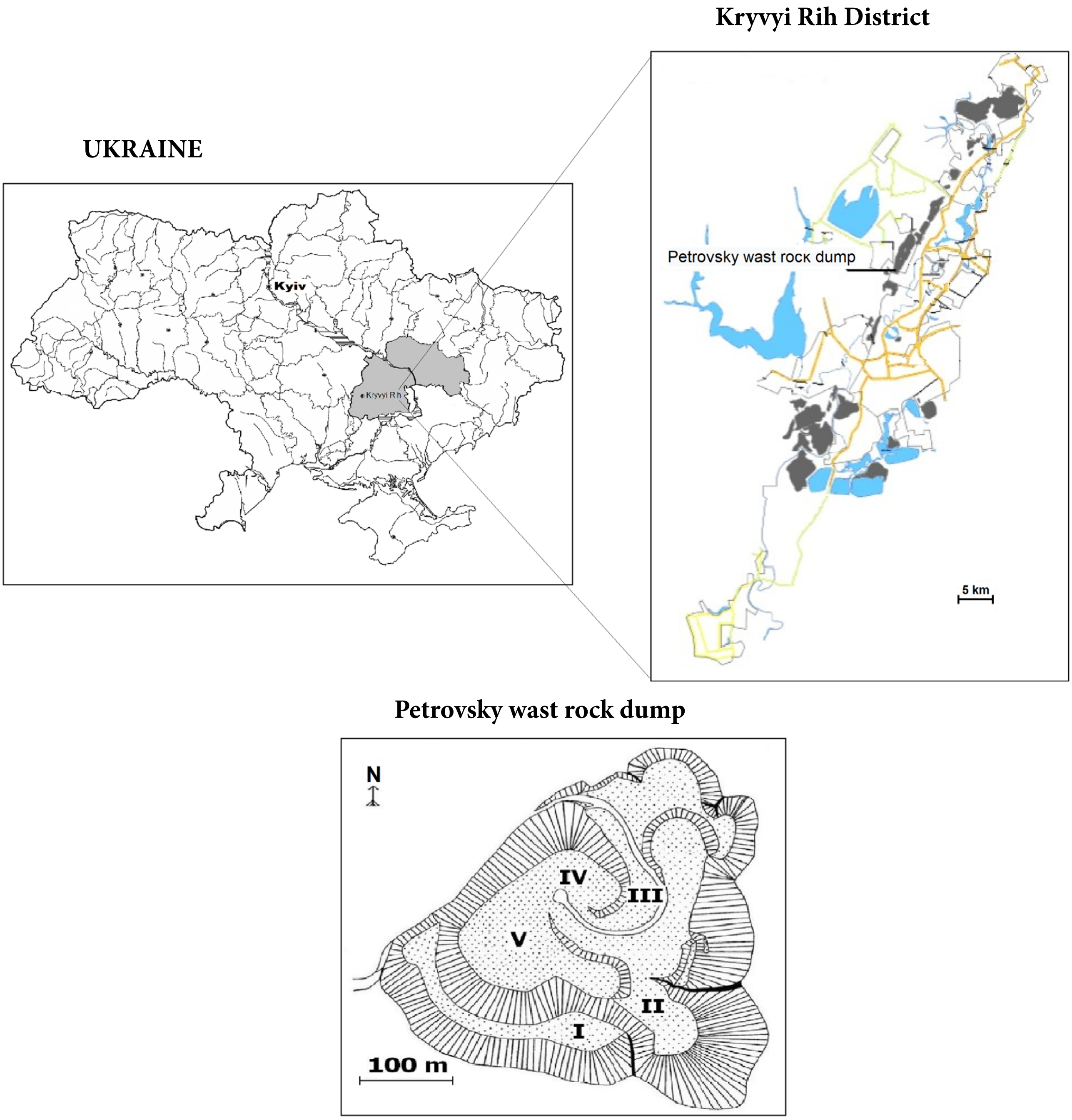
Study area

Kryvyi Rih Iron Ore Mining & Metallurgical District, Central Ukraine, was chosen for the present study. It is situated between 47°53’54” and 48°8’52” north latitude and 33°19’52” and 33°33’38” west longitude. The dominant soil type is Haplic Chernozems according to the FAO recommendations (IUSS Working Group WRB, 2015) or Chernozems Ordinary according to the Genetic Soil Classification of Ukraine (Polupan et al., 2005) or Mollisols according to the USA taxonomy (Soil Survey Staff, 2014).

The study area was located at the central part of Kryvyi Rih District in Petrovsky waste rock dump (Fig. 1) and was situated in the vicinity of Tsentralnyi Ore Mining and Processing Plant. It was in use since this quarry construction in 1960 and until 1965. This dump contained 5 834 000 m^3 of the waste (iron waste rock and overburden) on approximately 15.94 ha (Bielyk et al., 2020). These rocks was consisted of coarse, crushed or blocky material covering a range ofsizes, from very large boulders to fine sand-size particles and dust. The rehabilitation work of Petrovsky dump area was not performed. Now the revegetation and soil formation process occur on this dump.

Sampling site

The test plot study was designed to evaluate all factors controlling the initial soil formation, i.e. chemical/physical rock properties


UKRAINE

Kryvyi Rih District

Petrovsky wast rock dump

Fig. 1. Sketch of the study area (Legend: I, II, III, IV and V – sample plots).

and rock pile geometry, plant communities, topograthy, local microclimate conditions and time. The five sample plots were selected based on this information. The natural local background was used as a control level. The control area was distant from any industrial activities, urban area and major road but was stationed within the natural geochemical anomaly of district (Savosko, 2016). The control site located at a distance of 30 km from Kryvyi Rih City on natural ecosystems of the Gurivsky forest (Kirovograd region).

Sampling

The soil samples were taken in five plots in Petrovsky waste rock dump area and in one plot in control site. At each plot, 7-8 soil sub-samples (to obtain a representative sample) were collected from the top layer at a depth of 0-10 cm in accordance with classical sampling techniques and to ISO methodology (ISO 18400-203, 2018). In total, 43 soil samples were collected.

Table 1. Individual and Integrated indices of pollution used in this study.

Index	Formula and explanations	Limit values
Pollution index (PI) (Single pollution index)	$\mathrm{PI}=\frac{C}{B}$ C – metal content in soil from contaminated areas, B – metal content in soil from control site (Kowalska et al., 2018).	(i) low polluted (PI < 1), (ii) moderate polluted (1 ≤ PI < 3), (iii) considerable polluted (3 ≤ PI < 6), (iv) very high polluted (PI ≥ 6), (Hakanson, 1980).
Geo-accumulation index (I_{geo})	$\mathrm{Igeo}=\log_2\left(\frac{C}{1{,}5B}\right)$ C – metal content in soil from contaminated areas, B – metal content in soil from control site, 1,5 – the constant which represents the natural fluctuations (Mazurek et al., 2017).	(i) practically not unpolluted (Igeo<0), (ii) practically not unpolluted to moderately polluted (0≤Igeo<1), (iii) moderately polluted (1≤Igeo<2), (iv) moderately to highly polluted (2≤Igeo<3), (v) highly polluted (3≤Igeo<4), (vi) highly to extremely highly polluted (4≤ Igeo<5), (vii) extremely highly polluted (Igeo≥5), (Muller, 1969).
Enrichment factor (EF)	$\mathrm{EF}=\frac{\mathrm{C/Fe(c)}}{\mathrm{B/Fe(b)}}$ C – metal content in soil from contaminated areas, B – metal content in soil from control site, Fe(c) – Fe content in soil from contaminated areas, Fe(b) – Fe content in soil from control site (Mazurek et al., 2017).	(i) minimal polluted (EF<2), (ii) moderate polluted (2<EF<5), (iii) significant polluted (5<EF<20), (iv) very high polluted (20<EF<40), (v) extremely high polluted (EF>40), (Sutherland, 2000).
Contamination factor (CF)	$\mathrm{CF}=\frac{C}{Cpic}$ C – metal content in soil from contaminated areas, Cpic – pre-industrial concentration of individual metal (Hakanson, 1980).	(i) low polluted (Cf<1), (ii) moderate polluted (1<Cf<3), (iii) considerable polluted (3<Cf<6), (iv) very high polluted (Cf>6), (Holtra, Zamorska-Wojdyła, 2020).
Nemerow pollution index (PI_{nem})	$\mathrm{PInem}=\sqrt{\frac{\left(1/m\sum_{i=1}^{m}\mathrm{PI}\right)^2+(\mathrm{PImax})^2}{m}}$ PI – pollution index of individual heavy metals, PI max – maximum value of pollution index of all heavy metals, m – number of studied heavy metals (Kowalska et al., 2018; Mazurek et al., 2017).	(i) clean (PI nem≤0.1), (ii) warning limit (0.7≤PI nem<1), (iii) slight polluted (1≤PI nem<2), (iv) moderate polluted (2≤PI nem<3), (v) heavy polluted (PI nem≥3) (Kowalska et al., 2018).
Pollution load index (PLI)	$PLI=(PI1^2 * PI2^2 * PIm^2)^1/m$ PI – pollution index of individual heavy metals, m – number of studied heavy metals. (Tomlinson et al., 1980).	(i) no polluted (LPI<1), (ii) moderate polluted (1≤LPI<2), (iii) heavy polluted (2≤LPI<3) (v) extremely heavy polluted (PLI>3) (Holtra, Zamorska-Wojdyła, 2020).
Degree of contamination (C_d)	$\mathrm{Cd}=\sum_{i=1}^{i=n} Cfi$ Cfi – contamination factor of individual metal, n – number of studied heavy metals, (Holtra, Zamorska-Wojdyła, 2020).	(i) low degree of polluted (Cd<n), (ii) moderate degree of polluted (n<Cd<2n), (iii) considerable degree of polluted (2n<Cd<4n), (iv) very high degree of polluted (Cd>4n), (Holtra, Zamorska-Wojdyła, 2020).
Modified degree of contamination (mC_d)	$\mathrm{mCd}=\frac{Cd}{n}$ Cd – degree of contamination, n – number of studied heavy metals (Holtra, Zamorska-Wojdyła, 2020).	(i) nil to very low degree of polluted (mCd<1.5), (ii) low degree of polluted (1.5<mCd<2), (iii) moderate degree of polluted (2<mCd<4), (iv) high degree of polluted (4<mCd<8), (v) very high degree of polluted (4<mCd<8), (vi) extremely high degree of polluted (16<mCd<32), (vii) ultra high degree of polluted (mCd>32), (Holtra, Zamorska-Wojdyła, 2020).

Analytical methods

The soil samples were air-dried at 25 °C, grounded in a ceramic mortar, passed through a 2-mm plastic sieve (in order to remove large debris, stone, gravel, plant materials and other waste materials) and kept in polyethylene packages till analysis according to ISO methodology (ISO 11464, 2015).

The soil samples were analyzed in terms of total forms of As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sn and Zn. In order to determine the total content of these metals, 20 mg of a mixture of Na_2CO_3 and K_2CO_3 (ratio 1:1) was added to 100 mg of the soil sample and mixed thoroughly. The resulting mixture was placed in a muffle furnace and kept at a temperature of 700 °C for 5 hours. The cooled samples were dissolved in a mixture of acids (HF and HCl) and an aliquot was taken (Pansu, Jacques, 2006).

The content of heavy metals was determined using a ICP-MS X-Series 2 (Thermo Fisher Scientific, USA) – an inductively coupled plasma atomic emission spectrophotometer. The laboratory studies were carried out in Institute of Biosciences, Freiberg University of Technology and Mining Academy (Freiberg, Germany).

Statistical analysis

The results were statistically analysed using the descriptive statistics. The differences between mean values of features from waste rock dump and control were tested by a student's t-test for independent variables (at $p = 0.05$) (McDonald, 2014).

Pollution indices calculation and assessment

In this study, the individual (Pollution index, Geoaccumulation index, Enrichment factor, Contamination factor) and the integrated (Nemerow pollution index, Pollution load index, Degree of Contamination, Modified degree of contamination) indexes of pollution were used. These indexes were determined and were classified according to the classic approach as demonstrated in Table 1.

Results and discussion

Natural background concentrations of heavy metals in soils

Assessment of heavy metals contents in initial soils in post-mining landscapes requires that a natural background level be established as a reference point. That is why the accurate analysis of a local background sample is very important (Alfaro et al., 2015; Ander et al., 2013).

Data about heavy metals contents control sites of Kryvyi Rih District were already partially presented in our previous publications (Savosko et al., 2021). The local background concentrations of these elements and the representative descriptive statistics are summarized in Table 2. The heavy metal levels varied (mg×kg^{-1}) 30.98-35.03, 0.11-0.19, 12.21-20.84, 81.19-110.86, 26.60-30.15, 39 2400-47 513.00, 705.84-810.79, 0.21-0.34, 17.00-21.85 and 3.56-5.09 for As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, and Sn, respectively. The concentrations of these metals decreased in the following order: Fe (42 510.50) > Mn (761.70) > Cr (94.48) > Zn (90.51) > As (31.85) > Cu (28.10) > > Pb (18.73) > Co (16.21) > Sn (4.64) > Mo (0.28) > Cd (0.16) (mg×kg^{-1}).

According to obtained results, the least and the highest coefficient of variation (CV) for metals contents in soils from a background area were obtained for Cu (4.72%) and Cd (23.52%), respectively. Low CV was recorded for Cu, Zn, As, Mn, Pb and Fe (CV of between 5.04 and 8.88% – weak variability), moderately varied (CV of between 10.05 and 23.52% – medium variability) in Sn, Cr, Co, Mo and Cd content. The Co, Mo and Cd had a relatively high CV of 17.24, 21.47 and 23.52 %, respectively, which could be linked to geochemical features of parent and low levels concentration of these metals in continental crust.

Skewness and kurtosis were calculated for the studied heavy metals to perform the test of normality for each of them (Table 2). The values of skewness for heavy metals content varied from -1.77 (Sn) to 2.16 (As) with an average of 0.22. The Sn, Mn, Cd,

Table 2. Natural background concentrations of heavy metals in soils at Kryvyi Rih Iron Ore Mining & Metallurgical District (central part of Ukraine).

Descriptive statistics	**Heavy metals concentrations, mg×kg^{-1} dry weight**										
	As	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Mo**	**Pb**	**Sn**	**Zn**
M	31,85	0.16	16.21	94.48	28.10	42 510.00	761.70	0.27	19.73	4.64	90.51
Me	31,00	0.18	18.00	95.00	28.00	40 001.00	775.00	0.28	20.90	4.80	89.10
m	0.51	0.01	0.93	4.30	0.44	1 258.33	13.58	0.02	0.57	0.16	1.44
SD	1.54	0.04	2.79	12.89	1.33	3 775.00	40.75	0.06	1.71	0.47	4.31
CV	4.85	23.52	17.24	13.64	4.72	8.88	5.35	21.47	8.67	10.05	4.76
Min	30.98	0.11	12.21	81.19	26.84	39 245.00	705.84	0.21	17.80	3.56	84.62
Q1	31.00	0.12	15.00	82.00	27.00	40 000.00	718.00	0.22	18.00	4.60	87.40
Q3	31.50	0.19	18.00	109.30	29.00	47 000.00	800.00	0.33	21.00	4.90	94.10
Max	35.03	0.19	20.84	110.86	30.15	48 000.00	810.79	0.34	21.85	5.09	98.25
Skewness	1.69	-0.27	0.20	0.30	0.68	0.83	-0.31	-0.04	-0.17	-1.79	0.55
Kurtosis	1.43	-2.46	-0.63	-1.95	-1.21	-1.64	-1.76	-2.39	-2.36	3.56	-0.41

Notes: M – Mean; Me – Median; m – Standard Error of Mean; SD – Standard Deviation; CV – Coefficient of Variation; Min – Minimum Value of Sampling; Q1 – 1st quartile; Q3 – 3rt quartile; Max – Maximum Value of Sampling.

Pb and Mo data are negatively skewed apart. The Co, Cr, Zn, Cu, Fe and As data are positively skewed apart. According to Bulmer (1979), the distributions of Mn, Cd, Pb, Mo, Co and Cr are 'fairly symmetrical' (skewness in absolute value is between 0 and 0.5). The distributions of Zn, Cu and Fe are 'moderately symmetrical' (skewness in absolute value is between 0.5 and 1.0).

The distributions of Sn and As are 'highly skew' (skewness in absolute value is more than 1.0). This is important to recognize as it gives a a measure of how far from a normal distribution that these samples are and indicates that for each sample there is a distinctive distribution of data points. That is, the values for Cd and Mo are strongly skewed towards lower values.

The values of kurtosis (Table 2) for heavy metals content varied from -2.46 (Cd) to 3.56 (Sn) with an average of -0.89. The Cd, Mo, Pb, Cr, Mn, Fe, Cu, Co and Zn datasets have negative kurtosis values, showing that the tails of the distribution are of less weight than those found in a normal distribution but when compared to the normal distribution indicating a relatively 'peaked distribution'. The As and Sn datasets have positive kurtosis values showing that the 'outliers' are of minimal significance relative to the whole dataset and indicating a relatively 'flat distribution' (Bulmer, 1979).

Therefore, the kurtosis and skewness assessment facilitated the understanding of heavy metals content, such as elements distribution in background soil at Kryvyi Rih District, as compared with previous studies. Lastly, it appears that Sn and As contents in the soil are rarely normally distributed with skewness statistics often greater than 1,0.

The comparison of natural background heavy metals concentrations in soils with worldwide soils (Kabata-Pendias, 2011) has indicated that these soil contents of As, Co, Fe and Zn were higher than those values recorded for all the countries (Table 2). However, Cd and Mo values were lower than those values of world's soils. On the other hand, the Cr, Cu, Mn, Pb and Sn concentrations were within the range of average values of worldwide soils (Kabata-Pendias, 2011). Such patterns can be explained by geochemical features of the rocks composition and pattern material in the Kryvyi Rih District.

Heavy metals concentrations in initial soil of devastated lands

The summary of descriptive statistics for heavy metals concentrations in initial soils of devastated lands at Kryvyi Rih Iron Ore Mining & Metallurgical District is shown in Table 3.

Data about heavy metals contents in this area were already partially presented in our previous publications (Savosko et al., 2021). The range and averaged values of metal contents (mg×kg^{-1}) in initial soils are: As, 10.50 – 1 412.33 (533.75); Cd 0.15 – 1.06 (0.57); Co, 12.65 – 29.07 (22.53); Cr, 25,67 – 106.44 (73.06); Cu, 23.89 – 339.70 (134.49); Fe, 49 858.67 – 118 205,60 (95 129.65); Mn, 179.28 – 1 339.00 (794.51); Mo, 0.51 – 2.46 (1.44); Pb, 8.52 – 26.20 (13.73); Sn, 2.37 – 17.10 (7.38) and Zn, 74.34 – 137.60 (92.73).

Mean concentration of metals in the area from highest to lowest was recorded in the following pattern: Fe > Mn > As > Cu > Zn > Cr > Co > Pb > Sn > > Mo > Cd. This model was different from the one obtained at the control site (with the exception of Fe, Mn, Sn, Mo and Cd). This phenomenon is quite natural and is explained by the pedogeochemical features of initial soils in the devastated lands.

In the initial soils of the devastated lands at Petrovsky waste rock dumps, only an increased content of Cd, Co, Fe and Mo was revealed. The concentration of these metals were about 1.5-5.9 times higher than the background values. The soil As, Cr, Cu, Mn, Pb, Sn and Zn concentrations were slightly lower on some plots when compared to the control. Therefore, similar results were expected and finally confirmed.

Based on the our results from Table 3, in the initial soil of devastated lands, the CV values of metal content ranged from 21.13 (Co) to 124.13% (As) with an average of 50.60 %. In this study weak variability (CV < 10 %) was not obtained. The medium variability (CV of between 10 % and 100 %) was found for Co, Zn, Fe, Pb, Cr, Mo,

Table 3. Heavy metals concentrations in initial soil of devastated lands at Petrovsky waste rock dump (Kryvyi Rih District, central par of Ukraine).

Descriptive statistics	**Heavy metals concentrations, mg×kg^{-1} dry weight**										
	As	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Mo**	**Pb**	**Sn**	**Zn**
M	533.75	0.57	22.53	73.06	134.49	95 129.65	794.51	1.44	13.73	7.38	92.73
Me	17.92	0.56	22.84	80.43	31.79	101 859.20	911.04	1.45	13.15	6.76	84.37
m	171.07	0.07	1.23	6.57	35,31	5 513.41	87.68	0.15	1.15	1.28	5,18
SD	1 240.33	0.20	28.41	106.44	339.70	118 205,60	1 339.00	2.27	15,04	2.73	81.86
CV	124.13	47.06	21.13	34.83	101.68	22.45	42.74	41.56	32.51	67.03	21.64
Min	10.50	0.15	12.65	25.67	23.89	49 858.67	179.28	0.51	8.52	2.37	74.34
Q1	11.20	0.44	20.32	65.96	27.78	92 021.14	724.46	1.15	10.44	3.86	79.57
Q3	1 231.17	0.69	25.41	90.39	264.73	110 980.00	981.95	1.79	14.86	7.55	95.13
Max	1 412.33	1.06	29.07	106.44	339.70	118 205,60	1 339.00	2.46	26.20	17.10	137.60
Skewness	0.48	0.06	-0.63	-0.88	0.56	-1.23	-0.90	0.12	1.66	1.12	1.39
Kurtosis	-2.02	-0.38	-0.13	-0.26	-1.80	0.38	0.17	-0.76	3.52	0.10	0.70

Notes: M – Mean Me – Median; m – Standard Error of Mean; SD – Standard Deviation; CV – Coefficient of Variation; Min – Minimum Value of Sampling; Q1 – 1st quartile; Q3 – 3rt quartile; Max – Maximum Value of Sampling.

Table 4. Individual indices of pollution in initial soil of devastated lands at Petrovsky waste rock dump (Kryvyi Rih District, central part of Ukraine).

Heavy metal	**Sample plots**									
	I	**II**	**III**	**IV**	**V**	**I**	**II**	**III**	**IV**	**V**
	Pollution index					**Geoaccumulation index**				
As	44.14	0.56	0.33	0.35	38.37	4.88	-1.41	-2.16	-2.08	4.68
Cd	3.94	3.81	2.94	5.94	1.13	1.39	1.35	0.97	1.98	-0.42
Co	1.34	0.94	1.55	1.51	1.58	-0.16	-0.68	0.05	0.01	0.08
Cr	0.77	0.31	0.87	0.92	1.04	-0.95	-2.26	-0.79	-0.70	-0.53
Cu	0.47	0.37	0.50	0.66	0.47	-1.67	-2.02	-1.59	-1.18	-1.68
Fe	2.45	2.44	2.38	1.34	2.62	0.71	0.70	0.67	-0.16	0.80
Mn	0.26	1.16	1.23	1.33	1.35	-2.52	-0.37	-0.29	-0.18	-0.15
Mo	6.79	4.50	4.14	4.07	5.96	2.18	1.58	1.47	1.44	1.99
Pb	13.76	1.60	1.61	1.34	17.60	3.20	0.10	0.11	-0.16	3.55
Sn	3.50	0.84	1.52	1.52	5,30	1.22	-0.83	0.02	0.02	1.82
Zn	1.04	0.85	0.93	1.41	0.88	-0.53	-0.82	-0.69	-0.09	-0.77
	Enrichment factor					**Contamination factor**				
As	18.04	0.23	0.14	0.26	14.67	187.47	2.39	1.42	1.51	162.93
Cd	1.61	1.56	1.23	4.43	0.43	6.30	6.10	4.70	9.50	1.80
Co	0.55	0.38	0.65	1.13	0.61	2.18	1.52	2.52	2.45	2.57
Cr	0.32	0.13	0.37	0.69	0.40	0.81	0.33	0.91	0.97	1.09
Cu	0.19	0.15	0.21	0.49	0.18	0.66	0.52	0.70	0.93	0.66
Fe	1.00	1.00	1.00	1.00	1.00	3.47	3.46	3.37	1.90	3.71
Mn	0.11	0.48	0.52	0.99	0.52	0.40	1.77	1.87	2.02	2.06
Mo	2.77	1.84	1.74	3.04	2.28	12.67	8.40	7.73	7.60	11.13
Pb	5.62	0.66	0.68	1.00	6.73	17.18	2.00	2.02	1.67	21.97
Sn	1.43	0.35	0.64	1.14	2.03	6.49	1.57	2.82	2.83	9.84
Zn	0.42	0.35	0.39	1.05	0.34	1.56	1.28	1.41	2.12	1.32

Mn, Cd and Sn concentration in initial soils. The strong variability (CV > 100 %) was observed for Cu and As content.

The values of skewness for heavy metals concentrations ranged from -1.23 (Fe) to 1.66 (Pb) with an average of 0.16. In this case, the Fe, Mn, Cr and Co data are negatively skewed apart. Likewise, the Cd, Mo, As, Cu, Sn, Zn and Pb data are positively skewed apart. It has been found that the distributions of Cd, Mo and As are 'fairly symmetrical' (skewness in absolute value is between 0 and 0.5). The distributions of Mn, Cr, Co and Cu are 'moderately symmetrical' (skewness in absolute value is between 0.5 and 1.0). The distributions of Fe, Sn, Zn and Pb are 'highly skew' (skewness in absolute value is more than 1.0). In the initial soils of devastated lands the values of kurtosis for heavy metals concentrations ranged from -2.02 (As) to 3.52 (Pb) with an average of -0.04. The As, Cu, Mo, Cd, Cr and Co datasets have negative kurtosis values indicating a relatively 'peaked distribution'. The Sn, Mn, Fe, Zn and Pb datasets have positive kurtosis value indicating a relatively 'flat distribution'.

Finally, the results of this study can support the point of view that initial soils of devastated lands are young soils and that linked to weathering, soil formation and ecosystems development during the last last 50-60-year period (Sparks, 2002).

Individual indices of pollution

Pollution index (PI) is the easiest to calculate and helpful in the assessment of the most dangerous heavy metals within the studied elements (Kowalska et al., 2018). Moreover, this index is also used in the calculation of several integrated indices of pollution such as Nemerow pollution index and Pollution load index (Table 1).

In the initial soils of devastated lands at *Petrovsky* waste rock dump, the PI values varied from 0.26 to 44.14 with an average of 3.83 (Table 4). This index indicated that levels of contamination can be categorized into four classes: low polluted (32.73 % of samples), moderate polluted (41.82 %), considerable polluted (16.36 %) and very high polluted (9.09 %). The mean contamination levels of the heavy metals were in the order of As > Pb > Mo > Cd > Sn > Fe > Co > Mn > Zn > Cr >Cu and the sample plots therefore ranked, in descending order, as I > V > IV > III > II. Finally, the calculated PI shown that within the studied sample plots the most contaminated were the plot I (PI_{As} = 44.14; PI_{Mo} = 6.79; PI_{Pb} = 13.76) and the plot V (PI_{As} = 38.37; PI_{Pb} = 17.60).

Geoaccumulation index (I_{geo}) is also popular and commonly used for the assessment of soil pollution by heavy metals. This index was introduced by Muller (1969) to assess the level of metal accumulation in the sediments and has been used by a large number of scholars for sediments, rocks and soils (Muller, 1969). In the initial soils of devastated lands the means of I_{geo} values ranged between -2.52 and 4.88 (an average 0.17). This index indicated that samples can be categorized only into six classes: practically not unpolluted (52.73% of samples), practically not unpolluted to moderately polluted (21.82%), moderately polluted (16.36%), moderately to highly polluted (1.82%), highly pol-

Table 5. Integrated indices of pollution in initial soil of devastated lands at Petrovsky waste rock dump (Kryvyi Rih District, central par of Ukraine).

Index	**Sample plots**				
	I	**II**	**III**	**IV**	**V**
Nemerow pollution index	44.72	4.77	4.45	4.47	38.99
Pollution load index	5.97	1.25	1.69	1.96	7.33
Degree of contamination	239.18	29.34	29.46	33.50	219.08
Modified degree of contamination	21.74	2.67	2.68	3.05	19.92

luted (3.64%) and highly to extremely highly polluted (3.64%). The category extremely highly polluted was absent.

In the initial soils of devastated lands at *Petrovsky* waste rock dump, the main I_{geo} values were found in the order of Mo > Pb > Cd > As > Fe > Sn > Co > Zn > Mn > Cr > > Cu. The levels of pollution in different sample plots were in the order: V > I > > IV > III > II. As in previews case, the most contaminated were the plot I ($I_{geo}As = 4.88$; $I_{geo}Pb = 3.20$) and the plot V ($I_{geo}As = 4.68$; $I_{geo}Pb = 3.55$).

Enrichment factor (EF) is an effective tool for the comprehensive evaluation of the degree of soil contamination as well as the possible impact of anthropogenic activities on metal concentrations in the soils. The EF is given by standardization of a tested metal against a reference element (Sc, Mn, Al, Fe and Ca) with low occurrence variability (Dolezalova Weissmannova, Pavlovsky, 2017). In our study, Fe was used as a conservative tracer to differentiate natural from anthropogenic components (Table 1).

The results suggest that in the initial soils of devastated lands at Petrovsky waste rock dump, the values of EF fluctuated between 0.11 and 18.04 with an average of 1.66 (Table 4). The means of this index manifested that soil contamination levels can be categorized only into three classes: minimal polluted (83.64% of samples), moderate polluted (9.09%) and significant polluted (7.27%). In this study, the classes very high polluted and extremely high polluted were absent. On the grounds of mean EF levels, the studied metals were generally in the order of As > Pb > Mo > Cd > Sn > Fe > Co > > Mn > Zn > Cr > Cu and the sample plots were in the following order I > V > IV > > III > II. As in previous cases, the most polluted heavy metals were the plot I ($EF_{As} = 18.04$; $EF_{Pb} = 5.62$) and the plot V ($EF_{As} = 14.67$; $EF_{Pb} = 6.73$).

Contamination factor (CF) is not popular and not a much used index for the assessment of the soil contamination with heavy metals. The CF is defined as ratio of metal concentration in the pollution soil and metal background concentration. As the background concentration, metals content in Earth's crust, average upper continental crust, baseline values (mean worldwide soils) were used. In the present study, average heavy metals content in the Earth's crust had been used as the pre-industrial concentrations and is considered as a reference value for the evaluation of soil pollution by metals (Hakanson, 1980; Loska et al., 2004). On the whole, the background levels (preindustrial concentrations) for heavy metals were are 7.5 (As), 0.1 (Cd), 10 (Co), 90 (Cr), 20 (Cu), 30 000 (Fe), 500 (Mn), 0.15 (Mo), 15 (Pb), 2.5 (Sn) and 60 (Zn) $mg \times kg^{-1}$.

In the initial soils of devastated lands, the means values of CF were observed from 0.33 to 187.47, with an average of 10.01. CF indicated that levels of soil pollution can be classified into four categories: low polluted (18.18% of samples), moderate polluted (47.27%), considerable polluted (9.09%) and very high polluted (25.45%).

According to the mean values of CF the metals were in the order: As > Mo > > Pb > Cd > Sn > Fe > Co > Mn > Zn > Cr > Cu and the sample plots were in the order: I > V > IV > III > II. The mean CF shown that within the studied sample plots, the most polluted were the plot I ($CF_{As} = 187.47$; $CF_{Mo} = 12.67$; $CF_{Pb} = 17.18$) and the plot V ($CF_{As} = 162.93$; $CF_{Mo} = 11.13$; $CF_{Pb} = 21.97$).

Finally, based on the average values of individual indices of pollution the initial soils of devastated lands at *Petrovsky* waste rock dump were classified as very highly contaminated with As, Cd, and Pb; considerably contaminated with Fe, Mo and Sn and lower contaminated with Co, Cr, Cu, Mn and Zn. This observation agrees with earlier studies of Baghaie, Aghili (2019), Demkova et al., (2021) and Cheng (2019), who reported that the presence of heavy metals in soils remains at a serious level in the mining and post-mining landscapes.

Integrated indices of pollution

Nemerow pollution index (PI_{nem}) is the most popular among the integral indices of pollution. This index allows the assessment of soils pollution by heavy metals, also assesses the soil quality with using five classes and includes the contents of all the analyzed metals (Hakanson, 1980; Holtra, Zamorska-Wojdyla, 2020; Loska et al., 2004).

The results of calculation shown that in the initial soils of devastated lands at *Petrovsky* waste rock dump, the PI_{nem} values flocculated between 4.45 and 44.72 with an average of 19.48 (Table 5). The means of this index indicated that the initial soil can be classified only into one category: extremely heavy polluted. Based on the levels of contamination the sample plots were generally in the order of (V > I) >> (II > IV > III).

Pollution load index (PLI) is also popular and commonly used in environmental investigation to prioritization of areas with respect to quality of soils and to assess the level of environmental contamination by heavy metals in order to undertake monitoring. This index is the geometric average of the pollution indexes and and determines the contribution of all metals in studied sites. PLI provides simple but effective means for identification of the pollution of soils (Hakanson, 1980; Loska et al., 2004). In the initial soils of devastated lands the values of LPI were observed from 1.25 to 7.33, with an average of 3.64. The means of PLI manifested that levels of soil pollution can be classified only into two categories: no polluted (sample plots II, III and IV) and extremely heavy polluted (sample plots I and V). According to the PLI values, the sample plots in the area from highest to lowest were recorded in the following pattern: (V > I) >> (IV > III > II).

Degree of contaminated (C_d) was proposed by L. Hakanson (1980) to facilitate the aquatic pollution control as a new tool. This index is defined as a sum of contamination factors of the all heavy metals for each soil sample. In the initial soil, the values of C_d were from 29.34 to 239.18 with an average of 29.34 (Table 5).

The values of C_d demonstrated that sample plots II, III and IV fell beneath Class I (low degree of polluted) and the sample plots I and V fell beneath Class IV (very high degree of polluted). The order of the C_d values of the sample plots was (V > > I) >> >> (IV>III>II).

Modified degree of contamination (mC_d) was first used by Abrahin, Parker (2008) as modification of 'Degree of Contamination'. This index is the average value of C_d for all heavy metals, provided that at least three metals are used in the calculations (Abrahim, Parker, 2008). In the initial soils mC_d values were observed from 2.67 to 21.74, with an average of 10.10 (Table 4). Our results placed sample plots into Class III 'Moderate degree of polluted' (plots II, III and IV) and Class VI 'Extremely high degree of polluted' (plots I and V). The value of mC_d was found in the order of (V > I) >> (IV > III > II).

Therefore, the values of integrated indices of pollution indicated that the soil samples can be evaluated as no polluted – moderate degree of polluted (samples plots II, III and IV) and extremely heavy polluted – very high degree of polluted (samples plots I and V). According to the values of these indices of pollution, the sample plots in the area from highest to lowest were recorded in the pattern: (V > I) >> (IV > III > II).

The local background concentrations of heavy metals in soils in Kryvyi Rih District decreased in the following order: Fe (42 510) > Mn (761.7) > Cr (94.48) > > Zn (90.51) > As (31.85) > Cu (28.10) > Pb (18.73) > Co (16.21) > Sn (4.64) > > Mo (0.28) > Cd (0.16) (average values in parentheses, mg×kg^{-1}). The singularity of this pattern is: (i) Cr, Cu, Pb and Sn concentrations are within the range of *worldwide soils* values; (ii) Cd and Mo contents are lower than those values; (iii) for As, Co, Fe, Mn and Zn mean are higher than those values.

It should also be noted that in Kryvyi Rih District, there is a local geochemical anomaly that coincides closely with the up-rake projections of the principal iron ore shoots. The scholars suggest that this anomaly corresponds to the surface trace of channels through which migrating the weathering products. As a result, this anomaly is characterized by high concentrations of Fe and its accompanying chemical elements (Mn, Zn, As and Co) in groundwater, pattern material and consequently in soils. This conclusion are in agreement with previous studies, which demonstrated that highly significant correlations ($p<0.01$) were found between heavy metals (such as Pb, Mn, Zn, Cr, Sb and Co) and Fe content in background soils of Cuba (Alfaro at al., 2015).

In the initial of devastated lands at Petrovsky waste rock dumps in comparison with background values, there were an increased and a decreased concentration of heavy metals. The predominance of increased Cd, Co, Fe, Mm, Mo and Sn content and the predominance of decreased As, Cr and Pb content were observed. The slightly higher (about 1.2-1.6 times) than background values are contents: Co in plot I; Mn in plot II; Co, Fe, Mn, Sn and Zn in plot III; Cd, Co and Mn in plot IV and Co and Mn in plot V. The moderate higher (about 2.5-9.2 times) than background values are contents: Cd, Fe, Cu, Mo and Sn in plot I; Cd, Fe and Mn plots II and III; Cd and Mo in plot IV and Fe and Mo in plot V. The extra higher (about 40-44 times) than background values are contents: As in plots I and V, such effects were reported earlier in literature and one possible explanation for this is that initial soils of the devastated lands are geologically not sustainable because they were formed on variegated pattern materials.

The integrated indices of pollution also were calculated based on local (PI_{nem}, PLI) and reference (C_d, mC_d) backgrounds. The results of our study concur with the findings of previous research who reported that the initials soils are not homogenized (Sparks, 2002; Kabata-Pendias, 2011). As such, the values of all these indexes demonstrated that this soil in sample plots I and V was assessed as very high polluted by studied heavy metals. Contamination assessment according to evaluation on the PLI, C_d and mC_d indexes showed that levels of metals in samples from sample plots II, III and IV were evaluated only as moderate polluted. Our results provide good examples of the possible use of the individual and integrated indexes of pollution in environmental studies for the assessment of soil contamination.

Conclusion

The local background concentrations of heavy metals in soils of Kryvyi Rih Iron Ore Mining & Metallurgical District decreased in the following order (mg×kg^{-1}): Fe (42 510) > Mn (761.7) > Cr (94.48) > Zn (90.51) > As (31.85) > Cu (28.10) > Pb (18.73) > > Co (16.21) > Sn (4.64) > Mo (0.28) > Cd (0.16). In the initial soils of devastated lands at Petrovsky waste rock dumps in comparison with background values the predominance of increased Cd, Co, Fe, Mm, Mo and Sn content and the predominance of decreased As, Cr and Pb content were observed. Based on mean values of the individual indices of pollution, it can be assumed that in these soils As, Cd, Fe, Mo, Pb and Sn are mostly coming from industrial activities. Co, Cr, Cu, Mn and Zn are mostly related to their natural occurrence in devastated lands. The values of integrated indices of pollution indicated that the initial soils of post-mining landscapes can be evaluated as no polluted – extremely heavy polluted.

Acknowledgements

The authors are grateful to the DAAD program "Scientific Cooperation with Universities in Developing Countries" for the opportunity to perform analytical work on the basis of the laboratory of the Institute of Biosciences, Freiberg University of Technology and Mining Academy (Freiberg, Germany).

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