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The impact of forest plant communities on the content of heavy metals in soil profiles of the iron ore mining area, Kryvyi Rih District, Ukraine

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Abstract

The plant-soil interaction plays an important role in maintaining negative effects of soil pollution by heavy metals (HMs). Understanding HMs spatial variability in soils under plant communities is fundamental for soil restoration and predicting contamination by these elements. In this study, HMs content was estimated based on a soil survey conducted in Kryvyi Rih Iron Ore Mining and Metallurgical District, central Ukraine. The distribution of trace metals within a soil profile and their impacts on forest, steppe and agricultural land plant communities were also assessed. During field work, samples were collected from the whole soil profile (in 10 cm layers down to the parent rock). In total, 21 soil pits were sampled and 273 soil samples were collected. The contents of mobile Fe, Mn and Zn were assessed. The results showed that there was a specific pattern of HMs distribution in soil profile at the local background site of Kryvyi Rih District. The accumulation of HMs in soils in the vicinity of an iron ore mining and processing plant was found. Application of individual and integral indices of pollution demonstrated that Fe, Mn and Zn content was related to mining activity. The plant communities had a great impact on the HMs content in soils. According to the values of individual and integrated indices of pollution the plant communities form the following order: agricultural communities > forest communities > steppe communities. The forest plant communities, due to the presence of organic acids in forest leaf litter, promote the mobilization of heavy metals and may contribute to input of Fe, Mn and Zn irons to deeper soil layers. The differences observed between the plant communities located in the contaminated areas provide useful insight clues into the role and relative importance of major factors determining HMs contents in soil.

Keywords: plant communities, soil, plant-soil interactions, trace metals, indices of contamination, iron ore mining

Introduction

Plant communities in natural and planted forests ("forest phytocenoses") play a key role in mitigating the negative effects of industrialization and climate change (Faucon et al. 2016, Burns et al. 2017, Straigyte et al. 2019, Savosko et al. 2020b). Besides, the forest communities provide important ecosystem functions and services such as regulating carbon, nutrient and water cycles, providing timber for industries, wildlife habitat and opportunities for recreation, etc. (Savosko et al. 2018, Jogiste et al. 2020, Stanturf et al. 2021).

For decades, many researchers have focused on the multi-causal relationships and plant-soil feedbacks between plant communities and soil (Ehrenfeld et al. 2005, Li et al. 2017, Savosko and Tovstolyak 2017). On the one hand, forest soil properties have a significant impact on the richness and diversity of plants, the structure and dynamics of plant communities and the development of terrestrial flora (O'Neill et al. 2005, Bardule et al. 2017, Urbina et al. 2017, Savosko et al. 2018). On the other hand, plants as a primary factor in soil development, determine the most important soil properties that affect soil resistance to the degradation and pollution as well as sustainable development of soil (Straigyte et al. 2019, Naik et al. 2020, Pankiv et al. 2020). Finally, the plant-soil interactions are a prominent component of the plant communities that responds to environmental impact. However, little information is available regarding ecological relationships between forest communities and content of contaminants within the soil profile.

Numerous studies have revealed that in terrestrial ecosystems soil is the main store of many environmental contaminants such as trace metals (Gryshko et al. 2012, Baghaie and Aghili 2019, Kasiuliene et al. 2019, Savosko et al. 2021a). Heavy metals (HMs) are non-degradable and persistent components, therefore their presence in soil is very stable and very long-lasting (Demkova et al. 2017, Savosko et al. 2021b, Stofejova et al. 2021). Accumulation of HMs in soils have presented many problems for agricultural industry, food chains, biosphere functions and human health (Gryshko et al. 2012, Savosko 2016, Baghaie and Aghili 2019, Wang et al. 2020). The HMs in the soil are derived from the parent material and various anthropogenic sources, such as agriculture, urbanization and industrialization including mining (Demkova et al. 2017, Yi and Cheng 2019, Wang et al. 2020, Savosko et al. 2021a).

Modern mining activities are particularly recognized as important sources of HMs pollution due to the presence of high levels of metals in dust emissions (Demkova et al. 2017, Wang et al. 2020, Stofejova et al. 2021). All mining operations can emit huge amounts of airborne particles, usually as fugitive dust. After sedimentation, dust interacts with soil and causes accumulation of HMs in soil in the vicinity of mining areas (Demkova et al. 2017, Yi and Cheng 2019, Savosko et al. 2020a).

In most cases, the quality of soil polluted by HMs can be evaluated by several criteria such as absolute concentrations of HMs as a result of chemical tests, data of ecotoxicological tests or the use of bioindicators, as well as statistical methods (Loska at al. 2004, Baghaie et al. 2019, Wang et al. 2020). However, these methods do not provide a comprehensive information on the degree of soil contamination. Moreover, no generally accepted algorithm to identify the degree of soil pollution exists. One of the perspective methods for a comprehensive evaluation of the degree of HMs accumulation in soil is to use indices of pollution.

The most used indices are Pollution Index (PI), Geoaccumulation Index (Igeo), Enrichment Factor (EF), Nemerow Pollution Index (PI nem), Pollution Load Index (PLI) and Sum of Pollution Index (PI sm). These indices can also help to determine the accumulation of HMs in the result of anthropogenic activities as well as to estimate environmental risks (Dolezalova Weissmannova and Pavlovsky 2017, Mazurek et al. 2017, Kowalska et al. 2018).

According to the previous studies, the plant-soil interactions and the plant-soil feedbacks play a key role in mitigating the negative effects of an environmental pollution by HMs. During the previous decades, the main patterns of relationships between the plant communities and the soil media are well-studied. However, only very few publications have considered the possible impact of the forest on the content of pollutants within the soil profile.

Therefore, it is essential to evaluate the soil contamination with HMs under different plant communities. The objectives of this study were: (i) to quantify the local natural background level of mobile Fe, Mn and Zn forms in the soil profiles in Kryvyi Rih District, central part of Ukraine; (ii) to assess the soil pollution by mobile Fe, Mn and Zn in the vicinity of the Iron Ore Mining and Processing Plant using indices of pollution; and (iii) to determine the impact of the forest communities on the contents of Fe, Mn and Zn mobile forms within the soil profiles.

Material and methods

Study area

Kryvyi Rih Iron Ore Mining and Metallurgical District, central Ukraine, was chosen for this study (Figure 1). It is situated between 47°53’54” N and 48°8’52” N and 33°19’52” E and 33°33’38” E at the elevation of 80–120 m a.s.l. BSE. The climate of this area is characterized by short springs, hot and dry summers and cold winters with short-term snow cover. The monthly mean air temperature ranged from –3,5°C (in January) to 21,8°C (in July). The mean annual precipitation is from 400 to 450 mm (Gryshko et al. 2012).

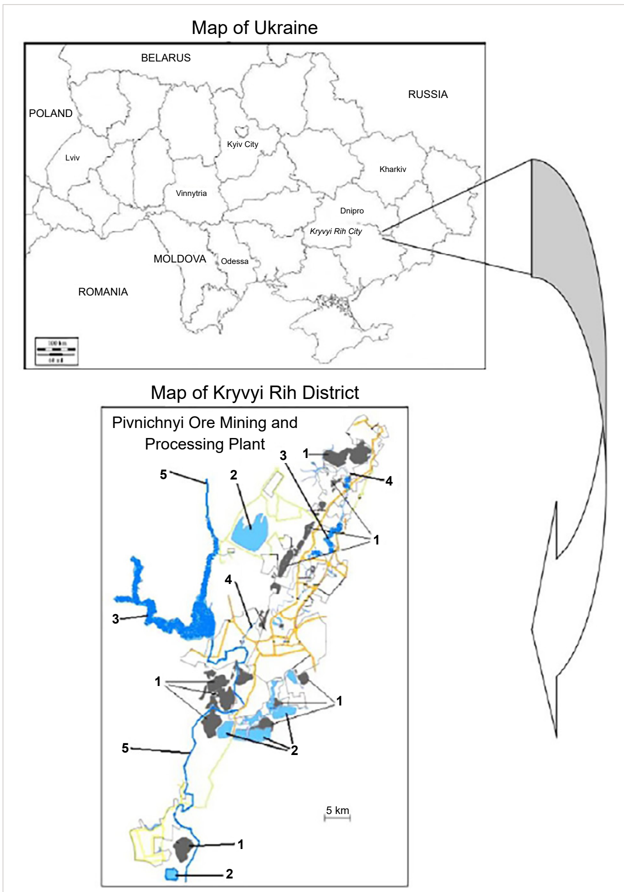

Figure 1. Sketch of the study area

Legend: 1 – quarry and waste rock dumps, 2 – tailing ponds, 3 – water storage reservoir, 4 – Saksagan river, 5 – Ingulets river.

The study area is situated at the northern part of Kryvyi Rih District in the vicinity of Pivnichnyi Ore Mining and Processing Plant. This is one of the largest iron ore mining enterprises in Europe, specializing in iron ore mining ($25–3·10^6$ t yr^{-1}) and production of iron ore concentrate ($12–15·10^6$ t yr^{-1}) and iron ore pellets ($7–10·10^6$ t yr^{-1}). The level of dust emissions from mining operations and from devastated lands (waste rock dumps, tailing ponds and quarry) was defined as $30·10^3$ t yr^{-1} (Gryshko et al. 2012, Savosko 2016, Bielyk et al. 2020).

In the northern part of Kryvyi Rih District, 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 *Chernozems's* soil profile is characterized by three soil horizons designated as: a humus surface horizon (Ah 0–30 cm), an illuvial subsoil horizon (Bk 60–90 cm) and a weathered horizon (Ck from 130 cm) and two intermediate layers: ABk (30–60 cm) and BCk (90–130 cm). The dominant texture of the *Chernozems Ordinary* is clay loam. The average humus concentrations in the soil profile ranged from 0.4–0.5% (in weathered horizon Ck) to 4.5–4.6% (in humus surface horizon Ah). Soils have pH H_2O and pH KCl values between 7.5 and 7.1 (in horizon Ck) and 7.1 and 6.5 (in horizon Ah), respectively.

Field sampling and soil analysis

The sampling was employed in two locations. Location I (Loc I) was characterized by a minimal input of metals to soil: from 0,040 to 10 000 mg m^{-2} yr^{-1}. Location II (Loc II) was characterized by maximal input of metals to soil: from 0,120 to 30 000 mg m^{-2} yr^{-1} (Savosko 2016).

In each location, three sub-locations were chosen. Sub-location A was selected in a planted forest – forest communities (FCs); sub-location B was selected in a natural grassland – steppe communities (SCs); and sub-location C was selected in a corn plantation – agricultural communities (ACs).

English oak (*Quercus robur* L.), European white elm (*Ulmus laevis* Pall.), European field elm (*Ulmus minor* Mill.), sycamore maple (*Acer pseudoplatanus* L.), black locust (*Robinia pseudoacacia* L.), European ash (*Fraxinus excelsior* L.), and honey locust (*Gleditsia triacanthos* L.) are the dominant tree species grown in forest plantations. The age of the forest is between 60 and 70 years (middle-aged-mature stand).

The local background concentrations of heavy metals were used as a control. The background area was distant from any industrial activities, urban areas and major roads but was located within the natural geochemical anomaly of the district. The control site was located 30 km from Kryvyi Rih city in a native steppe ecosystem in the proximity of natural Hurivskyi forest, Kirovohrad region (Savosko 2016).

In each sub-location (study plot), a soil pit was dug up to the depth of C-horizons. The soil samples were taken from topsoil up to 130 cm deep every 10 cm (ISO 2018). In total, 21 soil pits were sampled and 273 soil samples were collected.

The soil samples were air-dried, grounded in a ceramic mortar, and passed through a 2-mm plastic sieve (ISO 2015). For extracting, the soil samples (2 g) were digested with 20 mL mol L^{-1} nitric acid for 0.25 hours at 150°C. The digest was filtered through paper filter, made up to 25 mL (Sparks 2002). The concentrations of Fe, Mn, Zn in extracts were determined by the flame atomic absorption spectrophotometer (EPA 2007).

Data analyses and calculations

The results were statistically analysed with the descriptive statistics. The differences between mean values of features from locations and sub-locations were tested by Student's *t*-test for independent variables ($p < 0.05$) (McDonald 2014).

In this study the individual and integrated indices of soil pollution were calculated/defined. These indices were determined and classified according to the standard approach (Table 1).

Results

According to the obtained results, in the background site the content of Fe ranged from 636.54 to 1,348.51 mg kg^{-1} with an average of 1,184.23 ± 86.02 mg kg^{-1} within the soil profile (Figure 2). The maximum content of Fe was observed in the first intermediate layer (ABk). Notably, the content of this metal in soils ranked, in descending order, as ABk > Ah > Bk > Bck. The Fe distribution patterns in the soil profiles under different plant communities were different. Thus, under FCs content of Fe in horizons Ah, ABk, Bk and BCk were higher than the control values by 31–61%, 48–63%, 110–134% and 117–128%, respectively. Under SCs the concentrations of this metal only in surface horizons Ah and ABk were higher than background levels by 122–168% and 163–124%, respectively. Under ACs Fe content in horizons Ah, ABk and Bk were higher than the control values by 239–283%, 117–131% and 92–164%, respectively. According to means values of Fe content, the plant communities therefore ranked, in descending order, as ACs > FCs > SCs. Based on the average Fe values, it can be stated that the Fe content of 67% of soil samples at Loc II were higher by 11–46% than those at Loc I.

In the background site the Mn contents varied from 106.39 to 305.77 mg kg^{-1} with an average of 208.30 ± 23.26 mg kg^{-1} (Figure 3). Like in the previous case, the maximum value of this metal was found in layer ABk. According to Mn mean values the soil horizons ranked in the following order: ABk > Ah > Bk > BCk.

Results showed that under different plant communities, differences between the measurements of this pa-

Table 1. General information about indices of pollution

Index	Formula and explanations	Categories
	Individual indices of pollution	
Pollution Index (PI) (Single Pollution Index, Contamination Factor)	$$PI = \frac{C}{B}$$ C – metal content in soil horizon from contaminated areas, B – metal content in that soil horizon from background site (Kowalska et al. 2018)	(i) little polluted (PI < 1), (ii) moderately polluted (1 ≤ PI < 3), (iii) considerably polluted (3 ≤ PI < 6), (iv) very highly polluted (PI ≥ 6) (Hakanson 1980)
Geo-accumulation Index (Igeo)	$$Igeo = \log_2 \frac{C}{1.5B}$$ C – metal content in soil horizon from contaminated areas, B – metal content in that soil horizon from background site, 1,5 – the constant which represents natural fuctuations (Mazurek et al. 2017)	(i) practically unpolluted (Igeo < 0), (ii) practically 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)	$$EF = \frac{\frac{C}{Fe}}{\frac{B}{Fe}}$$ C – metal content in soil horizon from contaminated areas, B – metal content in that soil horizon from background site, Fe – iron content in that soil horizon from background site (Mazurek et al. 2017)	(i) minimally polluted (EF < 2), (ii) moderately polluted (2 < EF < 5), (iii) significantly polluted (5 < EF < 20), (iv) very highly polluted (20 < EF < 40), (v) extremely highly polluted (EF > 40) (Sutherland 2000)
	Integrated indices of pollution	
Nemerow Pollution Index (PI nem)	$$PInem = \sqrt{\frac{\left(1/m\sum_{i-1}^{m} PI\right)^2 + (PImax)^2}{m}}$$ PI – pollution index of particular heavy metals, PI max – maximum value of pollution index of all heavy metals, m – number of studied heavy metals (Mazurek et al. 2017, Kowalska et al. 2018)	(i) clean (PI nem ≤ 0.1), (ii) warning limit (0.7 ≤ PI nem < 1), (iii) slightly polluted (1 ≤ PI nem < 2), (iv) moderately polluted (2 ≤ PI nem < 3), (v) heavily polluted (PI nem ≥ 3) (Kowalska et al. 2016)
Pollution load index (PLI)	$$PLI = \left(PI1^2 \quad PI2^2 ... PIm^2\right)^{\frac{1}{m}}$$ PI – pollution index of particular heavy metals, m – number of studied heavy metals (Tomlinson et al. 1980)	(i) no polluted (LPI < 1), (ii) moderately polluted (1 ≤ LPI < 2), (iii) heavily polluted (2 ≤ LPI < 3) (iv) extremely heavy polluted (PLI > 3) (Holtra et al. 2020)
Sum of Pollution Index (PI sm)	$$Psm = \sum_{i-1}^{m} C$$ C – metal content in soil horizon from contaminated areas, m – number of studied heavy metals (Kowalska et al. 2016)	PI sm was used in soil quality assessment by heavy metals such as degree of contamination and as potential ecological risk index. But there are no limit values (Kowalska et al. 2016, Dolezalova Weissmannova and Pavlovsky 2017)

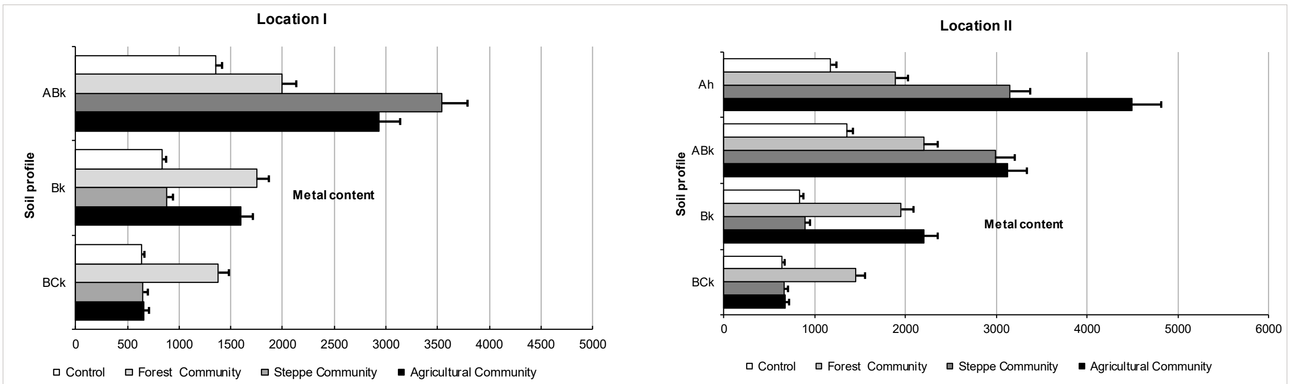

Figure 2. Iron content in soil profile under different plant communities

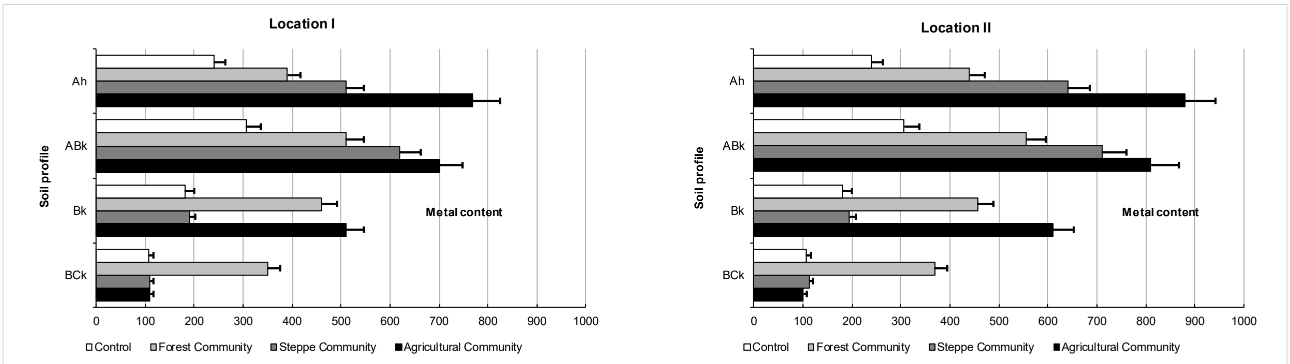

Figure 3. Manganese content in soil profile under different plant communities

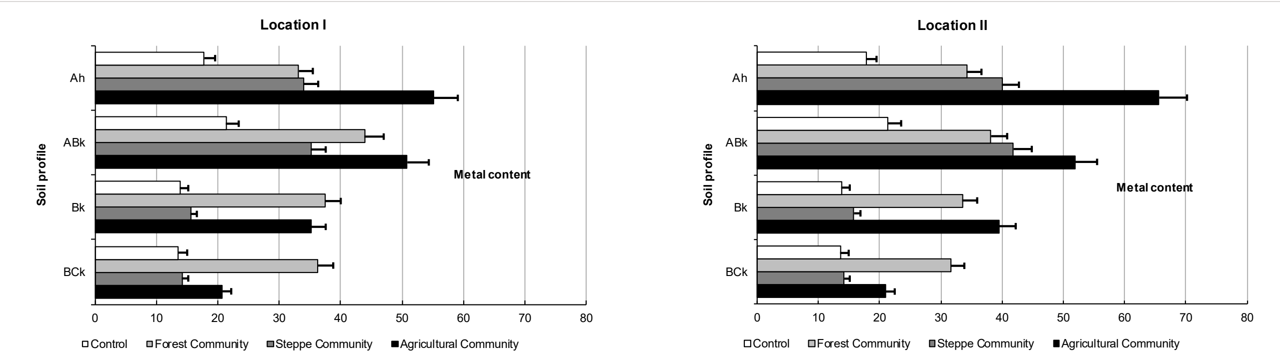

Figure 4. Zinc content in soil profile under different plant communities

rameter were significant. The levels of Mn in horizons Ah, ABk, Bk and BCk under FCs were found to be greater than the reference value by 63–84%, 67–82%, 154–153% and 229– 247%, respectively. Under SCs, the content of this metal was higher than control levels only in the surface Ah and ABk horizons by 113–167% and 103–132%, respectively. Under ACs, the Mn concentration in the Ah, ABk and Bk horizons was higher than background values by 221–167%, 129–132% and 181–237%, respectively. The plant communities by Mn levels in the soil ranked in the following order: ACs > FCs > SCs. The results demonstrate that in 75% of soil samples concentrations of this metal were higher by 15–85% at Loc II than at Loc I. At the same time, in horizons Bk under FCs, Bk and BCk under SCs no significant differences were observed between the mean contents of Mn throughout areas Loc I and Loc II.

The result of our study in the control site revealed that Zn contents in the soils ranged from 13.60 to 21.33 mg kg^{-1} with an average of 16.63 ± 1.29 mg kg^{-1} (Figure 4). As in the previous cases, the maximum concentration of Zn was detected in the ABk horizon. The soil horizons by mean value of Zn in the area from highest to lowest were recorded in the following order: ABk > Ah > Bk > BCk. Zn content in the soil profiles differed under different plant communities. Thus, under FCs the amounts of Zn accumulated in horizons Ah, ABk, Bk and BCk were higher than in the control by 86–93%, 107–79%, 171–143% and 167–139%, respectively. Under SCs the concentrations of this metal were higher than background values only in horizons Ah, ABk and BCk by 91–125%, 65–96% and 13–14%, respectively. Under ACs the Zn content in the horizons Ah, ABk and Bk were higher than in the control by 210–269%, 138– 143% and 154–186%, respectively. The plant communities by mean levels of Zn in soil ranked in the following order: ACs > FCs > SCs. The Zn values in soil profiles between Loc I and Loc II also differed significantly. Thus, only in 33% soil samples contents of this metal at Loc II were higher than at Loc I (by 31–58%). At the same time, in the ABk, Bk and BCk horizons under FC zinc concentrations at Loc II were lower than at Loc I (by 27–35%). The levels of Zn in horizons Bk and BCk under SCs, ABk and BCk under ACs did not differ significantly between Loc I and Loc II.

According to the data analyses (Tables 2–4), the PI values of all soil samples varied from 0.46 to 3.83 with an average of 1.93. The PI values indicated that levels of contamination can be categorized only into three classes: (i) little polluted (16.67% of samples), (ii) moderately polluted (72.22% of samples) and (iii) considerably polluted (11.11% of samples). In this study, the class of very high pollution was absent.

The values of PI in soil under plant communities fluctuated between 1.18 and 2.71 (average 1.86), 0.46 and 3.02 (average 1.59) and 0.46 and 3.83 (average 2.33) in the soil under FCs, SCs and ACs, respectively. The values of this index were categorized under Class II: 100% of samples at FCs, 62.50% of samples at SCs and 54.17% of samples at ACs.

According to mean values of PI, the plant communities therefore ranked, in descending order, as ACs > FCs >

SCs. The mean levels of PI in the soil samples were found to be 1.85 (ranged between 0.46 and 3.39) and 2.00 (ranged between 0.47 and 3.39), respectively, for soil on Loc I and Loc II. Most PI values were categorized under Class II for both locations (in 77.22% of samples).

The Igeo values of all soil samples varied from 0.55 to 3.83 with an average of 1.33 (Tables 2–4). The Igeo values indicated that samples can be categorized only into three classes: practically unpolluted (23.61% of samples), practically unpolluted to moderately polluted (63.89% of samples) and moderately polluted (12.50% of samples). In this study, classes moderately to highly polluted, highly polluted, highly to extremely highly polluted and extremely highly polluted were absent. The Igeo levels varied from –0.19 to 1.21 (with an average of 0.47), from 0.55 to 0.84 (with an average of 0.03) and from –0.54 to 1.35 (with an average of 0.62) for soil under FCs, SCs and ACs, respectively. Most of the soil samples belonged to Class II: 83.33% under FCs, 50.00% under SCs and 55.33% under ACs. Overall, the soil pollution levels under the plant communities ranked in the following order: ACs > FCs > SCs. The Igeo values observed in the soils at Loc I varied from –0.55 to 1.18 with an average of 0.31 while those in the soil at Loc II ranged from –0.53 to 1.35 with an average of 0.44. The majority of Igeo values were categorized under Class II: 61.11% of samples at Loc I and 66.67% of samples at Loc II.

The values of EF in all soil samples fluctuated between 0.55 and 3.83 with an average of 1.93 (Tables 2–4). The values of this index manifested that contamination levels observed in the soil samples studied can be categorized only into two classes: minimally polluted (88.99% of samples) and moderately polluted (11.11% of samples). In this study, the classes of significantly polluted, very highly polluted and extremely highly polluted were absent. The EF values varied from 1.02 to 1.87 with an average of 1.32,

Table 2. Individual indices of iron pollution in soil under different plant communities

Soil horizon	Plant community	Pollution Index		Geoaccumulation Index		Enrichment Factor	
		Loc I	Loc II	Loc I	Loc II	Loc I	Loc II
Ah	Forest	1.31	1.61	–0.19	0.10	1.31	1.61
	Steppe	2.22	2.68	0.57	0.84	2.22	2.68
	Agricultural	3.39	3.83	1.18	1.35	3.39	3.83
ABk	Forest	1.70	1.87	–0.02	0.12	1.70	1.87
	Steppe	3.02	2.55	0.81	0.56	3.02	2.55
	Agricultural	2.50	2.66	0.53	0.63	2.50	2.66
Bk	Forest	1.49	1.66	0.48	0.64	1.49	1.66
	Steppe	0.75	0.76	–0.51	–0.49	0.75	0.76
	Agricultural	1.36	1.87	0.35	0.81	1.36	1.87
BCk	Forest	1.18	1.24	0.53	0.60	1.18	1.24
	Steppe	0.55	0.56	–0.55	–0.53	0.55	0.56
	Agricultural	0.56	0.57	–0.53	–0.51	0.56	0.57

Note: Loc I – Location I, Loc II – Location II.

Table 3. Individual indices of manganese pollution in soil under different plant communities

Soil horizon	Plant community	Pollution Index		Geoaccumulation Index		Enrichment Factor	
		Loc I	Loc II	Loc I	Loc II	Loc I	Loc II
Ah	Forest	1.63	1.84	0.12	0.29	1.24	1.14
	Steppe	2.13	2.67	0.50	0.83	0.96	0.99
	Agricultural	3.21	3.67	1.10	1.29	1.10	0.96
ABk	Forest	2.13	2.32	0.15	0.28	1.25	1.11
	Steppe	2.59	2.96	0.43	0.63	0.77	1.05
	Agricultural	2.92	3.38	0.61	0.82	1.05	1.14
Bk	Forest	1.92	1.90	0.76	0.75	1.29	1.08
	Steppe	0.79	0.81	–0.52	–0.48	0.99	1.01
	Agricultural	2.13	2.54	0.91	1.17	1.47	1.28
BCk	Forest	1.46	1.54	1.13	1.21	1.24	1.52
	Steppe	0.46	0.47	–0.54	–0.51	1.01	1.02
	Agricultural	0.46	0.83	–0.54	0.33	1.00	1.79

Note: Loc I – Location I, Loc II – Location II.

Table 4. Individual indices of zinc in soil under different plant communities

Soil horizon	Plant community	Pollution Index		Geoaccumulation Index		Enrichment Factor	
		Loc I	Loc II	Loc I	Loc II	Loc I	Loc II
Ah	Forest	1.86	1.93	0.31	0.36	1.42	1.20
	Steppe	1.91	2.25	0.35	0.58	0.86	0.84
	Agricultural	3.10	3.69	1.05	1.30	0.88	0.9 · 6
ABk	Forest	2.06	1.79	0.46	0.25	1.40	1.10
	Steppe	1.65	1.96	0.14	0.39	0.63	0.88
	Agricultural	2.38	2.43	0.67	0.70	1.10	1.05
Bk	Forest	2.71	2.43	0.86	0.70	1.29	1.04
	Steppe	1.13	1.14	–0.41	–0.39	1.07	1.07
	Agricultural	2.55	2.86	0.76	0.93	1.33	1.08
BCk	Forest	2.67	2.32	0.83	0.63	1.23	1.02
	Steppe	1.04	1.04	–0.53	–0.52	1.02	1.01
	Agricultural	1.53	1.54	0.02	0.04	1.47	1.46

Note: Loc I – Location I, Loc II – Location II.

Table 5. Integrated indices of iron, manganese and zinc pollution in soil under different plant communities

Soil horizon	Plant community	Nemerow Pollution Index		Pollution Load Index		Sum of Pollution Index	
		Loc I	Loc II	Loc I	Loc II	Loc I	Loc II
Ah	Forest	1.32	1.48	1.58	1.79	1,963	2,364
	Steppe	1.76	2.13	2.08	2.52	3,153	3,829
	Agricultural	2.63	3.02	3.23	3.73	4,805	5,445
ABk	Forest	1.67	1.77	1.95	1.98	2,543	2,794
	Steppe	2.23	2.23	2.34	2.46	4,195	3,741
	Agricultural	2.26	2.15	2.59	2.79	3,680	3,981
Bk	Forest	1.96	1.82	1.98	1.97	2,247	2,439
	Steppe	0.69	0.84	0.87	0.89	1,085	1,100
	Agricultural	1.69	2.03	1.95	2.39	2,145	2,849
BCk	Forest	1.85	1.66	1.66	1.64	1,766	1,850
	Steppe	0.48	0.48	0.64	0.65	774.2	786.2
	Agricultural	1.01	1.05	0.73	0.90	790.8	890.9

Note: Loc I – Location I, Loc II – Location II.

from 0.55 to 3.02 with an average of 1.18 and from 0.56 to 3.83 with an average of 1.49 in the soils under FCs, SCs and ACs, respectively. In most samples, the values of this index were categorized under Class I: 100.00% of samples at FCs, 83.33% of samples at SCs and 83.33% of samples at ACs. Based on the EF contamination levels the studied plant communities were generally in the order of ACs > FCs > SCs. The values of EF fluctuated between 0.55 and 3.39 (average 1.31) and 0.56 and 3.83 (average 1.35) at Loc I and Loc II, respectively. The values of this index were categorized under Class I: 88.89% of the samples at all locations.

The values of PI nem in all soil samples ranged from 0.48 to 3.02 with an average of 1.68 (Table 5). The values of this index varied widely, ranging from Class 2 (warning limit) to Class 6 (heavily polluted). 50.00% of samples values were categorized under Class 3 (slightly polluted) and 29.17% of samples values were categorized under Class 4 (moderately polluted). 4.17% of samples values were categorized under Class 5 (heavily polluted).

The values of PI nem in the soils under the plant communities varied from 1.32 to 1.96 (average 1.69), from 0.48 to 2.23 (average 1.36) and from 1.01 to 3.02 (average 1.98) at FCs, SCs and ACs, respectively. The order of the plant communities according to PI nem values was ACs > FCs > SCs. The PI nem values in the soils at Loc I ranged from 0.48 to 2.63 (average 1.63) and in the soil at Loc II ranged from 0.48 to 3.02 (average 1.72). The values of this index were categorized under Class III: 58.33% of the samples at Loc I and 41.67% of the samples at Loc II.

In all soil samples the values of PLI fluctuated between 0.64 and 3.73 with an average of 1.89 (Table 5). The values of this index indicated that the soil samples can be classified into four PLI categories: no pollution (25.00% of samples), moderately polluted (37.50% of samples), heavily polluted (29.17% of samples) and extremely heavily polluted (8.33% of samples). The values of this index in the soils under the plant communities ranged from 1.58 to 1.98 (average 1.82), from 0.64 to 2.52 (average 1.56) and from 0.73 to 3.73 (average 2.29) at FCs, SCs and ACs, respectively. According to the contamination levels of the studied metals the plant communities were generally in the order of ACs > FCs > SCs. The PLI values observed in the soils at Loc I were from 0.64 to 3.23 with an average of 1.80 while those in the soils at Loc II ranged from 0.65 to 3.73 with an average of 1.98. Most values of this index was categorized under Class II: 41.67% of the samples at Loc I and 33.33% of the samples at Loc II, as well as Class III: 25.00% of the samples at Loc I and 33.33% of the samples at Loc II.

The values of PI sm in all soil samples varied from 774.2 to 5,445.6, with an average of 2,551.1 (Table 5). The results of the soil analyses indicate that the values of PI sm ranged from 1,766.3 to 2,794.2 (with an average of 2,246.2), from 774.2 to 4,195.2 (with an average of 2,333.4) and from 790.8 to 5,445.6 (with an average of 3,073.7) in soil under FCs, SCs and ACs, respectively. The levels of contamination in the areas under the plant communities were in the following order: ACs > FCs > SCs. The values of PI sm in the areas under different levels of metals contaminating the soils were in the range of 774.2 to 4,805.2 (with average of 2,429.3) at Loc I and in the range of 786.2 to 5,445.6 (with average of 2,672.9) at Loc II (Table 5).

Discussion

Numerous studies have revealed that certain HMs such as Fe, Mn and Zn are essential for the living organisms as structural and catalytic components of the proteins and enzymes. However, excessive accumulation of these metals in soil constitutes a risk for the plant communities, natural ecosystems, organisms and human health (Sparks 2002, Bashkin and Howarth 2003, Kabata-Pendias and Mukherjee 2007, Sposito 2008). Therefore, it is important to understand the patterns of the metal content in the soils of iron ore mining areas.

The natural content of metals in soils is influenced both by parent rock composition and by pedogenetic processes, which may cause the long-term accumulation and leaching of these elements in profile (Sparks 2002, Sposito 2008). Notably, a large number of scholars have indicated an enrichment of metals only in surface soil (Gryshko 2012, Wang et al. 2020, Stofejova et al. 2021). However, in our study, a different pattern of HMs distribution in the soil profile at Kryvyi Rih natural local background area was revealed (Savosko 2016). The content of Fe, Mn and Zn in the surface Ah horizon equalled 1,174 ± 78.94, 240 ± 13.56 and 18 ± 1.59 mg kg^{-1}, respectively. At the same time, in the sub-surface ABk horizon the mean levels of these metals were maximum and were about 1.15, 1.28 and 1.20 times greater than in the surface Ah horizon, respectively. Further, in deep horizons Bk and BCk the content of Fe, Mn and Zn gradually decreases to the levels of parent rock. This phenomenon can be explained as follows.

As it is known, soil is not only a passive recipient of chemical elements. In the soil media there are several pedogeochemical reactions which play an important role in retention, mobilization, and migration of HMs in soils and largely determine their availability to plants. The behaviour of these elements in soil depends on soil properties (organic matter and clay content, soil pH, cation exchange capacities) and on metal properties (ionic radius, ionic and redox potentials, electronegativity, ionization energy). As a result, the soil can mobilize/immobilize HMs by complexation/dissolution, oxidation/reduction, and sorption/desorption (Sparks 2002, Sposito 2008), and as such acts as a natural filter ("pedomembranes") for these compounds (Savosko 2016). That is why, the natural soil profile can be considered as a combination of pedogeochemical barriers to elemental migration. As we know it, these barriers are a part of the soil profile, where significant accumulation of several chemical elements occurs (Savosko 2019a, 2019b).

It is also important to note that these barriers can be manifested as a "subjective-reactionary phenomenon". The result of the investigation clearly indicated that in *Haplic Chernozems* the maximum organic matter and carbonate content takes place in the ABk horizon (Sposito 2008). In our opinion, these substances determine the maximum of Fe, Mn and Zn concentrations in this soil horizon (Savosko 2019a, 2019b).

The previous studies have demonstrated that in Kryvyi Rih District the soils are highly contaminated with Fe, Mn and Zn (Gryshko 2012, Gryshko et al. 2012). As we noted earlier, the results of many studies in other countries of the world also regularly indicated the elevated levels of soil contamination by Fe, Mn and Zn in the mining areas (Demkova et al. 2017, Yi and Cheng 2019, Wang et al. 2020, Stofejova et al. 2021). However, according to our results, predominantly low and moderate soil pollution levels of these metals were found in the vicinity of Pivnichnyi Ore Mining and Processing Plant. This phenomenon can be explained as follows.

First, as shown by results of our calculations (Savosko 2016), there are five levels of HMs input in the soils and therefore there are five areas of soil contamination with Fe, Mn and Zn at Kryvyi Rih District. But in this research, the study area included only two locations where pollution sedimentation on the surface of land was minimal. The presence of FCs, SCs and ACs in this area was the main reason why we made this choice for the sampling sites. Secondly, in most scholarly papers, authors give information about total concentrations of HMs in the soils of the mining areas. We studied the extractable contents of Fe, Mn and Zn in soils (digestion with 1 mol L^{-1} nitric acid). Such metals compounds are known as mobile forms, which are the most biologically available pools ("mobile portions") and which determines the environmentally dangerous concentrations in soils. According to scholarly papers, the share of each HM in the mobile fractions ranges from 5 to 75% of the total concentration (Sparks 2002, Kabata-Pendias and Mukherjee 2007, Sposito 2008). To summarize, the low levels of soil contamination in the vicinity of Pivnichnyi Ore Mining and Processing Plant could be explained by research of extractable contents of Fe, Mn and Zn. However, in the future these assumptions need to be verified in different conditions.

This study also demonstrated that according to the values of individual and integrated indices of pollution the plant communities ranged in the following order: ACs > FCs > SCs. This is consistent with the expected level of adaptation of plant communities to environmental pollution by HMs. Our observation also agrees with that of other authors (Loska et al. 2004, Urbina et al. 2017, Wang et al. 2020), who previously reported that agricultural phytocenoses are the least resistant to negative external influences in comparison with other plant communities.

The minimum concentrations of Fe, Mn and Zn and the smallest values of indices of pollution were found in the soil samples under natural steppe phytocenoses. This fact is due to the action of pedogeochemical barriers to elemental migration. As expected, these barriers strongly influenced both the natural elements content and the levels of contamination in undisturbed soil profile. Therefore, under the steppe phytocenoses a significant accumulation of Fe, Mn and Zn was detected only in the surface Ah and ABk horizons. With depth, the contents of these metals decreased and became constant on the background levels in horizons Bk and BCk.

Medium concentrations of Fe, Mn and Zn and medium values of indices of pollution were identified in the soils under semi-natural forest phytocenoses. Most likely, in this case, the forest leaf litter had a pronounced effect on the content of HMs in the soil profile. According to the scholarly literature, the forest leaf litter is a major bridge between the plant communities and soil, and it plays a key role in the biogeochemical cycle linking the biotic and abiotic part of forest ecosystems. Moreover, numerous studies have convincingly demonstrated that both 1) the biomass of the litter and 2) its chemical content (including HMs) are the important parameters for measuring, modelling, predicting and assessing the forest stand state (Bashkin and Howarth 2003, Shen et al. 2019, Saj et al. 2021, Yang et al. 2021). However, the modern researchers pay little attention to the existence of organic acids in the forest leaf litter biomass. In addition to other effects, after the input of leaf litter into soil, the organic acids can affect the mobility of HMs.

As it is known, the mobility of metals is closely related to the solubilisation processes that occur in soil. The presence of the organic acids significantly accelerates the pedogeochemical reactions in both cases between the soil solid phase and the soil solution, between the dust particles of pollution and the soil solution (Bashkin and Howarth 2003, Adeleke et al. 2017). The results of our investigation clearly indicated that in the soils under FCs the minimal levels of Fe, Mn and Zn were found in the surface Ah horizon. The level of soil pollution by these metals significantly increased with depth. In our opinion, one possible explanation for this is that the FCs due to existence of organic acids in the forest leaf litter fall promote the mobilization of HMs. As a result, such impacts may contribute to the migration of Fe, Mn and Zn mobile forms into lower horizons of soil profile. The analysis of Fe, Mn and Zn distribution in the soil profile has helped to identify the pattern of relationships between forest phytocenoses and soil. New and more thorough studies on forest and soil, with a larger number of macronutrient and HMs measurements, would certainly help to gain a better knowledge of soil restoration and reconstruction.

Conclusions

A specific pattern of the HMs distribution in the soil profile at natural local background areas of Kryvyi Rih District was revealed. The maximum metal concentrations were found in sub-surface soil horizon ABk of *Haplic Chernozems* profile. This phenomenon can be explained with pedogeochemical barriers to elemental migration.

The soils in the vicinity of the Ore Mining and Processing Plant were characterized by enrichment by Fe, Mn and Zn in the soil profile. Application of individual and integral pollution indices showed that concentrations of these metals were related to anthropogenic activity, mainly local pollution originating from ore mining and processing.

The results of our investigation indicated that under forest communities, minimal levels of Fe, Mn and Zn were found in surface horizon Ah. The intensity of soil pollution by these elements significantly increased with depth. The FCs due to existence of organic acids in forest leaf litterfall promote the mobilization of HMs and may contribute to intensive migration of mobile Fe, Mn and Zn into the deeper soil horizons.

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