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The total content of macronutrients and heavy metals in the soil on devastated lands at Kryvyi Rih Iron Mining & Metallurgical District (Ukraine)

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Abstract. The relevance of the research is due to the need to develop technologies for phytoremediation of the devastated lands in the mining and metallurgical regions of Ukraine and the world. In this regard, the creation of tree plantations adapted to the ecological conditions of such territories is considered by many experts as the most promising option for innovative technologies. However, the development of artificial woodlands requires knowledge of the pedogeochemical characteristics of devastated lands. The aim of the work was to carry out a comparative analysis of the macronutrients and heavy metals gross forms content in the soils of the devastated lands of the Kryvyi Rih mining and metallurgical region. The field studies focused on five contrasting monitoring sites of the Petrovsky dump (Central Kryvorizhzhya), which has a typical age and composition of rocks for the region. Soil sampling, drying, sieving, and sample preparation (sintering in a muffle furnace) were done in accordance with classical techniques. The concentrations of macronutrients (potassium, sodium, calcium, magnesium, sulfur, and phosphorus) and heavy metals (iron, manganese, zinc, copper, lead, and cadmium) were determined using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) X-Series 2 (Thermo Fisher Scientific, USA). The analytical part of our research was carried out on the basis of the laboratory of the Institute of Biosciences, Freiberg *University* of *Technology* and Mining Academy (Freiberg, Germany). At monitoring sites, significant differences were found in the content of macronutrients gross forms, and their variation relative to the control values as well. Potassium and sodium concentrations generally differed slightly or were close to control levels. The results of determining the content of calcium, magnesium and phosphorus indicate a significant deficiency or excess of these macronutrients in the soils of the devastated lands. An increased sulfur content was found in the soils of all monitoring sites, in some cases 4 times higher than the control level. The measured content of gross forms of iron, manganese, copper, cadmium and, partially, zinc in the soils of different monitoring sites exceeded the control values by 5.5 – 5.9 times. Thus, the analysis of the research results made it possible to establish that the soils of the devastated lands of the Petrovsky dump are characterized by unfavorable properties for the growth of most species of woody plants.

Key words: soil, devastated lands, waste rock dumps, macronutrients, heavy metals, gross forms, phytotoxicants, phyto-optimization

Валовий вміст макронутрієнтів та важких металів у ґрунтах девастованих земель Криворізького залізорудного гірничо-металургійного регіону (Україна)

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Анотація. Актуальність наших досліджень зумовлена необхідністю розробки технологій фіторемедіації девастованих земель у гірничо-металургійних регіонах України та світу. У зв’язку з цим створення деревних насаджень, адаптованих до екологічних умов таких територій, багато експертів розглядають як найбільш перспективний варіант інноваційних технологій. Однак розвиток штучних лісових масивів вимагає знання педогеохімічних характеристик девастованих земель. Метою роботи було провести порівняльний аналіз вмісту валових форм макронутрієнтів та важких металів у ґрунтах девастованих земель Криворізького гірничо-металургійного регіону. Польові дослідження були зосереджені на п'яти контрастних місцях модельного Петровського відвалу (Центральне Криворіжжя), який має типовий для регіону вік і склад гірських порід. Відбір проб ґрунту, висушування, просіювання та підготовка зразків (спікання в муфельній печі) проводили за класичними методиками. Концентрації макронутрієнтів (калію, натрію, кальцію, магнію, сірки та фосфору) та важких металів (заліза, марганцю, цинку, міді, свинцю та кадмію) визначали за допомогою мас-спектрометру з індуктивно-зв'язаною плазмою (ICP-MS) X-Серія 2 (Thermo Fisher Scientific, США). Аналітична частина нашого дослідження була виконана на базі лабораторії Інституту біологічних наук, Технологічного університету і гірничої академії Фрайберга (Фрайберг, Німеччина). На моніторингових ділянках були виявлені суттєві відмінності у вмісті валових форм макронутрієнтів та їх варіації щодо контрольних значень. Концентрація калію та натрію, як правило, незначно відрізнялася або були близькі до рівня контролю. Результати визначення вмісту кальцію, магнію та фосфору свідчать про значний дефіцит або надлишок цих макронутрієнтів у ґрунтах девастованих земель модельного відвалу. В ґрунтах усіх моніторингових ділянок було виявлено підвищений вміст сірки, в деяких випадках у 4 рази вище від контролю. Вміст валових форм заліза, марганцю, міді, кадмію та частково цинку в ґрунтах різних моніторингових ділянок перевищував контрольні значення у 5,5-5,9 разів. Аналіз результатів досліджень дозволив встановити, що ґрунти спустошених земель Петровського відвалу характеризуються несприятливими властивостями для росту більшості видів деревних рослин.

Ключові слова: ґрунт, девастовані землі, відвали гірських порід, макронутрієнти, важкі метали, валові форми, фітотоксиканти, фітооптимізація

Introduction.

Devastated lands are the surface new formations, where the soil and vegetation cover have been completely destroyed, and anthropogenic morphosculptures (medium or small forms of relief that have arisen under the influence of exogenous factors of technogenic genesis) have been formed. Now these lands are an integral component of the mining and metallurgical areas at Ukraine, at Europe and at Worldwide (Savosko, 2011; Adams, 2017; Bielyk, et al., 2019). Numerous studies have convincingly proved that such lands pose a serious threat to human safety and well-being, since they are a source of intense secondary pollution of atmospheric air, soil, surface and ground waters of adjacent territories. In addition, devastated lands generate the spread of weed, allergenic and invasive plant species in the regions of their deployment (Macdonald, et al, 2015; Pietrzykowski, 2019; Masiuk et al., 2020). These problems are exacerbated by a significant area of devastated land: more than 2 000 000 hectares in the world, about 200 000 hectares in Ukraine and about 100 000 hectares in Germany (Wong, 2003; Savosko, 2011; Kivinen, 2017; Shvaiko & Manyuk, 2017). Therefore, the development of effective, but inexpensive technologies for optimizing devastated lands is urgent.

Recently, numerous studies have been aimed at finding the innovative ways to optimize the territories of devastated lands (Skousen & Zipper, 2014; Shvaiko & Manyuk, 2017; Zipper, et al., 2011; Savosko, et al., 2019a). Since the classical technology of their reuse (reclamation / revitalization) does not stand up to criticism in the framework of modern research (Savosko, 2011; Skousen & Zipper, 2014; Adams, 2017; Kivinen, 2017). According to experts, the creation of the artificial tree plantations is the most promising way to restore the devastated lands (Adams, 2017; Macdonald, et al, 2015; Ranjan, et al, 2016; Savosko & Tovstolyak, 2017). However, the ecological conditions of these territories are very unfavorable for most species of ornamental woody (Savosko, 2011; Bielyk, et al., 2019; Pietrzykowski, 2019), fruit (Shcherbyna, et al., 2017; Khromykh, et al., 2018) and agricultural plants (Nazarenko & Lykholat, 2018; Nazarenko, et al., 2018; Palchykov, et al., 2019).

In most cases, the formation of a fragmented soil cover on the devastated lands was established, which is characterized by a thin profile, an insignificant content of humus and macronutrients, an unfavorable reaction of the soil solution, and the presence of an excessive content of phytotoxicants (Savosko, et al., 2018; Bielyk, et al., 2019; Savosko, et al., 2019b). It has been shown that such properties of the soil cover adversely affect the state of the organism of animals (Lykholat, et al., 2019; Pokhylenko, et al., 2019) and humans (Pertseva, et al., 2012; Lykholat, et al., 2019).

For woody plant species, one of the most significant environmental condition is the insufficient amount of leading macronutrients (nitrogen, phosphorus, potassium, etc.) in the soils of devastated lands, which predetermine the growth and development of these species (Adriano, 2001; Dobrovolskij, 2003; Bradl, 2005; Kabata-Pendias, 2011; Maathuis, 2019).

It should be noted that the heavy metals are among the priority phytotoxicants (Komarova, 2015b; Yakun, 2016; Antoniadisa, et al., 2017; Podolyak & Karpenko, 2019). Heavy metals in small concentrations are the actual trace elements for all living organisms (Adriano, 2001; Dobrovolskij, 2003; Sparks, 2003; Sposito, 2008), but a significant excess of their content in the soil has a negative effect on the growth and development of woody plant species (Ding, et al., 2015; Khalid, et all., 2017; Pogrzeba, et al., 2019).

Therefore, the urgent task is to study the chemical composition of the soil of devastated lands, and first of all, to identify the actual concentrations of the leading macronutrients (as potential nutrients for plants) and heavy metals (as potential phytotoxicants).

Purpose of the work: *t*o conduct a comparative analysis of the gross forms content of macronutrients and heavy metals in the soils of devastated lands of the Kryvyi Rih mining and metallurgical region.

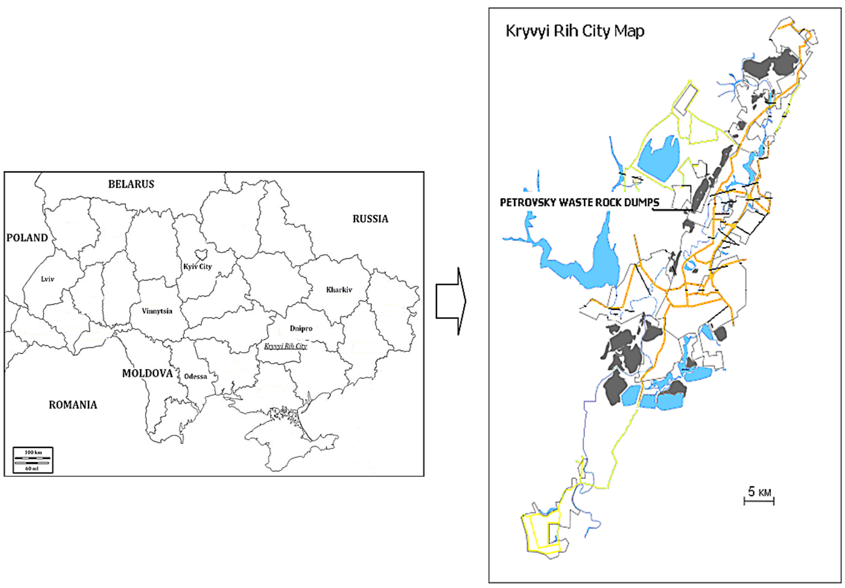
Materials and research methods.

The materials for the article were the results of research that were carried out at the Petrovsky waste rock dump, Central part of the Kryvyi Rih Iron Mining & Metallurgical District, Dnipropetrovs'k oblast, Ukraine (Fig. 1).

The Petrovsky waste rock dump was formed as a place for storing the unpromising iron ores, quartzite and loose rocks. In this dump the ecological conditions for the growth and development of plants are typical for the Kryvyi Rih region, which is due to the composition of rocks, their age and area (Savosko, et al., 2018; Bielyk, et al., 2019).

On the territory of the Petrovsky waste rock dump, five monitoring sites were selected, which differ in the age of the rock dump and are characterized by contrasting edaphic conditions. The control plot is located at a distance of 30 km from the industrial enterprises of the region in the Gurovsky forest (Dolinsky district, Kirovograd oblast).

At each plot, soil samples were taken from the top layer at a depth of 0 – 10 cm in accordance with classical sampling techniques. The procedures for soil samples drying, grinding and sifting through a metal



Map of the Petrovsky waste rock dumps

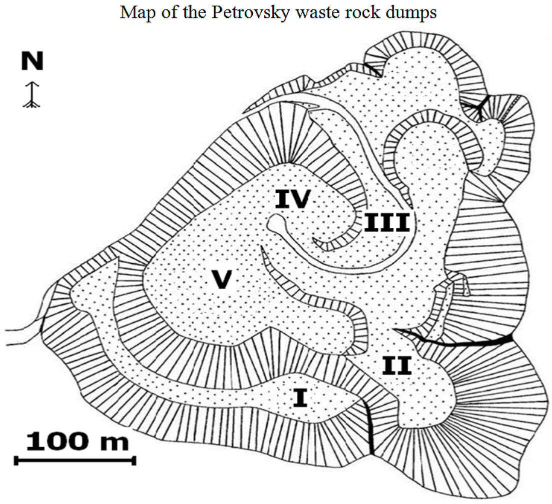


Fig. 1. Location of study area and structure of the Petrovsky waste rock dumps: I, II, III, IV, V – numbering of the monitoring plots

sieve (mesh size 1 mm) were carried out according to standard methods (Stehman, et al., 1999; Pansu & Jacques, 2006; Tykhonenko, et al., 2009). Briefly, 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 ºC for 5 hours. The cooled samples were dissolved in a mixture of acids (HF and HCl), and an aliquot was taken (Stehman, et al., 1999; Pansu & Jacques, 2006).

Determination of the macronutrients content (potassium, sodium, calcium, magnesium, sulfur and phosphorus) and the heavy metals (iron, manganese, zinc, copper, lead and cadmium) was performed using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) X-Series 2 (Thermo Fisher Scientific, USA). Laboratory studies were carried out at the Institute of Biosciences, Freiberg University of Technology and Mining Academy (Freiberg, Germany).

The content of macronutrients (MN) and heavy metals (HM) in the soil samples was expressed in ppm dry weight. The results obtained were processed using the methods of variation statistics; differences between the comparison groups were considered significant at the level of statistical significance $P < 0.05$ (McDonald, 2014).

Results.

Content of MN and HM in the soils of the control plot. We found that in the soils of the control plot, the potassium content ranges from 1.10% to 1.33%, with an average value of 1.22 ± 0.04 % (Table 1). According to scientific literature (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008), the average potassium content in soils ranges from 1.36 % to 4.20 %. Orlov (1992) showed that in the chernozem soils, the content of this element is 1.32 % (typical chernozems), 0.97 % (ordinary chernozems), and 1.75 % in southern chernozems.

In accordance with the results of our studies, the sodium concentration in the soils of the control plot varied in the range 0.65 – 0.83 %, with an average value of 0.70 ± 0.03 %. Scientific publications (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008;) indicate that the optimal sodium content in soil ranges from 0.63 % to 2.84 %. According to Orlov (1992) data, the amount of sodium in chernozem soils reaches the following values: 0.57 % in typical chernozems, 0.44 % in ordinary chernozems, and 1.19 % in southern chernozems.

The calcium content in the soils of the control plot fluctuated from 3.11 to 3.74 %, the average value was 3.41 ± 0.11 %. Literature sources (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008;) indicate that the average concentration of calcium in soils is 0.51 – 2.53 %. In the chernozem soils (Orlov, 1992), the content of this element reaches 2.47 % in typical chernozems, 4.20 % in ordinary chernozems and 2.10 % in southern chernozems.

According to our research, the magnesium concentration in the soils of the control plot ranged from 1.86 % to 2.57 %, with an average value of 2.06 ± 0.14 %. Previous studies (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008) have found that the average magnesium content in soils is in the range of 0.16 – 1.37 %. In typical chernozems, the concentration of this element comprises 1.01%, in ordinary chernozems 1.19 %, and in southern chernozems only 0.95 % (Orlov, 1992).

The sulfur concentration in the soils of the control plot varied in a narrow range from 0.75 % to 1.309 %, with an average parameter value of 0.89 ± 0.06 %. Scientific publications (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008) indicate that soils usually contain from 0.03 % to 0.085 % sulfur. According to Orlov (1992), the amount of sulfur is 1.69 % in typical chernozems, 0.22 % in ordinary chernozems, and 0.17 % in southern chernozems.

We found that the phosphorus content in the soils of the control plot ranges from 0.09 % to 0.13 %, with an average value of 0.11 ± 0.01 %. It is known that the average phosphorus content in soils is insignificant and amounts to 0.06 – 0.08% (Perelman, 1989; Alekseenko, 2000). The concentration of this

Table 1. Total content of the macronutrients in the soils of the control plot, %

Statistical parameters	Macronutrients					
	Potassium	Sodium	Calcium	Magnesium	Sulfur	Phosphorus
Minimum value, Min	1.10	0.65	3.11	1.86	0.75	0.09
Maximum value, Max	1.33	0.83	3.74	2.57	1.09	0.13
Average value, M	1.22	0.70	3.41	2.06	0.89	0.11
The absolute error of the arithmetic mean, m	0.04	0.03	0.11	0.14	0.06	0.01
Variation coefficient, V%	15.76	21.19	14.12	29.43	31.43	28.75

element in chernozem soils reaches 0.10 % in typical chernozems, 0.07 % in ordinary chernozems, and 0.06 % in southern chernozems (Orlov, 1992).

In our studies, it was found that in control plot soils the iron content varied from 3.92 to 4.75 %, with an average value of 4.25 ± 0.18 % (Table 2). The iron content in conventionally clean (uncultivated) soils comprises 0.47 – 4.30 %, and in the cultivated soils 1.40 % – 2.80 % (Bradl, 2005; Kabata-Pendias, 2011). The following concentrations of this metal were revealed in chernozem soils: in typical chernozems 3.69 %, in ordinary chernozems 3.04 %, and in southern chernozems 3.50 % (Orlov, 1992).

According to the scientific literature review (Bradl, 2005; Kabata-Pendias, 2011), the concentration of manganese in the untreated soils is detected in a very wide range of 60 – 1100 ppm, and in cultivated soils it varies from 990 to 7400 ppm. In the chernozem soils, the concentrations of this metal are as follows: 500 ppm in typical chernozems, 200 ppm in ordinary chernozems, and 500 ppm in southern chernozems (Orlov, 1992). We found (Table 2) that the content of manganese in the soils of the control plot is slightly higher than in chernozem soils (705 – 810 ppm, with an average value of 761.7 ± 18.02 ppm), but does not exceed the data established for the cultivated soil.

The concentration of zinc in uncultivated soils reaches 25 – 65 ppm, and in cultivated soils, 37 – 680 ppm (Bradl, 2005; Kabata-Pendias, 2011). According to the results of our research (Table 2), the zinc content in the soils of the control plot (85 – 98 ppm, with an average value of 90.51 ± 2.73 ppm) coincides with the published data for the cultivated soils.

The copper content in the uncultivated soils varies in the interval 8.70 – 33 ppm, while in cultivated soils, the concentration of this metal rises to 9.90 – 39 ppm (Bradl, 2005; Kabata-Pendias, 2011). We found (Table 2) that in the soils of the control plot, the copper content (26.84 – 30.15 ppm, the average value is 18.73 ± 0.78 ppm) does not go beyond the indicated ranges.

The average lead content in cultivated and uncultivated soils is 2.60 – 26.0 ppm (Bradl, 2005; Kabata-Pendias, 2011). The analysis of the obtained results showed (Table 2) that the concentration of this metal in the soils of the control plot (from 26.84 ppm to 30.15 ppm, with an average value of 28.10 ± 0.60 ppm) was slightly higher than these values.

Similar patterns were revealed for cadmium, the content of which in the background soils is 0.10 – 0.13 ppm (Bradl, 2005; Kabata-Pendias, 2011). The concentration of this metal revealed in the soils of the control plot exceeded the indicated level, varying in the range from 0.1 ppm to 0.19 ppm with an average value of 0.16 ± 0.01 ppm (Table 2).

Table 2. Total content of heavy metals in the soils of the control plot

Statistical parameters	Heavy metals					
	Iron	Manganese	Zinc	Lead	Copper	Cadmium
	%	ppm				
Minimum value, Min	3.92	705.84	84.62	17.80	26.84	0.11
Maximum value, Max	4.75	810.79	98.25	21.85	30.15	0.19
Average value, M	4.25	761.70	90.51	18.73	28.10	0.16
The absolute error of the arithmetic mean, m	0.18	18.02	2.73	0.78	0.60	0.01
Variation coefficient, V%	18.7	10.58	13.48	18.75	9.53	36.94

Content of MN and HM in the soils of devastated lands. The analysis of the obtained results showed that in the soils of the devastated lands of the Petrovsky dump, the potassium content varied in the range from 1.13 % (plot IV) to 1.39 % (plot I), with an average value of 1.26 %. The revealed concentrations of this macronutrient were less than its content in the lithosphere and the Earth's crust, but higher than in ultrabasic and basic rocks (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008).

It should be noted that a statistically significant excess of the control potassium content (13 % higher than the control, $P < 0.05$) was found only on the monitoring plot I (Fig. 2). At the same time, in sites II, III and IV, the concentrations of this macronutrient were at the level of control values, and on plot V concentration was slightly lower (by 8 %, $P < 0.05$).

We found that the concentration of sodium in the soils of devastated lands ranged from 0.64 % (plot V) to 0.77 % (plot I), with an average value of 0.74 %. These values are below the amount of this element in the Earth's crust and lithosphere, but close to the sodium levels found in shales and clays.

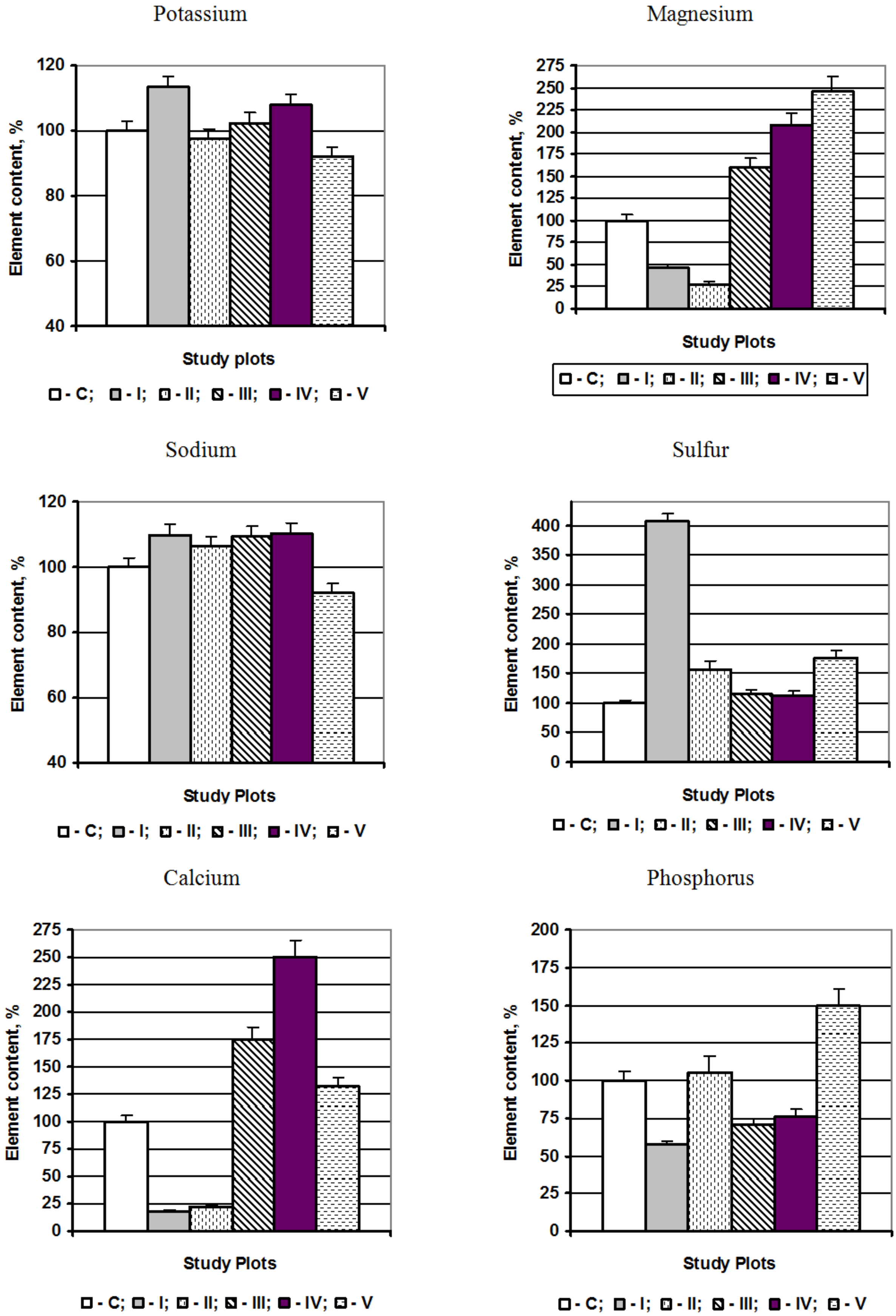


Fig. 2. Comparative content of the macronutrient's total forms in the soils of the devastated lands at Kryvyi Rih District
The content of the elements in the control is taken to be 100%.
Research areas: C – control; I, II, III, IV, V – monitoring sites of the devastated lands

The sodium content in the soils of the devastated lands was 6 – 10% (P <0.05) higher than the control level (Fig. 2). The exception is the soils of plot V, where the concentrations of this element were 7 – 8% (P <0.05) below the control value.

Calcium concentrations in the soils of the Petrovsky dump were determined in a very wide range of values: from 0.61 % (plot I) to 8.56 % (plot IV), with an average value of 4.08 %. Such content of this macronutrient corresponds to its Clarke in the Earth's crust, lithosphere, and in most rocks (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008). Compared with the control, calcium concentrations on the plots I and II were lower by 4.5 – 5.6 times (P <0.05), while on the plots III, IV and V they were higher by 1.3 – 2.5 times (P <0.05).

The range of magnesium content in the soils of devastated lands was also very wide: from 0.57 % (plot II) to 5.08 % (plot IV), with an average value of 2.83 %. These values of magnesium content correspond to its Clarke values in the Earth's crust, lithosphere and basic rocks. It was found (Fig. 2) that on the plots I and II, magnesium concentrations were 3.6 and 2.2 times lower than the control values, respectively (P <0.05), while in the rest of the sites they exceeded the control by 1.6 – 2.5 times (P <0.05).

The results of our research (Fig. 2) indicate that phosphorus concentrations in the soils of the devastated lands of Kryvorizhzha vary from 0.06 % (plot I) to 0.17 % (plot V), with an average value of 0.10 %. Such levels of this element correspond to its Clarkes in the Earth's crust, lithosphere, and basic rocks (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008). The amount of this macronutrient on the plots II and V was 7 – 49% higher than the control (P <0.05), while on the plots I, III and IV it was 24 – 44% lower (P <0.05).

The sulfur content in the soils of the Petrovsky dump varied from 1.02 % (plot IV) to 3.65 % (plot I), with an average amount of 1.73 %. Such concentrations of this element significantly exceed its Clarke in the Earth's crust, lithosphere and leading rocks (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008). Therefore, it is quite natural that the amount of sulfur in the soils of devastated lands was higher in comparison with the control values: 1.1 – 1.6 times (P <0.05) on the plots II, III, IV and V, and 4.1 times higher on the plot I (P <0.05).

The revealed values of calcium and magnesium in the soils of the plots I and II indicate a serious deficiency of these macronutrients (2 – 5 times lower than the control values). In the remaining plots, there is probably an excess amount of calcium and magnesium in the soils (1.3 – 2.5 times higher than the control). In the soils of all monitoring sites, increased sulfur content in comparison with the control values was revealed. On the plot I, high concentrations of this macronutrient (4.1 times higher than the control) may have a phytotoxic effect on woody plant species. The phosphorus concentration was at the control level only on plot II, while on the plots I, III and IV it was significantly higher than the control (by 24 – 42%), and on plot V it was 1.5 times lower than the control values.

The analysis of the obtained results showed that the iron content in the soils of the devastated lands of the Petrovsky dump varies from 5.70 % (plot IV) to 11.12 % (plot V), with an average value of 9.54 %. Such concentrations of this metal exceed its Clarkes in the lithosphere, Earth's crust and in the main rocks (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008). In comparison with the control values (Fig. 3), the iron content in the soils of all monitoring sites was significantly (P <0.05) higher by 1.4 – 2.6 times.

The concentration of manganese in the soils of the devastated lands ranged from 884 ppm (plot II) to 1030 ppm (plot V), with an average value of 962 ppm. Such concentrations of this metal are somewhat higher than its Clarks in the Earth's crust and lithosphere (Alekseenko, 2000; Chertko & Chertko, 2008; Perelman, 1989). In comparison with the control level, the concentration of manganese in the soils of all plots was significantly (P <0.05) higher by 16 – 35 % (Fig. 3).

The results of our research indicate that the concentration of zinc in the soils of the devastated lands of the Petrovsky dump varied from 77.1 ppm (plot I) to 127 ppm (plot V), with an average value of 92.4 ppm. These levels of element correspond to its Clarkes in the Earth's crust, lithosphere and basic rocks (Alekseenko, 2000; Chertko & Chertko, 2008; Perelman, 1989). The amount of zinc in the soils of devastated lands of the Petrovsky dump differs from its control values (Fig. 3). On the plots II, III and V, the amount of this metal was 8 – 14 % lower than the control (P <0.05), while on plot IV it was 1.41 times higher than the control level (P <0.05).

The copper content in the soils of the devastated lands of the Petrovsky dump varied in the range of 25.07 ppm (plot IV) – 32.96 ppm (plot V), with an average value of 28.82 ppm. Such concentrations do not exceed the Clarke values of this metal in the Earth's crust, lithosphere, and leading rocks, with the exception of ultrabasic rocks, sandstones, and carbonates (Alekseenko, 2000; Chertko & Chertko, 2008; Perelman, 1989). In comparison with the control values, the amount of copper in the soils of the Petrovsky dump at all monitoring sites was

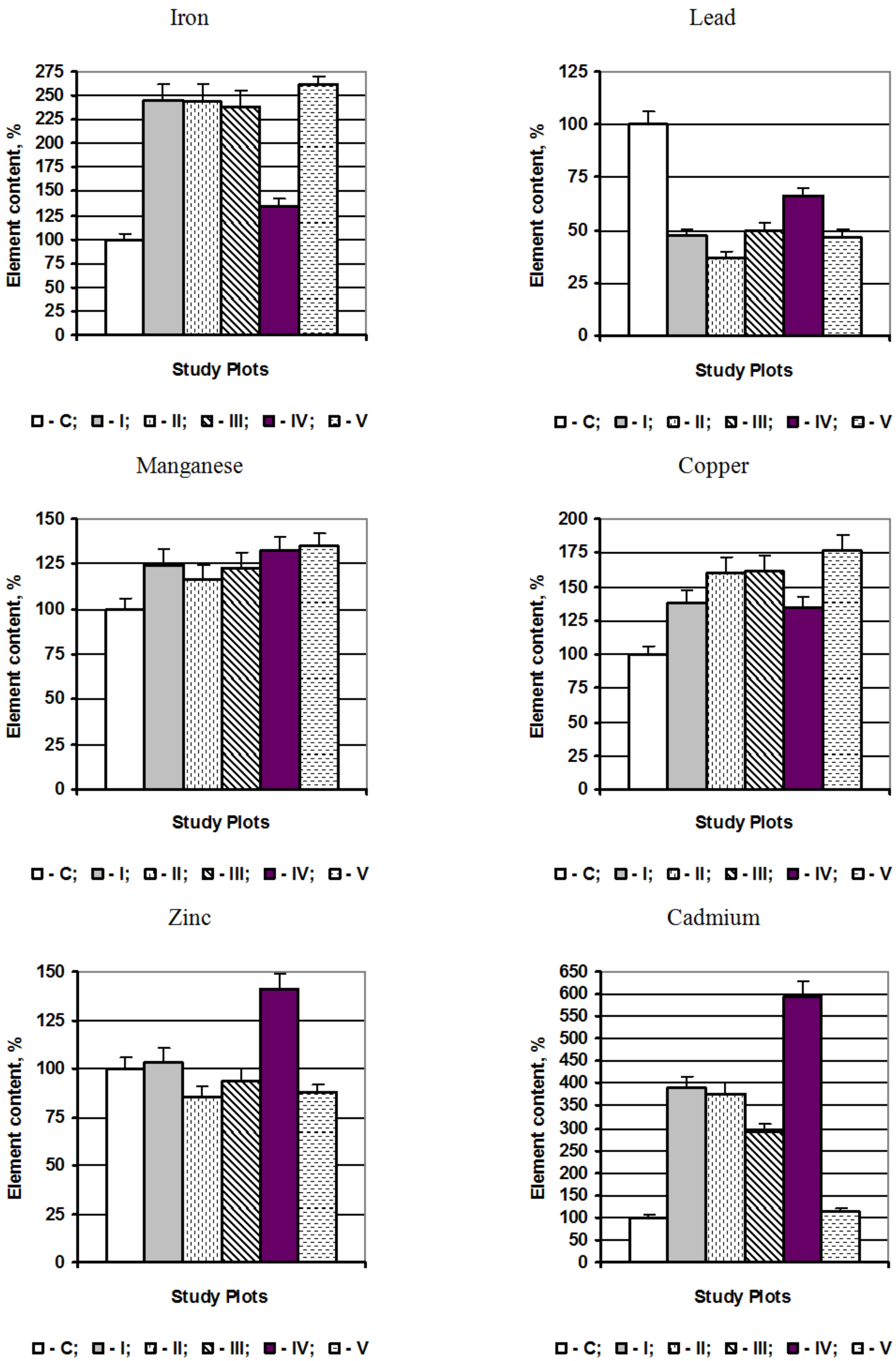


Fig. 3. Comparative content of the heavy metal's total forms
in the soils of the devastated lands at Kryvyi Rih District
The content of the elements in the control is taken to be 100%.
Research areas: C – control; I, II, III, IV, V – monitoring sites of the devastated lands

significantly ($P < 0.05$) higher by 1.3 – 1.8 times (Fig. 3).

Concentrations of lead in the soils of devastated lands were detected in a relatively small range from 10.9 ppm (plot II) to 18.60 ppm (plot IV), with an average value of 13.88 ppm. These metal levels are consistent with its Clarks in the Earth's crust, lithosphere, and leading rocks (Perelman, 1989; Alekseenko, 2000; Chertko & Chertko, 2008). The lead content in the soils of all studied plots significantly ($P < 0.05$) was below the control level by 34 – 64% (Fig. 3).

The cadmium content in the soils of the Petrovsky dump varied from 0.18 ppm (plot V) to 0.95 ppm (plot IV), with an average value of 0.57 ppm. Such values of the element content are not anomalous, since they correspond to its Clarks in the Earth's crust, lithosphere, and basic rocks (Perelman, 1989; Alekseenko, 2000). In comparison with the control values, the amount of cadmium in the soils of all monitoring sites was significantly ($P < 0.05$) higher by 1.1 – 5.9 times.

Discussion.

According to the results obtained, the soils of the control plot we chose were characterized by the typical regional content of the studied macronutrients (potassium, sodium, calcium, magnesium, sulfur and phosphorus). However, in comparison with chernozem soils in other regions, increased concentrations of calcium and magnesium were found. In our opinion, this may be due to the biogeochemical characteristics of the soils of the control plot. The revealed levels of macronutrient content in the soils of the control plot indicate their sufficient quantity for the growth and development of most species of woody plants.

In the soils of the control plot, only the concentration of copper was within the average values established for conditionally background, uncultivated soils. At the same time, the concentrations of other heavy metals (iron, manganese, zinc, lead and cadmium) were statistically significantly higher than the average values. We assumed that this phenomenon can be explained by the action of a regional geochemical and biogeochemical anomaly, which is characterized by an increased content of these metals.

The revealed patterns in the content of heavy metals in the soils of our control plot are consistent with the results of other studies carried out on the conditionally background areas of the Kryvyi Rih region (Savosko, 2009; Komarova, 2015a; Savosko, 2016) and the Dnipropetrovsk province as a whole (Gryshko et al., 2012; Tsvetkova et al., 2016). In our opinion, the increased content of biologically important metals (iron, manganese, and zinc) in the soils of the control plot may not be critical, but optimal for the growth of woody plant species.

The content of gross forms of macronutrients in the soils of the devastated lands of the Petrovsky dump was characterized by multidirectional differences from the control levels. The concentrations of potassium and sodium in the soils of the monitoring sites were at the level of control values or slightly exceeded them (by 10 – 13%). The exception is the soils of plot V, where the amount of potassium and sodium was slightly lower than the control (by 7 – 8%).

In the soils of the devastated lands of the Petrovsky dump, an increased content of gross forms of iron, manganese, copper, cadmium, and also zinc in some plots was revealed. The concentrations of these metals were by 1.2 – 5.9 times higher than the control values. It should be noted that, a lead content lower levels were revealed compared to the control (by 1.5 – 2.7 times). The zinc content in the soils of devastated lands characterized by multidirectional deviations from the control value. So, on the plots II, III, and V, the concentrations of this metal were slightly (by 7 – 14%) lower than the control; on plot IV they exceeded the control by 1.4 times, and on plot I they coincided with the control level.

Conclusion.

The soils of the devastated lands of the Petrovsky dump at all monitoring sites are characterized by very unfavorable conditions for the growth and development of most species of woody plants.

The concentrations of potassium and sodium in the soils of the devastated lands are mainly at the level of the control values. The content of calcium, magnesium and phosphorus in the soils of devastated lands indicates either a significant deficiency of these macronutrients (25 – 40 % lower than the control level), or their excessive amount (1.3 – 5.1 times higher than the control). In the soils of all monitoring sites, an excess of the control sulfur content was revealed (up to 4 – 5 times higher than the control).

The high content of gross forms of iron, manganese, copper, cadmium and, in some areas, zinc should also be attributed to unfavorable conditions at the monitoring sites of the Petrovsky dump. The concentrations of these metals in the soils of devastated lands exceed the control values by 5.5 – 5.9 times.

The established patterns of variation in the content of gross forms of macronutrients and heavy metals in the soils of the devastated lands of Kryvorizhzhya can be used in the development of innovative technologies for phyto-optimization of the territories of mining and metallurgical regions. In further studies, it is advisable to analyze the content of mobile forms of macronutrients and heavy metals in the soils of devastated lands, as well as their translocation into woody plants.

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