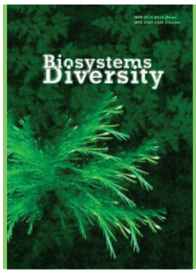

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Heavy metal accumulation by *Acer platanoides* and *Robinia pseudoacacia* in an industrial city (Northern Steppe of Ukraine)

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The role of tree species as a tool for bioaccumulation of heavy metals is an important current issue within the context of the increase of anthropogenic pressure in urban ecosystems. The article presents the results of research on the level of soil contamination with heavy metals and the processes of their accumulation by native and introduced tree species in green spaces of Dnipro city. Inductively coupled plasma mass spectrometry (ICP-MS) was used to detect concentrations of heavy metals (Zn, Cu, Cd, Pb) in soil samples and the assimilation component in trees of black locust (*Robinia pseudoacacia*) and Norway maple (*Acer platanoides*). The ranges of mean concentrations of heavy metals at different study sites within the city's green infrastructure were as follows (mg/kg): 30.7–185.5 for Zn, 5.7–22.4 for Cu, 9.0–31.3 for Pb, and 0.213–0.598 for Cd. With respect to all four of these metals, the soils of the Metallurgists Square location were characterized by the highest concentrations of the metals, and the Pridneprovsky Park in the area of the outskirts of Dnipro city was characterized by the lowest ones. Compared to soils, the two investigated tree species had a significantly lower content of all studied metals in leaves. The heavy metal accumulations in the leaves of both *R. pseudoacacia* and *A. platanoides* were observed in the following decreasing order: Zn > Cu > Pb > Cd. Regarding the migration of heavy metals in the soil-plant system, the concentrations of ecopollutants in the plants were found not to be dependent on their content in the soil environment. The calculated bioaccumulation coefficients of heavy metals for both tree species were < 1. However, the results of heavy metal concentration in leaves of both introduced and native tree species evidenced their special role in heavy metal bioaccumulation. Compared to *R. pseudoacacia,* such native species as *A. platanoides* can be considered to be a more "sensitive" bioindicator of environmental pollution caused by heavy metals. Planting fast-growing tree species such as *R. pseudoacacia* and *A. platanoides* can in a short time be an environmentally appropriate and cost-effective measure to mitigate the unfavourable effects of heavy metals on the environment.

Keywords: heavy metals; urban systems; leaves; bioaccumulation coefficient; *Robinia pseudoacacia*; *Acer platanoides*.

Introduction

Urban green park plantations provide economic, cultural, social, and food benefits to the population (Kosiorek et al., 2016; Abhijith & Kumar, 2019; Hrotko et al., 2021), and (along with other plant systems) they can be altered in response to climate and environmental changes, such as rising CO_2 levels, air temperatures, as well as soil and air pollution (Zhukov et al., 2021). The significant number of industrial enterprises within Dnipro city as the center of a powerful industrial agglomeration resulted in significant contamination of its area with heavy metals, as well as of the territories adjacent to Dnipropetrovsk region (Zverkovskyy et al., 2018; Lovynska et al., 2022). Environmental intoxication with heavy metals, especially soils, remains today one of the most serious challenges. This issue is investigated using methods of qualitative and quantitative determination of the localization of metals and the possibility of their extraction from soils.

Soil contamination is a form of land degradation caused by the spillage, migration, or burying petroleum and poly-nuclear hydrocarbons, solvents, pesticides, and heavy metals in the soil ecosystem (Kunakh et al., 2021). The problem of soil contamination with heavy metals is the most noticeable due to their heavy decomposition, easy accumulation, and presence of hysteresis (Chang et al., 2014; Zhang et al., 2020; Zhou et al., 2020; Vardhan et al., 2021; Wang et al., 2023). After accumulation in food chains, heavy metals migrate and accumulate again at subsequent trophic levels, further exacerbating the global degradation of soil, human health, and ultimately leading to a food security crisis (Miller et al., 2004; Khan et al., 2019; Rai et al., 2019). In a global sense, soil contamination with heavy metals has become a serious global challenge, especially in cities due to urbanization and industrialization (Andras et al., 2018; Vardhan et al., 2019; Cao et al., 2021).

Phytoremediation is a relatively new, potentially effective technology applicable to the recovery of contaminated soils and waters (Xiong et al., 2016; Wiche et al., 2017; Lata et al., 2019; Kayiranga et al., 2023). Historically, plant organisms have evolved, and they accumulate and store biologically essential elements to survive as the dominant biomass of the Earth (Kunakh et al., 2023). But in addition to this, plants also remove non-essential toxic metals from the polluted environment and thus act as passive samplers (Capuana et al., 2011). The direction which involves the use of plants that hyperaccumulate certain metals for detoxication of the environment, appeared in the last 30 years. The plant species having metal-accumulative ability may be used for phytoremediation (removal of soil pollutants) or phytomining (growing plants for "gathering" metals) (Rascio & Navari-Izzo, 2011). In addition to herbaceous plants that have hyperaccumulative properties, woody species are increasingly being used for this purpose (Skuza et al., 2022). Indeed, some of them (in addition to rapid growth) have deep roots, produce a significant amount of biomass, and are able to transport and accumulate heavy metals (Baycu et al., 2016; Viger et al., 2016; Ma et al., 2019). One of the aspects discussed in this article is the role of tree species as a tool for bioaccumulation of non-essential elements in urbanized areas. Studies on the mechanisms of heavy metal absorption and transfer open up prospects of global importance for a better understanding of the processes in the system "soil-woody plant" under conditions of an urban environment.

In recent years, significant progress has been made in the system of monitoring both autochthonous and introduced plant species in the urban environment of Dnipro city and its adjacent territories (Holoborodko et al., 2022). However, there is still no complete certainty regarding the characteristics of heavy metal accumulation by trees depending on their species (Zhukov et al., 2023).

Fast-growing woody species, such as black locust (*Robinia pseudoacacia* Linnaeus, 1753) and Norway maple (*Acer platanoides* Linnaeus, 1753) can effectively meet public needs ranging from a renewable energy source to environmental risk mitigation through phytoremediation, which involves the use of plants to clean up soil and water (Viger et al., 2016; Fan et al., 2018; Wilkaniec et al., 2021).

Robinia pseudoacacia, a non-native tree species of eastern North American origin, was introduced to Europe as early as 1601 (Bijak & Lachowicz, 2021). Right from the beginning, this species was used in parks and applied as a forest-forming species in the mid-1700s and 1800s. Today it is a species planted both for beekeeping purposes, as a hardwood species to produce high-quality wood, and as a tree valuable in terms of energy production (Sytnyk et al., 2023). In the steppe zone of Ukraine, *R. pseudoacacia* is very common and performs a number of beneficial functions (protective, soil-improving, anti-erosion, etc.). In the conditions of the Dnipropetrovsk region, this species belongs to one of the main forest-forming species, and its share in forest plantings is a third (Gorban & Huslystyi, 2018; Sytnyk et al., 2018). At the same time, this species is widely distributed in park areas, green areas of Dnipro city, and is an integral part of plantings in coastal areas.

In contrast to *Robinia*, another species such as Norway maple widely distributed within the park areas of industrial cities, belongs to the local native species. The use of this species in forest stands of the steppe zone is extremely limited, but it is widely used in park stands (Kowalski et al., 2016; Mleczek et al., 2023). First of all, this is conditioned by its decorative features and the capacity to form various landscapes in park areas.

The use of both species may define a new holistic approach for sustainable energy, agriculture and agroforestry development, and the use of marginal lands (Viger et al., 2016), and eventually for global mitigation of environmental risks (Celik et al., 2004; Haider et al., 2021). One of the priority benefits of the widespread use of both tree species is their resistance to a number of abiotic (drought, lack of nutrients in the substrate, salinity) and anthropogenic factors that occur in the steppe zone (Kunakh & Kovalenko, 2019). Being undemanding to environmental conditions, these species are optimal candidates for the absorption, accumulation, and storage of pollutants (heavy metals, pesticide residues, fertilizers and nitrates, salts, etc.) with appropriate improvement, or at least slowing down of the effects of toxic heavy metals on the environment (Lovynska et al., 2022).

The primary objective of this study was to examine (i) accumulation characteristics of individual heavy metals in the soils of various locations in the urban-technogenic environment; (ii) specifics of accumulative properties of toxicants by leaves of *R. pseudoacacia* and *A. platanoides* (iii) comparative assessment of the bioaccumulation characteristics of heavy metals in the leaf part of native and introduced woody plant species.

Materials and methods

Study area. For conducting this investigation, nine different sites in the urban zone of Dnipro city (Ukraine) were selected (Fig. 1). The study area is situated in the temperate continental climate zone of Central Europe and is characterized by warm, often hot summers and cold, humid winters. The average annual precipitation in the region is approximately 475 mm, and the average annual air temperature is +8 °C. The length of a growing season for plants is about 210 days.

The studied locations were situated on both the right (6 sites) and left (two sites) banks of the Dnieper River (Table 1). According to geographical zoning, Dnipro city is located in the center of the Dnipropetrovsk Oblast, in the southeast of Ukraine. The area of the territory of Dnipro city consists of app. 410 km^2 and its elevation is within the limits of 51–188 m.

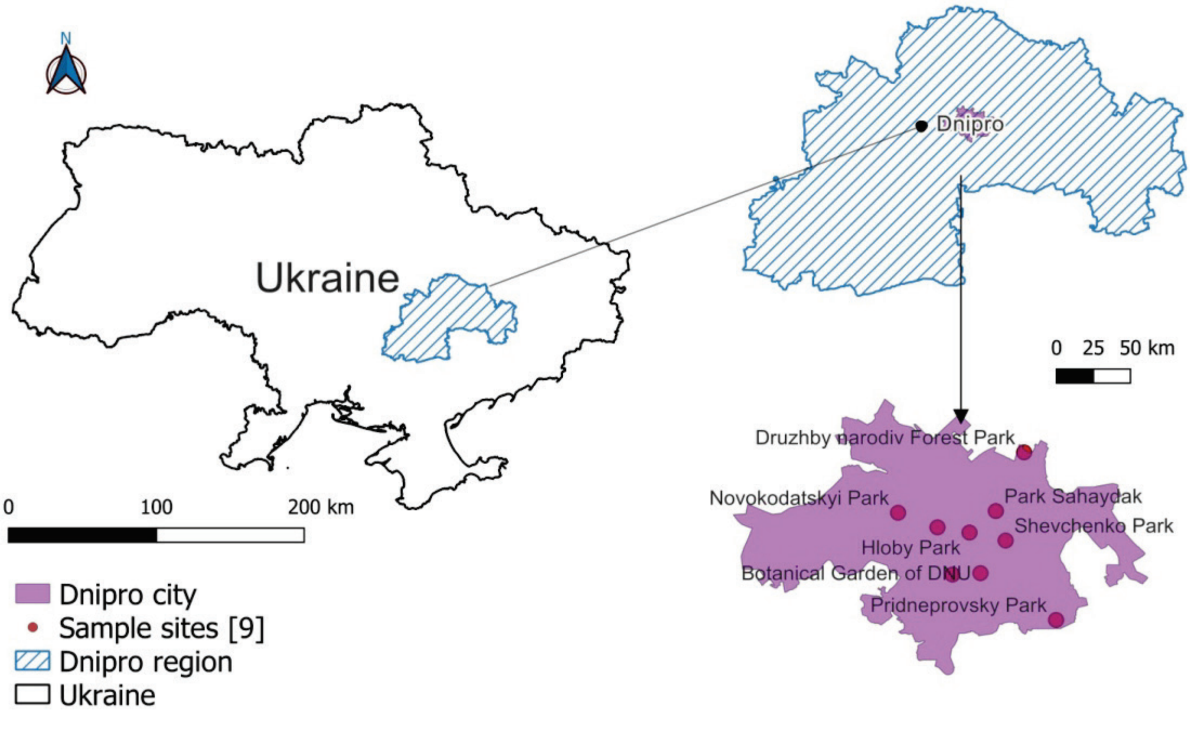

Fig. 1. Sample sites within Dnipro region

Table 1
Characteristics of different sample sites used in the field condition experiment

No.	Name (abbreviation)	The park coordinates / the altitude above sea level, m	Park area, ha	Landscape type	Terrain element (sampling location)	Soil	Share of a target tree species of all the trees in the park, %
Right bank of the Dnieper River							
1	Taras G. Shevchenko Park (TShP)	48°27'40" N, 35°04'21" E / 90	45.0	Near-valley ravine	Right-bank slope (upper third of slope, slope angle 3–4°)	Calcic chernozem (siltic)	*Robinia pseudoacacia* – 20 *Acer platanoides* – 11
2	Lazaria Hloby Park (HP)	48°28'11" N, 35°01'48" E / 56	26.0	Valley ravine	Floodplain	Calcic chernozem (siltic)	*R. pseudoacacia* – 9 *A. platanoides* – 11
3	Metallurgists Square (MS)	48°28'26" N, 34°59'31" E / 65	3.8	Watershed-gully	Upland	Calcic chernozem (siltic)	*R. pseudoacacia* – 50 *A. platanoides* – 7
4	Botanical Garden of DNU (BG DNU)	48°26'14" N, 35°02'35" E / 127	46.0	Watershed-gully	Upland	Calcic chernozem (siltic)	*R. pseudoacacia* – 27 *A. platanoides* – 10
5	Green Grove Park (GGP)	48°26'10" N, 35°00'35" E / 145	53.6	Watershed-gully	Ravine (plateau within the north-eastern slope)	Calcic chernozem (siltic)	*R. pseudoacacia* – 16 *A. platanoides* – 9
6	Novokodatskyi Park (NP)	48°29'08" N, 34°56'42" E /8 2	35.0	Valley ravine	Floodplain	Calcic chernozem (siltic)	*R. pseudoacacia* – 25 *A. platanoides* – 10
The left bank of the Dnieper River							
7	Pridneprovsky Park (PP)	48°23'59" N, 35°07'59" E / 75	7.0	Valley ravine	Sandy terrace	Fluvisol (loamic)	*R. pseudoacacia* – 35 *A. platanoides* – <1
8	Druzhby Narodiv Forest Park (DNFP)	48°32'02" N, 35°05'42" E / 65	90.0	Valley ravine	Saline terrace	Calcic chernozem (siltic)	*R. pseudoacacia* – 15 *A. platanoides* – 12
9	Park Sahaydak (PS)	48°29'13" N, 35°03'41" E / 50	34.0	Valley ravine	Floodplain	Anthrosol (loamic)	*R. pseudoacacia* – 15 *A. platanoides* – <1

Notes: soil classification was presented in accordance with the International Classification System IUSS Working Group WRB 2015 [IUSs Working Group WR, 2015]; World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps; World Soil Resources Reports No. 106. FAO, Rome]; evaluation of soil granulometric composition was carried out according to the FAO method of field soil description [FAO, 2006]; Guidelines for soil description, 4th edition, Food and Agriculture Organization of the United Nations, Rome].

In the studied six parks representing the right part of Dnipro city, the analysis of soil profiles showed the presence of a similar type of soil: Calcic chernozem (siltic) (Table 1). In addition to the above-specified soil type, the surface soil horizon Fluvisol (loamic) (Pridneprovsky Park) and Anthrosol (loamic) (Park Sahaydak) were also found in the areas of the left part of the city. Experimental sites were characterized by the presence of tree stands represented by species *R. pseudoacacia* and *A. platanoides*; their shares were unequal and to a greater extent were marked by the predominance of *Robinia* within the experimental site.

Soil and plant samples assessment. Generally, 27 field samples were taken to determine the elemental composition of the soil. The sampling depth was 0–20 cm; the weight of each sample was about 300–350 g. Additionally, plant leaf samples were collected from each soil sampling site; they were randomly sampled in 5–10 tree specimens of *R. pseudoacacia* and *A. platanoides*. All leaf samples were stored in plastic bags at –4 °C prior to the analysis.

The concentration of heavy metals (Zn, Cu, Pb, Cd) in the soil was estimated using a modified method of extraction in aqua regia (Midula et al., 2017). For this, a 100-mg sample of fine soil dried at 105 °C was mixed with 200 μL of water and four acids (900 μL of hydrochloric acid, 300 μL of nitric acid, 300 μL of hydrofluoric acid, and 150 μL of perchloric acid). The resulting mixture was subjected to microwave cleavage (Ullrich et al., 1999), then centrifuged (5000 rpm), and the supernatant was harvested to determine the concentration of the elements.

Part of the biomass of leaves sampled from both studied tree species was dried in a drying cabinet at 60 °C for 24 hours. Dried leaf samples were ground to a fine powder using an ultra-centrifugal mill (Retsch ZM 1000). 100 mg of each sample was mixed in centrifuge sample tubes with 200 μL of ultrapure water and 1.9 mL of 65% nitric acid. This mixture was incubated for 1 hour under a fume hood. The samples were then mixed with 600 μL of an aqueous solution of 4.8% hydrofluoric acid and placed in a microwave oven for 1–2 hours. After processing in a microwave oven, ultrapure water was added to liquid phase of the supernatant to restore its volume. Prior to the direct measurement of element concentration in solutions, samples were diluted 1:10. The concentrations in the samples were measured by mass spectrometry using an ICP-MS instrument (model X Series 2, Thermo Fisher Scientific, Dreieich, Germany).

To assess the bioaccumulation properties of the leaves of the studied tree species, the biological accumulation coefficient was calculated using the following formula:

$$K_{HM} = C_{leaf} / C_{soil}$$

where: K_{HM} – biological accumulation coefficient; C_{leaf} – mean metal content in the leaves of the plant (mg/g); C_{soil} – metal content in the substrate (mg/g).

Data proceeding and statistical analysis. The heavy metal content (mg/g dry matter) in plant biomass and soil extracts was calculated taking into account the dilution and accurate weight of selected leaf samples. The given results were presented as the mean value x ± SD (standard deviation). Differences in the mean values of element concentrations in soil fractions and samples of black locust and maple leaves at different experimental sites were detected by one-way analysis of variance (ANOVA) using the Statistica Software Package (version 8, StatSoft, USA). Multivariate generalized linear model GLM (Statistica software package) was used to test the significance of the dependence of heavy metal content on growing conditions and plant species. In each analysis, the compared groups were tested for equality of variances using Levene's test. In the case of equal variances, significant differences were identified using the Tukey HSD post-hoc test at $\alpha = 5\%$.

Results

The data on the mean content of heavy metals in the soil and plant material of woody species are presented in Table 2. The total concentrations of Zn in the soils of green plantings were quite high and showed significant variations in the Dnipro city region, with statistically significant differences between the values (in all cases $P < 0.05$, Table 2). The range of variability of changes in the concentrations of this metal was 30.7–138.7 mg/kg respectively. The range of mean Cu, Pb, and Cd concentrations was significantly narrower and varied from 5.7 to 22.4, 9.0–31.3, and 0.213–0.598 mg/kg respectively. Zn content was the lowest in the areas of Druzhby Narodiv Forest Park and Pridneprovsky Park. An excess concentration of this metal was detected in the area of Park Sahaydak and Metallurgists Square by approximately 6.0 and 4.5 times.

Comparison of the results with the values of environmental quality standards (maximum permissible concentrations) for the soil (on approval of Hygiene Regulations for the permissible content of chemicals in the soil, 2020) showed the presence of excess Zn content in all nine locations studied. To the greatest extent, it was characteristic of Park Sahaydak (8.0 times), Metallurgists Square (6.0), and Hloby Park (5.2).

In comparison with the values specified in the standard for maximum permissible concentrations in the soil, the mean concentrations of copper did not exceed the limit (66.0). However, as in the case of determining Zn concentrations, the lowest copper content was indicated in the site of Druzhby Narodiv Forest Park and Pridneprovsky Park, and the highest content was found in Shevchenko Park, Park Sahaydak, and Metallurgists Square. The mean concentrations of Pb and Cd in the soil also did not exceed the values of the established maximum permissible concentrations. However, as can be seen from the data presented in the table, the sites containing the highest concentrations of these toxicants included Metallurgists Square; in the case of cadmium, this was Novokodatskyi Park.

Compared to soils, the leaves of the studied plants had a significantly lower content of heavy metals with obvious differences between the two tree species (Table 2). The range of zinc concentrations in the leaves of woody plants was 6.9–15.9 mg/kg (*R. pseudoacacia*) and 11.4–40.4 mg/kg (*A. platanoides*).

The concentrations of other studied elements (Cu, Pb, and Cd) in all samples were quite low and had values approximately similar in both studied species. A persistent trend to accumulation of the maximum content of heavy metals by plant organs should be noted in such locations as Park Sahaydak and Metallurgists Square, a similar trend was previously detected in soil samples. It is possible that these data demonstrate a higher level of industrialization and a relatively high concentration of pollutants in the atmosphere at these two sites. The lowest levels of Pb and Cd were found in the plant leaves sampled in the territory of Pridneprovsky Park.

As for the distribution of the obtained bioaccumulation coefficient values, it should be pointed out that all the results for both species were quite low, and almost all the calculated indicators did not exceed 1 (Table 3). Copper bioconcentration was the most significant, with a range of the resulting coefficient of 0.11 to 0.58 (*Robinia*) and 0.11 to 0.36 mg/kg (maple). For zinc, the variability of changes was as follows: 0.06–0.40 (*Robinia*) and 0.17–0.55 mg/kg (maple).

Table 2
Heavy metal content (mg/kg) in soil and tree leaves (n = 5, x ± SD)

Location	Soil or plant	Zn	Cu	Pb	Cd
Shevchenko Park	Soil	79.08 ± 12.40^{d}	22.38 ± 2.93^{a}	15.32 ± 1.28^{f}	0.271 ± 0.029^{c}
Hloby Park		124.83 ± 13.91^{b}	15.91 ± 2.05^{cd}	24.79 ± 3.44^{c}	0.472 ± 0.065^{ab}
Park Sahaydak		185.49 ± 8.50^{a}	17.74 ± 1.62^{bc}	25.47 ± 1.68^{b}	0.359 ± 0.039^{bc}
Druzhby Narodiv Forest Park		37.87 ± 3.67^{f}	7.09 ± 0.71^{fg}	10.23 ± 1.34^{g}	0.213 ± 0.026^{c}
Metallurgists Square		138.25 ± 19.21^{b}	16.88 ± 2.16^{b}	31.28 ± 3.50^{a}	0.557 ± 0.067^{a}
Botanical Garden of DNU		105.09 ± 8.72^{c}	14.53 ± 2.11^{de}	17.63 ± 2.01^{de}	0.516 ± 0.074^{ab}
Novokodatskyi Park		68.01 ± 6.34^{e}	12.76 ± 1.65^{e}	14.30 ± 0.82^{ef}	0.598 ± 0.040^{a}
Green Grove Park		93.17 ± 6.02^{d}	9.77 ± 1.45^{f}	19.05 ± 1.85^{d}	0.556 ± 0.048^{ab}
Pridneprovsky Park		30.65 ± 3.22^{f}	5.66 ± 0.51^{g}	9.00 ± 0.46^{h}	0.289 ± 0.024^{c}
Shevchenko Park	*R. pseudoacacia*	13.24 ± 0.81^{d}	2.56 ± 0.31^{e}	0.53 ± 0.07^{g}	0.013 ± 0.002^{c}
Hloby Park		10.56 ± 1.07^{f}	2.78 ± 0.25^{f}	1.00 ± 0.06^{c}	0.024 ± 0.004^{b}
Park Sahaydak		15.93 ± 1.58^{a}	4.57 ± 0.60^{a}	1.04 ± 0.09^{b}	0.026 ± 0.004^{ab}
Druzhby Narodiv Forest Park		15.18 ± 1.43^{b}	3.47 ± 0.25^{b}	1.04 ± 0.07^{c}	0.025 ± 0.003^{ab}
Metallurgists Square		8.38 ± 1.31^{g}	3.00 ± 0.39^{d}	0.72 ± 0.09^{e}	0.010 ± 0.001^{cd}
Botanical Garden of DNU		6.93 ± 0.81^{h}	2.57 ± 0.36^{e}	1.56 ± 0.14^{a}	0.029 ± 0.003^{a}
Novokodatskyi Park		13.91 ± 1.31^{c}	2.07 ± 0.28^{h}	0.64 ± 0.08^{f}	0.012 ± 0.001^{c}
Green Grove Park		12.60 ± 1.81^{e}	2.45 ± 0.13^{g}	0.80 ± 0.11^{d}	0.013 ± 0.001^{c}
Pridneprovsky Park		11.83 ± 0.79^{i}	3.26 ± 0.29^{c}	0.17 ± 0.03^{h}	0.004 ± 0.001^{d}
Shevchenko Park	*A. platanoides*	15.19 ± 2.06^{e}	2.39 ± 0.17^{c}	0.97 ± 0.06^{e}	0.045 ± 0.003^{d}
Hloby Park		21.58 ± 2.25^{b}	3.30 ± 0.41^{b}	1.08 ± 0.11^{c}	0.026 ± 0.003^{ef}
Park Sahaydak		40.39 ± 5.29^{a}	3.89 ± 0.50^{a}	2.61 ± 0.16^{a}	0.118 ± 0.013^{b}
Druzhby Narodiv Forest Park		20.66 ± 1.04^{c}	2.51 ± 0.18^{d}	0.61 ± 0.07^{f}	0.241 ± 0.021^{a}
Metallurgists Square		12.13 ± 0.81^{g}	2.66 ± 0.33^{c}	0.90 ± 0.05^{e}	0.024 ± 0.003^{f}
Botanical Garden of DNU		15.55 ± 1.81^{d}	2.07 ± 0.19^{f}	1.05 ± 0.11^{d}	0.032 ± 0.004^{def}
Novokodatskyi Park		11.84 ± 1.32^{g}	2.02 ± 0.14^{g}	1.14 ± 0.14^{d}	0.035 ± 0.004^{de}
Green Grove Park		17.22 ± 1.03^{d}	2.32 ± 0.18^{e}	1.39 ± 0.14^{b}	0.028 ± 0.002^{ef}
Pridneprovsky Park		11.35 ± 0.95^{f}	1.97 ± 0.18^{f}	0.39 ± 0.03^{g}	0.067 ± 0.009^{c}

Notes: presented values were shown as mean ± SD; significant differences between means were identified by one-way ANOVA, and Tukey's posthoc test; the different letters within the same column indicate significant differences between heavy metal concentrations in different locations at 0.05 level ($P < 0.05$).

Table 3
Heavy metal bioaccumulation in tree leaves compared to soil (n = 5, x ± SD)

Location	Plant species	K_{Zn}	K_{Cu}	K_{Pb}	K_{Cd}
Shevchenko Park	*R. pseudoacacia*	0.171 ± 0.027^{d}	0.112 ± 0.011	0.031 ± 0.005	0.052 ± 0.013
Hloby Park		0.093 ± 0.012^{f}	0.180 ± 0.031	0.040 ± 0.006	0.058 ± 0.015
Park Sahaydak		0.092 ± 0.010^{a}	0.265 ± 0.040	0.048± 0.006	0.074 ± 0.013
Druzhby Narodiv Forest Park		0.404 ± 0.012^{b}	0.493 ± 0.049	0.104 ± 0.016	0.121 ± 0.022
Metallurgists Square		0.065 ± 0.015^{g}	0.182 ± 0.037	0.020 ± 0.005	0.020 ± 0.003
Botanical Garden of DNU		0.078 ± 0.011^{h}	0.188 ± 0.015	0.091 ± 0.007	0.064 ± 0.011
Novokodatskyi Park		0.211 ± 0.032^{c}	0.165 ± 0.029	0.058 ± 0.006	0.082 ± 0.001
Green Grove Park		0.142 ± 0.024^{e}	0.260 ± 0.055	0.046 ± 0.004	0.022 ± 0.000
Pridneprovsky Park		0.393 ± 0.031^{i}	0.584 ± 0.103	0.024 ± 0.003	0.014 ± 0.002
Shevchenko Park	*A. platanoides*	0.203 ± 0.049^{e}	0.115 ± 0.012	0.063 ± 0.008	0.177 ± 0.028
Hloby Park		0.170 ± 0.029^{b}	0.217 ± 0.041	0.044± 0.008	0.061 ± 0.013
Park Sahaydak		0.227 ± 0.024^{a}	0.220 ± 0.044	0.101 ± 0.011	0.335 ± 0.068
Druzhby Narodiv Forest Park		0.552 ± 0.054	0.366 ± 0.063	0.062 ± 0.011	1.150 ± 0.213
Metallurgists Square		0.091 ± 0.015	0.165 ± 0.015	0.034 ± 0.004	0.044 ± 0.007
Botanical Garden of DNU		0.155 ± 0.018	0.154 ± 0.030	0.061 ± 0.010	0.065 ± 0.009
Novokodatskyi Park		0.182 ± 0.032	0.163 ± 0.029	0.089 ± 0.013	0.067 ± 0.006
Green Grove Park		0.192 ± 0.021	0.249 ± 0.051	0.072 ± 0.002	0.051 ± 0.007
Pridneprovsky Park		0.377 ± 0.039	0.351 ± 0.014	0.042 ± 0.004	0.230 ± 0.028

Note: see Table 2.

Even lower values of bioaccumulation coefficients were calculated for the other two metals studied, Pb and Cd, the levels of which were almost zero. However, it is noteworthy that the bioaccumulation coefficient of cadmium for maple in the location of Druzhby Narodiv Forest Park was 1.15. In the soil sampled in Druzhby Narodiv Forest Park, the concentration of this metal was the lowest of the studied locations. At the same time, cadmium concentration in the leaves was the highest, clearly indicating possible ways of absorbing cadmium from the air.

Evaluation of the results on heavy metal accumulation in soil and leaves of the studied tree species in various locations was performed using a generalized linear model (GLM). In all cases, statistically significant ($P < 0.001$) effects of the environmental factor (location) and tree species on the bioaccumulation coefficient of metals were detected (Table 4).

The results of comparing the accumulative features of the two studied tree species revealed better accumulative properties of *A. platanoides* compared to *R. pseudoacacia* in relation to Zn, Pb, and Cd, which was reflected in the calculated bioconcentration coefficient (Fig. 2).

With regard to cadmium, this feature was detected in each of the studied locations; to zinc, the exception was the results obtained from Novokodatskyi Park, to lead, it was found in all locations except for Druzhby Narodiv Forest Park and Botanical Garden of DNU.

Discussion

Several dangerous heavy metals and metalloids (including Pb and Cd) are classified as unnecessary for the vital functions of biotic organisms. A number of ecosystems located near cities are predominantly contaminated with heavy metals such as lead (Pb) and cadmium (Cd) (He et al., 2023). Moreover, these metals are harmful in various aspects, so the United States Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry (ATSDR) included them in the list of the 20 most dangerous substances (Xiong et al., 2016; Rai et al., 2019). Lead belongs to the category of carcinogenic, mutagenic elements, as well as to the group of elements that have toxic effects on reproduction (Haider et al., 2021).

Table 4

General Linear Models analysis of the effect of location and tree species on the bioconcentration of heavy metals

Bioconcentration	R_{adj}^2	SS Model	Df Model	MS Model	SS Residual	Df Residual	MS Residual	*F*-ratio	*P*-level
K_{Zn}	0.96	1.56	17	0.09	0.06	72	0.0008	115.41	<0.001
K_{Cu}	0.89	1.41	17	0.08	0.13	72	0.0019	44.34	<0.001
K_{Pb}	0.91	0.06	17	0.00	0.00	72	0.0001	52.44	<0.001
K_{Cd}	0.96	5.97	17	0.35	0.21	72	0.0030	119.01	<0.001

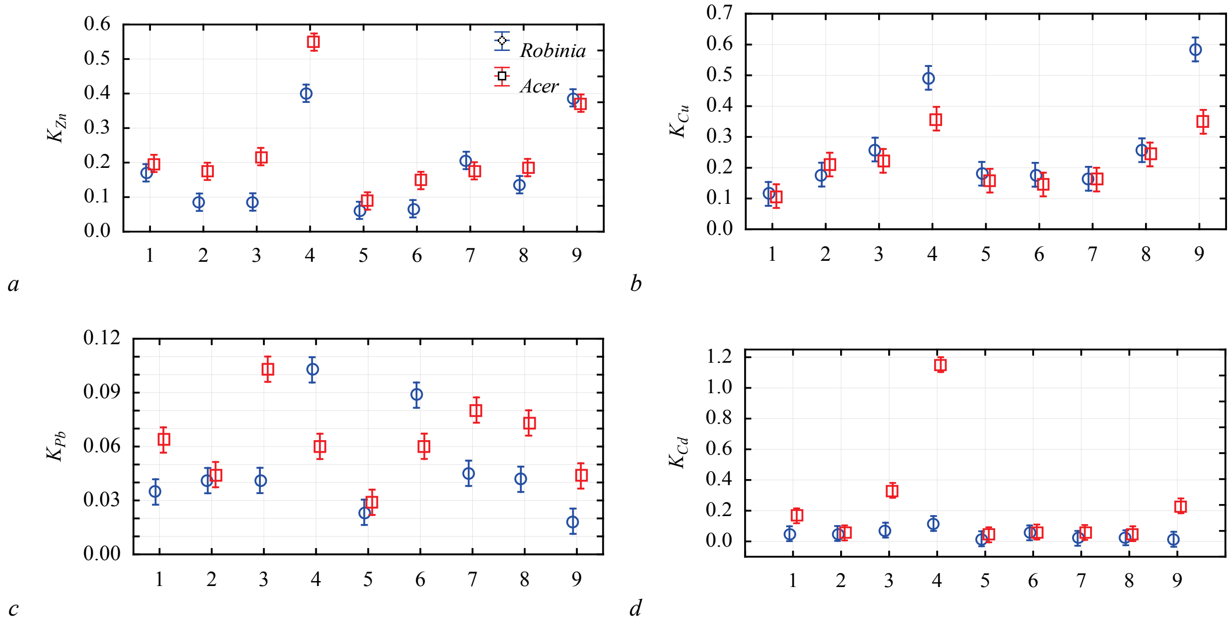

Fig. 2. Variation of heavy metal bioconcentration depending on tree species and location (mean ± 95% conf. interval): the numbers on the abscissa axis show 1 – Shevchenko Park, 2 – Hloby Park, 3 – Park Sahaydak, 4 – Druzhby Narodiv Forest Park, 5 – Metallurgists Square, 6 – Botanical Garden of DNU, 7 – Novokodatskyi Park, 8 – Green Grove Park, 9 – Pridneprovsky Park; the ordinate axis shows a is KZn, b is KCu, c is KPb, d is KCd

In urbanized areas, lead concentrations are highest in soils and biota near roads with high traffic intensity. High concentrations of this metal in the surface soil layer can significantly affect human health through inhalation or ingestion, which is particularly well observed in densely populated areas of the city (Steindor et al., 2016). In soil and vegetation, the concentration decreases exponentially with distance from the road.

Plants absorb lead from the air mainly through the leaves (Gjorgieva et al., 2011). According to Kabata-Pendias & Pendias (2001), the concentration of this metal in a plant is considered to be normal within the range of 0.1–10.0 mg/kg. According to some sources, the concentration of metal in plant samples is considered toxic if it is greater than 30 mg/kg (Kloke et al., 1984). The values of lead concentrations in black locust and maple leaves were consistent with the level of industrial activity in the green part of the city district and vehicle traffic density.

The accumulation of heavy metals in the soil of urbanized areas and their bioaccumulation by similar plant species have been reported by a number of authors (Celik et al. 2005; Oliva & Rautio, 2010; Stafilov et al., 2010). At the grand scale, the absorption of heavy metals by woody plants may be more effective compared to herbaceous plants. This is mainly explained by the deeper root system and greater biomass yield (Capuana, 2011). Representatives of the family Fabaceae including *R. pseudoacacia* belong to plants which have favourable phytomeliorative properties (Lata et al., 2018). This is primarily related to the existence of soil bacterial communities and their beneficial functions in the rhizosphere of *R. pseudoacacia* in response to soil contamination with heavy metals (Fan et al., 2018). A number of authors recommend using *R. pseudoacacia* as passive biomonitors and bio-mitigators in industrial urban ecosystems (Shojaee Barjoee et al., 2023).

To establish the potential role of plants in an urban-technological environment, similar studies were conducted on 25-year-old *Robinia* trees in plantings of various pollution levels in the industrial zone of Bulgaria (Tzvetkova & Petkova, 2015). This article states that the authors observed a gradual increase of Pb, Zn, and Cu contents in *R. pseudoacacia* leaves simultaneously with their accumulation in the soil, but such a pattern was not found in our studies. In our research, the result of matching for the same metals (Pb, Zn, and Cu) was recorded only in one of the least "polluted" areas (Pridneprovsky Park) and for another studied tree species, Norway maple. For *Robinia*, the correspondence of the highest concentrations in the substrate and the assimilation part of plants was registered for one of the metals, specifically for zinc (Park Sahaydak).

Distinctive trends in the bioaccumulation characteristics of the studied tree species were found only for copper. The bioconcentration coefficient of copper in black locust was greater in almost all the studied sites (except Hloby Park) compared to the maple. The differing values of the heavy metal bioaccumulation compared to our data were shown in Nadgórska-Socha et al. (2017). Thus, according to the results obtained by researchers, the bioaccumulation index for *Robinia* growing in one of the industrially developed regions of Poland was equal to 10.8, being significantly greater than the value of the bioaccumulation coefficient obtained by us. The authors emphasize the high potential of *R. pseudoacacia* to accumulate Cd and Pb not detected during our experiments. However, it is important to note that a big difference in the obtained data can be obviously explained by the different levels of contamination of the studied soils and the environment in different regions of the study.

Cadmium (Cd) is a non-essential trace element widely distributed in the environment. Its sources of various origins can increase Cd concentration in soils, which affects the biogenic cycles of nutrients, food, and water reserves. According to WHO recommendations, Cd dose exceeding 3 μg/L for drinking water is carcinogenic to humans. Cd generally occurs in the divalent form and is one of the most mobile heavy metals in the environment. Increased mobilization potential is the reason for faster Cd release from the soil into groundwater than other metals (Kubier et al., 2019). Normal Cd concentrations in plants ranged from 0.2 to 0.8 mg/kg. Concentrations of this metal above 5 mg/kg are considered to be toxic (Kloke et al., 1984; Kabata-Pendias & Pendias, 2001). The obtained values were compared with previously published data on the heavy metal accumulation in woody plants associated with urban-technogenic areas. Despite the large variability, the values of concentration of this metal in black locust and maple leaves were clearly lower than those obtained in similar experiments (Aksoy et al., 2000; Hrotkó et al., 2021). Other metals studied in this paper, Cu and Zn, are essential for a number of metabolic processes and therefore are inextricably linked to the metabolic functioning of biota (Marschner, 2012). In particular, excess Zn concentrations in plants >100 mg/kg (Allen, 1989) can cause a decrease in leaf biomass production (Gupta et al., 2016; Zverkovskiy et al., 2018). Copper is an important structural element for many enzymes, but its excess in the soil environment can pose a danger even greater than non-essential lead (An, 2006). In soils, Cd was rarely found as the single heavy metal pollutant; it is often accompanied by Zn present in the soil (Hammer et al., 2003; Mertens et al., 2005; Rai et al., 2019). After all, cadmium uptake in plant tissues tends to occur mainly via transporters, including Zn^{2+} (Rascio & Navari-Izzo, 2011).

Inhibition of Cd entry processes is often observed under zinc deficiency conditions (Naeem et al., 2015; Farooq et al., 2020). Based on the results of correlative analysis obtained for the soil environment, our data confirm the nature of such synergistic bonding between these two metals, although the coefficients obtained by us have a medium strength of positive correlative relationships ($r = 0.38$, $P = 0.047$). Further, functional studies of HMAs (heavy metal ATPases) have shown these transporters to be divided into two subgroups based on their metal-substrate specificity: a copper (Cu)/silver (Ag) group and a zinc (Zn) / cobalt (Co) / cadmium (Cd) / lead (Pb) group (Tangahu et al., 2011).

Compared to black locust, there are not many studies conducted on the other species studied by us, Norway maple. Plants with a wider leaf plate usually have a higher transpiration rate compared to that with smaller leaf plates (Cicek et al., 2004; Baldacchini et al., 2019). Thus, metal uptake by the roots of plants having wide leaf plates can be enhanced, it leads to the movement of metals from the roots to other plant tissues (Stalikas et al., 1997; Zheng et al., 2007). In addition, due to the wide leaf area, these plants are more susceptible to the accumulation of pollutants from dust and rainwater (Esfandiari & Hakimzadeh, 2022). As in our experiment, Steindor et al. (2016) sampled leaves of *A. platanoides* and soil in the Katowice area to assess the level of environmental contamination by Pb, Zn, Cd, and Cu. Similar to the data obtained both by the previous scientists and by us, when the soils were relatively heavily contaminated with Pb, Zn and Cd, then the plant material contained a small amount of these metals. The concentrations of the studied elements were lower in the adjacent forest zone of the city (Druzhby Narodiv Forest Park) and in areas the most distant from central part of the city (Pridneprovsky Park); it was consistent with data obtained for some European cities (Turan et al., 2011; Pfleiderer et al., 2012; Steindor et al., 2016). Also, similar to the data obtained by us and the results of the abovementioned authors, there was no clear relationship between the content of various heavy metals in the soils of the settlement studied. In publications devoted to the study of the heavy metal effects on plants, the accumulation coefficient or bioconcentration coefficient is increasingly used as a factor of plant potential to uptake toxic elements (Efroymson et al., 2001; Hammer et al., 2003; Mertens et al., 2005; Algreen et al., 2013). Due to this coefficient, the research on soil, the water system, and precipitation was expanded, as well as the assessment of heavy metal pollution in environmental geochemistry.

Conclusions

The data obtained as a result of the research indicate an uneven distribution of heavy metal contents in the soil environment of urbanized territories of Dnipro city. The excess over the maximum permissible concentrations in the soil of green plantings was found only for Zn. Comparison of Zn, Pb, and Cd concentrations between the two tree species showed greater concentrations in *A. platanoides* leaves compared to *R. pseudoacacia*, but such differences were generally insignificant. According to the results of this study, plantings of *A. platanoides* should be given first priority in lead- and cadmium-polluted areas, as this tree species accumulates such metals more intensively compared to *R. pseudoacacia*. On the background of rising interest in the use of woody plant species in urban green space systems to mitigate the negative environmental risks caused by rising levels of heavy metals, further research is needed to fill in the gaps related to the features of transportation, accumulation, and mechanisms of interaction of such elements in various separate plant organs.

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