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# STUDY ON ACCUMULATION OF HEAVY METALS BY GREEN PLANTATIONS IN THE CONDITIONS OF INDUSTRIAL CITIES

**Purpose.** Determination of the relationships between the concentrations of Zn, Cu, Pb, Cd in the atmospheric air and in the assimilative organs of the false acacia (*Robinia pseudoacacia*) trees – the most common species in the system of landscaping of industrial cities. The objectives of the study included finding out the peculiarities of the spatial distribution of metal pollutants in green spaces of Robinia pseudoacacia in Dnipro city.

**Methodology.** The study was conducted in the system of green spaces of the industrial city of Dnipro, in the atmospheric air of which pollutants dominate, whose source is emissions from metallurgy, energy and motor transport. To carry out the experiment, the method of atomic absorption spectrophotometry was used to determine the concentrations of heavy metals. The trend of technogenic emissions into the atmosphere was estimated by statistical methods. The spatial distribution of accumulation of essential and toxic metals in the Robinia plantations of the industrial city was built on the basis of the obtained experimental data.

**Findings.** Among the studied pollutants, the maximum concentration in the assimilation organs was found for Zn, whose range was 15–30 $mg \cdot kg^{-1}$. Almost the same level of accumulation was reached for Cu and for Pb: 3.9–17.2 and 8.6–10.8 $mg \cdot kg^{-1}$, respectively. The presence of Cd, which is not an essential element, has been established, which allows considering Robinia plantations as a potential depositor of Cu and Cd in conditions of polyelemental pollution of industrial cities.

**Originality.** It was established that Robinia plantations as an element of the green infrastructure of industrial cities are characterized by the maximum effect of Cu (among other heavy metals) translocation and are effective potential depositors of Pb when its normative values in the atmospheric air are exceeded..

**Practical value.** On the basis of the obtained experimental data, the spatial distribution of accumulation of metals as pollutants in Robinia plantations was constructed, which can be considered in the plane of optimization of the state of atmospheric air in the city. The cartographic materials that can be used by the subjects of environmental monitoring and green construction of industrial cities were obtained.

**Keywords:** *Robinia pseudoacacia, technogenic emissions, metal pollutants of atmospheric air, urban greening system, spatial distribution of pollutants in green spaces*

**Introduction.** Ecological risks of the environment are caused by the technogenic factor – the increased level of atmospheric air and soil pollution. Industrial enterprises of mining and metallurgical, fuel and energy, chemical sectors, and transport are the main sources of air pollution in Dnipro.

The concept of environmental risk reduction in the study area includes two components – risk assessment and risk management.

Human health hazards associated with atmospheric pollutants can arise mainly from the inhalation of metal elements together with dust, mainly in urban areas with high population density [1]. Currently, phytotechnologies, or approaches based on the use of plants as objects of bioindication research, are attracting attention due to their economic feasibility [2, 3]. Plants can be used as accumulators of particulate matter and associated pollutants, including toxic metals, because the leaves themselves capture dust from the environment [4].

Studies related to the absorption and accumulation of heavy metals by plant organisms concern the problem of metal transport through the root system [5]. However, in addition to plant roots, metal elements are absorbed by aboveground plant organs, among which foliar uptake is predominant. Xiong, et al. (2014) showed leaf accumulation of Cd, Zn and Pb [6]. Schreck, et al. (2012) showed foliar uptake of Zn, Cu, Cd and Pb by different plant species [7]. Accumulation of metallic elements such as Cr, Cu and Pb in plant leaves occurs mainly as a result of atmospheric dust deposition on the leaf surface through stomata, cuticular cracks, lenticels, ectodesmata and water pores [8].

Actually, according to a number of authors, metals can accumulate in plant leaves by leaf transfer through the deposition of atmospheric particles on the leaf surface [9].

Most studies on metal uptake usually focus on metal concentration without investigating the pathways of their transfer or focus exclusively on biomonitoring of precipitation. Foliar uptake of heavy metals has been primarily evaluated for those metals that are well known to play a significant role in plant metabolic and biochemical reactions.

Several studies have reported foliar uptake of metals, including Cu and Zn [10]. These metals penetrate the cuticle and then accumulate in the leaf tissues of plants. It is known that lead (Pb) and cadmium (Cd) can also enter the leaves of plants by foliar transfer.

Xiong, et al. [6] and Edelstein, Ben-Hur [8] have made a significant contribution to the study on the biogeochemical behavior of heavy metal uptake by leaves with the establishment of mechanisms of heavy metal uptake by plants, factors affecting the foliar uptake of heavy metals, transport, speciation and distribution of heavy metals within plants, as well as toxicity and detoxification of heavy metals after leaf uptake.

The level of heavy metals in the aboveground vegetative organs of plants is often described in studies of environmental risk assessment, which are presented in the form of indices of atmospheric pollution [11]. In industrial regions, some authors report that the concentrations of heavy metals in plant tissues are several times higher than the threshold levels.

False acacia, an introducer from North America, occupies a dominant position in the landscaping system of the Dnipro city. This species is ecologically and economically feasible when used in green construction of industrial cities of the natural zone of the Steppe of Ukraine.

**The purpose** of the work is to evaluate the relationship between the accumulation of metal elements (essential Cu and Zn) and toxic (Cd and Pb) in the assimilative vegetative organs of the false acacia and the concentrations of these elements in the atmospheric air of Dnipro city. The objectives of the study were to find out the peculiarities of the spatial distribution of concentrations of metal elements in the aboveground vegetative organs of Robinia plantations in the city of Dnipro.

**Research methods.** The study was conducted in the period 2018–2020 in the city of Dnipro (natural zone – Northern Steppe of Ukraine). The city is located in the zone of temperate latitudes with a fairly active atmospheric circulation with a predominant movement of air masses from east to west. The climate is temperate continental. One of the features of the climate of the territory is significant fluctuations in weather conditions from year to year. Moderately wet years alternate with sharply arid years, dry winds are not uncommon. In general, the climate is characterized by rather cool winters and hot summers.

In the green spaces of Dnipro city, as an object of the research, seven groups of model trees of Robinia common 20–30 years old with similar morphological and taxonomic characteristics were identified. Plots were established in 6 park zones of Dnipro city and in the nature reserve "Dniprovsko-Orilskyi", which represented the whole range of habitats of this species in the study area.

*Site 1* is located in Druzhby Narodiv forest park. It is located in the left-bank part of the city. The main stationary source of emissions of harmful substances into the atmosphere is the K. Liebknecht Pipe Rolling Plant.

*Site 2* is located in Taras Shevchenko Central Park. Trees are located in the central part of the park at a distance of 100 m from the road.

*Plot 3* is located in the park named after Lazar Hloba. It belongs to the central part of the city, which is characterized by heavy traffic.

*Site 4* is located in the center of the Botanical Garden of Oles Honchar National University. It belongs to the central part of the city, which is characterized by intensive traffic of motor transport port.

*Site 5* is located on the territory of the Park of the *40th* anniversary of the liberation of Dnipropetrovsk at a distance of 50 m from the highway. It also belongs to the western right-bank part of the city and is characterized by a large number of industrial enterprises and intensive traffic.

*Site 6* is located on the territory of Prydniprovskyi Park. The largest source of emissions in this eastern part of the city is the Prydniprovska TPP, which does not have a significant impact on the pollution of the park, as emissions are carried out through high pipes, which leads to the removal of the zone of maximum pollution.

*Site 7* is located on the territory of the nature reserve "Dniprovsko-Orilskyi". The territory of the reserve lies on the left bank of the Dnipro River floodplain, outside the city limits. There are no industrial enterprises within a radius of 50 km.

Material from five different model trees was collected on each plot. Leaves of the middle formation of 20 pieces were selected on the annual vegetative growth from the lower third of the crown of the southern exposure in dry clear weather, simultaneously from each experimental plot.

Leaf plates were dehydrated in porcelain crucibles using a drying oven at $t = 100$ °C. Using an AXIS AD500 electronic balance, the dry leaf residue was weighed to the nearest 0.001 g (the required mass for analysis was 0.5–1.0 g). Then ashing was carried out in a muffle furnace at $t = 450$ °C. The ash was poured into a conical flask and 0.5 ml of concentrated nitric acid and 0.5 ml of distilled water were added. The resulting solution was made up with 10 ml of distillate and filtered with ashless filters, then the crucible was washed with 10 ml of distilled water and the volume of the solution was made up to 25 ml. The content of such elements as Zn, Cu, Pb, Cd was analyzed in the samples. The content of heavy metals in leaf blades was determined using the method of atomic absorption spectrophotometry on the spectrophotometer AAS-30 according to the standard method of I. P. Khavezov (1983).

To assess environmental risks, the trend of anthropogenic emissions into the atmosphere was analyzed. According to the data of the Main Department of Statistics in Dnipropetrovsk oblast, annual emissions of pollutants are estimated at 641.1–3680.0 thousand tons, among which Zn and Pb dominate, with emissions ranging from 59 to 34.8 thousand tons per year (Zn) and from 8.2 to 18.4 thousand tons per year (Pb).

Comparison of the actual concentrations of the studied metals in the atmospheric air of the city of Dnipro with the values of the average daily maximum permissible concentration in the atmospheric air made it possible to establish the excess of legal environmental standards (Order of the Ministry of Health of Ukraine No. 156/34439 as of 10.02.2020).

The concentration of Pb (*1st* hazard class) in the air of Dnipro city is in the range of 0.001–0.029 mg·m$^3$. Given the value of the MPCs.d. of this element is 0.0003 mg·m$^3$, the excess of the normative value is critical and reaches 96 times.

The concentration of Cd (*1st* hazard class) in the air corresponds to the range of values 0.001–0.005 mg·m$^3$. Exceedance of the MPCs.d. (0.003 mg · m$^3$) is insignificant and amounts to 1.6 times.

Cu content (*2nd* hazard class) is 0.06–0.63 mg · m$^3$. Under the condition of MPCs.d. of 0.002 mg · m$^3$ the exceedance corresponds to a very significant range from 30 to 316 times.

Zn concentrations (*3rd* hazard class) are 0.34–2.31 mg · m$^3$. MPCs.d. is 0.05 mg · m$^3$, that is, the excess of the standard in the atmospheric air is also quite significant – 23–46 times.

**Results.** The assessment of environmental safety should be based on the data of studies on the accumulation of metal elements in the assimilation organs and the leveling of the impact of pollutants from anthropogenic emissions by recreational stands of one of the most common species in Dnipro greening system. The content of the studied elements in the assimilative organs of false acacia is given in Table 1.

On the basis of the values of concentration of metal elements in the phytomass of *Robinia pseudoacacia* leaves established in the study, the development of cartographic material of the spatial distribution of accumulation of metal contaminants – Zn, Cu, Pb, Cd in Robinia plantations of recreational areas of Dnipro city was carried out using GIS technologies (Figs. 1–4).

The above cartographic materials allow us to state that the accumulation of Cd in the phytomass of Robinia plantations is in the range of 0.21–0.39 mg · kg$^{-1}$. The maximum concentration (≥ 0.39 mg · kg$^{-1}$) is observed in trees that form recreational plantations Lazar Hloba Park, Park of the *40th* Anniversary of the Liberation of Dnipropetrovsk and Prydniprovskyi Park.

*Table 1*

Concentration of metallic elements in the assimilative organs of false acacia trees

| Location | Metal element, mg·kg$^{-1}$ | | | |
|---|---|---|---|---|
| | Zn | Pb | Cu | Cd |
| Druzhby Narodiv Forest Park | 30.28 ± 1.13 | 8.78 ± 2.21 | 8.23 ± 2.13 | 0.35 ± 0.07 |
| Taras H. Shevchenko Park | 15.03 ± 2.22 | 10.8 ± 2.12 | 6.43 ± 2.79 | 0.28 ± 0.07 |
| Lazar Hloba Park | 24.54 ± 1.17 | 9.52 ± 0.96 | 17.2 ± 3.15 | 0.41 ± 0.11 |
| Botanical Garden of DNU | 17.61 ± 1.87 | 8.25 ± 1.13 | 7.06 ± 0.67 | 0.18 ± 0.29 |
| Park of the *40$^{th}$* Anniversary of the Liberation of Dnipropetrovsk | 21.17 ± 1.78 | 10.59 ± 1.12 | 16.43 ± 1.16 | 0.42 ± 0.13 |
| Prydniprovskyi Park | 15.8 ± 1.93 | 8.58 ± 2.12 | 4.77 ± 0.32 | 0.39 ± 0.19 |
| Dniprovsko-Orilskyi Nature Reserve | 9.62 ± 1.45 | 10.68 ± 1.77 | 3.96 ± 0.11 | 0.17 ± 0.04 |

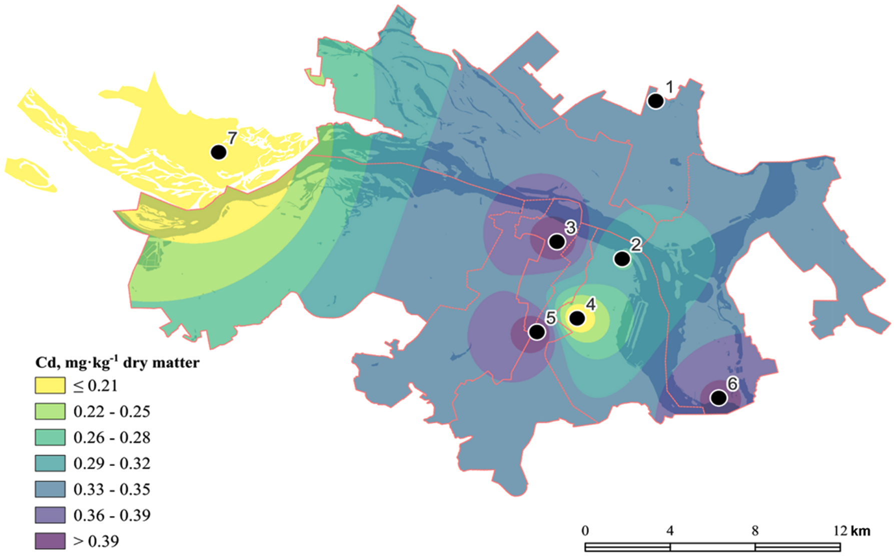


*Fig. 1. Spatial distribution of Cd in the foliage fraction of Robinia tree stands in the greening system of Dnipro city*

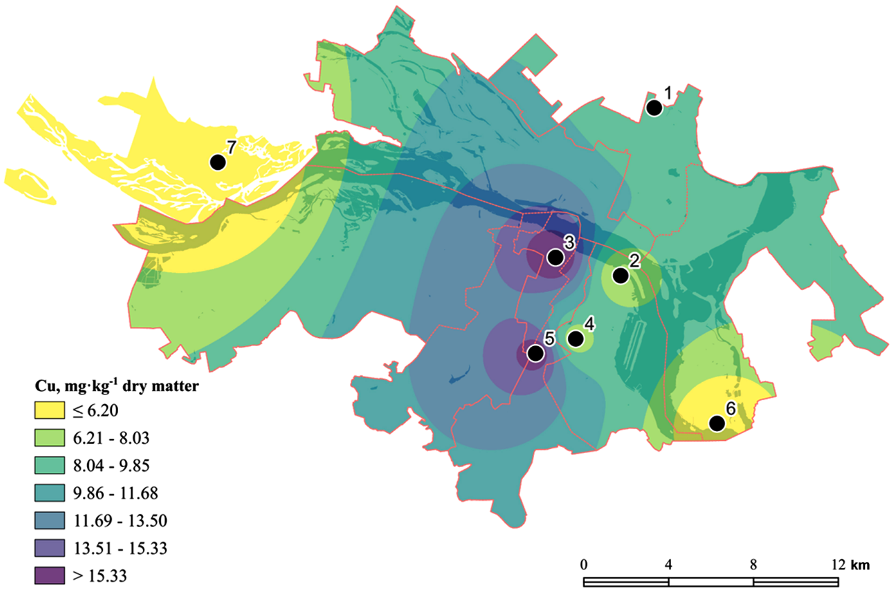


*Fig. 2. Spatial distribution of Cu in the foliage fraction of Robinia tree stands in the greening system of Dnipro city*

Most of the area is occupied by plantations that accumulate Cd in the range of 0.33–0.35 mg · kg$^{-1}$. The concentration decreases towards the west of the city. Localities of Dniprovsko-Orilskyi Nature Reserve and Botanical Garden of DNU are characterized by minimal concentration of this metal element.

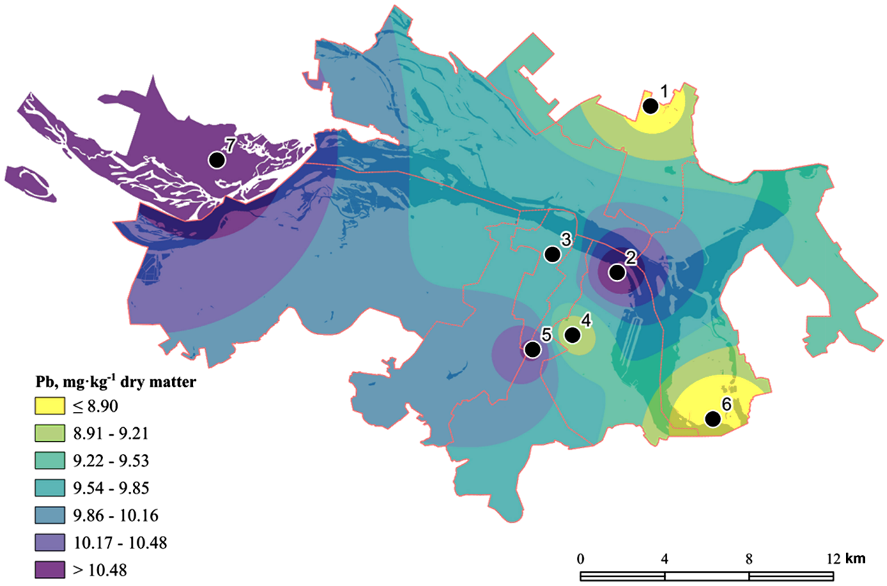


*Fig. 3. Spatial distribution of Pb in the foliage fraction of Robinia stands in the greening system of Dnipro city*

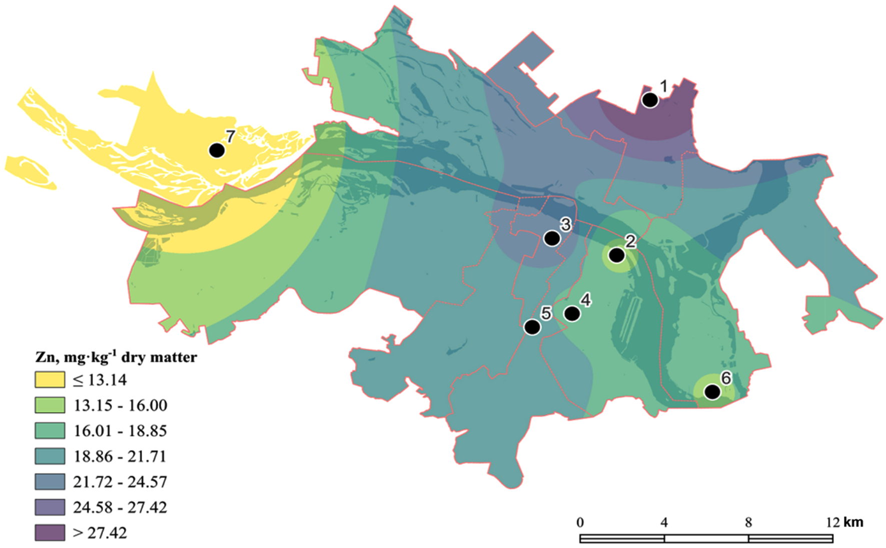


*Fig. 4. Spatial distribution of Zn in the foliage fraction of Robinia stands in the greening system of Dnipro city*

According to the distribution of Cu concentration in the fraction of assimilative vegetative organs, we can observe the predominance of recreational plantations that accumulate Cu in the range of 9.86–11.86 mg · kg$^{-1}$. Attention is drawn to the location with the maximum accumulation of more than 15.3 mg · kg$^{-1}$ of this metal element in the recreational plantations of the Park of the *40$^{th}$* Anniversary of the Liberation of Dnipropetrovsk and Prydniprovskyi Park. The areas where urban Robinia plantations with a minimum Cu concentration of less than 6.2 mg · kg$^{-1}$ are concentrated are in the western part and in the southeast of the city.

The gradation of concentrations demonstrates the accumulation of Pb in the Robinia stands of the left-bank part of the city, where plantations with 9.5–9.9 mg · kg$^{-1}$ of this element in the assimilation organs are concentrated. On the left bank of the Dnipro in Dniprovsko-Orilskyi Nature Reserve the maximum accumulation of this toxic element in the concentration of 10.5 mg · kg$^{-1}$ is recorded. The minimum Pb deposition (less than 8.9 mg · kg$^{-1}$) occurs in the phytomass of plantations growing in the south and northeast of the city in the area of Druzhby Narodiv Forest Park and Prydniprovskyi Park.

Between the established gradations of Zn accumulation in urban plantations, the areas with Robinia, which accumulates 18.7–21.7 mg · kg$^{-1}$, prevail, which are the average values determined for this metal element.

Locations of a small area with maximum concentrations (>27.4 mg · kg$^{-1}$) of Zn in the assimilation fraction of Robinia phytomass, which are concentrated in the area of Druzhby Narodiv Forest Park, were identified. The zone of minimal accumulation of this essential element was recorded in the plantations of false acacia Dniprovsko-Orilskyi Nature Reserve.

The accumulation of heavy metals by plant leaves depends on a number of factors, including the distance from the source of pollution, differences between plants in anatomy and physiology (such as evergreen/deciduous), physical properties and intensity of heavy metal emissions, edaphic and climatic factors (wind and precipitation, pH, redox state) [12].

Due to the ubiquitous presence of the majority of streets and parks of urban agglomerations in the phytocoenoses, as well as due to the appropriate morphology, canopy structure, and the capacity of leaves to accumulate heavy metals, many species of hardwoods are often used for biomonitoring of heavy metal pollution [5, 13–15].

*Table 2*

Ratio coefficients of metal elements in the phytomass of assimilative organs of false acacia trees to the end of their exposure to atmospheric air

| Experimental plots | Metals, mg · kg$^{-1}$ | | | | Cu/Zn |
|---|---|---|---|---|---|
| | Zn | Pb | Cu | Cd | |
| Druzhby Narodiv Forest Park | 13.1 | 13.1 | 8780.0 | 350.0 | 0.27 |
| Taras H. Shevchenko Park | 6.5 | 10.2 | 10800.0 | 280.0 | 0.43 |
| Lazar Hloba Park | 72.2 | 287.7 | 328.3 | 82.0 | 0.70 |
| Botanical Garden of DNU | 51.8 | 117.7 | 305.2 | 36.0 | 0.40 |
| Park of the *40$^{th}$* Anniversary of the Liberation of Dnipropetrovsk | 62.3 | 273.8 | 365.2 | 84.2 | 0.78 |
| Prydniprovskyi Park | 6.8 | 7.6 | 8580.0 | 390.0 | 0.30 |
| Dniprovsko-Orilskyi Nature Reserve | 4.2 | 6.3 | 10,680.0 | 170.0 | 0.41 |

*Table 3*

Correlation coefficients of metallic elements in phytomass of assimilative organs of *Robinia pseudoacacia* trees

| Metal elements | Zn | Pb | Cu | Cd |
|---|---|---|---|---|
| Zn | 1 | – | – | – |
| Pb | –0.388 | 1 | – | – |
| Cu | 0.570 | 0.162 | 1 | – |
| Cd | 0.599 | –0.036 | 0.666 | 1 |

The use of vegetative parts of trees as bioindicators in environmental biomonitoring is effective due to the ability of leaves to retain/absorb heavy metals from air and soil [3, 16]. In addition, heavy metals can be absorbed by roots, then transferred to the aboveground part and accumulate in leaves [17, 18].

Table 2 shows the coefficients that demonstrate the ratio of the concentration of a metal element in the phytomass of assimilative organs to the concentration of the corresponding element in the atmospheric air, Table 3 – correlation coefficients.

The maximum values of the coefficients of translocation of metals from the atmospheric air to the aboveground phytomass are characteristic of Cu. For this metal element, the concentration in the phytomass of leaves exceeds the concentration of this element in the air from 305 to 10,800 times.

The calculated correlation coefficients between the studied metal elements revealed the closest positive correlation between Cu and Cd, Zn and Cd, as well as Cu and Zn.

A moderate negative correlation is observed for such metallic elements as Pb and Zn, while for Pb and Cu it is weak. In fact, there is no connection between the most toxic elements studied – Cd and Pb.

The Cu/Zn ratio determines the degree of proportionality in the provision of metal elements for enzyme synthesis processes. The range of values of the Cu/Zn ratio in the assimilation organs of Black locust of recreational plantations in Dnipro city was 0.27–0.78, which is due to the high concentrations of Zn in the phytomass of the studied plants.

The ratio of essential metals, which was calculated for the plantations of Druzhby Narodiv Forest Park and Prydniprovskyi Park, is characterized by close to optimal values in conditions of different levels of concentrations of metal elements in the atmospheric air of the studied locations of the city of Dnipro.

The greatest imbalance in ensuring the processes of enzyme synthesis is experienced by the Robinia plantations of the Park of the *40$^{th}$* Anniversary of the Liberation of Dnipropetrovsk and Lazar Hloba Park, in which the values of the Cu/Zn ratio are 2.8–2.6 times.

Copper (Cu) is a true bioelement, as it is always present in plant tissues and participates in metabolic processes. This metal is part of plastocyanin, which transfers electrons between photosystem II and photosystem I, and is a component of enzymes that catalyze the oxidation of ascorbic acid, diphenols and hydroxylation of mono-phenols. The value in the assimilation organs of the studied plants in different areas of Dnipro city corresponds to the range of 3.9–17.2 mg · kg$^{-1}$.

Zinc (Zn) in plants takes part in redox processes that stabilize gas exchange, and participate in the synthesis of tryptophan [19]. The phytotoxic concentration is 300 mg · kg$^{-1}$ of dry matter, which was not exceeded in the phytomass of the studied Robinia plantations and corresponds to the range of 9.6–30.3 mg · kg$^{-1}$. Similar results were obtained in the study on metal elements accumulated in plantations of woody species [20].

**Conclusions.** The studied metal elements in the assimilative vegetative organs of the surface phytomass of Robinia plantations are accumulated in descending order of concentration in the sequence Cu > Zn > Cd > Pb. Phytotoxic values of the content of essential elements – Zn and Cu in the phytomass of plantations, under conditions of exceeding their concentrations in the atmosphere, are not exceeded. Metal elements Pb and Cd are not used by plant organisms, therefore, their presence in the phytomass can be considered an indication of the state of the ambient air in relation to these metals. Phytotoxic concentrations of Pb (5.0 mg · kg$^{-1}$) were exceeded in the studied assimilation organs of Robinia plantations in all locations of the city. The actual concentrations of Cd determined in the urban Robinia plantations were an order of magnitude lower than 2.5 mg · kg$^{-1}$, which is defined as the phytotoxic level of this toxic element. Robinia plantations in the landscaping system of Dnipro city can be considered as a potential depositor of Pb in case of exceeding its normative values in the atmospheric air.

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# Дослідження акумуляції важких металів зеленими насадженнями в умовах промислових міст

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**Мета.** Визначення взаємозв'язків між концентраціями Zn, Cu, Pb, Cd в атмосферному повітрі та в асиміляційних органах дерев робінії несправжньоакації (*Robinia pseudoacacia*) – найбільш розповсюдженого виду у системі озеленення промислових міст. До задач дослідження входило з'ясування особливостей просторового розподілу металічних полютантів у зелених насадженнях робінії несправжньоакації в місті Дніпро.

**Методика.** Дослідження проведене у системі зелених насаджень промислового міста Дніпро, в атмосферному повітрі якого домінують забруднюючі речовини, джерелом яких є викиди підприємств металургії, енергетики та автомобільного транспорту. Для здійснення експерименту застосовано метод атомно-абсорбційної спектрофотометрії для визначення концентрацій важких металів. Статистичними методами оцінено тренд техногенних емісій в атмосферне повітря. На основі отриманих експериментальних даних побудовано просторовий розподіл акумулювання есенціальних і токсичних металів у робінієвих насадженнях промислового міста.

**Результати.** Із досліджуваних полютантів максимальне концентрування в асиміляційних органах виявлено для Zn, діапазон вмісту якого становив 15–30 мг · кг$^{-1}$. Майже однакового рівня акумулювання сягали Cu і Pb: 3,9–17,2 та 8,6–10,8 мг · кг$^{-1}$ відповідно. Встановлена наявність Cd, який не є есенціальним елементом, що дозволяє розглядати робінієві насадження в якості потенційного депонатора Cu і Cd в умовах поліелементного забруднення промислових міст.

**Наукова новизна.** Встановлено, що робінієві насадження, як елемент зеленої інфраструктури промислових міст, характеризуються максимальним ефектом транслокації Cu (серед інших важких металів) і виявляються ефективними потенційними депонаторами Pb при перевищенні його нормативних значень в атмосферному повітрі.

**Практична значимість.** На основі отриманих експериментальних даних побудовано просторовий розподіл акумулювання металів як елементів-забруднювачів у робінієвих насадженнях, що можна розглядати у площині оптимізації стану атмосферного повітря в умовах міста. Отримані картографічні матеріали, що можуть бути використані суб'єктами екологічного моніторингу й зеленого будівництва промислових міст.

**Ключові слова:** *робінія несправжньоакація, техногенні емісії, металічні полютанти атмосферного повітря, система озеленення міст, просторовий розподіл забруднювачів у зелених насадженнях*

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