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Factors of Accumulation of Heavy Metals by Above-ground Phytomass of the Predominate Plants of Urban Ecosystems of Kursk

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Abstract. The article deals with the data on accumulation of heavy metals in the above-ground phytomass of common vegetation in urban ecosystems of Kursk. The accumulation of heavy metals by woody and grassy plants vegetating on soils of various genesis and structure of land-use experiencing contrast technogenic burden is studied. It is established that the priority element among heavy metals polluting plants is plumbum which exceeded limits of normal concentrations (norm) in 47% of samples which are taken in ecosystems of the city. Plants accumulators of manganese and zink are revealed. The proportion of the samples polluted by Pb in *Tilia cordata* Mill. in parks, squares and ecosites of Kursk reaches 100%. The role of two complex factors determining rates and volumes of deposition of plumbum in above-ground phytomass of common species of flora of Kursk is defined.

1. Introduction

Technogenic emissions of heavy metals to the environment lead to strengthening of their concentration in different components of ecosystems. The heavy metals (HM) emitted by the industry and motor transport are deposited in the soil and are fixed in ground geochemical barriers and also reach the food web and water bodies (surface and ground waters). High content of HM is registered in technogenic landscapes and urban areas. As a rule, they represent a gradually growing aureole of impact or local pollution [1, 2].

One of relevant problems of the modern ecology is to reduce pollutant emissions and to reduce the rates of their migration in the environment thus ensuring stable functioning of biogeochemical cycles and maintaining the ecosystem balance. The important role in these processes is assigned to geochemical barriers [1, 3].



The biogeochemical barrier of migration of HM promotes immobilization of a part of HM in the soil-plant system. The ions of Pb, Zn, Cd, Cu, Ni and of other HM deposited by cells of the plants are limited in their possibility of leaching out of a soil profile. However they can be spread to biomass of consumers of food webs with quite high speed [1, 3] that negatively affects the biological variety and the health of city dwellers.

Plants possess a wide range of responses and reactions to environmental pollution by HM. Plants can be divided into accumulators and excluders according to the ability to accumulate HM in the organs [4]. The fundamental difference is that the first accumulate HM in the above-ground phytomass, while the second – in roots. Biological features (tolerance, metals specificity, existence of compartments) and soil characteristic influencing the availability of HM to plants from factors of the plants defining ability to take HM from the polluted soils (distribution of HM between liquid and solid phase of soils, redox and acid-base conditions, granulometric texture, humus level) are the factors that influence the availability of plants to accumulate HM from the polluted soils [4].

Topical issue is studying the accumulative ability of the above-ground phytomass in the cities which plays a role of a dynamic component of an ecological framework. It is essential to assess the effectiveness of barrier function, to predict the dynamics of a vegetable component of ecosystems and define the plant species potentially used for phytoremediation of the polluted soils [5, 6].

The goal of work is the assessment of heavy metals pollution of the above-ground phytomass and identification of the factors that influence their accumulation in the predominate plant species of urban ecosystems of Kursk.

2. Objects and methods of research

The research was carried out in the territory Kursk in 2018. As key sites the urban ecosystems with contrast anthropogenic burden and soils of various genesis and structure of land use were chosen (Table 1).

Table 1. Key sites of the research of the above-ground phytomass in Kursk

№	Key sites	Soil type*	Total HM pollution of soils index, Zc	Functional zone	Land-use type
1	Forest-park Znamenskaya grove	Dark-grey soil –	10.6	Recreational	Forest land
2	North west district	Urban grey soil –	7.8	Borderline between industrial and residential	Hay meadow
3	Floodplain of Seim river near the ash-disposal area of CHP-1	Alluvial gleyic soil	48.5	Borderline between industrial and residential	Hay meadow
4	Forest-park Gorelii forest	Podzols illuvial-ferruginous	6.1	Sanitary protection zone	Forest land
5	Forest-park Mokva	Sod-podzols illuvial-ferruginous	3.5	Recreational	Forest land

*Remark: diagnostics и classification of soils of key sites has been carried out before [2, 7, 8]

At the five above-mentioned key sites, at the end of the vegetation season, the phytomass of predominant trees (leaves and needles) or herbs (stems and leaves) was taken.

To assess the impact of anthropogenic burden on the biotic component of urban soils in parks, squares and forest-parks of the city, before the beginning of leaf fall, leaves of the same age of *Tilia*

cordata Mill were sampled. Samples were taken in nine popular city resorts – parks, squares and forest-parks of the city, located in the city center and on its outskirts (Figure 1).

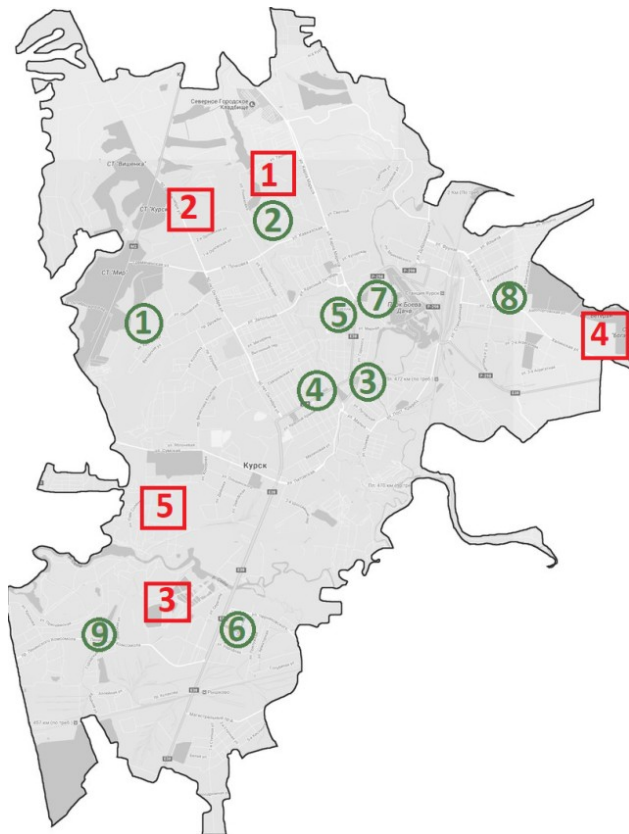


Figure 1. Location of the key sites of the research on the map of Kursk.

Number in the circle – key sites of forest-parks of Kursk: 1 – Forest-park Krutoi ravine, 2 – Forest-park Znamenskaya grove, 3- 1 of May park, 4 – Dzerzhinsky park, 5 – Civil War Heroes Park, 6 – Rokossovsky park, 7 – Pioneers park, 8 – Minipark «Three oceans», 9 – Minipark «Recreation Centre Lira». Number in the square – key urboecosystems of the research of HM pollution in the above-ground phytomass of plants: 1 – Forest-park Znamenskaya grove, 2 – North west district, 3 – Floodplain of Seim river near the ash-disposal area of CHP-1, 4 – Forest-park Gorelii forest, 5 – Forest-park Mokva

Key areas – Forest-park Krutoi ravine and Forest-park Znamenskaya grove were selected as control sites. At each of the key site 3 middle samples were taken, consisting of 10 point samples. The mass of the average sample was 1 kg. Determination of concentrations of heavy metals in plant samples was carried out by atomic absorption spectrometry in accordance with reference document – GOST 30692 and Methodology Guidelines for the determination of heavy metals in soils of farmlands and plant production 1992.

To assess the total soil pollution, an index proposed by Yu. E. Saet (Z_c) was used [9].

Statistical data processing, regression analysis and ANOVA were done using Microsoft Office Excel.

3. Concentration of accumulated heavy metals in predominate plants of urban ecosystems of Kursk

The results of the carried out research showed that plumbum is the highest priority pollutant of plant in Kursk. Exceeding the norm of the content of the technophilic element was observed in all the key sites without exception in 47% of the plant samples. Excess of MAC of manganese was observed in two

samples of woody plants- *Acer platanoides* L. and *Quercus robur* L. (11.7% of samples). One sample showed the excess of MAC of zinc – *Betula pendula* Roth. (5.8% of samples). The concentration of cadmium above the MAC is recorded only in the sample *Taraxacum officinale* Webb. s.l. (5.8% of samples). Excess of MAC of copper was not revealed in the phytobiomass samples of the plants under analysis (Table 2).

Table 2. Concentration of heavy metals in predominate grassland and woody vegetation of Kursk

№ Site	Plant	Concentration of heavy metals in the above-ground phytomass of the plants, ppm				
		Cu	Zn	Mn	Pb	Cd
1	<i>Picea abies</i> (L.) H.Karst	4.4±0.4	19.7±2.9	22.9±2.1	3.1±0.3	0.1±0.1
	<i>Acer platanoides</i> L.	6.3±0.5	27.9±3.3	338.3±8.7	2.7±0.1	0.2±0.1
	<i>Plantago major</i> L.	9.6±1.4	30.2±4.2	18.8±1.4	5.4±0.7	0.2±0.1
	<i>Quercus robur</i> L.	10.1±2.3	22.4±2.5	1103.1±19.5	3.3±0.2	0.1±0.1
	<i>Asarum europaeum</i> L.	10.4±2.7	34.1±3.7	190.1±6.4	5.6±0.4	0.1±0.1
	<i>Aegopodium podagraria</i> L.	11.2±2.5	47.4±6.1	113.3±6.9	3.7±0.1	0.1±0.1
2	<i>Achillea millefolium</i> L.	13.6±3.0	27.2±3.0	16.0±1.1	1.7±0.1	0.1±0.1
	<i>Poa pratensis</i> L.	2.8±0.2	13.5±1.1	66.5±4.9	13.5±1.1	0.1±0.1
3	<i>Medicago falcata</i> L.	6.5±0.8	18.6±1.8	17.7±2.5	3.3±0.3	0.7±0.1
	<i>Fragaria vesca</i> L.	6.1±0.8	13.4±0.9	19.8±2.3	9.7±1.4	0.5±0.1
	<i>Betula pendula</i> Roth.	5.1±0.7	154.2±9.2	20.1±3.7	39.1±2.1	0.4±0.1
	<i>Taraxacum officinale</i> Webb. s.l.	14.1±3.4	63.2±2.5	21.8±4.1	38.2±3.2	1.1±0.2
4	<i>Carex</i> L.	6.7±0.5	18.9±0.8	81.1±7.0	3.3±0.2	0.1±0.1
	<i>Pinus sylvestris</i> L.	6.1±0.5	39.6±2.9	217.0±9.4	2.8±0.1	0.2±0.1
	<i>Bryophyta</i>	9.1±0.9	36.6±3.1	234.2±9.9	23.1±2.2	0.3±0.1
5	<i>Pinus sylvestris</i> L.	6.2±0.4	27.1±1.6	76.8±5.1	3.5±0.3	0.2±0.1
	<i>Sorbus domestica</i> L.	5.8±0.4	19.8±1.0	156.4±7.7	6.9±0.6	0.1±0.1
Norms and MAC of HM*		15-20	150	300	1-5	1

*Remark: data on MAC (Mn) [10], data on MAC (Ni, Cu, Zn) and norms (Cd, Pb) [11]

The maximum variability of contamination of plants with heavy metals is characteristic of the site located in the residential zone, next to the floodplain of Seim river. This site is located near the ash-disposal area of CHP-1 and is experiencing a powerful anthropogenic impact. Here there were samples with the highest concentrations, usually exceeding the norms and MAC for Pb, Cd, Zn and Cu. This is due to the high level of total heavy metals pollution of alluvial-floodplain gleyic soil ($Z_c = 48.5$) [2, 9].

Among the studied plants, manganophils — plants capable to accumulate a significant amount of manganese — from 113.3 to 1103.1 ppm — could be clearly determined [10]. The examples of manganophils were woody plants (*Acer platanoides* L., *Plantago major* L., *Pinus sylvestris* L., *Sorbus domestica* L.), herbs (*Asarum europaeum* L., *Aegopodium podagraria* L.) and moss (*Bryophyta*) that grow in the Znamenskaya roscha, Gorelii les and Mokva. This accumulation effect can be explained by the high availability of the element in the dark-grey soils and sod-podzols illuvial-ferruginous [3].

The greatest depositing ability of plants with respect to Cu is characteristic of the herbs *Taraxacum officinale* Webb. s.l. > *Aegopodium podagraria* L. > *Achillea millefolium* L., which accumulate in the above-ground phytomass from 11.2 to 14.1 ppm of metal. As for zinc, the maximum accumulation reaching 154.2 ppm was recorded in the following plants placed in descending order — *Betula pendula* Roth. > *Taraxacum officinale* Webb. s.l. > *Aegopodium podagraria* L. Plumbum concentrators were *Betula pendula* Roth. > *Taraxacum officinale* Webb. s.l. > *Bryophyta*, accumulating in their above-ground organs from 23.1 to 39.1 ppm. The greatest accumulating effect was observed in herbs (from 0.5 to 1.1 ppm), representing the following descending order

in accordance to the metal concentration *Taraxacum officinale* Webb. s.l. > *Medicago falcata* L. > *Fragaria vesca* L.

In general, among the plants under analysis universal accumulators can be picked out – *Taraxacum officinale* Webb. s.l., *Betula pendula* Roth., *Bryophyta*, that showed the ability to intense phytoextraction of Pb, Cd and Zn from both the highly polluted and background soils of Kursk. *Acer platanoides* L. and *Quercus robur* L. vegetating on Dark-gray soils are selective manganese accumulators. *Poa pratensis* L. and *Sorbus domestica* L. in Urban gray soils and Sod-podzols illuvial-ferruginous are selective plumbum accumulators.

4. Heavy metals in leaves of *Tilia cordata* Mill. in forest-park of Kursk

In the studied forest-parks of Kursk pollution by plumbum was noted in all samples of leaves of *Tilia cordata* Mill., including control sites (Krutoi Log forest-park and Znamenskaya grove) that proves high technogenic burden on all urban ecosystems and confirms the priority of this pollutant for Kursk. Excess of MAC and standards of concentration of Zn, Cd, Cu and Ni in leaves of *Tilia cordata* Mill. wasn't found out that can be explained by biological barriers limiting accumulation of these elements in leaves of *Tilia cordata* Mill. (Table 3)

Table 3. Concentration of heavy metals in leaves of *Tilia cordata* Mill. in parks, miniparks and forest-parks of Kursk

Site / Soil	Концентрация элемента, ppm				
	Pb	Zn	Cd	Cu	Ni
Forest-park Krutoi ravine / grey soil	36.9±4.3	25.4±2.4	0.3±0.08	4.9±0.7	1.3±0.07
Forest-park Znamenskaya grove / dark-grey soil	21.3±1.8	22.7±2.1	0.1±0.01	5.7±0.1	1.4±0.3
1 of May park / urbanozem	33.2±6.4	17.7±0.1	0.2±0.05	5.34±0.9	1.53±0.3
Dzerzhinskiy park / urbanozem	72.4±8.3	25.3±3.5	0.3±0.02	7.9±1.1	2.9±0.4
Civil War Heroes Park / urbanozem	32.2±3.7	26.3±2.0	0.2±0.02	5.8±1.3	1.5±0.2
Rokossovsky park / urbanozem	46.9±5.2	24.9±3.0	0.3±0.01	5.6±1.2	1.2±0.3
Pioneers park / urbanozem	28.1±4.4	23.1±1.9	0.2±0.03	4.1±0.9	1.46±0.4
Minipark «Three oceans» / urbanozem	29.1±2.7	22.6±2.2	0.2±0.04	5.5±1.3	2.0±0.5
Minipark «Recreation Centre Lira» / urbanozem	30.1±2.0	17.9±1.7	0.2±0.06	4.3±0.9	0.8±0.1
Norms and MAC of HM *	1-5	150-200	1	15-20	20-30

* Remark: data on MAC (Ni, Cu, Zn) and norms (Cd, Pb) [11]

The received results demonstrate that *Tilia cordata* Mill. is a selective plumbum accumulator. Plumbum concentrations in *Tilia cordata* Mill leaves exceeded the norm from 4.2 to 14.5 times. The maximum (72.4 ppm) is recorded in the samples taken in. Dzerzhinsky park. It is explained by the peculiarities of its location. Along the perimeter of the park there are the main traffic arteries of the city, and traffic jams are the reason of the increase of local pollutant emissions. The minimum (21.3 ppm) is in the samples taken from the control site is the Znamenskaya Grove. Such a powerful accumulative effect shown by *Tilia cordata* Mill. in relation to plumbum is explained by phytoextraction of the element from the soil and sedimentation of aerotechnogenic plumbum-containing dust on the surface of the leaf plates and the subsequent absorption of Pb by leaf cells.

It should be noted that the leaves of trees in the parks located both in the center and on the outskirts of the city are polluted. Pb pollution of leaves of *Tilia cordata* Mill. in the control sites is the result of atmospheric transfer of the emissions of finely dispersed aerodynamical dust produced by motor transport and HPC.

The content of zinc, cadmium, copper and nickel in the leaves of *Tilia cordata* Mill. has a small range of variation: Zn – 17.9-25.3 ppm, Cd – 0.1-0.3 ppm, Ni – 0.8-2.9 ppm, Cu – 4.3-7.9 ppm. This is due to the phytoextracting capacity of the plant in relation to these heavy metals, the relative uniformity of the characteristics of urbanozems and the uniformity of the chemical constitution of the soil material.

5. Factors of accumulation of Pb in the phytomass of plants.

Results of regression analysis and ANOVA

On the basis of the results of the carried-out regression analysis curvilinear relationship between amount of the accumulated Pb in the phytomass of plants and ion concentration of metal in soil solution was determined (Figure 2).

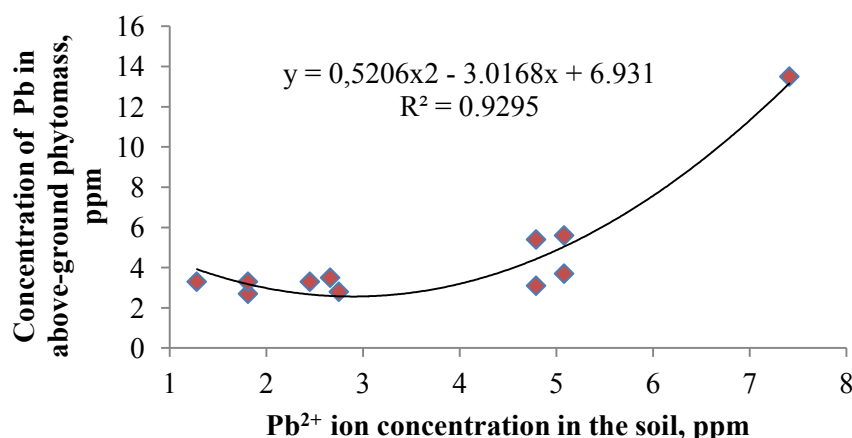


Figure 2. Dependence of Pb concentration in the phytomass of the above-ground phytomass in urban ecosystems of Kursk from Pb²⁺ ion concentration in soil solution

It should be noted that this dependence isn't characteristic of plants-hyperaccumulators of Pb and plants-excluders.

Generally accumulation of HM in plants depends on two complex factors – metal specificity of the phytoextraction of elements measured in the selective or universal absorption of HM and also capture rate of an element from the soil solution and the bioavailability of an element caused by a number of the soil characteristics defining distribution of HM between liquid and firm phases of soils. 2-way-ANOVA was carried out to determine the influence of the factors – capture rate of Pb by plants (it was made on the basis of species identification) and bioavailability of an element in the soil (was determined according to the ratio of mobile forms of Pb in soil solution in 5 key sites (Table 1)) [2]. Both factors under analysis and their combination had significant impact on accumulation of Pb in the phytomass of the above-ground phytomass in key urboecosystems of the city ($R^2 = 0.28$, $P < 0.05$ for each of the factors). The capture rate of Pb had dominating impact and defined 74.9% of total variance while the bioavailability of an element in the soil made 12.8%, and a combination of factors -12.0%.

6. Conclusion

The priority pollutant among heavy metals was plumbum, the proportion of the polluted samples of phytomass of plants reached 47% of total number of the samples under analysis taken on all key sites of urban ecosystems of Kursk. Carrying out the research Pb accumulators are determined: *Betula pendula* Roth., *Taraxacum officinale* Webb. s.l., *Bryophyta* accumulating from 23.1 to 39.1 ppm in the their above-ground phytomass that exceeds 4.6 – 7.82 times the standard of concentration of an element in organs of a plant and toxicity limit in 1.2 – 1.9 times. Among the studied plants in the territory of Kursk manganese hyperaccumulators – *Quercus robur* L. depositing 1103.1 ppm and *Acer platanoides* L. depositing 338.3 ppm are revealed. The universal accumulators are found out – *Taraxacum officinale* Webb. s.l., *Betula pendula* Roth., *Bryophyta* possessing the capability

to extract Pb, Cd and Zn. The received data of accumulating ability of plants can be used in practice for further phytoremediation in Central Chernozem region.

Forest-parks of Kursk also experience powerful anthropogenic burden that was proved by the results of *Tilia cordata* Mills samples exceeding the standard of contents from 4.2 to 14.5 times absolutely in all sites located both in the center and on the outskirts of the city.

The leading factors defining accumulation of Pb in the above-ground phytomass of plants in Kursk are plants capture rate of Pb and bioavailability of the element in soils.

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