

Spatial and Specific Variance in Accumulation of Heavy Metals in Tree Vegetation of Moscow City South-Western Administrative District

Belozubova N.¹, Zubkova V.¹, Kirillov N.¹

¹ Department of Ecology and Technospheric Safety, Russian State Social University, (RUSSIA)

gerlinger_natali@mail.ru, zubkovavm@rgsu.net

Abstract

Research of Moscow residential and transportation landscapes was performed in 2018. Examined parameters included spatial and specific variance of Zn, Pb, Cu, Cd, and Cr accumulation by small-leaved linden (*Tilia cordata*), ash-leaved maple (*Acer negundo*), and hard maple (*Acer saccharum*). Non-uniform spatial distribution of heavy metals in tree leaves was determined, depending upon tree species, and location of the trees. Areas with top total concentrations of pollutants were located along the motorways with extensive traffic, and in industrial zones. It was found that zinc is the prevailing biogenic element within the examined spectrum. For *Tilia cordata* it comprises close to 77%, for *Acer negundo* – close to 80%, and for *Acer saccharum* – from 66% to 80% of the determined pollutants' content. At the same time the share of copper varies within the 16-20% range. Increasing pressure causes anomalous changes in chemical composition of the plants, both in terms of biogenes, and polluting elements. That was demonstrated using an example of an ash-leaved maple growing in a 23rd public garden of Novye Chermushki, and hard maple growing in 5 meters from a motorway. Specific property of tree foliage in city environment is high pollutant accumulation capacity. Top summary pollutant concentration coefficients in tree foliage were determined for the most heavily polluted areas. At the same time the content of heavy metals in leaves at some sites differed for Cu by a factor of 2, for Cr – 4, Zn – 14, Cd – 42, and Pb – 45.

Keywords: pollution, heavy metals, tree vegetation, accumulation, metals association, city landscapes.

1. INTRODUCTION

Soil pollution with heavy metals is a common problem for industrial centers and urban territories all over the world (Yang et al., 2018; Cai et al., 2019; Stepanova et al., 2018; Kaur et al., 2018; Jafari et al., 2018; Sawut et al., 2018; Ma et al., 2018; Li et al., 2018; Gabarrón et al., 2017; Peng et al., 2017).

Soils of the city of Moscow are subject to increased anthropogenic pressure that damages ecological functions of these soils, namely processing of organic residue, atmosphere and surface water cleansing, forming microclimate, topsoil fixation, and support of biological and geological cycles of matter (Zubkova et al., 2018). Today Moscow is among the largest actively developing global megalopoli, where up to 90% of emissions to atmosphere are due to vehicle exhaust fumes.

Air pollution and adverse soil status (salination, compaction, and heavy metals pollution) are key adverse factors for trees in city environment. Taking these factors into account is essential for sustainable development of cityscape diversity (Egorov et al., 2018).

Wide spread of pollution with heavy metals in city soils requires understanding of special specifics about heavy metals transfer patterns within plants. Key mechanisms include exclusion, passive, and active accumulation. These mechanisms are known for a very limited number of tree species. Other independent from soil sources of pollution for trees growing in the cities can include hard particles and atmospheric substances. Metals in the air can get immediately into fruits, or be sucked through stomata, and transfer later (Gori et al., 2019).

For most metals content increases with leaf age, causing remobilization of the metals from soil, then metals return to topsoil (Almahasheer et al., 2018).

Barrier functions play an important role in the input of heavy metals into plant organs. For example, excessive concentrations of zinc and copper in soils affected city trees - accumulation of heavy metals in their accumulation apparatus is higher than one for the trees growing at reference sites

Belozubova N., Zubkov N., Kirillov N.

(Voskresenskiy et al., 2017). At the same time maximum permitted concentrations for tree leaves and needles is not specified, which demonstrates plant root system barrier function.

Protective reaction of *P. alba berolinensis* leaves with regard to Pb stress depend upon both concentration of Pb, and exposure duration, and Pb concentration level in soil equal to 300 mg/kg causes strongest protective reaction of poplar plantings, substantially exceeding reactions displayed at higher concentrations equal to 500 and 700 mg / kg (Jiang et al., 2018).

Plants (*Arundo donax*, *Broussonetia papyrifera*, *Robinia pseudoacacia* and *Cryptomeria fortunei*), planted directly into zinc melting slag, substantially increase accumulation of nutrients, and decreased bioaccessibility of heavy metals (Cu, Zn, and Cd), except for *A. done* regarding Zn and Cd. These trees display high resistivity to heavy metals, and their low accumulation (Luo et al., 2019).

Research by Woch (2018) demonstrated that in case of very complex and productive ecosystems, even under heavy pollution with heavy metals key role belongs to biotic factors. Despite high content of heavy metals, namely, Cd, Pb, and Zn, in soils, key factor affecting differences in undergrowth phytocenosis was tree canopy shade density. Species composition changes substantially with increase of coverage of trees, stress-resistant species became more common. Cd to Ca ratio caused decrease in the number of trees and endangered species.

Results obtained by Wang et al., (2019) demonstrated that the presence of root system changes distribution and interaction of Cd and Cu in plant organs and increases plant tolerance and phytoextraction capabilities. Initial sprigs can incept and accumulate heavy metals at early stages of willow growth without roots. Cu inhibited Cd inception and accumulation by the plants and facilitated Cd transfer. In turn, Cd inhibited Cu-inception of the root system.

Similar position of Cd and Pb in the row of heavy metals accumulation in soils and plants was demonstrated. These metals were usually efficiently transported from roots to shoots. Metals were distributed within the plants according to plant life form, higher levels were present in perennial plants, for example, concentrations in wood matter of *S. polaris*, *D. octopetala*, *D. corymbosa*, were higher than in redivives (Hanaka et al., 2019).

Therefore, knowledge of the laws of heavy metals accumulation by different tree species can become basis for city landscape design and management.

Research goal was to determine spatial and specific heavy metals accumulation by trees growing in the South-Western administrative district of Moscow.

2. RESEARCH METHODS

Research took place in residential and transport city landscapes in 2018 and included testing of the most common tree species - small-leaved linden, ash-leaved maple, and hard maple. Sampling sites included Academic Glushko street, 12 (1); northern side of Moscow beltway, 35 km waypoint (2); Koktebelskaya street, 8 (3); General Tyulenev street, 5, bldg. 1 (4); 23rd public garden of Novye Cheremushki (5), Profsoyuznaya street, 43 (6); and Profsoyuznaya street, (7). The sites were selected as the ones being part of complex research related to studying environmental effects of deicing reagents (Zubkova et al., 2018).

Samples were taken in early September. At each site three tree leaf samples were taken; total number of samples was equal to nine for each species. Sampling method was due to presence a single trees at sampling sites.

Leaves were collected at the end of vegetation period, washed with distilled water, dried and then incinerated. Total content of heavy metals was determined using atomic absorption method in the lab of Moskovskiy Federal State Budgetary Institution – State Agrochemical Service Center.

In order to perform environmental and geochemical assessment, pollutants concentration coefficient (K_c) was determined using formula:

$K_c = C_i:C_{\phi}$, where C_i is actual analyte content, and C_{ϕ} – reference analyte content. A minimum value from the obtained range was used as reference concentration. In order to describe pollution, impact the total pollution value (Z_c) was used, determined using a formula:

$Z_c = \sum (K_{ci} + \dots + K_{cn}) - (n - 1)$, where K_{ci} is a concentration coefficient for i -th pollutant, and n – is the number of pollutants.

3. RESULTS AND DISCUSSION

Based on research results it is possible to state that there is a non-uniform spatial distribution of heavy metals in tree leaves. Distribution is affected by tree species and location of the trees (Table 1).

Table 1 – Content of heavy metals in the leaves of different tree species, mg/kg

Site	Tree species	Zn	Pb	Cu	Cd	Cr
1	Tilia cordata	30.8 ± 6.5	0.64 ± 0.22	8.1 ± 1.9	0.081 ± 0.028	0.31 ± 0.02
2	Tilia cordata	34.3 ± 7.2	0.67 ± 0.23	8.7 ± 2.0	0.037 ± 0.013	0.85 ± 0.08
3	Acer negundo	31.3 ± 6.6	0.21 ± 0.07	6.6 ± 1.5	0.044 ± 0.015	0.69 ± 0.07
4	Acer negundo	31.3 ± 6.6	0.71 ± 0.25	5.9 ± 1.4	0.069 ± 0.024	0.88 ± 0.07
5	Acer negundo	370.0 ± 55.0	1.82 ± 0.64	8.6 ± 2.0	1.542 ± 0.540	1.24 ± 0.1
6	Acer saccharum	27.0 ± 5.7	0.43 ± 0.15	6.7 ± 1.5	0.081 ± 0.028	0.43 ± 0.02
7	Acer saccharum	32.8 ± 6.9	9.47 ± 3.31	5.5 ± 1.3	0.846 ± 0.296	1.08 ± 0.10

Accumulation row for the examined elements was the following: - Zn > Cu > Pb (Cr) > Cd. It is necessary to note that widest variation of pollutant contents for single species was displayed by Tilia cordata about cadmium and chrome (2.2 and 2.7 times, correspondingly).

Anomalous content of all pollutants was revealed in Acer negundo leaves from the 23rd park of Novye Cheremushki (site 5), and hard maples, growing on Profsoyuznaya street display severe differences in elements content - for lead by a factor of 22, for cadmium – by a factor of 10, and for chrome – by a factor exceeding 2. One of the reasons for that is the distance from a motorway (5 and 40 meters).

While comparing summary pollution coefficients, is necessary to point out that differences in accumulative capacity of the trees depend upon their species and location.

For example, for ash-leaved maples growing in three different places total concentration of pollutants differed by a factor of 22 and more. It can be also noted that sites with maximum total coefficients of pollutant concentration are located close to major roads with intensive traffic and industrial zones (table 2).

Table 2 – Heavy metals concentration coefficients for tree leaves of different species

Pollutant	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
Zn	1.14	1.27	1.16	1.16	13.70	1.00	1.21
Pb	3.05	3.19	1.00	3.38	8.67	2.05	45.10
Cu	1.72	1.85	1.40	1.26	1.83	1.43	1.17
Cd	2.19	1.00	1.19	1.86	41.68	2.19	22.86
Cr	1.00	2.74	2.23	2.84	4.00	1.39	3.48
ΣC	5.10	6.05	2.98	6.50	65.88	4.05	69.83

From the data different associations of heavy metals were accumulated in the examined leaf samples, depending upon the species and functional zone where trees grow. Foreexample, leaves of Tilia cordata growing in industrial and residential areas lead concentration values exceed ones for chrome and cadmium. At the same time in industrial zones concentration of chrome in Tilia cordata leaves is higher than in residential areas. Another important factor is distance from the roads. Samples of Acer saccharum collected at the distances of 5 and 40 meters from the road displayed different concentrations of analytes.

Another important factor of assessing environmental and geochemical parameters of ecosystems is an accumulation coefficient of accumulative index (K_i) calculated as a ratio of element content in dry mass of plant leaves to the content of element acid-soluble form in soil (mg/kg): $K_i = C_p/C_i$, where C_p – is the average contents of an i -th element in leaves, mg/kg; C_i – average soil content of an i -th element, mg/kg (see Table 3).

Table 3 – Heavy metals bioaccumulation coefficients for tree leaves

Sampling site	Zn	Pb	Cu	Cd	Cr
1	0.52	0.07	0.38	0.08	0.02
2	0.31	0.04	0.44	0.93	0.06
3	0.48	0.03	0.53	4.40	0.06
4	0.52	0.04	0.47	6.90	0.09
5	31.7	0.46	1.84	20.05	0.17
6	2.25	0.10	1.03	0.81	0.05
7	0.39	1.05	0.10	1.41	0.06

Depending on the key sources of heavy metals for the trees different associations of heavy metals can form at different sites, but the main role is played by the ratio of element contents which is usually genetically determined. Table 4 contains presence of examined elements for different pollutant species growing under different anthropogenic pressures.

Table 4 – Content of heavy metal pollutants in leaves of different tree species (percent)

Sampling site	Tree species	Zn	Pb	Cu	Cd	Cr
1	<i>Tilia cordata</i>	77.1	1.6	20.3	0.2	0.8
2	<i>Tilia cordata</i>	77.0	1.5	19.5	0.1	1.9
3	<i>Acer negundo</i>	80.6	0.5	17.0	0.1	1.8
4	<i>Acer negundo</i>	80.5	1.8	15.2	0.2	2.3
5	<i>Acer negundo</i>	96.6	0.5	2.2	0.4	0.3
6	<i>Acer saccharum</i>	77.9	1.2	19.4	0.2	1.3
7	<i>Acer saccharum</i>	66.0	19.0	11.1	1.7	2.2

Zinc prevails in the overall composition of examined element. This biogenic comprises close to 70% of heavy metal pollutants for *Tilia cordata*, close to 80% for *Acer negundo*, and 66-80% in *Acer saccharum*. Chemical composition of the plants changes under increased environmental pressure, and this process causes both changes in ratios of biogenic elements, and pollutants. This point is illustrated by results obtained for *Acer negundo* trees growing in the 23rd part of Novye Chermushki district, and *Acer saccharum* growing 5 meters away from a motorway.

Thus, distinctive feature of tree leaves in urban environments is a high pollutants accumulation capacity. Highest total pollutant concentration coefficients were determined for leaves from trees growing in the most polluted areas. At the same time at some sites the content of heavy metals in leaves varied for Cu by a factor of 2, Cr – 4, Zn – 14, Cd – 42, and Pb – 45.

Study of leaves' chemical composition can assist in making optimal decisions in terms of species and location of trees used for greening the city of Moscow.

REFERENCES

- [1] Almahasheer, H., Serrano, O., Duarte, C. M., & Irigoien, X. (2018). Remobilization of heavy metals by mangrove leaves. *Frontiers in Marine Science*, 5, 484.
- [2] Cai, L. M., Wang, Q. S., Luo, J., Chen, L. G., Zhu, R. L., Wang, S., & Tang, C. H. (2019). Heavy metal contamination and health risk assessment for children near a large Cu-smelter in central China. *Science of The Total Environment*, 650, 725-733.
- [3] Egorov, A., & Fatianova, E. (2018). ACTUAL CONDITION OF WOODY PLANTS AND DEVELOPMENT OF SUSTAINABLE ASSORTMENT FOR GREENING OF SAINT PETERSBURG (RUSSIA) IN CHANGING CLIMATE. *International Multidisciplinary Scientific GeoConference: SGEM: Surveying Geology & mining Ecology Management*, 18, 597-604.
- [4] Gabarrón, M., Faz, A., & Acosta, J. A. (2017). Soil or dust for health risk assessment studies in urban environment. *Archives of environmental contamination and toxicology*, 73(3), 442-455.
- [5] Gori, A., Ferrini, F., & Fini, A. (2019). Reprint of: Growing healthy food under heavy metal pollution load: Overview and major challenges of tree based edible landscapes. *Urban Forestry & Urban Greening*.
- [6] Hanaka, A., Plak, A., Zagórski, P., Ozimek, E., Rysiak, A., Majewska, M., & Jaroszuk-Ścisel, J. (2019). Relationships between the properties of Spitsbergen soil, number and biodiversity of rhizosphere microorganisms, and heavy metal concentration in selected plant species. *Plant and Soil*, 436(1-2), 49-69.
- [7] Jafari, A. J., Kermani, M., Kalantary, R. R., & Arfaeinia, H. (2018). The effect of traffic on levels, distribution and chemical partitioning of harmful metals in the street dust and surface soil from urban areas of Tehran, Iran. *Environmental Earth Sciences*, 77(2), 38.
- [8] Jiang, D., Wang, Y. Y., Dong, X. W., & Yan, S. C. (2018). Inducible defense responses in *Populus alba berolinensis* to Pb stress. *South African Journal of Botany*, 119, 295-300.
- [9] Kaur, M., Kumar, A., Mehra, R., & Mishra, R. (2018). Human health risk assessment from exposure of heavy metals in soil samples of Jammu district of Jammu and Kashmir, India. *Arabian Journal of Geosciences*, 11(15), 411.
- [10] Li, G., Sun, G. X., Ren, Y., Luo, X. S., & Zhu, Y. G. (2018). Urban soil and human health: a review. *European Journal of Soil Science*, 69(1), 196-215.
- [11] Luo, Y., Wu, Y., Qiu, J., Wang, H., & Yang, L. (2019). Suitability of four woody plant species for the phytostabilization of a zinc smelting slag site after 5 years of assisted revegetation. *Journal of Soils and Sediments*, 19(2), 702-715.
- [12] Ma, W., Tai, L., Qiao, Z., Zhong, L., Wang, Z., Fu, K., & Chen, G. (2018). Contamination source apportionment and health risk assessment of heavy metals in soil around municipal solid waste incinerator: A case study in North China. *Science of The Total Environment*, 631, 348-357.
- [13] Peng, C., Wang, M., Chen, W., Chang, A. C., & Crittenden, J. C. (2017). Mass balance-based regression modeling of Cd and Zn accumulation in urban soils of Beijing. *Journal of Environmental Sciences*, 53, 99-106.
- [14] Sawut, R., Kasim, N., Maihemuti, B., Hu, L., Abliz, A., Abdujappar, A., & Kurban, M. (2018). Pollution characteristics and health risk assessment of heavy metals in the vegetable bases of northwest China. *Science of The Total Environment*, 642, 864-878.
- [15] Stepanova, N. V., Fomina, S. F., Valeeva, E. R., & Ziyatdinova, A. I. (2018). Heavy metals as criteria of health and ecological well-being of the urban environment. *Journal of Trace Elements in Medicine and Biology*.

- [16] Voskresenskiy, V. S., Sarbayeva, E. V., Alyabysheva, E. A., & Voskresenskaya, O. L. (2017). Heavy Metals In Soils And Plants Of Urban Ecosystems (on The Example Of The City Of Yoshkar-ola). In *Heavy Metals and Other Pollutants in the Environment* (pp. 143-160). Apple Academic Press.
- [17] Wang, W. W., Ke Cheng, L., Hao, J. W., Guan, X., & Tian, X. J. (2019). Phytoextraction of initial cutting of *Salix matsudana* for Cd and Cu. *International journal of phytoremediation*, 21(2), 84-91.
- [18] Woch, M. W. (2018). Factors of variation in beech forest understory communities on waste heaps left by historical Zn-Pb ore mining. *Ecotoxicology and environmental safety*, 164, 681-689.
- [19] Yang, Q., Li, Z., Lu, X., Duan, Q., Huang, L., & Bi, J. (2018). A review of soil heavy metal pollution from industrial and agricultural regions in China: Pollution and risk assessment. *Science of The Total Environment*, 642, 690-700.
- [20] Zubkova, V. M., Belozubova, N. Y., Arslanbekova, F. F., & Dryabzhinsky, O. E. (2018, December). Development of Soils Containing Heavy Metals in Southwestern Administrative District of Moscow. In *International Symposium" Engineering and Earth Sciences: Applied and Fundamental Research"*(ISEES 2018). Atlantis Press.