POLISH JOURNAL OF SOIL SCIENCE
VOL. LIII/2 2020 PL ISSN 0079-2985

DOI: 10.17951/pjss/2020.53.2.199

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CD AND PB IN THE "SOIL-PLANT" SYSTEM OF HOLOSIYIV GREEN PARK AREA IN KYIV

Received: 11.11.2019
Accepted: 08.09.2020

Abstract. In this paper, the content of metals (Cd and Pb) was investigated in soil-plant system of Holosiyiv green park area in Kyiv. Kyiv is the capital and largest city of Ukraine, and has an anthropogenic load. Metals pollution in various degrees in green park areas may affect people's health through different paths. We propose to control the lead contamination in soil because Pb concentration levels were above when compared with background values in almost all samples of soil and exceeded the maximum permissible concentration in sites of top of hills in park. Moreover, the obtained results indicated high concentrations of lead in studied plants; most of them are medicinal and traditionally used by people. The highest phytomass concentration of Pb was observed in *Asarum europaeum* L., whereas *Impatiens parviflora* DC and *Urtica dioica* L. had the highest plant up-taking indexes for both studied metals.

Keywords: trace metals (Cd, Pb), Holosiyiv green park zone, soil-plant system, plant up-taking indexes

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INTRODUCTION

Toxic metals are one of the most common and dangerous pollutants in the environment. Content of metals in soil and plants in big cities increases and exceeds the background values due to the continuous expansion of human production and living activities (Marjanović *et al*. 2009, Tangahu *et al.* 2011, Zhang and Chen 2018). Green parks in big cities are also considerably affected by metal contamination. Holosiyiv green park area is one of the most popular and unique recreation places in the city of Kyiv and has become an important place for people's daily leisure. Kyiv is the capital and largest city of Ukraine and has a significant anthropogenic load. Metal pollution in various degrees in green park areas may affect people's health through air, water, and other sources (Zhang and Chen 2018, Marjanović *et al.* 2009, Wang *et al.* 2016, Yang *et al*. 2017). Therefore, it is becoming more and more important to study the content of metals in soil and plants of urban parks and assess the risk of metal contamination.

The abilities of plants to take up metals and their distribution in the soil and plants help to observe pollutants' behavior and give the possibility to forecast their influence on the green parks ecosystems. Cd and Pb concentration levels were investigated in two locations: Didorivska and Horikhuvatska. Both locations belong to subaquatic landscapes with steep slopes and they are situated near ponds which were artificially formed thanks to natural streams (Dydorivskiy and Horikhuvatskiy). Metals' distribution in soil (0–20 cm) highlights their tendency to "migrate".

The special attention in our research was also paid to uptake of metals by plants and their concentration in medicinal plants that are traditionally widely used by the people in Ukraine. However, there are no standards for maximum permissible concentrations for metals in the phytomass of wild medicinal plants. The aim of the current study was to investigate the content of metals (Cd and Pb) in soil-plant system of Holosiyiv green park zone in Kyiv in order to control the metal pollution in this area.

MATERIALS AND METHODS

Holosiyiv green park area is a part of National Nature Park "Holosiyivskyi" located at the junction of the Right-bank Polissia and the Forest-Steppe of Ukraine. Holosiyiv green park area is a forest area; oak plantations cover most of the territory (≈62%) with an average age of 86 years (Yakubenko and Grigora 2007, Pryadko *et al*. 2014). Samples were collected from two sites which are of high recreational significance (Fig. 1).

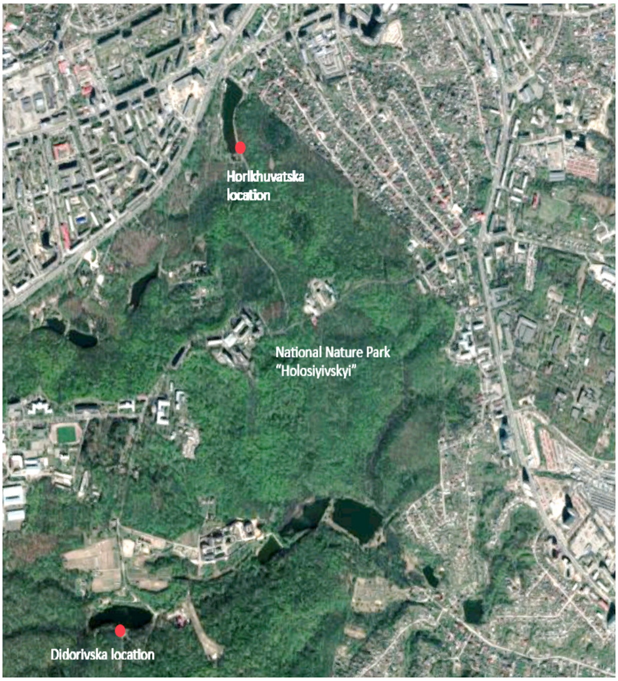
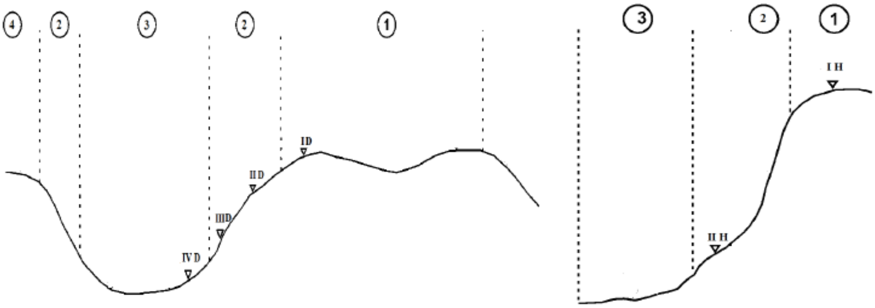


Fig. 1. Sampling sites

The scheme of sampling points is presented in Fig. 2.



a) b)

Fig. 2. Fragment of the scheme of landscape profile (Kavetsky *et al*. 2002)

a) Didorivska location (I D–IV D – sampling points of soil and plant; 1 – watershed, 2– slope, 3 – flood-plain, 4 – high sand terrace); b) Horikhuvatska location (I H–II H – sampling points of soil and plant; 1 – watershed, 2 – slope of gorge, 3 – flood-plain)

Mean standard deviations, variance, and minimum, maximum, and standard errors were calculated in four replicates. The total amount of analyzed samples was 60. The experimental results were interpreted using standard statistical methods. Soil and plants were sampled in the phase of plants flowering in 2019. We investigated aboveground phytomass of such plant species as: *Impatiens parviflora* DC, *Achillea millefolium* L., *Plantago media* L., *Urtica dioica* L., *Sambucus nigra* L. (berries), *Cichorium intybus* L., *Asarum europaeum* L. Most of these plants are medicinal. The investigated soil was grey forest sandy loam on loess loam (grey forest soil). Investigated soil has the following physicochemical characteristics pH salt: 6.2; organic matter by Turin, Walkley-Black: 2.5%. The studied elements were extracted by ammonium acetate buffer (pH 4.8) from the soils. Trace element determination in the plants was carried out after wet digestion by the mixture of HNO_3 and HCl. Analysis of Cd and Pb concentration in soil and in plants was carried out by atomic absorption spectroscopy (AAS) (the spectrophotometer AAS-3; flame atomization; flame type "acetylene – air" is used for analysis). Determination of Cd and Pb in soil and plant samples was carried out in the laboratory of the National Institute of Agriculture (National Academy of Agrarian Sciences of Ukraine) in 2019. Cd and Pb concentration levels in soil (0–20 cm) were assessed by existing standards for maximum permissible concentrations for metals in the soil in Ukraine (*Maximum…1987*, Sozinov and Prister 1994, Korsun *et al.* 2019). The plant up-taking index (PUI) for each metal was calculated as follows:

$$PUI = \frac{C_p}{C_s} \quad (1)$$

where: *Cp* – concentration in plant, $mg \cdot kg^{-1}$ (dry weight); *Cs* – concentration in soil, $mg \cdot kg^{-1}$.

RESULTS AND DISCUSSION

Cd and Pb in soil

All investigated samples did not exceed the Cd maximum permissible concentration in soil (Table 1). Soil may be contaminated with Cd by fallout from aerial sources, by application of waters, or by the discharge of Cd-containing waste materials from industrial, metallurgical or urban activities (Kabata-Pendias and Mukherjee 2007, Yao *et al.* 2017). Comparison of the level of Cd content in soil with the background values of metal revealed an excess of metal content in the samples from the foot of slope in Didorivska location and from the watershed in Horikhuvatska location. Generally, concentration of Cd in soil was decreased in the direction from the watershed to the foot of slope. Cadmium concentration in the Didorivska and Horikhuvatska locations were at the same level ($F_{theor} > F_{exper}$, P_{05}).

Table 1. Cd and Pb content in soil (0–20 cm), P_{05}

Point of sampling	Cd	Pb
	Mobile form in soil (ammonium acetate buffer, pH 4.8), $mg \cdot kg^{-1}$	
I D	0.10±0.02	2.8±0.45
II D	0.08±0.01	1.5±0.23
III D	0.12±0.02	1.1±0.16
IV D	0.08±0.01	0.5±0.07
I H	0.15±0.02	2.3±0.34
II H	0.09±0.01	0.9±0.13
Background values in Ukraine	0.1	0.5
The maximum permissible concentration in Ukraine, $mg \cdot kg^{-1}$	0.7	2.0

Pb exceeded the maximum permissible concentration in watershed of both investigated locations. Pb concentration levels were above the background values in almost all samples of soil. In this regard, the monitoring and control of metals contamination in soil should be carried out primarily for Pb. Lead exists in many forms in nature and is now one of the most widely and evenly distributed trace metals. Soil can be contaminated with lead from car exhaust, dust, and gases from various industrial sources, lead-based paint, etc. (Brown *et al.* 1998, Kabata-Pendias and Mukherjee 2007, Pan *et al.* 2016). Lead is non-volatile and therefore extremely persistent in soil. The fate of lead in soils is dependent upon specific or exchange adsorption at mineral interfaces. Most lead is retained in soil as it is strongly adsorbed to organic matter, and only a limited fraction can be transported into surface water or groundwater (Bertrand *et al.* 2011, Tangahu *et al.* 2011). This occurs principally if the soil is acidic. In current studies, the gradient of lead concentration decreased in the direction from the watershed to the foot of slopes at both investigated locations. That could be explained by horizontal migration of Pb from watershed (I D, I H) to the foot of slopes (III D, II H) in subaquatic landscapes. The concentration of Pb in samples from floodplain (IV D) was the lowest, which obviously may be due to the leaching of metal by water in the floodplain. Lead concentration in the Didorivska and Horihuvatska locations were at the same level ($F_{theor} > F_{exper}$, P_{05}).

Cd and Pb in plants

The Cd and Pb concentration levels in the aboveground plant phytomass are presented in Table 2.

Table 2. The content of Cd and Pb in the aboveground plant phytomass, P_{05}

Point of sampling	Plant	Cd	Pb
		mg·kg^{-1} dry weight	
I D	*Urtica dioica* L.	0.3±0.04	3.8±0.50
I D	*Impatiens parviflora* DC	0.7±0.10	2.7±0.40
II D	*Plantago media* L.	0.5±0.07	4.5±0.60
II D	*Sambucus nigra* L.	0.1±0.02	1.3±0.20
III D	*Impatiens parviflora* DC	0.4±0.06	4.4±0.65
III D	*Cichorium intybus* L.	0.5±0.08	2.7±0.40
III D	*Achillea millefolium* L.	0.3±0.04	2.8±0.45
I H	*Asarum europaeum* L.	0.4±0.05	5.7±0.80
II H	*Urtica dioica* L.	0.4±0.06	4.4±0.70
s^2		*0.02*	*1.57*
v, %		*39.10*	*34.90*

The highest concentration of Cd was observed in *Impatiens parviflora* DC, *Cichorium intybus* L., *Plantago media* L. Such plants as *Asarum europaeum* L., *Plantago media* L., *Impatiens parviflora* DC, *Urtica dioica* L. were characterized by the highest concentration of lead. The lowest concentration of both metals in phytomass was observed in *Sambucus nigra* L. The coefficient of variation ($30 < v < 70\%$) indicates a moderate variation in phytomass concentrations of certain metals for different species. Each metal is characterized by its own range of concentration in the conditions of relatively low levels in soil. In previous papers we observed the results for metals concentration and plant up-taking in the conditions of extra high metals concentration in soil (experiment with artificial metals' contribution to soil) (Ryzhenko *et al.* 2017). Very high concentration of Cd and Pb in soil resulted in very high metals concentration in plant; Cd had much higher phytomass concentration and up-taking indexes than Pb (Ryzhenko *et al*. 2015). In current investigation we observed much higher concentration of lead than of cadmium in plant ($F_{theor} < F_{exper}$, P_{05}). In addition, each species of plants has a specific ability of up-taking metals from the soil. Qualitative composition of the chemical components of plants within the certain species is quite constant. Plants growing in nature can accumulate metals to a certain extent depending on their individual properties (Gasser *et al*. 2009, Sharma *et al.* 2014, Rachit *et al*. 2016). Plants have evolved highly specific and very efficient mechanisms to obtain essential micronutrients from the environment, even when present at low levels. Plant roots, aided by plant-produced chelating agents and plant-induced pH changes and redox reactions, are able to solubilize and take up micronutrients from very low levels in the soil, even from nearly insoluble precipitates. Plants have also developed highly specific mechanisms to translocate and store micronutrients. The same mechanisms are also involved in the uptake, translocation, and storage of toxic elements, whose chemical properties simulate essential elements (Tangahu *et al.* 2011).

Currently, sanitary and hygiene standards, in particular, maximum permissible levels of metals, have not been set for medicinal plants in Ukraine. However, most of the studied plants are medicinal and traditionally used by people. The World Health Organization recommends the need for quality assurance of herbal products. It is critical to analyze metals in medicinal plants in order to ensure that their levels do not exceed the required limits established by special regulations. Herbal products should be subjected to adequate quality control requirements (WHO 1999, Mousavi *et al.* 2014). The World Health Organization recommends limits for various medicinal plants of not more than 10 $mg \cdot kg^{-1}$ Pb and 0.3 $mg \cdot kg^{-1}$ Cd in the final dosage form of the plant material (Gasser *et al.* 2009). According to the European Commission, the following limits have been set for herbs: lead 0.3 $mg \cdot kg^{-1}$, cadmium 0.05 $mg \cdot kg^{-1}$ (*Commission*… 2006). Kenya standard recommends limits for herbal and fruit infusions of 5 $mg \cdot kg^{-1}$ Pb and 1 $mg \cdot kg^{-1}$ Cd (*Kenya*… 2017). The limits of metals in Ukraine are set for fresh vegetables and fruits: lead 0.3 $mg \cdot kg^{-1}$, cadmium 0.03 $mg \cdot kg^{-1}$ (*Regulation*… 2013). Thus, relatively high concentrations of lead in studied plants are of concern.

Up-taking of Cd and Pb by plants

Plant up-taking indexes are presented in Table 3.

Table 3. Plants up-taking indexes (PUI) of Cd and Pb

Point of sampling	Plant	Cd	Pb
I D	*Impatiens parviflora* DC	7.0	1.0
I D	*Urtica dioica* L.	3.0	1.4
II D	*Plantago media* L.	0.6	3.0
II D	*Sambucus nigra* L.	1.2	0.9
III D	*Impatiens parviflora* DC	3.3	4.0
III D	*Achillea millefolium* L.	2.5	2.5
III D	*Cichorium intybus* L.	4.2	2.5
I H	*Asarum europaeum* L.	2.7	2.5
II H	*Urtica dioica* L.	4.4	4.9
s^2		*3.2*	*1.6*
v, %		*55.4*	*49.9*

The lowest PUI was observed in *Plantago media* L. (Pb), *Sambucus nigra* L. (Cd). Generally, PUI of Cd and Pb were at the same level for all studied plants ($F_{theor} > F_{exper}$, P_{05}). The variation between PUI for all plants was moderate both for Cd and Pb; coefficients of PUI variation were 55.4% (Cd) and 49.9% (Pb). On the one hand, each metal has its own concentration range of availability for plants. The availability of soil lead and cadmium depends on how tightly they are held by soil particles and on their solubility (the extent to which they dissolve in water) (Meyers *et al*. 2008). At low soil pH (pH < 5, acidic conditions) lead is held less tightly and is more soluble. At near neutral or higher pH (pH > 6.5, neutral to basic conditions) lead is held more strongly, and its solubility is very low (Bertrand *et al.* 2011, Fahr *et al.* 2013, Amin *et al*. 2018). Lead and cadmium are held by soil organic matter, so as organic matter increases, lead and cadmium availability decreases (Clemens 2006, Gill 2014, Gunawardana *et al.* 2015, Khan *et al*. 2017). On the other hand, species barrier mechanisms of plants also play the key role in the uptake of trace elements by plants. *Impatiens parviflora* DC and *Urtica dioica* L. were characterized by the highest plant up-taking indexes for both metals (Fig. 3).

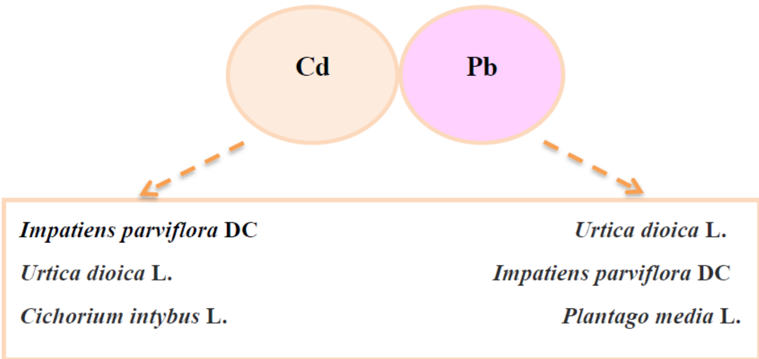


Fig. 3. Plants with the highest bioaccumulation capacity

According to the value of Cd plant up-taking index, the plants can be ranked in the following descending order: *Impatiens parviflora* DC > *Urtica dioica* L. > *Cichorium intybus* L. > *Asarum europaeum* L. > *Achillea millefolium* L. > *Sambucus nigra* L. > *Plantago media* L. According to the value of Pb plant up-taking index, the plants can be ranked in the following descending order: *Urtica dioica* L. > *Impatiens parviflora* DC > *Plantago media* L. > *Achillea millefolium* L. = *Cichorium intybus* L. = *Asarum europaeum* L. > *Sambucus nigra* L.

The results obtained in our experiment are analogous to those of other researchers dealing with the subject of the metals bioaccumulation for the same species of plants (Ross 1994, Fritioff and Greger 2003, Grubor 2008, Aksoy 2008, Tangahu *et al.* 2011, Anilova *et al* 2013, Trubina and Vorobeichik 2013, Balabanova *et al*. 2015, Viktorova *et al*. 2016, Dimitrijevic *et al*. 2016, Popova 2018, Fuentes *et al.* 2019). In the case of *Urtica dioica* L., it has been shown that the level of Cd and Pb was reduced, as well as polychlorinated biphenyls content in polluted soil. According to Viktorova *et al.* (2016), after four months, up to 33% of the less chlorinated biphenyls and 8% of Pb and Cd had been removed. Therefore, *Urtica dioica* L. could be used as a considerable phyto remediator for toxic metals such as cadmium and lead and other xenobiotics. Moreover, phytoremediation is a low-cost and effective method of detoxication of metals in soil. Numerous authors suggested that *Urtica dioica* L. is a very suitable phytoextraction plant in highly contaminated as well as in moderately polluted soils although the nettle is not associated with hyper accumulators (Balabanova *et al*. 2015). On the other hand, content of Cd and Pb in *Urtica dioica* L. plants should be controlled when consuming the nettle as a herb. A special attention should be paid when someone individually collects the plant material (Dimitrijevic *et al*. 2016). In the papers of other researchers, the *Impatiens parviflora* DC is also noted as a plant with high bioaccumulative properties of Zn, Cu, Cd, and Pb (Fritioff and Greger 2003, Tangahu *et al.* 2011). Trubina and Vorobeichik (2013) highlighted the correlation between arising of Cd concentration in soil and an increased level of this metal in aboveground organs of *Asarum europaeum* L. plants. However, in present studies, *Asarum europaeum* L. revealed the moderate bioaccumulative potential for cadmium and lead. Results of current studies on the bioaccumulative properties of *Cichorium intybus* L. are similar to those obtained by other authors (Ross 1994, Aksoy 2008, Fuentes *et al.* 2019). For example, *Cichorium intybus* L. was suggested as a possible biomonitor of toxic metals (Pb, Cd, Cu and Zn) pollution, particularly in urban areas (Aksoy 2008). What is most important is the use of *Cichorium intybus* L. as a potential biomonitor for green park areas in the big city. Some authors' research results concerning the metals' content in *Plantago media* L. plants are in line with present results (Anilova *et al.* 2013, Popova 2018). Various studies have reported about quite high concentrations of lead in plantain. Although the content of Cr, Mo, Ni, Pb, Sr in *Plantago media* L. is usually much less than in *Plantago major* L., Popova (2018) had obtained the large range of positive correlation in concentration of Pb in soil and plants of the species *Plantago media* L. (r = 0.48–0.98); that obviously might be related with different paths (root and foliar) of uptake of this metal by the plant. Lead is generally added to the environment by aerial deposition alongside the roads depending on the density of traffic and distance from the roadside (Aksoy 2008).

CONCLUSIONS

As far as the level of Cd is concerned, in the Holosiyiv green park area of Kyiv it did not exceed the maximum permissible concentration in soil. The monitoring and control of metal contamination of soil should be carried out primarily for lead. Pb exceeded the maximum permissible concentration in watershed of both investigated locations. Pb concentration levels were above the background values in almost all samples of soil.

According to the value of Cd concentration in plant phytomass, the plants can be ranked in the following descending order: *Impatiens parviflora* DC > *Plantago media* L., *Cichorium intybus* L. > *Asarum europaeum* L., *Urtica dioica* L. > *Achillea millefolium* L. > *Sambucus nigra* L. According to the value of Pb concentration in plant phytomass, the plants can be ranked in the following descending order: *Asarum europaeum* L. > *Plantago media* L. > *Urtica dioica* L. ≥ *Impatiens parviflora* DC > *Cichorium intybus* L. > *Sambucus nigra* L. In the current investigation we observed much higher concentration of lead than of cadmium in plant. Moreover, the obtained results indicated high concentrations of lead in studied plants; most of them are medicinal and traditionally used by people. Therefore, medicinal plants should be subjected to adequate quality control requirements.

The lowest plant up-taking indexes was observed in *Sambucus nigra* L. (Pb), and *Plantago media* L. (Cd). *Impatiens parviflora* DC and *Urtica dioica* L. were characterized by the highest plant up-taking indexes for both metals. *Urtica dioica* L. and *Impatiens parviflora* DC could be proposed as biomonitors of toxic metals (Cd, Pb) for green park areas in the city of Kyiv.

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