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REMEDIATION POTENTIAL OF FOREST FORMING TREE SPECIES WITHIN NORTHERN STEPPE RECLAMATION STANDS

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Abstract

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The aim of the research was to study the features of accumulation of heavy metals by assimilation apparatus of coniferous and deciduous arboreous plants. The research identified excess of factual concentrations for Arsenic in mining rock in relation to values stated in IPC (indicative permissible concentrations). It is stated that the metals can be divided into three groups according to their absolute content in unit of foliage biomass. The element of excessive concentration is Mn, medium concentration is characteristic for Pb and Zn and low concentration is observed for Sb, Cr, As, Cu, Ni and Sn. Calculation of coefficient of biological accumulation of the metals under research has shown its high values for Crimean pine. The data presented for Black locust indicate low values of coefficient of biological accumulation, which is best noticeable for Chromium, Antimony and Tin. It is determined that a small amount of Sb and Sn are a subject to uptake by Black locust leaves, whilst for Crimean pine needles, Sb and As are characterised by the lowest inflow. The average content of lead is 209.11 kg·ha^{-1} for Crimean pine in all age groups of trees, whilst for Black locust, this index is only 15.52 kg·ha^{-1}, which is 13.5 times less. Zinc accumulation is better performed by Black locust leaves, and it gradually decreases with increasing age. No definite trend of redistribution and subsequent accumulation of copper depending on tree species and age was found.

Key words: Black locust (*Robinia pseudoacacia* L.), Crimean pine (*Pinus pallasiana* L.), northern steppe of Ukraine, mining rock, heavy metals, bioaccumulation coefficient.

Introduction

Rapid development of industry in all countries of the world leads to local pollution due to emissions from industrial enterprises that has significantly exceeded the maximum permissible sanitary norms during recent decades (Jarup, 2003). Large-scale coal mining activities result in substantial erosion and pollution of vast areas (Kuznetsova et al., 2010; Alekseenko et al., 2017). Technogenic influence leads to global disturbances of ecological systems; therefore, an important task is to forecast changes occurring in ecological systems under the influence of anthropogenic factors (Alexander, 2000; Risto et al., 2005; Shahid et al., 2014).

In the process of coal mining, particularly under conditions of operation of mines, significant disturbance and pollution of land occurs, being especially relevant for agricultural lands. Also, withdrawal of significant areas from use is being carried out (Allen et al., 1995; Kaar, 2002). As a result, poly-elemental man-made anomalies are formed, which can cover all components of the biosphere. Arboreous vegetation that grows in such conditions primarily serves as a mechanical barrier for aerogenic migration of metals and prevents involvement of elements in the process of small biological cycling of substances (Chodak, Niklińska, 2010; Khokhotva, 2010; Marmiroli et al., 2011; Fernández et al., 2017).

Soil and plant objects are involved in all processes of transformation and migration of substances occurring in the biosphere and associated with functioning of ecosystems and with metabolism of substances in living organisms (Hüttl 1998; Prasad, Hagemeyer, 1999; Hüttl, Weber, 2001; Marko-Worłowska et al., 2011; Thapa et al., 2012). Heavy metals coming from different sources are accumulated in the soil; their subsequent redistribution depends on chemical nature of the elements as well as on specific properties of soils and plants (Kabata-Pendias, 2011).

In modern conditions of anthropogenic pressure intensification, with the constant 'enrichment' of habitats of plants with compounds of heavy metals, the environmental factor often impedes implementation of a genetic programme for absorption of chemical elements by plants (Saarelaa et al., 2005; Verbruggen et al., 2009; Appenroth, 2010; Chudzińska et al., 2016).

Many authors believe that the state of assimilation apparatus of arboreous plants can be used as an object of environmental monitoring, which is associated with the assessment of their environment stabilising role, as a mediator of pollutants spreading into the environment (Dmuchowski, Bytnerowicz, 1995; Pöykiö et al., 2010; Kabata-Pendias, 2011; Pietrzykowski, Socha, 2011; Pietrzykowski et al., 2014).

The purpose of this research was studying the peculiarities of accumulation of elements of the group of heavy metals in assimilation apparatus of coniferous and broadleaved tree species that grow under conditions of mining rock.

Material and methods

Sample plots for the research were established on the forest reclamation site of mine 'Pavlohradska' in Pavlohrad city, Dnipropetrovsk region, Ukraine. Samples of vegetal material were taken only from living plants, without any signs of damage and diseases, that were growing on mining rock. The object of the study was represented by foliage biomass (leave and needle biomass) of Black locust (*Robinia pseudoacacia* L.) and Crimean pine (*Pinus pallasiana* L.) trees.

Mine rock was defined as heavy loam, light and middle clays. Mine rock was characterised by adverse water–physical properties. The sulphur content in mine rocks indicated that the amount of pyrite was changing from 1.8% to 3.3%. Acidity (pH) of mine rock was 4.8.

Determination of concentrations of chemicals in mine rock and vegetal material was carried out by the method of inductively coupled plasma-optical emission spectrometry (ICP-OES) using Technologies 5100 (Agilent) spectrometer with an inductively coupled plasma.

Content of the following inorganic contaminants was researched: Cu, Ni, Cd, Zn, Pb, Cr, Sb, Sn and Mn, amongst which Ni, Mn, Co and Cu represent the so-called transition metals, compounds of which have significant biological activity.

To estimate the processes of intake and accumulation of heavy metals in foliage biomass of the woody species under research, the coefficient of biological accumulation was applied, as a ratio of an average content of heavy metals in foliage to their average content in mine rock:

$$K_{bac} = C_f / C_{sub},$$

where K_{bac} is the bioaccumulation coefficient, C_f is the metal content in foliage biomass expressed in mg/g and C_{sub} is the metal content in mining rock expressed in mg/g.

In order to calculate the gross content of elements belonging to the group of heavy metals in foliage live biomass of the tree species, on the first stage of research, their average values were determined in dry state using the approach and methodology described by Lakyda (2003). The research was conducted at different ages of the investigated species and indicated as young-age (1–20 years), middle-age (21–40 years), maturing (41–60 years), mature (61–80 years), overmature (81–100 years) age groups.

For quantification of assimilation component of the aboveground live biomass, 45 model trees of each investigated tree species were analysed and biometric parameters of 250 model trees were determined. In order to determine dependency from the main biometric indices (diameter, height) for foliage biomass of Black locust and Crimean pine trees, analytical search for adequate models by means of Statsoft STATISTICA 10 software was performed.

Results

At the first stage of this research, the content of chemicals in the substrate for growing arboreous plants was determined and their compliance with the state ecological and sanitary standards was assessed (Table 1).

The results of analysis of the actual concentrations of chemicals in mine rock with pH 4.8, in relation to the IPC values, has shown an excess for only one metal – arsenic (5.2 times). The comparative analysis of compliance with the normative values of maximum permissible concentrations (MPC) has demonstrated the absence of excess for only one amongst the nine substances under research – manganese. Indicators of content of other inorganic contaminants in mine rock have exceeded the MPC values for chemical sub-

T a b l e 1. Content of inorganic contaminants in mine rock on the area of forest reclamation.

Index	**Chemical elements**								
	As	**Sb**	**Zn**	**Pb**	**Cr**	**Ni**	**Cu**	**Mn**	**Sn**
Concentration, mg/kg	25.8 ± 2.70	40.5 ± 1.44	56.5 ± 1.57	40.6 ± 4.58	93.9 ± 2.21	43.1 ± 2.53	27.5 ± 0.19	164.5 ± 1.25	40.5 ± 1.40
Maximum permissible concentration*, mg/kg	2.0 g/q*****	4.5 g/q	23.0 m/f***	32.0 g/q	6.0 m/f	4.0 m/f	3.0 m/f	1500.0 g/q	n/r***
Indicative permissible concentration**, mg/kg	5.0	n/r	110.0	65.0	n/r	40.0	66.0	n/r	n/r

Notes: * – values of maximum permissible concentrations (MPC) of chemical substances in soils by indices of harmfulness; ** – values of indicative permissible concentrations of gross content of chemical substances in soils for different types of land use; n/r*** – content of chemical substance is not regulated; m/f*** – mobile form of chemical substance; g/q***** – gross quantity of chemical substance.

stances in soil to various extent: Pb exceeded 1.3 times, Zn 2.5 times, Sb 9.0 times, Cu 9.2 times, Ni 10.8 times, As 12.9 times, Cr 15.7 times and Sn 20.3 times.

As metals are present in soils in two forms – in solid form and in soil solution – their form of existence, transformation and, most importantly, availability to plants are determined by medium reaction, chemical composition of soil solution and content of organic substances (Wuana, Okieimen, 2011).

The phytotoxicity of substances depends on their chemical properties as well as their ability to form complexes and, above all, their concentration. In most cases, metals are ranked by degrees of toxicity as follows: Cu > Ni > Cd > Zn > Pb > Hg > Fe > Mo > Mn (Brown et al., 1990; Grishko et al., 2012). Changes may occur in the given series because of genetic, physiological and biochemical characteristics of plants and their growing conditions.

A complex of edaphic factors determines the transformation and direction of migration of chemicals into vegetal organs and tissues. The inorganic contaminants under research on acidic substrates (represented by the studied mine rock with pH 4.6–4.8) have the following degrees of mobility: Ni, Cr, Pb and As have low mobility and Mn, Cu and Zn are mobile (Wuana, Okieimen, 2011).

The next stage of the research was aimed at the determination of concentrations of inorganic contaminants in foliage biomass of Black locust and Crimean pine, the results of which are presented in Fig. 1.

The studied chemical substances in the assimilating fraction of aboveground live biomass of tree species were divided into three groups based on the concentration: (1) substances with excess concentration (113.7–510.6 mg/kg of dry mass), Mn; (2) substances

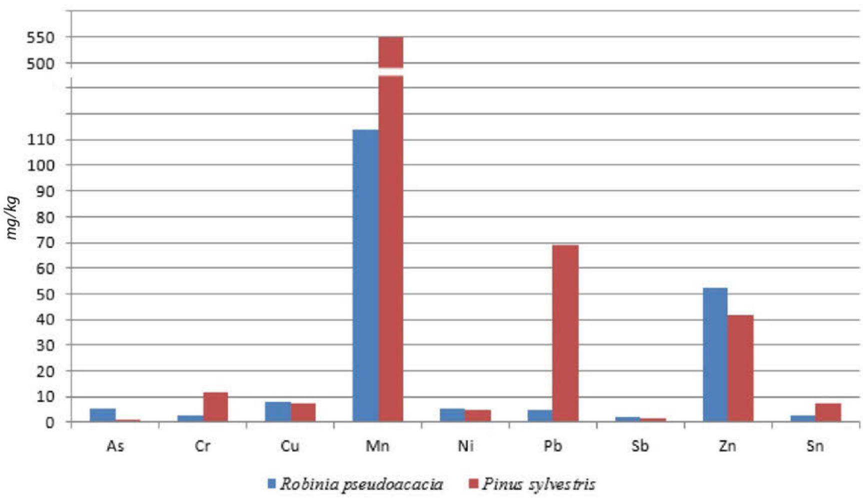


Fig. 1. Inorganic contaminants concentration in foliage biomass of Black locust and Crimean pine.

with medium concentration (41.5–69.2 mg/kg of dry mass), Pb, Zn; and (3) substances with low concentration (0.8–11.9 mg/kg of dry mass), Sb, Cr, As, Cu, Ni and Sn.

A comparative analysis of concentration of chemical substances under research in foliage biomass of Black locust and Crimean pine has enabled to reveal significant differences in the concentration of metals such as manganese, arsenic, chromium, lead and tin.

The most significant difference is recorded for the concentration of lead: in the needles of Crimean pine, the concentration of this element was more than 12 times higher than that in Black locust leaves. More significant accumulation in Black locust foliage biomass compared to the concentration in Crimean pine needles was found for only two metals: arsenic (6.7 times) and antimony (2.2 times). The reverse trend was observed in relation to manganese, chromium and tin: their accumulation in Crimean pine needles exceeded those found in the leaves of Black locust, which are 4.5, 4.4 and 2.9 times, respectively. The presence of identical concentrations in foliage biomass of Crimean pine and Black locust was found for copper, nickel and zinc. These substances are physiologically significant for plants; therefore, their concentration is identical in assimilation apparatus of different tree species without any signs of either damage and lesions of different abiotic and biotic aetiology, or intoxication, which demonstrates physiologically optimal value for the performance of physiological and biochemical reactions.

Excessive gross content and significant concentration of mobile forms of inorganic contaminants in soils result in their accumulation and higher concentration in vegetal tissues. However, this process is species specific. Therefore, to characterise remediation potential for the tree species under research, the coefficient of biological accumulation of metals by foliage fraction of their aboveground live biomass was calculated (Table 2).

T a b l e 2. Values of bioaccumulation coefficients for inorganic contaminants.

Tree species	**Chemical substances**								
	As	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**	**Sn**
Robinia pseudoacacia	0.178	0.029	0.282	0.691	0.127	0.152	0.043	0.924	0.069
Pinus pallasiana	0.031	0.127	0.281	3.104	0.107	1.702	0.020	0.734	0.184

According to scale developed by Avessalomov (1987), manganese and lead are recognised as elements of high accumulation ($10 > K_{bac} \geq 1$); all other metals under research are considered amongst elements of weak accumulation ($1 > K_{bac} \geq 0.1$). High coefficient of biological accumulation values for these metals was recorded only for the specimens of Crimean pine. The data presented for another studied tree species, Black locust, has shown very low values of coefficient of biological accumulation for substances such as chromium, antimony and tin.

The results of determining the accumulative properties of assimilative fraction of arboreous plants have allowed to establish that when growing on mine rock, this fraction of live biomass is capable of accumulating inorganic contaminants from 1.46 to 2134.35 kg/ha for Crimean pine and from 4.42 to 441.08 kg/ha for Black locust, depending on the age of the model trees (Table 3).

T a b l e 3. Content of inorganic contaminants in foliage biomass of Black locust and Crimean pine.

Age group, years	**Foliage biomass, $kg\cdot ha^{-1}$**	**Elements of the group of heavy metals, $kg\cdot ha^{-1}$**								
		As	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Zn**	**Sn**
1–20	3880 / 1830	20.91 / 1.46	10.63 / 21.87	30.11 / 14.16	441.08 / 934.42	21.30 / 8.44	18.20 / 126.54	6.84 / 1.46	202.65 / 75.87	10.20 / 13.63
21–40	3480 / 4180	18.76 / 3.34	9.53 / 49.95	27.00 / 32.35	395.61 / 2134.35	19.11 / 19.27	16.32 / 289.05	6.12 / 3.34	181.76 / 173.30	9.15 / 31.14
41–60	3370 / 3350	18.18 / 2.68	9.23 / 40.03	26.15 / 25.93	383.10 / 1710.54	18.50 / 15.44	15.80 / 231.65	5.93 / 2.68	176.02 / 138.89	8.86 / 24.96
61–80	2510 / 3130	13.53 / 2.50	6.88 / 37.4	19.48 / 24.23	285.34 / 1598.21	13.78 / 14.43	11.77 / 216.44	4.42 / 2.50	131.10 / 129.77	6.60 / 23.32
81–100	2630 / –	2.10 / –	31.43 / –	20.36 / –	1342.90 / –	12.12 / –	181.86 / –	2.10 / –	109.04 / –	19.59 / –

Notes: numerator – *Robinia pseudoacacia*, denominator – *Pinus pallasiana*.

Significant differences were found regarding nature of accumulation of individual metals, which is mainly reasoned by their content in mine rock, nature of intake and translocation of a metal in vegetal tissues and by different potential for accumulation of the two tree species under research.

When researching the content of inorganic contaminants in Black locust foliage biomass, it was determined that the lowest accumulation in assimilation organs is characteristic for metals such as Sb and Sn, whereas for Crimean pine, minimal accumulation is observed for Sb and As. On the contrary, translocation of manganese in assimilation fraction of both the hardwood and coniferous wood species occurs most intensively. Significantly higher concentrations of this metal were recorded in foliage biomass of Crimean pine, especially in the second age group, which is primarily due to the formation of predominant assimilation live biomass in trees of the specified age group.

The second position in terms of gross content in foliage fraction of both investigated wood species is presented by lead and zinc, which are elements with synergistic action when accumulated in soils (Grishko et al., 2012). Upon intake in the aboveground live biomass, lead with low mobility is accumulated in substantial quantities in assimilative fraction of trees of all ages ranging from 126.54 kg/ha (young-age stands) to 289.05 kg/ha (middle-age group). An average content of the analysed element for Crimean pine included in this research is 209.11 kg/ha, whereas that for Black locust is only 15.52 kg/ha^{1}, which is 13.5 times less. Such differences can be explained by different lifetime of assimilative apparatus in coniferous and broadleaved tree species.

Another tendency of gross content variability depending on the age of Crimean pine and Black locust trees was found for zinc. Unlike lead, this metal is easily available to plants, and its accumulation increases linearly with increasing concentrations in soils (Eide, 2006). Sequestration of this metal is greater in foliage biomass of Black locust and gradually decreases with increasing age of the model trees, which is directly proportional to decrease in the ability to form assimilative organs for this tree species. The difference between maximal and minimal content of this metal in the young-age and the mature age groups is 35%. For Crimean pine needles, it was found that zinc is accumulated in lower quantities, with maximum accumulation in live biomass of trees belonging to the middle-age group.

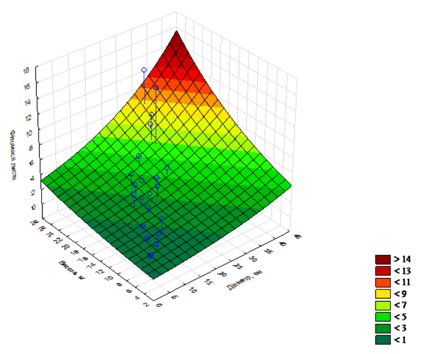
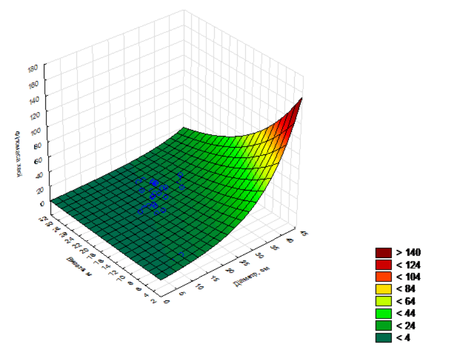
Distribution of copper in photosynthetic organs of the studied tree species did not reveal any particular age-dependent variability and specificity of its accumulation. A tendency towards age-driven decrease in gross content of nickel in foliage biomass was found for Black locust (Table 3). The mentioned pattern was also found for the coniferous species with a noticeable decrease in the concentration of this metal in the needles of overmature trees. The research did not reveal species-specific peculiarities of build-up, redistribution and subsequent accumulation of this metal.

According to the results of our research, it was found that for Crimean pine, processes of translocation of metals such as As, Sb and Ni to assimilation apparatus are slowed down as compared to Cr, Mn and Zn, whereas for Black locust, the minimal content in foliage is registered for metals such as Cr and Sn. The maximal gross content is found for manganese; Crimean pine accumulates this metal at a 5 times higher rate than Black locust, and lead is accumulated 16 times more intensively by Crimean pine than by Black locust.

The content of chromium is highest in specimens of Crimean pine aged between 21 and 40 years and lowest in young-age group. The content of this metal in foliage biomass of *R. pseudoacacia* logically decreases with increase in age and reaches its minimum – 6.88 kg/ha – in leaves of mature model trees.

In order to determine the dependency of accumulation of inorganic contaminants in assimilative organs of the two tree species, a search for an adequate mathematical model

T a b l e 4. Equations describing dependency of foliage biomass on the main biometric indices of model trees.

Robinia pseudoacacia		*Pinus pallasiana*	
Equation type	R^2	Equation type	R^2
$P_{fol} = 0.7909 \cdot \exp(0.3512\ d) \cdot \exp(0.0499\ h)$	0.46	$P_{fol} = 3.2256 \cdot \exp(0.0891\ d) \cdot \exp(0.0683h)$	0.42
			

T a b l e 5. Main distributional statistics of indices of model trees' foliage fraction.

Index	Minimal value	Maximal value	Mean value	Standard deviation	Skewness	Kurtosis
Robinia pseudoacacia						
Foliage biomass, kg	0.14	13.36	3.61	0.02	1.877	3.755
Diameter, cm	2.70	40.00	17.22	0.09	0.255	-0.294
Height, m	3.70	25.80	15.05	0.07	-0.208	-0.789
Pinus pallasiana						
Foliage biomass, kg	0.95	19.62	5.82	0.03	1.493	3.761
Diameter, cm	4.00	38.90	20.61	0.12	-0.468	0.754
Height, m	4.20	30.00	19.06	0.42	-1.268	1.027

was performed, in order to account for dependency of formation of foliage biomass on the main mensurational indices of model trees (Tables 4, 5).

The presented dependencies are the most significant and envisage further practical application of the developed two-factor models accounting for two mensurational indices – height and diameter of a sample tree.

Discussion

To consider all the variety of soil and geochemical conditions when establishing maximum permissible concentrations of inorganic substances is hardly possible. Therefore, certain concentrations of chemical substances in mine rock reveal an understanding of their phytotoxic effects on arboreous plants. An important point in substantiating soil toxic safety for formation of artificial plantation systems is the consideration of concentrations of inorganic contaminants that alter physiological and biochemical processes and are toxic to plants. Regarding location and transformation of chemical substances in the soil and their availability to plants, the literature presents data proving different directions of migration of inorganic contaminants from soil to plants and their absorption. According to Appenroth (2010), inorganic contaminants are predominantly concentrated in a 10-cm layer; however, given low pH values, which is characteristic for the substrate under research, a large proportion of metals are transferred to soil solution, which makes them more accessible to root systems of plants.

The results of comparative analysis of determined actual concentrations of chemical substances in foliage biomass of aboveground live biomass of Crimean pine and Black locust with concentrations indicated by different authors as optimal for functioning of plants are shown in Table 6.

According to the results of our research, the highest migration capacity and sequestration in assimilation fraction of aboveground live biomass of the two tree species are observed for zinc and manganese, which are physiologically significant substances for plant metabolism. It is worth noting that gross content of these metals in mine rock does not exceed the values indicated in MPC (Mn) or are slightly excessive (Zn). The obtained data are

T a b l e 6. Limits of fluctuations of optimal concentrations of chemical substances in plants.

Inorganic contaminants, mg/kg	Mineev V.H., 1990	Chertko N.K., 2008	Kovalskyy V.V., 1974	Kabata-Pendias A., 1989	Nieber et. al., 1978	Concentrations in foliage biomass of the researched plants
Chromium	0.2 – 1.0	–	–	0.02 – 0.2	–	2.8 – 12.0
Copper	2.0 – 12.0	5.0 – 30.0	3.0 – 12.0	2.0 – 20.0	≤ 30	7.7
Nickel	0.4 – 3.0	≤ 1.0	–	0.1 – 2.7	–	4.6 – 5.5
Lead	0.1 – 5.0	1.5 – 14.0	–	0.05 – 5.0	≤ 30	4.7 – 69.1
Tin	0.8 – 6.0	–	–	–	–	2.6 – 7.5
Zinc	15.0 – 150.0	15.0 – 150.0	20.0 – 60.0	–	≤ 100	41.6 – 52.3
Manganese	–	20.0 – 300.0	20.0 – 60.0	17.0 – 334.0	–	113.7 – 510.6

consistent with the results obtained by Grishko et al. (2012), which indicate that the depth of penetration of chemicals in contaminated soils is usually not more than 20 cm, but in cases of severe contamination, they can penetrate down to a depth of 1.5 m. According to Grishko et al. (2012), amongst all the metals, zinc has the highest migration potential and uniformity of distribution in the soil layer of 0–20 cm. The research results state that a decrease in pH by two units leads to 3.8–5.5 times increase in mobility of zinc. Phytotoxicity of zinc is noted by many authors, especially on acid soils (Alexander, 2000; Eide, 2006; Fernandez et al., 2017). Manifestation of toxicity signs of zinc in plants is noted when its content in tissues reaches 300–500 mg/kg of dry matter. Tolerant species may weaken the effect of excessive zinc concentrations by metabolic adaptation and formation of complexes or by limiting the presence of the element in cells or by converting it into insoluble form in storage tissues. According to Prasad and Hagemeyer (1999), zinc concentration of 200 mg/kg of dry plant material causes a toxic effect on plants.

The literature does not contain data indicating an undoubted need for lead for functioning of any plant species; only information on growth stimulating effect of low concentrations of compounds of this metal is available. The described effects of inhibition of plants' metabolism arise from low level of the element. Interaction of lead with other elements under different environmental conditions does not allow to reliably determine which metal concentrations are toxic to plants. Data on interaction of lead with other microelements are available only for zinc and cadmium. Stimulating effect of Pb^{2+} ions on the absorption of cadmium by plant roots may be a secondary effect associated with the disturbance of transmembrane transport processes. Antagonism of zinc and lead is manifested in a mutually unfavourable effect on the transport of both the elements from roots to aboveground part of plants (Itoh et al., 2006).

Regarding migration of lead, it is mainly indicated that the element is able to be accumulated in the soil. According to Lin et al. (2004), this metal accumulates only in the surface layer, 0–2.5 cm, and its ions are characterised by low mobility even at low pH values. For different types of soils, the rate of leaching of this metal varies from 4 to 30 g/ha/year. However, our research has found that when the total amount of lead in the substrate was within the range of indicative permissible concentrations, Crimean pine needles revealed a significant sequestration capacity in relation to lead, which is confirmed by high value of accumulation coefficient.

Significant migration potential in acidic environment is observed for copper and nickel. Migration of the latter is complex: on one hand, this metal enters plants from the soil in a form of soil solution; on the other hand, its amount in the soil is replenished as a result of destruction of soil minerals, dieback of plants and microorganisms. Coefficients of biological accumulation of these metals in assimilation fraction of the researched tree species that were calculated in the course of our research have shown a considerable similarity: Crimean pine needles and Black locust leaves concentrated copper (K_{bac}Cu = 0.28) and nickel (K_{bac}Ni = 0.11) with the same intensity, provided a significant excess over MPC of these substances in the substrate.

High concentrations of copper may cause toxic effects on plants. Copper is referred to as inactive metal, which actively binds mainly with cell membranes in plant roots. This is confirmed by the high metal concentrations in the soil, and a significant decrease in its concentration in assimilation fraction of plants. Owing to its important role in functioning of enzymes and variable valency, other ions with similar protein affinity may exhibit antagonistic interaction. The mechanism for copper and zinc absorption is identical, and therefore, each of them, because of mutual competition, can inhibit the absorption of the other by a root system. Signs of copper deficiency in plants are observed at different content in cells: content of copper below 2 mg/kg is unfavourable for most plants (Pietrzykowski et al., 2014).

Currently, the necessity of nickel for plants is a controversial question, but toxicity of its high concentrations is obvious. For different plant species, a range of toxic concentrations of nickel varies widely, and concentrations of excessive and toxic levels vary from 10 to 100 mg/kg of soil. With an excess of nickel, absorption of nutrients is drastically reduced. Jarup (2003) has found a fact of reduction in inflow and transfer of a number of elements – Zn, Cu, Ca, Mg and Mn – in plants. However, when nickel concentration is excessive, inhibition of the activity of meristem was observed, which was expressed in the suppression of differentiation of tissues, decrease in number of cell layers and vascular beams. Before the appearance of visually noticeable symptoms of acute toxicity, elevated concentrations of nickel in plant tissues suppress transpiration and photosynthesis processes, whilst replacing the central magnesium atom with the nickel atom. Thapa et al. (2012) indicate that mobility of nickel in soil depends on the concentration of organic matter, mainly humus acids, and pH of the medium. The determined coefficients of biological accumulation for nickel in relation to the researched tree species have shown a considerable resemblance: foliage of both tree species was absorbing and concentrating the element with same insignificant intensity (K_{bac}Ni = 0.11).

Antimony is not considered to be a vital metal for plants. It is known that its soluble forms are actively absorbed by plants from the soil. The physiological impact of antimony is similar to that of arsenic: it binds with thiol groups of proteins and participates in enzymatic reactions as a competitor of vital metabolites. In our studies, given the high content of antimony in technosol and excess over MPC, its concentration in foliage of the researched tree species was taking place identically: concentration of Sb in leaves of Black locust and needles of Crimean pine was between 0.02 and 0.04 mg/kg, which is very low for accumulation. Kubatbekov et al. (2012) indicate that the content of antimony in tissues of trees and shrubs growing in areas of ore mineralisation was 7−50 mg/kg, whereas according to our data, the concentration of this metal in foliage of Black locust was 1.7 mg/kg and in needles of Crimean pine was only 0.8 mg/kg, which cannot compete with plants that are recognised as antimony accumulators.

Conclusion

Mine rock, which served as a substrate for growing arboreous plants of a remediation stand, was characterised by excessive content of inorganic contaminants, with the exception of manganese. Actual concentrations of metals in mine rock exceeded those stated in state MPC norms: Pb exceeded 1.3 times, Zn 2.5 times, Sb 9.0 times, Cu 9.2 times, Ni 10.8 times, As 12.9 times, Cr 15.7 times and Sn, 20.3 times.

Per unit of foliage biomass of Black locust and Crimean pine, the metals were divided into three groups: (1) substances with excess concentration (113.7–510.6 mg/kg), Mn; (2) substances with medium concentration (41.5–69.2 mg/kg), Pb, Zn; and (3) substances with low concentration (0.8–11.9 mg/kg), Sb, Cr, As, Cu, Ni, Sn.

In Crimean pine needles, sequestration of lead was 12 times higher in comparison with its content in leaves of Black locust. The tendency for higher accumulation in Crimean pine needles was detected in relation to manganese, chromium and tin: their accumulation exceeded the corresponding values in Black locust leaves by 4.5, 4.4 and 2.9 times, respectively. Higher accumulation in Black locust foliage biomass compared to Crimean pine was detected for arsenic (6.7 times) and antimony (2.2 times). Same concentrations in foliage biomass of the two researched tree species for physiologically significant metals have been established for copper, nickel and zinc.

Determination of content of heavy metals in mine rock and foliage biomass – Crimean pine needles and Black locust leaves – tree species used for biological reclamation of mine dumps shows stabilisation of content of heavy metals in the substrate. According to the bioaccumulation coefficient, Crimean pine can be considered a hyperaccumulator of lead, which substantiates its use as a phytoremediation agent.

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