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BIOCONSERVATION OF TECHNOGENIC METALS BY BIRCH ON INDUSTRIAL WASTE DUMPS IN BASHKORTOSTAN

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Abstract

The features of the accumulation of heavy metals in the organs of the birch (Betula pendula Roth) which growing on industrial dumps within the Republic of Bashkortostan were studied. The studied birch stands grow on the dumps of the copper-pyrite deposits of the Sibay branch of the Uchaly mining and processing plant and the Uchaly mining and processing plant. The content of copper, zinc, cadmium, manganese, cadmium, strontium, iron, nickel, chromium and lead was determined. Analyzes were carried out on an ICP-MS (Plasma quad pq2-turbo plus, Usa) installation using inductively coupled plasma mass spectrometry. The content of heavy metals was determined in the vegetative organs (leaves), in the shoots, in the bark and in the root system of birch. The content of metals in soils under plantings and in non-forested areas was also determined. It is shown that metals accumulate to the greatest extent in perennial birch organs on dumps in Uchaly (bark) - 576.91 and 7942.52 ppm, and also in leaves on dumps in Sibay - 97.1 ppm. It can be recommended to use birch when reclaiming industrial waste dumps within the Republic of Bashkortostan.

Keywords: Adaptation, birch, bioaccumulation, technogenic metals.

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1. Introduction

The development of industrial production in the XX century led to the formation of anthropogenically transformed areas, the restoration of which in the XXI century becomes a priority. The formation of significant volumes of highly toxic industrial waste caused the primary and secondary pollution of large areas, including urban and agricultural lands. The imperfection of technology with a low level of purification measures at industrial enterprises leads to the fact that huge amounts of toxic compounds, which often include metals, are released into the environment with emissions (Clemens, 2006, p. 14). Toxicants have a negative impact on the health of the population and the state of vegetation in large areas.

Restricting the migration of toxicants in the environment is a prerequisite for ensuring integrated environmental safety of the population and sustainable development. It is well known that woody vegetation is able to accumulate significant amounts of ecotoxicants, while maintaining growth energy and durability while performing a complex of sanitary, hygienic and aesthetic functions. Of particular relevance is this direction of environmental improvement in those regions where a specific geochemical background has been formed, which is characterized by a high background content of metals.

2. Problem Statement

The nature of accumulation and redistribution of heavy metals in an ecosystem largely depends on the characteristics of the soil and vegetation cover, as well as the level of anthropogenic stress. The soil accumulates the incoming pollutants and can become a secondary source of pollution of surface air, natural waters, and crop production. The need to determine the content of heavy metals in the soil is of particular importance, since having a buffer capacity, the soil reduces the mobility of metals and thereby reduces their flow into the plants (Fernández-Calviño et al., 2017). As an indication of the anthropogenic impact on the objects of study, an approach was chosen based on a comparison of the concentration of heavy metals in the soils and plants of the anthropogenic zone with indicators of the local geochemical background of the studied metals.

3. Research Questions

Heavy metals are the most toxic for living organisms, including woody plants. Heavy metals are part of enzymes that play an important role in redox processes, contribute to the formation of chlorophyll, increase the intensity of photosynthesis, positively affects carbohydrate and nitrogen metabolism, increase resistance against fungal and bacterial diseases. However, an excess of heavy metals causes negative changes in plants. So the toxic effect of copper manifests itself in reducing the formation of phytomass, reducing tissue hydration and chlorophyll content, inhibiting the absorption of ions of some other metals and their translocation (Kalinovic et al., 2015; Pająk, Halecki, & Gąsiorek, 2016). Lead is necessary for plants in small quantities and therefore is relatively weakly absorbed by plants, while its excess inhibits respiration and inhibits the process of photosynthesis, resulting in reduced accumulation of phytomass (Chrzan, 2015; Chropeňová et al., 2016; Matin, Kargar, & Buyukisik, 2016). Cadmium is one of the most toxic heavy metals for plants (Clemens, 2006; Campos, Abrantes, Keizer, Vale, & Pereira, 2016;

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Fernández-Calviño et al., 2017); it significantly slows down the growth rate and development of the plant organism, weakens the intensity of photosynthesis, leads to changes in the permeability of cell membranes and the activity of a number of enzymes.

It is known that woody plants perform the most sanitary protection functions. Pollutants have a serious integrated effect on vegetation, and often powerful anthropogenic press is fatal or lethal to plants. At the same time, environmental improvement is impossible without the creation of a fitofilter and among the many tree species the birch (Betula pendula Roth) is a species that is widely used in "green construction" both in Bashkortostan and throughout Russia (Matin, Kargar, & Buyukisik, 2016).

4. Purpose of the Study

Studied the content of a number of metals in the birch (Betula pendula Roth), growing on industrial dumps near the cities Sibay (Sibay branch of Uchaly mining and processing plant, SF UGOK) and Uchaly (Uchaly mining and processing plant, UGOK).

5. Research Methods

The selection, laying and description of test plots in the birch trees were carried out according to standard methods (Snowdon et al., 2001). To determine the content of metals in the bodies of birch and in the soil during the field work, more than 1500 pooled soil and plant samples were taken. To analyze the content of individual elements in soils and plants, the selected samples were dried to an air-dry state, then weighed samples (2.0 g each). The content of elements in plant samples and soil was determined in the analytical laboratory of the Institute of Geology, RAS (Moscow) using ICP-MS (Plasma quad pq2-turbo plus, Usa) mass spectrometry with inductively coupled plasma (Medhe, 2017) The content of individual elements was expressed as the mass fraction of impurities - in parts per million (ppm). The actual material was selected for 10 years - from 2010 to 2018. All measurements were performed at least 10 times. Mathematical processing of the data was performed using the statistical package Microsoft Excel 2000. The tables show the average arithmetic data and errors of the mean for all the years of research.

6. Findings

Birch plants are highly everybiontic. It should be noted that development in various conditions makes a serious imprint on the nature of the formation of birch stands. Thus, when growing on the dumps of UGOK and SF UGOK, birch, along with pine, is one of the pioneer species of woody vegetation and develops free territories, forming at the same time uneven plantations. The number of birch trunks can reach 3000 pieces per hectare, while the fact that the birch plants perform the stabilizing functions in technogenic landscapes is obvious.

Considering the issue of the formation of birch stands on technogenically polluted areas, it should be noted that the stands were created as crops and today are closed tree stands that can fully fulfill the role of a phytofilter in the spread of industrial environmental pollutants. It has been established that the calcium content in plants is estimated in thousands of ppm, with the greatest amount accumulating in the bark (6610 ppm), and the smallest - in the shoots (3318 ppm). The content of iron and manganese amounts to hundreds

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of ppm and to the greatest extent these metals accumulate in the bark (1090 and 440 ppm), the minimum content of these metals falls on the shoots (284 and 151 ppm). The copper content in the bark is also the largest and exceeds its content in the leaves by 2.3 times and is 23 ppm.

It is shown that the largest amount of lead, cadmium and mercury accumulates in the leaves of birch, while the smallest amount is contained in the bark. Shoots occupy an intermediate position. The content of these metals in plants does not exceed 1.5 ppm. Describing the accumulation of strontium, it should be noted that this element is not detected in plants, while its content in the soil is 22 ppm. Due to the bioaccumulative properties of birch, the metal content in plants exceeds that of the soil, and the maximum total amount of technogenic metals in the forest floor is explained by the constant flow of metals with litter.

It was established that the total copper content in the above-ground part of the birch is significantly higher than the content of this metal in the underground part of the plant. Thus, it can be concluded that perennial perennial above-ground organs of the birch hang and play a depositing role and are capable of accumulating significant amounts of copper. The greatest amount of copper is contained in the shoots (92 ppm), while copper is not found in the leaves. The intermediate position is occupied by the root system (44 ppm) and the bark (32 ppm). The copper content in the soil under the planting and in the bare forest areas is insignificant and approaches zero.

The manganese content, as one of the most important physiological elements, is in the hundreds of ppm. Analyzing the data on the quantitative content of manganese in various birch organs, the marked accumulation of this element in the leaves is up to 424 ppm, while the content of manganese in roots, bark and shoots does not exceed 200 ppm. The maximum accumulation of metal in the leaves causes repeated intoxication during the fall of leaves. In the soils under the plantings of woody plants, the manganese content is 30% lower relative to the non-forested areas of the dumps of brown coal deposits.

It is established that the accumulation of zinc in the organs of birch is in the series: shoots> root system> bark. Most of the accumulation of zinc occurs in the above-ground organs of birch, but it should be noted that zinc is not concentrated in the leaves. The quantitative ratio of zinc in soils shows that under planting the metal content is more than 7 times higher than in comparison with the non-forested areas.

In the course of analyzing the determination of nickel content in various organs of birch, it was found that there is no nickel in the leaves. The metal content in the shoots is 2 times less than in the bark and 4 times less than the root system and is 13 ppm. The protective mechanisms of birch provide the deposition of metal in the older organs of the plant, thereby preventing nickel from entering the young developing organs and tissues. Due to the metal storage capacity of woody plants, the nickel content in the soils under planting is more than 4 times less than that of the unpolished land (Kangas & Maltamo, 2007, p. 123).

Analysis of the distribution of lead in various organs of woody plants growing in the dumps of a brown coal field shows that the root system and bark are the main place of deposition of lead in birch plants: the content of this metal in the bark is 7.9 ppm and in the roots is 9.3 ppm . Shoots are also able to accumulate lead, but the metal content in them is significantly lower compared to the bark and root system and is 1.7 ppm. It has been shown that hung lead does not accumulate in the birch leaves. Despite the significant ability of birch to accumulate lead, the content of this metal in the soils under plantings is almost 10 times higher compared to the soils of the unforested areas.

Strontium accumulates in all parts of the birch and its content amounts to tens of ppm. Its greatest content is noted in the root system (93 ppm) and shoots (68.3 ppm), the smallest - in the leaves (22 ppm) and bark (52 ppm) (Titus, 2004). Thus, the distribution of strontium in birch plants can be characterized as uniform. The total amount of metal in the aerial part is higher than in the root system, which is the basis for making an assumption about the high penetrating power of strontium into the plant organism (in this case – the birch). The high content of strontium in plants causes a decrease in its amount in soils under planting by more than 2 times compared with the soils of the non-forested area.

Chromium in the greatest amount accumulates in the root system of birch hung to 107 ppm. The chromium content in the bark and shoots varies slightly and is 68 and 71.3 ppm, respectively. The smallest amount of chromium is found in leaves (29 ppm), which suggests the possibility of internal regulation of the distribution of this metal in plants. It is obvious that the bulk of the highly toxic metal is concentrated in the tissues of the roots and enters the assimilation organs in a minimal amount. Despite the significant abilities of birch to accumulate Cr, its amount in the soil under planting is more than 34 times higher than the same indicator for unforested areas. This fact can be explained by significant root excretions of plants with a high content of this metal (there is a lot of it in the roots), as well as by additional ingress into the soil with residues.

It is shown that the total content of cadmium in the aboveground part of birch is 3 times higher than in the underground part of the plant. The greatest amount of cadmium is found in the bark (0.78 ppm) and shoots (0.74 ppm), and the smallest - in the leaves (0.4 ppm) and roots (0.6 ppm). The greatest amount of cadmium accumulates in the older parts of the birch. The content of cadmium in the soils under birch is much less compared to the soils of the unforested areas - 0.55 and 5.4 ppm, respectively.

It is noted that the content of mercury in the bodies of birch varies in the range of 0.12-0.01 ppm, in the shoots and root system, respectively. The greatest amount of mercury is concentrated in the shoots, while this metal is not transported to the leaves - its content in the assimilation organs is 0. The bark of trees occupies an intermediate position, the mercury content of which is about 0.06 ppm. The amount of mercury in the soil under the stands of birch is 7 times greater than the content of this metal in the soils of the unforested areas and is 0.21 ppm. A significant increase in mercury in soils under plantings is possible due to root excretions.

The zinc content in the birch plants when they grow on the dumps of the SF UGOK varies from 81.9-86.5 ppm. Significant differences between the indicators of Zn accumulation in various organs were not established. Compared to zinc, much less copper accumulates in birch plants. The copper maximum is concentrated in birch leaves (11.5 ppm), copper is slightly less in the root system (7.4 ppm), and the minimum amount is noted in wood and bark - 5.4 ppm. The results of analyzes show that the content of cadmium in plants obeys the laws: roots> wood and bark> leaves, which is not the case with zinc and copper. Describing the total metal content in plants, it should be noted that the largest amount of metals is contained in the leaves and somewhat lower in the roots, bark and shoots. Waste soils contain a significant amount of metals, despite the bioaccumulative properties of woody plants. Since the process of self-overgrowing of the dumps of the UGOK SF is very slow, and the dump soil under plantings differs little from the non-forested part of the dumps, the comparison of metal content is given relative to the LLC (limit of legal concentration) for the corresponding elements. So, it was found that the greatest excess is observed

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in the case of copper, the content of which in dump soil is 83.8 ppm with an LLC of 23 ppm. The gross content of zinc in dump soil approaches 100 ppm. Despite the high content of metal in the soil, its excess over the MPC is much less compared to copper and is 13.8 ppm. The cadmium content in the dump soil for the bioaccumulative properties of plants is 3 times less than the LLC, which is 1.5 ppm for this metal. The bioaccumulative properties of birch in conditions of chronic environmental pollution play an important role in limiting the migration of ecotoxicants (Tables 01 and 02).

Analyzing the quantitative characteristics of the bioaccumulation of metals, it was found that the iron content in both birch and soil plants amounts to thousands of ppm. It is shown that the smallest amounts of this metal are accumulated by leaves and shoots of plants - 3270 and 3720 ppm, respectively. The greatest amount of iron accumulates in the bark of plants and 2 times exceeds the indicators of leaves and shoots. The root system contains up to 7350 ppm of iron, which is an average value relative to other plant organs. Against the background of a high Fe content in plants, the soil under plantings contains a much larger amount of the metal under study as compared to the soils of the non-forested areas - 132,000 and 89900 ppm.

Table 01. The content of anthropogenic elements in the organs of birch (Betula pendula Roth) on the dumps of the copper-pyrite deposit in the town of Sibay

Element (ppm)	**Names of samples for analysis**				
	Leaves	**Mixed samples of shoots and bark**	**Roots**	**Soil under planting (gross content)**	**LLC (gross content)**
Cu	11,5±1,1	5,4±0,3	7,4±0,8	83,8±2,9	23
Zn	86,5±5,8	84,3±7,5	81,9±6,4	98,8±3,6	85
Cd	0,1±0,02	0,12±0,01	0,15±0,05	0,48±0,07	1,5
Total:	97,1	89,82	89,45	183,08	109,5

Birch plants also accumulate a significant amount of manganese when they grow on UGOK dumps. The highest content of manganese falls on leaves - up to 475.3 ppm and bark - 205.5 ppm, the smallest - on shoots (54.5 ppm) and root system (129 ppm). The significant bioaccumulative abilities of birch are the basis of a more than 3-times decrease in the manganese content in the soils under plantations as compared with the waste soil outside the stands - 1410 and 4260 ppm, respectively.

The chromium content of the birch plants growing on the dumps of UGOK is estimated in dozens of ppm. The largest amount of chromium is accumulated in the leaves (84.3 ppm) and bark (76.5 ppm), the smallest - in the shoots (26.5 ppm). The intermediate position is occupied by the root system, the chromium content of which is estimated at 58 ppm. At the same time, the amount of chromium in the soil under the plantings of birch is 735 ppm, which is significantly higher compared to the soils of the unforested areas (433 ppm). The increase in the amount of chromium in the soil under the plantings is explained by the additional intake of metal with residues and root secretions.

Copper is distributed in the organs of birch plants very evenly compared with other metals. Its content varies from 23.3 ppm in leaves to 31.5 ppm in the root system. The copper content in the shoots and bark varies slightly and is 28.5 and 24 ppm, respectively. Significant accumulation of copper in plants determines its rather low content in soil grounds under plantings relative to areas where there is no woody

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vegetation. Thus, it was found that in the soil under plantings the copper content is 57 ppm against 166 ppm in treeless areas.

It is established that perennial parts of birch are capable of accumulating significant amounts of zinc. In particular, the birch root systems contain up to 760, and the bark is 124.5 ppm zinc, moreover, that in the shoots zinc can be found only in trace amounts. The zinc content in birch leaves was 40.2 ppm. In the dump soil of UGOK, the zinc content is 242 ppm, with the trace content of this metal in the soils under birch plantations.

It was shown that in the birch plants growing on the UGOK dumps, the lead content in the largest amount is noted in the root system and shoots - 6 and 6.65 ppm, respectively. A slightly smaller amount of lead accumulates in the bark (4.5 ppm), and the minimum amount of metal accumulates in the assimilating organs of the birch - 1.46 ppm. It should be noted that the difference between the Pb content in the soil under planting and its content in the soils of treeless areas is more than 400%. The lead content in the soil under plantings is 9.2 ppm, and in the deforested areas - 43 ppm.

Table 02. The content of anthropogenic elements in the organs of birch (Betula pendula Roth) on the dumps of the copper-pyrite deposit in the town of Uchaly

Element (ppm)	**Names of samples for analysis**					
	Leaves	**Shoots**	**Bark**	**Roots**	**Soils under plantings**	**Soils of the non-forested area**
Cu	23,3±3,7	28,5±2,2	24±1,2	31,5±2,2	57±4,2	166±21
Zn	40,2±4,1	0	124,5±16,9	760±55	0	242±38
Mn	475,3±21,8	54,5±3,7	205,5±31,6	129,5±11	1410±98	4260±187
Cd	0,22±0,05	7,8±0,8	0,52±0,07	0,95±0,06	0,13±0,04	1,1±0,08
Sr	50,1±4,7	39,5±3	152±10,9	74,5±6,8	83±5,7	239±18
Fe	3270±212	3720±+169	7355±+265	4690±389	132000±1268	89900±948
Ni	10,3±0,9	0	0	0	937±89	0
Cr	84,3±6,7	26,5±1,4	76,5±5,1	58±4,3	735±25	433±15
Pb	1,46±0,2	6±0,7	4,5±0,6	6,65±0,88	9,2±1,1	43±2,1
Total:	3955,18	3882,8	7942,52	5751,1	133961,33	95284,1

The content of strontium in birch plants growing on the dumps of UGOK is estimated in tens of ppm. At the same time, the bulk of strontium is concentrated in the root system (74.5 ppm) and bark (152 ppm). The smallest amount of strontium accumulates in the birch sprouts - 39.5 ppm and a slightly larger amount of metal is concentrated in the leaves 50.1 ppm. The background content of strontium in the soils of the unforested area is 239 ppm, while in the soils under the plantations this figure is 83 ppm.

The highest content of cadmium is noted in the shoots (7.8 ppm) of birch, growing on the dumps of UGOK. In this case, the distribution of metal in the organs of birch as follows: shoots> roots> bark> leaves. Thus, it has been shown that in the perennial parts of the plant the content of cadmium is significantly

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higher as compared with the assimilation organs. Against the background of an increase in cadmium content in perennial birch organs, a 9-times decrease in its concentration in soil-grounds under plantings relative to the soils of the unforested area is observed - 0.13 and 1.1 ppm, respectively.

In perennial birch bodies, nickel does not accumulate when grown on UGOK dumps. However, a fairly high nickel content is noted in birch leaves - up to 10.3 ppm. As a result of analytical work, it was found that nickel content in soil samples under birch stands is 937 ppm, and in samples of dump soils in non-forested areas of Ni, it is not detected.

7. Conclusion

Studies of the bioaccumulative abilities of birch plants in man-made landscapes suggest that metals accumulate to the greatest degree in perennial organs in KBCM dumps (shoots) and UGOK (bark) - 576.91 and 7942.52 ppm or in leaves on dumps of SF UGOK - 97.1 ppm. The lowest bioaccumulation abilities of birch plants are characterized by: on the KBCM dumps - the bark (378, 74 ppm), UGOK - shoots (3882.8 ppm) and roots - on the dumps of the SF UGOK (89.45 ppm). It is shown that during the development of plants in the dumps of the KBCM and the SF UGOK, metals are evenly distributed in various organs, as evidenced by the insignificant difference between the maximum and minimum values of the metal content. With the development of the KBCM dumps, there is a decrease in the total amount of metals in the soil grounds under plantings relative to the unforested areas - by 35%. In Sibay, the largest amount of metals, as well as copper, cadmium, manganese, iron, accumulates in the bark, while lead, cadmium and mercury are concentrated in the leaves, and strontium - only in the soil. The total metal content in plants exceeds that for the soil under plantings, but the largest amount of metals accumulates in a well-developed forest floor.

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