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METAL BIOACCUMULATION BY SCOTCH PINE ON MINING INDUSTRY DUMPS (SOUTH URALS, BASHKORTOSTAN)

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Abstract

The features of accumulation of high-toxic metals in the organs of pine (*Pinus sylvestris* L.) were studied during growth on industrial dumps within the Republic of Bashkortostan. The studied pine stands grow on the handmade mountains of the Kumertau brown coal mine, copper-pyrite deposits of the Sibay dept. of the Uchalinsky 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. Analyses 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 vegetative organs (needles), in shoots, in the bark and in the root system of pine. In addition, the content of metals in soils under plantings and in non-forested areas was determined. It has been established that in the dumps of a brown coal field the largest amount of metals accumulates in the needles (682.37 ppm), and the smallest - in the crust (71.64 ppm). On the dumps of copper-pyrite deposits (Uchaly), the bark contains the largest amount of metals (4270.5 ppm), with the minimum amount of metals accumulating in the root system (878.44 ppm). On the dumps of the copper-pyrite deposit (Sibay), there is a uniform distribution of metals in the pines: in the shoots and bark - 93 ppm, and in the needles - 66 ppm.

Keywords: Bioaccumulation, heavy metals, industrial dumps, pine.

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1. Introduction

The growth process of pine trees in extreme man-made forest growing conditions (EFGC) is associated with the action of man-made exhalates. It should be noted that ecotoxicants have a negative effect on plants, due to excessive accumulation of a number of chemical elements in organs and tissues. Pine is characterized by exceptional wide range of adaptation, is used in "green building" everywhere, because it is able to perform environmental protection functions all year round. Heavy metals exhibit a toxic effect on all living organisms, including woody plants (Kangas & Maltamo, 2006). Many heavy metals play an important role in plant life, regulate enzymatic activity, participate in redox processes, regulate the rate of formation of chlorophyll and carotenoids, change the intensity of photosynthesis, participate in carbohydrate and nitrogen cycle reactions, increase plant resistance against various fungal and bacterial diseases. With an excessive influx of heavy metals into the environment, negative changes occur in woody plants (Medhe, 2017). The negative impact of copper reduces the rate of formation of phytomass, leads to fall the water content in plant tissues and chlorophyll content in assimilation organs. There is also a decrease in the rate of absorption of ions of other metals and their redistribution in plants (Kalinovic et al., 2015; Pająk, Halecki, & Gąsiorek, 2016). Lead is needed by woody plants in very small quantities and therefore is relatively poorly absorbed by root systems from the soil. Excessive lead content inhibits gas exchange and reduces the rate of formation of photosynthetic pigments, resulting in reduced accumulation of phytomass (Chrzan, 2015; Chropeňová et al., 2016; Matin, Kargar, & Buyukisik, 2016). Cadmium is one of the most toxic metal for plants (Campos, Abrantes, Keizer, Vale, & Pereira, 2016; Clemens, 2006), significantly slows down the growth rate and development of the plant body, weakens the intensity of photosynthesis, causes changes in cell membrane permeability and activity of a number of enzymes. Strontium is an integral part of plants. In optimal concentrations, plays a positive role in metabolism in plants. In small doses, it performs functions similar to those of calcium: it participates in the construction of the plant cell wall, increases the strength of plant tissues, and contributes to an increase in plant endurance. The initial processes of the development of the toxic action of strontium are associated with a decrease in the efficiency of light reactions of photosynthesis, which determines the further deterioration of production properties.

2. Problem Statement

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 including *Pinus sylvestris* L. is a tree that is widely used in “green construction” both in Bashkortostan and throughout Russia.

3. Research Questions

The character of the accumulation and redistribution of high-toxic metals depends on soil features and vegetation cover, on the level of anthropogenic stress. Man-made metals, entering the environment, accumulate in soils, which can cause secondary pollution of atmospheric air, natural waters, plant products (Snowdon et al., 2002).

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Determining the soil concentration of metalions allows us estimate soilbuffer capacity, degree of reduction in their mobility and the rate of their entry into plants. In the study of anthropogenic effects on plant objects, we chose an approach based on comparing the toxic ions concentration in soils and plants in anthropogenic zones with indicators of the local geochemical background of the metals were studied.

4. Purpose of the Study

Studied of the content a number of high-toxic metals in the plants (*Pinus sylvestris* L.), living on industrial dumps near the cities of Kumertau (Kumertau brown coal mine, KBCM), Sibay (Sibay branch of Uchaly mining and processing plant, SF UGOK) and Uchaly (Uchaly mining and processing combine, UGOK).)

5. Research Methods

The selection, laying and description of test plots in pine plantations were carried out according to standard methods (Titus, 2004).To determine the concentration of metal ions in the Scots pine organs and in the soil during the work, more than 1,200 pooled soil and plant samples were taken. To analyze the nuber 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 concentration of toxic materials in plant samples or in soil was determined in Institute of Geology, RAS (Moscow) using ICP-MS (Plasma quad pq2-turbo plus, USA) mass spectrometry with inductively coupled plasma (Chrzan, 2015; Kalinovic et al., 2015, p. 268; Pająk, Halecki, & Gąsiorek, 2016, p. 855). The content of elements was expressed as the mass fraction of impurities - in parts per million (ppm). The actual material was selected for 10 years - from 2008 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

We have conducted a cycle of studies on the peculiarities of the bioaccumulation of some technogenic elements of the pine. It should be noted that the composition of the metals to be determined in plant samples and soil grounds differs due to the peculiarities of environmental pollution, or the geochemical background of the studied territory. In addition, pine plants growing on the dumps of the SF UGOK have insignificant linear dimensions - their height does not exceed 2 m, therefore during the analytical work we studied the metal content in mixed samples of shoots and bark. The results of these studies to determine the bioaccumulative properties of pine forests are presented in Tables 1-3.

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Table 01. The content of some toxic metals (ppm) in the organs of pine (Pinus sylvestris L.) on Kumertau brown coal dumps

Element	Names of samples for analysis					
	Needles	Shoots	Bark	Roots	Soils under plantings	Soils of the non-forested area
Cu	0	0	0	0	0	0
Zn	0	0	0	0	0	12±2
Mn	619±79	204±11	62±5	130±20	515±153	996±262
Cd	Steps	0,41±0,08	0,15±0,011	1±0,1	staeps	5,5±1
Sr	12±2	15±2	10±1	22±3	55±14	183±50
Ni	0	0	0	0	2312±220	879±217
Cr	48±4	14±2	0	71±9	239±30	16±1
Pb	4±1	1,5±0,2	steps	23±3	11±2	2±0,3
Hg	0,079±0,012	0,0035±0,00071	0	0,035±0,0062	0,049±0,0038	0,038±0,0042
Total:	683,079	234,9135	72,15	247,035	3132,049	2093,538

The manganese content in various pine organs ranges from 62 (bark) to 619 ppm (needles). In the root system of pine, only one tenth of manganese accumulates (no more than 130 ppm). The shoots contain more than 204 ppm of manganese. The total content of manganese in the organs of woody plants is quite large, but it cannot be argued that this particular metal is the main pollutant of this technogenic landscape. Due to the high metal storage capacity of pine in relation to manganese, the soil under planting contains 515 ppm of metal, which is significantly less compared to the soils of the non-forested area - 996 ppm.

When trees growing on the dumps of the KBCM, the bulk of chromium accumulates in the root system of pine - 71 ppm. Somewhat less chromium is concentrated in pine needles (48 ppm) and shoots (14 ppm). It should be noted that chrome does not concentrate in the pine bark. Despite the significant amount of chromium accumulated in plants, its amount in the soil under planting is much higher than in the soils of the open unpolished area - 239 and 16 ppm, respectively. It has been established that in the organs of pine ordinary, strontium accumulates in significant quantities, estimated in dozens of ppm. It should be noted that strontium accumulates to the maximum extent in the root system and shoots - 22 and 15 ppm, respectively, and to a lesser extent - in the wood and needles of Scots pine (10 and 12 ppm). The fact of a sufficiently high accumulating capacity of pine with respect to strontium became the basis for reducing the amount of this metal in soil grounds under plantings to a value of 55 ppm as compared to dump soil, where the amount of this metal was 183 ppm.

In the course of testing for the determination of lead in various organs of pine, it was found that this element is contained in the root system (23 ppm), needles (4 ppm) and shoots (1.5 ppm). Lead is not detected in pine bark. Probably, the protective mechanisms of pine provide metal deposition in the plant root system and do not allow the penetration and distribution of lead in the plant organism. Against the background of the accumulation of a certain amount of lead by pine plants, its content in the soil under planting significantly exceeds the same indicator for the soils of the unpolished landfill site of KBCM - 11 and 2 ppm. Analyzing the data on the quantitative content of cadmium in various organs of pine, it is noted that the accumulation of this element occurs in the root system (1 ppm), shoots (0.41 ppm) and bark (0.15 ppm). In the needles, cadmium is contained only in trace amounts. Despite the insignificant amount of cadmium in plants, the content of this element in the soil under planting is estimated to be trace, while the amount of metal in the soil of the open bare forest site is 5.5 ppm, which exceeds the total amount of cadmium in the whole plant by more than 3 times. The total content of mercury in pine plants growing on the

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dumps of KBCM does not exceed 0.15 ppm. The greatest amount of this metal is concentrated in the needles and pine root system - 0.07 ppm or about 70% and 0.03 ppm or about 30%. An insignificantly small amount of mercury accumulates in the pine shoots (0.0035 ppm) while in the mercury crust is not detected. The content of mercury in the soils under the plantings and in the open areas of the dumps is not significantly different and makes up about 40% of the total content of this metal in plants.

Table 02. The content of some toxic metals (ppm) in the organs of pine (Pinus sylvestris L.) on Sibay (SF UGOK)

Element	Names of samples for analysis				
	Needles	Mixed samples of shoots and bark	Roots	Soil under planting (gross content)	LLC (gross content)
Cu	10±1	12±2	5±0,5	84±3	23
Zn	57±4	82±9	86±7	99±4	86
Cd	0,15±0,04	0,35±0,05	0,49±0,08	0,49±0,06	2
Total:	67,04	94,35	91,49	183,49	111

Commenting on the data on the content of copper, zinc and nickel in the organs and dump soil, it is necessary to note the fact that these metals do not accumulate in pine plants. As for the soil, copper is not detected in any of the selected samples, zinc is determined only in soil samples from the non-forested area (11 ppm), and nickel is found in significant quantities both under pine plantation (2310 ppm) and in the soil of the non-forested area (876 ppm). The needles of pine contains 66 ppm of heavy metals, which are the main environmental pollutants when the SB UGOK and UGOK operates. The main share among the studied metals in the needles is zinc, the amount of which is 57 ppm. Cadmium accumulates the least, the concentration of which in the needles does not exceed 0.15 ppm. The copper content in pine needles is 10 ppm. The largest number of metals studied is concentrated in perennial parts of plants. Thus, copper (11 ppm) accumulates in the greatest amount in shoots and bark, while the root system accumulates zinc (86 ppm) and cadmium (0.5 ppm) in an amount slightly exceeding the bark and shoots - 81 and 0.35 ppm, respectively. 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 SB UGOK is very slow and the dump soil under the plantations differs little from the non-forested part of the dumps, the comparison of the metal content is given relative to the MPC for the corresponding elements. So, it was found that the greatest excess is observed in the case of copper, the content of which in dump soil is 84 ppm with an LLC (limit of legal concentration) 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 LLC is much less compared to copper and is 14 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.

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Table 03. The content of some toxic metals (ppm) in the organs of pine (Pinus sylvestris L.) on of Uchaly (UGOK)

Element	Names of samples for analysis					
	Needles	Shoots	Bark	Roots	Soils under plantings	Soils of the non-forested area
Cu	35±2	33±3	37±2	254±16	57±4	167±22
Zn	47±4	115±8	21±3	0	0	244±35
Mn	663±54	727±49	336±26	75±6	1412±95	4261±188
Cd	0,8±0,02	3±0,4	1,4±0,3	0,25±0,05	0,15±0,03	1±0,05
Sr	33±2	67±2	47±6	14±1	84±5,5	239±15
Fe	1692±111	2232±180	3715±213	512±33	132000±1270	89900±950
Ni	6±1	14±1	2,5±0,5	0	938±84	0
Cr	23±1,5	39±3	111±22	24±3	7350±256	434±15
Pb	3±0,3	0,25±0,02	4±0,5	0	9±1	43±2
Total:	2502,8	3230,25	4274,9	879,25	141850,15	95289

In the pine organs when growing on the UGOK dumps there is a significant accumulation of iron. The greatest amount of iron is concentrated in shoots (2232 ppm) and bark (3715 ppm). The smallest amount of iron found in the root system of pine and is 512 ppm. The intermediate position is occupied by needles, in which 1692 ppm of iron accumulates. An analysis of the soil grounds showed that the loose rocks of the unforested area contain significantly less iron compared to the soils under the plantation, despite the significant accumulation of iron in the pine organs - 132,000 and 89900 ppm, respectively. The manganese content in pine plants amounts to hundreds of ppm. At the same time, the greatest amount of this metal is concentrated in the needles (663 ppm) and shoots (727 ppm), however, we have not established significant differences in the accumulation of manganese by these trees. Much less manganese accumulates in pine bark (336 ppm) and root system (75 ppm). Analysis of the distribution of manganese in the plant shows a clearly defined acropetal nature of the bioaccumulation of this metal in pine plants growing on the UGOK dumps. The ability of plants to accumulate significant amounts of manganese determines the nature of changes in its content in the soil under plantings compared with similar indicators for the non-forested plots of dumps - the difference in the content of manganese is very significant - 1412 and 4261 ppm.

The highest content of zinc falls on the shoots of pine and is 115 ppm. The assimilation organs concentrate up to 47 ppm of zinc, which is not a minimum for pine plants. Zinc accumulates in the bark in 2 times less compared to the needles, while in the root system of woody plants zinc is not detected. Zinc was not found in the soil under the pine forest soils, however, the amount of this metal in the soils of the non-forested area was 244 ppm, which indicates the highest degree of absorption of pollutant metals from the environment described earlier.

Chromium, being a metal highly toxic to living organisms, accumulates in the organs of pine in significant quantities. The smallest concentration was observed in the needles and root system - 23 and 24 ppm, respectively, and no significant differences were found in chromium bioaccumulation by these organs. Somewhat more chrome is concentrated in shoots (39 ppm), and in the greatest amount this metal is found in the bark of pine - 111 ppm. Along with the high bioaccumulation of chromium by pine ordinary plants, the content of this element in the soil under plantings is more than 15 times higher than that for the unforested area - 7350 and 434 ppm. In the pine organs, growing on the dumps of UGOK, copper is found

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in significant quantities. This fact is due to the high copper content in the soil under the pine plantations (57 ppm), while in the soils of the non-forested areas the copper content varies within 167 ppm. In the root system of pine, growing on UGOK dumps, the greatest accumulation of copper is noted - 254 ppm. Analyzing the magnitude of accumulation of copper in other organs, we conclude that in the shoots, bark and needles the content of the element under study is approximately the same and varies between 33-37 ppm. Strontium content in pine needles growing on UGOK dumps is lower compared to shoots (67 ppm) and bark (47 ppm), but significantly higher compared to the root system (14 ppm). At the same time, the content of strontium in the soil under pine plantations is 84 ppm, which is almost 4 times less in relation to the non-forested plots of dumps. In the pine organs, growing on the dumps of UGOK, nickel is found in insignificant quantities. The maximum nickel content we observed when studying shoots was 14 ppm. As a result of analytical work, data were obtained that nickel does not accumulate in the pine root system, as well as in the dump soil grounds of the unforested areas, but under plantings the content of this metal is quite high - up to 938 ppm. It is established that the nickel content in the needles and bark is insignificant and amounts to 6 and 2.5 ppm, respectively. In pine plants, when growing on dumps of UGOK, the following pattern of lead distribution by organs is noted: bark (4 ppm)> needles (3 ppm)> shoots (0.25 ppm). It has been established that lead does not accumulate in the root system, despite the fact that the soil under the plantings is equal to 9 ppm. The lead content in the soils of the non–forested area significantly exceeded the corresponding indicator for planting - 43 ppm.

Among all the elements analyzed that are toxic to animals and plants, cadmium accumulates in the least amount of plants. Its total content in various organs is about 5 ppm, and more than half (3 ppm) of metal accumulates in the pine shoots. The bark is also a deposit site for cadmium - 1.4 ppm of metal is concentrated here. The smallest amount of cadmium accumulates in the root system - 0.25 ppm and somewhat more in the needles (0.8 ppm). The ability of pine to accumulate a certain amount of cadmium in its organs became the basis for its tenfold decrease in the soil under plantings compared to the non-forested areas of dumps - 0.15 and 1 ppm.

7. Conclusion

Studies of the bioaccumulative potential of plants in technogenic landscapes allow us to conclude that the accumulation of anthropogenic metals by pine in different ecotopes is very different both in quantity and distribution within the plant. It has been established that in the dumps of a brown coal field the largest amount of metals accumulates in the assimilation organs (683 ppm), and the smallest - in the wood (72 ppm). At the copper-pyrite deposit of the UGOK dumps (pine-birch forest zone), the bark contains the largest amount of metals (4274.9 ppm), while the lower amount of metals accumulates in the roots (879.25 ppm). On copper-pyrite deposit SF UGOK dumps (the territory of the steppe), there is a uniform distribution of metals in the pine trees: 94.35 ppm in shoots and bark, and 67.04 ppm in the needles.

References

Campos, I., Abrantes, N., Keizer, J. J., Vale, C., & Pereira, P. (2016). Major and trace elements in soils and ashes of eucalypt and pine forest plantations in Portugal following a wildfire. *Science of The Total Environment*, *572,* 1363-1376. Retrieved from: http://dx.doi.org/10.1016/j.scitotenv.2016.01.190

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Corresponding Author: Gulshat Shakirova
Selection and peer-review under responsibility of the Organizing Committee of the conference
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Chropeňová, M., Gregušková, E. K., Karásková, P., Přibylová, P., Kukučka, P., Baráková, D., & Čupr, P. (2016). Pine needles and pollen grains of *Pinusmugo*Turra – A biomonitoring tool in high mountain habitats identifying environmental contamination. *Ecological Indicators, 66*, 132-142. Retrieved from: http://dx.doi.org/10.1016/j.ecolind.2016.01.004

Chrzan, A. (2015). Necrotic bark of common pine (*Pinussylvestris* L.) as a bioindicator of environmental quality. *Environmental Science and Pollution Research, 22*(2), 1066-1071. Retrieved from: http://doi.org/10.1007/s11356-014-3355-0

Clemens, S. (2006). Toxic metal accumulation, responses to exposure and mechanisms of tolerance in plants. *Biochimie, 88*(11), 1707-1719. Retrieved from: http://doi.org/10.1016/j.biochi.2006.07.003

Kalinovic, T. S., Serbula, S. M., Radojevic, A. A., Kalinovic, J. V., Steharnik, M. M., & Petrovic, J. V. (2015). Elder, linden and pine biomonitoring ability of pollution emitted from the copper smelter and the tailings ponds. *Geoderma, 262*, 266-275. http://doi.org/10.1016/j.geoderma.2015.08.027

Kangas, A., & Maltamo, M. (2006). *Forest inventory: methodology and applications*. Netherlands: Springer. Retrieved from: https://doi.org/10.1007/1-4020-4381-3

Matin, G., Kargar, N., & Buyukisik, H. B. (2016). Bio-monitoring of cadmium, lead, arsenic and mercury in industrial districts of Izmir, Turkey by using honey bees, propolis and pine tree leaves. *Ecological Engineering, 90*, 331-335. http://doi.org/10.1016/j.ecoleng.2016.01.035

Medhe, S. (2017). Ionization Techniques in Mass Spectrometry: A Review. *Mass Spectrometry & Purification Techniques, 04*(01). Retrieved from: https://doi.org/10.4172/2469-9861.1000126

Pająk, M., Halecki, W., & Gąsiorek, M. (2016). Accumulative response of Scots pine (*Pinussylvestris* L.) and silver birch (*Betula pendula* Roth) to heavy metals enhanced by Pb-Zn ore mining and processing plants: Explicitly spatial considerations of ordinary kriging based on a GIS approach. *Chemosphere, 168*, 851-859. Retrieved from: http://doi.org/10.1016/j.chemosphere.2016.10.125

Snowdon, P., Raison, J., Keith, H., Ritson, P., Grierson, P., Adams, M., & Eamus, D. (2002, January, 22). Protocol for sampling tree and stand biomass. Australian Greenhouse Office. http:// doi.org/10.13140/RG.2.1.2825.8967

Titus, S. J. (2004). *Manual of forest measurements and sampling. Course prospectus and session PowerPoint slides.* Edmonton: University of Alberta, Department of renewable resources.