Journal of Engineering and Applied Sciences 13 (Special Issue 11): 8746-8751, 2018
ISSN: 1816-949X

Bioaccumulation of Chemical Elements by Old-Aged Pine Trees in the Southern Urals

[1]Ilgiz Asylbaev, [2]Ilysja Gabbasova, [1]Ilgiz Khabirov, [2]Timur Garipov, [1]Nail Lukmanov, [1]Bulat Rafikov, [1]Anna Kiseleva, [1]Gulmira Khuzhakhmetova, [1]Aigul Mukhamedyanova and [3]Radik Mustafin
[1]Department of Soil Science, Botany and Plant Breeding, Federal State Budgetary Educational Institution, Bashkir State Agrarian University, ul.50-Letiya Oktyabrya, 34, Ufa, Russia
[2]Laboratory of Soil Science, Federal State Budgetary Institution of Science, Ufa Institute of Biology, Prospekt Oktyabrya, 69, Ufa, Russia
[3]Department of Environmental Management, Construction and Hydraulics, Federal State Budgetary Educational Institution, Bashkir State Agrarian University, ul.50-Letiya Oktyabrya, 34 Ufa, Russia

Abstract: The content and distribution of 37 chemical elements in rocks, soils and wood of old-aged pines of the Belebey plateau-like elevation have been studied. It is shown that soils have a low and very low level of availability of the elements studied. Their absorption by pine trees is largely derived from the soil-forming rock, Zn, Sc, Co, W, Sb, Cr and As are the maximum accumulation (the biophilicity coefficient is 1.17-0.60). From the soil, pine absorbs Mo, Zn, Sb, Sr and Pb most intensely (the biophilicity coefficient is 1.09-0.14) and very weakly Be, Ba, W and V (the biophilicity coefficient is 0.03-0.01). Rare-earth elements are almost equally absorbed from the soil and more selectively from the rock. Eu, Nd, Sm and Pr are accumulated to a greater extent and much less Cs, Lu, Er and Tm. The uranium content in soil and rock is almost 6 times greater than thorium but its biological absorption by pines is much lower.

Key words: Bioaccumulation, chemical elements, biophilicity coefficient, soil-forming rock, soil, old-aged pines

INTRODUCTION

In soils, there are practically all elements of the periodic system of Medvedev *et al*. (2015) in excess of the norm and subcritical concentrations due to geochemical features, transregional transfer and the activities of industrial enterprises. Currently, one of the important environmental problems is the involvement in the biological cycle not only necessary for the normal functioning of plants but also toxic chemical elements. This is due primarily to the geochemical, specificity of the territory: the features of soil-forming processes the content of chemical elements in the indigenous and soil-forming rocks and their ability to bioaccumulate. Another source of income is the trans-regional transfer of emissions from industrial enterprises.

When studying the geochemical ecology of plants, special attention should be given to the character of the accumulation of chemical elements in the system: soil-growth and the establishment of biological absorption coefficients (Ermakov, 2015). In general, bioaccumulation in the chain "parent rock-soil-plant-animal-man" is of great importance for ecology,biology, rational use of natural resources and health (Dobrovol'skiy and Grishina, 1985; Kabata-Pendias, 2011). This phenomenon has specific features in various ecosystems: agricultural (Mortvedt, 1987), wetland (Schaller *et al*., 2016), meadow (Tyler, 2004), forest (Ganjali *et al*., 2016; Schaller *et al*., 2016; Borgulat *et al*., 2018; Olajire and Ayodele, 2003; Giniyatullin and Kulagin, 2016). Higher plants can perform the function of bioindication of environmental pollution (Geagea *et al*., 2007; Prasetia *et al*., 2018). In addition to the widely known negative effect of the accumulation of toxic elements, primarily in agricultural products, bioaccumulation can also have positive aspects for the growth and development of plants (Ganjali *et al*., 2016; Tyler and Olsson, 2001; Kastori *et al*., 2010). At the same time in spite of great attention to the geochemistry of the

Corresponding Author: Ilgiz Asylbaev, Department of Soil Science, Botany and Plant Breeding, Federal State Budgetary Educational Institution, Bashkir State Agrarian University, ul.50-Letiya Oktyabrya, 34 Ufa, Russia

elements, some aspects related to the barrier function of soil and old-aged trees have not been studied sufficiently (Chiang *et al*., 2012; Gonzalez-Nunez *et al*., 2012; O'Carroll *et al*., 2013; Vodyanitskiy, 2017) including in the South Ural Region (Starova, 2003).

The purpose of this research was to study the content of chemical elements in the rocks and soils and their bioaccumulation with old aged pine forests of the Belebey plateau like elevation of the Southern Urals.

MATERIALS AND METHODS

Studies were carried out in the Southern Urals in conditions of a flat plateau alternating with hilly ridges (Belebey plateau like elevation). The altitude of the terrain varies from 194-350 m above sea level. The basis of the geological structure of the elevation is the deposits of the Kazanian stage of the Upper Permian system, represented by sandstones, fine-dispersed carbonate clays, tile dolomites and limestones, marls with interlayers of gypsum and conglomerates.

Soil-forming rocks are deluvial carbonate clays, loams and eluvium of limestones. The soil cover is mainly represented by black soils (Chernic Chernozems) to a lesser extent gray soils (Albic Luvisols) and dark gray soils (Greyi-Luvic Phaeozems). Soil pits are laid under pine forests, pit 6-under broad-leaved forest.

Black soils are characterized by intense dark gray coloration of the humus horizon, lumpy-granular structure, loose composition, increased level of effervescence from HCL. The humus content in the humus-accumulative horizons is medium or high the reaction of the medium is close to neutral or slightly alkaline and the soil is saturated with bases (Table 1).

The color of gray soils is lighter, the structure is lumpy-powdery the texture is loose. The humus content in the upper horizons is average the reaction of the medium is weakly acidic. The humus content of both soils is sharply reduced with depth.

The content of the gross forms of elements in rocks, soils and pine wood (about 180 years old) was determined by inductively coupled plasma mass spectrometry (IPC-MS) using the VG Plasma Quad and Elan-6100 mass spectrometer under standard conditions of variation using reference samples.

For the general characteristics of soils the concentration of elements was determined by their weighted average content in the soil profile and the level of availability on the scales developed for the Southern

Table 1: Physical and chemical properties of soils

		pH		Resin (eq) / kg soil	
Horizon, depth (cm)	Humus (%)	H_2O	KCL	Ca^{2+}	Mg^{2+}
R.1. Medium- thick medium-humus heavy-loamy black soil					
AU 3-36	8.14	7.6	-	41.2	7.5
AUBCA 36-54	2.45	7.9	-	25.0	8.3
BCA 54-67	1.03	8.0	-	28.1	10.1
Cca 70-85	1.18	7.9	-	22.3	6.4
R.2 Medium-thick high-humus heavy loamy black soil					
AU 3-35	10.30	7.1	-	46.4	10.1
AUBCA 35-50	5.34	7.8	-	37.6	8.3
Cca 70-85	2.28	8.0	-	22.0	6.2
R.3. Gray metamorphic low- thick heavy loam					
AY 3-19	4.09	5.8	5.1	32.4	8.8
AEL 19-33	1.56	6.1	5.3	32.8	6.8
BM 33-80	0.83	6.0	4.9	31.6	7.2
C 80-120	0.48	8.1	-	35.1	6.8
R.4. Dark gray low- thick light clay AU 4-18	7.87	5.9	5.3	36.6	9.7
BEL 18-33	2.08	6.1	5.1	33.4	5.8
BT 33-62	0.85	7.3	-	41.8	6.8
C 62-120	0.43	7.6	-	38.2	7.6
R.5 Medium-thick high-humus heavy loamy black soil					
O 0-3	12.84	6.7	6.3	44.0	9.8
AU 3-36	6.63	7.8	-	43.5	8.7
AUBCA 36-72	3.63	8.1	-	28.4	8.8
BCA 72-90	0.68	8.2	-	23.3	8.2
Cca 90-130	0.41	8.4	-	24.1	8.3
R.6. Clay-illuvial low-thick high-humus black soil					
AU 3-34	7.29	5.8	5.0	32.8	12.9
AUBI 34-50	4.03	6.2	4.1	31.4	8.7
BI 50-70	1.95	7.4	-	35.5	10.3
Cca 70-120	0.67	7.9	-	36.0	6.9

Urals (Asylbaev and Khabirov, 2015; Asylbaev *et al*. 2017). Determination of physicochemical, physical, morphological properties of soils was carried out by conventional methods (Agrochemical methods of soil investigation (Sokolove, 1975).

RESULTS AND DISCUSSION

The soils of the Belebey plateau like elevation are characterized by a predominantly low and very low level of availability of the chemical elements studied (Table 2). Only copper, rubidium, strontium, sodium and barium have an average level of supply which is apparently due to the geological structure of this elevation which is based on the deposits of the Kazan and Tatar stages of the Upper Permian system.

At the same time, among these elements only the strontium content in the parent rock is much higher than in the soil. At a low and very low level of supply, molybdenum is also recognized as an obvious input from the rock. The higher content of most elements in the soil as compared to the soil-forming rock may be caused to some extent by their trans-regional transport but mainly due to the ability of living organisms to absorb and accumulate chemical elements in their bodies. Calculations of the biophilicity coefficients (the ratio of the element content in the wood to its content in soil or rock), characterizing the intensity of the absorption by the pine trees of a particular element showed that the pine roots largely absorb t he chemical elements from the parent rocks. The pine most intensively absorbs the following elements from the soil: molybdenum (1.09)> zinc (0.36)> antimony (0.22)> strontium and lead (0.14) and very slightly beryllium (0.03)> barium and tungsten (0.02)> vanadium (0.01). It is interesting to note that zinc (1.17) and antimony (0.8) also intensively enter pine wood from the rock and strontium mainly from the soil. The maximum accumulation from the rock along with zinc and antimony are scandium (1.15), cobalt (1.00), tungsten (0.94), chromium (0.63) and arsenic (0.60). The absorption of rare

Table 2: Content of chemical elements in soil forming rocks, soils and pine wood of the Belebey plateau-like elevation (average values, n = 18)

	Content (mg/kg)			Biophilicity coefficient		
Elements	Species	Soil	Pine	Species	Soils	Coverage level
Lithium	9.170	19.1	1.260	0.14	0.07	Low
Beryllium	0.140	0.7	0.023	0.16	0.03	Low
Scandium	0.520	12.6	<0.600	1.15	0.05	Low
Vanadium	8.560	57.5	4.480	0.52	0.08	Very low
Chromium	5.810	60.0	3.640	0.63	0.06	Low
Cobalt	0.690	9.2	0.690	1.00	0.08	Low
Nickel	7.130	63.6	2.900	0.41	0.05	Low
Copper	23.300	46.8	5.930	0.26	0.13	Average
Zinc	11.400	37.5	13.300	1.17	0.36	Very low
Arsenic	<0.500	3.5	0.300	0.60	0.09	Very low
Selenium	<0.500	0.2	<0.010	0.02	0.05	Low
Rubidium	3.360	34.8	<1.500	0.45	0.04	Average
Strontium	290.800	126.8	17.600	0.06	0.14	Average
Yttrium	2.340	11.7	0.590	0.25	0.05	Average
Molybdenum	1.410	0.8	0.820	0.58	1.03	Low
Cadmium	0.050	0.1	0.036	0.67	0.36	Very low
Antimony	0.320	1.1	0.240	0.75	0.22	Low
Cesium	0.300	2.9	0.110	0.37	0.04	Low
Barium	29.500	416.2	11.600	0.37	0.02	Low
Lanthanum	2.150	13.1	0.980	0.46	0.08	Low
Cerium	4.260	22.5	1.400	0.33	0.06	Low
Praseodymium	0.560	3.2	0.340	0.61	0.11	Low
Neodymium	1.650	11.1	1.180	0.72	0.11	Low
Samarium	0.290	2.0	0.180	0.62	0.09	Low
Europium	0.073	0.7	0.058	0.80	0.08	Low
Gadolinium	0.380	2.3	0.220	0.58	0.10	Low
Terbium	0.066	0.4	0.036	0.55	0.09	Low
Dysprosium	0.330	1.9	0.170	0.52	0.09	Low
Holmium	0.074	0.4	0.039	0.53	0.10	Low
Erbium	0.170	0.9	0.070	0.41	0.08	Low
Thulium	0.032	0.2	0.014	0.44	0.07	Low
Ytterbium	0.180	0.9	0.081	0.45	0.09	Low
Lutetium	0.029	0.2	0.013	0.35	0.07	Low
Tungsten	0.170	0.6	0.160	0.94	0.02	Very low
Lead	2.440	8.7	1.180	0.48	0.14	Very low
Thorium	0.340	4.5	0.180	0.53	0.04	Moderate
Uranus	2.010	5.5	0.039	0.02	0.01	Moderate

earth elements from the soil is almost the same, the biophilicity coefficients varies in the range 0.07-0.10. Absorption from the rock is more selective, mostly accumulating europium (0.89), neodymium (0.72), samarium (0.62) and praseodymium (0.61), much less cerium (0.33), lutetium (0.35), erbium (0.41) and thulium 0.44). Relatively low coefficients of biophilicity indicate the preferential absorption of elements from rock and soil, rather than industrial emissions.

The accumulation of heavy metals in pines seems to depend not only on their content in rocks and soil but also on gas-dust emissions from one side and on the age of trees on the other. If at a high concentration of toxic elements in the soil they accumulate primarily in the roots of the pines (Andras *et al*., 2018) then at atmospheric contamination, iron, manganese, arsenic and other elements are first adsorbed by the bark of trees and then can be absorbed by internal tissues (Olajire and Ayodele, 2003; Catinon *et al*., 2009). In particular a lot of lead is absorbed in the pine bark due to air pollution by vehicles (Osma *et al*, 2017; Jaworska *et al*., 2015). The maximum accumulation of some heavy metals is observed in the central part of the trunk of pine (Kilyusheva *et al*., 2017). In the wood of pines growing in the zone of influence of the mining and metallurgical plant “Pechenganikel” (Alekseev, 1987) the content of zinc is 8.9 times, copper is 2.9 times, nickel is 4.2 times, lead is 10.7 times, cadmium is 23.6 times higher than at the Belebey plateau-like elevation. In conditions of pollution by industrial emissions in the South Urals the biophilicity coefficients of a number of elements were 2-3 times greater than in an ecologically clean area of research (Giniyatullin and Kulagin, 2016).

At the same time in the wood of younger pines of urban forest parks the accumulation of these elements is 3-10 times lower (Demakov *et al*., 2011). Later when the requirements of plants in microelements are reduced there is a general tendency to reduce the content of heavy metals with the age of trees (Medvedev *et al*., 2015).

Bioaccumulation of radioactive elements depends on the physical and chemical characteristics of soil and rock the content and form of radionuclides and the biological features of plants (Barnett *et al*., 2000; Shaposhnikova, 2017; Rachkova and Shuktomova, 2015). Among the radioactive elements in the rocks of the Belebey plateau-like elevation, the uranium content is almost 6 times greater than that of thorium. This fact confirms the previously revealed regularity of uranium accumulation in soils west of the Ural fault line and thorium to the east. At the same time, biological uptake of thorium by pines from soil and rock is significantly higher than that of uranium: the biophilicity coefficient is 0.04 versus 0.007 and 0.53 versus 0.02, respectively (Asylbaev *et al*., 2017).

CONCLUSION

In general the soils of the Belebey plateau-like upland of the Southern Urals have a low and very low level of supply with chemical elements. In this case, only the content of strontium and molybdenum in the parent rock is much higher than in the soil. The absorption of chemical elements by pines is largely derived from the soil-forming rock. Pine most intensely absorbs molybdenum, zinc, antimony, strontium and lead (the coefficient of biophilicity is 1.09-0.14) from the soil and very little beryllium, barium, tungsten and vanadium (biophilicity coefficient is 0.03-0.01). The maximum accumulation from the rock is zinc, scandium, cobalt, tungsten, antimony, chromium and arsenic (biophilicity coefficient is 1.17-0.60).

Absorption of rare earth elements from the soil is almost the same. Absorption from the rock is more selective with more accumulation of europium, neodymium, samarium and praseodymium, significantly less of cerium, lutetium, erbium and thulium. The uranium content in soil and rock is almost 6 times greater than thorium but its biological absorption by pines is much lower.

The definition of regional and subregional biogeochemical indicators can serve as the basis for biogeochemical zoning, as well as long-term and retrospective monitoring of the ecological state of the ecosystem.

REFERENCES

Alekseev, Y.V., 1987. Heavy Metals in Soils and Plants. Agroindustrial Publishing House, Saint Petersburg, Russia, Pages: 148.

Andras, P., J.X. Matos, I. Turisova, M.J. Batista and R. Kanianska *et al*., 2018. The interaction of heavy metals and metalloids in the soil-plant system in the Sao Domingos mining area (Iberian Pyrite Belt, Portugal). Environ. Sci. Pollut. Res., 25: 20615-20630.

Asylbaev, I.G. and I.K. Khabirov, 2015. Features of the accumulation of rare-earth elements in soils and rocks of the Southern Urals. Agrochemistry, 7: 71-80.

Asylbaev, I.G., I.K. Khabirov, I.M. Gabbasova, B.V. Rafikov and N.A. Lukmanov, 2017. Geochemistry of uranium and torium in soils of the Southern ural. Soil Sci., 12: 1468-1476.

Barnett, M.O., P.M. Jardine, S.C. Brooks and H.M. Selim, 2000. Adsorption and transport of uranium (VI) in subsurface media. Soil Sci. Soc. Am. J., 64: 908-917.

Borgulat, J., M. Metrak, T. Staszewski, B. Wilkomirski and M. Suska-Malawska, 2018. Heavy metals accumulation in soil and plants of polish peat bogs. Pol. J. Environ. Stud., 27: 1-8.

Catinon, M., S. Ayrault, R. Clocchiatti, O. Boudouma and J. Asta *et al*., 2009. The anthropogenic atmospheric elements fraction: A new interpretation of elemental deposits on tree barks. Atmos. Environ., 43: 1124-1130.

Chiang, Y.W., R.M. Santos, K. Ghyselbrecht, V. Cappuyns and J.A. Martens *et al*., 2012. Strategic selection of an optimal sorbent mixture for in-situ remediation of heavy metal contaminated sediments: Framework and case study. J. Environ. Manage., 105: 1-11.

Demakov, Y.P., S.M. Shvetsov, V.I. Talantsev and K.K. Kalinin, 2011. Dynamics of ash elements content in annual layers of old-aged pine trees growing in floodplain biotopes. Bull. Mari State Univ., 3: 25-35.

Dobrovol'skiy, G.V. and L.A. Grishina, 1985. Conservation of Soils. Moscow State University, Moscow, Russia, Pages: 224.

Ermakov, V.V., 2015. Geochemical ecology and biogeochemical criteria for estimating the ecologic state of biospheric taxons. Geochem. Intl., 53: 195-212.

Ganjali, M.R., V.K. Gupta, F. Faridbod and P. Norouzi, 2016. Lanthanides Series Determination by Various Analytical Methods. Elsevier, Amsterdam, Netherlands, ISBN:9780124200951, Pages: 448.

Geagea, M.L., P. Stille, M. Millet and T. Perrone, 2007. REE characteristics and Pb, Sr and Nd isotopic compositions of steel plant emissions. Sci. Total Environ., 373: 404-419.

Giniyatullin, R.K. and A.Y. Kulagin, 2016. The state of protective poplar balsamic plantations (Populus balsamifera L.) in the conditions of the Sterlitamak industrial center: The accumulation of metals in the organs of healthy and weakened trees. Rev. Ufa Sci. Center Russ. Acad. Sci., 2: 62-68.

Gonzalez-Nunez, R., M.D. Alba, M.M. Orta, M. Vidal and A. Rigol, 2012. Remediation of metal-contaminated soils with the addition of materials-Part II: Leaching tests to evaluate the efficiency of materials in the remediation of contaminated soils. Chemosphere, 87: 829-837.

Jaworska, H., H. Dabkowska-Naskret and S. Rozanski, 2015. [Lead in soils and pine tree bark (Pinus sylvestris L.) from the park area exposed to automotive contamination/lead in soils and pine bark (Pinus sylvestris L.) from the park area, exposed to automotive pollution (In Polish)]. Environ. Prot. Nat. Resour., 26: 12-16.

Kabata-Pendias, A., 2011. Trace Elements in Soil and Plants. 4th Edn., CRC Press, Boca Raton, FL., USA.

Kastori, R.R., I.V. Maksimovic, T.M. Zeremski-Skoric and M.I. Putnik-Delic, 2010. Rare earth elements: Yttrium and higher plants. Prose Serb. Matrix Nat. Sci., 118: 87-98.

Kilyusheva, N.V., P.A. Feklistov, N.V. Ezhova, I.N. Bolotov and B.Y. Filippov, 2017. Comparative analysis of mineral content in pine and spruce wood. For. J., 5: 64-70.

Medvedev, I.F., S.S. Derevyagin, M.A. Kozachenko and N.N. Gusakova, 2015. Evaluation of the chemical elements content in wood of various tree species. Agrar. Sci. J., 11: 12-14.

Mortvedt, J.J., 1987. Cadmium levels in soils and plants from some long term soil fertility experiments in the United States of America. J. Environ. Q., 16: 137-142.

O'Carroll, D., B. Sleep, M. Krol, H. Boparai and C. Kocur, 2013. Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Adv. Water Resour., 51: 104-122.

Olajire, A.A. and E.T. Ayodele, 2003. Study of atmospheric pollution levels by trace elements analysis of tree bark and leaves. Bull. Chem. Soc. Ethio., 17: 11-17.

Osma, E., M. Elveren and G. Karakoyun, 2017. Heavy metal accumulation affects growth of Scots pine by causing oxidative damage. Air Qual. Atmos. Health, 10: 85-92.

Prasetia, H., M. Sakakibara, K. Omori, J.S. Laird and K. Sera *et al*., 2018. Mangifera indica as bioindicator of mercury atmospheric contamination in an ASGM Area in North Gorontalo Regency, Indonesia. Geosci., 8: 1-9.

Rachkova, N.G. and I.I. Shuktomova, 2015. Distribution of uranium and thorium in podzolic soil contaminated with their soluble compounds. Geochem., 2: 187-195.

Schaller, J., J. Schoelynck, M. Murray-Hudson, P.J. Frings and D. Van Pelt *et al*., 2016. Input, behaviour and distribution of multiple elements in abiotic matrices along a transect within the Okavango Delta, Northern Botswana. Environ. Monit. Assess., Vol. 188, 10.1007/s10661-016-5696-2

Shaposhnikova, L.M., 2017. The main factors influencing the absorption of uranium, radium and thorium by plants. Bull. Inst. Biol. Komi Sci Center Ural Branch Russ. Acad. Sci., 3: 49-57.

Sokolov, A.V., 1975. Agrochemical Soil Research Methods. Nauka Publisher, Moscow, Russia, Pages: 656.

Starova, N.V., 2003. Ecological Problems: The Principles of their Solution in the Example of the Southern Urals. Nova Science Publishers, Hauppauge, New York, Pages: 288.

Tyler, G. and T. Olsson, 2001. Concentrations of 60 elements in the soil solution as related to the soil acidity. Eur. J. Soil Sci., 52: 151-165.

Tyler, G., 2 004. Rare earth elements in soil and plant systems-a review. Plant Soil, 267: 191-206.

Vodyanitskiy, Y.N., 2017. Assessment of the total toxicological contamination of soils with heavy metals and metalloids. Agrochemistry, 2: 56-63.