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The content and distribution of lead in the permafrost soils of the northern-taiga landscapes of Yakutia

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Abstract. We studied the content and nature of the distribution of lead in permafrost soils of the "Burannyi" site of the Tomtor rare-earth deposit. We explored three types of permafrost soils with low power of the soil profile: permafrost fawn-brown podzolized, permafrost fawn-brown and homogeneous non-gleyed cryozem. An experiment on lead sorption by genetic horizons of permafrost soil was constructed in the laboratory. The contents of the mobile forms of Pb in the studied soils are arranged in the ascending order: homogeneous non-gleyed cryozem < permafrost fawn-brown < permafrost fawn-brown podzolized. The experiment identified high correlation dependence of the lead content on humus values, as well as the average negative dependence on pH. Based on the constructed sorption model, it claims that the mineral horizons have the highest sorption capacity.

1. Introduction

In recent years, the content of pollutants in the environment has increased due to the rapid industrial growth. The pollutants which present interest to various environmental services include the heavy metals [1, 5].

Once entered the soil, the heavy metals accumulate in it, especially in the upper humus horizon, and are slowly removed during leaching and erosion. The first period of removal of half of the initial concentration of heavy metals varies significantly in different elements and takes an extremely long period: for Zn — 70-510 years; Cd — 13-110 years; Cu — 310-1500 years; Pb — 770-5900 years [7, 11, 13].

Lead is one of the most toxic metals, as well as the most highly toxic elements (1st hazard class). Lead dust is deposited on the surface of the soil, adsorbed by organic matter, moves along the profile with soil solutions, but is carried outside the soil profile in small quantities [2, 4].

The study shows that at present, the content of this metal in the soils of mining areas significantly exceeds its background concentrations. In this regard, the study of the content of lead and its compounds in the soils of the site "Burannyi" of the Tomtor deposit of rare-earth metals is highly relevant.

The study area is located in the north-west of the Republic of Sakha (Yakutia) of the Russian Federation in the Olenyokskyi administrative district 400 km south of the coast of the Laptev Sea on the watershed of the Udya and Chimara rivers (Figure 1).

Figure 1. The territory of site the "Buranny" of the Tomtorskoe rare-earth deposit.

As of today, the Tomtorskyi deposit is a rightful leader among rare metal giants. It is unique in terms of reserves and concentrations of Nb_2O_5 and TR_2O_3 and exceeds all known global analogues [12].

Primary components of complex ore are the niobium, yttrium, scandium, rare-earth elements of cerium (lanthanum, cerium, praseodymium, neodymium) and yttrium (europium, samarium) groups. Niobium is central to the main useful components. The study analysed and evaluated all the major and associated components in the contours of its distribution.

The associated components estimated in the contours of niobium ores are the titanium, vanadium, aluminium, phosphorus, zirconium, strontium, uranium and rare earth elements of yttrium group (gadolinium, terbium, holmium, erbium, dysprosium, thulium, ytterbium, lutetium).

This paper aims to study the patterns of distribution and content of lead in the permafrost soils of the northern-taiga landscapes of Yakutia.

2. Material and Methods

The objects of study were permafrost fawn-brown podzolized, permafrost fawn-brown and homogeneous non-gleyed cryozem. These soil types are characterized by a small thickness of the soil profile, permafrost water regime and the presence of ice permafrost.

2.1. Determination of soil physicochemical characteristics

Chemical analysis was carried out in the laboratory of physicochemical analysis of NEFU Research Institute of Applied Ecology of the North by generally accepted methods in soil science. The determination of the total content of organic carbon (humus) was carried out according to the Tyurin method; the determination of the reaction of the soil solution was carried out in suspensions at a ratio of soil: solution = 1: 2.5 using the potentiometric method. Analysis of the content of mobile forms of lead in soil samples was performed by atomic absorption spectrometry at MGA-915, using 1N. extract. HNO_3, which unlike H_2O and 1N. HCl extracts extract acid-soluble forms, more firmly associated with the soil.

2.2. An experiment to study the processes of absorption of lead by permafrost soils
A solution of pollutant ($Pb(NO_3)_2$) in a ratio of 1:20 was added to the air-dry soil samples. The suspension was shaken in a rotator (160 rpm) for 1 h; then, it was settled for a day, and then filtered. The lead concentration in the filtrates was determined by atomic absorption spectrometry on MGA-915.

The amount of absorbed lead was calculated by the formula (1):

$$q = \frac{(C_0 - C_{eq})V_{sol}}{M_s} \quad (1)$$

where q is the amount of adsorption of heavy metals per unit weight within soil (mg/kg), C is the initial concentration of heavy metal solution (mg/dm^3), C_{eq} is the equilibrium concentration of the solution (mg/dm^3), V_{sol} is the volume of solution (dm^3) and M_s is the mass of soil (kg).

The adsorption rate was calculated by the formula (2):

$$\mathrm{a} = \frac{m_{Sorb}}{m_{Intro}} \times 100\ \% = \frac{m_{Intro} - m_{Sol}}{m_{Intro}} \times 100\ \% = \frac{C_0 \times V_0 - C_i \times V_i}{C_0 \times V_0} \times 100\ \% \quad (2)$$

where m_{Sorb} is the mass of lead adsorbed by the soil (mg), m_{Intro} is the mass of lead in the initial solution (mg), C_0 and C_i are at the initial and fixed time points of the concentration of lead ions in the solution, respectively (mg/dm^3), V_0 and V_i are the solution volumes at initial and fixed points in time (dm^3) [9].

Model experience is based on the works of S V Kruglov, V S Anisimova, G V Lavrentieva, L N Anisimova, T M Minkina, A A Statova, V S Kryshchenko [6, 8].

3. Results and Discussion

The studied samples of permafrost soils are characterized by medium acid and the weak acid reaction of the medium of soil (pH 4.4-5.9). Also, it is observed that humus content decreases with depth (Table 1). The highest value of humus is recorded in the upper layers of permafrost pale-brown podzolized soil, which is associated with the content of coarse-decomposed humus, while the lowest value is found in the homogeneous non-gleyed cryozem.

Table 1. The content of mobile lead, pH and humus in the permafrost soils of the territory of the "Burannyi" site of the Tomtor rare-earth deposit.

№	Soil type	Sampling depth (cm)	Pb (mg/kg)		pH	Humus (%)
			result	±		
1	Permafrost fawn-brown podzolized	0(1) - 5(8)	2.94	0.71	4.4	18.5
2		5(8) - 26(33)	1.86	0.45	5.3	0.9
3		26(33) - 55	2.31	0.55	5.9	1.1
4	Permafrost fawn-brown	0(2) - 8(9)	2.56	0.61	4.9	10.7
5		8(9) - 20	2.81	0.67	5.5	2.8
6		20 - 29	2.48	0.60	5.8	1.1
7	Homogeneous non-gleyed cryozem	2(3) - 4(7)	2.46	0.84	4.7	7.6
8		4(7) - 12(18)	2.52	0.52	5.3	4.5
9		12(18) - 25	1.63	0.55	5.9	5.7

The content of humus has a decreasing distribution character over the soil profile in the permafrost fawn-brown podzolized soil type; it has sharply decreasing character in permafrost fawn-brown soil, and has a bimodal character in a homogeneous non-gleyed cryozem. The accumulation of organic matter in the lower part of the soil profile is a consequence of cryogenic processes associated with the mobility of humus and permafrost destruction, or mixing and intrusion through cracks.

The content of the mobile form of lead in permafrost soils varies from 1.63 to 2.94 mg/kg. Moreover, the maximum Pb content is noted in the upper layers of the soil profile (Figure 2).

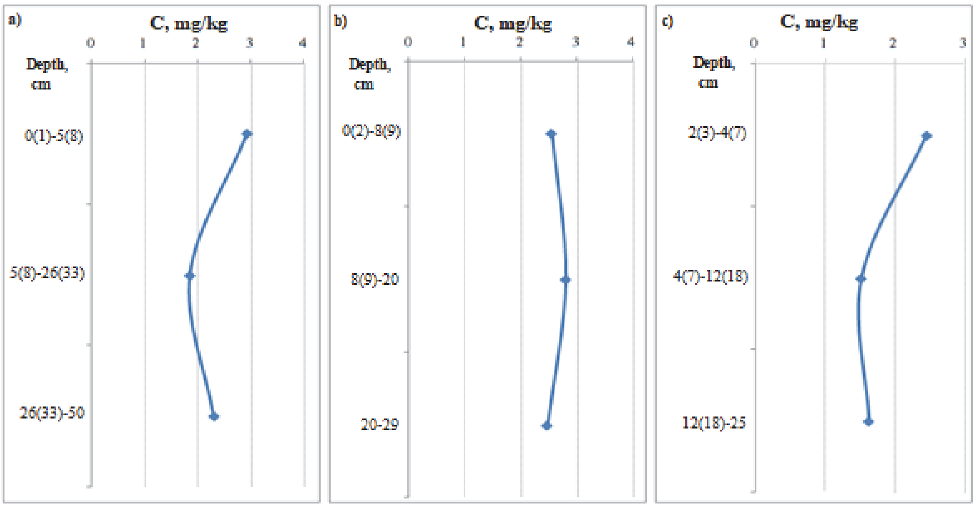

Figure 2. Lead distribution by soil profile in various types of permafrost soils - a) permafrost fawn-brown podzolized, b) permafrost fawn-brown, c) homogeneous non-gleyed cryozem.

The Pb content is increased in the lower horizons in permafrost pale-brown podzolic and homogeneous non-gleyed cryozem, which associated with strong fixation with organic matter. The high correlation dependence is proof of the connection of lead with organic matter (r = 0.91 и r = 0.96 respectively) (Figure 3).

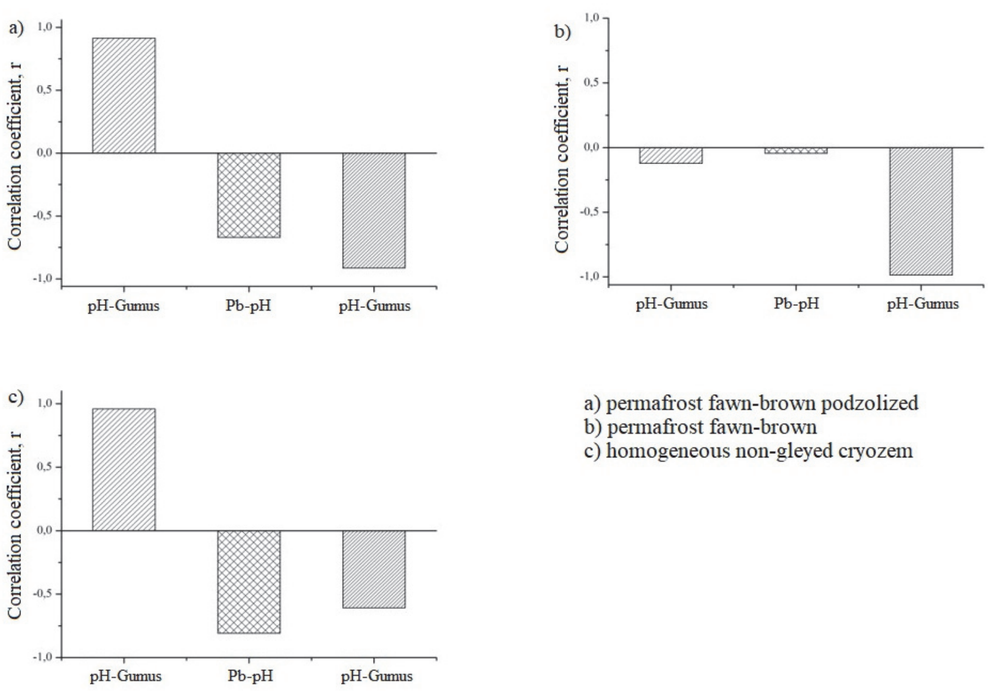

Figure 3. Dependence of lead content on humus and pH values in permafrost soils.

Also, the correlation analysis established the average negative dependence of the lead content on the pH in the permafrost fawn-brown podzolized and homogeneous non-gleyed cryozem (r = -0.67 and r = -0.81 respectively).

The correlation dependence of the lead content on pH and humus was not recorded in the permafrost fawn-brown type of soil.

The content of heavy metals in the soil and their accessibility to plants largely depends on the sorption properties of the soil. High sorption activity of the soil contributes to a greater fixation of metals and their reduced mobility [10].

Table 2 presents the experimental data on the redistribution of lead between the solution of a pollutant and the adsorbent on the example of permafrost fawn-brown podzolized soil. The graphical distribution of the degree of lead adsorption over the soil profile is shown in figure 4.

Table 2. Characteristic of adsorption processes of lead in permafrost fawn-brown podzolized soil.

№	Soil type	Sampling depth (cm)	Pb content in solution (mg / kg)	The amount of sorbed lead (*q*, mg / kg)	Degree of sorption (a,%)
1	Permafrost fawn-brown podzolized	2(6) - 8(11)	14.07	105.67	88.25
2		8(11) - 26(35)	17.46	102.28	85.42
3		26(35) - 44(48)	39.74	80.00	66.81
4		44(48) - 57(63)	7.00	112.74	94.16
5		57(630-98)	6.89	112.85	94.25

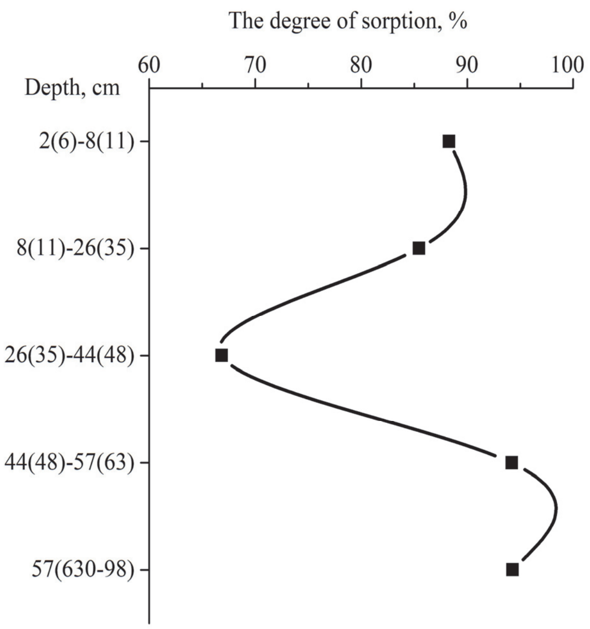

Figure 4. The degree of sorption of lead by permafrost fawn-brown podzolized soil (%).

The obtained data demonstrate that the lead absorption is the highest in the lower supra permafrost horizons (below 44 cm), where the degree of sorption reaches 94 %. Lead is sorbed less at a depth of 26–44 cm (the maximum degree of adsorption is 67 %). It is absorbed quite well in the upper organogenic and organo-mineral horizons (85 – 88 %). It is explained by the presence of biogenic and suprapermafrost geochemical barriers in permafrost soils [3].

Thus, the obtained data confirm that under normal conditions, the permafrost soil can almost completely absorb and deposit anthropogenic emissions of lead ions over the entire soil profile.

4. Conclusion

The paper researched three types of permafrost soils with low power of the soil profile. According to the content of mobile forms of Pb the studied soils can be arranged in the ascending order: homogeneous non-gleyed cryozem <permafrost fawn-brown <permafrost fawn-brown podzolized. The analysis also defined the high correlation dependence of the lead content on humus values and average negative dependence on pH. Moreover, the developed model experiment allowed for the determination of the degree of sorption of the genetic horizons of permafrost fawn-brown podzolized soil. Finally, it is established that mineral horizons have the highest sorption capacity.

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