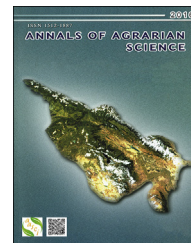


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Chemical evolution of soil profile from humid regions: The role of the rare elements



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ABSTRACT

Eluvial-illuvial distribution of rare metals in forest soils is expressed more vividly than the distribution of Fe and Al the more. This is applies primarily to lanthanides: Y, La, Ce. In particular, this difference is noticeable in light Al–Fe-humus podzols, where highly differentiated elements of platinum group. The type of metals exposed to eluvial-illuvial distribution depends on the mineralogical composition of the parent rock and has a pronounced regional dimension.

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Introduction

The profile change of the chemical composition of the soil is occur in the process of soil formation as a result of the destruction and formation of new minerals. This phenomenon is accompanied by a variety of basic soil formation processes (BSFP). As an example of the transformation of the parent substrate lead form system the soil profile horizons: O – A – E – B1t – B2t – C [1], which is formed by eluvial-illuvial distribution of substances. Classifying types of distribution of substances in the soil profile [2], selects the type of eluvial-illuvial distribution, which is especially the case for podzol series soils.

Let us discuss chemical aspect of eluvial-illuvial distribution of substances in the soil profile of humid regions. For those regions currently emit one broad division of soils, where the differentiation manifested itself most clearly. According to the soils classification and diagnostics of Russia [3], this division is Al–Fe-gumus soils. The soil of this division only

influenced by BSFP: organic humic acid influence of hostile to the mineral mass. In other words: differentiation of chemical composition has a chemical nature. In this regard, Al–Fe-gumus soil constitutes the most pure example of differentiation through chemical composition.

Al–Fe-gumus soils are differing morphologically and chemically pronounced accumulation of Al-, Fe- and humic compounds. They form spodic horizon BHF brown or buff-brown tones. Coloring a horizon depends on the ratio of it organic matter and iron oxides. The Division of soils characterized by: acid reaction to the entire profile, desaturated bases, fulvic or gumic-fulvic type of humus. Al–Fe-gumus soils are distributed mainly in the taiga and tundra zones. They are formed in a free drainage on unconsolidated sandy sediments. Let's take a look at different kinds of spodosols, containing in profile spodic horizon [4].

Spodic horizon is also evident in soils other genesis humid regions. Consideration the differentiation of metals in these soils profile is also of interest. Among these soils will highlight the division texture-differentiated soil, where also clearly

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expressed eluvial-illuvial differentiation of chemical composition. The formation of these soils is going through multiple heterogeneous mechanisms. Highly-differentiated soil diagnosed clear mineral and texture differentiated profile. In the profile has two horizon necessarily: one of them is EL clarified with a lightweight particle-size composition, and other textured BT. This type of profile structure is the result of several differentiating processes. The main process is the selective destruction of very silty minerals leaching fractions with the destruction of products beyond the profile.

In past years, changing the chemical composition of soils profile was assessed on a limited list of main elements: Si, Al, Fe, Ca, Mg, K, Ti [5]. This was due to the difficulty and expense of “wet” bulk chemical analysis of soils. Therefore, profile differentiation detected items only for iron and aluminum. On the basis of the selected soils are appointed as cambisols type in the Soil Taxonomy [4].

But by analyzing only main elements, soil scientists for many years did not pay attention to the differentiation of rare elements with content <1000 ppm. Later, in connection with the development of X-ray soil analysis [6], the situation changed radically. The cost of bulk analysis was decreased and the set of elements analyzed had increased, mainly due to heavy metals: Cr, Mn, Ni, Cu, Zn, Ge, Sr, Y, Pb. Most recently, the possibilities of the method were further expanded at the expense of radiometric modification of X-ray analysis that allows analyze several lanthanides: La, Ce and so on [7]. Thus, it is now possible to analyze profile differentiation of large amount of chemical elements.

The aim of this research: to evaluate the degree of evolution of soil profile based on redistribution of rare elements.

Theory

Let us assess the extent of profile migration of chemical elements by using the indicator: $K_{s/a} = C_{spodic} : C_{albic}$, where C_{spodic} – element content in spodic horizon and C_{albic} – element content in albic horizon. This indicator is equivalent coefficient of differentiation of silt in the profile.

Spodic-albic distribution of matter in forest soils is largely determined by the action on minerals, organic acids produced during the disintegration of the forest floor. Among the most important acids are dominated fulvic acids, as well as oxalic acid and citric [8]. It is clear that the influence of acids on minerals will be different depending on the strength of the relationship of organic ligands from metals, which are present in these minerals. Main elements are different in strength of connection with organic ligands very greatly. So, logarithms

oxalic resistance constants of metals data $\lg K_{ox}$ form number: $Fe^{3+} (9.4) > Al^{3+} (7.3) \gg Mg^{2+} (2.5) > Ca^{2+} (1.7)$ [9]. In harmony with this next, connect Fe- and Al-(hydr)oxides and clay minerals are destroyed in the horizons E and EL and their degradation products migrate to the horizon B in or out of profile.

The eluvial-illuvial distribution is not limited to two main metals: Fe and Al. Certain rare metals: copper, chromium, also named “heavy metals” are form strong complexes with oxalic enough, comparable in strength with complexes with Fe^{3+} and Al^{3+} . Of course, you have to keep in mind many causes differentiation of chemical elements. So, not only organic oxalate ligand soil solution, essential for chelating has also citrate. Here is some constants sustainability of metals with citrate $\lg K_{cit}$: $Fe^{3+} (11.4) > La^{3+} (8.4) > Ce^{3+} (7.4) > Cu^{2+} (5.9) > Zn^{2+} (5.0) = Co^{2+} (5.0) > Mg^{2+} (3.7) > Ba^{2+} (2.9)$ [9]. It is slightly different than with oxalate. In citrate series stand out high position rare earth metals lanthanum and cerium, which form strong complexes with citrate.

The number of metals $K_{s/a}$ are not fully consistent with the theory. But high strength of metal complexes with organic ligands is indicate the possibility of differentiation of rare (heavy) metals in Al–Fe-humus soils.

As a traditional example of spodic/albic differentiating substances give the distribution in sod-podzol soil on loam silt particles are only two metals (Al and Fe) [2]. The value of $K_{s/a}$ is for the oxides 2.0.

The sod-podzolic soils on acid intrusion of the Middle Urals is observed sodic/albic character profile distribution of some rare metals. In terms of $K_{s/a}$ rare metals are placed in a row: $Cu (5.5) > Zn (1.5) > Mn (1.2) > Ni (1.2)$. At the same time, this should not be distribution of vanadium: the $K_{s/a} = 0.8$ [10].

Note that eluvial-illuvial character profile distribution of some metals is typical not only for podzols, but also in soils of more southern regions. For example, this type of distribution is typical of light gray soils of the Central black earth region, Russia [11]. So, by the values of $K_{s/a}$ are form a series: $Zn (2.8) = Ni (2.8) > Co (2.2) > Cr (2.0) > V (1.9) > Cu (1.8) = Ti (1.8)$. In contrast, the figure for manganese 0.8, which is consistent with weak strength it with many ligands of organic acids that impact the minerals in the eluvial horizon EL.

Other authors confirm eluvial-illuvial differentiation of rare (heavy) metals in forest soils. Value of $K_{s/a}$ for copper is 2.8, for cobalt is 1.6, whereas manganese that character profile distribution does not meet (0.4) [12]. A particularly interesting results were obtained on podzolic sandy soils of Karelia [13]. Here is marked by eluvial-illuvial character of the profile distribution of copper, cobalt, molybdenum, zinc and sometimes.

Table 1 – The physicochemical properties of the soil in town Chusovoy, Perm Krai, Russia [15].

Horizon	Depth, cm	Cation exchange capacity, mg-equiv./100 g	V, %	pH KCl	P ₂ O ₅ mg/100 g	K ₂ O mg/100 g	C org, %	Clay, %
AY	3–12	19	80	4.9	4.9	19.2	7.3	14
EL	12–27	12	80	4.2	2.0	11.2	1.2	17
BEL	27–59	16	70	3.8	1.0	12.8	0.9	29
BT1	59–85	17	85	4.1	3.4	16.0	0.9	36
BT2	85–104	25	>90	5.1	4.0	14.0	0.9	26
C	104–150	25	>90	5.4	5.0	7.6	0.5	17

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