Migration of microelements in the profile of Cryozem in North-west Yakutia

Jana Borisovna Legostaeva
"Scientific Research Institute of Applied Ecology of the North,"the Federal State Autonomous Educational Institution of Higher Professional Education "North-Eastern Federal University named after MK Ammosova", Russia

Abstract. One of the specific features of the soil formation process in cryolithic zone, which distinguishes it from other processes, including the geological one (geochemical eolation), lies in the fact that migration of microelements in cryogenic soils is controlled by living organisms only to a certain extent, while in extreme continental climate of Northwest Yakutia it is controlled mainly by plants. The most important factor is the presence of permafrost horizon in the soil profile, which serves as a retainer and forms over-permafrost geochemical barrier. The article describes the intraprofile migration of microelements in dominant types of soils of north taiga landscapes of Yakutia, called Cryozems.

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Introduction

Attention of geochemists and mineralogists, as well as chemists and physicists currently is being increasingly focused on the processes taking place in geochemical systems at subfreezing temperatures [1]. Following a series of geochemical studies, which have shown that permafrost is not a zone of chemical quiescence, as it was previously believed, theoretical and experimental works of chemists began to appear in scientific literature; these studies addressed the properties of the film moisture at subfreezing temperatures, the behavior of cryogenic heterogeneous systems, the rates of chemical reactions, and etc. [2, 3, 4, 5].

Cryogenesis processes are one of the leading factors in the formation of soil in the territories of continuous permafrost expansion. In the Northwest Yakutia the permafrost thickness ranges from 250-400 m. In flat terrain (river terraces and flat watersheds) mollisoil reaches the maximum thickness of 1-2.5 m on well-drained slopes as well as alluvial floodplain and sand-gravel deposits. In the areas of fine-grained peaty soils the defrost depth is just 0.5-0.7 m. As the content of fragmentary material increases, the defrost depth augments to 0.8-1.10 m [6].

Ice content of the soils depends on the geomorphological and geological conditions of their formation. On the tops of watersheds, composed of carbonate rocks and their eolation crusts, ice content ranges from 5-6% to 18%. Smooth slopes, consisting of alluvial clay-loamy deposits, are characterized by ice content that changes from 14.5% to 40.5%.

Cryogenic microrelief is clearly pronounced: it is knotty hummocky with well-marked permafrost cracking.

Complex physical and geographical conditions of soil formation predetermined soils nature. Northwest Yakutia is characterized by dominating heavy-textured, usually gleic or gley thixotropic soils with a thin crush stony profile named Cryozem.

Methodology

Complex soil geochemical studies were carried out during the period from 1994-2013 on the territory of Daldyno-Alakitsky industrial area, located in terms of its natural and climatic conditions within the West and Northwest Yakutia.

During field observations 35 soil profiles were laid within the natural and technogenic landscapes with the morphological description and sampling of all genetic horizons.

Regional background values were taken as statistically significant (n=1241) average geometrical parameters of microelements containment in soil continuum of natural intact landscapes of Northwest Yakutia, based on long-term data of our research, as well as the results involving reputed geochemical studies of the region [7].

Concentration factors K_c and accumulation factors K_0, K_1, K_2, etc. are calculated. Concentration factor relative to the regional background K_c is a measure of excess multiplicity of microelements content at sampling point over the regional background values $K_c = C/C_b$. Where K_0 is the ratio of the average content of microelement in a particular soil profile to the average content of the same microelement in a soil-forming substrate $K_0 = C_{soil}/C_{ettle}$.

Main part

Microelements take a special place in the soil chemistry; therefore they can be considered from the point of view based on both formation of the main migration flows within the soil profile, and as specific markers of natural and technogenic component [8, 9].

Formation of the modern soil continuum of the Northwest Yakutia takes place against a backdrop of preceding period of a long-term denudation, which, at the level of modern erosional truncation, resulted in dominant position that has been acquired by early Paleozoic carbonate rocks. They act as soil-forming substrate, thereby determining the "carbonate" trend of existing geochemical processes at a dominant position of Ca-Fe-Mg components of the environmental media.

Because soil formation is a combination of geochemical and biochemical processes, soil profile of permafrost soils of northern taiga landscapes of the area under study, is a two-tier system, in which the lower part (BC и C horizons) accumulates the microelements, i.e. the products of geochemical eolation of parent rocks. Whereas the upper part of the profile accumulates biophil elements and the elements, transferred into the organo-mineral horizons under the effect of biogenic-accumulating and alluvial-accumulating processes. It is necessary to take into account that the cryogenic soil profile is characterized by low thickness, strong gravelly and relative homogeneity. Thus, when isolating lithogenic component, which is characterized by the highest concentrations of elements, we obtain the microelement characteristic of cryogenic soils, formed under the influence of the geological and geochemical conditional specifics of the region and the interaction of climatic factors, particularly permafrost conditions, and development of living organisms.

In Cryozems of Northwest Yakutia active organo-mineral layer rests at a depth of 30-40 cm; below are located usually over-permafrost horizons BC or C, which characterize microelement composition of the parent rocks. Therefore, for characteristic of the dominant soil types in terms of microelements it is sufficient to confine by soil layer of 0-30 cm that includes upper humus horizons (A_0, A_1) and mineral or transitional organic-mineral horizons (B and AB). In general, the soil continuum of the area under study, formed by the biogenic-accumulative, alluvial-accumulative and cryoturbation processes is characterized by concentrations of microelements that are at or slightly below the regional background values. Three element groups are identified based on the concentration factor values:

1. Kc< 0,5 - Co;
2. Kc = 0,5 – 0,9 - Li, Be, B, P, V, Cr, Cu, Ga, Nb, Mo, Ag, Pb;
3. Kc > 1,0 - Sc, Ti, Mn, Ge, Y, Sn, Yb.

The first group includes only cobalt, because the main concentration of this element is confined to the lower part of the soil profile. This is especially evident in soils formed over the magmatic rocks of alkaline-ultrabasic and basic compositions, over blue earths and dolerites.

The second group of elements is the most numerous one, comprising of biophil (B, P), lithophile and litho-siderophile (Li, Be, Nb, Cr, V, Mo) and chalcophile (Mo, Ag, Pb) elements. Maximum concentrations of these group of elements, significantly exceeding the regional background parameters, are recorded in mineral over-permafrost horizons of the soil profile. At higher profiles the values tend to decrease and in the organic and mineral parts remain at or slightly below the background level. Second peak is observed in the A_0 horizon due to the effects of biogenic accumulation. Exceptions are biophilic elements, which have the maximum values in the humus horizons. Thus, taking the levels of lithogenic component, we got a microelements group that characterizes the specificity of soil-forming substrate and exhibits a pronounced tendency to accumulate.

Third group of elements is accumulated in cryogenic soil and is characterized by chalco-siderophile properties, designating sedimentary carbonate rocks of the Early Paleozoic that predominate in the soil-forming substrate of the given territory.

An analysis of the obtained data was used to build the accumulative series, characterizing microelement composition of the dominant soil types of Northwest Yakutia. Cryozem Homogeneous humus gley: $Sc_{1.4} \rightarrow Mn_{1.3} \rightarrow Yb_{1.2} \rightarrow Ti\ (Ag)_{1.1} \rightarrow Ge_{1.0}$. Cryozem Homogeneous over-permafrost gleysolic: $Sc_{1.3} \rightarrow Ti(Ge – Y- Yb)_{1.2} \rightarrow Mn(Nb – Sn)_{1.1} \rightarrow Ni(Zn)_{1.0}$. Cryozem Homogeneous non-gleic: $Sc_{1.4} \rightarrow Ge(Y- Yb)_{1.2} \rightarrow Be(Ti –Sn)_{1.1}$ and Cryozem Thyrotrophic: $Ge_{1.6} \rightarrow Ni\ (Zn)_{1.3} \rightarrow Sn_{1.2} \rightarrow Li\ (Y)_{1.1}$.

It should be noted that the studied area is located within the formation of the natural geochemical anomaly, associated with the formation of blue earth of Mirninsky, Daldyn, Alakit-Markhin and Verhnemunsk ore fields. Natural geochemical anomaly of parent rocks is inheritably recognized in formed soils and thus changes the microelement structure of the soil profile, forming a qualitatively new accumulative series, and thus changing the spatial distribution of microelements in the soil continuum. Consequently, as a result of variations in the petrochemical and geochemical specificity of the parent rocks, microelement associations of accumulative series of dominant soil types are changing. At that accumulation factors K_1 vary within the broad range. For example, Cryozem Homogeneous humus gley formed on the rocks of Meiksk formation of early Silurian period, are characterized by the following accumulative series (Table 2): Li $_{9.2}\rightarrow$ Ti $_{3.9}\rightarrow$ V$_{3.3}\rightarrow$ Zn $_{2.2}\rightarrow$ Mn $_{1.2}\rightarrow$ Pb (Ni)$_{1.1}$. Cryozem Homogeneous over-permafrost gleysolic, formed on blue earth of "Yunost" pipe, are characterized by the accumulation of the following elements in the soil profile: Ni $_{1.7}\rightarrow$ V$_{1.4}\rightarrow$ Co$_{1.3}\rightarrow$ Cr(Mn)$_{1.2}\rightarrow$ Cu$_{1.0}$. Cryozem Homogeneous non-gleic, formed above dolerite dykes, accumulate in their profile in terms of soil-forming substrate just Y$_{2.3}$. Cryozem Thyrotrophic, formed on carbonate rocks of Sohsolohsk set of early Ordovician period, are characterized by the following accumulative sequence: Y$_{12.5}\rightarrow$ Sn$_{5.3}\rightarrow$ Zn$_{3.8}\rightarrow$ Li$_{3.3}\rightarrow$ Ti$_{2.7}\rightarrow$ Co$_{2.1}\rightarrow$ Cr$_{1.7}\rightarrow$ Ni$_{1.1}$.

The main components that enhance the reactivity of migrating moisture fluxes are organic substances which are taken from the soil and involved into the geochemical processes [10]. The possibility of the partial removal of organic carbon from the biological cycle is inherent in the nature of thermodynamically and biologically sustainable colloidal complex, accumulating in the soil, and providing a specific soil material namely humus, or humic substances, more precisely.

The majority of Cryozems are characterized by acidic or weakly acidic pH in the upper humus horizons and pH parameters, changing to neutral values, in the mineral part of the soil profile. The soils of the area under study are dominated by anaerobic conditions, strong moisturizing and in most cases the oxidation of sesquioxides in the mineral part of the soil profile. In the composition of organic matter of Northwest Yakutia Cryozems prevails non-hydrolyzable residue, while humus is of pronounced humate-fulvic or fulvic character. Redistribution of microelements in the soil profile is due to cryogenic mixing of soil material and retinization of organic matter in over-permafrost horizons, as well as mobile properties of fulvic acids, predominating in the composition of organic matter.

When analyzing the above derived reference model of the microelement composition of Cryozem Homogeneous humus gley and the data on accumulation factors, recalculated depending on soils bedrock, the accumulation of Li, V, Mn, Ni, Zn and Pb in the mineral part of the soil profile (horizon BCg) becomes obvious (Table 1). The distribution of these microelements along the depth of Cryozem Homogeneous humus gley is of regular character and increases with the depth.

Table 1. Distribution pattern of the microelements along the cryogenic soil profile in Northwest Yakutia

Accumu-lation factor	Elements													
	Li	B	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Nb	Sn	Pb
Cryozem Homogeneous humus gley formed on the rocks of Meiksk formation of early Silurian period														
K_3	0.6	0.8	**1.7**	0.3	0.3	**2.5**	**14.0**	0.3	0.8	0.5	0.7	0.3	0.3	0.6
K_2	0.9	0.7	**16.6**	**1.4**	**4.9**	0.6	**2.2**	**6.0**	**1.7**	0.8	**2.3**	**2.8**	0.5	0.7
K_1	**3.6**	0.7	0.1	**3.3**	0.6	**1.2**	0.2	**1.1**	0.3	**2.2**	**4.4**	0.8	-	**1.1**
Cryozem Homogeneous over-permafrost gleysolic formed on blue earth of "Yunost" pipe														
K_3	0.8	**6.2**	0.7	**3.5**	0.3	0.6	0.5	0.2	0.5	0.6	**1.7**	-	0.6	0.2
K_2	1.3	0.1	1.0	0.5	0.8	0.1	0.9	0.5	0.9	1.0	1.7	-	1.0	1.2
K_1	0.9	0.2	0.01	**1.4**	**1.2**	**1.2**	**1.3**	**1.7**	1.0	0.5	0.7	-	0.9	0.7
Cryozem Homogeneous non-gleic formed above dolerite dykes														
K_1	**1.3**	**1.1**	**1.4**	**1.2**	0.8	**1.3**	0.9	1.0	0.7	**1.2**	0.7	-	0.8	0.8
K_1	-	0.6	0.6	0.7	0.9	0.5	0.7	0.4	0.1	0.3	**2.3**	-	0.3	0.6
Cryozem Thyrotrophic formed on carbonate rocks of Sohsolohsk set of early Ordovician period														
K_3	**1.4**	0.7	2.8	**1.9**	0.7	0.7	0.3	**1.3**	0.3	0.6	**1.5**	0.4	**1.7**	0.6
K_2	0.9	**1.9**	0.5	**2.8**	**2.2**	**1.9**	**7.9**	**4.7**	**6.1**	**1.7**	**1.7**	**4.5**	0.5	1.0
K_1	**3.3**	**1.9**	0.4	0.1	0.6	0.3	0.1	0.04	0.02	0.3	0.9	0.2	0.5	0.5

Note: accumulation factor values: elements marked in bold (**2.3)** are accumulated by organic matter, while the elements given in regular font (4.2) are transferred from the underlying horizon.

$K_1 = C_{\text{hor. BC (or C)}} / C_{\text{ettle}}$

$K_2 = C_{\text{hor. B(or AB)}} / C_{\text{hor. BC (or C)}}$

$K_3 = C_{\text{hor. Ao}} / C_{\text{hor. B (or AB)}}$

Humus-accumulative horizon A_1 is characterized by a more broad range of microelements accumulation with wider variations of accumulation factors with regard to horizon BCg, which, of course, is due to the essential involvement of organic matter and at the same time the subtraction of the elements, such as V, Ti, Ni and Y, from the underlying horizon.

The elements, such as Ti, Mn and Co, concentrating in A_0 horizon, may have a double origin: biogenic accumulation with gradual dilution down the profile and, at the same time, transfer from the lower horizons accompanied by the accumulation by organic matter. Thus, Cryozem Homogeneous humus gley are characterized by the accumulation of Mn and Ti; the rest of the microelements composition depends on the geochemical properties of the soil-forming substrate.

Cryozem Homogeneous non-gleic is characterized by accumulation of yttrium with K_1=2.3 relatively to soil-forming substrate. Humus horizon differs by wider composition of microelements such as Li, B, Ti, V, Mn, Zn, though with low accumulation factors varied between 1.1 and 1.4. It should be noted that Cryozem Homogeneous non-gleic differ by most thin homogeneous profile among frozen cryogenic type soils. Therefore, though the distribution of microelements over the soil profile is relatively uniform, whereas slight accumulation in the upper part of the profile is associated with the sorption of organic matter.

Soil profile of Cryozem Thyrotrophic, according to the reference model, is characterized by the following microelement composition: Ge-Ni-Zn-Sn-Li-Y. According to the values of accumulation factors, the following elements accumulate in the mineral part of the soil profile: Li, B, V, Cr, Mn, Co, Ni,Cu, Zn, Y and Nb with a sufficiently high K_1-K_2 (1.7 - 7.9); at that the main accumulation of the microelements occurs in the B horizon that confirms the presence of differentiated profile with a pronounced eluvial-accumulative horizon in thixotropic cryogenic soils. The humus horizon is characterized by organogenic accumulation of lithium, vanadium, nickel, yttrium and tin with small accumulation factors changing from 1.3 to 1.9 due to their subtraction from the mineral part of the profile.

Conclusions

In terms of microelement composition of the soil profile, zonal types of soils in Northwest Yakutia, namely Cryozems, are characterized by the two-level accumulation system, which is based on the accumulation of microelements in the mineral horizons as a result of their subtraction from parent rocks, as well as biogenic sorption and distribution over the soil profile with organic matter as a result of cryogenic stirring. Each subtype of cryogenic soil is characterized by the accumulation of a certain microelements variety, and specific multielement associations are created as a result of geochemical influence of soil-forming substrate.

Corresponding Author:
Dr.Legostaeva Jana Borisovna
"Scientific Research Institute of Applied Ecology of the North," the Federal State Autonomous Educational Institution of Higher Professional Education "North-Eastern Federal University named after MK Ammosova", Russia.

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