INTERNATIONAL JOURNAL OF ENVIRONMENT

Volume-3, Issue-2, Mar-May 2014 ISSN 2091-2854

Received:13 April *Revised:28 April* *Accepted:16 May*

REGULARITIES OF LA DISTRIBUTION IN HUMIC PSAMMOZEM PROFILE OF TRANSBAIKALIA AND SOIL-ROOT LAYER MICROZONES OF MAIZE DURING THE VEGETATION PERIOD

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Abstract

In Transbaikalia information about accumulation, distribution of rare earth elements (REEs) in soils, their transportation from soil to plants is very rare. The aim of this study was to assess the migration of lanthanum in a soil profile and soil-root layer microzones of maize during the vegetation period. The study is based on a field approach in non-polluted natural sites. Concentration of total content La and its mobile form (acid-soluble, exchangeable and water-soluble) in the soil and soil root layer of maize was determined using method of selective extraction Gobran and Glegg. Maximum concentration total La was founded in the upper part of the soil (0 to 15 cm depth). The content of the La mobile forms is 6.9-11.2% from the total amount. The distribution of the element mobile forms within the profile is relatively even. Results indicated that concentration La mobile forms changed in accordance with the phase of maize development. The higher concentration of mobile forms (17-120% from germination period) was founded in soil-root layer microzones in the blossom period.

Key Words: humus psammozem, lanthanum, microzones of soil-root layer, maize, Transbaikalia

Introduction

Rare earth elements (REE) are chemical elements from La to Lu, whose atoms differ from each other in structure of internal 4f-electron orbitals. The feature of REE is their joint presence in the Earth's crust where the REE minerals of Cerium subgroup are dominant, which persentage is about 10^{-3}%. Only some rare earth minerals such as monazite, xenotime, bastnaesite, loparite, apatite, obruchevite, chernovite, rabdofanite contain significant amount of REE (Kostov, 1971; Balashov, 1976; Evans, 1990; Hu *et al.*, 2006). The difference in properties of REE is due to the decrease of ionic radius from La to Lu, as a result redistribution and selective concentration of REE in minerals takes place. REE are concentrated in granitoids and alkaline rocks during magmatic processes (Ripp *et al.*, 2000). Monazites enriched in LREE (La, Ce, Nd, Eu) are part of granites, pegmatites, alkaline rocks, carbonatites. Bastnaesites enriched in La and Y are major REE-minerals of carbonatites. Carbonatite laterites are used as an ore for the extraction of REE.

REE concentration in soils varies from 0.2 to 86.4 mg kg^{-1} depending on its level in soil-forming rock, on how much the rock is weathered, genesis of soil, clay minerals content, organic matter and other factors. In a humid climate top soils are depleted in REE compared to the parent material (Perelomov, 2007). It was found that the REE relocate from the upper acid horizons to the deeper horizons and deposit in the secondary minerals, Mn-and P-containing concretions (Gouveia *et al.,* 1993; Aide *et al.,* 1999; Perelomov, 2007). The behavior of lanthanides in soil depends on organic matter containing different negative charge groups sorbing REE cations. Being high reactive REE interact with proteins, substitute calcium and magnesium in the structure of proteins, stimulate biological nitrogen cycle and nitrification ability of cryo-arid and permafrost soils (Kabata-Pendias, Pendias, 1992; Diatloff *et al.*, 1996).

In Transbaikalia the distribution of Cerium subgroup REE in the profile of chestnut soil and grey forest soil is studied (Kozhevnikova, 2010; Kozhevnikova and Ermakova, 2010). Uniform distribution of REE in the profile of the soils mentioned, with some accumulation in the carbonate horizon was founded. Accumulation and distribution of REE in other soils of Transbaikalia peculiarities needed for the assessment of influence of REE nature on their distribution in the profile of different genetic types of soils are not studied.

The root systems of plants change the physical, chemical and biological properties of the soil in the zone of contact (Gobran, Gleegg, 1996). The microzones of rhizosphere soil and soil-root surface are different from the soil in general by the amount of available nutrients, organic matter, pH, composition of microorganisms and other indicators. The root exudates - organic acids, sterols, enzymes, cellular active ingredients contribute to increasing of mobility and availability of phosphorus, potassium and trace elements for plants (Efimov, 1988). However, the similar information for the humic psammozem of Transbaikalia in the literature is absents.

Therefore, the purpose of this work is to study the distribution of total content and mobile forms of La in the humic psammozem profile and in soil-root layer microzones of maize in Transbaikalia.

Materials and methods

Research was carry out in the territory of the Republic Buryatia (Transbaikalia, 51°52′32″N, 107°32′8″E). The humic psammozem is distributed mainly on sandy terraces-ridges and occupied the area about 30 thousand hectares (1.2% in the structure arable fund of Republic). In the region the humic psammozem is located in the bottom of the forest zone, predominantly under the steppe pine forests (the height is 700-1000 m ASL). The soil-forming rocks of these soils are the products of weathering of the various deposits.

The humic psammozem has the sandy granulometric composition, low-alkaline reaction of soil solution, very low content of the humus, nitrogen and absorbed cations (Ubugunov, Kashin, 2004). These soils have the high heat availability, the short period of thawing after the winter freezing, but they have the moisture deficit, which depend on unfavorable water-physical properties of the soils (the weak water retention capacity, the high porosity of the soil and moisture permeability).

The soil incision was made in the pine-forest near township Glassworks (city Ulan-Ude) to study features of the La distribution. It was located on the right side of the Selenga river, the height is 800 m ASL. The main forest-forming species is Scots pine (*Pinus sylvestris* L.). The grass cover is sparse, the total projective cover is 40-45%. The gramineous-forbs community is dominated.

The soil profile has the following characteristic of the horizons

A_1 (0-15 cm) Light brown color, moist, density, structureless, sand with inclusions of the plant roots; does not effervesce with HCl. The transition to the lower layer is clear and expressed in color and density.

A_1B (15-25 cm) Brown color, with humus pocket, moist, loose, structureless, sand with inclusions of the plant roots; does not effervesce with HCl. The transition to the lower layer is sharp in color and density.

B (25-40 cm) Brownish-yellow color with a whitish tinge, moist, density, structureless, medium sand, does not effervesce with HCl. It has few roots. The transition to the lower layer is weakly expressed in color.

BC (40-70 cm) Brownish-yellow color, moist, density, sand, does not effervesce with HCl. It has not roots and other inclusions.

The soil was classified in agreement with the new classification system of Russian soils based on the genetic principle (Shishov *et al.*, 2004). The agrochemical properties of the soil were determined by routine methods (Agrochemical…, 1975). The agrochemical characteristic of humic psammozem was: pH $_{(H_2O)}$ – 7.4, humus content – 1.03%, N – 0.11%, the mobile form of P_2O_5 – 31 mg kg^{-1}, the exchangeable form of K_2O – 96 mg kg^{-1}, the exchangeable cations of calcium and magnesium – 6.8 and 1.7 mg.eq. 100 g^{-1} soil.

The soil samples were taken from each horizon. They were calcined for 4 hour in a muffle furnace at 500-550°C to delete organic matter. For determination of the La total content the mineral part of the soil was decomposed with mixture of acids HF, HNO_3 and HCl (concentrated). The concentration of La was measured by AAS SOLAAR M6. For atomization in flame the mixture of acetylene-air was used (Obukhov, Plekhanov, 1991). The La mobile forms from the soil were extracted sequentially by ammonium acetate buffer (CH3COONH4 (ABB), pH 4.8) (the ion-exchangeable form) and 1M HCl (acid-soluble form, non-exchangeable, related with oxides, hydroxides of iron, organic matter) (Rinkis *et al.*, 1987; Tulupov, Zhuravleva, 1987).

The content of the La mobile forms in soil-root layer microzones of maize during the vegetation period was studied by microfield experience. The crop investigated in this study was maize varieties Bukovina-3TV. The experience had 20 record plots with an area 1x1 m^2 each.

The soil samples were taken from the rhizosphere, the soil-root surface and the soil in general. The selection of the soil samples was carried out by the method Gobran and Glegg (Gobran, Gleegg, 1996). The root system of maize was released from the soil, but the thin soil layer on the roots (1-2 mm) was leave. The roots were separated from the shoots and dried. After drying soil layer was carefully shaken off (rhizosphere), adhering soil particles from the root surface was removed by the brush (soil-root surface). The total sample of soil was selected on the same plot, free of the maize roots. The La mobile forms were measured in the each sample. They were extracted sequentially by bidistilled water, ammonium acetate buffer (CH3COONH4 (ABB), pH 4.8) and 1M HCl (Rinkis *et al.*, 1987). The whole data were subjected to statistical analysis (Dospekhov, 1985).

Results and discussion

Soil forming processes lead to the REE differentiation in genetic soil horizons. LREE, which include La, have low migration capacity in neutral and alkaline conditions (Balashov, 1976).The typical increase of REE concentrations was detected with the increase of clay particles, loess deposits, carbonates in the soil profile causing organo-mineral REE complexes formation.

The data on distribution of La in the humic psammozem profile are displayed in Table 1. In the upper soil horizon the maximum total amount of La was found which was 16.9 mg kg^{-1} and gradually reduced to 11.3 mg kg^{-1} in accordance to the depth (horizon BC). Perhaps, such a distribution character of the element within the humic psammozem profile is caused by low content of organic matter and physical clay, lack of carbonates which leads to the decreased La compounds fixation in the lower part of the soil profile and causes the further their gradual washing out of the lower horizons.

The content of the La mobile forms is 6.9-11.2% from the total amount. The distribution character of La mobile form in the soil profile was almost uniform with some increase in the horizon A_1B.

Table 1: The distribution of total content and mobile forms of lanthanum in the humic psammozem profile (mg kg^{-1})

Horizon, cm	Form of lanthanum		
	Total	Ion-exchangeable	Acid-soluble
A_1 (0-15)	16.9[a)] ±0.54[b)]	0.98±0.015	1.21±0.020
A_1B (15-25)	15.4±0.51	1.41±0.020	1.73±0.020
B (25-40)	13.8±0.52	0.81±0.015	1.13±0.015
BC (40-70)	11.3±0.49	0.78±0.012	1.11±0.015

Here and next table [a)] - average value; [b)] - error average value.

The decrease of the content both as an ion-exchangeable form and acid-soluble forms La in the lower horizons B, BC was shown. The level of acid-soluble La form was higher than the ion-exchangeable form. In the sands the content of metal mobile forms is usually higher than in the loams. It confirms the converging role of soil forming processes in formation of the La concentration levels. The study of the dynamics of the La content in soil-root layer microzones of maize during the vegetation period showed that the processes of the soil-root interactions did not effect significantly the total content of the element. It changed slightly during the vegetation period and was almost identical to the content of the element in the "general" soil (Table 2). Probably in short period of time the roots of maize did not have a significant effect on the total quantity La. The content of acid-soluble, ion-exchangeable and water-soluble forms of the La compounds in soil-root layer microzones was 1.1-2.8 times higher than in "general" soil. The acid-soluble form of La accumulation in the contact zone of the root system with the soil was found. Acid-soluble form of La compounds is ions associated with the oxides of iron, aluminum, manganese, clay minerals, humus compounds (Ripp *et al.*, 2000; Perelomov, 2007), the content of which in rhizosphere soil samples and soil-root surface exceeded their content in general soil of 1.1-1.2 times.

The concentration of La compounds mobile form extracted using ABB extraction in soil-root layer microzones was 1.1-1.3 times over its concentration in soil in general. The mobile form includes the ions transferred into the buffer solution extract and a definite amount of the substance, earlier closely bound with soil and having become more mobile due to the effect of soil root interaction, and sorbed in a specific way.

The concentration of water-soluble La compounds form in soil-root layer microzones of maize has increased by 1.6-2.8 times in comparison with the concentration "general" soil. The accumulation of the ion-exchangeable, acid- and water-soluble La forms in the microzones of soil-root layer is significantly caused by organic matter secreted by roots into the environment,

Table 2: The total content and mobile forms of lanthanum in the microzones of soil root layer of maize during the vegetation period (mg kg^{-1})

Form of compound	Lanthanum		
	Rhizosphere	Soil-root surface	General soil
Germination period			
Total content	35.8 ± 0.44	36.1 ± 0.42	35.3 ± 0.41
Acid-soluble	4.1 ± 0.13	4.3 ± 0.10	3.8 ± 0.12
Ion-exchangeable	2.4 ± 0.07	2.8 ± 0.06	2.1 ± 0.08
Water-soluble	0.4 ± 0.03	0.5 ± 0.02	0.2 ± 0.03
Stooling period			
Total content	36.0 ± 0.51	36.3 ± 0.49	35.7 ± 0.37
Acid-soluble	4.2 ± 0.08	4.1 ± 0.07	4.0 ± 0.07
Ion-exchangeable	2.4 ± 0.08	2.6 ± 0.006	2.2 ± 0.04
Water-soluble	0.5 ± 0.02	0.8 ± 0.05	0.3 ± 0.05
Blossom period			
Total content	37.5 ± 0.48	35.8 ± 0.47	34.1 ± 0.42
Acid-soluble	4.8 ± 0.11	5.2 ± 0.12	4.2 ± 0.11
Ion-exchangeable	3.0 ± 0.09	3.4 ± 0.10	2.6 ± 0.09
Water-soluble	0.8 ± 0.02	1.1 ± 0.02	0.4 ± 0.03

such as amino acids, aromatic and aliphatic acids, carbohydrates, styrols, enzymes, cell substances. The root secrets form the conditions in the soil under which destroy the mineral structure, change the content of compounds, increase the cation exchange capacity thus stimulating the transition of some amount into mobiles forms (Aide *et al.*, 1999; Gouveia *et al.*, 1993). It's necessary to note the contribution of the root suction force elements in the increase of mobile forms concentration. It causes the mass transfer of substance to the root surface and providing accumulation of water-soluble form of elements in the root zone soil. A definite part in accumulating metals in root zone soil belongs to root microorganisms the amount of which on the root surface hundreds times over than in the soil in general (Kabata-Pendias and Pendias, 1992).

The concentration of all the La mobile forms in the root zone soil has changed in accordance with the phase of maize development. The maximum concentration of mobile forms of elements microzones of soil-root layer is observed in the blossom period. The acid-soluble La compounds during the blossom period have increased by 14-23% compared to the germination period. The content of La compounds extracted using ABB extraction microzones of soil-root layer during the blossom period has increased by 15-31%. The content of water-soluble La form microzones of soil-root layer during the blossom period has increased by 100-180%. The increase of La compounds probably results from the fact that roots secrete maximum amount of substances during the blossom period. Due to the presence of big amount of organic acids in the maize blossom period the intense accumulation of water-soluble La forms was observed as organic acids can to form soluble complexes with the REE ions under consideration.

Conclusion

Thus in the course of the research it was stated that total amount of La decreases with the increase of the humus psammozem profile depth. The distribution of the element mobile forms within the profile is relatively even. Total content of La in the microzones of soil-root layer of maize has changed insignificantly and didn't have any considerable differences with its content in the soil in general. The concentration of mobile forms of La compounds in the root zone was higher than in the rest soil mass as a result of transition of some total amount of elements in the mobile state. The maximum concentration of mobile forms of element in the microzones of soil-root layer is observed in the blossom period.

Acknowledgment

The reported study was partially supported by RFBR, research project № 12-05-00020-a.

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