Content of Rare-Earth Elements Lanthanum and Neodymium in the Phytomass of Corn and Pea

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Abstract

It is established that the content of lanthanum and neodymium accumulated in plant roots is several times higher than their content in the top mass. Rare-earth elements are most actively accumulated in pea roots. With respect to the coefficients of biological absorption, lanthanum and neodymium are characterized by low and middle level of absorption in the top mass of corn and pea.

INTRODUCTION

Literature data on the content of rare-earth elements (REE) in plants are scarce and exhibit a broad range of variations of the quantitative parameters. In particular, lanthanum content varies from 3.0 to 15000 μg and neodymium is present at a level up to 300 μg per 1 kg of the dry mass. The most active concentrators of REE are lichen and moss, which accumulate lanthanum in the amount of 400–3000 μg per 1 kg of the dry mass, and vegetables (0.4 to 2000 μg per 1 kg of the dry mass). Neodymium content in these plants is 240 to 3000 μg and up to 10 μg per 1 kg of the dry mass, respectively [1]. These data provide evidence that plants can concentrate substantial amounts of REE, depending on biological features and growing conditions. However, no cases of their toxic effect on human or animal organisms have been revealed. At the same time, determination of the distributive function of plants towards REE is important for the characterization of ecological stability of plant – soil system and for compliance with sanitary and hygienic requirements to food and forage crops.

At present, because of limited data on REE content of soil and plants under different natural climatic conditions, as well as of animal and human organisms, no permissible concentrations in soil and in biological objects have been adopted for these elements. The REE physiological and biochemical functions in plants and other organisms are as yet imperfectly understood.

The goal of the present work was to determine lanthanum and neodymium content in the organs of corn (stem, leaves, roots) and pea (top mass, roots) which are used in the Baikal region as forage crops in cattle breeding, and also to determine the coefficient of biological absorption (CBA) by plants using the data on the amount of lanthanum and neodymium in the ash of plants and in soil.

EXPERIMENTAL

Investigation was carried out by vegetation experiments in the vessels 6 l in volume (6 kg of the dry soil mass). Corn "Bukovinskiy-3TV" and forage pea "Pelyushka" were grown on dark chestnut sandy loam and gray forest medium-loamy soils with the humus content of 2.91 and 3.82 %, respectively, with sufficient content of mobile phosphorus, and with medium content of exchange potassium. Total amount of lanthanum and neodymium in soil was 30 and 18 mg/kg of soil, respectively. Three corn plants were left in each vessel to the phase of panicle; 15 pea plants were left in each vessel at the phase of mass blooming.

Lanthanum was introduced into the soil on the background of complete mineral fertilizer (NPK background) in the form of sulphate (3 and 6 mg/kg of soil, calculated for the element) and in the form of microfertilizer (MF) obtained according to sorption technology by saturating natural mordenite-containing tuff from 0.01 % $La_2(SO_4)_3$ solution. Lanthanum content of mordenite tuff was 3 mg/g of zeolite. Lanthanum-containing zeolite was introduced in the amount of 1 and 2 g per 1 kg of soil.

Neodymium was introduced on the NPK background in the form of sulphate in doses 0.5, 1.0, 2.0, 3.0 and 6 mg/kg of soil, for pea in the amount of 0.25, 0.5, 1.0 and 2.0 mg/kg of soil, and also by wetting the seeds in 0.001 M $Nd_2(SO_4)_3$ solution.

The soil with the introduced NH_4NO_3, $Ca(H_2PO_4)_2$ and KCl [2] was chosen as a reference background.

In order to prepare MF according to the sorption technology, we used mordenite-containing tuff from the Mukhor-Talinskoye perlite-zeolite deposit (Buryatia) of the following composition, mass %: SiO_2 70.96, Al_2O_3 11.97, MgO 0.18, CaO 0.92, Na_2O 2.38, K_2O 5.22, the ratio Si/Al = 5.2. Concentration of zeolite in the rock was 60–62 mass %. Tuff grain size was 1–2 mm, the mass ratio of zeolite to lanthanum sulphate solution was 1 : 10.

Lanthanum and neodymium in soil were determined after decomposition with a mixture of acids HF, HNO_3 and HCl according to the procedure described in [3], and in plants – through dry ashing followed by atomic absorption analysis with AAS SOLAAR M6 spectrometer [4]. Acetylene–air mixture was used for flame atomization. The data on plant productivity were processed with the help of dispersion method [5]. Coefficients of biological absorption of REE were determined according to A. I. Perelman [6].

RESULTS AND DISCUSSION

The data shown in Table 1 suggest that the introduction of lanthanum in different doses and forms does has no substantial effect on the change in concentration of this element in the top organs of corn. At the same time, 1.5–4 times larger amount of lanthanum is accumulated in roots than in the top mass. One can see that the concentration of this element in roots depends both on its dose and on its form. The concentration of the element increases with an increase in dose; lanthanum enters the roots more actively when sorbed by the zeolite (especially for MF dose equal to 2 g/kg of soil).

The income of the element into the roots from MF is nearly 4 times higher than its income from sulphate. So, lanthanum sorbed by zeolite is more available for roots than that introduced in the form of salt, maybe due to fixation of water-soluble form by soil with the formation of difficultly assimilable form.

TABLE 1

Lanthanum and neodymium content of corn phytomass, mg/kg of dry mass

Version	Lanthanum			Version	Neodymium		
	Leaves	Stem	Roots		Leaves	Stem	Roots
NPK (background) – reference	0.27	0.29	0.32	NPK (background) – reference	0.28	0.29	0.82
Background + La (3 mg/kg)	0.27	0.29	0.41	Background + Nd (0.5 mg/rg)	0.28	0.28	1.03
Background + La (6 mg/kg)	0.28	0.28	0.49	Background + Nd (1.0 mg/kg)	0.27	0.29	0.84
Background + MF (1 g/kg)	0.27	0.29	0.74	Background + Nd (2.0 mg/kg)	0.28	0.30	0.98
Background + MF (2 g/kg)	0.29	0.30	1.16	Background + Nd (3.0 mg/kg)	0.30	0.32	0.90
				Background + Nd (4.0 mg/kg)	0.32	0.34	0.94

TABLE 2

Coefficient of biological absorption of rare earth elements by corn phytomass

Version	Lanthanum		Version	Neodymium	
	Leaves	Stem		Leaves	Stem
NPK (background) – reference	0.073	0.104	NPK (background) – reference	0.169	0.142
Background + La (3 mg/kg)	0.098	0.107	Background + Nd (0.5 mg/kg)	0.173	0.147
Background + La (6 mg/kg)	0.096	0.105	Background + Nd (1.0 mg/kg)	0.155	0.156
Background + МУ (1 g/kg)	0.081	0.104	Background + Nd (2.0 mg/kg)	0.167	0.136
Background + МУ (2 g/kg)	0.090	0.111	Background + Nd (3.0 mg/kg)	0.175	0.160
			Background + Nd (4.0 mg/kg)	0.196	0.182

According to the value of CBA, lanthanum is characterized by weak (leaves) and medium (stems) levels of absorption in the top organs of corn (Table 2).

With an increase in intake of lanthanum from sulphate into corn roots, an increase in the productivity of the top mass of corn is observed with some decrease in the yield of roots. The absorption capacity of roots is likely to be higher in the case of La dose equal to 6 mg/kg of soil than in the case of a smaller dose of this element. For the introduction of lanthanum sorbed by zeolite (in the form of MF), we observe no increase in the top mass but a noticeable increase in the yield of roots and in lanthanum concentration in roots in comparison with the case of lanthanum introduced in the form of sulphate (Table 3).

So, it was shown in experiments that roots playing the role of a barrier for lanthanum intake into the top organs stimulate the development of the top mass of corn only to a definite level of lanthanum concentration in roots. When lanthanum concentration in roots is higher than 0.49 mg/kg of dry mass, a depression of the growth of plant top mass is observed.

Similarly to lanthanum, neodymium is distributed over corn leaves and stems uniformly somewhat increasing in the case of the higher dose (4 mg/kg of soil). La and Nd exhibit almost no differences in the concentrations in the top mass (see Table 1) but neodymium intake in roots is 2.0–2.5 times higher than that of lanthanum. With an increase in the dose of neodymium, a trend to a decrease in its concentration in roots is observed, which is in agreement with the results of the laboratory experiment.

The effect of different doses of neodymium on germination of corn seeds in an inert substrate (quartz sand) was determined. The experiment was carried out at the stage of the formation of two true leaves. It was established that with an increase in neodymium content from 0.5 to 6 mg/kg of sand the roots of plants got longer to the length of 13 cm as a mean (against 9 cm in the reference with neodymium dose 0.5 mg/kg of sand). However, an increase in the dose of neodymium caused thinning of corn roots while total root mass decreased.

According to the value of CBA, neodymium is characterized by a middle level of ab-

TABLE 3

Effect of lanthanum-containing microfertilizers on the bioproductivity of corn, g/vessel of dry mass

Version	Yield of top mass	Increase		Underground mass	
		g/vessel	%	Yield	Top/underground
NPK (background) - reference	59.4	–	–	26.0	2.3
Background + La (3 mg/kg)	63.0	3.6	11	29.0	2.2
Background + La (6 mg/kg)	68.8	9.4	16	27.1	2.5
Background + MF (1 g/kg)	60.2	0.8	1.3	32.2	1.9
Background + MF (2 g/kg)	58.0	–	–	34.6	1.7
$LSD_{0.5}$*	2.5				

*Least significance difference (test by Dospekhov [5]).

TABLE 4

Effect of neodymium on the yield of corn, g/vessel of dry mass

Version	Yield of top mass	Increase*	Underground mass	
			Yield	Top/underground
NPK (background) + reference	54.1	–/–	24.4	2.2
Background + Nd (0.5 mg/kg)	60.5	6.4/12	29.2	2.1
Background + Nd (1.0 mg/kg)	58.3	4.2/8	20.2	2.9
Background + Nd (2.0 mg/kg)	57.9	3.8/7.0	19.5	3.0
Background + Nd (3.0 mg/kg)	56.2	2.1/4	17.6	3.1
Background + Nd (4.0 mg/kg)	56.2	2.1/4	21	2.7
$LSD_{0.5}$	3.7			

*The first value: g/vessel, the second: percentage.

sorption in the top organs of corn (see Table 2). The barrier for neodymium income into the plants is at the level of root – top mass, too. More active increase in the vegetative mass of corn was observed for small doses of neodymium: 0.5 and 1.0 mg/kg of soil (Table 4). With further increase in dose, the yield of the top mass and especially of roots decreases, thus the ratio of top to underground mass increases.

In pea, the amount of lanthanum in the top mass does not differ much from the same parameter for corn (Table 5). Only a more noticeable increase in the element content with an increase in the dose of lanthanum in the form of sulphate from 3 to 6 mg/kg of soil is observed.

At the same time, it was established that lanthanum is accumulated in pea roots in the amount 4–5 times larger than that in the top mass. During a shorter vegetation period (30–35 days), the amount of lanthanum income into pea roots was 3–4 times more than that into corn roots during 60 days. Lanthanum sorbed by zeolite enters the roots with a lower activity when the dose of MF increases to 2 g/kg of soil. According to CBA value for top mass, pea is characterized by a low level.

The productivity of the top mass in all the versions turned out to be higher than in the reference, while an increase caused by lanthanum introduction in the form of MF varied within 23–29 % with respect to the reference (Table 6).

Neodymium content in the top mass of pea for the dose of 0.5 mg and above decreased by a factor of 2.3–2.8 in comparison with its introduction in a small dose (0.25 mg/kg) (see Table 5). Neodymium income into roots decreases most noticeably with an increase in the content of the element to 2.0 mg/kg. One can see from the data shown in Table 5 that for different doses and forms of introduction, the concentrations of lanthanum and neodymium in the top mass of pea do not change significantly; however, an increase in the top mass of pea under the action of neodymium is not so essential than that under the action of lanthanum. An increase in the dry top mass of pea

TABLE 5

Lanthanum and neodymium content of pea phytomass, mg/kg of dry mass

Version	Lanthanum		Version	Neodymium	
	Top mass	Roots		Top mass	Roots
NPK (background) – reference	0.27	1.08	NPK (background) – reference	0.32	1.12
Background + La (3 mg/kg)	0.31	1.19	Background + Nd (0.25 mg/kg)	0.39	1.39
Background + La (6 mg/kg)	0.34	1.61	Background + Nd (0.50 mg/kg)	0.17	1.43
Background + MF (1 g/kg)	0.33	1.26	Background + Nd (1.0 mg/kg)	0.14	1.36
Background + MF (2 g/kg)	0.33	1.25	Background + Nd (2 mg/kg)	0.14	0.86

TABLE 6

Effect of lanthanum-containing microfertilizers on the yield of pea top mass on gray forest soil, g/vessel of dry mass

Versions	Yield	Increase*
NPK (background)	22.7	–/–
Background + La (3 mg/kg)	28.2	5.5/24
Background + La (6 mg/kg)	29.3	6.6/29
Background + MF (1 g/kg)	27.9	5.2/23
Background + MF (2 g/kg)	28.4	5.7/25
$LSD_{0.5}$	1.3	

*The first value: g/vessel, the second: percentage.

over the reference (NPK background) did not exceed 7 %. The most efficient neodymium dose turned out to be 2 mg/kg of soil, that is, in the version involving the lowest neodymium content of pea roots and relatively low one in the top mass (see Table 5). According to the value of CBA, neodymium is characterized by the low level of income into the top mass of pea.

It was also established in experiments that lanthanum and neodymium, though in smaller amounts, enter the plants from the soil of the reference version (NPK background) where lanthanum and neodymium were not introduced. It is known that apatite is the raw material for the production of superphosphate. Mean RRE content of apatite-nepheline ores is 0.3–0.4 %, while apatite concentrate contains about 1.1 % R_2O_3 [7]. REE content of superphosphate obtained from this raw material may vary from 0.1 to 0.3 % [8], so plants extract not only phosphorus but also REE from the fertilizer.

CONCLUSIONS

On introduction of lanthanum and neodymium into soil, the income of these elements into corn and pea roots is several times greater than their income into the top organs. The biological barrier of REE concentrating in plants was established to exist at the level of root–top mass. According to the coefficient of biological absorption, lanthanum is characterized by low and medium levels of absorption. An increase in lanthanum concentration in corn roots above 0.49 mg/kg of dry mass causes depression of the growth of vegetative mass of plants. Neodymium has a positive effect on the development of corn in small doses (0.5 mg/kg of soil); with an increase in the dose, the top mass yield decreases. According to the coefficient of biological absorption, neodymium is characterized by the medium level. For the corresponding doses, neodymium content of pea roots is 1.4–1.6 times higher than that in corn roots. Neodymium income into the roots and top mass decreases already for its dose 1.0 mg/kg of soil. Pea is more sensitive to an increased neodymium content in the nutrient medium than corn is. According to the coefficient of biological absorption, neodymium is characterized by weak absorption by the pea top mass. The data obtained confirm previously formulated conclusions [2, 9, 10].

It was demonstrated that lanthanum and neodymium in small doses (0.5–3 mg/kg of soil) activate nitrogen exchange, stimulate the income of potassium, calcium into the top mass of corn and pea, and improve forage characteristics of the plants. The effect of lanthanum on soil is activation of microbiological functioning, elevation of nitrifying ability, which is an index of the biological activity of the investigated microdoses of REE.

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