

## Rare Earth Element Distribution (La, Nd, Sm) in the Aerial Phytomass and Roots of Pasture Herbage for Different Methods of Introducing REE into Soil

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### Abstract

It has been established that the biological absorption coefficient for rare-earth elements corresponds to a low entrapment level inherent in the aerial phytomass of pasture herbage. The content of lanthanum, neodymium and samarium in the aerial phytomass of a natural pasture of the Transbaikalian cryozone is 2.3–4.5 times lower than that in roots.

**Key words:** cerium, neodymium, samarium, chestnut soil profile, mobile elemental species

### INTRODUCTION

It is known, that the content of the majority of rare-earth elements (REE) in aerial phytomass does not exceed 3–15 mg/kg with respect to dry solid matter [1–6]. The most high REE concentration level is registered for lichens, mosses, ferns (up to 30–40 mg/kg of dry solid matter) [2]. REE distribution in different organs of plants [1, 4] has not been adequately investigated. Data published indicate that an influence of biological features of plants and the conditions of plant growth upon the absorption of REE occurs. The determination of the REE content level of in forage crops is important from the standpoint of estimating sanitary-and-hygienic standards as well as biological and biogeochemical role of REE, since a number of papers describes a negative influence of REE upon photosynthesis in plants and upon physiological processes in the cells of organisms [2–4]. REE cations tend to substitute

calcium in cellular membranes of such plants as peas and rape influencing the activity of  $\alpha$ -amylase and NAD kinase are capable to penetrate into chloroplasts and to bind with chlorophyll then substituting magnesium and forming REE-containing chlorophyll [5–7].

The purpose of the present work consisted in the investigation of lanthanum, neodymium and samarium distribution in the aerial mass and roots of pasture herbage for different methods of introducing REE into soil, as well as the determination of the biological absorption coefficient (BAC) for plants from the content of REE in plant ash and in soil.

### EXPERIMENTAL

The studies were carried out under field conditions with the allotment size amounting to 1 m<sup>2</sup> on a natural pasture of the Northern Transbaikalia (the Eravnino depression, Buryatia). The registration area of the allotments was

equal to 1 m<sup>2</sup> with the shelterbelt of 0.5 m in width. The replication of the experiments was quadruple. There is a sparse growth of plants on the experimental plot of a sedge-bluegrass pasture, the specific composition of the plant growth is few in number; the age structure is presented by perennial plants, with the prevalence of xerophytes.

The ground of the experimental plot represented sod-gley permafrost soil with the following initial characteristics (the layer of 0–20 cm): pH<sub>H2O</sub> 6.9, humus content 6.1 %, total nitrogen content 0.35 %, mobile species of P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O (according to Machigin) being equal to 2.63 and 6.75 mg/100 g of soil, respectively; the cation exchange capacity amounting to 40 mg-eq/100 g of soil. The total content of individual REE in soil amounted to 23.47 mg/kg for lanthanum, 8.83 mg/kg for neodymium, and 1.64 mg/kg for samarium. The content of mobile REE species amounted to (mg/kg): 0.85 for La, 0.48 for Nd, 0.13 for Sm.

Rare-earth elements were introduced into the soil against the background of complete mineral fertilizing (the background represented N<sub>40</sub>P<sub>40</sub>K<sub>40</sub>) in the form of lanthanum, neodymium and samarium sulphates (REE<sub>3</sub> и REE<sub>6</sub>) at a doze equal to 3 and 6 mg/kg of soil as calculated for an RE element and as a microfertilizer MF (REE<sub>3</sub> и REE<sub>6</sub>) obtained by means of the sorption technology *via* the saturation of natural mordenite-containing tuff in 0.01 % solutions of lanthanum, neodymium and samarium sulphates during 32 h.

The content of REE in mordenite-containing tuff is equal to 3 mg/g zeolite [6]. We introduced into soil either 1 or 2 g of REE-containing zeolite per 1 kg of soil.

The reference background represented a variant whereby we introduced into soil each of NH<sub>4</sub>NO<sub>3</sub>, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and KCl in 40 kg/ha.

In order to obtain MF according to the sorption technology, as a sorbent we used mordenite-containing tuff taken from the Mukhor-Tala perlite and zeolite deposit (Buryatia), with the following composition, %: SiO<sub>2</sub> 70.96, Al<sub>2</sub>O<sub>3</sub> 11.97, MgO 0.18, CaO 0.92, Na<sub>2</sub>O 2.38, K<sub>2</sub>O 5.22. The ratio Si/Al = 5.2 [3]. The mass fraction of zeolite in the tuff amounted to 60–62 %. The grain size of tuff 1–2 mm, the mass ratio between zeolite and the solution of REE sulphate was equal to 1 : 10.

The total content of REE in soil was determined after decomposition by a mixture of acids such as HF, HNO<sub>3</sub> and HCl. Mobile REE species were determined in an extract of ammonium acetate buffer solution (pH 4.8) [6, 8]. The determination of REE in plant samples was carried out after dry ashing with a subsequent atomic absorption analysis using an AAS S0LAAR M6 spectrophotometer. An acetylene-air mixture was used for the flame-atomizing procedure.

Data concerning the productivity of phytomass and the content of REE in phytocenosis were processed by means of the dispersion method [9]. The biological absorption coefficients were determined according to A. I. Perelman [10] as a ratio between the content REE in plant ash and the REE content in soil.

TABLE 1

Content of rare-earth elements in pasture herbage phytomass, mg/kg of dry solid matter

Variants	Lanthanum		Neodymium		Samarium	
	Aerial phytomass	Roots	Aerial phytomass	Roots	Aerial phytomass	Roots
N <sub>40</sub> P <sub>40</sub> K <sub>40</sub> (background)	0.32±0.009	0.83±0.021	0.18±0.004	0.61±0.011	0.06±0.001	0.27±0.006
Background + zeolite	0.30±0.008	0.81±0.020	0.15±0.004	0.57±0.010	0.06±0.001	0.25±0.004
Background + REE <sub>3</sub>	0.34±0.009	0.91±0.022	0.21±0.003	0.64±0.011	0.08±0.001	0.31±0.007
Background + REE <sub>6</sub>	0.35±0.007	0.98±0.024	0.25±0.004	0.67±0.012	0.09±0.002	0.38±0.008
Background + MF (REE <sub>3</sub> )	0.31±0.008	0.81±0.021	0.22±0.005	0.64±0.011	0.09±0.002	0.32±0.006
Background + MF (REE <sub>6</sub> )	0.33±0.009	0.84±0.022	0.21±0.004	0.60±0.012	0.10±0.002	0.37±0.009

TABLE 2

Influence of lanthanum-, neodymium- and samarium-containing microfertilizers upon pasture herbage bioproductivity

Variants	Lanthanum		Neodymium		Samarium	
	Crop yield, c/ha	Crop increase, % of the reference	Crop yield, c/ha	Crop increase, % of the reference	Crop yield, c/ha	Crop increase, % of the reference
N <sub>40</sub> P <sub>40</sub> K <sub>40</sub> (back-ground)	12.6	–	12.3	–	12.2	–
Background + zeolite	13.4	6.3	13.8	12.2	14.5	18.8
Background + REE <sub>3</sub>	14.5	15.1	14.2	15.5	13.5	13.1
Background + REE <sub>6</sub>	14.8	17.5	14.3	16.3	12.9	5.7
Background + MF (REE <sub>3</sub> )	15.3	21.4	14.7	19.5	13.0	6.6
Background + MF (REE <sub>6</sub> )	15.8	25.4	14.9	21.1	14.3	17.2
HCP <sub>0.5</sub>	0.22		0.28		0.19	

## RESULTS AND DISCUSSION

The results of the investigations demonstrate that the introduction of lanthanum, neodymium and samarium into soil at various doses and in different forms causes the REE content in herbage to increase (Table 1). It should be noted that the content of REE in roots is 2.3–4.5 times higher as compared to that in aerial phytomass irrespective of the nature of a rare-earth element, which indicates the active barrier role of the roots of pasture phytocenoses. One could reveal that the REE entry from sulphate is somewhat higher than that from MF; thus, the REE absorbed are to a much less extent accessible for plants than those introduced in the form of sulphate. This fact could be caused by a good solubility of sulphates in the soil solution (*i. e.* in the liquid phase of soils), since these REE ions are to a lesser extent fixed by soil as compared to REE ions introduced into a natural zeolite matrix in the process of obtaining microfertilizers via the sorption technology.

As the result the investigations we have established that the level of REE absorption by the aerial phytomass of the pasture herbage is nit high. The biological absorption coefficient inherent in the aerial phytomass is equal only to 0.12–1.14 for lanthanum, 0.22–0.25 for neodymium and 0.44–0.55 for samarium.

Introducing the microfertilizers containing REE promotes an increase in the productivity of pasture herbage within the range of 5.7–

25.4 %. The application of zeolite modified by lanthanum, neodymium and samarium allows one to increase the herbage productivity to a considerable extent, particularly with the introduction of lanthanum-containing microfertilizers: the productivity increase with respect to the reference in this case amounted to 21.4–25.4 %. In the case of neodymium-containing microfertilizer the productivity increase against the reference was equal to 19.5–21.1 %, whereas for samarium-containing microfertilizer this value amounted to 6.6–17.2 %.

Thus, we have established under field conditions that the roots playing the role of a barrier for REE entry stimulate the development of the aerial mass of pasture herbage. The content of REE in roots in amounts of 0.25–0.98 mg/kg with respect to dry solid matter no inhibition of aerial organs is observed to occur in pasture phytocenoses. Depending on the nature of REE, there is a difference revealed concerning the accumulation of an element both in the aerial, and in the root phytomass.

The increase in the dose of neodymium up to 6 mg/kg with the application of modified zeolite has been noted to result in a decrease of its accumulation level in the aerial phytomass and roots of the phytocenosis (see Table 1).

Samarium adsorbed onto zeolite enters into roots and aerial mass with a lower activity than adsorbed lanthanum and neodymium. When samarium in the form of sulphate is introduced, a minimal (5.7 %) increase in pasture herbage

productivity is observed (Table 2). It could be assumed that at the content of samarium in roots amounting to 0.38 mg/kg with respect to dry solid matter a decrease in the growth intensity of herbage aerial mass is observed. For a great accumulation level in roots (0.81–0.98 mg/kg for lanthanum, 0.60–0.67 mg/kg for neodymium) such a tendency is not pronounced.

#### CONCLUSION

The introduction of REE into soil results in the fact that the level of REE entering into roots is 2.3–4.5 times higher as compared to the level of REE entering into the aerial mass of pasture phytocenosis plants. The biological barrier of REE entering into plants is established to be at the level between the root and aerial phytomass. As far as the biological absorption coefficient is concerned, lanthanum, neodymium and samarium are characterized by a low entrapment level. Pasture crops absorb samarium in a

more active manner when one introduces this element in the form of sulphate. Increasing the doze of samarium up to 6 mg/kg corresponds to a minimal (by 5.7 %) increase in the productivity of pasture herbage.

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