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Original article

PHOSPHATE FERTILIZERS MARKETED IN RUSSIA AS A SOURCE OF RARE EARTH ELEMENTS IN THE SOIL

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Phosphate fertilizers actively used in agriculture can serve as a source of various impurities in the soil, which can have a negative impact on environmental components. In this work, the content of rare earth elements (REEs) in phosphate fertilizers marketed in Russia was evaluated. REEs are a group of elements that are actively studied due to possible negative and positive effects on living organisms. Currently, there are no standards for the content of REEs in soil and fertilizers. Also, in the literature there are no data on REEs content in phosphate fertilizers marketed on the territory of Russia and assessment of the significance of fertilizer application as a factor of REEs input into agricultural soils. Using the method of optical emission spectrometry with inductively coupled plasma, we obtained data on the REEs content in samples of phosphate rock, single and double superphosphate (22 samples). It is shown that phosphate fertilizers can differ significantly in REEs content, high REEs content (over 1000 mg/kg) was observed in some samples of single and double superphosphate. The group of phosphate rock samples is the most homogeneous in terms of REE content in the samples. Light REEs predominate over heavy REEs in the composition of fertilizers. According to the results of the study, it can be concluded that there is potentially no significant effect of the application of the studied phosphate fertilizers on the REEs content in the soil. However, the high REEs content in some fertilizer samples requires monitoring of REEs content in soils of agrocenoses, as well as the development of standards for REE content in mineral fertilizers.

Keywords: mineral fertilizers; impurities; lanthanides; phosphate rock; superphosphate

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Научная статья

ФОСФОРНЫЕ УДОБРЕНИЯ, РЕАЛИЗУЕМЫЕ В РОССИИ, КАК ИСТОЧНИК ПОСТУПЛЕНИЯ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В ПОЧВУ

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Активно применяемые в сельском хозяйстве фосфорные удобрения могут служить источником поступления в почву различных примесей, способных оказывать негативное воздействие на компоненты окружающей среды. В работе проведена оценка содержания редкоземельных элементов (РЗЭ) в фосфорных удобрениях, реализуемых на территории России. РЗЭ – группа элементов, которая активно изучается в связи с возможными как негативными там и положительными эффектами влияния на живые организмы. На настоящий момент не разработаны нормативы содержания РЗЭ в почве и удобрениях. Также в литературе отсутствуют данные о содержании РЗЭ в фосфорных удобрениях, реализуемых на территории России, и оценка значимости внесения удобрений как фактора поступления РЗЭ в сельскохозяйственные почвы. С применением метода оптико-эмиссионной спектроскопии с индуктивно-связанной плазмой получены данные о содержании РЗЭ в образцах фосфоритной муки, простого суперфосфата и двойного суперфосфата (выборка включала 22 образца). Показано, что фосфорные удобрения могут существенно различаться по содержанию РЗЭ, высокое содержание РЗЭ (свыше 1000 мг/кг) отмечалось в отдельных образцах простого и двойного суперфосфата. Группа образцов фосфоритной муки наиболее однородна по содержанию РЗЭ в образцах. Легкие РЗЭ преобладают в составе удобрений над тяжелыми РЗЭ. По результатам проведенного исследования, можно сделать вывод о потенциальном отсутствии существенного влияния применения изученных фосфорных удобрений на содержание РЗЭ в почве. Однако, высокое содержание РЗЭ в некоторых образцах удобрений требуют мониторинга содержания РЗЭ в почвах агроценозов, а также разработки нормативов содержания РЗЭ в минеральных удобрениях.

Ключевые слова: минеральные удобрения; примеси; лантаноиды; фосфоритная мука; суперфосфат

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Introduction

Phosphate fertilizers are among the most widely used fertilizers in the world, with demand reaching 47.4 million tons in 2020 and growing [5]. The need to consider fertilizer use as a potential source of contamination of agricultural soils and the surrounding environment has been recognized by researchers for some time [15]. While existing standards mainly define nutrient standards for fertilizers, some countries have developed standards for heavy metals in fertilizers. However, it should be noted that the use of fertilizers can be a source not only of heavy metals but also of rare earth elements [14].

The rare earth elements (REEs) are a group of metals that have attracted particular attention in recent decades. This group includes: Ce, La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y [2]. The applications of REEs and their importance to the global economy are detailed in the literature [2; 4; 12]. In addition to exploring their beneficial properties, many studies have been carried out on the effects of REEs on living organisms and ecosystem components due to their increasing concentrations in the environment [3; 6; 16]. Despite the controversy, there is more consensus among researchers about the negative effects of high concentrations of REEs on organisms and the possible hormesis effect of low concentrations. In this respect, the presence of REEs in fertilizers can be a positive factor, contributing additionally to plant growth and development, as has been shown in a number of studies [20]. On the other hand, in the case of long-term use, REEs may accumulate in the soil and it is then necessary to assess the permissible concentrations in the soil and the safety of the products, since they may be transferred to plants [18; 25; 26]. In addition to the total content, it is also important to get an idea of the bioavailability of REEs from mineral fertilizers, as this is not established and can be one of the criteria for assessing the quality of mineral fertilizers.

Limestone, a component of superphosphate fertilizers, contains REEs in the form of impurities, which are expected to increase their concentrations in soil and plants with long-term use of phosphate fertilizers [1; 7]. The concentration of REEs in apatite has been estimated and may exceed 1600 mg/kg, or 9000 mg/kg according to other sources due to the replacement of calcium by these elements [20]. It has been shown that up to 50-60% of the REEs is transferred to the superphosphate during the production of fertilizers from this raw material [18]. Superphosphate produced from Kola Peninsula apatite has been shown to have a total REEs content of approximately 2600 mg/kg [24]. According to the results of the Egyptian researchers, the REEs content of the superphosphate was La – 18.09 mg/kg, Ce – 8.55 mg/kg, Eu – 0.33 mg/kg [1], which is significantly lower than

for superphosphate produced from apatite from the Kola Peninsula. Australian phosphate fertilizers contain an average of 45.2 mg/kg La and 61.0 mg/kg Ce [9].

Thus, it is currently known that the REEs content of phosphate fertilizers can vary considerably. Existing work on the assessment of the REEs content of phosphate fertilizers is sparse and does not provide an indication of the possible input of these elements to the soil for different areas. There are references in the literature to high REE content in phosphate fertilizers produced from Russian raw materials, which can be explained by the high REE content of the raw materials. Russian phosphate rock is estimated to contain 2150 mg/kg La, 3420 mg/kg Ce, 131 mg/kg Sm and 54 mg/kg Eu [21]. These rocks appear to be significantly enriched in REEs, with average crustal contents of La 30-35 mg/kg, Ce 64-66 mg/kg, Sm 4.5-7 mg/kg, Eu 0.8-2.1 mg/kg [8; 23]. The aim of the work is to assess the REE content in a number of phosphate fertilizers marketed in Russia and to evaluate their potential inputs into soils of agrocenoses.

Materials and methods

Fertilizer samples. Samples of phosphate fertilizers of different brands available on the local market were purchased for the study. A selection of 22 samples representing three groups of fertilizers was obtained: rock phosphate (RP, 6 samples), single superphosphate (SSP, 8 samples) and double superphosphate (DSP, 8 samples). The short designation of the samples used in the following text and the phosphorus content according to the manufacturer's specifications are given in Table 1.

Determination of total REEs content in fertilizer samples. The fertilizer samples were ground in a ball mill using agate bowls and balls. To avoid cross-contamination of the samples during sieving, a special sieve was designed and 3D printed. Circles cut from 0.5 mm mesh sieve cloth were placed in the sieve and the sample bag was attached. In this way, contact of the samples with the surface of the sieve and of the samples with each other was avoided.

To determine the total REEs content of the fertilizer samples, a complete acid digestion of the samples was carried out. A sample of fertilizer (0.2-0.25 g) was placed in a PTFE beaker, moistened with a few drops of distilled water and a mixture of concentrated acids (1 ml HNO₃, 1 ml HClO₄ and 6 ml HF) was added. The beakers were placed on a hotplate, covered with a PTFE lid, brought to the boil and heated for 30 minutes. The lids were then removed and evaporated until an intense white vapor appeared. The beakers were removed from the hotplate, cooled, washed on the walls with a small amount of distilled water and evaporated again to wet salts. Then 4 ml of HCl and 0.4 ml of H₃BO₃ were

added to each beaker, placed on a hotplate and evaporated to 1-2 ml. The solutions were transferred to 10 ml plastic tubes and made up to the mark with distilled water. Acid digestion of the fertilizer samples was carried out in triplicate.

The solutions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (5800 ICP-OES, Agilent Technologies, USA). Concentrations of REEs group representatives were determined: light REE (LREE) subgroup – La, Ce, Pr, Nd, Sm, Eu; heavy REEs (HREEs) subgroup – Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. Sc is most often excluded from consideration due to its small ionic radius, and Pm has no stable isotopes [13].

Solubility of REEs in fertilizer samples. The aqueous extract was prepared at a ratio of 1:5 fertilizer sample to distilled water. The samples were shaken on a rotator at 230 rpm for one hour and then centrifuged at 4000 rpm for 10 minutes. To prepare the citric acid extract, 100 ml of a 2% citric acid ($C_6H_8O_7$) solution was added to 1 g of fertilizer. The samples were shaken in a rotator at 230 rpm for 15 minutes and then centrifuged at 4000 rpm for 6 minutes. Extraction was carried out in triplicate for each sample.

The solutions were analyzed by ICP-OES (5800 ICP-OES, Agilent Technologies, USA). REEs solubility was defined as the ratio of the concentration of soluble forms of elements to the total content in the fertilizer sample, expressed as a percentage [22].

Statistical analysis. Mean values and 95% t-confidence intervals were calculated using the STATISTICA 10.0 program.

Results and discussion

Analysis of the samples provided data on the REEs total content of phosphate fertilizers (Fig. 1). A subgroup of RP samples is the most homogeneous in terms of REEs content, with the maximum total content of REEs found in sample RP-3 (359 ± 25 mg/kg). In the subgroups of SSP and DSP samples, there were samples with significantly higher REEs concentrations. Three SSP samples (SSP-4, SSP-6, SSP-7) and two DSP samples (DSP-5, DSP-8) stand out with the maximum total REEs content in sample SSP-7 – 3467 ± 134 mg/kg. The average Σ REEs content of the Earth's crust is 189 mg/kg, and most uncontaminated soils are close to this [11; 19; 27]. Thus, most of the phosphate fertilizer samples analyzed appear to be comparable to the Earth's crust and soils in terms of total REEs content. However, in a number of samples the excess over the average content in the Earth's crust was 5 to 18 times. Differences in REEs concentrations between fertilizer samples may be due both to differences in the raw material used for production and to the specifics of the production process [19].

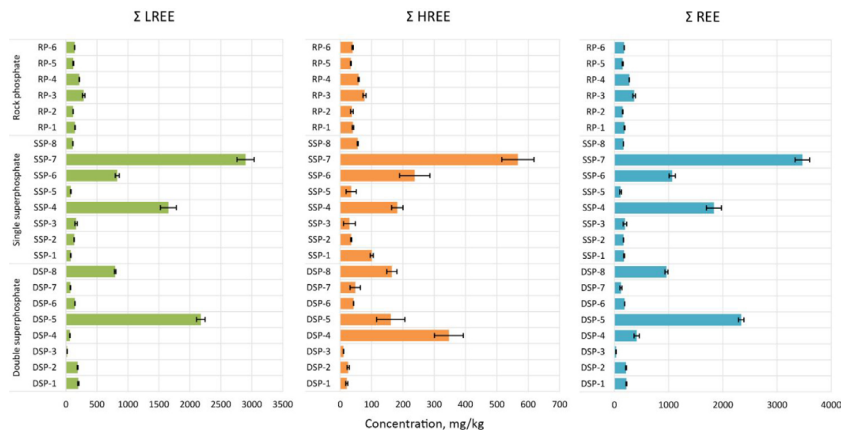


Fig. 1. Total content of LREE subgroup, HREE subgroup and total REE content in phosphate fertilizer samples.

We do not have information on the raw materials used to produce the fertilizers. However, we can be confident that most of Russia's phosphate rock deposits are of igneous origin. And these igneous ores – apatite ores – are mainly used to produce superphosphate and double superphosphate, while phosphate rock fertilizer is essentially ground phosphate ores – sedimentary ores. The origin of the raw materials can largely determine the REEs content of phosphate fertilizers. The absence of phosphate rock fertilizer samples (sedimentary origin) with extremely high REEs concentrations in our samples is in line with data reported by Brazilian researchers, who show higher concentrations in samples of igneous origin compared to sedimentary origin [22].

In most of the fertilizer samples the total content of the LREEs representatives fell into the pattern $Ce > Nd \approx La > Pr > Sm \approx Eu$ (the order of Sm and Eu varied greatly from sample to sample). The exceptions were two samples (SSP-3, DSP-2) in which the Ce content was below the detection limit, the La concentration was relatively low and the dominant element was Nd. It is noteworthy that both samples are sold under the same brand name. Both samples also have an extremely low phosphorus content and the highest pH among the samples analyzed (Table 1). The manufacturer of these fertilizers appears to have introduced methods to extract valuable REEs from the raw materials used. However, this extraction process may have significantly reduced the phosphorus content of the fertilizer produced. The order of HRREs content in the fertilizer samples was predominantly in the ratio $Y > Gd > Dy > Er > Yb > Tb > Ho > Lu > Tm$ (with a predominance of Gd or Dy in

some samples). The resulting patterns are generally characteristic of the distribution of REEs in the Earth’s crust, with LREEs predominating over HREEs, which are much less abundant [27]. This distribution pattern is due to the Oddo-Harkins rule, which states that the concentration of a rare earth element decreases with increasing atomic number [22]. An exception was the double superphosphate sample DSP-4, in which the proportion of LREEs from total REEs content was 16% due to relatively high concentrations of Y and Gd.

	Ce	La	Nd	Pr	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	
Rock phosphate	RP-1	57.8 ±2.9	26.2 ±1.3	41.7 ±3.0	13.7 ±0.8	0.5 ±0.8	1.6 ±0.1	3.7 ±0.5	1.3 ±0.4	3.8 ±0.1	26.0 ±2.2	0.7 ±0.1	2.8 ±0.2	<0.4	2.3 ±0.1	0.2 ±0.2
	RP-2	47.7 ±2.1	22.0 ±0.1	30.7 ±1.5	10.7 ±0.4	0.3 ±0.5	1.3 ±0.1	7.6 ±4.1	0.2 ±0.3	3.0 ±0.2	22.0 ±1.0	0.7 ±0.1	2.0 ±0.1	<0.4	1.9 ±0.1	<0.4
	RP-3	133.3 ±11.5	45.3 ±2.1	66.3 ±4.0	30.0 ±1.7	3.1 ±1.0	3.2 ±1.0	7.4 ±1.2	1.7 ±0.4	6.1 ±0.3	51.7 ±3.2	1.4 ±0.1	4.8 ±0.4	<0.4	3.8 ±0.3	0.7 ±0.1
	RP-4	100.0 ±0.1	35.3 ±0.6	50.0 ±1.0	21.7 ±0.6	1.8 ±1.2	2.4 ±0.1	4.7 ±2.0	<0.4	3.9 ±0.1	41.3 ±0.6	1.2 ±0.2	3.8 ±0.1	<0.4	3.3 ±0.1	0.6 ±0.1
	RP-5	32.0 ±3.6	17.0 ±1.5	20.0 ±1.0	7.4 ±0.5	0.2 ±0.6	0.6 ±0.1	20.2 ±0.3	<0.4	1.5 ±0.1	11.1 ±1.2	0.5 ±0.1	0.9 ±0.2	<0.4	1.0 ±0.1	<0.4
	RP-6	58.0 ±2.0	25.7 ±0.6	38.3 ±0.6	13.0 ±0.1	0.2 ±0.3	1.3 ±0.1	2.1 ±1.5	1.0 ±0.2	3.6 ±0.1	27.0 ±0	0.7 ±0.1	2.7 ±0.1	<0.4	2.3 ±0.1	0.3 ±0.3
Single superphosphate	SSP-1	17.3 ±1.2	27.0 ±1.7	19.0 ±1.0	5.2 ±0.6	2.4 ±0.3	1.1 ±0.1	3.1 ±0.9	1.3 ±0.2	5.4 ±4.2	77.7 ±2.2	1.6 ±0.2	5.0 ±0.3	<0.4	5.6 ±0.3	1.2 ±0.1
	SSP-2	52.7 ±3.1	23.7 ±1.2	38.0 ±2.6	12.3 ±0.6	0.2 ±0.4	1.5 ±0.1	1.1 ±1.8	1.1 ±0.1	3.4 ±0.1	24.3 ±0.6	0.7 ±0.2	2.3 ±0.3	<0.4	2.1 ±0.1	0.1 ±0.2
	SSP-3	<0.4	7.8 ±0.6	150.0 ±17.3	3.4 ±0.2	0.2 ±0.4	0.5 ±0.1	21.3 ±18.5	3.6 ±0.5	0.3 ±0.2	4.2 ±0.2	<0.4	<0.4	0.2 ±0.3	<0.4	<0.4
	SSP-4	723.3 ±70.9	406.7 ±30.6	313.3 ±15.3	180.0 ±10.0	19.0 ±1.0	9.4 ±1.1	10.6 ±15.1	<0.5	21.0 ±1.0	129.7 ±9.6	4.4 ±0.4	9.5 ±0.6	<0.4	6.0 ±0.4	1.0 ±0.1
	SSP-5	32.0 ±1.7	17.0 ±1.0	20.0 ±1.0	7.4 ±0.5	0.2 ±0.3	0.6 ±0.1	20.2 ±16.2	<0.4	1.5 ±0.1	11.1 ±0.3	0.5 ±0.1	0.9 ±0.2	<0.4	1.0 ±0.1	<0.4
	SSP-6	356.7 ±15.3	140.3 ±6.8	206.7 ±5.8	96.3 ±3.5	19.3 ±0.6	8.7 ±0.6	85.3 ±47.9	1.4 ±0.2	19.0 ±1.0	114.3 ±3.5	3.3 ±0.2	8.7 ±0.3	<0.4	5.0 ±0.2	0.8 ±0.1
	SSP-7	1233.3 ±57.7	496.7 ±28.9	723.3 ±32.1	340.0 ±17.3	73.7 ±1.5	33.0 ±1.7	41.0 ±58.9	7.9 ±0.4	69.7 ±2.9	386.7 ±11.5	13.5 ±0.6	30.3 ±1.5	1.0 ±0.1	15.0 ±1.0	2.0 ±0.1
	SSP-8	43.0 ±0.1	18.7 ±0.6	34.3 ±1.5	11.8 ±0.3	3.0 ±0.3	1.1 ±0.1	2.8 ±1.0	<0.5	3.1 ±0.1	46.0 ±2.6	0.4 ±0.4	2.1 ±0.1	<0.4	1.7 ±0	<0.4
Double superphosphate	DSP-1	80.0 ±10.0	39.3 ±2.5	50.0 ±7.2	20.3 ±1.2	4.7 ±0.4	1.8 ±0.2	2.5 ±4.3	0.1 ±0.2	5.6 ±0.4	4.8 ±0.3	0.9 ±0.3	3.6 ±0.1	<0.4	2.9 ±0.2	0.6 ±0.1
	DSP-2	<0.4	9.2 ±0.3	173.3 ±5.8	3.8 ±0.2	0.2 ±0.4	0.6 ±0.1	0.8 ±0.7	4.5 ±0.1	0.6 ±0.2	19.0 ±2.6	<0.4	0.4 ±0.4	0.3 ±0.3	<0.4	<0.4
	DSP-3	6.7 ±0.6	3.4 ±0.9	4.7 ±0.8	1.8 ±0.2	2.2 ±0.1	<0.4	1.1 ±0.1	<0.4	0.6 ±0.2	6.7 ±0.2	0.1 ±0.3	1.0 ±0.1	<0.4	1.1 ±0.1	<0.4
	DSP-4	25.7 ±1.2	15.4 ±0.6	16.3 ±1.2	5.9 ±0.6	0.2 ±0.4	0.5 ±0.1	54.4 ±46.1	<0.4	1.0 ±0.1	290.0 ±0.1	0.3 ±0.3	0.6 ±0.1	<0.4	0.6 ±0.1	<0.4
	DSP-5	933.3 ±57.7	363.3 ±5.8	543.3 ±11.5	253.3 ±5.8	56.0 ±0.1	23.7 ±0.6	31.3 ±46.5	4.9 ±0.8	51.7 ±0.6	27.7 ±0.6	9.6 ±2.2	22.7 ±0.6	0.7 ±0.1	11.4 ±0.1	1.5 ±0.1
	DSP-6	61.3 ±1.2	26.7 ±0.6	41.3 ±1.5	14.0 ±0.1	0.2 ±0.3	1.5 ±0.1	3.9 ±0.3	1.1 ±0.1	3.8 ±0.1	27.7 ±0.7	0.7 ±0.1	2.7 ±0.1	<0.4	2.4 ±0.1	0.3 ±0.3
	DSP-7	24.7 ±1.2	12.9 ±0.7	26.0 ±1.0	6.8 ±0.4	1.6 ±0.5	0.6 ±0.1	19.7 ±15.2	<0.4	2.1 ±0.1	23.0 ±1.0	0.2 ±0.3	1.6 ±0.1	<0.4	1.6 ±0.1	<0.4
	DSP-8	343.3 ±5.8	137.7 ±2.1	193.3 ±5.8	92.0 ±1.0	19.7 ±0.6	8.4 ±0.3	14.5 ±14.4	0.7 ±0.1	19.0 ±0.1	113.3 ±1.5	3.3 ±0.1	8.3 ±0.3	<0.4	4.9 ±0.1	0.7 ±0.1

Fig. 2. Heat map showing mean values and standard deviation (n=3) of REEs content in phosphate fertilizer samples, mg/kg (see designations in Table 1). For each column, darker color reflects higher REE content

Table 1.

**List of fertilizer samples analyzed in the study and their characteristics:
mass fraction of phosphorus according to the manufacturer's specifications,
pH of the aqueous suspension, and total phosphorus content**

Sample	Mass fraction of P ₂ O ₅ according to manufacturer's specifications, %	pH of aqueous suspension	P total concentration, mg/g
Rock phosphate (RP)			
RP-1	22	7.3	19.3±1.2
RP-2	22	7.5	17.0±1.0
RP-3	22	7.6	25.7±2.5
RP-4	22	7.3	29.7±1.2
RP-5	22	7.1	8.3±1.2
RP-6	17	6.6	22.0±0.1
Single superphosphate (SSP)			
SSP-1	20	3.5	35.0±2.6
SSP-2	29	8.2	17.3±0.6
SSP-3	26	9.6	0.5±0.1
SSP-4	30	3.5	33.7±3.8
SSP-5	26	7.2	8.3±0.6
SSP-6	26	7.0	44.3±5.1
SSP-7	26	4.5	33.3±2.3
SSP-8	26	6.6	24.3±0.6
Double superphosphate (DSP)			
DSP-1	35	4.5	38.7±2.5
DSP-2	46	9.8	0.6±0.1
DSP-3	49	6.3	31.0±2.6
DSP-4	36	7.1	3.8±0.2
DSP-5	41	5.3	26.3±0.6
DSP-6	46	7.1	22.0±0.1
DSP-7	44	6.6	24.3±1.5
DSP-8	48	6.9	41.0±1.7

Currently, there are no developed standards for REEs content in both soils and mineral fertilizers. In Russia, regulatory document GOST R 58658-2019 regulates the permissible content of the following impurities in mineral fertilizers: Cd, Hg, As, Ni, Pb, Cr (VI), Cu, Zn. Calculating the impurity content per percentage point of P₂O₅ in the fertilizer can be used as an approach to estimating the impurity content of fertilizers. For example, some authors suggest using a threshold of 40 mg/kg per percentage point of P₂O₅ in the fertilizer (the value for Cr established in Brazilian legislation) for the approximate assessment of the REE content in fertilizers [22]. Fig. 3 shows the results of such calculation for

the studied fertilizer samples. Data are presented only for the LREEs subgroup, since the content of heavy REEs in fertilizers is lower than that of light REEs. The increased value is noted for Ce concentration in sample SSP-7 (47.4 ± 2.2 mg $\text{kg}^{-1}/\% \text{P}_2\text{O}_5$). The values of Nd concentration in the same sample (27.8 ± 1.2 mg $\text{kg}^{-1}/\% \text{P}_2\text{O}_5$), as well as Ce concentration in samples SSP-4 and DSP-5 (27.8 ± 2.7 and 20.3 ± 1.3 mg $\text{kg}^{-1}/\% \text{P}_2\text{O}_5$, respectively) also fall within the range of 20 to 40 mg/kg/% P_2O_5 . Thus, 97% of the calculated REEs concentrations in the studied fertilizer samples were below the proposed threshold of 20-40 mg $\text{kg}^{-1}/\% \text{P}_2\text{O}_5$.

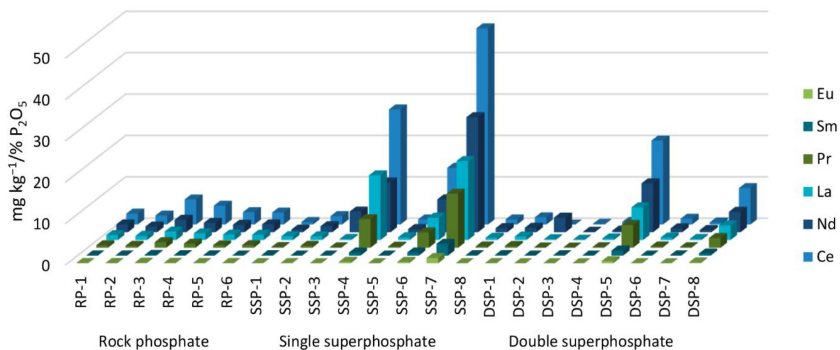


Fig. 3. LREEs content in phosphate fertilizer samples per % of fertilizer phosphorus content

To assess the possible REEs input into the soil with phosphate fertilizers, the potential REEs input per unit area (hectare) was calculated using the maximum dose recommended by the manufacturers (Table 2). Despite the different fertilizer masses required for the same dose of active ingredient, the maximum possible REE input with fertilizer per unit area is also observed for the samples with the highest REE content (RP-3, SSP-4, SSP-6, SSP-7, DSP-5).

If we calculate the value by which the concentration of REEs in soil will increase with annual application of phosphorus fertilizers to the surface layer of soil (0-20 cm) per one hectare of area for 100 years, these values will be insignificant in comparison with the average known concentrations of REEs in soil (Table 2). Total REEs content in the surface layer of uncontaminated soil can be as high as 100-200 mg/kg [10, 17]. The maximum possible increase in the Σ REE content will be 47 mg/kg when simple superphosphate (SSP-7) is applied. It should be noted, however, that this value will actually be even lower due to leaching of REEs into the underlying soil layers and partial removal with biomass, which will vary for different crops.

Table 2.

REEs input to the soil from a single application of fertilizer at the maximum dose recommended by the manufacturer (g/ha) and potential added REE concentration after 100 years of fertilizer application in the 0-20 cm soil layer

Group	Sample	Element																	Potential added Σ REEs concentration over 100 years of fertilizer application, mg/kg	
		Ce	Eu	La	Nd	Pr	Sm	Dy	Er	Gd	Ho	Lu	Tb	Tm	Yb	Y	Σ LREEs	Σ HREEs		Σ REEs
RP	RP-1	87	2	39	63	21	2	6	4	6	1	0	2	0	3	39	214	61	275	5
	RP-2	72	2	33	46	16	1	4	3	11	1	0	0	0	3	33	170	56	226	4
	RP-3	200	5	68	100	45	5	9	7	11	2	1	3	0	6	78	422	116	538	10
	RP-4	150	4	53	75	33	3	6	6	7	2	1	0	0	5	62	317	88	405	8
	RP-5	26	0	14	16	6	0	1	1	16	0	0	0	0	1	9	62	28	90	2
	RP-6	87	2	39	58	20	1	5	4	3	1	0	2	0	4	41	205	60	265	5
SSP	SSP-1	14	1	22	15	4	2	4	4	2	1	1	1	0	4	62	58	81	138	3
	SSP-2	37	1	17	27	9	0	2	2	1	0	0	1	0	1	17	90	25	115	2
	SSP-3	0	0	2	41	1	0	0	0	6	0	0	1	0	0	1	44	8	52	1
	SSP-4	217	3	122	94	54	6	6	3	3	1	0	0	0	2	39	496	55	550	11
	SSP-5	22	0	12	14	5	0	1	1	14	0	0	0	0	1	8	54	25	79	2
	SSP-6	250	6	98	145	67	14	13	6	60	2	1	1	0	4	80	580	167	746	14
	SSP-7	863	23	348	506	238	52	49	21	29	9	1	6	1	11	271	2030	397	2427	47
	SSP-8	30	1	13	24	8	2	2	1	2	0	0	0	0	1	32	78	39	118	2
DSP	DSP-1	24	1	12	15	6	1	2	1	1	0	0	0	0	1	1	59	6	65	1
	DSP-2	0	0	3	52	1	0	0	0	0	0	0	1	0	0	6	56	8	64	1
	DSP-3	2	0	1	1	1	0	0	0	0	0	0	0	0	0	2	6	3	9	0
	DSP-4	14	0	8	9	3	0	1	0	30	0	0	0	0	0	160	35	191	226	4
	DSP-5	560	14	218	326	152	34	31	14	19	6	1	3	0	7	17	1304	97	1401	27
	DSP-6	28	1	12	19	6	0	2	1	2	0	0	0	0	1	12	65	19	85	2
	DSP-7	7	0	4	8	2	0	1	0	6	0	0	0	0	0	7	22	14	36	1
	DSP-8	103	3	41	58	28	6	6	2	4	1	0	0	0	1	34	238	49	288	6

Evaluation of the solubility of REEs in phosphate fertilizers allows estimation of the potential mobility of REEs. Only Ce and Sm were detected in the aqueous extract of the fertilizer samples. The water solubility of REEs in fertilizers did not exceed 1% for the whole sampling (Table 3). REEs solubility in 2% citric acid was significantly higher for most of the phosphate fertilizer samples. At the same time, for a number of fertilizer samples (SSP-3, SSP-7, DSP-3, DSP-6), including the sample of simple superphosphate with the highest total REEs concentration (SSP-7), the REEs solubility was rather low – 1-6%. Thus, the subgroup of rock phosphate samples appears to be more homogeneous with

respect to the potential mobility of the REEs contained in phosphate fertilizers compared to the single and double superphosphate subgroups.

Table 3.

Solubility of REEs contained in phosphate fertilizers in water and citric acid solution

Group	Sample	Water solubility Σ REEs, %	Acid solubility Σ REEs, %
RP	RP-1	0.0	40
	RP-2	0.2	44
	RP-3	0.2	27
	RP-4	0.1	27
	RP-5	0.0	52
	RP-6	0.0	36
SSP	SSP-1	0.7	35
	SSP-2	0.3	42
	SSP-3	0.0	5
	SSP-4	0.0	26
	SSP-5	0.7	65
	SSP-6	0.0	86
	SSP-7	0.0	1
	SSP-8	0.2	96
DSP	DSP-1	0.1	97
	DSP-2	0.0	6
	DSP-3	0.0	133
	DSP-4	0.0	16
	DSP-5	0.0	3
	DSP-6	0.0	35
	DSP-7	0.2	78
	DSP-8	0.0	97

Conclusions

The study allowed us to obtain data on the REEs content in samples of phosphate rock, single superphosphate and double superphosphate. It is shown that the group of phosphate rock samples is the most homogeneous in terms of REEs content. At the same time and within this group of samples, the difference between the maximum (359 ± 25 mg/kg) and minimum (151 ± 8 mg/kg) REEs content exceeded 2 times. Among the samples of single and double superphosphate, the samples with significantly higher REE content – up to 3467 ± 134 mg/kg in single superphosphate and up to 2334 ± 51 mg/kg in double superphos-

phate, the minimum values were 112 ± 16 and 29 ± 3 mg/kg, respectively. The predominance of the LREEs subgroup over the HREEs in the composition of phosphate fertilizers was observed. The calculation of the potential REEs intake at the application of the studied phosphorus fertilizers to the soil indicates that there is no significant influence of this factor on the REEs content in the soil. However, the rather high REEs concentrations observed in some samples require the monitoring of REEs content in soils of agrocenoses, as well as the development of standards for REEs content in mineral fertilizers.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

1. Abdel-Haleem A.S., Sroor A., El-Bahi S.M., Zohny E. Heavy metals and rare earth elements in phosphate fertilizer components using instrumental neutron activation analysis. *Appl. Radiat. Isot.*, 2001, vol. 55, pp. 569–573. [https://doi.org/https://doi.org/10.1016/S0969-8043\(01\)00098-7](https://doi.org/https://doi.org/10.1016/S0969-8043(01)00098-7)
2. Balaram V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geosci. Front.*, 2019, vol. 10, pp. 1285–1303. <https://doi.org/https://doi.org/10.1016/j.gsf.2018.12.005>
3. Brown P.H., Rathjen A.H., Graham R.D., Tribe D.E. Rare earth elements in biological systems. *Handb. Phys. Chem. rare earths*, 1990, vol. 13, pp. 423–452. [https://doi.org/10.1016/S0168-1273\(05\)80135-7](https://doi.org/10.1016/S0168-1273(05)80135-7)
4. Castor S.B., Hedrick J.B. Rare earth elements. *Ind. Miner. Vol. 7th Ed. Soc. mining, Metall. Explor.* Littleton, 2006, pp. 769–792.
5. FAO. *World fertilizer trends and outlook to 2022*. Rome, 2019, 40 p.
6. Gonzalez V., Vignati D.A.L., Leyval C., Giamberini L. Environmental fate and ecotoxicity of lanthanides: Are they a uniform group beyond chemistry? *Environ. Int.*, 2014, vol. 71, pp. 148–157. <https://doi.org/10.1016/j.envint.2014.06.019>
7. Gorbunov A.V, Frontasyeva M.V, Gundorina S.F., Onischenko T.L., Maksjuta B.B., Pal C. Effect of agricultural use of phosphogypsum on trace elements in soils and vegetation. *Sci. Total Environ.*, 1992, vol. 122, pp. 337–346. [https://doi.org/https://doi.org/10.1016/0048-9697\(92\)90051-S](https://doi.org/https://doi.org/10.1016/0048-9697(92)90051-S)
8. Greenwood N.N., Earnshaw, A. *Chemistry of the Elements*. Oxford: Butterworth-Heinemann, 1997, 1359 p.

9. Hu Z., Haneklaus S., Sparovek G., Schnug E. Rare earth elements in soils. *Commun. Soil Sci. Plant Anal.*, 2006, vol. 37, pp. 1381–1420. <https://doi.org/https://doi.org/10.1080/00103620600628680>
10. Liang T., Zhang S., Wang L., Kung H. Te, Wang Y., Hu A., Ding S. Environmental biogeochemical behaviors of rare earth elements in soil-plant systems. *Environ. Geochem. Health*, 2005, vol. 27, pp. 301–311. <https://doi.org/10.1007/s10653-004-5734-9>
11. Liu C., Yuan M., Liu W.-S., Guo M.-N., Huot H., Tang Y.-T., Laubie B., Simonnot M.-O., Morel J.L., Qiu R.-L. Element case studies: rare earth elements, in: *Agromining: Farming for Metals*. Springer, 2018, pp. 297–308. https://doi.org/https://doi.org/10.1007/978-3-319-61899-9_19
12. Massari S., Ruberti M. Rare earth elements as critical raw materials: Focus on international markets and future strategies. *Resour. Policy*, 2013, vol. 38, pp. 36–43.
13. Migaszewski Z.M., Gałuszka A. The characteristics, occurrence, and geochemical behavior of rare earth elements in the environment: a review. *Crit. Rev. Environ. Sci. Technol.*, 2015, vol. 45, pp. 429–471.
14. Naccarato A., Tassone A., Cavaliere F., Elliani R., Pirrone N., Sprovieri F., Tagarelli A., Giglio A. Agrochemical treatments as a source of heavy metals and rare earth elements in agricultural soils and bioaccumulation in ground beetles. *Sci. Total Environ.*, 2020, vol. 749, pp. 141438. <https://doi.org/10.1016/j.scitotenv.2020.141438>
15. Otero N., Vitoria L., Soler A., Canals A. Fertiliser characterisation: major, trace and rare earth elements. *Appl. geochemistry*, 2005, vol. 20, pp. 1473–1488.
16. Pagano G., Guida M., Tommasi F., Oral R. Health effects and toxicity mechanisms of rare earth elements—Knowledge gaps and research prospects. *Ecotoxicol. Environ. Saf.*, 2015, vol. 115, pp. 40–48. <https://doi.org/https://doi.org/10.1016/j.ecoenv.2015.01.030>
17. Paoli L., Fiorini E., Munzi S., Sorbo S., Basile A., Loppi S. Uptake and acute toxicity of cerium in the lichen *Xanthoria parietina*. *Ecotoxicol. Environ. Saf.*, 2014, vol. 104, pp. 379–385. <https://doi.org/https://doi.org/10.1016/j.ecoenv.2014.02.028>
18. Ramos S.J., Dinali G.S., de Carvalho T.S., Chaves L.C., Siqueira J.O., Guilherme L.R.G. Rare earth elements in raw materials and products of the phosphate fertilizer industry in South America: Content, signature, and crystalline phases. *J. Geochemical Explor.*, 2016, vol. 168, pp. 177–186.
19. Ramos S.J., Dinali G.S., Oliveira C., Martins G.C., Moreira C.G., Siqueira J.O., Guilherme L.R.G. Rare earth elements in the soil environment. *Curr. Pollut. Reports*, 2016, vol. 2, pp. 28–50. <https://doi.org/https://doi.org/10.1007/s40726-016-0026-4>

20. Ribeiro P.G., Dinali G.S., Boldrin P.F., de Carvalho T.S., de Oliveira C., Ramos S.J., Siqueira J.O., Moreira C.G., Guilherme L.R.G. Rare Earth Elements (REEs) Rich-Phosphate Fertilizers Used in Brazil are More Effective in Increasing Legume Crops Yield Than Their REEs-Poor Counterparts. *Int. J. Plant Prod.*, 2021, vol. 15, pp. 1–11. <https://doi.org/10.1007/s42106-021-00129-5>
21. Sabiha-Javied, Waheed S., Siddique N., Shakoor R., Tufail M. Measurement of rare earths elements in Kakul phosphorite deposits of Pakistan using instrumental neutron activation analysis. *J. Radioanal. Nucl. Chem.*, 2010, vol. 284, pp. 397–403.
22. Silva F.B.V, Nascimento C.W.A., Alvarez A.M., Araújo P.R.M. Inputs of rare earth elements in Brazilian agricultural soils via P-containing fertilizers and soil correctives. *J. Environ. Manage.*, 2019, vol. 232, pp. 90–96. <https://doi.org/10.1016/j.jenvman.2018.11.031>
23. Taylor S.R., McLennan S.M. *The continental crust: its composition and evolution*. Oxford, Melbourne: Blackwell Scientific Publications, 1985, 312 p.
24. Todorovsky D.S., Minkova N.L., Bakalova D.P. Effect of the application of superphosphate on rare earths' content in the soil. *Sci. Total Environ.*, 1997, vol. 203, pp. 13–16.
25. Turra C. Sustainability of rare earth elements chain: from production to food—a review. *Int. J. Environ. Health Res.*, 2018, vol. 28, pp. 23–42.
26. Turra C., Fernandes E.A.D.N., Bacchi M.A., Sarriés G.A., Reyes A.E.L. Uptake of rare earth elements by citrus plants from phosphate fertilizers. *Plant Soil*, 2019, vol. 437, pp. 291–299.
27. Tyler G. Rare earth elements in soil and plant systems - A review. *Plant Soil*, 2004, vol. 267, pp. 191–206. <https://doi.org/10.1007/s11104-005-4888-2>

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