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РЕДКОЗЕМЕЛЬНЫЕ ЭЛЕМЕНТЫ В ПОЧВАХ ЗАСОЛЕННЫХ АГРОЛАНДШАФТОВ БАРАБИНСКОЙ РАВНИНЫ

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Изучено валовое содержание редкоземельных элементов в профиле почв катены засоленных агроландшафтов Барабинской равнины в пределах Новосибирской области. Определено валовое содержание циркония, иттрия, скандия, галлия, в том числе лантаноидов – церия, лантана и иттербия. Редкоземельные элементы крайне слабо изучены. В настоящее время влияние их на растения, организмы животных и человека активно исследуют, хотя предельно допустимые и ориентировочно допустимые концентрации для них пока не разработаны. Валовое содержание редкоземельных элементов, определяемое в почвах катены, зависит от гранулометрического состава и степени гумусированности почвенных горизонтов. Выявлено, что в изученных почвах они в основном содержатся в количестве кларков земной коры, за исключением лантана в гумусовых горизонтах, где его содержание почти в 1,5 раза (44–48 мг/кг) больше кларка в земной коре (29 мг/кг) и иттербия (в 10 раз больше кларка). По профилю почв отмечено незначительное передвижение редкоземельных элементов как в вертикальном, так и в горизонтальном направлении, что свидетельствует о малой подвижности их соединений. В профиле изучаемых почв из группы редкоземельных элементов преобладает цирконий. Его содержание в гумусовых горизонтах почв элювиальных позиций находится в пределах кларка земной коры, колебания по профилю незначительны. В больших количествах содержится иттербий – от 1,89 до 4,05 мг/кг почвы, что значительно больше кларка земной коры (0,3 мг/кг почвы). Роль лантаноидов в системе почва – растения – животное – человек требует дальнейшего глубокого изучения.

Ключевые слова: Барабинская равнина, засоленные агроландшафты, катена, редкоземельные элементы, лантаноиды

RARE EARTH ELEMENTS IN SOILS OF SALINE AGROLANDSCAPES OF THE BARABA PLAIN

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The total content of rare earth elements in the soil profile of saline agricultural landscapes catena of the Baraba plain within Novosibirsk region was studied. The total content of zirconium, yttrium, scandium, gallium, including lanthanides – cerium, lanthanum and ytterbium was determined. Rare earth elements are extremely poorly analyzed. At present, their influence on plants, organisms of animals and humans is being actively studied, although the maximum permissible and tentatively permissible concentrations for them have not yet been developed. The total content of rare earth elements, determined in the soils of the catena, depends on the granulometric composition and the degree of humus content of the soil horizons. It was revealed that in the studied soils they are mainly contained in the number of clarkes of the earth's crust, with the exception of lanthanum in the humus horizons, where its content is almost 1.5 times (44–48 mg/kg) higher than the clarke in the earth's crust (29 mg/kg), and ytterbium (10 times higher than the clarke). Along the soil profile, an insignificant movement of rare earth elements in both vertical and horizontal directions was noted, which indicates a low mobility of their compounds. Zirconium predominates in the profile of the studied soils from the group of rare earth elements. Its content in the humus horizons of soils of eluvial positions is within the clarke of the earth's crust; variations along the profile are insignificant. Ytterbium is contained in large quantities – from 1.89 to 4.05 mg/kg of soil, which is significantly higher than the clarke of the earth's crust (0.3 mg/kg of soil). The role of lanthanides in the soil – plant – animal – human system requires further in-depth study.

Keywords: Baraba plain, saline agricultural landscapes, catena, rare earth elements, lanthanides.

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Conflict of interest

The authors declare no conflicts of interest.

INTRODUCTION

At present, due to challenging ecological conditions both in Russia as a whole and in Western Siberia, when studying the properties of agricultural landscapes special attention is paid to their microelement composition. It is important to know not only its average content for a particular territory, but also more detailed information for each agricultural landscape. The data obtained are necessary for the development of adaptive landscape farming systems: scientifically grounded systems of processing, crop rotations, fertilizers, etc. The main goal of scientifically grounded farming systems is to obtain high and stable yields of ecologically clean and high-quality agricultural crops. This is possible only with a deep knowledge of the elemental chemical composition of soils and parent rocks. The chemical composition of soils is directly determined by the composition of the parent rocks, in which, in turn, the composition of the original rocks is preserved, which is discussed in detail in the works of V.B. Ilyina, A.I. Syso [1, 2]. The soil cover of the Novosibirsk region is characterized by a large variegation of the total content of trace elements (heavy metals), which is inherited from the parent rocks. In the process of soil formation, they are somewhat redistributed along the soil profile, relief elements, and biogenic accumulation is manifested in the humus horizons. It has been established that the main carriers of heavy metals are silt particles, humic substances and hydroxides [2].

According to A.P. Vinogradov, "... all the chemical elements of the earth's crust, including soils, may be necessary or useful for plants and living organisms. There can be no toxic elements in nature, there are their toxic concentrations "[1].

At present, a certain part of microelements in soils has been studied rather thoroughly. Hazard standards for different territories, maximum permissible concentrations, tentatively permissible concentrations, etc. have been developed. However, devices have appeared that make it possible to determine more accurately a large number of microelements. The significance of some of them for the life of plants, animals and humans has not yet been established, but the very constant presence in plants indicates their importance.

In the process of studying microelements in the soils of saline agricultural landscapes of the Baraba Plain, the content of 37 macro- and microelements was determined by atomic emission spectroscopy.

In the present paper the gross content of rare earth elements (REE), the significance of which is currently underexplored for plants and living organisms has been reviewed.

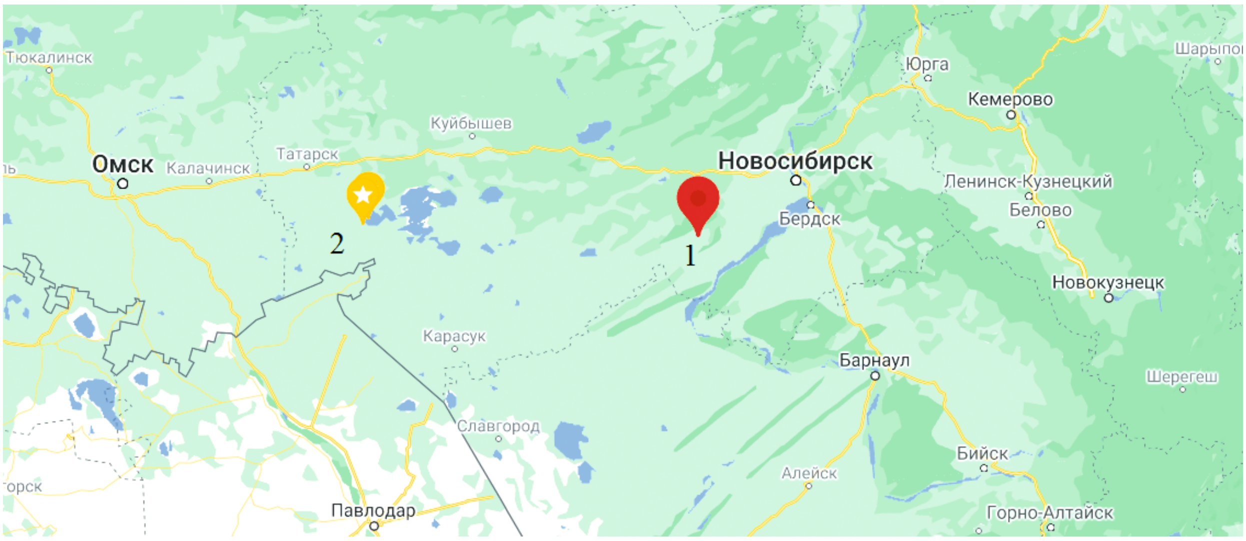
The aim of the study is to investigate the total content of rare earth elements in the soil profile of the saline agricultural landscapes catena of the Baraba Plain within the Novosibirsk region.

MATERIALS AND METHODS

The studies were carried out in two key areas of the Baraba Plain: in the wide valley of the Karasuk River and in the basin of the lake Chany. The first site is located in the Chulym district of the Novosibirsk region near the village Bolshenikolskoe. Three soil sections were laid in the saline agrolandscape along the catena. Section No. 1 is located at the eluvial position of the mesorelief (a gently sloping ridge). The coordinates are - 54˚31′28.9 ″ N. and 81˚29′45.3 ″ E, the altitude above sea level is 203.3 m. The soil is meadow-chernozemic ordinary leached medium-thick medium loamy. Section 2 was excavated in the transit zone. The coordinates are - 54 ° 35'14.5 ″ N. and 81 ° 29′45.3 ″ E. The soil is chernozem-meadow saline sandy loam, in which, at a depth of 72 cm, the profile of the buried soil with horizons A of burials and B of burials is clearly distinguished. Section No. 3 was laid in the accumulative zone. The coordinates are - 54˚35′37.4 ″ N. and 81˚29′11.5 ″ E, the altitude above sea level is 229 m. The soil is a deep solonchak heavy loamy meadow solonetz (see the figure).

The second site is located on the drying Yudinsky reach of Lake Chany. Two cuts were laid along the catena. In the eluvial position, section no. 40 was dug at the summit of the ridge at an altitude of 120 m above sea level. The coordinates are - 54˚74'58.98 ″ N and 76˚06'94.00 ″ E. Soil - meadow-chernozem ordinary, slightly salted, medium-thick sandy loam. In the accumulative zone in geochemical subordination, section No. 20 was laid. The coordinates are - 54˚78′11.33 ″ N. and 76˚83'95.28 ″ E, absolute elevation above sea level 103m. The ridge, with

[1]Vinogradov A.P. The main regularities in the distribution of trace elements between plants and the environment // Microelements in the life of plants and animals. Moscow: Publishing House of the Academy of Sciences of the USSR, 1952.



Географическое расположение объектов исследования
Geographic location of research objects

a sharp ledge, is transformed into a gently sloping surface of the dried bottom of the Yudinsky reach. Ground water was found at a depth of 60 cm. The soil is meadow-boggy, saline, heavy loamy (see the figure).

The morphological description of the soil profiles was carried out and soil samples were taken from the genetic horizons. Analyzes were carried out in them according to generally accepted methods: granulometric composition according to Kachinsky, absorbed bases - according to Schollerberger, humus - according to Tyurin, pH - potentiometrically[2]. Trace elements were determined on a two-jet atomic emission plasmatron (DAEP) by atomic spectroscopy in the laboratory of soil biogeochemistry of the Institute of Soil Science and Agrochemistry of the Siberian Branch of the Russian Academy of Sciences.

RESULTS AND DISCUSSION

The total content of seven rarely detected trace elements - zirconium (Zr), yttrium (Y), scandium (Sc) and gallium (Ga), including lanthanides - cerium (Ce), lanthanum (La) and ytterbium (Yb) has been studied in the soils of saline agricultural catena landscapes. Since they exhibit similar properties, they have been combined into one group of rare earth elements. This name is due to the fact that these elements are believed to be rare and their concentrations are widely scattered both inside the earth's crust and in soils. However, in-depth studies of recent years have shown that REEs are not rare. In terms of total prevalence, they exceed lead by 10 times, molybdenum by 50 times [5].

In the last decade, rare earth elements have begun to be used in various industries, and their release into the environment has increased accordingly. The effect of REEs on plants and organisms of animals and humans is currently being actively studied.

As our studies have shown, zirconium predominates in the soils of both catenas from the REE group (see Tables 1, 2). Its content in the humus horizons of soils in the eluvial positions of catena is 179–200 mg / kg of dry soil. Down the profile, the fluctuations are insignificant, but its amount is somewhat less - about 170 mg / kg of soil, which corresponds to the clarke of this element in the earth's crust[3].

In the transit position of the first catena in the profile of chernozem-meadow soil at a depth of 72–90 cm, horizon A of the buried soil is clearly distinguished, in which the zirconium

[2]Workshop on agrochemistry / ed. by V.G. Mineev. M.: Publishing house of Moscow State University. 2001. 687 p.
[3]Alekseenko V.A. Environmental geochemistry: textbook. M.: Logos, 2000. 627 p.

Табл. 1. Содержание редкоземельных микроэлементов в почвах засоленных агроландшафтов первой катены

Table 1. The content of rare earth trace elements in the soils of saline agricultural landscapes of the first catena

Geomorphological position, section No., soil	Horizon, cm	Trace element (heavy metal), mg / kg dry soil						
		Zr	Y	Sc	Ga	Ce	La	Yb
Eluvial, R, No. 1, meadow chernozem medium thick medium loamy	$A_{пах}$ 0–18	200	29,9	14,9	10,6	68,7	31,4	3,01
	A_1 18–45	270	41,6	18,4	10,3	92,5	44,9	4,05
	AB 45–65	198	32,4	17,8	15,7	94,7	41,4	3,38
	B 65–85	254	42,9	20,8	12,4	87,5	48,6	4,29
	$B_к$ 85–135	215	36,1	18,0	10,5	77,7	42,4	3,52
Transit, R, No. 2, chernozem-meadow slightly salty heavy loamy	A_d 0–10	208	20,7	10,3	11,7	43,8	28,2	1,94
	A_1 10–24	129	15,1	10,8	8,75	80,4	33,5	2,08
	AB_q 24–43	174	13,5	9,09	7,25	14,0	22,6	1,59
	B_q 43–72	113	15,5	9,38	5,67	54,2	24,7	1,83
	$A_{пог}$ 72–90	222	28,6	14,6	11,1	61,0	37,5	2,98
	$B_к$ 90–130	135	15,2	11,2	8,85	66,3	32,5	1,91
Accumulative, R, No. 3, deep meadow saline solonchak heavy loamy	$A_{пах}$ 0–20	276	19,4	12,2	8,39	69,3	29,7	2,18
	B_1 25–35	126	19,3	10,6	9,11	51,3	22,8	1,89
	B_{2q} 35–50	149	24,6	11,7	9,8	60,8	26,7	2,36
	B_{3q} 50–68	168	31,2	13,2	10,1	84,7	35,6	3,25
	B_{4q} 68–80	195	28,9	14,9	8,17	71,0	32,3	2,82
Clarke element in the earth's crust [5]		170	20	10	19	70	29	0,3

Табл. 2. Содержание редко определяемых микроэлементов в почвах засоленных агроландшафтов второй катены

Table 2. The content of rarely detected trace elements in the soils of saline agricultural landscapes of the second catena

Geomorphological position, section No., soil	Horizon, cm	Trace element (heavy metal), mg / kg dry soil						
		Zr	Y	Sc	Ga	Ce	La	Yb
Eluvial, P, 40, meadow chernozem solodized sandy loam	A_1 3–18	193,0	26,2	12,1	8,87	50,2	30,4	2,62
	A_1 18–30	224,0	26,9	11,4	9,93	39,7	24,8	2,72
	AB 35–45	177,0	19,1	8,4	8,41	38,7	23,3	1,86
	B_{ca} 61–93	178,0	24,5	16,9	8,65	58,2	34,1	2,28
	C_{Ca} 90–100	178,0	25,5	11,9	8,62	52,5	29,5	2,41
Accumulative, R, No. 20 meadow-swamp saline heavy loamy	A_q 0–7	179,0	21,3	24,1	14,9	69,6	49,0	3,57
	A_{1q} 10–20	171,0	30,7	21,0	13,0	59,4	39,3	3,37
	B_q 40–50	136,0	24,9	17,4	12,3	46,6	25,5	2,68
	G 65–75	174,0	31,5	22,8	12,0	55,6	39,4	3,34
Clarke element in the earth's crust [5]		170	20	10	19	70	29	0,3

content is high - 222 mg / kg. In the accumulative position, the largest amount of zirconium was found in the humus horizon of the deep solonetz - 276 mg / kg; it decreases down the profile. It is known that zirconium belongs to low-mobile elements, does not form water-soluble compounds within the landscape, and weakly migrates with organic complexes [3, 4]. In our opinion, some of its accumulation in the humus horizon of soils in the accumulative zone is associated with the erosional processes of the movement of clay fractions from the upper positions of the catena to the lower water flows. In the second catena, approximately the same zirconium content was found in the profiles of the studied soils.

The gross content of yttrium in the soil profiles of the studied catenas is also close to the clarke of this chemical element in the earth's crust. In the first catena at the eluvial position in the meadow chernozem soil, the amount of yttrium is somewhat higher than in the second, due to the heavier granulometric composition (see Table 3). V.V. Ivanov noted that there are no reliable soil clarkes of yttrium, since "soils are rarely analyzed for yttrium." He believes that

Табл. 3. Физико-химические свойства почв катены
Table 3. Physical and chemical properties of catena soils

Geomorphological position, section No., soil	Horizon, cm	Physical and chemical properties		
		pH	Humus,%	Physical clay, particles <0.01 mm,%
Eluvial, R, No. 1, meadow chernozem medium-power medium loamy	$A_{пах}$ 0–18	6,6	9,7	36,5
	A_1 18–45	6,6	7,7	31,1
	AB 45–65	6,3	1,3	53,5
	B 65–85	6,7	Not ident.	53,9
	$B_к$ 85–135	8,4	» »	56,3
Transit, R, No. 2, chernozem-meadow slightly salty heavy loamy	A_d 0–10	7,9	10,8	14,0
	A_1 10–24	8,2	4,5	8,8
	AB_q 24–43	8,3	1,0	21,4
	B_q 43–72	8,4	0,6	22,6
	$A_{пог}$ 72–90	8,9	0,9	53,3
	$B_к$ 90–130	9,1	0,6	56,1
Accumulative, R, no. 3, deep meadow saline solonchak heavy loamy	$A_{пах}$ 0–20	9,8	5,2	60,6
	B_1 25–35	10,1	2,6	60,2
	B_{2q} 35–50	10,2	0,9	41,2
	B_{3q} 50–68	10,0	Not ident.	41,2
	B_{4q} 68–80	10,0	» »	54,6
Eluvial, R, No. 40, meadow chernozem solodized sandy loam	A_1 3–18	6,8	5,7	14,8
	A_1 18–30	7,1	4,5	14,1
	AB 35–45	7,3	1,1	36,1
	B_{ca} 61–93	8,9	0,5	29,4
	C_{Ca} 90–100	9,0	0,2	26,9
Accumulative, R, no. 20, meadow-swamp saline heavy loamy	A_q 0–7	8,9	5,9	72,2
	A_{1q} 10–20	9,0	2,8	88,1
	B_q 40–50	8,6	2,8	66,1
	G 65–75	8,9	2,5	51,1

yttrium is in the clay fraction of soils, where its average content is 33 mg / kg, in sandy and calcareous soils - 18 and 8 mg / kg of dry soil, respectively [5]. This conclusion is consistent with the conclusions of other researchers [1, 2], including ours.

Scandium is a typical scattered lithophilic element. Due to its very low concentration in the earth's crust, its geochemistry is poorly studied, although it has a rather high clarke - 10 mg / kg. This is higher than tin and almost the same as lead. In the last decade, it was established that the content of scandium in soils depends on its content in the parent rock. Its lowest concentration is typical for sandstones and light soils; in heavy and clayey soils, the scandium content is much higher [6].

It should be noted that the scandium content in the soils of both catenas is equal to the clarke or is slightly higher. In the first catena, it is more abundant in the profile of the meadow-chernozemic medium loamy soil of the eluvial position, in the second, in the meadow-boggy saline heavy loamy accumulative position. Along the profile, fluctuations in the content of scandium are not so significant, which indicates a weak movement of its compounds.

The average content of this element in land plants is 0.008 mg / kg dry weight[4], in vegetables - 0.005 mg / kg, in grass - 0.07, while in barley roots - 0.63 mg / kg. The content of scandium in old leaves is higher than in young ones [7]. The biological role of scandium and its migration along biological chains is very poorly studied. It has now been established that scandium, like other REEs, is not a necessary chemical element for the life of plants, animals and humans, especially since it is not a "mineral of death" - a potent poison [8, 9].

The gross gallium content in the catena soil profile is almost 2.0–2.5 times lower than its clarke value in the earth's crust - 19 mg / kg. Its fluctuations along the profile are insignificant. In the soils of the first catena, the amount of gallium is greater in the meadow chernozemic medium loamy soil of the eluvial position than in the meadow chernozem solodized sandy loamy soil of the second catena (see Table 1). In the accumulative position, an inverse dependence of the gallium content in soils was found, which is associated with both the granulometric composition and the location of the sections along the relief. The gallium content probably depends on the humus content: with a decrease in humus in the A horizons of the soils, its amount decreases. In the buried horizon A of the soil, it is approximately the same as in the upper horizon A (see Table 1).

The gross content of cerium, the clarke of which is 70 mg / kg (see footnote 3), in the soil profile of the second catena is significantly lower than in the soil profile of the first catena, which is probably due to their lighter granulometric composition along the genetic horizons and the content of cerium in parent rock.

In the humus horizon of the chernozem-meadow soil of the transit zone, it is somewhat less than in the eluvial and accumulative ones. There is little data on the role of cerium in the life of plants, animals and humans, but recently there have been studies to study its effect on the elemental composition and development of plants [5].

The gross content of lanthanum is approximately the same in the soils of both catenas, and it is within the clarke of the earth's crust - 29 mg / kg of soil (see Tables 1, 2). Only the profile of the meadow chernozem soil of the eluvial position in the first catena is distinguished, where the total content of lanthanum along the profile is in an amount higher than the clarke - from 41.4 to 48.6 mg / kg, while in the profile of the soils of the transit and accumulative position it is slightly less - from 22.6 to 37.5 mg / kg. Much attention has been paid to this element by Yu.N. Vodyanitsky [10]. It has been established

[4]Scandium. it's Occurrence, Chemistry, Physics, Metallurgy and Technology. London, New York, Krancisco: Acad. Press, 1975. 598 p.

[5]Kotelnikova A.D., Volkov D.S., Fastovets I.A., Rogova O.B. The influence of cerium on the elemental composition of barley plants when introduced into sod-podzolic soil. Soil Science: Horizons of the Future: Proceedings of the III Intern. conf. (Soil Institute named after Dokuchaev). M., 2019.

that lanthanum in micro doses has a stimulating effect on plants, in high doses it has a depressive effect [11, 12].

It was found that the total content of ytterbium in the soil profile of catena in saline agricultural landscapes of Baraba significantly exceeds the clarke in the earth's crust. Clarke of ytterbium - 0.3 mg / kg, and in soils of catena it contains from 1.6 to 4.3 mg / kg of soil. Its greatest amount is in the meadow chernozem soil of the first catena, the smallest is here in the transit zone, which is directly related to the granulometric composition. It should be noted that plants are able to resist the accumulation of REE. They block their transfer into the human body and do not accumulate in it.

Statistical processing of the material.

To perform statistical processing, consider the physicochemical properties of catena soils, presented in table 3. The granulometric composition of soils in the first catena varies along the profile in the eluvial position from medium loamy to heavy loamy, in the transit one - from sandy loam in horizon A to heavy loamy in the lower horizons. The humus content in the studied soils is rather high in the upper horizons (9.7–10.8%). It falls sharply down the profile. The pH value in soils increases from the eluvial position to the accumulative one.

In the soils of the second catena in the eluvial position, the granulometric composition of soils in horizon A is sandy loamy, and becomes heavier downward to light loamy. In the accumulative position, it becomes heavily heavier to heavy clay. The soils of the second catena are less humus-rich than the first. The pH value in the soils of the eluvial position in the upper horizons is neutral, becoming alkaline with depth. In the accumulative one, an alkaline medium is preserved throughout the profile.

Statistical processing of the research results was carried out in the applied statistics package of standard Excel programs. In particular, a correlation analysis was carried out between

Табл. 4 Коэффициенты корреляции между распределением редкоземельных элементов по профилю и физико-химическими свойствами почв

Table 4. Coefficients of correlation between distribution of rare earth elements along the profile and the physical and chemical properties of soils

Geomorphological position, section No., soil	Physical and chemical properties	Trace element						
		Zr	Y	Sc	Ga	Ce	La	Yb
Eluvial, R, No. 1, meadow chernozem medium-power medium loamy	Physical clay	–0,34	0,01	0,45	0,51	0,12	0,37	0,08
	Humus	0,32	0,10	–0,55	–0,96	–0,73	–0,47	–0,06
	pH	–0,10	0,05	0,05	–0,48	–0,42	0,08	–0,06
Transit, R, No. 2, chernozem-meadow slightly salted heavy loamy	Physical clay	0,20	0,43	0,66	0,20	0,18	0,52	0,51
	Humus	0,37	0,14	–0,15	0,61	–0,01	–0,03	–0,10
	pH	–0,09	0,22	0,56	–0,05	0,32	0,50	0,41
Accumulative, R, No. 3, deep meadow solonchak heavy loamy	Physical clay	0,39	–0,70	–0,17	–0,81	–0,46	–0,42	–0,64
	Humus	0,85	–0,79	0,41	–0,99	0,57	0,53	–0,27
	pH	–0,93	0,19	–0,22	0,46	–0,46	–0,42	–0,06
Eluvial, R, No. 40, meadow chernozem solodized sandy loam	Physical clay	–0,78	–0,85	–0,11	–0,78	0,05	–0,06	–0,95
	Humus	0,68	0,49	–0,17	0,57	–0,32	–0,17	0,68
	pH	–0,49	0,04	0,58	–0,34	0,70	0,58	–0,21
Accumulative, R, no. 20, meadow-swamp saline heavy loamy	Physical clay	0,09	–0,10	0,32	0,43	0,32	0,16	–0,09
	Humus	0,43	–0,82	0,81	0,96	0,81	0,70	0,58
	pH	0,61	0,82	0,22	–0,21	0,22	0,34	0,37

the content of rare earth elements in soils with particle size distribution, humus and pH (see Table 4).

Certain regularities between the content of rare earth elements, granulometric composition, humus and pH are weakly manifested, although it can be noted that this relationship is absent in soils of eluvial positions. Only between zirconium and ytterbium, granulometric composition and humus is a close inverse relationship established. In the accumulative position, a close inverse relationship was also established between cerium, lanthanum, yttrium, ytterbium, scandium, and humus.

CONCLUSIONS

1. Rare earth elements zirconium, yttrium, scandium, gallium, including lanthanides - cerium, lanthanum, ytterbium are currently poorly studied, their significance in the life of plants, animals and humans has not been established. However, the constant presence of rare earth elements in the chemical composition of plants indicates their need.
2. Rare earth elements were found in all soils of the studied saline agrolandscapes. Their content is determined by the content in the parent rock, depends on the granulometric composition and the amount of organic matter in the humus horizon.
3. In the soils of saline agricultural landscapes of the Baraba Plain, rare earth elements, including lanthanides, are mainly found in the amounts of clarkes of the earth's crust, with the exception of lanthanum in the humus horizon (1.5 times the clarke value) and ytterbium (up to 10 times higher than the clarke value). Some changes in the content of rare earth elements are observed along the soil profile. However, these changes are insignificant, which indicates a weak movement of REE compounds both in the vertical and horizontal directions.

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