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Lanthanides in Soils of the Cherepovets Steel Mill

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Abstract

Content of forms of the lanthanides in soddy-calcareous soils at a different distance from the Cherepovets steel mill (Vologda region, Russia) has been studied. In soils near the steel mill, an increased content of Pr and Tb was found, while the content of other light lanthanides (from La to Gd inclusive) is less increased. In addition to increasing of the total content, technogenic pollution leads to increasing the amount and the degree of extraction of acid-soluble forms of the lanthanides from soils. About 80–95% of Ln is located in the residual fraction strongly bound to aluminosilicates. As a result of the processes in the soil, 5–18% of the total content of lanthanides is bound to organic matter and 0.1–5% to Fe and Mn (hydr)oxides. The lanthanides' individual properties are manifested in this interaction: medium lanthanides are mostly bound to organic matter and whole heavy lanthanides to Fe and Mn (hydr)oxides.

Keywords: soddy-calcareous soils, soil pollution, lanthanides, forms of compounds, sequential fractionation, soil organic matter, Fe and Mn (hydr)oxides

1. Introduction

The lanthanides (Ln) comprise a group of 15 elements of which only 1, promethium (Pm), does not occur naturally in the Earth's crust. The lanthanides are placed in the sixth period of the periodic table, the secondary subgroup of the third group. Together with scandium (Sc) and yttrium (Y), the lanthanides are commonly referred to as the rare-earth elements (REE). Due to their special chemical properties, content and peculiarities of accumulation in soils, and the use of methods of determination in natural objects, the lanthanides are usually considered as a group of elements isolated from other TM.

The use of REE in industry, and as a consequence, contamination of the biosphere, has become noticeable only in recent decades, which is related to the development of new technologies

and materials on their basis [1, 2]. The lanthanides are generally considered to be of low toxicity for living organisms. Moreover, the efficiency of lanthanide-containing fertilizers, widely used in agriculture in China, is proved [3]. However, environmental risks related to changes in the lanthanide content, mobility, and proportions in soils, caused by enhanced technogenic pollution of soils, are still unknown.

Objective: to study the lanthanides in soils under anthropogenic impact of the Cherepovets steel mill (CSM), Vologda region, Russia

Tasks: (1). To study the total and acid-soluble form content of the lanthanides in soils. (2). To study the forms of the lanthanide compounds in soils using the sequential fractionation

2. Chemical properties of the lanthanides and their distribution

The REE are extremely similar to each other in electron shell structures and, accordingly, in chemical properties. Scandium and yttrium have one *d* and two *s* electrons on their outer electron levels. The lanthanides have also 4f sublevel, gradually filled from Ce to Lu. This structure of electron shells is the reason that 3+ is the main oxidation state for the REE. Although 4+ oxidation state is known for Ce, Pr, and Tb, and 2+ for Sm, Eu, and Yb, in natural conditions only Ce and Eu have oxidation state different from 3+ [4, 5].

La, Ce, Tb, and Er were isolated in pure form in the first half of the nineteenth century and the remaining lanthanides a bit later [6]. The difficulties in isolation of individual elements from rocks, containing their mixture, led to the formation of a sustainable opinion that these elements have similar chemical properties and geochemical behavior [7]. Investigations, carried out later, showed that in the lanthanide series, there are regular changes in chemical properties, associated with structural features of their electron shells. Unlike other heavy metals (HM), whose variation in chemical properties from element to element is not always obvious, in the lanthanide series, there are some interesting regularities.

In the La-Lu series, there is a gradual decrease in ionic radii (so-called lanthanoid compression). This is a consequence of the filling of the 4f level by electrons [5]. As a result, the stability of complex compounds increases, and the pH of the beginning of precipitation of lanthanide hydroxides decreases [4, 8, 9].

Since there are no cases of formation of own solid phases of the lanthanides under soil conditions, it can be assumed that the redistribution of the lanthanides between soil components during soil-forming processes and technogenic pollution is proceeding mainly due to ion exchange, sorption interactions, and complexation. The regularities of sorption of the lanthanides by the main soil components influencing the behavior of heavy metals—(hydr) oxides of iron and manganese, clay minerals, and organic matter—were studied [10–12]. The adsorption of the lanthanides increases significantly with increasing of pH of the soil liquid phase [13–15].

Investigations of lanthanide adsorption by various soil components showed the dependence of the amount of absorbed element on the ionic strength of the solution. In addition, under adsorption from solutions with high ionic strength, the amount of absorbed element increases with increasing atomic number of the element, corresponding to a change in ionic radii. This regularity is absent in adsorption from solutions with low ionic strength [13, 16].

It can be assumed that the differences in individual chemical properties of lanthanides will have a great effect on formation of their compounds in soils, both in background conditions and under technogenic pollution [10–12].

The average content of lanthanides in different rocks depends on their origin and is described in detail in [17]. The most rich in lanthanides are acid magmatic and clay sedimentary rocks.

Another specific distribution feature of the lanthanides in the Earth crust and its individual components is the "sawtoothness" of the graphs, where the atomic number is plotted on x-axis and its content on y-axis (so-called geochemical spectra) (**Figure 1**). This kind of graphs clearly demonstrates one of the basic rules of geochemistry: the Oddo-Harkins rule states that an element with an even atomic number is more abundant than adjacent elements with odd atomic numbers.

Differences in the abundance of even and odd elements, as well as significantly higher abundance of light lanthanides, make difficult to compare characteristics of their behavior and location in natural objects, including soils. To exclude the influence of these differences, in geochemistry, it was suggested to normalize the content of elements in the studied objects to their content in standard objects.

Data on the content of lanthanides in geological rocks are usually to be normalized on composition of chondrites or shales [17–24]. However, chondrites are not suitable for studying lanthanides in soils of different compositions and origins.
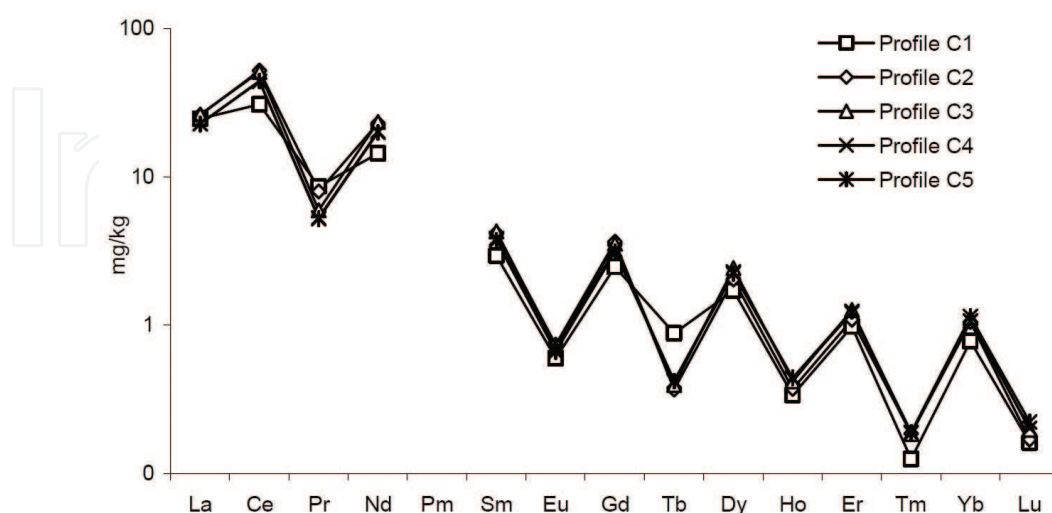
Figure 1. Total content of the lanthanides in the surface horizons of soils in the CSM impact zone, mg/kg.

The clay of the Russian platform [19] is the best object for normalization of the content of lanthanides in the soils studied. The soils of the taiga-forest zone of the European part of Russia, formed on quaternary sediments as a result of the glacier activity, have similar elemental ratio for most of HM. These rocks were formed as a result of processing of the same source material by glaciers [25]. The main differences in the elemental composition of the sediments are related to their granulometric composition. They depend on the ratio of clay minerals with the maximum content of HM and quartz depleted by them.

3. Objects and methods

We've studied the content of lanthanides in the soils of the impact zone of the Cherepovets steel mill. CSM is one of the most powerful sources of technogenic impact on the European territory of Russia. Pollution with heavy metals on the investigated territory has been monitored since 1955 [26, 27]. We selected soil samples from five soil profiles at different distances from the CSM. Profile C1 is located near the CSM boundary, and profiles C2–C5 are at a distance of 2, 5, 12, and 30 km to the north from it.

The soil of profile C1 is represented by an industrizem—strongly technogenic-transformed soil. The top layer of this soil contains a large number of fallout particles, containing heavy metals, which adhere the soil mass, making it difficult to take samples from deeper layers (only one sample from 0 to 20 cm layer was selected).

The soils in other profiles are represented by soddy-carbonate leached (Rendzic Leptosols) also formed on light cover loam and underlain by carbonate calcareous moraine. The profiles of these soils include humus-accumulative A horizons with thickness from 10 to 25 cm, gray color, of medium granular structure, transitional B horizons from 15 to 30 cm, and calcareous C horizons of parent rock. Samples for chemical analysis have been taken from these horizons.

According to their chemical properties (**Table 1**), the investigated soils are quite typical representatives of soddy-carbonate leached soils.

The upper humus-accumulative horizon is characterized by a rather high content of organic carbon (in comparison with the underlying horizons) and weakly acid reaction, which becomes weakly alkaline down the profile. Near the source of pollution, weakly alkaline reaction is observed throughout the profile because of the input of a large number of technogenic compounds on the soil surface. The content of exchangeable cations is typical for light loamy soils.

To determine the total content of the lanthanides, soil samples were treated with a mixture of hydrofluoric, hydrochloric, and nitric acids in medium-pressure autoclaves in the laboratory microwave Ethos One (Milestone) according to [28].

Acid-soluble forms of the lanthanides were extracted from soils by the treatment with 1M HNO_3 with a ratio of soil:solution equal to 1:10 [29].

Profile	Horizon, depth, cm	pH_{H_2O}	Total organic carbon, %	Sum of exchangeable cations, $cmole_c$/kg
C1	U, 0–20	7.60	Not determined	
C2	A, 0–20	7.14	2.65	18.79
	B, 20–35	7.05	0.68	15.05
	C, 35–65	7.25	0.15	12.31
C3	A, 0–23	6.89	3.17	21.10
	B, 23–41	6.92	0.51	16.32
	C, 41–70	7.12	0.12	13.58
C4	A, 0–21	6.77	2.95	19.21
	B, 21–38	6.89	0.57	14.39
	C, 38–70	7.10	0.14	11.06
C5	A, 0–23	6.85	2.86	20.36
	B, 23–45	6.93	0.49	16.54
	C, 45–75	7.14	0.17	11.88

Table 1. Some chemical properties of soils in the CSM impact zone.

The sequential fractionation of the lanthanides in soils was carried out by using the McLaren and Crawford scheme [29]. The following fractions were separated: exchangeable cations, fraction of specifically sorbed ions, fraction bound to organic matter, fraction bound to (hydr) oxides of iron and manganese, and residual (strongly bound to aluminosilicates) fraction.

The quantitative determination of the lanthanides in the obtained extracts was carried out by the inductively coupled plasma mass spectrometry on 7500a ICP-MS (Agilent Technologies), according to [28]. The lower determination limit of measured concentrations of the lanthanides does not exceed 0.001 mg/L, which corresponds to a total metal content equal to 0.05 mg/kg or forms of compound content of 0.01 mg/kg. The relative error of determination did not exceed 20%.

4. Results and discussion

4.1. Total content of the lanthanides

Total content of the lanthanides in soils is given in **Table 2**.

The analysis of the results shows that changes in total content of the lanthanides are observed in profiles C1 and C2 located in close vicinity to the pollution source. We observe either a significant increase or some decrease in the total content of the lanthanides (primarily Pr and Tb) compared to soils, located at a considerable distance from the CSM.

Profile	Horizon	La	Ce	Pr	Nd	Sm	Eu	Gd
C1	U	24.76	30.88	8.65	14.39	2.95	0.60	2.49
C2	A	26.15	52.10	7.98	23.02	4.20	0.74	3.66
	B	28.52	55.45	6.42	24.46	4.44	0.77	3.92
	C	29.57	56.25	6.48	25.22	4.76	0.89	4.74
C3	A	26.40	51.09	5.98	23.55	4.31	0.71	3.55
	B	27.79	52.17	6.12	25.47	4.74	0.81	3.90
	C	28.64	55.48	6.63	26.21	5.32	0.87	4.51
C4	A	22.98	44.28	5.31	20.36	3.85	0.70	3.22
	B	24.15	48.95	5.80	22.61	4.26	0.76	3.66
	C	27.30	52.78	6.63	26.20	5.15	0.98	4.52
C5	A	22.86	44.38	5.23	20.05	3.74	0.66	3.13
	B	27.10	52.68	6.16	23.48	4.31	0.74	3.64
	C	27.90	54.46	6.41	24.08	5.29	0.84	4.29
Profile	Horizon	Tb	Dy	Ho	Er	Tm	Yb	Lu
C1	U	0.88	1.72	0.34	0.98	0.13	0.78	0.16
C2	A	0.37	2.04	0.37	1.09	0.19	1.06	0.17
	B	0.40	2.50	0.47	1.27	0.20	1.18	0.21
	C	0.46	2.69	0.49	1.39	0.25	1.96	0.21
C3	A	0.40	2.43	0.42	1.27	0.19	1.12	0.20
	B	0.49	2.44	0.46	1.29	0.21	1.34	0.20
	C	0.56	2.76	0.51	1.48	0.22	1.64	0.23
C4	A	0.42	2.29	0.44	1.22	0.19	1.07	0.20
	B	0.49	2.53	0.48	1.30	0.20	1.10	0.20
	C	0.53	3.31	0.63	1.83	0.27	1.62	0.29
C5	A	0.42	2.24	0.44	1.24	0.19	1.15	0.22
	B	0.49	2.55	0.48	1.40	0.21	1.24	0.23
	C	0.51	2.78	0.57	1.75	0.24	1.41	0.26

Table 2. Total content of the lanthanides in soils of the CSM impact zone, mg/kg.

Content of the lanthanides in the upper horizons of the investigated soils is given in **Figure 1**. The different levels of elemental content in soils and sawtooth character of the distribution of elements in the figure make it difficult to identify the similarities and differences in the behavior of studied elements in the soil and the effect of the CSM emissions on their content in the soil.

When normalizing data to the clay of the Russian platform, the graphs of the content of the lanthanides in unpolluted soils are gently sloping, almost horizontal, without clear maxima or minima (**Figures 3** and **4**). Thus, a high content of quartz and other minerals with low content of rare-earth elements in light loamy deposits affects equally the level of all lanthanides in the soils.

Normalized content of the lanthanides in the surface horizons of industrizem (profile C1) and soddy-calcareous soil (profile C5), which are the most contrast in chemical composition and technogenic impact, is given in **Figures 2** and **3**. The results of normalization show that the studied soils are strongly enriched with the lanthanides compared to chondrites and the degree of enrichment gradually decreases with increasing of atomic numbers of elements.

In the background soil C5 (**Figure 3**), europium stands out, whose point lies below the general trend line, as well as lutetium, a bit above it. This feature manifests at the normalization of all objects and is typical for all investigated soils (**Figure 4**).

The potential effect of technogenic pollution is of greater interest than the changes in the content of the lanthanides in soils on the geological time scale (which can be estimated by normalization to chondrites); therefore, rocks, whose composition is most similar to that of the studied soils, were used as objects for normalization. The normalization to the content of the lanthanides in the world shale and, especially, to clay of the Russian platform shows good correspondence with these objects in uncontaminated soils. Since the investigated soils are formed on light loamy sediments, the content of many chemical elements will be deliberately underestimated compared to shales or clays because of dilution with quarts.

Soil contamination by CSM emissions strongly changes the elemental relationships in contaminated soils (**Figures 2** and **4**). A noticeable increase in the content of Pr and Tb is observed at normalization to all abovementioned objects. The maximum increase in Tb content is registered in profile. Pr content is slightly lower in C1 profile, but this element is also found in
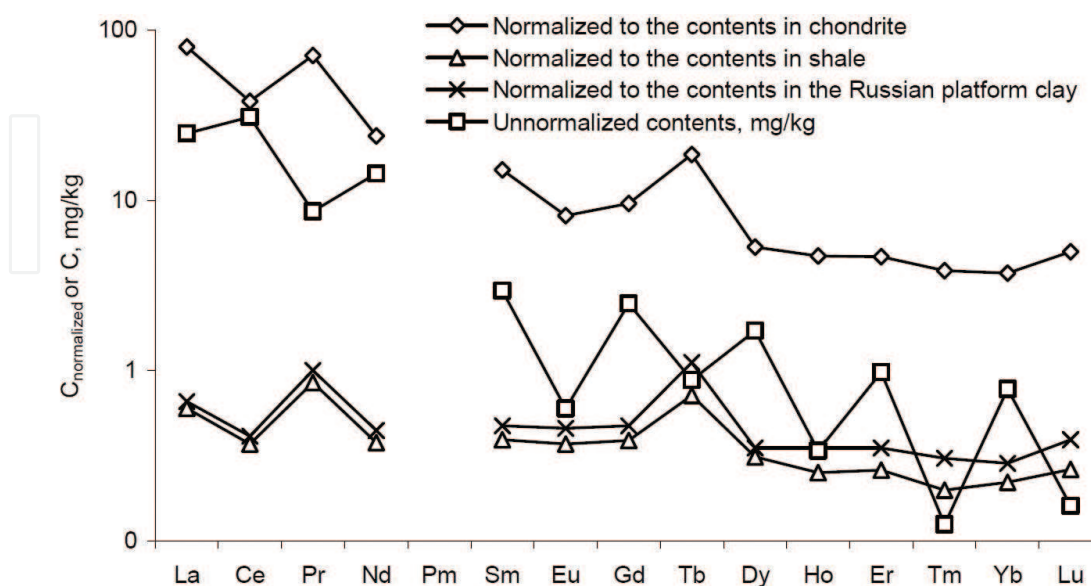
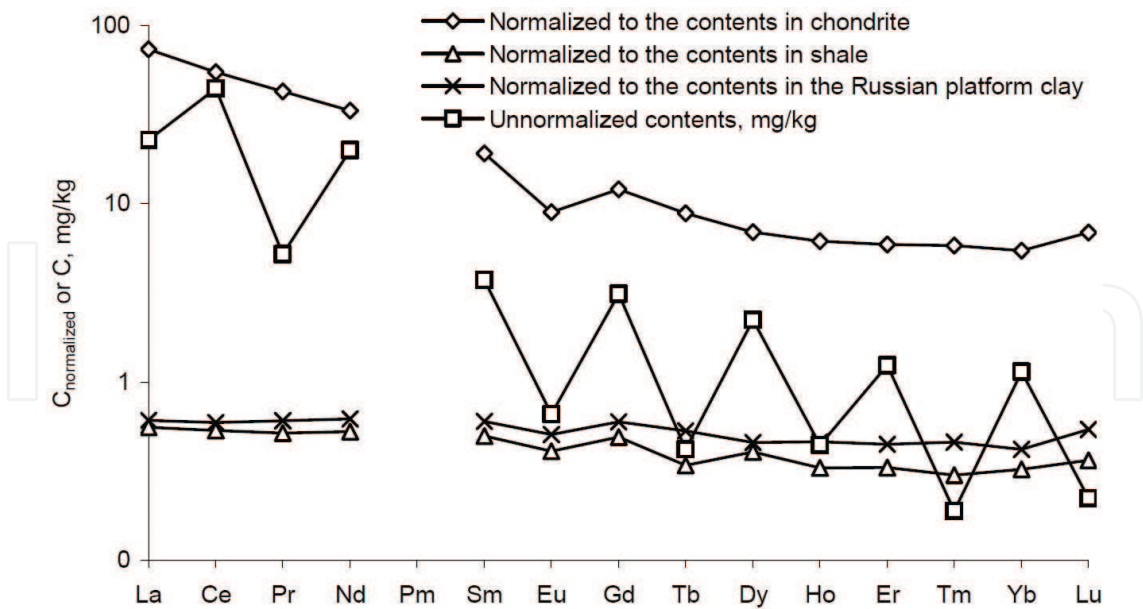**Figure 2.** Total content of the lanthanides in the surface horizons of profile C1.

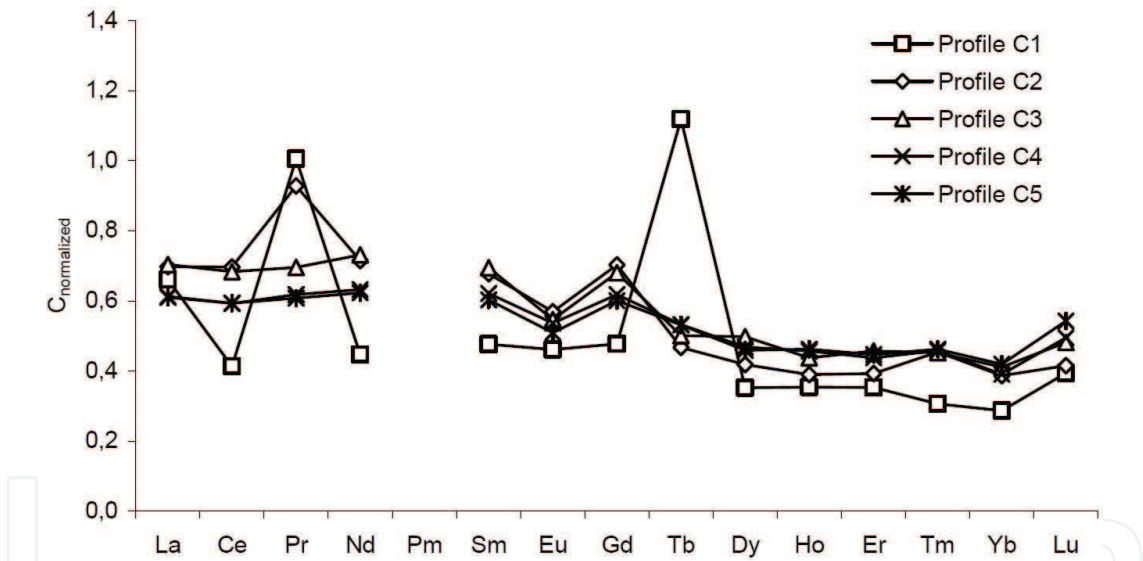**Figure 3.** Total content of the lanthanide in the surface horizons of profile C5.

Figure 4. Total content of the lanthanides in the surface horizons of soils in the CSM impact zone, normalized to the content in the Russian platform clay.

profile C2. This may indicate significant changes in the elemental composition of atmospheric fallout with the distance from the pollution source. Along with Pr, a tendency of content increasing of other light lanthanides, from La to Gd, is observed in soils in profiles C2 and C3.

4.2. Content of acid-soluble forms of the lanthanides

Content of acid-soluble lanthanides in the surface horizons in the studied soils is given in **Table 3**. It can be seen that the main trend of the lanthanide distribution soils regulated by the Oddo-Harkins rule basically is saved at transition from total content to acid-soluble forms of elements.

| Profile	Horizon	La	Ce	Pr	Nd	Sm	Eu	Gd
C1	U	5.19	11.58	1.27	4.98	1.03	0.28	0.97
C2	A	4.20	8.89	1.11	4.26	0.78	0.18	0.77
C3	A	1.63	5.64	0.66	2.47	0.54	0.11	0.57
C4	A	1.67	5.07	0.58	2.57	0.50	0.10	0.51
C5	A	1.45	4.83	0.51	2.48	0.49	0.12	0.45
Profile	Horizon	Tb	Dy	Ho	Er	Tm	Yb	Lu
C1	U	0.15	0.72	0.13	0.35	0.05	0.27	0.04
C2	A	0.11	0.56	0.10	0.25	0.03	0.17	0.02
C3	A	0.09	0.36	0.07	0.15	0.02	0.12	0.02
C4	A	0.09	0.48	0.09	0.23	0.03	0.18	0.03
C5	A	0.09	0.45	0.08	0.18	0.03	0.13	0.02

Table 3. Content of acid-soluble forms of the lanthanides in the surface horizons of soils in the CSM impact zone, mg/kg.

The content of acid-soluble forms of the lanthanides in soddy-calcareous soils (profiles C1 and C2) is higher than in other profiles. Obviously, this is a consequence of their fall-out near the CSM, their presence in ore, and their use in technological process of steel production.

Not only technogenic pollution but also the original contents of elements in rocks, their chemical properties, and their affinity to soil components affect the amount of acid-soluble HMs in soils; thus, it is necessary to conduct more detailed analysis of acid-soluble forms of lanthanides in the investigated soils. For this purpose, the extraction degree of acid-soluble lanthanides from soils was calculated, and their contents were normalized using data for the Russian platform clays.

The extraction degree of acid-soluble lanthanides expressed in percentage to their total content is shown in **Figure 5**. There is a significant increase in the extraction degree for all lanthanides (except Pr and Tb) in the soil of profile C1 and a less significant for a set of elements from La to Er in the soil of profile C2. The results of determination of the content of acid-soluble forms clearly show a tendency to increase the degree of extraction from the soil of medium lanthanides, from neodymium to erbium. Primarily, this is due to stronger hardening of heavy lanthanides by the soil (due to increase in adsorption that corresponds to published data [9, 13–15]). This leads to the worst extraction of heavy lanthanides from the soil by nitric acid. On the other hand, this may be a result of a decrease in lanthanide distribution in soils as the number of the element increases.

Based on the results of determining the extraction degree of acid-soluble forms, we can divide lanthanides into three groups, depending on extraction degree of acid-soluble forms from the soils of the CSM impact zone (**Figure 5**). The first group included praseodymium and terbium, which, despite a strong increase in the total content in the most polluted soil C1 (**Table 2**), is characterized by the lowest degree of extraction of acid-soluble forms (less than 16%). The
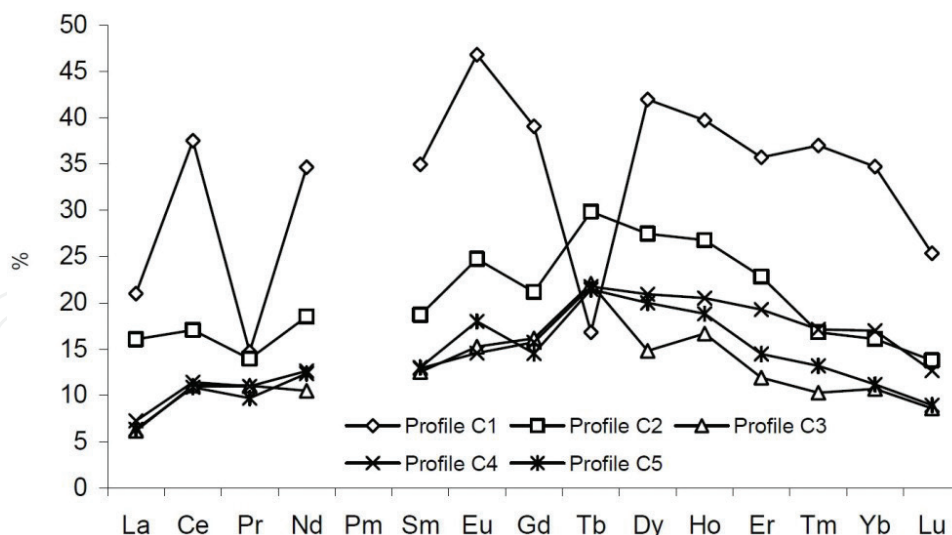
Figure 5. Content of acid-soluble forms of the lanthanides in the surface horizons of soils in the CSM impact zone, share in the total content.

majority of lanthanides—La, Ce, Nd, Sm, Eu, Gd, Dy, Ho, and Er—belong to the second group, and the extraction degree of acid-soluble forms increases in the first two most polluted soils. The third group of elements consists of three heavy lanthanides—Tm, Yb, and Lu—with the lowest changes in the extraction degree of acid-soluble forms, determined only in the most polluted soil C1.

Based on grouping of the lanthanides, we suggested that praseodymium and terbium of technogenic origin in soils in near the CSM are found in poorly soluble acid-technogenic particles of a large size. The lanthanides' content in finer and lighter technogenic particles is more homogeneous, and they are spread to a longer distance from the pollution source and are extracted by acid better. As the atomic number of lanthanides increases, their involvement in technogenic emission flows in the CSM impact zone gradually decreases.

Additional information on the lanthanides' redistribution in the studied soils can be obtained by normalizing the contents of acid-soluble forms to the contents of elements in the Russian platform clay (**Figure 6**). The comparison of the content of total and acid-soluble forms of the lanthanides has shown that almost horizontal curves are typical for the distribution of the total content of the lanthanides, and more complicated with clear maximum—for acid-soluble forms of medium lanthanides (Eu, Gd, and Tb).

As the content of acid-soluble lanthanides (**Figure 6**) is not related to their total content in the studied soils, then it is difficult to estimate soil contamination with the lanthanides using these data. So, the minima for Pr and Tb in **Figure 5** are absent in **Figure 6**.

Nevertheless, with this exception, the general shape in **Figures 5** and **6** is similar, which confirms our assumptions about changes in the extraction degree of acid-soluble forms of the lanthanides depending on their atomic number, with the maximum for medium lanthanides.
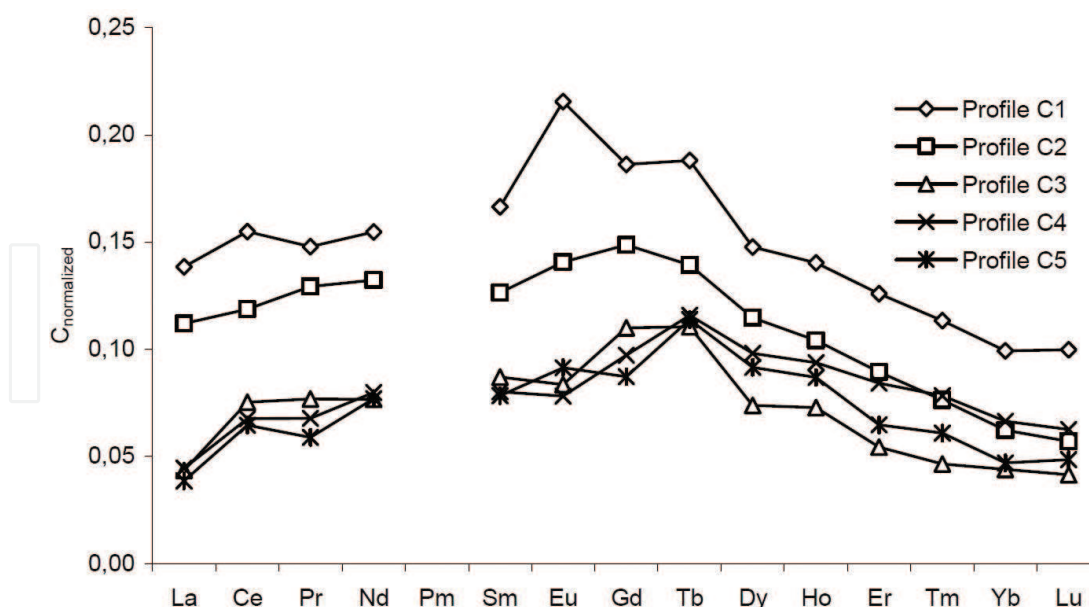
Figure 6. Content of acid-soluble forms of the lanthanides in the surface horizons of soils in the CSM impact zone, normalized to the content in the Russian platform clay.

4.3. Fractional composition of the lanthanide compounds

For all lanthanides in all studied soils, regardless of a distance from the source of pollution, a significant predominance of the residual (strongly bound to aluminosilicates) fraction (80–95% of the sum of fractions) is typical. This indicates that the main soil components determining the background level of the lanthanides in soils are aluminosilicate minerals, which strongly fix lanthanides in their structure, and lanthanide compounds, fallen into the soil under the impact of the CSM, are also chemically stable. As a result, most of the technogenic lanthanides are detected in the residual fraction. This corresponds to the data available in the literature [10–12].

Soil-forming processes have no significant influence (compared to the share of residual fraction and many other HMs in the studied soils) on redistribution of lanthanides among soil components [30–32]. The highest effect of pedogenesis on the fractional composition of lanthanides has been determined in the fraction bound to organic matter (**Figure 7**).

This fraction is reached from 5 to 18% of the sum of all fractions, depending on the element. The largest content of the fraction, associated with organic matter, is typical for the middle lanthanides. This is similar to the regularity observed for acid-soluble forms of lanthanides (**Figures 5** and **6**). Both light and heavy lanthanides have low affinity to soil organic matter. This, certainly, requires further study.

The content of the fraction associated with (hydr)oxides of Fe and Mn is much lower than the fraction considered above and amounts to only 0.1–5% of the sum of all fractions (**Figure 8**). The maximum part of this fraction in contaminated soils C1 and C2 corresponds to heavy lanthanides. In soil C1 the maximum of this fraction was detected for ytterbium and in soil C2 for dysprosium and holmium.
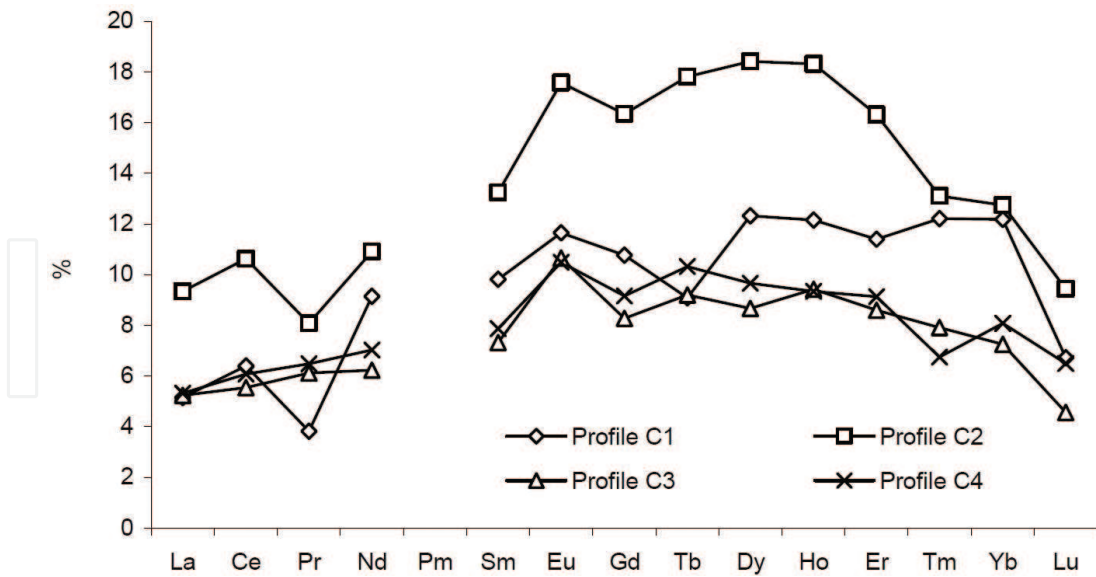
Figure 7. Fraction of the lanthanides, bound to organic matter, percentage of the sum of fractions.
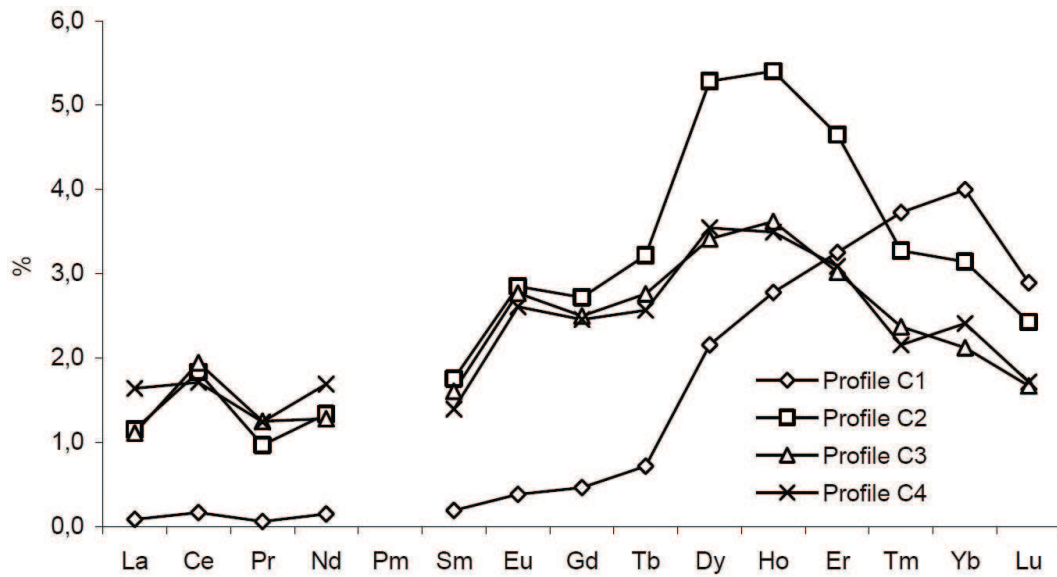
Figure 8. Fraction of the lanthanides, bound to Fe and Mn (hydr)oxides, percentage of the sum of fractions.

The obtained regularities reflect an increase in the affinity of lanthanides to iron oxides, which are the main component of the CMP emission substance, according to the number of the element raising. The decrease in the fraction share for heavy lanthanides in weakly contaminated soils of profiles C2–C4 is more significant than in profile C1. This is related to the lower technogenic input of these elements into the soil, as well as an increase in the strength of fixation of the lanthanides on the surface of ferruginous minerals as their number increases, that is corresponds to generally accepted understanding of chemical properties of the lanthanides [4, 8, 33].

The amount and share of the specifically sorbed fraction of the lanthanides are expectedly low because of their low mobility in the studied soils and moderate level of pollution. There are

only two cases when the content of this fraction reaches significant values. The first case is the high content of this fraction of europium in soil C1 (4% of the sum of extracted fractions). This may be due to the peculiarities of this element and its entry into the soil with contamination, as in this soil we observe the maximum extraction degree of acid-soluble forms of europium (**Figures 5** and **6**).

The second case is a high content of a specifically sorbed terbium fraction in all soils (4–7% of the sum of all fractions). This is a consequence of technogenic contamination of soils, as it is terbium that falls down in the largest of all lanthanide quantities into the soils near the CSM (**Figure 4**). It must also be remembered that both europium and terbium can exist in two different states—Eu(II)/Eu(III) and Tb(III)/Tb(IV) [4]. The changes in redox conditions during the smelting of metal may have an effect on the state of lanthanides entering the soil during contamination.

The content of the exchange fraction of lanthanides in the investigated soils is very low and is at the level of the detection limit of the ICP-MS method that confirms the extremely low mobility of these elements in the soils.

The largest part of the sum of fractions is the residual fraction of lanthanides that corresponds to the literature data [10, 11]. There are no significant differences between soils located at different distances from CSM. Because of the absence of extractive solutions in the fractionation schemes to extract stable technogenic TM compounds from the soil, this method is inapplicable to adequate estimating of soil pollution without additional investigations.

In this context, the comparison of the total extraction capacity of sequential fractionation and 1M HNO_3 is of great interest. The shares of acid-soluble lanthanides in the total lanthanide content in all fractions separated from the soil (except the residual fraction) are shown in **Figure 9**.
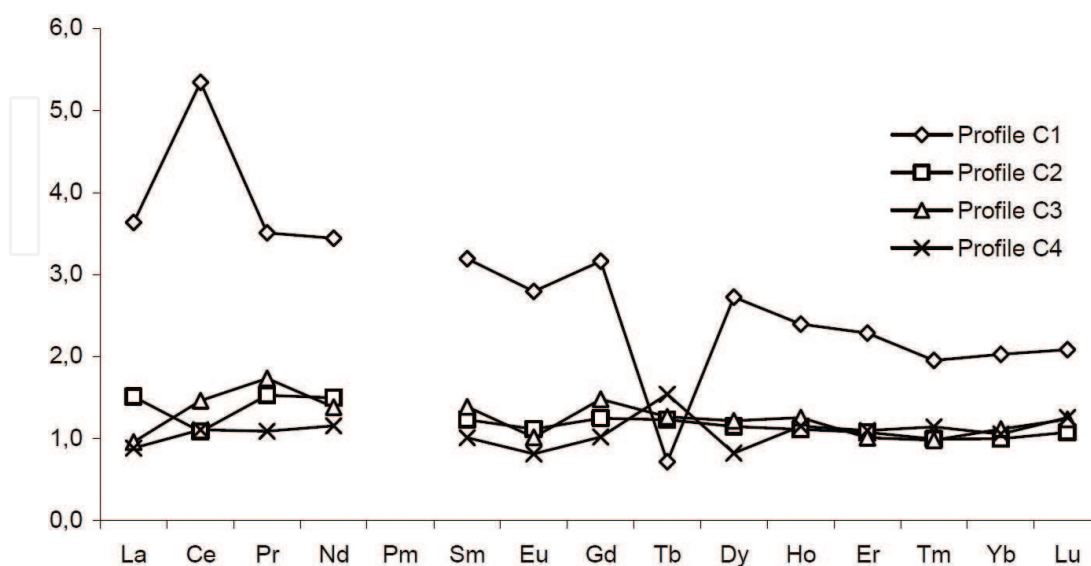
Figure 9. Ratios between the content of acid-soluble forms of the lanthanides and the sum of fractions (without the residual fraction).

It is clearly shown in **Figure 9** that the content of lanthanides in nitric acid extract from the most contaminated soil C1 significantly exceeds the sum of isolated fractions. In other less polluted soils, both these indices are practically equal. Terbium and cerium are out of the general trend in soil C1, and the differences in the behavior of cerium hadn't been noticed earlier and can be associated not with soil contamination by this element but its variable valency and its variation when forms are extracted from the soil. The extraction of lanthanides by nitric acid from the soil of C1 is higher than the amount of other fractions; the inflow of chemically resistant technogenic compounds of lanthanides (presumably oxides) into the soil that could not be extracted under sequential fractionation is clearly indicated.

5. Conclusions

1. Because of different natural abundances of lanthanides, their comparative study in soils is impossible without techniques that allow eliminating this factor: the normalization of the content of elements by a standard object similar to the investigated soils in terms of composition and conditions of formation and determination of extraction degree of various forms of lanthanide compounds. Comparison of distribution diagrams of lanthanides constructed with these indicators allows deriving both qualitative and sometimes quantitative differences in the behavior of these elements and in the technogenic contamination of soils with lanthanides.

2. The soils of the investigated territory are contaminated with the lanthanides due to CSM activities. The lanthanides are characterized by a high degree of extraction of acid-soluble forms (5–40% of the total content).

3. A significantly increased content of praseodymium and terbium was found in soils near CSM. In these soils a less increase in the content of other light lanthanides, from lanthanum to gadolinium inclusive, was also determined. Technogenic contamination also leads to an increase in the amount and to changes in extraction degree of acid-soluble forms of lanthanides from soils.

4. About 80–95% of the total content of lanthanides in the soils of the impact zone of CSM is concentrated in the residual fraction; thus, they are represented by extremely chemically stable compounds. The main soil components determining the background level of the lanthanides in investigated soils are aluminosilicate minerals, strongly fixing the lanthanides in their structure, and the compounds fallen into the soils as a result of the CSM impact are also chemically stable.

5. As a result of soil processes, a part of the lanthanides is bound to organic matter and Fe and Mn (hydr)oxides (5–18% and 0.1–5% of the total content correspondingly). The individual properties of the lanthanides are clearly manifested in their interaction with these soil components. The largest part of the fraction, bound to organic matter, contains medium lanthanides; the part bound to Fe and Mn (hydr)oxides contains heavy lanthanides.

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