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RARE-EARTH ELEMENTS IN SOIL AND PINE NEEDLE FROM NORTHERN TERRESTRIAL ECOSYSTEMS

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The experimental data on heavy metal and rare-earth element concentration in the environmental objects (pine needle and soil) caused by the enterprise for the production of mineral phosphoric fertilisers in Apatity (the industrial region in the Murmansk region, Kola Peninsula) have been obtained. The investigation was performed by the neutron activation analysis at the IBR-2 research reactor in the Joint Institute for Nuclear Research. The analysis of nearly 40 element distributions in pine needle and soil from different geographical sites testifies about their contamination by a spectrum of elements, including REEs. Their contamination levels in the soil in the vicinity of the enterprise are significantly high.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Редкоземельные элементы в почвах и хвое земных северных экосистем

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Получены экспериментальные данные по концентрациям тяжелых металлов и редкоземельных элементов (РЗЭ) в объектах окружающей среды (почвах и хвое) в окрестностях комбината для производства минеральных фосфорных удобрений (г.Апатиты Мурманской области). Работа выполнена с использованием нейтронного активационного анализа на реакторе ИБР-2. Анализ поведения концентраций ~ 40 элементов в хвое и почвах свидетельствует об их загрязнении рядом элементов и особенно РЗЭ.

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Introduction

Monitoring of the environment is actual in connection with significantly increasing technogenic load in many regions of the globe during the past decades. The important objectives of the monitoring are the control and prognosis of the environment state. This requires investigation of interactions between different surroundings as well as the migration processes of contaminating substances. To reliably estimate the quality of the environment systematic studies of different parameters of the environment, including atmospheric air, soil, vegetation, water, etc., need to be carried out. Obtaining of experimental data is an important stage of environmental monitoring.

At present, analysis of the content of different elements and thier combinations is being conducted by different methods. Most suitable are the methods that allow the largest number of elements in biomonitors to be determined reliably. The neutron activation analysis is an effective method and has been used for monitoring different ecosystems of Russia in the NAA department of FLNP, JINR during the recent years.

As is well known, northern ecosystems are especially sensitive to technogenic load and their recovery is a slow process that takes decades. Therefore, timely monitoring is most important. The objective of the performed investigation was to obtain by NAA the new experimental data on the concentrations of different elements, including REEs in soils and pine needle in the industrial region of the Kola Peninsula (in the vicinity of the plant producing mineral phosphoric fertilisers in the town of Apatity). Till recently, the attention paid to studies of the REEs content in ecosystems, as well as to the REEs accumulation processes by vegetation and to their influence on the vegetable and animal world, was not adequate. This is mainly connected with a low content of REEs in vegetation. Their usual concentrations in clean vegetation are on the low level of $\approx ng/g$ and the ratio of the REE content in plants to that in soils is in the range of $n^{*}(10^{-5}–10^{-4})$.

Experimental

This is a continuation of our collaboration with Kola Science Centre of the Institute of North Industrial Problems (Apatity, Murmansk region, Russia). In 1995, pine-needle of 1–3 year-age and soil from different genetic horizons were collected in the vicinity of a plant for production of mineral phosphoric fertilisers in Apatity (at 0.5 and 2 km) and in the nearby regions at the distances of 30 and 100 km from the enterprise. The nearby (background) sites were studied for comparison with the data for Apatity. Nearly 40 elements were identified in the samples of soil and pine-needle by the NAA at the IBR-2 high flux research reactor. The procedures of irradiation and elemental analysis by the gamma-spectrometry of short-, middle-, and long-life nuclides were applied. The neutron energy spectra in the irradiation channels of the IBR-2 reactor are characterised by the presence of thermal, epithermal, and fast neutrons with high flux densities [1] and allow one to realize two regimes of sample irradiation, including by thermal, epithermal, fast neutrons and epithermal and fast neutrons. In the first regime, the analysis sensitivity may be higher for Na, Al, Si, S, Cl, K, Sc, Ca, Cr, Ti, V, Mn, Co, Fe, Cu, Zn, La, Ce, Pr, Nd, Eu, Gd, Dy, Lu, Os, Pt; in the second regime — for F, Mg, Ga, Ge, Se, As, Br, Sr, Rb, Y, Zr, Nb, Ru, Mo, Tc, Ph, Cd, Pd, Ag, In, Sn, Te, Sb, I, Ba, Cs, Pr, Sm, Tb, Ho, Tm, Er, Hf, Yb, W, Ta, Re, Ir, Hg, Au, Th, U. This is connected with the difference in the cross-section values for different nuclides in thermal and epithermal neutron energy regions. Thus, the specific character of the neutron energy spectrum and the possibility of sample irradiation in two different regimes (with and without Cadmium) allow us to provide selectivity of the analysis for interesting trace-elements.

Processing of the NAA data was performed by the computer programs and a well-tested bank of nuclear data. Most nuclides were identified by several gamma-lines. The elemental concentrations were calculated by absolute and reference methods (with Standard Reference Materials from MAGATE and the National Institute of Standards (US)). In the gamma-spectrometry, interference during processing was partially avoided by the choice of interference-free photo-peaks. When necessary, contributions from the interfering reactions and the reactions caused by the fast neutrons were accounted for.

Results and Discussion

On the basis of the obtained elemental concentrations in the samples of soil and pine needle (36 and 32, respectively) average concentrations of elements and their confidence intervals were calculated for each geographical point (0.5, 2, 30, and 100 km). The distributions of all determined elements were analysed versus the distance from the enterprise and, for some of them, are presented in Figs.1–3. These distributions testify the conta-

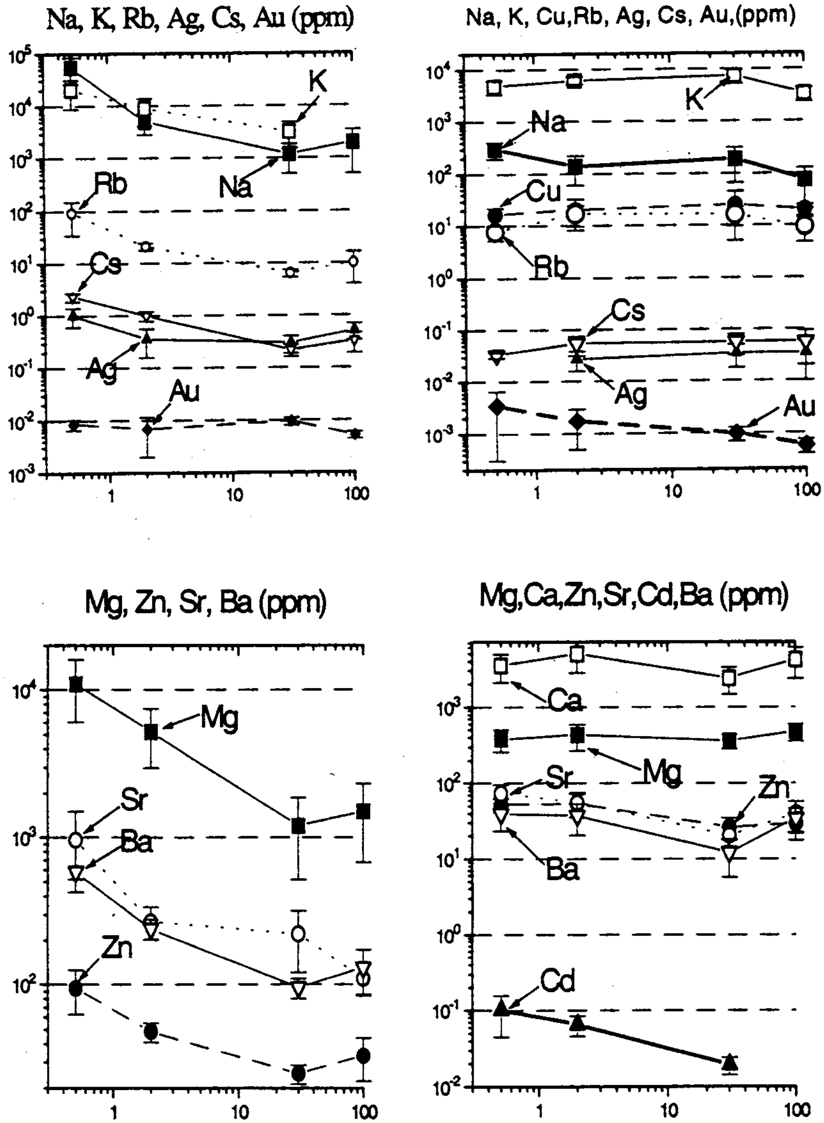

Fig.1. Distributions of elemental concentration for Kola soil and pine needle (left and right, respectively) versus the distance from the enterprise

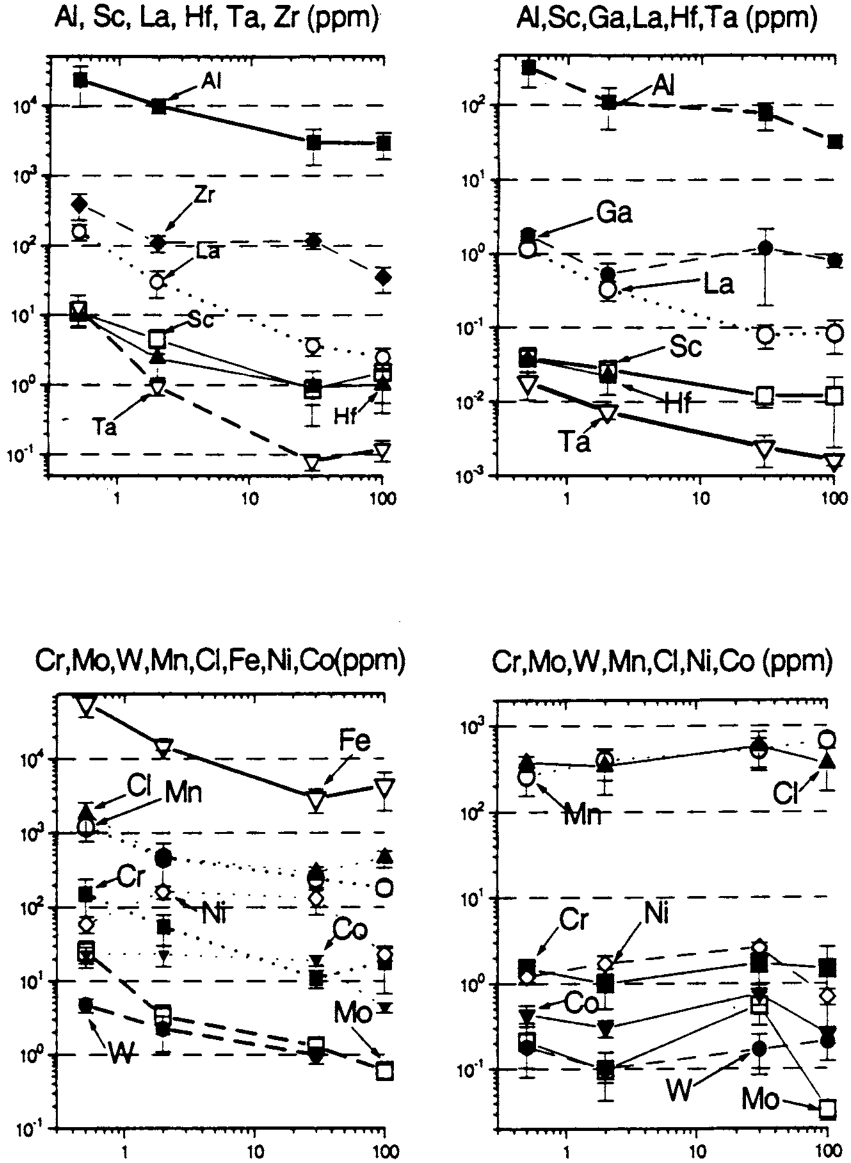

Fig.2. Distributions of elemental concentration for Kola soil and pine needle (left and right, respectively) versus the distance from the enterprise

mination of the biomonitors by the row of elements released in atmosphere by the enterprise in Apatity. Particularly, the increased concentration of Na, K, Rb, Cs, Mg, Sr, Zn, Ba, Al, Zr, Sc, La, Hf, Ta, Fe, Cl, Mn, Cr, Mo, W, Ce, Nd, Sm, Eu, Tb, Yb, Th, and U were observed in superficial soil at distances of 0.5 and 2 km compared to the nearby regions

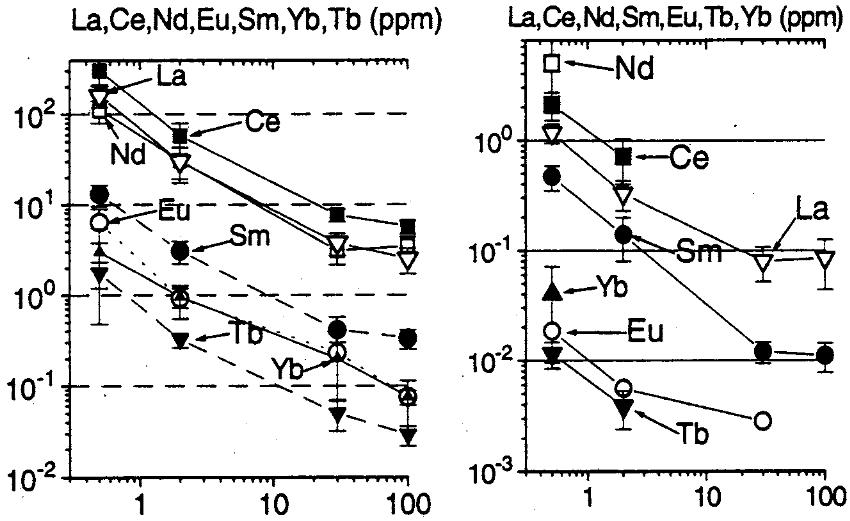

Fig.3. Distributions of elemental concentration for Kola soil and pine needle (left and right, respectively) versus the distance from the enterprise

(30 and 100 km). The concentration of the elements in soil and pine needle with their confidence intervals (in per cent) for Apatity and nearby regions are presented in columns 2–3 of Tables 1–2. The ratios of the maximal REEs concentration in soil (point 0.5 km) to the minimal one (30, 100 km) are high and lay in the range of values from 27 up to 85 (Tab.1, col.4). So, for this specific source of atmospheric pollutions an increased emission of REE is characteristic, what is understandable because the apatit concentrate used as a raw material for the production of mineral phosphoric fertilisers is an intense source of REEs.

In the pine-needle, the increased content of a smaller number of elements, namely — Al, Cd, La, Sc, Ta, Ce, Sm, Eu, Th, and U, is observed. For the content of K, Na, Cu, Rb, Cs, Ag, Ca, Mg, Sr, Zn, Ba, Ga, Hf, Mn, Cl, Cr, Ni, Co, Mo, and W no significant distance-dependence is measured. The concentration of these elements in pine-needle at points 0.5 and 2 km are close to nearby one at points 30 and 100 km. The observed difference in the distributions of concentration of the same elements in soil and pine needle versus the distance from Apatity is, apparently, connected with that in soil, we deal with long-time accumulated amounts of contaminating elements. In pine needle, the contaminating elements were accumulated during a relatively short time and therefore, not exceed significantly their natural concentrations.

Content of REEs in pine-needle in Apatity is higher (1.5–10 times) than in Monchegorsk [7] and significantly higher (10–500 times) than their concentration or upper detection limit in the Tver region (near Moscow). In accordance with Fig.3 we cannot clarify the background content for all REEs in pine-needle. For soil samples we see the complete distance dependence including the suburban points for Sc, La, Ce, Nd, Sm, Eu, Tb, and Yb. As is mentioned above, the natural abundance of REEs in clean vegetation is close to values of the order of ng/g [8]. Therefore, the problem of determination of their suburban content in vegetation is not a very simple one. At the same time, this problem is copmlicated by

Table 1. Concentrations of elements (ppm) in soils of the Kola Peninsula (Apatity)

	Literary data	Apatity Maximal	Apatity Minimal	Ratio 2/3	Toxic in Plants
Na	17700 [6]	55000 (50)	1200 (58)	**46.0**	
Mg	17200 [4]	11000 (45)	1200 (57)	**9.2**	
Al	71100 [2]	23000 (58)	2900 (40)	**7.9**	
Cl	1000 [4]	1800 (43)	290 (20)	**6.2**	
K	10500 [4]	20000 (56)	3200 (53)	**6.2**	
Sc	2.5 [4]	11 (40)	0.86 (40)	**12.8**	
V	90 [2]	120 (55)	14 (35)	8.6	50–100
Cr	70 [2]	150 (58)	11 (27)	13.6	60–600
Mn	- 300 [4]	1200 (36)	180 (20)	**6.7**	> 2200
Fe	13100 [4]	57000 (35)	2900 (36)	**19.7**	
Co	8 [2]	23 (25)	4.3 (15)	5.3	
Ni	50 [2]	160 (25)	58 (25)	2.8	
Zn	50 [4]	94 (32)	25 (15)	3.8	
Se	0.37 [3]	1.7 (25)	1.4 (25)	1.2	
As	1 [4]	18 (30)	6.1 (24)	3.0	$15–10^3$
Rb	20 [4]	91 (60)	6.3 (25)	**14.4**	
Sr	70 [4]	960 (55)	110 (25)	**8.7**	
Zr	50 [4]	390 (40)	35 (40)	**11.1**	
Mo	1.0 [2]	25 (40)	0.6 (21)	**41.7**	
Ag	0.015 [4]	1.0 (39)	0.3 (33)	3.3	
Cd	0.8 [4]	0.67 (20)			
Sb	0.07 [4]	1.0 (30)	0.5 (20)	2.0	
Ba	60 [4]	580 (11)	95 (16)	**6.1**	
Cs	1.5 [4]	2.3 (18)	0.22 (25)	**10.5**	
La	0.8 [4]	160 (25)	2.5 (32)	**64.0**	
Ce	5.5 [5]	300 (30)	5.7 (20)	**52.0**	
Nd	2.4 [5]	110 (25)	3.1 (27)	**35.5**	
Sm	0.43 [5]	13.0 (26)	0.33 (23)	**39.0**	
Eu	0.083 [5]	6.4 (40)	0.075 (18)	85.3	
Tb	0.08 [5]	2.5 (25)	0.05 (36)	**50.0**	
Yb	0.8 [4]	2.0 (50)	0.075 (52)	**26.7**	
Hf	0.4 [4]	10 (30)	0.93 (67)	**10.8**	
Ta	0.023 [4]	13 (46)	0.08 (25)	**162.0**	
W	0.7–3 [3]	4.7 (21)	1.0 (25)	**4.7**	
Au	0.007 [4]	0.0095 (18)	0.005 (16)	1.8	
Th	1 [4]	13 (26)	0.33 (37)	**39.4**	
U	0.4 [4]	6.4 (40)	0.075 (19)	**85.3**	

Table 2. Concentration of elements in pine-needle (ppm) of the Kola Peninsula (Apatity)

	Tver Average	Apatity Maximal	Apatity Minimal	Ratio 2/3	Toxic in Plants	Cereal Grains
Na	14 (64)	300 (35)	**74 (71)**	4.1		
Mg	785 (19)	430 (38)	360 (22)	1.2		
Al	148 (46)	300 (45)	33 (15)	**9.1**		
Cl	177 (28)	580 (48)	340 (53)	1.7		
K	2830 (33)	7400 (30)	3300 (30)	2.2		
Sc	0.013 (30)	0.04 (36)	0.012 (30)	3.3		
Cr	< 0.1	1.7 (41)	**1.0 (50)**	1.7	4–30	
V	< 1	2.0 (25)	0.3 (58)	**6.7**		
Mn	234 (51)	670 (20)	260 (40)	2.5		
Fe	55 (43)	412 (29)	67 (44)	**6.2**		25–80
Co	0.039 (89)	0.75 (26)	**0.25 (21)**	3.0	20–50	4–20
Cu		25 (80)	16 (36)	1.6		
Ni	2.4 (70)	2.6 (25)	0.7 (20)	3.7	10–100	0.2–0.6
Zn	33 (36)	52 (21)	26 (33)	2.0	70–400	22–33
Se	< 0.02	0.24 (20)	0.067 (22)	3.6	0.8–22	0.02–0.5
As	< 0.01	0.57 (32)	**0.063 (31)**	**9.1**	2–20	0.05
Rb	21 (76)	17 (44)	7.5 (30)	2.3		4
Sr	3.4 (12)	73 (27)	**20 (28)**	**3.6**	> 600	0.5–2
Mo	< 0.4	0.21 (66)	0.033 (25)	**6.4**	2–10	0.2–0.6
Ag	0.031 (23)	0.05 (30)	0.026 (40)	1.8	5–10	
Cd	< 0.03	0.10 (55)	0.019 (26)	**5.3**	5–30	0.01–0.2
Sb	0.033 (42)	0.028 (45)	0.009 (25)	3.1	> 0.15	0.002
Ba	1.2 (58)	39 (40)	**12 (50)**	3.3	> 500	4–6
Cs	0.081 (91)	0.056 (42)	0.033 (40)	1.7		
La	< 0.01	1.2 (20)	**0.08 (35)**	**15.0**		
Ce	< 0.09	2.1 (28)	< 0.5	**> 40**		
Nd	< 0.2	5.0 (60)	< 0.84	**> 6**		
Sm	< 0.001	0.47 (26)	0.011 (30)	**42.7**		
Eu	0.024 (66)	0.019 (48)	< 0.0028	**> 6.8**		
Tb	< 0.003	0.011 (24)	< 0.00034	**> 32**		
Yb	0.03 (60)	0.04 (50)	< 0.0022	**> 18**		
Hf	0.34 (67)	0.036 (25)	0.022 (43)	1.6		
Ta	0.0015 (40)	0.018 (82)	0.0016 (25)	**11.3**		
W	< 0.02	0.18 (42)	**0.10 (57)**	1.8	> 3	
Au		0.0034 (90)	0.0006 (30)	5.7		
Th	0.07 (12)	0.069 (23)	0.026 (27)	**2.7**		
U	< 0.004	0.022 (30)	0.0073 (25)	**3.0**		

the presence of other contaminating and interfering elements in pine-needle besides REEs. This leads to a decrease in the sensitivity of REEs determination. It can be also noted that in fact, we do not know a priory to what extent the background (suburban) regions are clean. Elucidation of this circumstance was also one of the objectives of this investigation. But we see that pine-needle from the suburban sites is characterised by a sufficiently high content of some other elements, such as Na, Cr, Co, As, Sr, Ba, and W, whose concentration is 5–10 times higher than, for example, in the pine needle from Tver region (Table 2, cols.3,1, respectively). The obtained concentrations and upper detection limits for REEs in the pine needle and soils from suburban sites are in reasonable agreement with analogous ones in [5,8]. Thus we can conclude that for the reliable determination of the majority of REEs in the pine-needle from suburban regions, the maximum sensitivity of analysis must be achieved, possibly, by individual and more suitable regimes of irradiation for some REEs.

Conclusions

As a result, of this work the new experimental data on the concentration of nearly 40 elements in environmental biomonitors, such as soil and pine needle, were obtained. It was elucidated that the investigated enterprise for production of mineral phosphoric fertilisers is a specific source of atmospheric pollution and releases into the environment a wide spectrum of different elements, including REEs. On the basis of the obtained data the emission power of this industrial source of atmospheric pollution can be estimated and used for prognosis of the future state of the environment in this region.

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