UDC 504.3.054:620.26+663

Geochemical Features of Aerosol Pollution in the Region of the Siberian Chemical Combine

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(Recieved 30.05.11; revised 12.07.11)

Abstract

Results of the investigation of aerosol in the region of Seversk (Tomsk Region) performed in 2010 using mass spectrometry and atomic emission with inductively coupled plasma are presented. With the help of GIS methods, geochemical indicators of technogenic aerosol of the Siberian Chemical Combine were revealed, and the basic aureoles of their distribution were determined. Comparative analysis of the results and the data published previously is presented.

Key words: Siberian Chemical Combine, aerosol pollution, emissions, snow cover, technogenic aerosol, geochemical indicators, rare earth elements, natural radionuclides, isotopes, ecological risk, mass spectrometry with inductively coupled plasma, atomic emission spectrometry with inductively coupled plasma

INTRODUCTION

Enterprises related to Minatom of the Russia manufacturing enriched uranium and plutonium, and processing radioactive wastes have always been the objects of rapt attention of the society and ecologists. Researchers at the Tomsk Polytechnic University were the first to start the investigation of geochemical features of aerosol in the region of Seversk (Tomsk Region) within the boundaries of the Siberian Chemical Combine JSC (SCC), a city-forming plant of the nuclear fuel cycle. During the period of operation of the reactors producing plutonium, the solid precipitates in snow cover of the region were shown to contain high concentrations of X-ray amorphous matter, spherical particles of mullite and magnesioferrites, graphite, asbestos, badelleite (ZrO_2), uranium oxides, ferrites, hematites, metal Au, Pb, Co, Fe, Ni of technogenic origin [1]. The same complex of technogenic minerals except uranium oxides was extracted from soil and ground in the region [2]. As the geochemical indicators of SCC emissions, U, Lu, Zn, F, Cs were determined in the snow cover [3], Sr, Eu, Lu in soil [4]. It was revealed that in the soil of the zone affected by SCC the ratio $(La + Ce)/(Yb + Lu) < 22$, the ratio $Ce/Eu = 14–26$, $Th/U < 2.5$ [2, 4].

The goal of the present work was to study the elemental composition of modern technogenic aerosol in the Seversk region after the reactors were stopped and the major kind of production at the SCP is only processing of radioactive wastes (uranium hexafluorides). Under the conditions of Siberia, snow is an ideal object to study the composition and dynamics of emissions from industrial enterprises because solid aerosol particles and gaseous products partially sorbed on solid phases are fixed in stable snow cover since the beginning of November till the end of March.

The winds of southern and southwestern direction dominate in the region of Seversk,

similarly to the south of West Siberia in general. This explains the major fluxes of aerosol pollution from the industrial chimney stalks and power stations: wind-induced transport of aerosol particles to the north and northeast dominates.

OBJECTS AND METHODS OF INVESTIGATION

Large-scale samples of snow cover (50–70 L each) were taken in March 2010 along three routes to the north and northeast from Seversk (Fig. 1). To exclude the effect of automobile roads, sampling sites were chosen at a distance not less than 200 m from roads. Site binding was performed with the help of the GPS navigator Etrex GARMIN with the error of 7–10 m.

Samples were left to melt in the vessels 70 L in volume. The upper part of settled melted water was decanted; the lower layer of water with the suspension was filtered through a "blue ribbon" paper filter. The dust content was determined as the ratio of the mass of suspended matter to the volume of melted snow, the dust and aerosol load was measured as the ratio of the mass of suspended matter to the product of sampling area and the dumber of days since the formation of stable snow cover till sampling day.

Fig. 1. Scheme of sampling sites near Seversk: *1* – sampling sites (Nos. 1–10) of snow cover in 2010; II – cities; III – settlements; IV – territories of settlements; insert shows the positions of sampling sites.

Snow precipitation was transferred into solution using two methods: 1) fusion with KOH and Na_2O_2 at 550 °C after preliminary ashing for 2 h at 450 °C; 2) decomposition with concentrated acids $HClO_4$ and HF in autoclaves at a temperature of 120 °C for 2 days. The concentrations of macroelements Ca, Mg, Na, K, S, Si, B, Tl, Fe, Mn, P and As were determined by means of atomic emission with inductively coupled plasma using an IRIS Advantage spectrometer (the USA) [5, 6]. Relative error is not more than 15 %, while the lower detection limits are 0.1 to 0.0005 ppm. The concentrations of heavy metals, rare earths (lanthanides), highly charged elements (Hf, Nb, Ta, Zr, Ba, Rb, Sr, Y, radionuclides Th and U) were determined by means of mass spectrometry with inductively coupled plasma (MS-ICP) using the ELEMENT instrument (Finnigan Mat GmbH, Germany) [7, 8]. To correct the matrix effect and to control the instrumental drift, In in the concentration of 1 ng/L was used as the internal standard. Rare earth elements (REE) and highly charged elements, as well as Cd, Tl, Cu, Zn, Pb were determined at the low resolution because there are no substantial overlapping elements (except superposition of Ba oxides on the isotopes of Eu). The elements Al, Ca, Co, Cr, Cu, Fe, Ga, Mn, Na, Ni, P, Mo, Sc, Si, Ti, V, Sb were analyzed with medium resolution, while K, As at high resolution to isolate the signals of elements from spectral overlaps. The limits of element detection (except macroelements) are 0.1 to 0.01 ppb. The relative standard deviation, independent of elements, does not exceed 10 % if the concentration under determination is above the detection limit by an order of magnitude or more. The isotope ratio $^{235}U/^{238}U$ was determined using the MS-ICP method with the relative error of ≤2 %. When measuring isotope ratios, scanning was performed for 1 min 50 s (1000 and more scans for each isotope) [9].

The elemental composition of separate aerosol particles was studied with a LEO 1430 VP scanning electron microscope equipped with an OXFORF energy disperse spectrometer (EDS). The diameter of the scanning beam of

the spectrometer was about 0.5 μm, which allowed us to determine the composition of aerosol particles 0.5–1 μm in size.

On the basis of the Landcat geo-coded photos, a GIS project of the region under study was prepared with the help of ArcView 3.3 software package with Spatial Analyst module and ENVI 4.01 software. The elemental and ion composition of melted snow and aerosol particles was introduced into the GIS project in the form of separate thematic layers. The GIS project was created in the UTM coordinate system (zone 45, geoid WGS-1984) compatible with point coordinates according to the ETREX GARMIN GPS navigator.

RESULTS AND DISCUSSION

The distribution of dust content in snow cover provides evidence that the major aerosol transport from Seversk goes to the north and northeast according to the wind rose: the dust and aerosol load during the winder of 2010 in this direction at a distance up to 21 km was 31.2–102.3 mg/(m^2 · day), the average value being 53.4 mg/(m^2 · day) (Fig. 2, *a*). These data are in good correlation with previously obtained results at approximately the same area (20–124 mg/(m^3 · day), the average value 51.6 mg/(m^2 · day)) [1] but much lower than the dust and aerosol load within the city territories (16–303 mg/(m^2 · day) in Tomsk) [10]. With an increase in the distance from Seversk, the dust and aerosol load decreases and becomes only 22.8 mg/(m^2 · day) at a distance of 27.8 km to northeast (see Fig. 2, *a*). The minimal dust load was detected in the samples of the north-northwestern route in the vicinity of Samus settlement: only 11.9 to 17.3 mg/(m^2 · day).

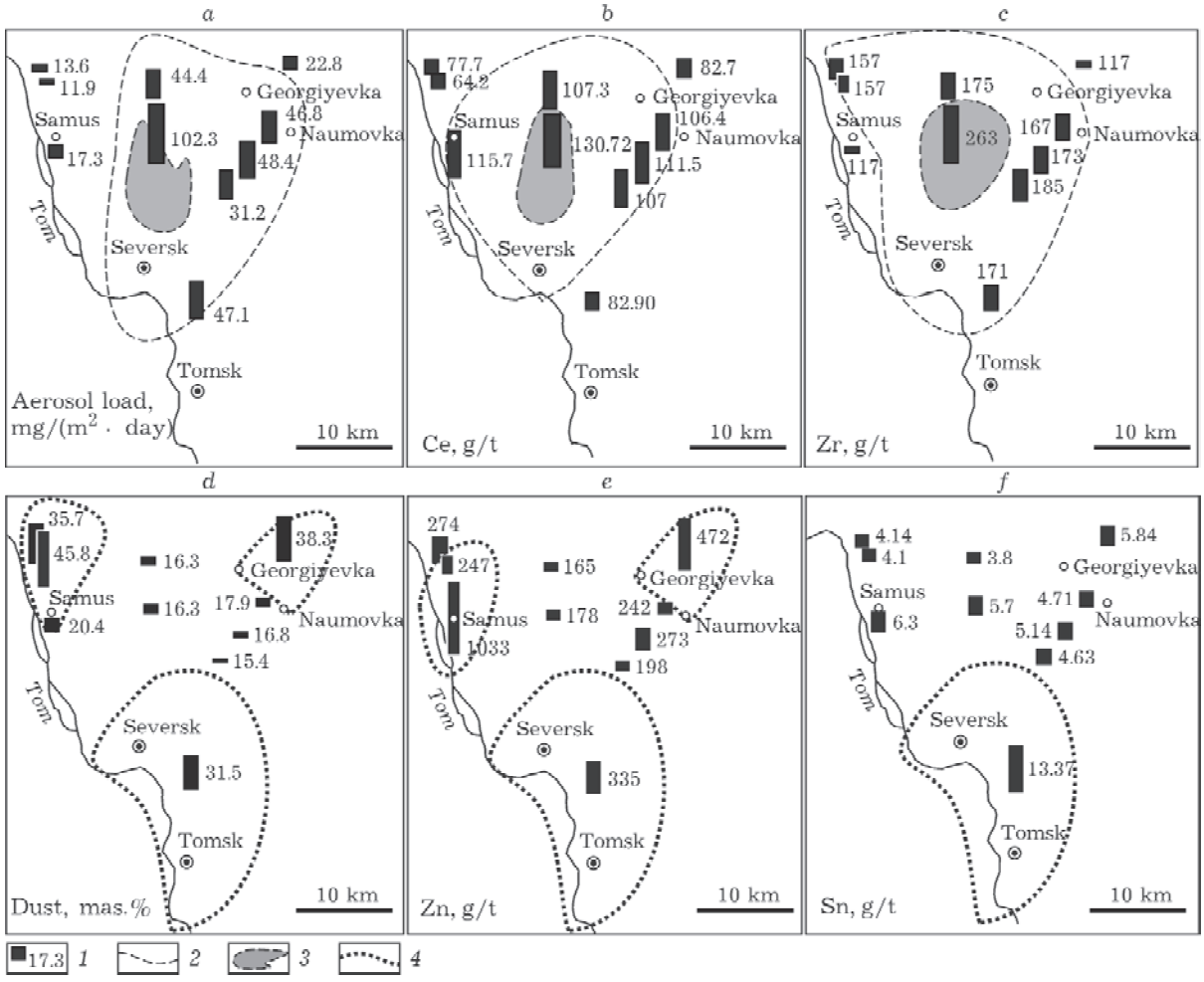

Fig. 2. Data on dust and aerosol load in the region of Seversk (*a*) and content in aerosols: Ce (*b*), Zr (*c*), soot (*d*), Zn (*e*), Sn (*f*): *1* – diagram and component content in aerosol samples; *2* – major plume of high-temperature emissions from SCC; *3* – region of maximal precipitation of emissions from SCC; *4* – plumes of local low-temperature aerosol emissions.

Three sites were revealed in which aerosol was enriched with soot: 1) near Naumovka and Georgiyevka villages; 2) near Samus settlement; 3) in the suburbs of Seversk and Tomsk (see Fig. 2, *d*). Soot content in the samples taken at these sites is 32–46 % and originates from local pollution due to furnace heating in villages, from boiler plants in Samus, as well as from city "breathing" (understood as integral emissions of small city industrial enterprises and vehicles). At the same time, to the north and northeast of Seversk under high dust and aerosol load low soot content in aerosol is observed: only 15–16 mass %, which is 2–3 times lower than its content in the aerosol of three sites indicated above. According to the data of the spectrogram of individual soot particles, they are composed of amorphous carbon by 80–100 %, with admixtures (%): O up to 7–10, Si 2–5, Al, S, K, Ca 0.*n*.

The basis of the mineral component of aerosol is formed by SiO_2, Al_2O_3 and Fe_2O_3, with their average fractions of 64, 21.7 and 7.65 %, respectively. The aluminosilicate composition of aerosol is the same for all samples from this region; the fraction of silica is about three times larger than alumina (Fig. 3). An increase in Fe_2O_3 content (up to 9.85 %) was detected in the samples taken in the vicinity of Samus along the north-northwestern route. In this direction also SO_2 content increases in aerosol samples (up to 3.1 %; average 0.66 %), K_2O (up to 1.46 %, average 0.75 %), P_2O_5 (up to 0.58 %, average 0.26 %) (see Fig. 3). It was established that SO_2, P_2O_5, K_2O content is substantially connected with soot content of aerosol: correlation coefficient R for these elements is 0.56, 0.78 and 0.49, respectively. A weak increase in SO_2, P_2O_5 content, as well as an increase in CaO content (up to 2.61 %, average 1.98 %) is observed in aerosol samples from the suburbs of Seversk and Tomsk (see Fig. 3, sample No. 10). The concentrations of other macrocomponents are insignificant and varies from one tenth of a per cent to 2 % (see Fig. 3).

The microelement composition of aerosol (Table 1) obtained with the help of MS-ICP is substantially enriched with a number of elements in comparison with the clarke (K) [11]. Thus, excess was detected for the following chalcophilic elements: Cd maximally 117.3 times (19.8 times as average), Bi 97 and 19 times, respectively, Sb 36.5 and 14.9 times, Mo 34.1 and 6.8 times, Zn 15.4 and 4.8 times, Cu 10.7 and 3.4 times, Pb 9.1 and 5.9 times, Ni 6.5 and 2.1 times, Co 2.1 and 1.1 times, respectively. The content of lithophilous elements exceeds the clarke as follows (times): Sn maximally 6.4 (average 2.7), W 2.7 and 1.6, respectively, Ba 2.6 and 1.9, Nb 2.3 and 1.6, Y 2.1 and 1.7, Sr 1.8 and 1.3, radionuclides Th 2.3 and 1.7, U 3.6 and 2.6, respectively. The maximal excess for

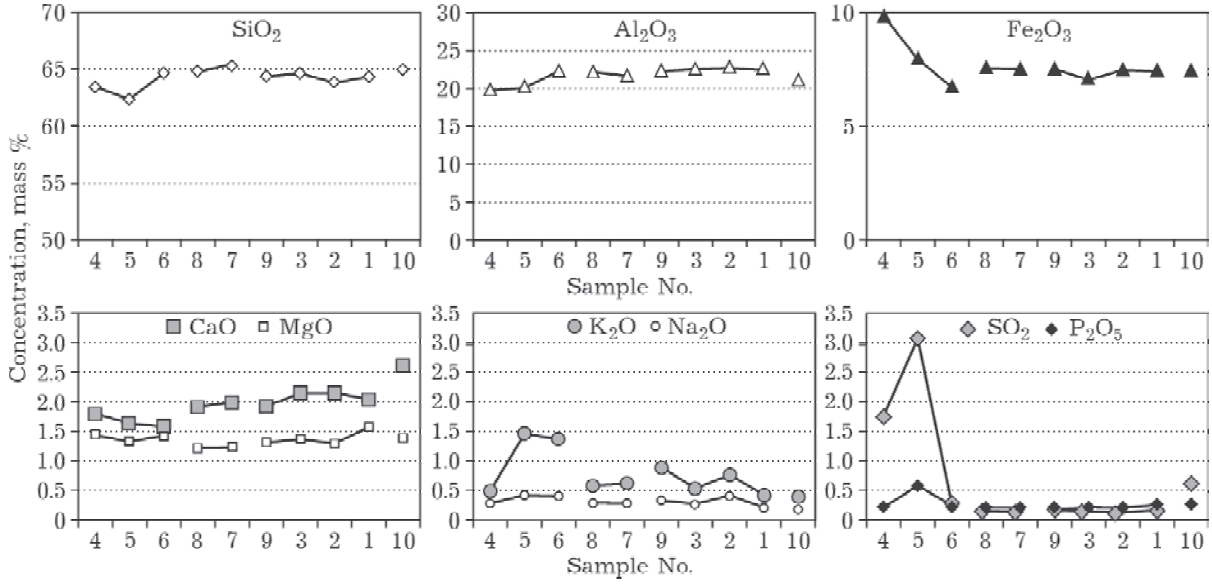

Fig. 3. Concentrations of macrocomponents in the mineral part of aerosol in the region of Seversk in the samples taken in 2010 (without taking soot into account).

TABLE 1

Microelement composition of aerosol, ISP-MS, ppm

Profiles	Sample No.*	D**, km	Pb	Zn	Sb	Co	Ni	Cu	Cd	Bi	Mo	W	Sn	Sr	Ba	Y	Nb	Zr	Hf
Clarke			17	67	0.4	17.3	47	28	0.09	0.16	1.1	1.9	2.1	320	624	21	12	193	5.3
NNW	4	16.2	152	1 033	14.6	36	304	130	10.6	15.5	38	5.17	6.30	452	1 401	39.7	18.0	117	n.d.
	5	22.8	89	247	5.2	14.1	112	299	1.19	4.9	16.9	2.68	4.09	255	919	23.4	14.4	157	n.d.
	6	24.7	109	274	5.4	15.7	61	80	0.76	1.42	3.0	2.77	4.14	343	1 079	28.1	14.0	157	n.d.
N	8	14.7	117	178	5.3	24	83	77	0.84	1.70	3.5	2.79	5.70	588	1 620	44.7	28.0	263	13.0
	7	20.1	65	165	3.4	17.2	66	54	0.50	1.06	2.6	2.80	3.78	435	1 228	37.2	21.9	175	n.d.
NNE	9	13.2	103	198	5.5	19.0	70	70	0.88	1.58	3.0	2.59	4.63	428	1 263	36.8	21.1	185	n.d.
	3	16.9	106	273	6.2	20	79	66	0.95	1.57	2.9	2.44	5.14	478	1 355	38.9	22.7	173	n.d.
	2	21.0	90	242	4.9	20	89	67	0.81	1.42	2.5	2.54	4.71	489	1 373	37.5	21.8	167	7.1
	1	27.8	154	472	8.1	16.5	69	67	1.07	1.62	2.3	2.02	5.84	348	1 018	28.8	16.3	116	n.d.
SE	10	6.85	64	335	3.4	16.3	65	100	1.26	1.74	4.9	4.74	13.37	359	1 033	29.4	15.7	171	n.d.

Profiles	Sample No.*	D**, km	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Tl
Clarke			31	63	7.1	27	4.7	1.0	4.0	0.7	3.9	0.83	2.3	0.3	2.0	0.31	10.5	2.7	0.9
NNW	4	16.2	59	116	14.9	51.4	9.3	1.90	9.17	1.33	9.50	1.90	5.77	0.90	5.30	0.77	15.6	9.1	0.78
	5	22.8	43	64	9.3	32.1	6.1	1.01	5.54	0.76	5.40	1.09	3.33	0.54	2.61	0.40	14.1	4.3	0.38
	6	24.7	43	78	10.4	35.7	7.2	1.27	5.65	0.90	6.22	1.30	4.01	0.67	3.07	0.57	14.2	5.4	0.30
N	8	14.7	68	131	17.0	58.2	11.1	1.89	9.93	1.42	10.25	2.07	6.20	1.01	6.00	0.88	24	9.8	1.73
	7	20.1	55	107	13.7	46.8	8.5	1.55	7.82	1.11	8.58	1.74	5.13	0.79	4.98	0.72	18.7	7.5	1.13
NNE	9	13.2	56	107	13.7	47.2	8.5	1.60	7.96	1.14	8.57	1.73	5.00	0.79	4.75	0.71	19.6	7.5	0.90
	3	16.9	58	111	14.5	49.6	9.0	1.63	8.14	1.22	8.89	1.75	5.14	0.81	5.12	0.72	20	7.9	1.36
	2	21.0	57	106	13.7	48.1	8.5	1.52	8.25	1.14	8.61	1.71	5.14	0.83	5.01	0.73	19.6	7.2	0.94
	1	27.8	43	83	10.7	36.7	6.5	1.18	6.20	0.86	6.53	1.26	3.81	0.60	3.59	0.53	14.3	5.6	0.84
SE	10	6.85	44	83	10.9	39.0	7.1	1.23	6.11	0.94	7.22	1.39	4.02	0.62	2.63	0.62	16.0	6.1	0.51

Note. n. d.– not determined. .

* Sample No. corresponds to the numbers of sampling sites (see Fig. 1).

** Distance from the centre of Seversk, km.

light lanthanides was 2.4 times (1.7 as average), heavy lanthanides 3.5 times (2 times as average).

The features of element distribution in the aerosol of the region under study provided the separation into two groups formed by the emissions from different technogenic sources. The first group of elements, mainly chalcophilic, is concentrated within three sites of local aerosol pollution revealed previously on the basis of soot content: 1) near Naumovka and Georgiyevka villages, Pb content in aerosol samples increases to 8.9 of the clarke (K) for the upper part of the Earth's crust [11], Zn to 7K, Sb to 20.3 K (see Fig. 1), 2) near Samus settlement in

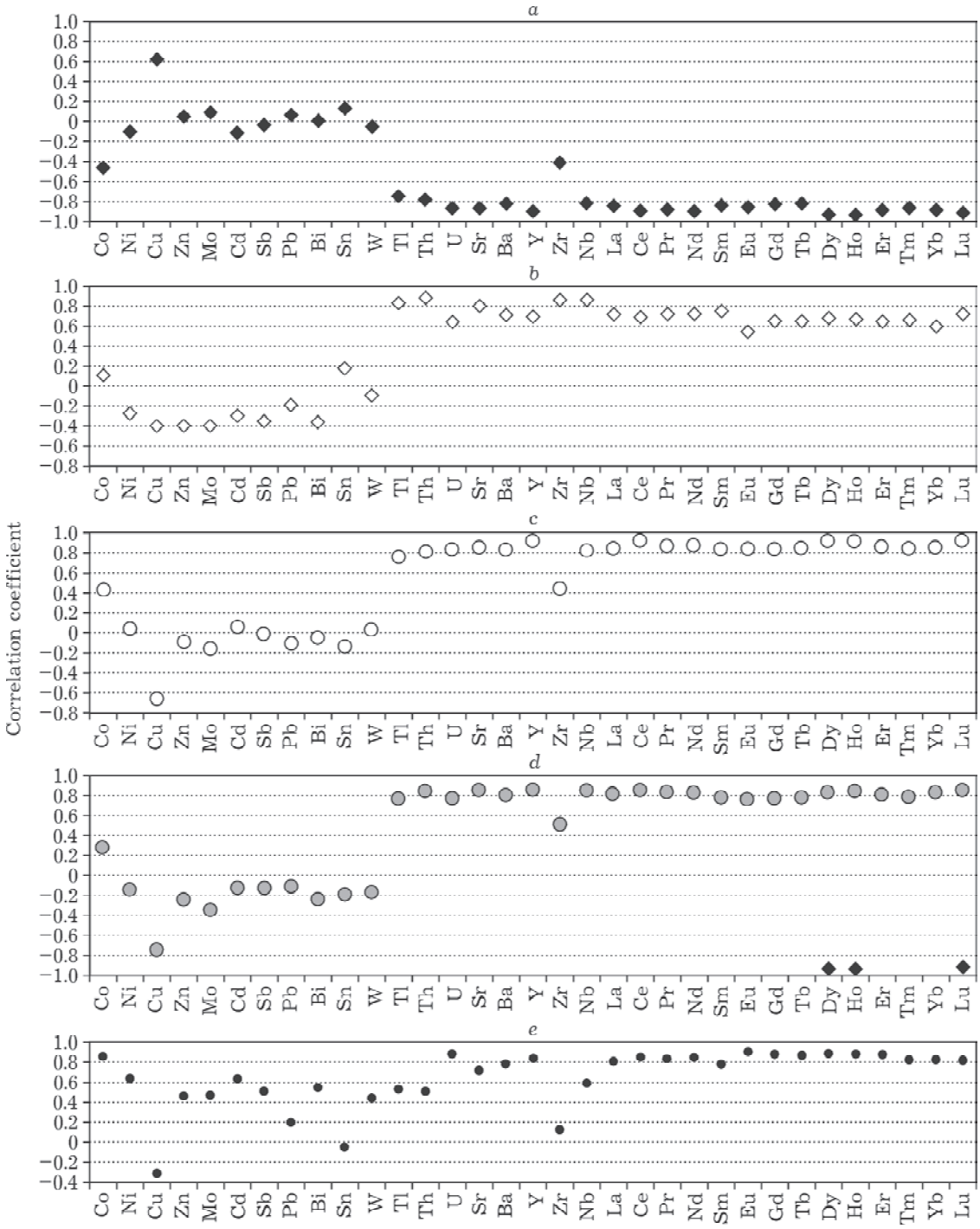

Fig. 4. Correlation coefficients between microelement content in aerosol of Seversk and soot content in aerosol (*a*), with the dust and aerosol load (*b*), with the concentrations of silica (*c*), alumina (*d*), and total iron (*e*) in 2010.

aerosol samples, in addition to an increase in Pb content (up to 8.9K) Zn, Sb (to 36.5K), the concentrations of the following elements are sharply increased: Cd (to 117.3K), Bi (to 97K), Mo (to 34.1K), Cu (to 10.7K), Ni (to 6.5K), Co (to 2.1K), and lithophilous W (to 2.7K); 3) in the suburbs of Seversk and Tomsk aerosol samples exhibit increased content of chalcophilic elements (Cd to 14K, Zn to 5K, Mo to 4.4K, Cu to 3.6K) and lithophilous ones (W to 2.5K, Sn to 6.4K) (see Fig. 2, Table 1).

Except for copper, no clear correlation of the concentrations of these elements with soot content is observed (Fig. 4).

These three regions of local distribution of the 1st group elements are overlapped by the local distribution of the 2nd group elements including lithophilous ones (Sr, Ba, Y, Nb, Zr), natural radionuclides (NRE) U, Th, as well as REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and likely chalcophilic rare Tl. The values of correlation coefficients between REE, NRE and lithophilic elements of this group are not less than 0.9, which points to their close genetic connection, that is, a sole common source. The concentrations of elements exceed the clarke by a factor of 1.5?5 (see Table 1) and are most substantial in the points of northern routes that are the closest to Seversk: point 4 of the north-northwestern route, points 9, 3, 2 of the northeastern route. Their maximal content was detected in the sample taken in point 8 of the northern route. With an increase in the distance from the city, element concentrations in aerosol decrease not so substantially: 1.65 times as average along the north-northwestern route when passing from point 4 (at a distance of 15.8 km from Seversk) to point 5 (at 22.6 km) and almost 1.3 times in the northern route (passing from point 8 to point 7, at a distance of 14.8 and 20 km from Seversk, respectively) and northeastern direction: from point 2 to point 1 (at 21 and 27.8 km, respectively). In point 10 situated at a distance of 6.85 km to southeast from Seversk and 9 km to the northeast from Tomsk the concentrations of the 2nd group elements is not high and comparable with their content in point 1 which is situated at the largest distance from the cities (27.8 km). The ratio of 2nd group element concentrations in the sample of point 1 to that in the sample of point 10 is 0.99. This distribution of the concentrations of the 2nd group elements in aerosol points to the fact that the source of this group of elements is in Seversk rather than in Tomsk, and agrees with the dominant northern and northeastern direction of aerosol mass transfer (see Figs. 1, 2, Table 1).

A correlation is observed between the concentrations of the 2nd group elements and the dust and aerosol load of the region, with the average value of correlation coefficient $R = 0.74$, and with its basic mineral components: silica ($R = 0.85$), alumina ($R = 0.81$) and iron ($R = 0.75$) (see Fig. 4, *b*–*d*). The prevailing plume of SCC emissions to the north and northeast creates a field of heavy dust and aerosol load and provides the high concentrations of the 2nd group elements in aerosol, which is indicated by the data for samples taken in points 2–4, 7–9. At the same time, a reverse correlation between the concentrations of the 2nd group elements and soot content is characteristic of aerosol: $R = -0.85$, which points to the absence of their connection with three previously outlined regions of local aerosol pollution (see Fig. 4, *a*). Among the elements of the 2nd group, Zr is distinguished because it exhibits a weaker correlation with silica ($R = 0.47$), alumina ($R = 0.51$) and iron ($R = 0.15$) (see Fig. 4). The Zr content may be connected not only with the aluminosilicate and iron components but also with other components of aerosol from SCC. The presence of another significant source is also admitted, which would explain the observed effect of a decrease of the correlation of Zr with other elements of the 2nd group.

So, it may be stated that the emissions of SCC in Seversk form the major dust and aerosol load in the region and thus serve as the dominating regional technogenic source. The emissions of SCC are distinguished by high temperature and low soot content, predominance of SiO_2, substantial Al_2O_3 content, the presence of CaO admixture; they are enriched with a complex of microelements of the 2nd group. The latter corresponds to the geochemical specificity of the emissions of nuclear fuel cycle of SCC. The author of [3] established that Lu, F, Zn, U, Cs are connected with SCC emissions but we expanded this group to include

the entire sequence of REE, as well as Th, Ba, ,Y, Nb, Zr, Tl. However, Zn is excluded from this group because of the absence of its correlation with the elements of this group and the presence of a strong correlation with the elements of the 1st group.

The authors of [1, 12] in 2004 studied aerosol (snow precipitation) at three regions at a distance of 15–20 km to the northeast from Seversk, at 2–10 km to the southwest from Seversk and Tomsk, at 85–110 km to the northeast and east from Seversk near six villages at the left bank of the Chulym River (see Fig. 1).

Additionally, we attracted for comparison the background data on aerosol samples collected at a distance of 480 km to the northwest from Tomsk (regional background [10] – G1); at 75 km to the southwest from Tomsk (local background [10] – G2); at 15 km to the southeast from Tomsk (G3). We also used the published data of studies carried out in 1995 for soil and aerosol of Seversk [13], the data of 2008 for soil of Seversk and Tomsk [4], as well as the data of 2010 for soil and aerosol of Tomsk [10].

It is necessary to stress that the monograph of 2010 [10] presents the data on samples taken within the boundaries of Tomsk. (Unfortunately, the information on sampling date is absent; most probably the samples were taken before the year 2010.) Our works in 2010 were dealing with fixing the major plume of wind-related transport of emissions from Seversk to the northern and northeastern directions from the city (according to the dominating directions of wind in winter), so the boundaries of our sampling region do not coincide with those in [10].

At two regions situated within the radius of 20 km from Seversk, the authors of [1, 12] also studied soil [2]. The first site coincides with boundaries of the region of dominating plume

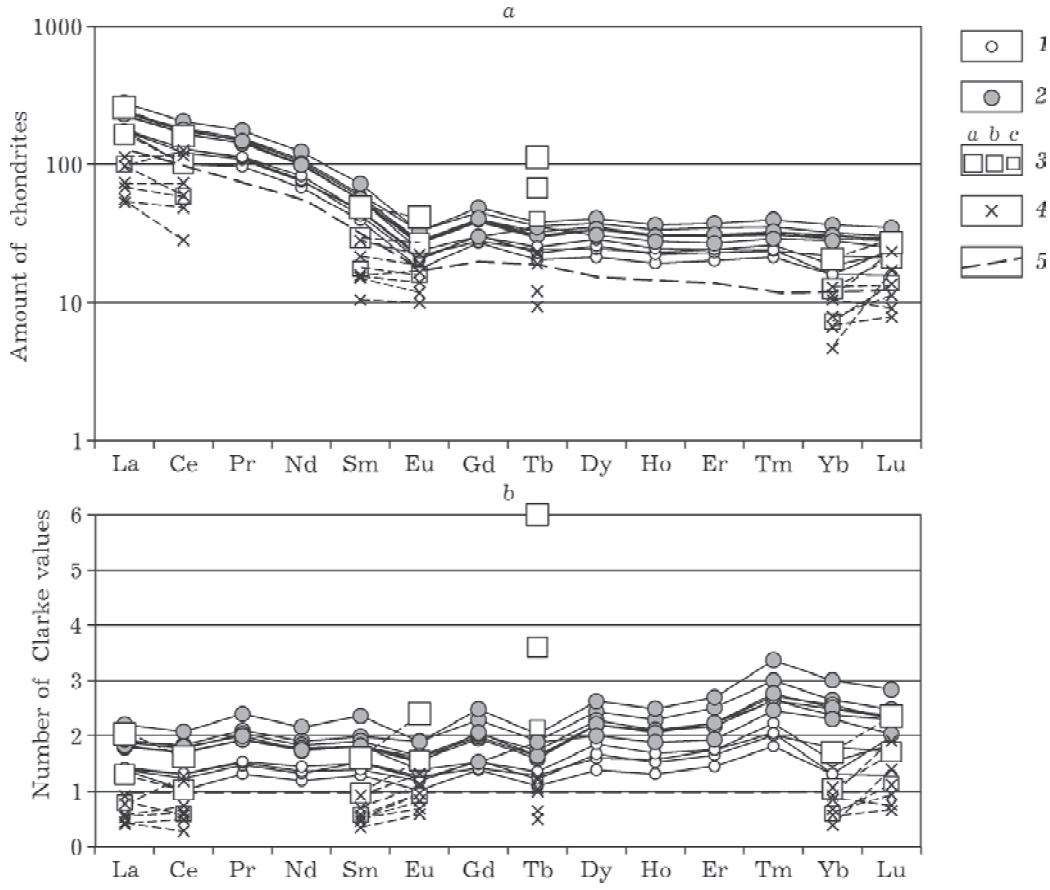

Fig. 5. REE profiles normalized for carbonaceous chondrite [14] (*a*) and the clarke [11] (*b*): *1*, *2* – aerosol samples taken by us in 2010 outside (*1*) and within the major SCC emission plume (*2*); *3*, *4* – data of 2004 on aerosol samples taken at a radius of 20 km from Seversk (*a*–*c* – maximal, average and minimal concentrations of elements, respectively [1]) (*3*) and at a distance of 85–110 km to the northeast and east from Seversk [12] (*4*); *5* – the clarke.

due to emissions from SCC outlined by us – to the northeast from the city; the second region is situated in the southwestern direction from Seversk. Judging from the distribution of technogenic dust and aerosol load in the region, increased element concentrations with respect to average values, as described in [1, 2, 12], should be related to the northeastern leeward region under study, while decreased element content should be related to the southwestern windward region.

Smooth profiles were obtained in normalizing the REE content in our aerosol samples in 2010 with respect to carbonaceous chondrites C1 [14], similarly to the REE profile for the Earth's crust, which points to their regular distribution and the absence of random errors during sample preparation and in analytical works (Fig. 5, *a*). A clear negative europium anomaly is observed: $Eu/Eu^* = Eu_n/(Sm_n \cdot Gd_n) = 0.58$, while for the Earth's crust $Eu/Eu^* = 0.71$, and for I-granites it is 0.63 [15]. Therefore, mobile bivalent Eu was likely to survive more intense carry-out during technological processes, which promoted Eu depletion of technogenic emissions and aerosol. The concentrations of light REE in aerosols are higher than the clarke by a factor of 1.7 as average, while for heavy REE the excess is almost 2 times (see Fig. 5, *b*). A shift of the profiles to heavier REE caused a decrease in La/Lu ratio (light REE/heavy REE) as an average to 7.81 (varied within the range 7.28–7.91) while in the earth's crust La/Lu = 9.33.

According to the data of the year 2004, the concentration of REE in the aerosol within the major emission plume of SCC [1] is 0.63–1.1 of REE content in the samples of 2010, except for Eu and Tb (see Fig. 5). Unexpected and unexplainable exclusion from the data of 2004 [1] became increased concentration of Tb in aerosol (almost by a factor of 2–3), Eu (1.5 times) and 1.5–1.75 times decreased concentrations of Ce, Yb [1] in comparison with our data of the year 2010. As a consequence, according to the data of 2004, first of all, the Eu anomaly is almost levelled off in the REE profiles. Second, a sharp jump is detected in their tail part, unlike for REE profiles in our samples taken in 2010 (see Fig. 5, *a*).

According to the data obtained in 2014 [1], in the aerosol collected at the southwestern windward side from Seversk and Tomsk REE content is almost the same or less than the clarke, and 2.5 (as an average) lower than that for the samples collected in 2010. Exclusion is Tb: its amount is 40 % larger in comparison with the data of 2010. In general, low concentrations of REE to the southwest from cities are quite expectable and logical because this region is situated at the windward side from the SCC.

According to the data obtained in 2004 [1, 12], the REE content of aerosol collected at a distance of 85–110 km to the northeast from Seversk (except for Eu, Tb, Lu) decreases by a factor of 3.2 as average in comparison with the data for the surroundings of Seversk and Tomsk in the radius of 20 km and is equal to about 0.85 of the clarke. The concentrations of Eu, Tb, Lu in some samples taken at the remote area are somewhat higher than the clarke but no anomalous peak of Tb as described previously (at the radius of 20 km) appeared (see Fig. 5, *b*).

In our aerosol sample, relying on the ratios (La + Ce)/(Yb + Lu), Ce/Eu, it is possible to distinguish two geochemical fields marked as A-2010 and B-2010 (Fig. 6, *a*, *b*). The A-2010 field is formed by points 2–4, 7–9, situated to the north and northeast from Seversk (see Fig. 1) within the major plume of SCC emissions. The B-2010 field is formed by remote points and/or those situated apart from the major plume: these are points 1, 5, 6, 10 (see also Fig. 1 and 6, *a*). One can see in the data shown in Fig. 6, *a* that REE concentrations, especially those of heavy REE, are increased in the aerosol samples of the major plume of SCC emissions (the A-2010 field) because the weighted mean straight line (curve *1*) passes below the weighted mean straight line for the B-2010 field (curve *2*). For the A-2010 field the average ratio (La + Ce)/(Yb + Lu) = 28.9 (the range: 28.4–29.9), and for the field B-2010 – 34.6 (the range: from 30.6 to 35.6) (see Fig. 6, *a*).

Let us compare our data with previously published results.

The REE content in aerosol samples collected by the authors of [1] at the regions in the radius of 20 km from Seversk and Tomsk are substantially lower in comparison with the data

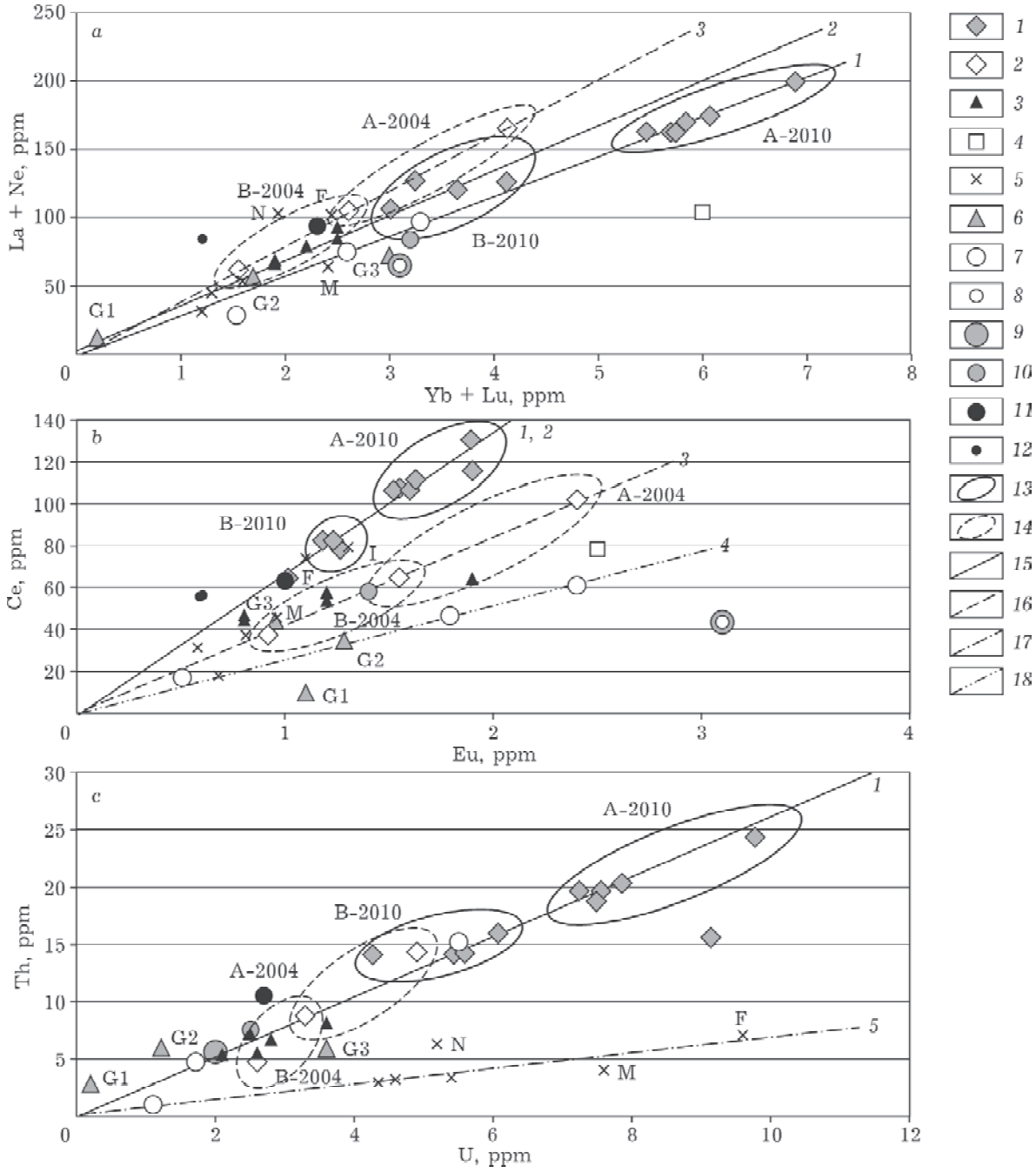

Fig. 6. Ratios (La + Ce)/(Yb + Lu) (*a*), Ce/Eu (*b*), Th/U (*c*) in aerosol and soil in the region of Seversk: *1–6* – data on aerosol samples (*1* – our data of 2010; *2* – in the radius of 20 km from Seversk, 2004 [1]; *3* – in Tomsk, 2010 [10]; *4* – in Seversk, 1995 [13]; *5* – at a distance of 85–110 km to north and northeast from Seversk, G3 – 15 km to southeast from Tomsk, 2010 [10]); *7–12* – data on soil samples (*7* – in the radius of 20 km from Seversk, 2006 [2]; *8*, *9* – in Seversk, 1995 [13] and 2008 [4], respectively; *10* – in Tomsk, 2008 [4]; *11* – the clarke [11]; *12* – soil of the USSR, 1997 [16]; *13*, *14* – geochemical fields according to aerosol data (*13* – A-2010 within the major SCP emission plume, northern and northeastern direction from Seversk, B-2010 – outside the major SCP emission plume, 2010; *14* – within the radius of 20 km of Seversk, 2004 [1]: A-2004 – within the major SCP emission plume, B-2004 – to the southwest from Seversk and Tomsk; *15–17* – mean weighted aerosol sample data: *15* – our samples, 2010 (*1*, *2* – for fields A-2010 and B-2010, respectively); *16* – within the radius of 20 km of Seversk, 2004 [1]; *17* – at 85–110 km to the northeast and east of Seversk, 2004 [12]; *18* – soil samples, 2006 [2]; F, M, N – Filimonovka, Minayevka, Novonikolayevka villages, respectively.

of 2010 (see Fig. 6, *a*). According to the data obtained in 204, aerosol is especially depleted of heavy REE – Yb, Lu, which follows from the position of curve *3* with respect to curves *1*, *2*. For these samples, the average ratio (La + Ce)/(Yb + Lu) = 40.2, which is close to the ratio in the Earth's crust (40.7).

According to REE content, aerosol samples from the region at a distance of 85–110 km from Seversk and Tomsk [12] also can be divided into two parts. The first group will include aerosol sampled near Filimonovka, Novonikolayevka and Minayevka villages situated in the section line of the main northeastern plume of SCC emissions (see Fig. 1). These samples are distinguished by increased REE content in comparison with samples taken in the radius of Novokuskovo, Zyryanskoye, Semyenovka villages that comprised the second group. For the samples of the fist group, the average ratio (La + Ce)/(Yb + Lu) = 40.5; for the second group it is 26.3 to 33.9.

Because of the very small REE content point G1 corresponding to the region background value is localized in the left lower corner of Fig. 6, *a*: (La + Ce)/(Yb + Lu) = 37.4.

According to the data obtained in 1995, the samples of aerosol taken in Seversk are close in REE content to the samples of the A-2010 field but are substantially depleted of light REE [13]: (La + Ce)/(Yb + Lu) = 17.3 (see Fig. 6, *a*).

The samples of aerosol of Tomsk [10] with the average ratio (La + Ce)/(Yb + Lu) = 36.0, as expected, fall into the B-2010 field formed by the aerosol of the windward southwestern region within 20 km of Tomsk (see Fig. 6, *a*).

Soil is a perennial depositing component responding to the long-term effect of technogenic action. In the regions situated within 20 km from Seversk and Tomsk, the range of REE content in soil in 2006 [2] was noticeably less than that in aerosol samples taken in 2004 [1]. According to the data obtained in 2006 [2], REE content in soil samples is lower in comparison with the similar data obtained in 2004 for aerosol samples [1]. The average ratio (La + Ce)/(Yb + Lu) = 28.8 [2]. In the soil of Seversk, the ratio (La + Ce)/(Yb + Lu) is smaller and is equal to 20.9 [4] and 21 [13], while in soil of Tomsk it is 26.3 [13]. As estimated by the author of [16], the average ratio (La + Ce)/(Yb + Lu) = 70. in the background soil in the USSR. So, under the conditions of long-term technogenic emission of REE, heavy REE are likely to get accumulated in the soil cover with more intense washout (migration) of light REE. This secondary redistribution of REE in soil leads to a decrease in (La + Ce)/(Yb + Lu) ratio in soil in comparison with the initial REE composition in technogenic emissions (aerosols).

The average Ce/Eu ratio in aerosol of the A-2010 field (see Fig. 6, *b*) is equal to 67.4 (the range: 60.9 to 69.8) and comparable with the average Ce/Eu ratio of the B-2010 field (65.4, range: 61.2–69.8). The fields A-2010 and B-2010 differ from each other only in the absolute content of Ce and Eu (their amount in the A-2010 field is much higher).

In aerosol collected in 2004 at the areas to the northeast and southwest from Seversk, due to lower Ce content, the average ratio Ce/Eu = 41.6, which is much lower than that for aerosol samples of 2010 (see Fig. 6, *b*). The A-2010 and B-2010 fields differ from each other in the diagram in the absolute concentrations of elements but are described by the same mean weighted straight line (see Fig. 6, *b*, curve *3*).

According to the data obtained in 1995 [13], aerosol of Seversk contains less Ce than aerosol of the A-2004 field and approaches in this parameter to the B-2004 field, with the average ratio Ce/Eu = 45.0 (see Fig. 6, *b*).

The average Ce/Eu ratio for aerosol samples of 2004 collected at a distance of 85–110 km to the northeast and east from Seversk was 50.4. Nevertheless, the concentrations of Ce and Eu are also increased in aerosol samples taken near Filimonovka and Novonikolayevka villages situated in the northeastern section. Aerosols from the vicinity of Semyenovka and Novokuskovo villages contain the smallest amounts of REE.

The aerosol of background sites contains especially small amounts of Ce: for G1 Ce/Eu = 13.1, for G2 27.3 (see Fig. 6, *b*).

In 2004 the ratio Ce/Eu in soil of the territories situated at the radius of 20 km from Seversk and Tomsk was 26.0 [2], and the mean weighted straight line (curve *4*) was less inclined in comparison with the weighted mean straight lines for aerosol (see Fig. 6, *b*). According to the data of [2],

in 1995 the ratio Ce/Eu for the soil of Seversk was even smaller: only 14.0. Similar data are reported by the authors of [4] (2008). Lower Ce/Eu ratio for the soil of Seversk and adjacent territory in comparison with aerosol points to more intense Ce carry-off from soil and accumulation of Eu. According to estimates made by the authors of [16], the average Ce/Eu ratio in the soil of the USSR was 93.3, while the clarke ratio is 63.0. On this ground, it may be stated that the soil of the region under study is enriched with rare earths and to a larger extent by Eu.

Not less informative is the ratio Th/U. The average U content in aerosol of the A-2010 field (within the major SCC plume) is 8.2 g/t, or 3K, Th 19.7 g/t (1.9K), while outside the SCP emission plume (B-2010 field) radionuclide content is smaller (g/t): U 5.3, Th 14.6. Aerosol sample form the fields also in the Th/U diagram: A-2010 and B-2010. Aerosol in the major SCP emission plume (A-2010 field) is enriched with Th and U in comparison with the B-2010 field (see Fig. 6, *c*). At the same time, however, Th/U ratio is almost the same in both fields; it is described by the same mean weighted straight line (curve *1*), similarly to the Ce/Eu ratio. For the A-2010 field, the average ratio Th/U = 2.4 (range: 2.49–2.71), while for the B-2010 field it is 2.8 (range: 2.55–3.3). These points to a weak trend to enrich aerosol of the major SCC plume with uranium in comparison with aerosol outside this plume.

According to the data of 2004, for aerosol samples collected within 20 km from Seversk and Tomsk the average ratio Th/U = 2.5, average U content is 3.3, Th 8.8 g/t. The maximal thorium content in aerosol collected in 2004 is less by a factor of 1.4 and uranium by a factor of 1.7 in comparison with the data for aerosol samples of 2010. These fields are close to each other in the value of the Th/U ratio (see Fig. 6, *c*).

The data on aerosol from Tomsk [10] fit within the B-2010 field. One can see that G3 point with the low Th/U ratio (1.64) stands apart in the diagram.

For aerosol samples taken from the remote region (at a distance of 85–110 km from Seversk) the Th/U ratio is much smaller and equals 0.75, with average concentrations (g/t): Th 4.5, U 6.1 [12]. At the same time, in the samples collected near Filimonovka and Minayevka villages, uranium content is higher in comparison with the data for other samples from this region and reaches 9.6 and 7.6 g/t, respectively, with comparable levels of Th content. A sharp depletion of aerosol from remote region in thorium is described by the mean weighted straight line appressed to the abscissa axis (see Fig. 6, *c*, curve *5*). This fact allows assuming that thorium is mainly bound with heavier and (or) larger aerosol particles depositing at a shorter distance from their source, so aerosol gets depleted of this element. At the same time, it is possible that uranium is mainly bound with light fine fractions of aerosol, maybe also gaseous, which provides uranium transfer at long distances.

Aerosol of the regional background G1 is characterized by the low Th content and lower U content. For G1 Th/U= 14.5, for the point of local background G2 Th/U = 5.0 (see Fig. 6, *c*).

With the clarke ratio Th/U ~ 3.9, the average Th/U ratio in soil in the radius of 20 km from Seversk and the city itself is 2.8 [2, 3], in soil of Tomsk it is 3.0 [4], which is close to the ratios for aerosol samples according to the data obtained in 2010 and 2004. The range of U, Th content in soil is wider than in aerosol (see Fig. 6, *c*). Enrichment of aerosol and also soil with uranium within the major SCP plume is undoubtful.

Natural uranium is a mixture of three isotopes: 238, 235 and 234, with the percentage of 99.28 : 0.714 : 0.006, respectively. The natural ratio $^{238}U/^{235}U = 139.05$. With the measurement error of ±2 %, the range of natural ratios of uranium isotopes is 136.27–141.83. Measurements showed for the first time that in the aerosol of A-2010 field the average ratio $^{238}U/^{235}U = 127.315$, and the minimal one is 74.28 (point 4). For aerosol of B-2010 field, the average ratio $^{238}U/^{235}U = 137.667$. One can see that the ratio of uranium isotopes in the aerosol of the major SCC plume is shifted to the side of enrichment with U-235, while outside the major plume of SCC emissions it corresponds to the natural ratio. This fact proves that SCC is the source of substantial technogenic aerosol pollution of the adjacent territory.

CONCLUSIONS

The distribution of dust in snow cover confirmed our assumptions that the major aerosol

carry-off from Seversk occurs in the northern and north-eastern directions according to the wind rose: at a distance up to 21 km the dust and aerosol load was 31.2–102.3 mg/($m^2 \cdot$ day), 53.4 mg/($m^2 \cdot$ day) as average.

Soot content in aerosol was revealed to vary within 15 to 46 mass %, in connection with local aerosol pollution from low-temperature sources. The basis of the mineral part of aerosol is formed by SiO_2, Al_2O_3 and $Fe_2)_3$ (about 64, 21.7, 7.65 %, respectively).

Investigations allowed us to distinguish three sources of local aerosol pollution in the region of Seversk and adjacent territories, connected with emissions from boiling plants, industrial enterprises and furnace heating of Samus settlement, furnace heating in Georgiyevka, and Naumovka, and "breathing" of the city. City breathing is created by the integral emissions from numerous small industrial enterprises and transport in Tomsk and Seversk. Indicators of the pollution of this kind are: abundance of soot, high concentrations of chalcophilic elements Pb, Zn, Sb, Co, Ni, Cu, Cd, Bi, Mo, and S. Additional feature of the aerosol "breathed" out by the city is the presence of lithophilous W, Sn. Presumably, the pollution of city breathing has a larger scale in comparison with other sources of local aerosol pollution of the region under study.

Emissions from the SCC in Seversk have regional nature and predetermine the geochemical specificity not only of aerosol but also of soil cover in the region. The effect of SCC is fixed in aerosol at a distance up to 100 km but more clearly within the major emission plume (in the radius of 20 km to the north and northeast from Seversk). Geochemical indicators of aerosol pollution by SCC are increased concentrations of radionuclides U, Th, rare earths (REE) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu in aerosol. Enrichment of aerosol with heavy REE decreasing the ratio (La + Ce)/(Yb + Lu) to ~28.9 and with technogenic uranium enriched with ^{235}U leading to a decrease in the isotope ratio $^{238}U/^{235}U$ to 74.28 are typical.

During different periods of time, aerosol pollution from SCC was different. For example, in 2010 it was more intense in comparison with the previous period: REE, U and Th content in aerosol samples was higher in comparison with the data obtained in 2004, except for Eu, Tb. According to the data of 2004, relatively low Ce content in the REE profiles of aerosol caused the disappearance of the europium anomaly, and lower Yb content caused changes of the tailing part in comparison with the REE profiles of aerosol recorded in 2010. The difference of REE composition in the aerosol of 2004 and 2010 can be due to the changes in technological processes at SCC during its operation.

According to the data of [1, 12], with an increase in the distance from SCC to 20–110 km the Th/U ratio in aerosol decreases from 2.4–2.8 to ~0.8. This may be due to the prevailing bonding of uranium with light and fine aerosol particles able to be transferred by the air for longer distances. A trend was revealed for the secondary enrichment of soil with heavy REE and Eu in comparison with the primary composition of aerosol entering soil, likely as a result of more intense washing light REE out of soil. This is confirmed by the lower (La + Ce)/(Yb + Lu) and Ce/Eu ratio in soil in comparison with aerosol.

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