UDC 504.3.054:620.2–403.8

Uranium in Technogenic Aerosol of the Industrial Areas of Novosibirsk

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(Received November 18, 2011)

Abstract

Results of the mineralogical and geochemical investigation of technogenic aerosol samples collected in 2011 in the northeastern direction from Novosibirsk in the plume of the Novosibirsk Chemical Concentrates Plant JSC, as well as aerosol collected near the Novosibirsk Tin Plant JSC and Heat and Electric Power Plant No. 3 are reported for the first time. Uranium content and its mineral formations were determined by means of ICP-MS, ICP-AES and scanning electron microscopy.

Key words: technogenesis, technofilic elements, natural radionuclides, isotopes, aerosol, emission, technogenic pollution, ecological risk

INTRODUCTION

Investigation of the selective ecological impact of industrial enterprises situated within the boundaries of large cities is one of the urgent problems of geochemistry of technogenesis. Determination of the contribution from separate sources of pollution among many others is rather complicated scientific problem, but its solution can become determinative for realization of the measures aimed at ecological sanitation of territories. Integrated mineralogical and geochemical examination of aerosol particles accumulated during winter in the snow cover of Novosibirsk allowed for the first time to reveal the contribution from separate industrial enterprises into the general technogenic pollution of the megapolis [1]. The next step was the analysis of the distribution of separate groups of technophilic elements in urban aerosol.

In the present paper we report the results of the investigation of technogenic aerosol sampled in 2011 to the northeast of Novosibirsk in the plume of emissions from the Novosibirsk Chemical Concentrates Plant (NCCP) and aerosol collected near Novosibirsk Tin Plant (NTP) and Heat and Electric Power Plant No. 3 (HEPP-3).

Under the conditions o Siberia, snow serves as an ideal model object for the studies of the composition and dynamics of emissions of industrial enterprises because solid aerosol particles and gaseous products partially sorbed on solid phases are fixed in the stable snow cover since early November till the end of March. Winds of southern and southwestern direction dominate in the surface atmospheric layer in winter in the region of Novosibirsk, while in summer the wind rose becomes more isometric [2]. At the height of 0.5 km in the boundary atmospheric layer the winds of southwestern and western direction dominate in winter. This fact determines the major directions of aerosol pollution from the chimney-stalks of industrial objects under investigation.

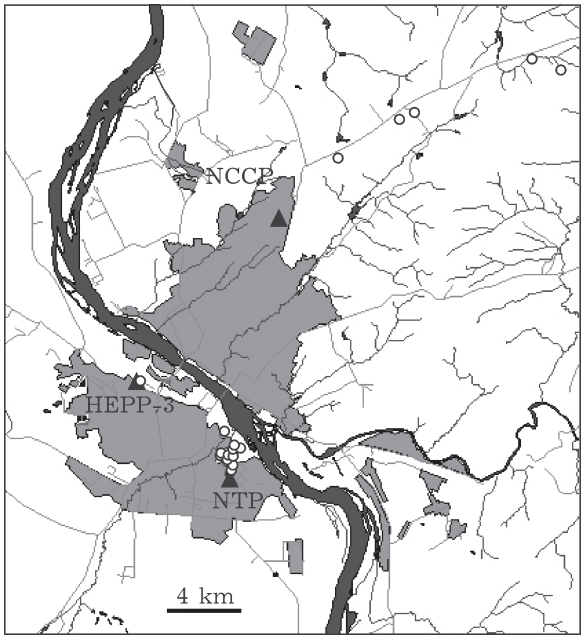

Fig. 1. Scheme of snow cover sampling regions in Novosibirsk and its outskirts. Triangles mark industrial enterprises, circles mark sampling sites.

EXPERIMENTAL

The samples of snow cover (50–70 L in volume) were collected during the years 2009–2011 along the route to the northeast from Novosibirsk in the plume of emissions from NCCP (region No. 1) and aerosol sampled in the region of NTP (region No. 2) and HEPP-3 (region No. 3) (Fig. 1).

To exclude the effect of roads, sampling sites were chosen at a distance not less than 200 m from the roads. The sites were bound with the help of GPS navigator Etrex GARMIN with the error of 7–10 m.

The samples were allowed to melt in the tanks 70 L in volume, the upper part of settled melted water was decanted; the lower part of water with the suspension was filtered through the Blue Ribbon paper filter. The dust content (suspension content) was determined as a ratio of the mass of suspension to the volume of melted snow. Precipitates from snow were transferred into solution using two methods: by alloying with alkali KOH and lithium metaborate. The content of Ca, Mg, Na, K, Al, S, Si, B, Ti, Fe, Mn, P was determined in melted snow and in aerosol particles transferred into solution by means of atomic emission with inductively coupled plasma (AES-ICP) using an IRIS Advantage spectrometer (the USA). Relative error does not exceed 10 %; the lower limits of element detection are 0.001–0.005 ppm. Heavy metals, rare earths, natural radionuclides U and Th were determined by means of mass spectrometry with inductively coupled plasma (ICP-MS) with ELEMENT (Finnagan Mat, Germany) equipped with ultrasonic sprayer U-5000AT+ [3]. To correct the matrix effect and control the instrumental drift, In was used as an internal standard. The detection limit for the elements under study, estimated from the 3σ variation of background signal, was 0.001–0.1 ppb. Relative standard deviation for the determination of concentrations does not exceed 10 %. The ratio of isotopes $^{238}U/^{235}U$ was determined by means of ICP-MS with the error ≤2 %.

The elemental composition of solid aerosol particles was determined quantitatively using the X-ray fluorescence method with synchrotron radiation (SR-XRFA) at the station of elemental analysis of VEPP-3 at Budker Institute of Nuclear Physics, SB RAS (Novosibirsk). According to the standard procedure, the samples were ground to ~200 mesh and pressed into tablets 6 mm in diameter, with the mass of 30 mg [4]. Up to 35 elements were determined using this method: Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Br, Mo, Ag, Cd, Sn, Sb, Te, Hg, Tl, Bi, Th, Pb *etc.*) with the detection limit down to 0.1 ppm, depending on the energy of emission line excitation. Relative standard deviation of the determination of concentrations of these elements was 10–15 %. The international soil standard SOIL-7 IAEA was used as the external standard sample.

The morphology and substance composition of separate aerosol particles were studied on a help of LEO 1430 VP scanning electron microscope equipped with OXFORD energy dispersive spectrometer (EDS). The diameter of the scanning beam of the spectrometer was about 0.5–1 μm. Aerosol particles were deposited as a thin layer on the substrates and examined in the mode of back-scattered electrons under graphite spraying. To search for metal-containing and other heavy particles (especially uranium oxides), the sweep brightness reduction method was used (with the help of

built-in software package) to damp the particles composed mainly of light elements: soot particles, aluminosilicate slag spheroids. The level of brightness was chosen to leave only the particles containing 15–20 % and more iron visible (dead-gray). At this background, the particles composed of the elements with atomic mass not less than 56 (heavier than Fe) are distinguished by bright glow. The larger is the atomic mass of an element, the larger number of electrons it attracts and reflects, and the brighter is particle glow at the background of dead grey hematite spheroids and ferrites. Through sequential stepwise displacements over the substrate, with the magnification of 1500, not less than 5000 sweeps 212 × 159 μm were examined; each of them contained 300 to 500 (visible (larger than 0.5 μm) aerosol particles.

RESULTS AND DISCUSSION

Uranium content in melted snow from both regions under study was insignificant and approximately the same (μg/L): near NCCP – 0.04 as an average, with the range 0.02–0.06, near NTP – 0.05 as an average, with the range 0.03–0.04. The concentration of Th in melted snow near NCCP at the detection limit is 0.01–0.02 μg/L, near NTP 0.02–0.05 (0.04 μg/L as an average), which is comparable with uranium content. For the samples of melted snow collected near NCCP and NTP, the ratio Th/U is 0.42 and 0.95, respectively. Unexpectedly high uranium content (0.13 μg/L) was detected in the sample of melted snow from the region of HEPP-3, Th was about two times less, and the ratio Th/U = 0.46 (Fig. 2).

Thorium content was about two times higher than uranium content in the solid aerosol particles from the regions of NCCP and NTP; Th/U ratio is 2.12 and 2.09 as an average, respectively. In aerosol from the region of HEPP-3, the relative thorium content is even higher, while the average Th/U = 2.57.

The regularity in the distribution of U and Th in aerosol was revealed only near NCCP: at a distance of 0.5 to 25 km from the plant these values decrease almost by a factor of 2,

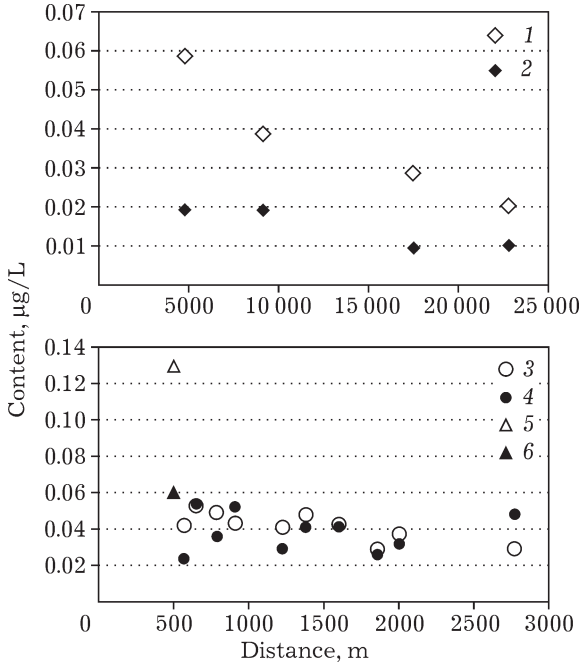

Fig. 2. U and Th content in melted snow from different regions of Novosibirsk at different distances from plant chimney-stalks: to the northeast from NCCP (*1* – U, *2* – Th), north from NTP (*3* – U, *4* – Th) and near HEPP-3 (*5* – U, *6* – Th). The distance from plant chimney-stalks is shown as abscissa.

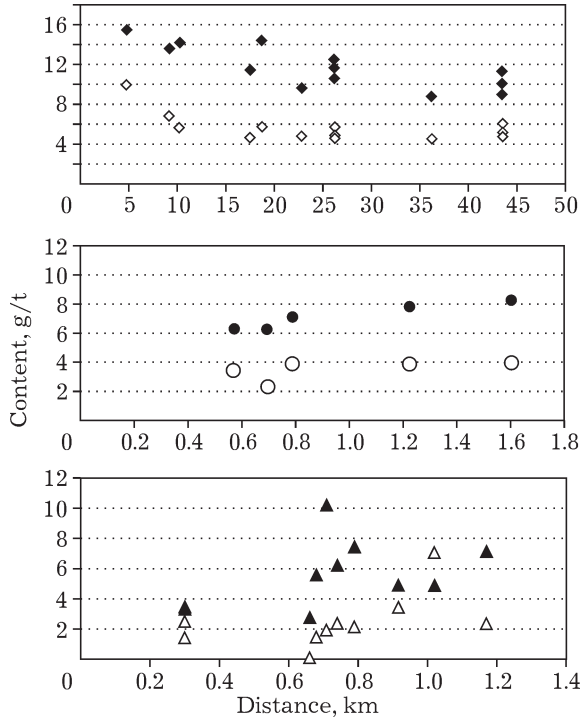

Fig. 3. U and Th content in aerosol from different regions of Novosibirsk. For designations, see Fig. 2.

similarly to their concentrations in melted snow (see Figs. 2, 3).

The concentrations of U and Th in aerosol remains almost unchanged with an increase in the distance from NTP, and the range of values is narrow, while broad scattering is observed in the region of HEPP-3.

Aerosol from the region of NCCP is distinguished by its absolute U and Th content: U – 5.64 g/t as an average, with the range 4.50–9.93 g/t; Th – 11.74 g/t as an average, with the range 8.80–15.49 g/t; in aerosol from the region of NTP, average U and Th content was 3.49 and 7.17 g/t, respectively. The lowest U and Th content was detected in general in aerosol from the region of HEPP-3: 2.6 and 5.9 g/t, respectively. As a confirmation of these data, aerosol from the region of NCCP forms a separate field in the upper right sector of U-Th diagram (Fig. 4).

Natural uranium is a mixture of three isotopes: ^{238}U, ^{235}U and ^{234}U at the percent ratio 99.28 : 0.714 : 0.006; for natural uranium ^{238}U/^{235}U = 139.05. With the error of ^{238}U and ^{235}U measurements using ELEMENT (Finnigan Met, Germany) ±2 %, the range of natural ^{238}U/^{235}U is 136.27–141.83. It was revealed for the first time that uranium in aerosol of the region of NCCP has technogenic origin and is strongly enriched with ^{235}U isotope: the ratio ^{238}U/ ^{235}U is much lower than the natural value and varies within the range 77.43–129.26, with the average value 107.78 (Fig. 5).

The ratio ^{238}U/^{235}U in the region of NTP varies within the range 125.15–138.71; the average value is 134.94, which is somewhat lower than the natural ratio, too. One can see in Fig. 5 that the lower ratio is characteristic of two sampling sites at a distance of 700 m from the chimney-stalk of NTP or within the nearest zone around NTP [1]. At a larger distance within the region of NTP, ^{238}U/^{235}U ratio does not differ from the natural value (see Fig. 5).

The isotope ratio for the sample collected in the nearest zone of HEPP-3 corresponds to the natural value and may be corresponding to the initial ratio of U isotopes in fuel.

A shift of ^{238}U/^{235}U isotope ratio and high total concentrations of U, Th in aerosol serve as the geochemical indicators of emissions from NCCP. It is evident that this plant is a source of significant technogenic aerosol pollution of the adjacent territory.

Mineral inclusions of uranium in aerosol from the region of NCCP were revealed with the help of scanning electron microscopy: at a dis-

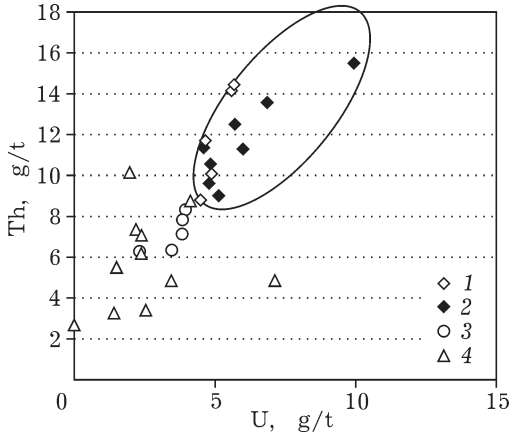

Fig. 4. Diagram of Th–U content in aerosol of Novosibirsk: *1*, *2* – the region of NCCP, determined by means of ICP-MS and SR-XRFA, respectively; *3* – the region of NTP, determined by means of ICP-MS; *4* – the region of HEPP-3, determined by means of ICP-MS and SR-XRFA; oval shows the distribution of aerosol from the region of NCCP.

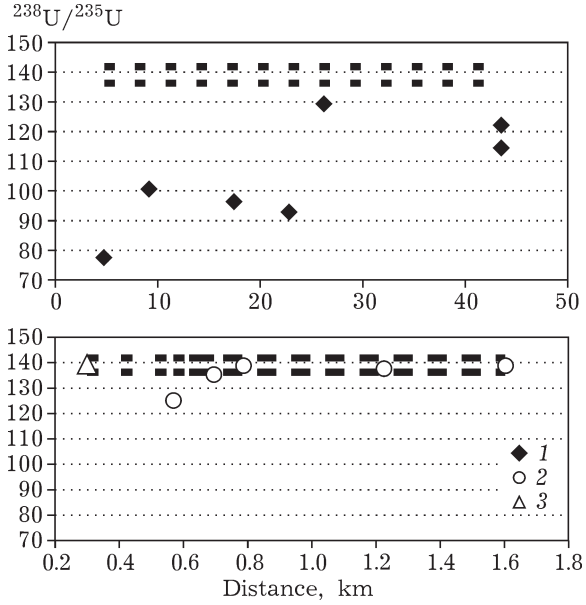

Fig. 5. Diagram of ^{238}U/^{235}U ratio in aerosol of Novosibirsk: *1* – the region of NCCP; *2* – the region of NTP; *3* – the region of HEPP-3; X axis shows the distance from the chimney-stalks of plants; dashed lines show the corridor of natural ^{238}U/^{235}U isotope ratio.

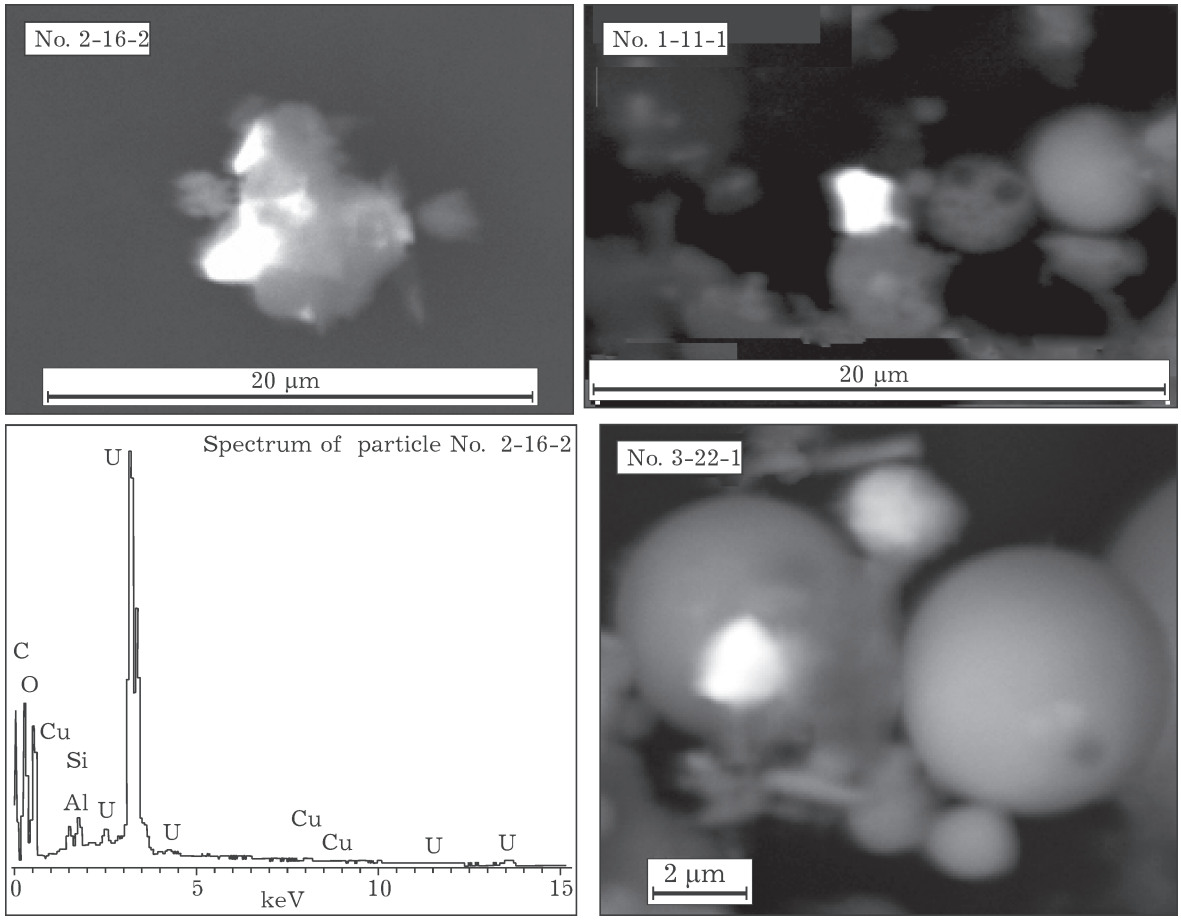

Fig. 6. Particles of uranium oxides in technogenic aerosol of Novosibirsk in the region of NCCP (image in the mode of back-scattered electrons).

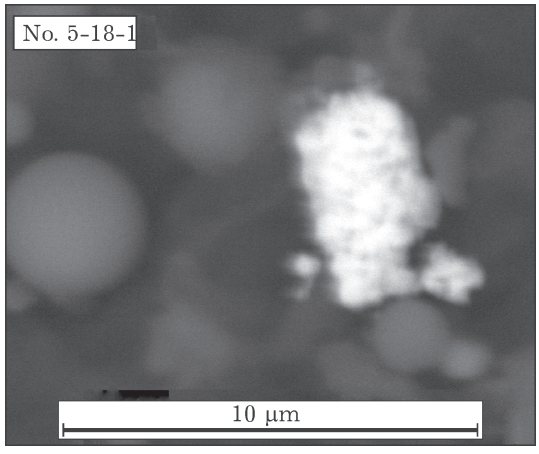

Fig. 7. Slag-like shape of uranium oxide in technogenic aerosol of Novosibirsk in the region of NCCP (image in the mode of back-scattered electrons).

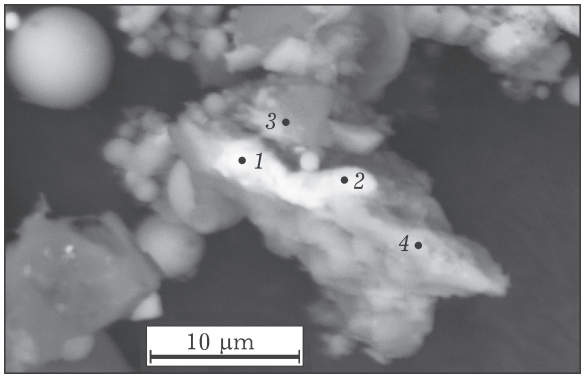

Fig. 8. Conglomerate of aluminosilicate aerosol particles containing uranium (image in the mode of back-scattered electrons): *1–4* – points of conglomerate composition scanning (see Table 2).

TABLE 1

Composition of particles – uranium oxides in technogenic aerosol from the region of NCCP

Particle No.	Distance from NCCP, km	Particle size, μm^2	Content, %			
			O	Fe	Cu	U
1-11-1	4.8	9	27.88	0	0	72.12
1-38-1	4.8	6	49.49	0.85	0	49.66
1-48-1	4.8	3	37.72	1.68	1.23	59.38
2-16-2	9.15	64	28.16	0.00	0.82	71.02
2-18-1	9.15	6	34.39	0.98	0	64.63
2-32-1	9.15	8	23.90	0.99	0	75.11
3-22-1	9.15	3.9	65.18	0.98	0	33.83
4-14-1	17.5	12	26.00	1.54	1.09	71.37
4-22-2	17.5	2.25	37.18	2.11	0	60.71
5-9-1	22.8	3	25.89	1.34	0	72.77
5-18-1	22.8	18	21.20	0.00	0	78.80

TABLE 2

Element content in different points of aerosol composition scanning (see Fig. 8), %

Scanning points	O	Na	Mg	Al	Si	P	K	Ca	Ti	Fe	Y	Zr	U
1	48.31	0.77	0.55	3.71	13.02	1.74	0.37	0.85	–	17.83	3.77	6.8	2.28
2	48.92	1.49	–	4.28	14.9	1.95	2.04	1.06	–	6.96	6.05	9.87	2.47
3	56.76	1.37	1.98	8.98	22.07	1.09	1.76	0.58	0.37	5.04	–	–	–
4	45.68	2.22	–	10.69	33.24	–	3.07	–	–	5.11	–	–	–

Note. Dash means a value below detection limit.

tance up to 10 km – approximately three grains per dust layer 0.5 cm^2 in area, with the mass of about 1–2 mg; at a distance of 10 to 23 km – somewhat more rarely: two grains per the same dust area. The sizes of particles vary from 3 to 64 mm^2. The particles are mainly irregular with angular shape and clear boundaries, often adhered to aluminosilicate mass or spheroids (Fig. 6). One particle resembles slag and has uneven wavy surface (Fig. 7). Uranium content varies within the range from 33.83 to 78.80 %, Fe and Cu admixtures account for 3.19 and 1.23 %, respectively (Table 1).

It is possible that attachment to light aluminosilicate particles, in particular hollow spheroids, provides higher mobility of heavy particles with uranium for long-range wind mass transport.

A conglomerate composed of slag aluminosilicate particles in which one of the particles is enriched with rare elements was revealed (%): Zr 9.87, Y up to 6.05, U up to 2.47 (Fig. 8, Table 2).

CONCLUSION

It was established in the studies that substantial aerosol pollution is characteristic of the northeastern outskirts of Novosibirsk; the source of pollution is most likely NCCP (Rosatom State Nuclear Energy Corporation). Aerosol from this region is enriched with Th and U in comparison with aerosol from the regions around HEPP-3 and NTP. Uranium in substantially enriched with U-235 isotope in aerosol from the region of NCCP, which is confirmed

by the shift of the average isotope ratio $^{238}U/^{235}U$ to 107.78, while the natural ratio is equal to 139.05. The particles of uranium oxides in technogenic aerosol from the region of NCCP were established for the first time by means of scanning electron microscopy.

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