Monitoring of aerosol fallouts at background areas of Tomsk Region in wintertime of 2006–2007

A.V. Talovskaya,[1] E.G. Yazikov,[1] M.V. Panchenko,[2] and V.S. Kozlov[2]

[1]*Tomsk Polytechnical University*
[2]*Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk*

Received January 23, 2008

Investigation results on spatial-temporal variability of aerosol fallout flows in winter period 2006–2007 for two background observation stations of IAO SB RAS (Akademgorodok and the Kireevsk village, 60 km from Tomsk) are presented. Stereoscopic binocular and electron microscopic methods, as well as X-ray diffraction and instrumental neutron-activating analysis were used in studying the mineral-matter and geochemical composition of snow samples. From January to April of 2006 and 2007, the concentration of submicron aerosol and soot in the ground air layer was investigated. Insignificant differences in mineral-matter and geochemical compositions of the samples were noted. Samples of 2007 are characterized by lower aerosol flows as compared to 2006, which is explained by the air temperature at that time and the corresponding power efficiency of the Heat Power Stations. Measurements in Akademgorodok qualitatively agree with results of geochemical investigations.

Tomsk Region has a diverse industry (fuel, timber, metallurgy, chemical, and petrochemical plants, mechanical engineering, agriculture, as well as the transport), which are main anthropogenic sources, influencing the regional natural complexes and urban territories. The region consists of 16 districts. The Tomsk district, where more than 30% of industrial objects are concentrated, is the most polluted. South-west direction is the main wind rose, therefore most stresses fall on the north-north-eastern and south-south-western region sectors. They are located close to the city and belong to a 30 km zone of influence of the Siberian chemical complex.[1,2]

The snow cover, being an accumulator of atmospheric fallouts in cold period, is widely used by researchers for the study of material and chemical composition of the pollutants, the power of their flows, and the range of transfer. All these characteristics were analyzed via snow sampling.[2–4]

This work is a continuation of the earlier one,[9] started in 2006 winter period, and devoted to the study of aerosol fallout flows with the help of geochemical methods, as well as of the spatial-temporal variability of aerosol pollutant distribution at two background sites of the Tomsk Region.

Measuring techniques and data processing

Snow was sampled at two observation stations of IAO: at the Akademgorodok (eastern suburb) and at Kireevsk (forest zone 60 km away from the town) sites (areas of 2×2 m in size). To estimate the flows of aerosol fallouts, snow was sampled in January and April, 2006 and March, 2007 in Akademgorodok, as well as in April, 2006 and March, 2007 in Kireevsk. The samples taken in January characterize the total level of aerosol pollution in the period from November to January, while the samples taken in March and April characterize the level of pollution for the whole winter period.

The snow samples were selected and prepared following technical recommendations given in Refs. 5–7 and the Manual of the atmospheric pollution control.[8]

The mineral-matter composition of solid snow residuals was analyzed with the help of stereoscopic binocular microscope (MBS-9) at the department of geoecology and geochemistry of the Tomsk Polytechnic University (TPU). The additional samples taken in April, 2006 were analyzed with the help of electron microscopy and *X*-ray analysis in a laboratory of Karlsruhe Institute of Mineralogy and Geochemistry (Germany).

All samples underwent instrumental neutron-activating analysis in order to determine the content (concentration mg/kg) of 23 chemical elements in the laboratory of nuclear-geochemical research methods at the Department of Geoecology and Geochemistry of TPU.

Using the MBS-9, the percentage of all natural and anthropogenic particles was determined by comparing them with standards.[10] The *X*-ray structural analysis allowed determination of the qualitative content of natural minerals in samples. Samples were studied with the use of LEO 1530 Gemini (now "Carl Ceiss Iena") electron microscope. The samples were placed in the cell with the help of conductive adhesive and covered with a 10-nm carbon layer. From 10 to 11 types of particle in each sample were analyzed. Each particle under analysis was photographed and the spectrum of the chemical element content was recorded.

0235-6880/08/06 432-05 $02.00

Analytical measurements were used, following Ref. 6, for estimation of the dust load P_n [mg/(km^2·day) or kg/(km^2·day)], total load P_t [mg/(m^2·day)], produced by each chemical element arrival into the environment, and the concentration coefficient K_c. The K_c was calculated relative to background values, received earlier for Tomsk Region.[3,4] The description of the estimation procedure is presented in Ref. 9 in detail. We also used statistical methods with the use of the Statistica 6.0 program to process the analytical data.

The data on mass concentration of submicron aerosol and soot dry basis in the atmospheric ground layer for the periods from November, 2005 to April, 2006 and from November, 2006 to April, 2007 were also involved into analysis of snow measurements. These data were received at the IAO SB RAS aerosol station. They give evidence on temporal variations of characteristics of aerosol and soot in ground air layer for the above time intervals. Note that soot in the atmospheric aerosol characterizes the level of anthropogenic load on the environment, especially in winter period. The analyzed submicron aerosol has a significant lifetime in the atmosphere (about several weeks) and is transported with air masses to long distances, participating in the processes of precipitation on soil and snow cover at a regional scale.

Note that the results of simultaneous measurements of aerosol and soot concentration at the IAO aerosol station and at the Fonovyi site (Kireevsk) in 2001 winter–spring period have shown the level of aerosol concentrations, measured at the aerosol station, to be close to background (for more than 70% of realizations). Thus, they carry more information, firstly, on the dynamics of aerosol midregional background state.[11]

Results

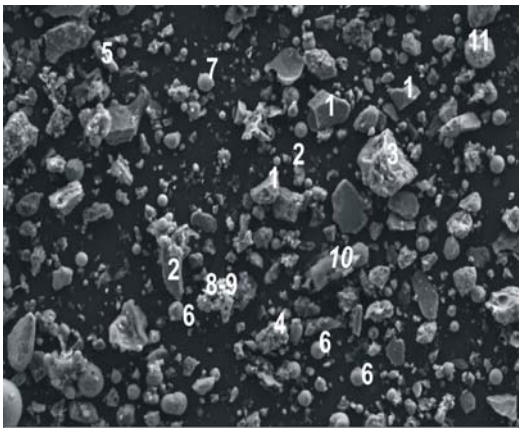
Dust load

The results of dust load estimation state that for the samples taken from Akademgorodok in 2006 this value changed within 20–40 mg/(m^2·day) in January at a mean value of 30 mg/(m^2·day), and within 20–30 mg/(m^2·day) in April at a mean value of 26 mg/(m^2·day). As for the samples from Kireevsk, it changed within 16–20 mg/(m^2·day) (April) at a mean value of 18 mg/(m^2·day). In March, 2007 the value of dust load in the samples from Akademgorodok changed from 17–37 mg/(m^2·day) at a mean value equal to 27.5 mg/(m^2·day) and from 20 to 30 mg/(m^2·day) at a mean value equal to 27 mg/(m^2·day) in Kireevsk. On the whole, according to gradation offered in Ref. 7, the received values of the dust load show a comparatively low pollution level (less than 250 mg/(m^2·day)). However, the comparison of this load with the background one for the Tomsk Region[3] (7 mg/(m^2·day)), we can see an excess of the dust load for Akademgorodok by four orders of magnitude (both in 2006 and 2007) and in Kireevsk by two orders of magnitude in 2006 and by four orders of magnitude in 2007.

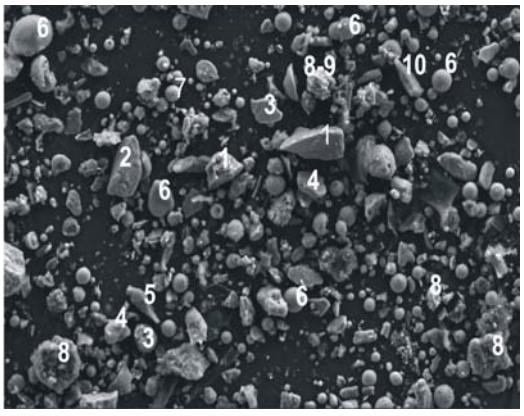
Mineral-matter composition

The study of mineral-matter composition with the help of binocular microscope has shown that anthropogenic particles (mullite, ferromagnesite, soot, slag, etc…) dominate (60–70%) in snow samples from Akademgorodok over natural components (quartz, feldspar, etc…) making up 30–40%. In the samples taken in Kireevsk the situation is opposite, i.e., the particles of natural origin (70–75%) prevail over anthropogenic ones (25–30%).

According to the data of electron microscopy the particles of natural (quartz, feldspar, amphiboles, clay and biogenic particles) and anthropogenic (Al–Si-smooth spheres, spheruls containing iron, porous cinder particles, slag, soot, and coal particles) origin were found in the samples taken in the areas of Akademgorodok and Kireevsk in 2006 (Fig. 1).



a



b

Fig. 1. General view of solid snow residuals, received with the help of electron microscopy (1000^x magnification): *a* is snow sample from Akademgorodok (20 mc resolution); *b* is snow sample from Kireevsk (10 mc resolution). Natural particles (1–5): (1) quartz, (2) feldspar (albite), (3) amphibole, (4) kaolin, (5) boigenic particles; anthropogenic particles (6–11): (6) Al–Si-smooth spherules, (7) spheruls containing iron, (8) slag, (9) soot, (10) coal particle, (11) spheruls containing mullit.

Data of *X*-ray structural analysis demonstrate the following minerals, found in the samples of Akademgorodok in 2006: quartz, cristobalite, amorphous quartz, feldspar (albite, K-containing feldspars), dolomite, kaolin, mica, mullit, ferric oxides (gematite, magnetite, magnesioferrite).

Such minerals and particles as cristobalite, amorphous quartz, Al–Si-smooth spheres, porous cinder particles, slag, soot, coal particles, and mullit are produced at high temperatures and are emitted by Fuel-Energy plants of Tomsk (Heat-power Station, Hydroelectric Power Station, etc…), and local boiler stations situated in villages. The sources of other minerals are mostly natural, e.g., the erosion of Tom' river banks and naked slopes, long-range transboundary transport.

Other sources of these elements in the atmosphere can be the building industry and the surface of buildings. The sources of ferric oxides and spheruls can be both natural and anthropogenic, for example, mechanical engineering and metal processing plants.

Geochemical composition

The estimation results of distribution of the heavy metals (Cr, Ba, Sr, Co), rare (Hf, Cs, Rb, Ta), rare-earth (Sm, Lu, Yb, La, Sc, Tb), radioactive (U, Th), noble metals (Au, Ag), macroelements (Na, Ca, Fe), and Br are presented in Table according to the instrumental neutron-activating analysis in the studied regions. To estimate the differences of chemical element content for two background sites, we used Mann–Witney and Kolmogorov–Smirnov nonparametric tests of samples difference.[12,13] The results of the comparison show that the difference of mean contents of Eu, Sc, Cs, and Hf is insignificant ($0.1 > p \geq 0.05$), while the mean content of other elements in the samples taken in Akademgorodok in January and April, 2006 is negligible ($p \geq 0.1$). The tendency to the decrease of the content of the analyzed elements from January to April is observed. The comparison of mean content of elements in the samples taken in Akademgorodok at the end of 2006 and 2007 winter period shows that the differences of

Table. Geochemical composition of snow solid residuals at the observational background stations of IAO SB RAS and dust load intensity in 2006 and 2007 winter periods

Chemical element	Content, mg/kg					Total load, mg/(km^2·day)				
	Akademgorodok			Kireevsk		Akademgorodok			Kireevsk	
	2006		2007	2006	2007	2006		2007	2006	2007
	January	April	March	April	March	January	April	March	April	March
Co	23.7	19.3	8.3	13.5	8.1	722.4	518.3	412.2	250.8	216.6
Sb	8.1	7.7	5.1	8.9	7.1	243.3	203.6	274.4	158.7	187
Cr	94.9	81.5	71.6	102.2	96.1	2789.8	2151.2	3601.5	1921	2556.3
Ba	1290	1030	653.2	716.7	522.2	38948	26765	33191.5	13243.3	14034.7
Sr	280	100	256.5	100	216.8	8452	2590	16478.9	1833.3	6201.7
Lu	0.4	0.4	0.3	0.4	0.3	13.2	10.6	12.6	7.4	7.6
La	38.9	35.1	21.3	30.6	22.1	1167.4	923.7	1065.9	556.6	593.4
Ce	75.5	64.2	38.4	52.1	37.4	2207	1692	1907.5	958.5	1007.1
Sm	5.8	6.0	3.7	5.1	4	175.4	159.8	183.5	92	108.7
Eu	1.7	1,2	0.6	1.0	0.6	51.0	31.4	28.4	19	17.3
Tb	1.0	0.8	0.4	0.7	0.5	29	20.6	20.8	13.1	14.5
Sc	12.3	10.2	6.2	9.0	6.9	365.3	269.2	311.3	165.5	185.5
Yb	3.2	2.9	1.7	2.4	2.1	93.9	76.1	83.8	44.2	57
Rb	58.0	49.7	34.3	49	36.8	1677.0	1276.4	1572	904.3	996.4
Cs	5	3.4	2.7	3.8	3.4	141.8	87.7	126.6	71.1	90.8
Hf	6.2	5.2	3.8	4.7	3.9	183.2	137	178.8	87.6	104.7
Ta	1.2	1.0	0.5	0.7	0.7	34.7	26.4	26.4	13.2	19.7
U	4.6	4.5	1.6	3.1	2.0	127	117.2	84.6	57.6	52.2
Th	11.4	8.5	5	6.8	4.6	319.8	221.7	247.2	125.1	123.3
Ca	1.1	1.1	1.2	1	0.9	34.6	30	49.3	18.6	23.1
Na	0.8	0.8	0.5	0.8	0.7	25.9	21.2	24.7	15.1	18.5
Fe	3.9	3.4	1.9	3.7	1.9	115.5	89.3	94.7	69.9	50.5
Br	6	6.7	4.8	8.3	4.7	180.3	171.4	210.6	149.4	129.6
Au	0.1	0.1	0.1	0.7	0.1	3.4	2.9	3.8	12.8	2.4
Ag	1	1	1	1	1	29.8	25.9	44.4	18.3	26.7
Th/U	2.5	1.9	3.0	2.2	2.3					
P_n	30	26	27.5	18	26.7					

Comment. Ca, Na, Fe (content, %); total load, g/(km^2·day); P_n is dust load, mg/(m^2·day).

Co, Ba, Lu, La, Ce, Eu, Tb, Yb, Rb, Hf, Ta, U, Th, and Fe are insignificant, while the differences of other elements are negligible.

The comparison of mean concentrations in the samples taken in Kireevsk in 2006 and 2007 shows insignificant differences for such elements as Co, Ba, Lu, La, Ce, Eu, Tb, Sc, U, Th, Fe, Br, and Au, while the differences for other elements are negligible.

Note that for insignificant differences a small increase of element concentrations is observed in 2006 as compared to 2007 in both sites of monitoring.

It should be also noted that aerosols of the analyzed regions have a pronounced uranium specialization (Th/U < 3) according to the gradation presented in Ref. 4.

The total load caused by the inflow of these chemical elements is characterized by low quantityes in the samples from Kireevsk, as compared to the samples taken in Akademgorodok.

Mutual tendencies to the decrease of chemical element concentrations and total load closer to spring season of 2006 are connected with the end of the heating season (Fuel-Energy complex activity), as well as with the seasonal variability of temperature conditions in the atmospheric boundary layer.

Using the results presented in Table, we constructed a geochemical associative series in the decreasing order of concentration coefficients relative to background.[3,4] As is seen, the content of the analyzed elements in the samples exceeds background values: April, 2006 – Akademgorodok – U_{22}–Yb_{14}–Tb_{13}–La_{12}–Sm_{11}–$Ba_{10.3}$–$Ta_{10.2}$–Ce_6–$Lu_{5.4}$–$Na_{5.2}$–Ag_4–$Sb_{3.3}$–Th_3–$Hf_{2.4}$–$Br_{2.3}$–$Co_{1.9}$–$Fe_{1.8}$; Kireevsk – U_{16}–Yb_{12}–$Tb_{11.8}$–La_{11}–Sm_9–$Ta_{7.2}$–$Ba_{7.2}$–$Na_{5.4}$–$Lu_{5.4}$–Ce_5–Ag_4–$Sb_{3.9}$–$Au_{3.3}$–Br_3–$Th_{2.3}$–Hf_2–$Co_{1.3}$ [9]; March, 2007 – Akademgorodok – $Yb_{7.8}$–$U_{7.4}$–La_7–$Tb_{6.6}$–$Ba_{5.9}$–$Sm_{5.8}$–$Ta_{4.6}$–Ag_4–$Ce_{3.4}$–$Lu_{3.2}$–$Na_{2.7}$–As_2–$Sb_{1.9}$–$Sr_{1.7}$–$Hf_{1.7}$–$Br_{1.7}$–$Th_{1.6}$; Kireevsk – $Yb_{10.6}$–$U_{9.8}$–Tb_9–$La_{7.9}$–$Ta_{7.3}$–$Sm_{7.1}$–$Ba_{5.2}$–$Na_{4.7}$– Ag_4–$Lu_{3.8}$–$Ce_{3.6}$–$Sb_{3.1}$–$Sr_{2.2}$–As_2–$Hf_{1.8}$–$Br_{1.6}$–$Th_{1.6}$.

To estimate the similarity of the results received in background sites, we have conducted the cluster analysis. The task was to divide a set of elements into groups of elements with the highest degree of similarity of the Pirsons correlation coefficients r.[12,13] According to the results of building the correlation matrix of the geochemical spectrum of elements in snow cover solid residual, the following associations of elements with significant positive coefficients are distinguished: April, 2006 Akademgorodok – La–Lu, Eu–Sm, Br–Rb, Yb–Ba and noble metals (Ag, Au) with radioactive elements (U, Th); April, 2006 – Kireevsk – Sm–Sb, Eu–Ba, Na–Co [Ref. 9]; March, 2007 – Akademgorodok – Sr–Sb, Au–Na–Eu–Ba, Ta–Cr, Hf– Sm; March, 2007 – Kireevsk – Au–Cr, Eu–Sb, Br–Cs–La, Na–Sr. As is seen from association data, geochemical spectra of elements in the solid residuals of snow from the analyzed sites differ between each other during one observational period and yearly. This fact characterizes the specificity of each background site under study.

We consider emissions of Thermal Power Stations to be the sources of rare, rare-earth and radioactive elements, because they use coal, which contains all these elements.[14] Heavy, noble metals, and Fe can inflow into the environment with emissions from mechanical engineering and metal processing plants. The majority of natural minerals contain noble metals, calcium, magnesium, sodium, and Fe, however, building surfaces and building plants can be the anthropogenic sources of calcium and sodium.

Winter concentrations of submicron aerosol and soot in the atmosphere

Figure 2 illustrates the time dependence of daily mean concentrations of dry basis of the submicron aerosol and soot in the ground layer for the period corresponding to the time necessary to accumulate the pollutants in the analyzed snow samples, i.e., from November, 2005 to April, 2006 (curve *1*) and from November, 2006 to April, 2007 (curve *2*). These data were obtained at the IAO Aerosol Station.

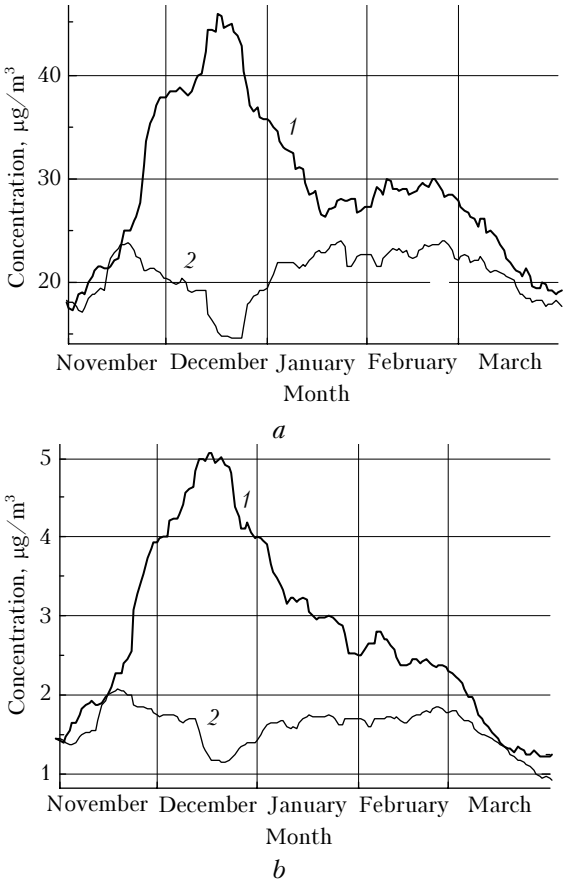


Fig. 2. Time dependences of mass concentrations of aerosol (*a*) and soot (*b*) in winter periods of 2005/06 (curves *1*) and 2006/07 (curves *2*).

As is seen from Fig.2, where data are presented with a 30-days smooth averaging, there are qualitative and quantitative differences in time scans for two winter periods. Thus, time dependence of aerosol

characteristics in 2005/06 (curves *1*) in the period of snow accumulation has prominent winter maxima. According to the results of long-term investigations this fact corresponds to the typical annual behavior of aerosol and soot concentration in the ground layer.[15] However, for 2006/07 period (curves *2*) winter maxima are not prominent. Besides, aerosol concentrations for all months of the first winter period regularly exceed the values, which correspond to the second winter period. The most significant differences are observed in December: on the average three-fold for aerosol (Fig. 2*a*) and 4.4-fold for soot (Fig. 2*b*). As it is seen in Fig. 2, the differences in absolute values of concentrations decrease from January to April.

In the beginning of January, the concentration difference of aerosol is on the average equal to 33.6–22 $\mu g/m^3$ and the same value for soot is equal to 3.6–1.6 $\mu g/m^3$. The same concentration differences decrease to 27–22 and 2.3–1.7 $\mu g/m^3$, respectively, in the beginning of March. Thus, in 2005/06 winter period much higher level of aerosol and soot concentration is observed as compared to the similar period of 2006–2007. These data agree with those for dust load, obtained from the results of snow investigation, presented in Table.

Conclusion

In general, according to the data of mineral-geochemical observations in 2006 and 2007 winter periods at the IAO SB RAS background observational stations, we can note that particles of anthropogenic origin prevail over natural ones in the snow solid residuals of samples taken in Akademgorodok, while in the samples taken in Kireevsk, natural particles prevail over anthropogenic ones. The main sources of inflow of anthropogenic particles are emissions of the Fuel-Energy complex, while the main source of natural particles is the erosion of Tom' and Ob' banks and naked slopes. The magnitude of dust load is characterized by increased values for Akademgorodok as compared to dust load in Kireevsk. This trend is characteristic for the whole observational period. The content of chemical elements and the total load of each element have insignificant or negligible difference. This trend held true for two observational sites during the time of investigation, i.e., the tendency of element inflow with aerosol fallouts from industrial and natural sources persists.

The decrease of aerosol fallout flows in the snow of investigated areas in 2007 in comparison with 2006 can be caused by the decrease of polluting component inflows from the Fuel-Energy complex, as well as by the annual variability of the temperature conditions in the atmospheric boundary layer. According to weather station data, the winter period of 2007 was warmer than the corresponding period of 2006, this fact influenced the work of city and town Heat Power Stations, resulting in a certain decrease of intensity of the aerosol pollutant emission.

Acknowledgements

The authors are grateful to V.V. Pol'kin and A.B. Tikhomirov for their help in snow sampling in March, 2007, as well as E.P. Yausheva for the processing of data on aerosol and soot mass concentration.

This work was financially supported by Russian Foundation for Basic Research (Grant No. 06–05–64393).

References

1. A.M. Adam, ed., *Ecological Monitoring: The Environmental Condition of Tomsk Region in 2002* (Tomsk Region Administration, "Oblkompriroda," Tomsk, 2003), 156 pp.
2. L.P. Rikhvanov, E.G. Yazikov, Yu.I. Sukhikh, N.V. Baranovskaya, V.T. Volkov, N.N. Volkobva, V.V. Arkhangelskii, T.A. Arkhangelskaya, O.A. Denisova, A.Yu. Shatilov, and E.P. Yankovich, eds., *Ecological and Geochemical Peculiarities of Tomsk Region and Sickness Rate* (Tomsk, 2006), 216 pp.
3. A.Yu. Shatilov, "Material constitution and geochemical characteristics of atmospheric fallouts on the territory of Ob' basin," Author's Abstract of Cand. Geol.–Min. Sci. Dissert., Tomsk (2001), 22 pp.
4. E.G. Yazikov, *"Ecogeochemistry of south west Siberian urban territories,"* Doct. Geol.–Min. Sci. Dissert., Tomsk (2006), 420 pp.
5. V.N. Vasilenko, I.M. Nazarov, and Sh.F. Fridman, *Snow Cover Pollution Monitoring* (Gidrometizdat, Leningrad, 1985), 185 pp.
6. Methodological Recommendations on Geochemical Estimation of Urban Territory Pollution with Chemical Elements (Moscow, 1982), 111 pp.
7. Yu.E. Sayet, B.A. Revich, E.P. Yanin, and R.S. Smirnova, *Environmental Geochemistry* (Moscow, 1990), 335 pp.
8. *Environment Pollution Control Manual*, RD 52.04.186, No. 2932–83 (Goskomgidromet, Moscow, 1991), 693 pp.
9. A.V. Talovskaya, E.G. Yazikov, M.V. Panchenko, and V.S. Kozlov, Atmos. Oceanic Opt. **20**, No. 6, 474–479 (2007).
10. S.A. Vakhromeev, in: *Mineralogy Manual* (Moscow, 1950), pp. 178–181.
11. M.V. Panchenko, V.S. Kozlov, S.A. Terpugova, V.V. Pol'kin, and E.P. Yausheva, in: *Abstracts of Reports at the VIII Workshop "Siberian Aerosols,"* Tomsk (2001), pp. 18–19.
12. V.P. Borovikov, *Statistica. Computer Data Analysis Skill* (St. Petersburg, 2003), 688 pp.
13. A.A. Mikhalchuk, E.G. Yazikov, and V.V. Ershov, *Statistic Analysis of Ecological and Geochemical Information: Manual* (TPU Publishing, Tomsk, 2006), 235 pp.
14. S.I Arbuzov, V.V. Ershov, A.A. Potseluev, and L.P. Rikhvanov, *Rare Elements in the Coal of Kuznetskii Basin* (Tomsk, 2000), 246 pp.
15. V.S. Kozlov, M.V. Panchenko, and E.P. Yausheva, Atmos. Oceanic Opt. **19**, No. 6, 434–440 (2006).