Estimation of the content of some components in the industrial emissions of the South Urals and Norilsk

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Analysis is performed of temporal variability of $Ca^{2+} + Mg^{2+}$ and SO_4^{2-} ions and Ni, Cu, and Ca chemical elements in the composition of atmospheric aerosols of Tarko-Sale settlement (65°N, 78°E) in winter of 1999 and of Krasnoselkup settlement (66°N, 82°E) in summer of 1999. In every series of observations the periods were observed when the content of all the components increased drastically. It is assumed that such an increase of concentrations is due to simultaneous emission of these pollutants from one and the same source. Using the back trajectories technique (model HYSPLIT, NOAA, ARL), the region is determined where the industrial sources emitting pollutants are located, and the areas of pollutant spread are calculated. The sampling sites of Tarko-Sale and Krasnoselkup are within the pollution areas. The annual industrial emissions of Ni, Cu, Ca, and $Ca^{2+} + Mg^{2+}$ cations are approximately estimated using the available emission power of sulfur dioxide from industrial sources of Urals and Norilsk and the ratio between the measured component concentration and the sulfate ion concentration.

Since 1991, in the framework of the project "Siberian Aerosols," a systematic study of atmospheric aerosols (AA) over Siberian region has been performed.[1] Goals and the tasks of the project have been presented in Ref. 2. The results of the experimental research of basic characteristics of atmospheric aerosols over Siberia, such as disperse and chemical composition of AA, as well as their space-time variations are described in Ref. 1, 3, 4, 5. One of the problems of this project is the study of the effect of long-range transport of industrial emissions on the formation of regional and global pollution of distant territories.

At present, much attention is paid to the effect of distant transport of continental AA to polar regions. The investigations in Norway and in Alaska have shown that western and central parts of Siberia can be essential pollution sources of the air basin over the Arctic.[6] The atmosphere of the cities and many regions in the south of Siberia is very strongly polluted by heavy metals. The level of such pollution is higher than in well-developed countries of Europe and America. Special attention should be paid to the following characteristic properties of AA in Siberia, where some territories are far remote from large industrial centers. According to the commonly accepted opinion, AA in these regions are referred to a category of "background" aerosols, i.e., those formed as a result of natural processes, with only small admixture of pollutants.

Long-term investigations of AA characteristics at different points of the world have shown that a considerable part of atmospheric pollutants are the particles formed at wind erosion of the land surface and the surface of seas and oceans. These are the so-called dust particles and the particles consisting of sea salts. The content of other particles of natural and anthropogenic origin in AA, as a rule, is much less. Central Siberia is at a distance of several thousand kilometers from the sources of soil-erosion aerosols. In winter period in Siberia the ground is covered with snow and the seas, oceans, and other water basins are covered with ice. Thus, during this period the conditions are very favorable for investigating the long-distance transport of industrial emissions to the north regions of Siberia.

Starting in 1996, at several points in the north of Western Siberia systematic observations are made of the space-time variations of chemical composition and the concentration of surface atmospheric aerosols. Some results of the research, which enable us to clarify the influence of sources of natural and anthropogenic types, are presented in the papers.[3,7] If in Ref. 3 the type of the source was estimated by the relative change of multielement composition of AA, then in Ref. 7 to identify possible pollution source, the experimental data were used on time variation of the concentration of some components of AA chemical composition and the data on variation of wind velocity and direction at an observation point. This paper describes analysis of time variability of some ions and chemical elements in AA composition in Tarko-Sale settlement (65°N, 78°E) in winter of 1999 and of Krasnoselkup settlement (66°N, 82°E) in the summer of 1999.

Figures 1 and 2 show the daily mean concentrations of some components over the observation periods from January 9 to February 7 and July from 1 to 30 of 1999. In Fig. 1 the values for Ni concentrations are multiplied

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by 40. It is evident from Figs. 1 and 2 that in every series of observations there are periods characterized by a sharply enhanced content of all the components. It is assumed that such concentration increase is due to a simultaneous emission of these pollutants from one and the same source. This hypothesis is supported by the results of the correlation and factor analysis.

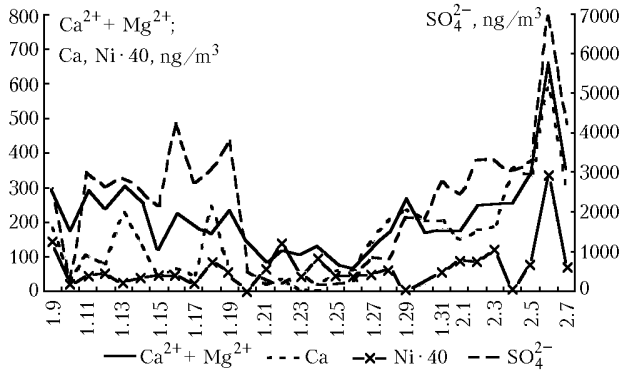

Fig. 1. Daily mean concentrations (ng/m³) of $Ca^{2+} + Mg^{2+}$, SO_4^{2-} ions, and elements Ca and Ni in Tarko-Sale settlement from January 9 to February 7, 1999.

In the first case in Tarko-Sale settlement on February 6 a significant increase is noted of the concentration of ions $Ca^{2+} + Mg^{2+}$, SO_4^{2-} and chemical elements Ni and Ca. The correlation coefficients increased over a period from February 2 to February 7 as compared with the entire observation period between all these components but especially between sulfate and the other components. The factor analysis was made for a complete series of observations, all the indicated components fell within the first factor with high weights (Table 1).

In the second case, as is seen from Fig. 2, in Krasnoselkup settlement we observed a sharp increase of concentration of sulfate ion, nickel and copper (SO_4^{2-}, Ni, and Cu) in July 13–15. Their correlation is very high, when considering over a month period and increases from July 10 to July 20; the largest increase is in correlation between nickel and copper. Factor analysis has made it possible to determine all three components of SO_4^{2-}, Ni, and Cu, as well as in the preceding case, as components of the same factor with high factor weights (Table 2).

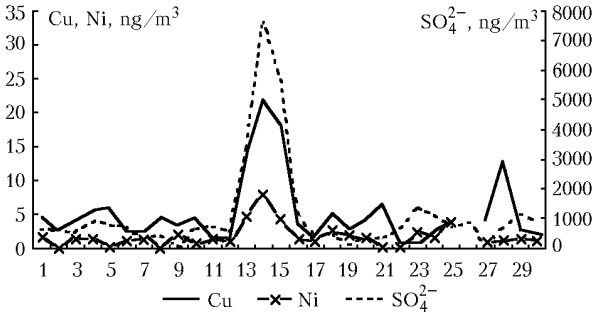

Fig. 2. Daily mean concentrations (ng/m³) of SO_4^{2-} ion and elements Cu and Ni in Krasnoselkup settlement in July 1–30, 1999.

To determine the region, from which these pollutions can be transported to the observation points, from Tarko-Sale in February 6–7 and from Krasnoselkup in July 13–15, the back trajectories were constructed of air mass motion at altitudes 10, 100, 300, 500 and 1000 m by the HYSPLIT model.[8] In Fig. 3 some of the trajectories are shown.

Table 1. The correlation coefficients and factor weights of Ca, Ni, $Ca^{2+}+Mg^{2+}$, and SO_4^{2-} in Tarko-Sale

Chemical element and ion	Factor weight	Correlation coefficients from January 9 to February 7				Correlation coefficients from February 2 to 7			
		Ca	Ni	$Ca^{2+} + Mg^{2+}$	SO_4^{2-}	Ca	Ni	$Ca^{2+}+Mg^{2+}$	SO_4^{2-}
Ca	0.81	1	0.72	0.83	0.69	1	0.87	0.99	0.93
Ni	0.79		1	0.69	0.53		1	0.91	0.92
$Ca^{2+} + Mg^{2+}$	0.87			1	0.86			1	0.97
SO_4^{2-}	0.88				1				1

Table 2. The correlation coefficients and factor weights of Ni, Cu, and SO_4^{2-} concentrations in Krasnoselkup

Chemical element and ion	Factor weight	Correlation coefficients from July 1 to 30			Correlation coefficients from July 10 to 20		
		Ni	Cu	SO_4^{2-}	Ni	Cu	SO_4^{2-}
Ni	0.80	1	0.77	0.87	1	0.93	0.92
Cu	0.75		1	0.88		1	0.98
SO_4^{2-}	0.86			1			1

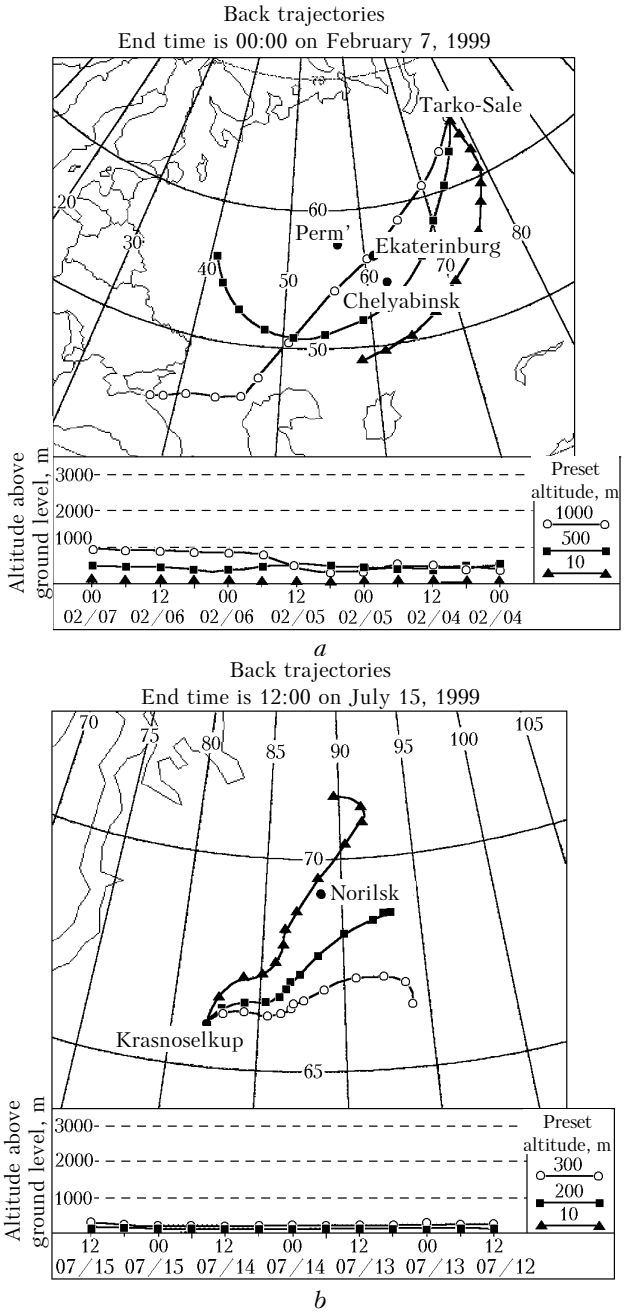

Fig. 3. Back trajectories of air mass motion; from Tarko-Sale, 00.00, February 7, 1999 (*a*); from Krasnoselkup, 12.00 a.m. July 15, 1999 (*b*).

Figure 3*a* shows that the air mass, which arrived on February 7 in the region of Tarko-Sale, passed over the territory of the South Urals, and from Fig. 3*b* it is seen that over the period from July 13 to 15 the air mass transport was observed in the north-east direction over the region studied. The trajectories passed near Norilsk.

Using the HYSPLIT model[8] we have calculated the areas of propagation of sulfur dioxide from large industrial centers, such as Perm', Chelyabinsk, Ekaterinburg, and Norilsk, for the above period. The parameters of calculations were the following: period of calculations – 48 hrs, time of emission – 48 hrs, horizontal step – 0.4°, emission velocity – $17 \cdot 10^{13}$ μg/h for the Urals (we proceed from the assumption that over one-year period the amount of industrial emissions is about 1.5 million tons of SO_2) and $23 \cdot 10^{13}$ μg/h for Norilsk (Norilsk Metallurgical Plant emits 2 million tons of SO_2 a year).

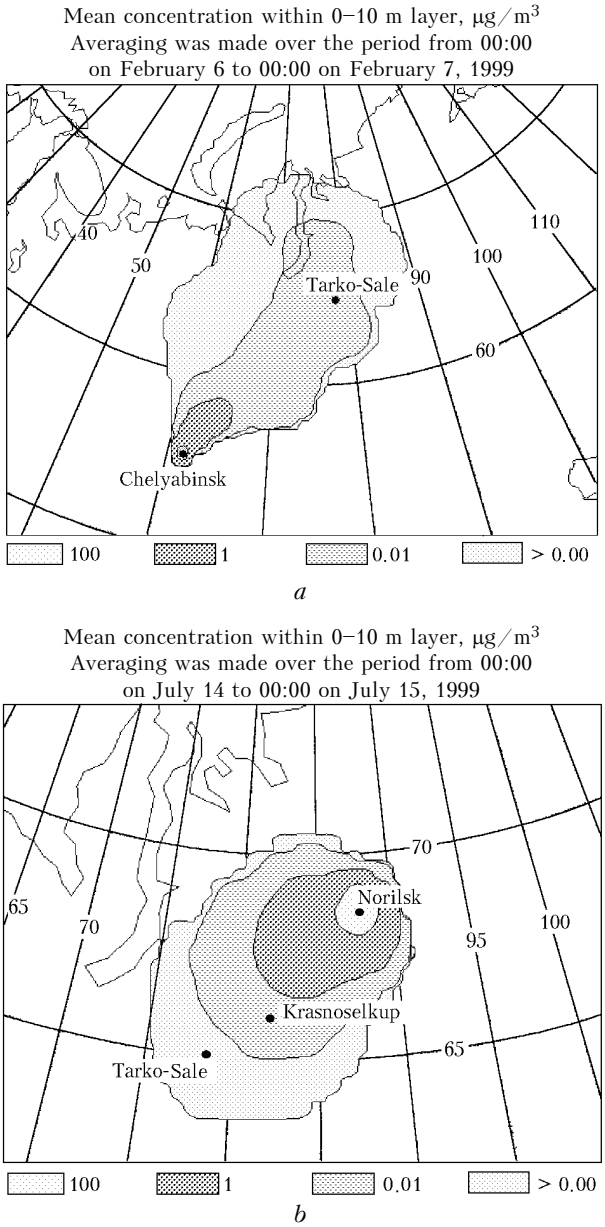

Fig. 4. Areas of SO_4^{2-} emission transport from industrial centers Chelyabinsk, February 5, 1999 (*a*); Norilsk, July 13, 1999 (*b*).

Figures 4*a* and *b* show the calculated results of, i.e., mean concentration of SO_2 in the layer of 0–10 m with the averaging over a period from 00.00 on February 6 to 00.00 on February 7, 1999 and from 00.00 on July 14 to 00.00 on July 15. It is evident that in the first period (Fig. 4*a*) Tarko-Sale area is that of mean pollution by industrial emissions from Chelyabinsk.

The calculations for the Ekaterinburg area give the same picture. Tarko-Sale settlement polluted area coincides with the Perm' polluted area with the lowest level of concentrations. In the second period (Fig. 4*b*) the areas of Krasnoselkup and Tarko-Sale settlements are polluted by industrial emissions from Norilsk Metallurgical Plant, but higher concentrations of pollutants are observed in the Krasnoselkup area. In Tarko-Sale during this period the AA samples were taken, and their analysis has shown that on July 14–15 in this area the sulfate ion content increased but not that high as in Krasnoselkup.

It should be noted that in the first case (February 5–7, 1999) over the territory of Europe a vast deep cyclone, transporting to the east, was located. This cyclone provided the air mass transport from the South Urals region to the north of Western Siberia. An extended shape of the area of emission propagation (Fig. 4*a*) can be explained by high wind velocity. In the second case (July 13–16, 1999) in the area under study a small-gradient baric field with weak winds in the north-east direction was observed. Therefore the area of industrial emission transport is not strongly extended (Fig. 4*b*). In this case the increase of concentrations of components being studied was observed during 3 days. This can be explained by the proximity of location of the assumed source of pollutants from the point of sampling – about 500 km. In the first case the distance between the observation point and the pollution source is about 1200 km.

We consider that the gaseous sulfur dioxide SO_2 is rapidly converted (during several hours), owing to chemical transformations, to a sulfate ion SO_4^{2-}, appearing in solid aerosol particles, and thus the relation between the $[SO_2]$ and $[SO_4^{2-}]$ concentrations was obtained:

$$[SO_4^{2-}] = 1.5 \cdot [SO_2]. \qquad (1)$$

If the SO_2 emission power is known, then based on the ratio of concentrations of Ni, Cu, Ca, and $Ca^{2+} + Mg^{2+}$ and SO_4^{2-} concentration in maximum we estimate the total annual emissions of Ni, Cu, Ca, and cation $Ca^{2+} + Mg^{2+}$.

$$Q_i = \frac{C_i^{\max}}{C_{SO_4^{2-}}^{\max}} Q_{SO_4^{2-}} = 1.5 \frac{C_i^{\max}}{C_{SO_4^{2-}}^{\max}} Q_{SO_2}, \qquad (2)$$

where Q_i is the emission power, $C_i^{\max}$ is the maximum value of daily mean concentration of ith pollutant (Ni, Ca, Cu, $Ca^{2+} + Mg^{2+}$). Using the ratio (2) we obtain the estimates of the annual industrial emission in tons (Table 3).

Table 3. Estimates of annual emission (in tons) of several components from industrial plants of the Urals and Norilsk

Components	The Urals	Components	Norilsk
Ni	2 600	Ni	3 000
Ca	193 000	Cu	8 250
$Ca^{2+} + Mg^{2+}$	225 000	–	–

Thus, using the mathematical models for constructing the back trajectories and pollutant transport, we can determine the location of pollution sources of local and regional scales and, using the measured concentrations of different AA components, the amount of industrial emissions can be evaluated.

Acknowledgments

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