Experimental investigation of the pollution transformation in industrial plumes

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The aim of this work was to determine the extent and character of the influence of Norilsk industrial center on the regional air basin. This problem was solved with the aid of the Optik-E flying laboratory (An-30 aircraft). It turned out that in the urban column the pollutants are mostly transported in the gaseous form, because the aerosol fraction deposits in the form of coarse particles just near the source. Gaseous pollutants spread to significant distances under the inversion layer (in the 300–400 m layer during the experiment). During the airborne experiment, we managed, for the first time in the past 15 years, to observe the gas-to-particle transition in the plume emitted from an industrial center. This process started 6 hours after the pollutants were emitted into the atmosphere and proceeded at the distance of 50 km from the point where the condensation began. Sulfurous anhydride was the main precursor gas. The estimates have shown that the deposition of sulfates formed in the plume can achieve 281 t/(km^2·year) in the region, where this process proceeds.

Introduction

Intensification of the industrial and agricultural activities becomes more and more noticeable and, as a rule, has negative effect on the environment. Urban building and construction of highways restrict the areas suitable for agriculture. Construction of cascades of hydroelectric power stations sharply upsets life processes in water systems, significantly worsens water quality, and hampers reproduction of fish resources. Mountains of empty rock extracted together with ore and coal rise near mines. Waste waters of industrial and communal enterprises containing alien to water medium and often toxic compounds, finally come to seas and oceans. Ineffective use of such important industrial products as fertilizers is quite dangerous. Emitted from fields to rivers, they lead to intensive growth of water plants, death of which causes pollution of water reservoirs. Migrating waste products of not complete technological processes, such as aerosol and gas emissions containing toxic substances, are even more dangerous.

The staff of the AN-30 "Optik-E" aircraft–laboratory of IAO SB RAS studies industrial emissions during the past 15 years. The original technique was developed for this purpose and tested in 12 cities, 6 regions, and 2 deposits. Its detailed description is presented in Ref. 1. In this paper we present the results of airborne sounding carried out over Norilsk industrial region.

Norilsk is the large industrial center in Arctic. Because of numerous emissions, the atmosphere over the city was characterized by the following parameters by the late 1980s.[2] Occasional concentrations of sulfur dioxide exceeded 40 MPC, and the concentrations of nitrogen oxides exceeded 36 MPC. Annual mean values of these compounds were 3–4 MPC. Occasional MPC of chlorine, phenol, hydrogen sulfide, carbon oxide were exceeded 4–6 times, and the nitrogen dioxide – 15 times.

The main sources of air pollution are non-ferrous metallurgy enterprises. Emissions of sulfur dioxide by these enterprises were the highest in the former USSR and reached 10% of the total emissions. It provided 96% of emissions, and 1–1.5% were dust, carbon oxide, and nitrogen oxides.

According to the data of regional committee on preservation of the environment,[3,4] the level of cleaning and utilization of sulfur dioxide at Norilsk mining and melting enterprise decreases from 20% in 1989 to 3.5% in 1994, that entailed additional amount of emissions (thousands tones) to the atmosphere[5–8]:

Year	Dust	SO_2	NO_2	CO
1996	24.1	2014.4	13.7	53.1
1997	26.0	2015.0	12.8	32.0
1998	20.1	2065.0	12.8	25.5
1999	20.4	2104.1	12.3	23.6

As economically justified techniques for utilization of sulfur anhydride are absent,[9] one cannot expect improvement of the air quality in the city in the nearest future.

Unhappy arrangement of the enterprises relative to residential areas in the city aggravates the situation.[2] The enterprises are located to the north and south from the city. Repetition of southward and south-eastward wind directions is 19%, northward and north-westward is 28%. Thus, the city is

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alternatively under the influence of emissions of one or another enterprise of non-ferrous metallurgy.

1. Instrumentation and techniques

In our experiment we used only some instrumentation installed onboard aircraft–laboratory (Ref. 10). Therefore in this Section we briefly describe instruments applied.

Air samplers for the devices based on the contact measurement methods were installed in the front part of the aircraft, in front of the propellers. They are intended for measurement of aerosol and gas composition of air at the flight height. Such an arrangement allowed recording meteorological parameters and collecting air samples in the undisturbed zone. The devices were mounted on the racks inside the salon, just next to the samplers. It is especially important when measuring the aerosol disperse composition and its concentration for determination of the chemical composition of particles.

Air sampling was realized by direct counter flow and additional rarefaction at the outlet of the measurement path. Such technical solution allows to get rid of application of pumps and various airflow actuators and regulators of airflow rate in the air sampling paths, because the Bernoulli principle of the change of air flow rate at the change of both the velocity and the flight height is automatically realized at the constancy of hydraulic resistance of the instruments.[11]

To measure the gas composition, the gas analyzers designed at OPTEK Company and tested and certified at D.I. Mendeleev R&D Institute of Metrology were used in the experiment. Their specifications are presented in Table 1.

Measurements of the aerosol composition were carried out in two ways. The disperse composition was promptly determined by means of the photoelectric counter PK-GTA produced at Priborostroitel Company (Vyborg) and checked at the plant, and the diffusion spectrometer of aerosol DSA designed at the Institute of Chemical Kinetics and Combustion SB RAS and checked in the same place. PK-GTA measures the number of particles in a unit volume in the size range 0.4 to 10 μm in 12 channels of combined non-linear scale, DSA measures in 10 channels in the size range from 3 to 200 nm.

Table1

Instrument	Parameter	Measurement principle	Range, error
C310	SO_2	chemiluminescent	0…2000 μg/m^3, ± 25%
R310	NO	»	0…1000 μg/m^3, ± 25%
	NO_2	»	0…1000 μg/m^3, ± 25%
3–02P	O_3	»	0…1000 μg/m^3, ± 15%
L-061-02	CO	electrochemical	0…400 μg/m^3, ± 20%
	CO_2	optical, non-disperse	0…10000 ppm, ± 20%

The aerosol chemical composition was determined using the preliminary concentrated samples on filters AFA-HP-20 of the NEL type. Airflow rate through the filter was controlled by means of the counter SGBd4-1 produced by Signal Company (Engel's) and checked at the plant. Three filters were exposed simultaneously in a flight. The specifications of aforementioned devices are presented in Table 2.

Table 2

Instrument	Parameter	Measurement principle	Range, error
PK-GTA	Disperse composition	photoelectric	0…300 cm^{-3}, ± 25%
DSA	Disperse composition	diffusion	0…1000 cm^{-3}, ± 25%
SGBd4-1	Airflow rate	rotation	0…6 m^3/h, ± 3%

The aerosol samples were processed in the Laboratory of Monitoring of the Environment of Tomsk State University (certified by the State Standard of RF No. 510338) using the techniques Atomic-Emission Spectral Analysis and Ion Chromatography, undergone an examination at the State Metrological Center of State Standard of RF (Ekaterinburg) No. 08-48/031 and 08-48/032 20.12.1994. The errors in determination are presented in Table 3. The data were referred to height and geographical site by means of the GPS system.

Table 3

Constituent	Method	Detection threshold, μg/filter	Error, %
Br^-, SO_4^{2-}	Ion chromatography	0.6	8
NO_3^-	–	0.6	8
Cl^-	–	0.1	12
F^-, NH_4^+, NO_3^-	Ionometry with selective electrodes	0.2	10
Na^+, K^+	Flame photometry	0.2	10
Al, Co, Cr, Mo, Ni, Ti, Zn, B, Si	Atomic-emission spectroscopy	0.02	20
Ag, Ba, Cu, Pb, Sn, V, Mg, Mn	–	0.01	20
Fe, Ga, W	–	0.1	20
Ca, Cd	–	0.2	20

2. Conditions and diagram of a flight on investigation of plumes

One of the negative effects of emissions of industrial enterprises of Norilsk on environment is fall-out of sulfur compounds from the atmosphere.[2,4,5] Table 4 includes the data on the content of sulfates in atmospheric precipitation obtained in Norilsk and at the nearest stations of Russian Hydrometeorological Service.[12] Two of them, Dickson and Turukhansk, are included into the list of the background stations of the world network of monitoring of acid precipitation.[13]

Table 4. Annual mean concentrations of ion SO_4^{2-} (mg/l) in atmospheric precipitation

Station	Year				
	1991	1992	1993	1994	1995
Dickson	11.1	18.2	17.6	2.9	21.1
Norilsk	124.8	125.3	112.4	182.0	150.9
Turukhansk	1.0	1.6	2.4	1.5	1.7
Urengoy	1.8	2.7	3.4	1.4	1.3
Zhigansk	1.3	1.2	0.9	1.4	1.2
Kusur	7.9	11.3	6.0	8.2	9.5
Polyarny	2.9	–	1.8	2.9	1.7
Tiksi	4.4	4.1	7.6	4.7	5.9

It is seen from Table 4 that the content of sulfates in Norilsk is two orders of magnitude greater than their concentration in other regions. The increase of the concentration of sulfates after disabling of the cleaning constructions (1994, 1995) of the enterprises of the city is also seen in the Table.

It is hard to consider the station Dickson as the background in sulfates, because their concentration here is an order of magnitude greater than at the neighbor stations. Most likely, it is in the zone of influence of the enterprises of Norilsk at northward direction of the air mass transfer. Taking into account the prevalent eastward transfer, one can assume that the enhanced content of sulfates observed in Kusur and Tiksi is also the consequence of the long-range transport of emissions of Norilsk. So the aim of this flight was to determine the spread of admixtures in the area surrounding the region.

Initially it was planned to make the maps of admixtures over the city and nearest vicinities, as was described in Ref. 1. However, some circumstances lead to the necessity of the change of the plan of the flight.

First, it was because of the meteorological conditions. Low inversion lead to the fact that emissions of the enterprises were spread in the lowest layer, under the inversion. To perform measurements in such a plume, it is needed to carry out a flight at super-low heights, but orography of Norilsk did not allow to do this.

Second, as was revealed in the preliminary flight, sulfur compounds are emitted from the city in the gas phase. It is unknown at what distance they are condensed. But fall-out is the most effective from aerosol phase.[14] Our previous experiments show that one should collect the aerosol fraction at the distance of no less than 20 km from the source of emission.[15]

Third, when moving in the city plume, the processes of transformation of compounds in it occur continuously. Then it is expedient to estimate their rate. It is asserted,[13] that the intensity of fall-out of sulfur compounds at the distance of 10–15 km from the city is several times (sometimes an order of magnitude) greater than the values accepted as the regional background. According to the data by A.G. Ryaboshapko, chemical processes of sulfur transformation occur in the way of its oxidation to the upper valency VI and neutralization[14]:

$$H_2S \to SO_2 \to H_2SO_3 \to H_2SO_4 \to MeHSO_4 \to Me_2SO_4,$$

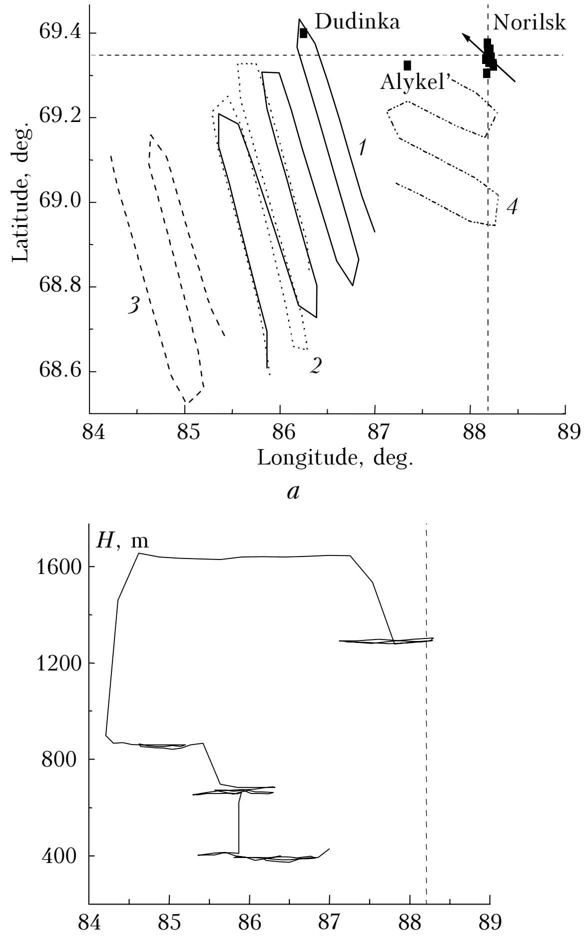
where Me is any cation. Really the principal part of emission consists of sulfur dioxide. The use of numerical methods[16,17] made it possible to determine the principal parameters of chemical transformations of sulfur and nitrogen compounds and their sink from the atmosphere. It was found that maximum of the sulfuric acid content in the atmosphere during the transfer is reached approximately in 20 hours, and the mean lifetime of sulfur dioxide due to dry absorption and chemical transformations is about 40 hours. In precipitation, the rate of sink of sulfur dioxide dramatically increases. The longer period of presence of sulfur anhydride in the atmosphere (from 4 to 9 days) was obtained in modeling.[18] The experiments[18,19] show that this period is from a few hours to 2–3 days. Obviously, such great differences are explained by the prevalence of mechanisms in the plume – chemocondensation, binary or triple nucleation.[21]

So it was decided to construct the maps of admixtures out of the city along the main direction of air mass transfer. Here one should pay attention to the fact that the directions of wind and air mass transfer often do not coincide. It was shown by S.P. Khromov,[22] that air mass carries its own wind field as if it is “frozen” in it. The example can be a moving cyclone, in which wind direction is counter-clockwise, while the cyclone itself moves as a whole along the leading flow.

The flight was carried out on November 10, 2002 in daylight time according to the diagram shown in Fig. 1. It is seen that horizontal flight legs were carried out at the heights of 400, 600, 800, and 1200 m over the sea level along the equidistant tacks. Three lower horizontal flight legs were carried out at the distances of 60 to 120 km far from the city. The flight at 1200 m was 20 km far; 6 paths were performed at the height of 400 m, 4 at 600 m, 3 at 800 m, and 4 at 1200 m.

The weather in Norilsk in the morning was determined by central part of filled cyclone with near-ground fronts, then the small-gradient field of low pressure was observed. The type of air mass was Arctic.

Vertical stratification of the atmosphere is shown in Fig. 2, where it is seen that the powerful near-ground inversion was formed in the nighttime, which favored accumulation of sulfur anhydride up to 1000 μg/m^3 and submicron aerosol fraction in the under-inversion layer. The intensity of inversion decreased by the end of the flight, and its height slightly decreased. Besides, weak precipitation led to cleaning of the lower layer of the atmosphere. The concentration of SO_2 approached the background value of 40–60 μg/m^3, as well as the number density of submicron aerosol fraction.



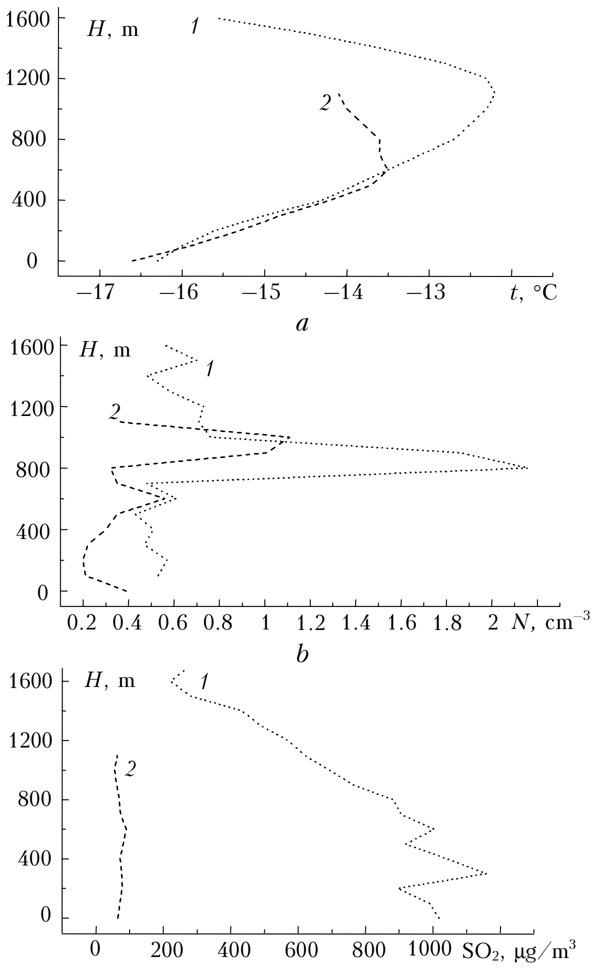
b

Fig. 1. Diagram of flights at the heights of 400 (*1*), 600 (*2*), 800 (*3*) and 1200 m (*4*).

The maps were constructed using measurement data obtained at the aforementioned heights, which show the distribution of admixtures in the plane close to horizontal.

Let us consider first of all the data collected at the height of 400 m in the plume of emission, as the most effectively representing the subject of analysis.

It is seen from Fig. 3 that urban air came to the square of measurements, the concentration of SO_2 reached 450 μg/m^3. Although the nearest boundary of the square was at the distance of 58 km from the city, and the far boundary was at 100 km, the trajectory analysis shows that air came to this region in 6 hours along an arc-shaped path.



c

Fig. 2. Vertical distributions over Norilsk on November 10, 2002 of air temperature (*a*), aerosol number density ($d \geq 0.4$ μm) (*b*), sulfur anhydride concentration at take off (*1*) and landing (*2*) (*c*).

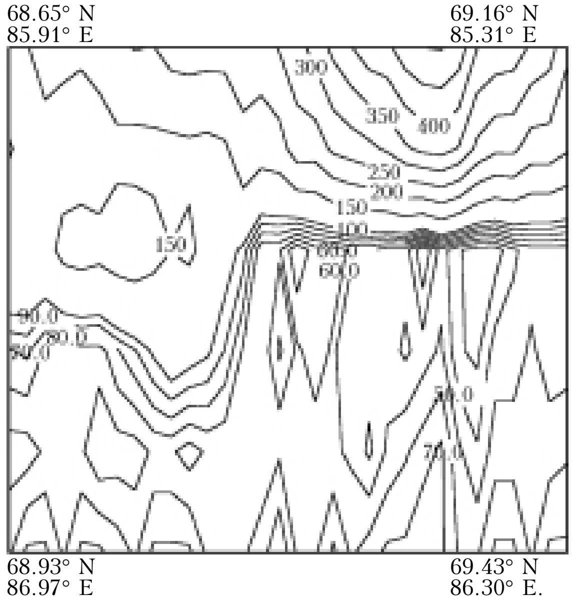


Fig. 3. Distribution of the sulfur anhydride concentration at the height of 400 m on November 10, 2002, μg/m^3.

The pass from urban plume to the background conditions is well seen. The content of sulfur anhydride under background conditions is 50–60 μg/m^3. It confirms the results from Refs. 16–21 that SO_2 can be in the plume during tens of hours. Thus, for the first time during the past 15 years we have managed to record the transformation from gas to aerosol in the plume. The transformation process shown in Fig. 3 has been displayed in concentrations of carbon oxide and dioxide and the aerosol characteristics.

The aerosol samples were collected during the flight in addition to direct measurements, from which one can follow the transformation from gas to particle. The paths were selected perpendicularly to the wind direction at different distance from the source (Fig. 4).

It is seen in Fig. 4 that in plume, as moving from the source, the mass portion of calcium decreases, and the portion of sulfates increases from 64 to 9 and from 4 to 51%, respectively.

As these measurements have shown, the change of the admixture contents above the inversion was inverse: the contribution of calcium is greater, and the portions of others were less as moving from the source. Its contribution to the total aerosol at the height of 800 m increases from 56% at the distance of 121 km to 81% at 142 km from the source. The contribution of calcium at the height of 1200 m at the distance of 10 km is 69% and increases up to 94% at the distance of 35 km.

Such different behaviors of the main aerosol components can be explained by two facts. In the plume, where the concentration of SO_2 is high, it actively condenses to the acids H_2SO_3 and H_2SO_4, which obviously interact with calcium. As a result, aerosol particles are formed, which fall down from the flow. Above the inversion, where the content of SO_2 approaches the background value, such processes are not observed. Calcium, which most likely came to the atmosphere at combustion of fuel is contained in microdisperse fraction, which is well transferred in the atmosphere and practically does not precipitate. At least, it is well known that aerosol generated in the process of combustion has the size within the range from 20 to 180 nm.[23]

It is also possible that particles containing calcium have bimodal distribution. One mode contains microdispersed particles, and another one contains submicron or coarse particles. However, one can test this assumption only experimentally, for which repeated sampling of aerosol and analysis with electron and optical microscopes are needed.

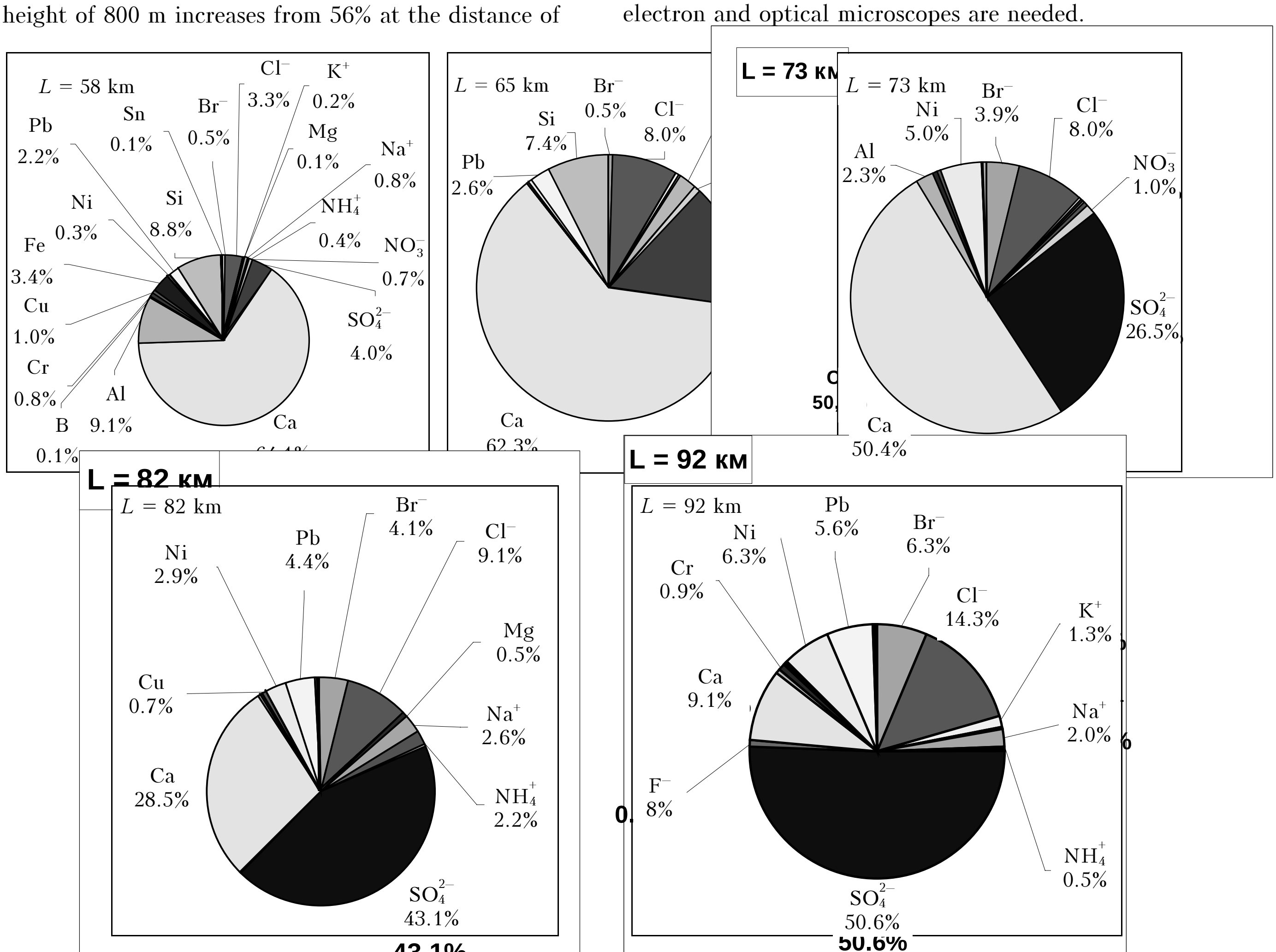


Fig. 4. Relative chemical composition of atmospheric aerosol at the height of 400 m on November 10, 2002.

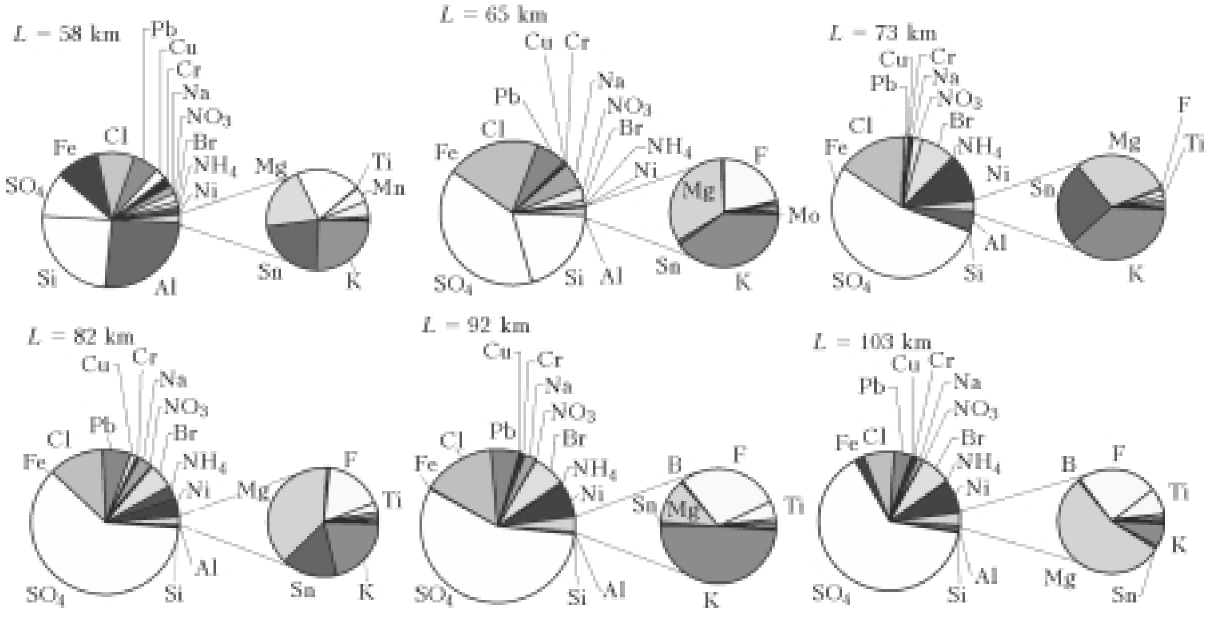


Fig. 5. Relative chemical composition of atmospheric aerosol without calcium at the height of 400 m on November 10, 2002 (indices of ion charge are missed).

As calcium clearly dominates in the aerosol composition, the aerosol composition without calcium is shown in Fig. 5.

It is seen from Fig. 5 that the aforementioned tendency of increase of the portion of sulfate in aerosol as moving from the source is also observed at the height of 400 m. Sulfate ion is the main component in the plume after calcium.

Thus, it follows from the experiment that the concentration of sulfur dioxide remains high in urban plume at significant distances. The effective transformation gas-to-particle begins at the distance more than 50 km from the source, which is accompanied by the change of the aerosol chemical composition. As a result, sulfate aerosol begins to dominate. Calcium and chlorine dominate in the composition of particles above the inversion. Possibly, it has marine origin.

Obviously, if gas-to-particle transformation occurs as nucleus formation but not condensation of vapor on already existing particles, it should be observed as increase of the concentration of the nucleus mode. Calculations[24] and experiments[25] show that the rates of generation of particles with the size of 1 and 10 nm can differ by an order of magnitude. To examine these statements, let us consider Fig. 6, where the distribution of the nucleation mode within the square under study is shown.

It is seen from Fig. 6 that the zone of the highest concentration of nanoparticles coincides with the area where the greatest concentration of sulfur anhydride has been observed (see Fig. 3). Concentrations of nanoparticles and sulfur anhydride out of this area approach the background values. Hence, generation of new particles occurs mainly from SO_2, where its concentration is enhanced.

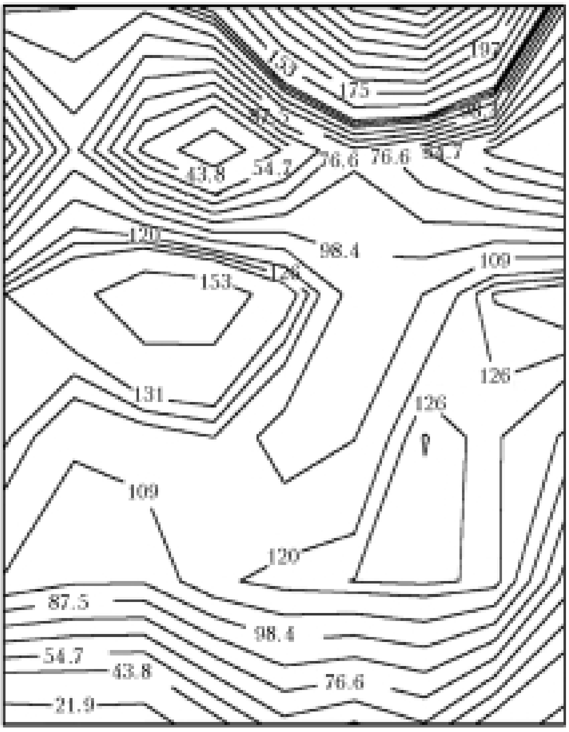


Fig. 6. Distribution of nucleation mode at the height of 400 m, cm^{-3} (see coordinates of the plate in Fig. 3).

Increase of the concentration of nucleation mode should reinforce coagulation processes. It is seen in Fig. 7, which shows the distribution of accumulative mode produced from nanoparticles during such processes. As is seen from comparison of Figs. 6 and 7, the zones of the maximum concentrations of both modes coincide. This means that nucleation and coagulation processes occur simultaneously in this part of the plume.

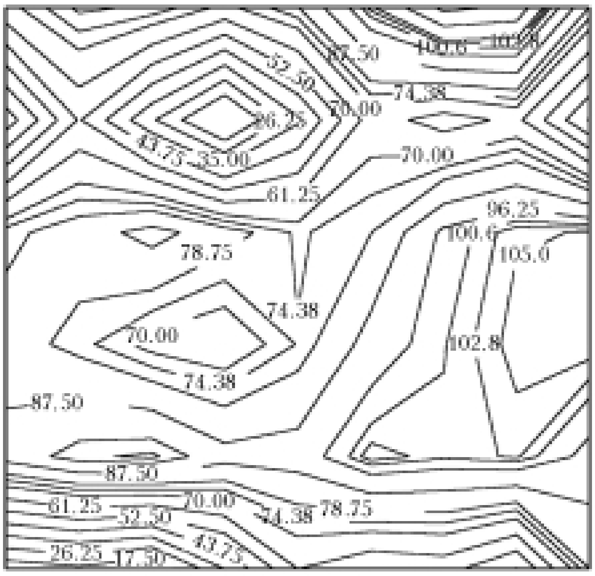


Fig. 7. Distribution of accumulative mode at the height of 400 m, cm^{-3} (see coordinates in Fig. 3).

If all existing and new generated particles remained in the plume, it should affect the concentration of submicron particles, the most long-lived in the atmosphere. To check this assumption, let us consider Fig. 8.

Submicron fraction (not only new generated particles in our case) is also close to the distribution of SO_2. One can see this in Fig. 8.

Submicron fraction concentration in the plume is not great – 2.4 cm^{-3}. Out of the plume it is 0.8 cm^{-3}. As compared with CO and SO_2, the excess of concentration of which in the plume is 5 to 7 times, this value for submicron fraction is only 3 times. Similar characteristics were also obtained in Ref. 26. The value for SO_2 presented is 6.2, and 1.5 for CO. Taking into account that coarse fraction ($d > 1$ μm) is also included into the number density, such difference in the behaviors of microdisperse and submicron fractions in the plume can mean that some particles reaching the size of 1 μm and more, precipitate.

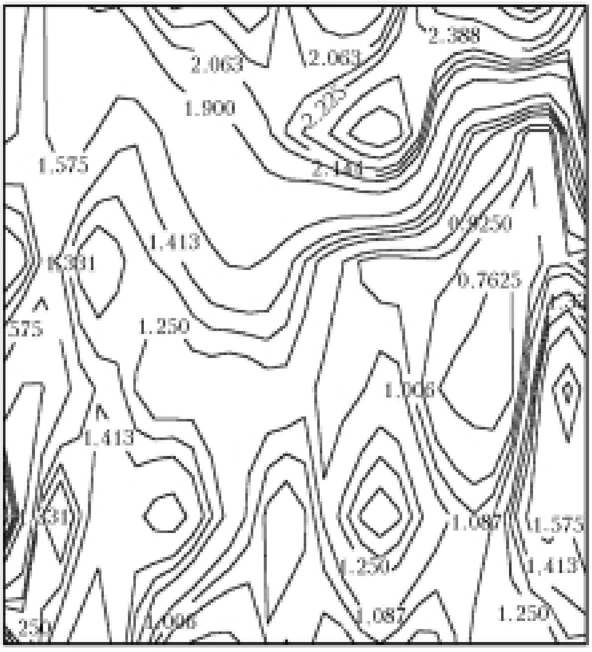


Fig. 8. Distribution (in cm^{-1}) of submicron aerosol fraction ($d \geq 0.4$ μm) at the height of 400 m on November 10, 2002.

The aforementioned data allow us to estimate possible fluxes of the chemical components of atmospheric aerosol to the underlying surface. For calculation, let us use the results obtained at the height of 400 m in the plume, where intensive process of aerosol formation and precipitation of some particles from the plume have begun. The initial data and the results of calculation are presented in Table 5, where the concentration of the elements and ions at the beginning and at the end of the process of gas-to-particle transformation are presented in the upper part. The beginning and the minimum are referred to the distance from the city.

Table 5. Concentration (μg/m^3) of admixtures in the plume before and at the end of aerosol generation and estimate of the volumes of fall-out

Distance from the source, km	Cu	Ca	Al	Si	Pb	Cr	Ni	SO_4^{2-}	NO_3^-	Cl^-
58	0.738	45.715	6.466	6.228	1.553	0.580				
65			0.006			0.109			0.523	4.092
73				0.700					0.256	
82							1.258	10.408		
92		1.269								
103	0.021				0.397		0.790	6.283		0.716
Difference in concentrations	0.717	44.446	6.460	5.528	1.156	0.470	0.468	4.125	0.266	3.376
Volume, km^3	10530	7956	1638	3510	10530	1638	4914	4914	1972	8892
Mass, kg	7552	353613	10582	19404	12170	770	2300	20270	525	30023
Area, km^2	2700	2040	420	900	2700	420	600	600	480	2280
Time, s	8100	6480	1080	2700	8100	1080	3780	3780	1440	6840
Flux, (g/$km^2 \cdot s$)	0.36	26.75	23.33	8.01	0.56	1.70	1.01	8.94	0.76	1.93
Flux, t/($km^2 \cdot$ year)	10.89	843.59	735.70	251.80	17.56	53.57	31.98	281.85	23.98	60.71

Second part of Table 5 contains: the volume, in which the process of sedimentation of particles occurred, the area, on which it occurred, and duration of sedimentation. The total mass of the substance fell down from the plume, specific and annual fluxes to the ground surface were calculated. The last row should be considered as conditional, because it is based on the data of the short-time experiment. The area was calculated based on the fact that the plume width was about 60 km, and the length was determined from the beginning and the end of the process of gas-to-aerosol transformation. Vertical size was determined from the lidar data, and was, on the average, 60 m.

The results of calculations need no comments. Let us only note that sedimentation of sulfate is not so great as expected. But the process of formation of SO_4^{2-}, as is seen in Table 5, is the most intense at the distance of 82 km. In addition to sedimentation of sulfates, the data of Table 5 reveal significant fluxes of ash components Al, Si, and Ca. The values of the sedimentation of Pb are relatively high. Possibly, it is used in technologies at the enterprises of Norilsk.

The estimate of sedimentation of Pb presented in Table 5 is significantly greater than the mean value obtained earlier for the territory of the former USSR,[27] and is close to the estimates obtained for the regions with high volumes of emissions of sulfur dioxide,[28,29] although it exceeds them by 1.5–2 times.

Conclusions

The moment of gas-to-particle transformation in the plume of emission of an industrial center was observed in airborne experiment for the first time during the past 15 years of such investigations. This process began 6 hours after the admixtures came to the atmosphere and occurred at the distance of 50 km from the moment of the beginning of condensation. The main gas-precursor is sulfur anhydride. The estimates have shown that precipitated amount of sulfates generated in the plume can reach the value of 281 t/(km^2 · year) in the region where this process occurs.

Acknowledgments

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