Complex assessment of the conditions of the air basin over Norilsk industrial region. Part 3. Dispersal of admixtures

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We analyze the composition of atmospheric emissions from the main industrial plants of Norilsk industrial region and their transformations occurring while the emissions are being spread in the atmosphere.

Introduction

One of the adverse environmental effects of the emissions from Norilsk industrial plants is deposition of sulfur compounds from the atmosphere.[1] Therefore, we have paid special attention to sulfur containing admixtures in our experiments.

Earlier we have considered the dispersal of admixtures over Norilsk region in winter period.[2] The present paper is mainly devoted to specific features of their behavior in summer and comparison of the results obtained in both seasons.

The main results of our first and second summer flights on the sizes of urban column and total balance of admixtures in Norilsk industrial region have been discussed in the first two parts of our study.[21,22]

Here we consider in detail composition of emissions from some local sources on the territory under study and their spreading down air stream. The emissions from the main industrial enterprises of Norilsk have been surveyed during the third and partially the forth summer flights.

The scheme of third flight is depicted in Fig. 1.

Measurement results

One of the tasks of this study was sampling the aerosol in emission plumes of the three biggest enterprises: nickel and copper plants and "Nadezhda" industrial complex. Sampling was performed at short distances from the stacks in order to determine the immediate release of the plant emission to the atmosphere (Fig. 2).

As seen from Fig. 2a, the emissions from nickel production plant mainly comprise sulfates and next silicon. Potassium, sodium, and ammonia are represented in noticeable amounts. Among secondary admixtures, lead makes main contribution.

At the copper production plant, sulfates are also the main compounds of emissions (Fig. 2b); there are

also chlorine, calcium, ammonia, nitrates, and sodium. Lead, chromium, molybdenum, and such less-common element as barium dominate in the group of secondary elements.

Composition of the emission from "Nadezhda" industrial complex slightly differs from composition of the emissions from other enterprises (Fig. 2c). Though sulfates dominate in the composition their contribution is evidently lower. The amount of chlorine and calcium increases; ammonia, nitrates, aluminum, silicon, sodium, iron, and copper are also present in noticeable amounts.

Since no such experimental measurements have been carried out in the cold season, there is nothing to compare with. However, the subplume measurements carried out in winter revealed the similar situation.

As follows from Fig. 2, sulfates dominate in the emissions from the three enterprises. The winter measurements have shown SO_2 to transform into aerosol at a considerable distance from sources. We return to this question later.

During the first flight, there occurred a forest fire near the city. Since vegetation is an effective accumulator of atmospheric aerosol which comes back to the atmosphere in case of a fire,[3] the comparison of compositions of both the plume of the industrial emission (see Fig. 2) and of the forest fire (Fig. 3) makes sense as this can serve as an indirect indicator of the environmental effect of an enterprise.

Samples in the plume of the fire were taken twice: at the height of 500 m at the distance of 10–15 km from the source and at the height of 1200 m at the distance of 80 km away from the fire (Fig. 3).

As seen from the comparison of Figs. 2 and 3a, the composition of forest fire aerosol essentially differs from those of the industrial emissions. Thus, chlorine and calcium dominate in the fire plume while sulfates dominate in the emissions from the enterprises, though they are present in the smoke of burnt plants in noticeable amounts too. The latter contains all terrigenous elements and nitrates.
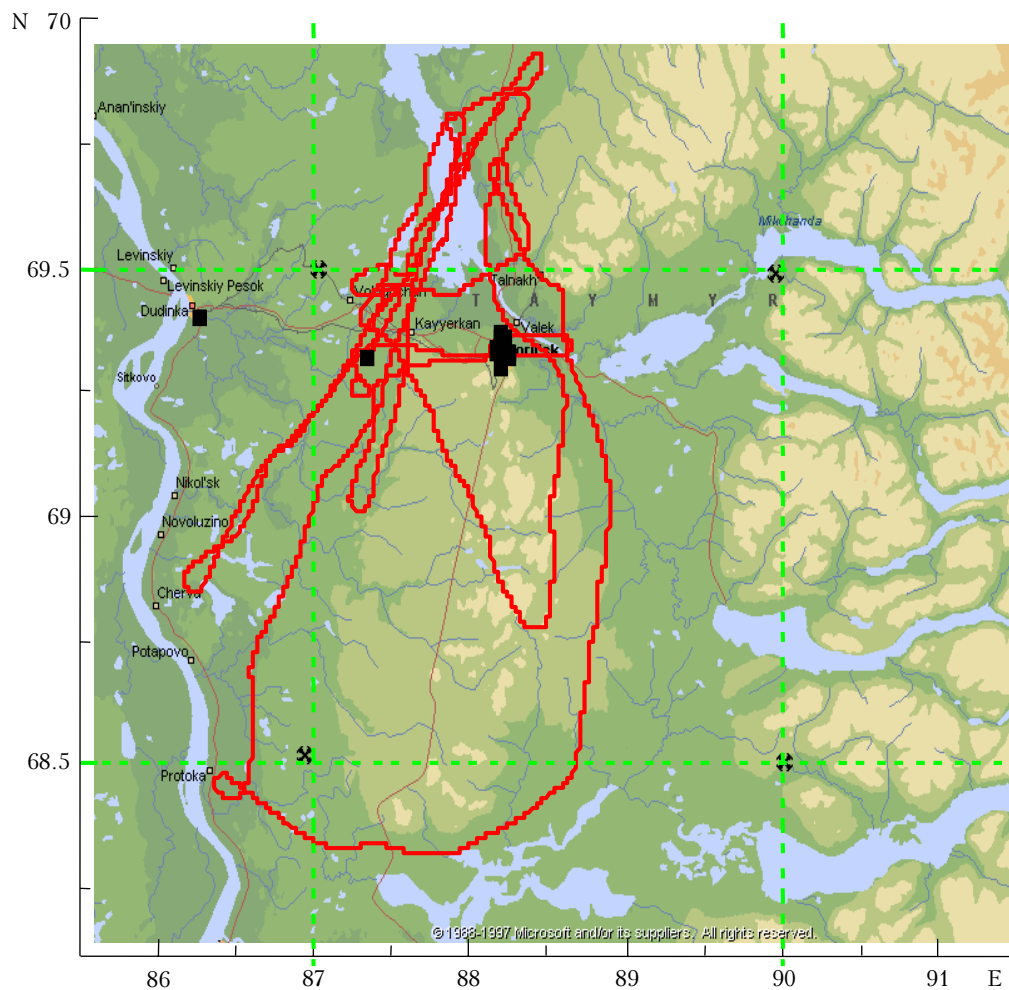
Fig. 1. The scheme of flights for sounding the propagating emission plumes.

No dominating element or compound is observed among secondary elements. In contrast to industrial emissions, all identifiable elements are present in the fire plume.

Transformation of the forest fire plume with its spreading is shown in Fig. 3b. It is seen that as the fire plume spreads the concentration of sulfates essentially decreases. As a result, the relative contribution of other elements and compounds has increased against this fading background. The most probable reason for this is the drop of heavy particles out from the plume. At least, the concentration of identifiable elements near the source was $90\,\mu g/m^3$, while at 80-km distance it was $40\,\mu g/m^3$, that is less than a half.

To check this hypothesis, consider the enrichment ratios presented in Fig. 4, which have significantly grown for sulfates, nitrates, ammonia, chlorine, sodium, nickel, chromium, and vanadium in the course of the plume spreading.

Since the last elements are presented in trace amounts the drop out of particles from the plume most probably removed NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, Na^+ ions

or their combinations in the form of $(NH_4)_2SO_4$, NH_4NO_3, and other possible compounds, e.g. $NaNO_3$, NaCl, etc. According to measurement results on $(NH_4)_2SO_4$ and NH_4NO_3 the average sizes of dropping out particles are 3.2 and 2.1 μm, respectively.[4]

Measurement data on aerosol chemistry near a source most likely reflect the first wave of condensation of compounds deposing not far from the source; this is mentioned in Ref. 5.

An attempt to analyze the behavior of an admixture inside the plume spreading from an emission source was made in the next flight. The idea of the experiment was to sample inside a plume at different distances from an emission source. Data of sampling at the distances of 15, 45, 110, and 150 km, respectively, are shown below (Fig. 5). Flight routes were chosen "by touch" because the lidar was not operated in the summer experiment. There number of routes was abundant so there were similar samples. We present here only the most characteristic ones.

As is seen from Fig. 5a, sulfates, nitrates, calcium, chlorine, ammonia, and sodium are present in the plume as it leaves the town yet in sufficient amount.

Seemingly, these elements and ions are contained in direct emissions, which have not deposed from the plume yet, because several further samples did not show such amounts of these substances (Fig. 5b).
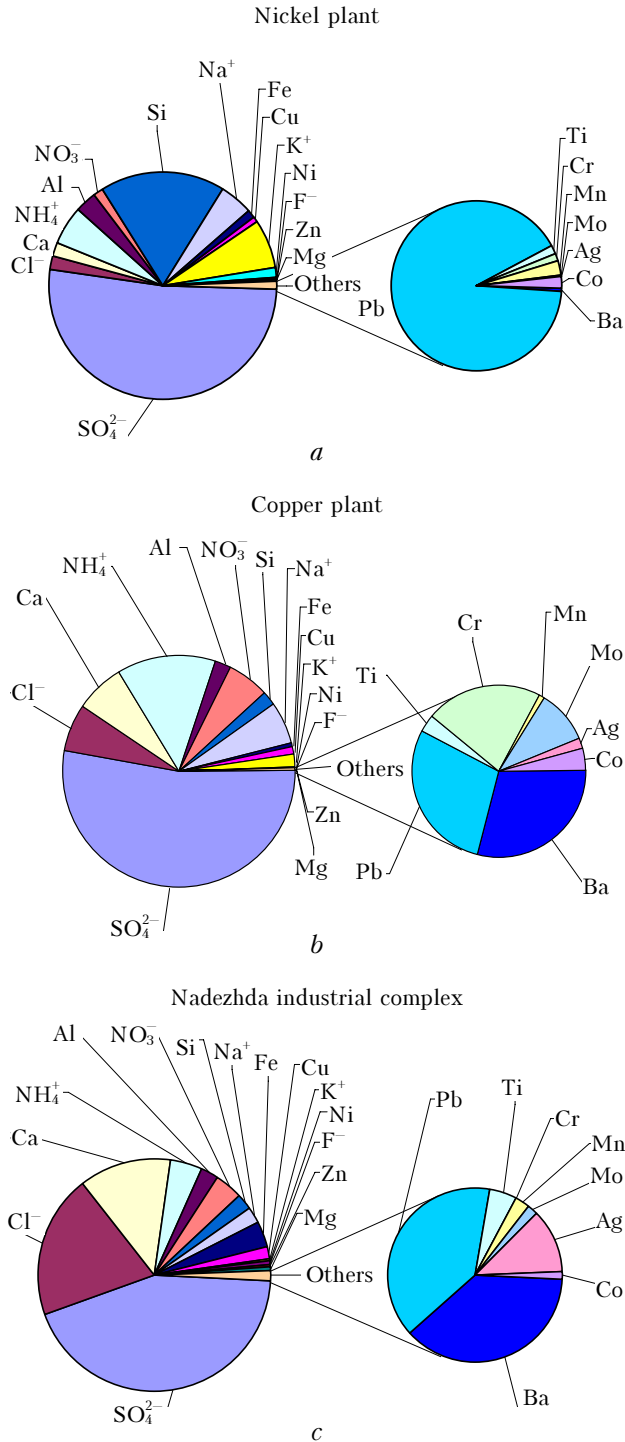
contribution of calcium has increased, which is in a good agreement with data for the winter period. This is only possible in case of aerosol deposition from the plume before secondary (atmospheric) condensation begins.[6] In winter experiment in Norilsk, this happened at the distances from 60 to 100 km from the source. Therefore, these distances were taken as the reference ones in our summer experiment.
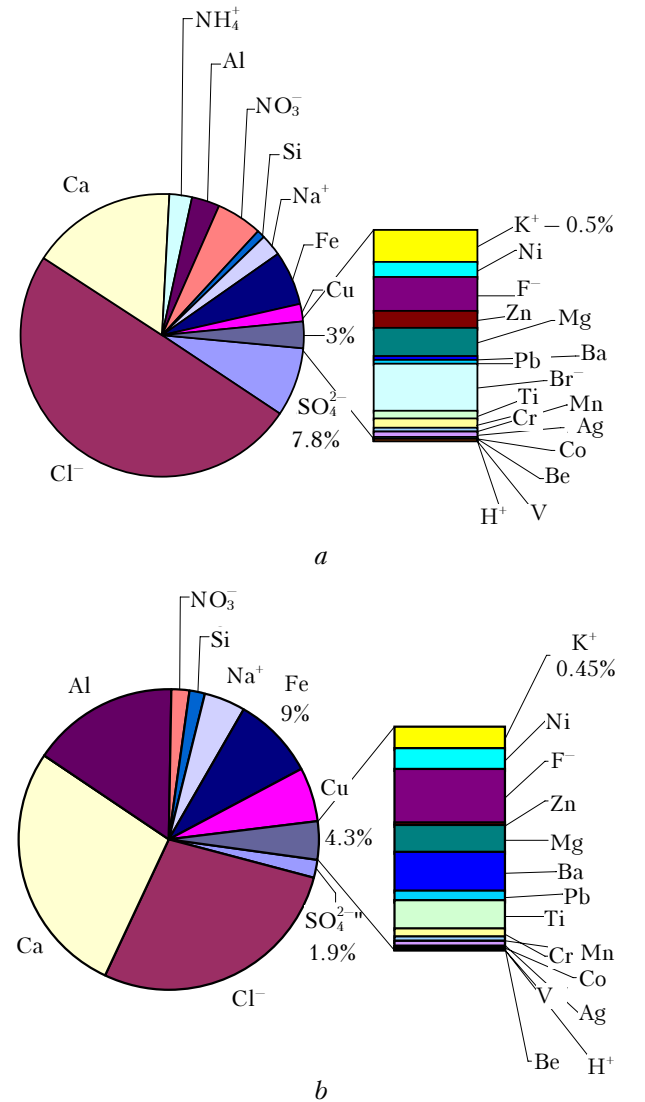

Fig. 2. Aerosol chemistry in emissions of the main plants of Norilsk.

Fig. 3. Aerosol chemistry in the forest fire plume at the distance of 10–15 (a) and 80 km (b).

Dilution of sulfates, chlorine, and nitrates follows from Fig. 5b. Mass of identifiable compounds has decreased nearly twofold. As a result, relative

Figure 5c shows that the second aerosol wave has formed at the distance of 110 km with increased sulfate and chlorine content. Thus, besides sulfates, chlorine and ammonium ions play an important role in Norilsk aerosol.

In moving further along the plume, the situation repeats: growing particles drop out of the plume and the concentration of the main ions decreases again (Fig. 5d).

Thus, after emission of admixtures, large particles drop out of the plume near a source, which have been formed yet in the gas flue due to chemocondensation.[7]
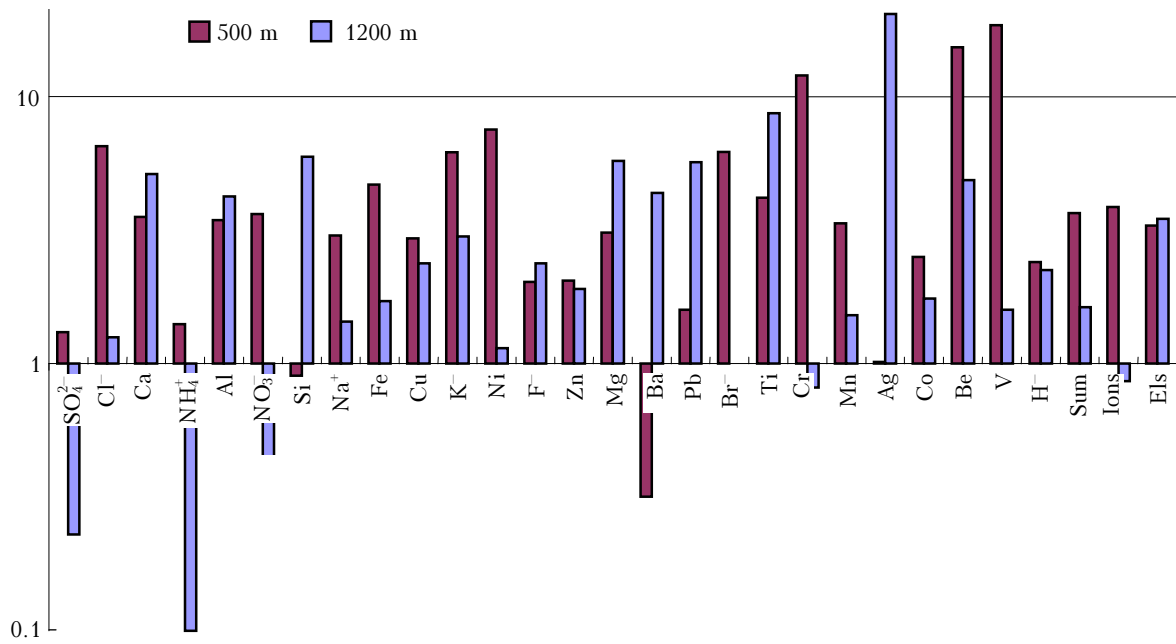
Fig. 4. Relative enrichment of elements and ions in the forest fire plume at the heights of 500 and 1200 m.
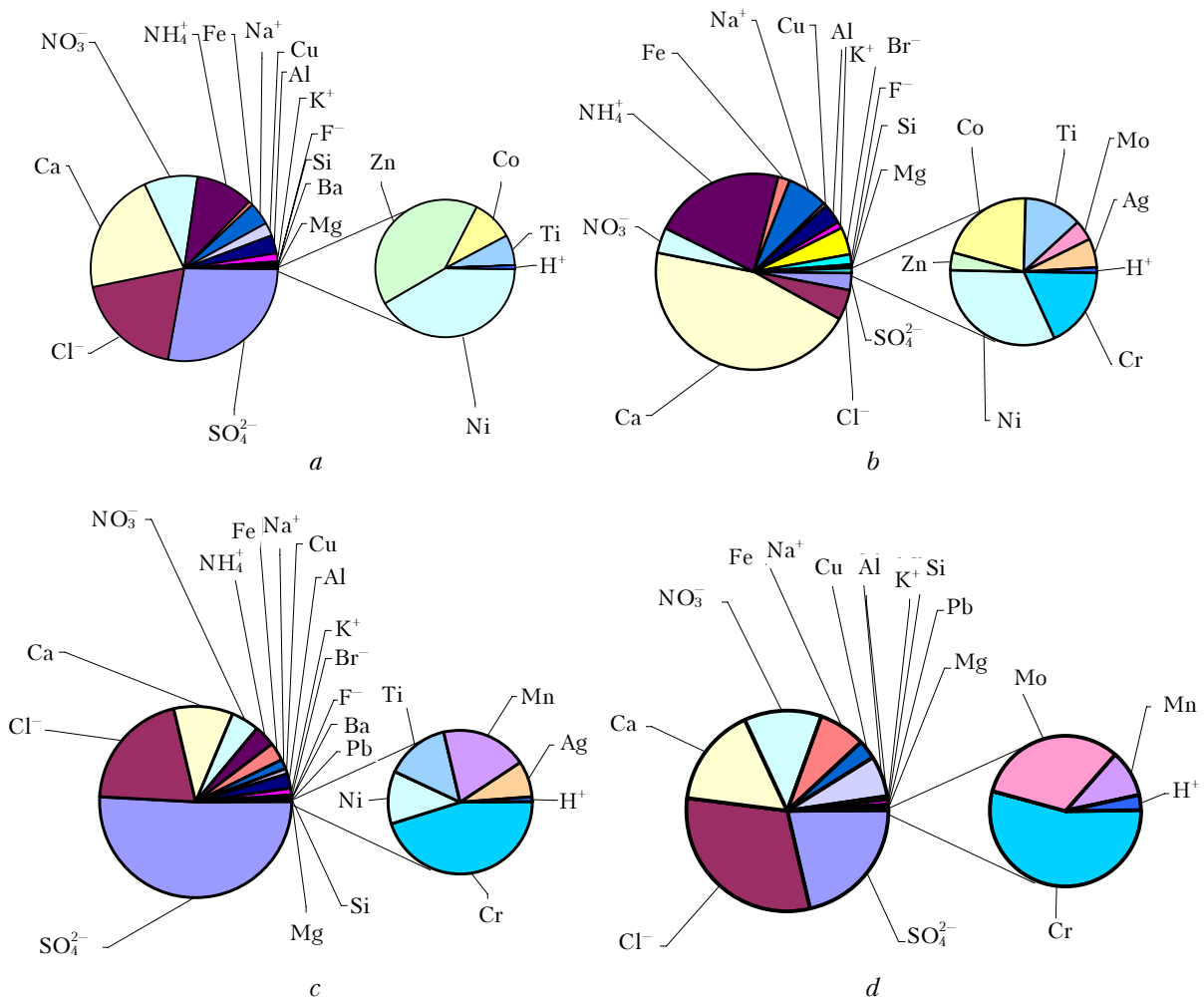

Fig. 5. Aerosol chemistry in the city plume at the distances of 15 (*a*), 45 (*b*), 110 (*c*), and 150 km (*d*).

Remind, that when mixing several gases in a closed volume, the saturation pressure for an individual gas in the mixture essentially decreases compared with that for each gas, if pure. While moving in a gas flue and then in the atmosphere, these particles quickly coagulate growing in size and drop down near the source after exceeding a certain mass. Some time is required for the second wave of particles deposition to occurr.[8] The scheme of triple nucleation ($NH_3-SO_2-H_2O$) works most often as air cools in the plume.[9] Catalysts, which are parts of aerosol particles (metals[10–12] and organic compounds[13,14]) can intensify the nucleation. Besides, the gas-to-particle conversion can be intensified due to the reaction of sulfur dioxide with hydroxyl.[15,16] According to assessments,[8] the gas-to-particle conversion lasts no less than 2 hours. Therefore, if wind speed equals to 10 m/s, next area of particle formation cannot be expected closer than at 70 km downstream the plume. This is evident from Fig. 6 showing the horizontal section of the plume spreading down the air stream.

Figure 6 shows two zones of nanoparticles generation from the gas phase: the first one is not far from the emission sources and the second one is at 80 to 120 km distance from them.

Thus, as the plume travels, the drop out of aerosol particles occurs twice: at the initial section of the path, where particles, just coming out from a stack, drop down to the surface and at a large distance where particles, formed during condensation and coagulation inside the plume, do the same. As is clear, the location of these zones with respect to sources depends both on the environmental (air temperature and humidity, wind speed, turbulence intensity, solar radiation) and initial conditions (concentration of an admixture, presence of catalysts, gas flue — atmosphere temperature and pressure jump, etc.). Thus, in our experiments, the second sedimentation wave began at 60-km away from a source in winter and 100 km in summer. We managed to trace the first sedimentation wave only from the ground-based measurements of the winter experiment.

The above data allow one to estimate probable fluxes of chemical elements of atmospheric aerosol to the underlying surface. The assumption that all the aerosol dropping out from a plume sediments on the underlying surface is to be the basic ones for making calculations. Having known the plume parameters for the first zone (40-km width, vertical thickness of 100 m, and 30-km distance between the reference routes) and the second one (60-km wide, vertical thickness of 200 m, and 40-km distance between the reference routes), concentrations at the zones' entrance and exits as well as wind speed along the routes (6 and 8 m/s), it is possible to calculate the mass of the compounds dropped out of the plume, the deposition time and thus to obtain fluxes by dividing the result by the plume area between the reference sections. The data are given in Tables 1 and 2.

No special comments are needed to these tables. Consider Table 3. It is seen, that the fluxes in summer and winter differ insignificantly by the anthropogenic elements except for lead while the contents of terrigenous elements differ by tens and hundreds times. This can be caused by the fact that the natural background of these elements increases in summer time, because soil is free of the snow screen, thus masking the anthropogenic component.

The estimates made using data from Tables 1 and 2 of sulfates deposition essentially exceed the average value previously obtained for the territory of the former USSR[17] and only 1.5 to 2 times are higher than those obtained for the regions with heavy sulfur dioxide emissions.[18,19] According to Ref. 20 the background flux is 0.0438 t/(km$^2 \cdot$ year).[20]

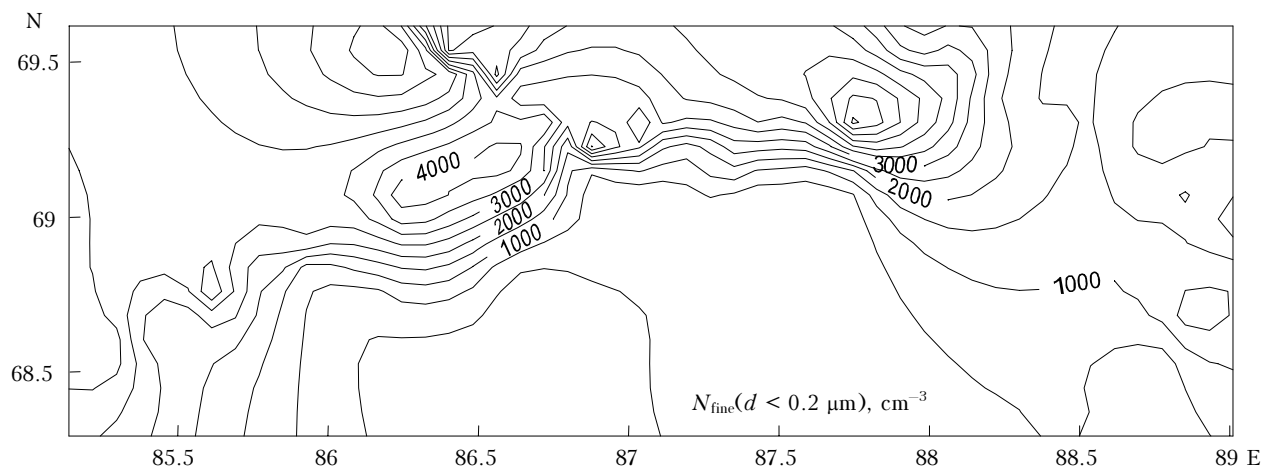**Fig. 6.** Horizontal distribution of fine aerosol along the plume at the sampling height.

Table 1. Concentration (μg/m³) of aerosol-chemical components in the first zone and their fluxes to the underlying surface

Chemical component	Concentration		Difference	Mass, kg	Flux, g/(km²·s)	Flux, t/(km²·year)
	initial	final				
SO_4^{2-}	6.82	0.41	6.41	7692	1.28	40.37
Cl^-	4.76	0.69	4.07	4884	0.81	25.54
Ca	6.50	5.31	1.19	1428	0.24	7.57
NO_3^-	2.30	0.57	1.73	2076	0.35	11.04
NH_4^+	3.18	2.49	0.69	828	0.14	4.42
Fe	0.28	0.17	0.11	132	0.022	0.69
Na^+	1.02	0.94	0.08	96	0.016	0.50
Cu	0.59	0.11	0.48	576	0.096	3.03
Al	0.71	0.45	0.26	312	0.052	1.64
K^+	0.35	0.17	0.18	216	0.036	1.14
F^-	0.23	0.17	0.06	72	0.012	0.38
Br^-	0.64	0.01	0.63	756	0.126	3.97
Mg	0.04	0.007	0.033	40	0.007	0.22
Cr	0.019	0.002	0.017	20	0.003	0.09

Table 2. Concentration (μg/m³) of aerosol-chemical components in the second zone and their fluxes to the underlying surface

Chemical component	Concentration		Difference	Mass, kg	Flux, g/(km²·s)	Flux, t/(km²·year)
	initial	final				
SO_4^{2-}	13.83	7.18	6.65	31920	2.66	83.89
Cl^-	10.20	5.59	4.67	22416	1.87	58.90
Ca	5.40	2.69	2.71	13008	1.08	34.18
NO_3^-	4.09	1.31	2.78	13344	1.11	35.07
NH_4^+	0.97	0.07	0.90	4320	0.36	11.35
Fe	2.51	0.82	1.69	9112	0.68	21.32
Na^+	1.03	0.43	0.60	2880	0.24	7.57
Cu	2.25	0.24	2.01	9648	0.80	25.35
Al	0.70	0.19	0.51	2448	0.20	6.43
K^+	0.27	0.24	0.03	144	0.012	0.38
Br^-	0.16	0.01	0.15	720	0.06	1.89
Mg	0.03	0.001	0.029	139	0.012	0.36
Cr	0.039	0.022	0.017	82	0.007	0.21
Pb	0.07	0.02	0.05	240	0.02	0.63

Table 3. Ratios between the component fluxes in the plume

Chemical component	I zone	II zone		
	summer	summer	winter	winter/summer
SO_4^{2-}	40.37	83.89	281.85	3.4
Cl^-	25.54	58.90	60.71	1.0
Ca	7.57	34.18	843.59	24.7
NO_3^-	11.04	35.07	23.98	0.7
NH_4^+	4.42	11.35	—	—
Fe	0.69	21.32	—	—
Na^+	0.50	7.57	—	—
Cu	3.03	25.35	10.89	0.4
Al	1.64	6.43	735.70	114
K^+	1.14	0.38	—	—
F^-	0.38		—	—
Br^-	3.97	1.89	—	—
Mg	0.22	0.36	—	—
Cr	0.09	0.21	53.57	255
Pb	—	0.63	17.56	27.8

Conclusion

Measurement results on the aerosol composition of emissions from the main Norilsk plants are as follows.

Sulfates dominate in emissions from nickel production plant, next goes silicon, potassium, sodium, ammonia, and lead as secondary admixtures.

In the emissions from copper production plant, sulfates are also at the first place followed by chlorine, calcium, ammonia, nitrates, and sodium. Lead, chromium, molybdenum, and such, less common element, as barium can be referred to the group of secondary elements.

Though sulfates dominate in emissions from "Nadezhda" industrial complex, their contribution is

evidently lower. The fractions of chlorine and calcium increase. Ammonia, nitrates, aluminum, silicon, sodium, iron, and copper are present in noticeable amounts.

Dropping out of aerosol from the plume occurs in two parts of the plume. First, this occurs in the initial one and then in the part, which is quite distant from a source. Of course, locations of these plume sections relative to the source will vary depending on both the technology used and atmospheric conditions. Thus, the second deposition wave in our experiments began at the distance of 60 km from the source in winter and at about 100 km in summer.

Assessments of the deposition flux show that the fluxes slightly differ by anthropogenic elements in winter and summer except for lead. Differences by tens and hundreds times in contents of the terrigenous elements have been revealed.

Acknowledgments

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