Complex assessment of the conditions of the air basin over Norilsk industrial region.
Part 5. Impurities in the atmospheric boundary layer.
The correspondence of air composition to hygienic norms.
Recommendations

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This paper completes a thematic series of papers. It describes the results obtained in the course of surface measurements using the ground mobile and stationary complexes similar to that mounted at the aircraft—laboratory. The interconnection between different compounds detected in the air of Norilsk was analyzed, and the clusters of the compounds interconnection were determined. A comparison between the detected concentrations and the hygienic norms was made. Recommendations on the improvement of air quality in city were worked out.

Introduction

In addition to the airborne measurements, in the course of both experiments, the impurity concentrations in the atmospheric boundary layer of Norilsk were measured. The instrumentation was similar to that mounted at the AN-30 "Optik-E" aircraft—laboratory. One complex of instruments was movable and measured sub-plume concentrations when traveling by the city streets; the second one was stationary (it was located on the forth floor of the hotel "Norilsk" and operated during 24 hours).

There are three plants in the measurement region of Large Norilsk polluting the city (Fig. 1). It was assumed to measure the gas and aerosol composition of the atmospheric boundary layer at some points in the vicinity of each plant: in windward and leeward points close to the plant, and at one or several points
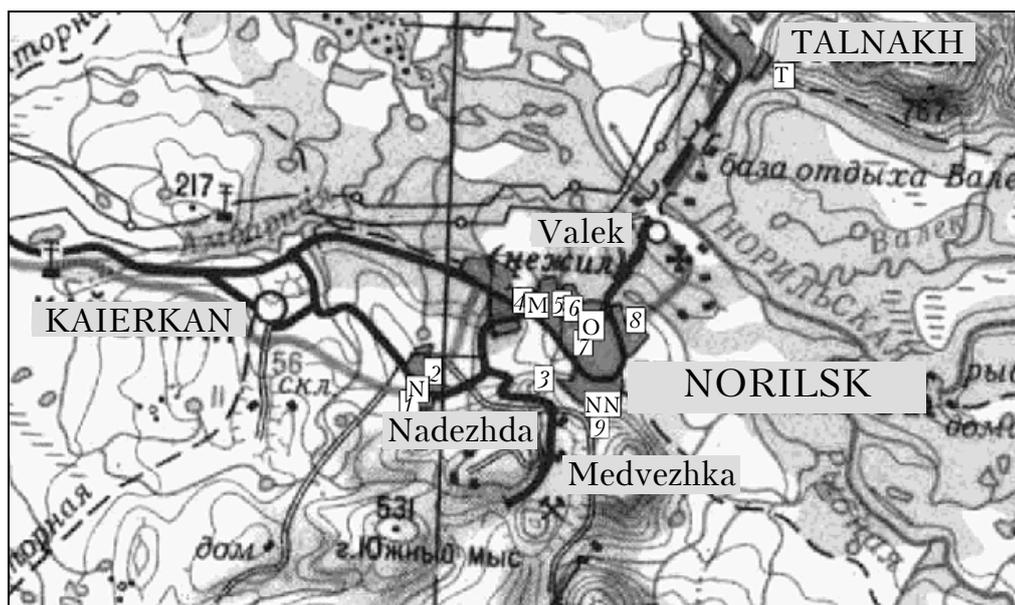
Fig. 1. Measurement map of 2004 with marked measurement sites: the hotel (O); mobile points in the city (*1, 4, 8*); windward or background points (T); points under plant chimneys ("Nadezhda"plant (N), copper plant (M), and nickel plant (NN)); leeward (under-plume) points (*2, 3, 5, 6, 7, 9*).

at a distance between 1 and 5 km. In spite of the poor conditions in the period of measurements: low cloudiness hiding the industrial plumes from the observers, unstable wind direction, and intermittent rain or snow (giving no way to collect all filters for analysis at all points), as well as a complicated landscape of the region, with poor roads, the equipment of the instrumentation complex with a self-contained supply source has made it possible to perform completely the planned amount of the work.

In this paper we consider the results obtained in housing and background districts.

Ground air composition in Norilsk

Most measurements were conducted at the stationary station. As a result of the processing of the data series, 208 significant values were obtained, presenting the hourly averaged data (Fig. 2).

Taking into account the location of the hotel and small dimensions of the housing estate of Norilsk, the stationary station may be considered as a representative point for the housing estate of the city. Diagrams of daily behavior of the measured parameters are presented in Fig. 2.
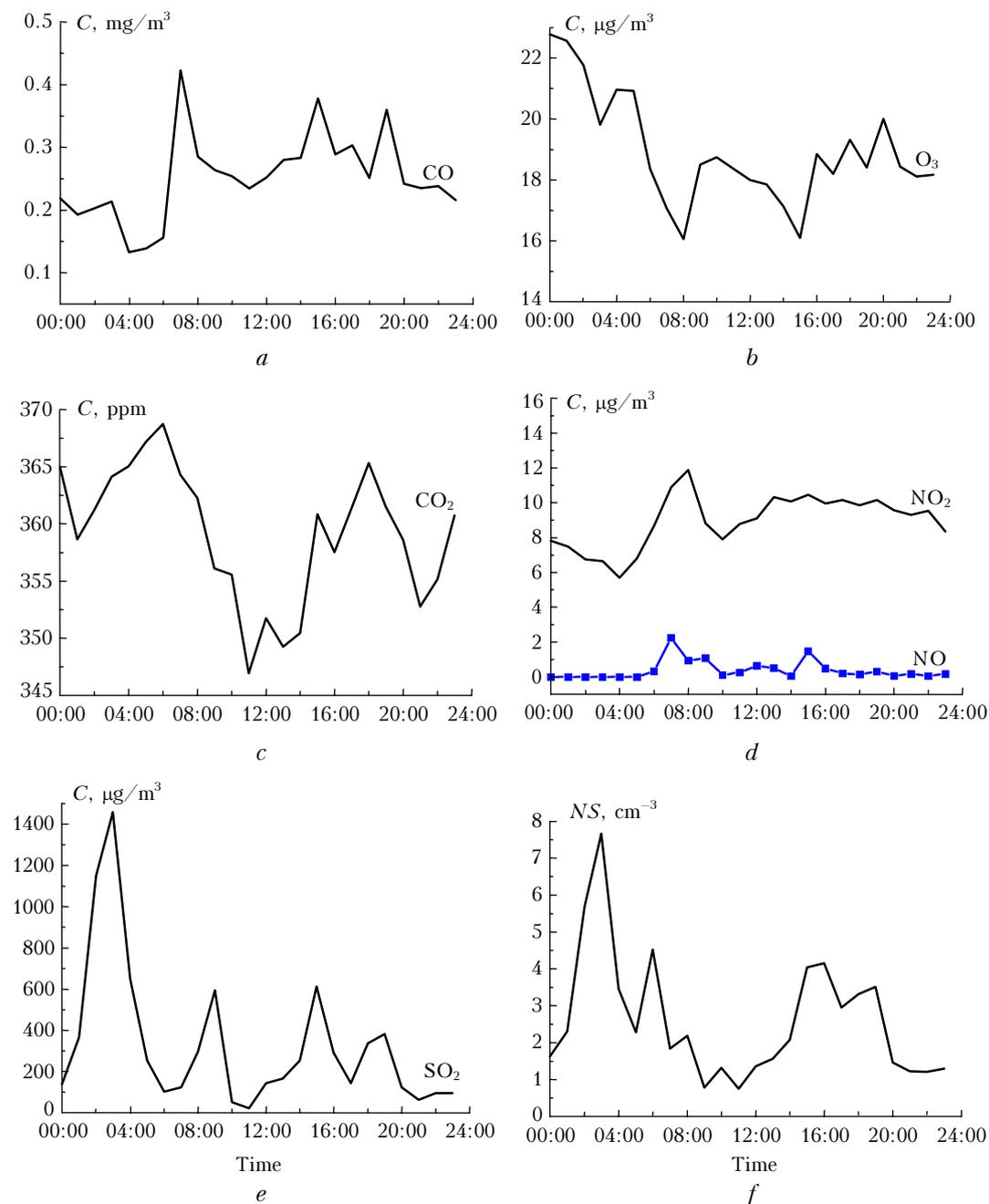
Fig. 2. Daily variation of parameters measured at the stationary station: gases (a–e); the aerosol number density (f).

Figures 2*c*, *d*, and *e* show a growth of industrial emissions in evening and morning hours, which is possibly connected with the technology of the pollution emission in the atmosphere by plants. Peaks and general elevation of the curve at daytime in Figs. 2*a* and *d* can be associated with the transport activity. Also, Fig. 2*b* shows that increasing or decreasing the concentration of emitted impurities is followed by the decay or growth of ozone concentration. During this period in the vicinity of Norilsk the ground inversion was lacking, the atmosphere has been cleanning intensively, and values of exhaust gases of motor transport in contrast to SO_2 industrial emissions did not exceed the available at the moment maximum permissible concentrations. Therefore, we can draw

the conclusion that this clear interconnection was due to the density of city buildings, resulting in stagnation of atmospheric air in the yards, and can be considered as a local phenomenon.

Figure 3 shows the time dependence of parameters measured at the Norilsk hotel point.

The NO_x concentration decrease during August, 7—8, (rest-days) is seen. The subsequent its growth is connected not only with the beginning of the working week, but also with the change of the basic air transfer direction from the northern to western, resulting in a greater effect of exhaust gases of the transport on the air pollution in this city. This once again shows the locality of such pollutions within the city boundaries.
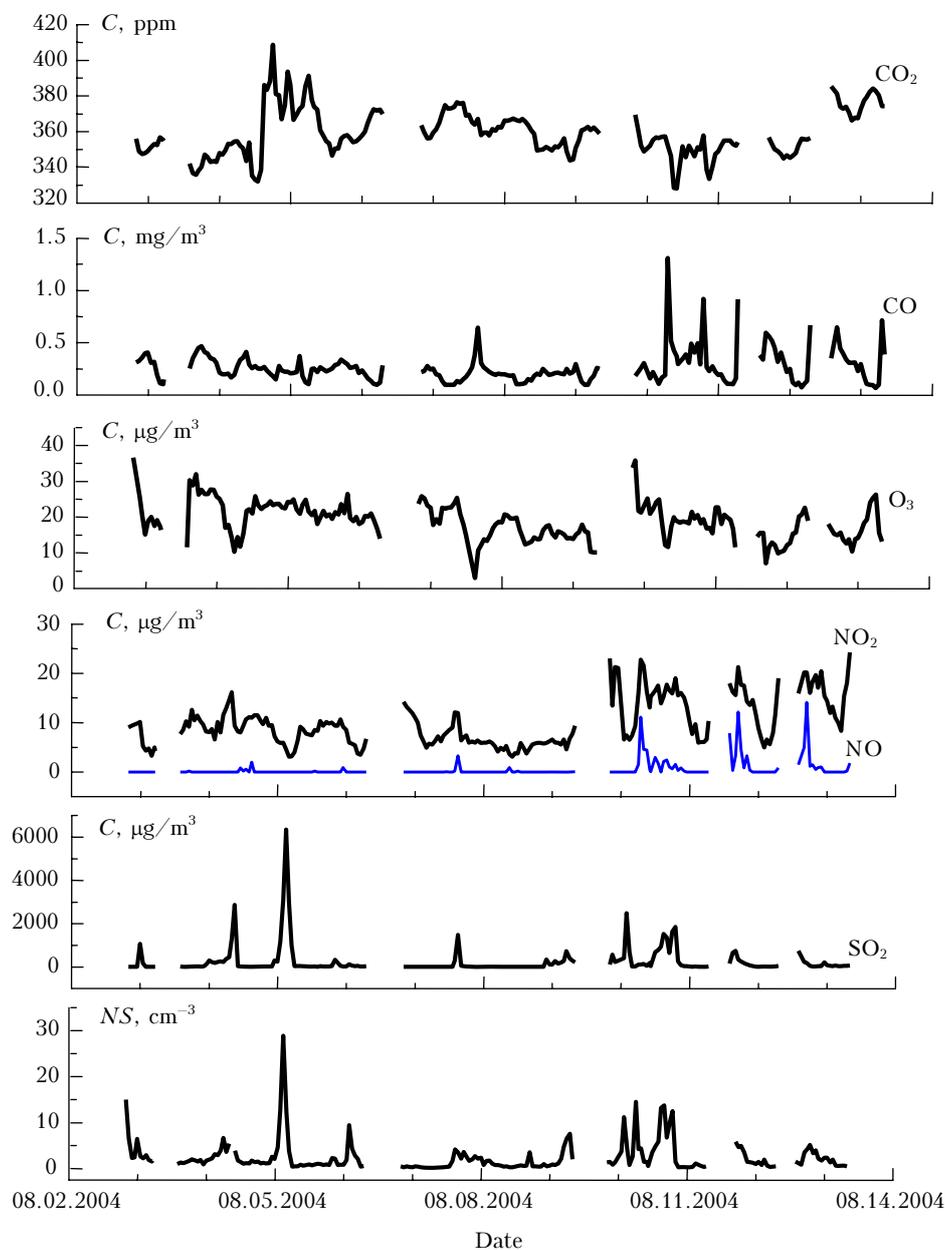
Fig. 3. Time variation of parameters measured at the stationary station.

When considering the data on the aerosol chemical composition for winter and summer periods in the vicinity of Norilsk, significant differences for individual groups of elements are seen, as well as in their percentage; however, there can be separated out a group of elements, the presence and amount of which do not depend on the season change.

Table 1 shows a considerable content of such elements as Ca, Fe and Si, Na^+ (excluding the background samples) in all samples of 2002. In addition, at the measurement points subjected to the effect of deposition from industrial plant plumes, the elements Al, SO_4^{2-}, Cl^-, NO_3^-, and K^+ are seen.

Table 1. Aerosol chemical composition ($\mu g/m^3$)
in the ground layer, November, 2002

Chemical substance	Place of sampling					
	CTB*, background, 11.02.02	Road to city disposal area, background	Communication center of railway, plume	Control room **CP/part of NN plume***	CTB, background, 11.08.02	CTB, plume
Ca	61.010	12.960	70.645	73.232	19.163	65.061
Fe	24.510	17.539	13.798	19.290	2.947	69.214
Al	0.900	1.744	7.200	2.010	3.998	69.214
Mg	0.000	0.000	0.230	0.176	0.254	69.214
SO_4^{2-}	0.660	0.443	38.670	3.179	10.028	46.603
Cl^-	0.940	0.273	6.894	20.616	1.554	47.985
Si	3.080	3.113	13.332	7.744	0.659	18.508
NO_3^-	0.180	0.420	0.582	1.365	1.130	4.773
Na^+	0.050	0.092	1.207	0.481	0.743	2.292
K^+	0.020	0.031	0.483	0.330	0.065	1.046
Ni	0.110	0.075	0.206	0.136	0.138	0.015
Cu	0.000	0.000	0.011	0.000	0.550	0.031
Ti	0.030	0.000	0.000	0.070	0.004	0.055
Mn	0.020	0.002	0.018	0.006	0.025	0.054
Cr	0.040	0.039	0.047	0.034	0.000	0.010
Pb	0.000	0.000	0.000	0.000	0.058	0.001
B	0.000	0.000	0.032	0.023	0.000	0.011

* CTB is the Central Transport Block; ** CP is the Cement works, *** NN is the Nickel Plant.

As to the data on the aerosol chemical composition in 2004 (Table 2), a considerable content in all samples of Ni, Pb, Na^+ (excluding the background samples) is observed. At the measurement points experienced depositions from industrial plumes, the additional elements NO_3^-, NH_4^+, SO_4^{2-}, Fe, Si, and K^+ are also observed.

The above data show that Na^+ at both seasons has a rather wide propagation area in the region of research, however, its concentration at a substantial distance from the emission sources decreases by orders of magnitude. The elements NO_3^-, SO_4^{2-}, K^+ behave similarly, but their propagation area is smaller and their high values are observed only in the region of impact of industrial plumes. For the period from winter 2002 to summer 2004, a change in the behavior

of Fe and Si is observed. They stopped their accumulation in the urban atmosphere and were detected only in the area of industrial emissions.

Table 2. Aerosol chemical composition ($\mu g/m^3$)
in the ground layer, August, 2004

Chemical substance	Place of sampling						
	Plume of Norilsk Nickel (NN)	Plume of Gubchikha (9)	Copper plant, windward (4)	Copper plant, leeward (5)	Metallurgists square (6)	Talnakh, background (T)	Norilsk, background (8)
SO_4^{2-}	87.200	20.580	9.910	36.130	4.200	2.310	2.950
Cl^-	2.450	5.420	3.480	3.250	2.280	1.220	1.240
Ca	2.594	2.607	0.253	0.368	0.633	0.124	0.125
NH_4^+	7.230	9.340	8.100	6.790	6.200	3.820	5.030
Al	3.896	0.161	0.046	0.018	0.273	0.088	
NO_3^-	1.950	3.600	2.770	2.830	3.680	1.470	1.620
Si	33.282	0.163			0.084	0.009	
Na^+	5.998	2.697	2.795	2.933	0.626	0.259	0.384
Fe	1.611	0.579	0.275	0.231	0.628	0.128	0.287
Cu	0.911	0.212	0.051	0.505	0.079	0.014	0.005
K^+	9.203	0.624	0.737	0.922	0.455	0.231	0.373
Ni	1.788	0.048	0.016	0.016	0.038	0.012	0.008
F^-	0.150	0.199	0.149	0.105			
Zn	0.125	0.048	0.007	0.015	0.030	0.002	
Mg	0.256	0.042	0.002	0.004	0.006	0.000	
Ba	0.010	0.023	0.006	0.020	0.012		0.009
Pb	1.433	0.003	0.006	0.007	0.004	0.004	0.008
Ti	0.026	0.011	0.002	0.002	0.006	0.000	
Cr	0.023	0.029	0.020	0.015	0.030	0.018	0.017
Mn	0.043	0.004	0.001	0.001	0.002	0.000	0.001
Mo	0.003	0.023	0.012	0.007	0.001	0.100	0.007
Ag	0.000	0.003	0.001	0.001	0.003	0.001	0.000
Co	0.035	0.004	0.004	0.003	0.002		0.014
H^+	0.001	0.001	0.001	0.001	0.000	0.000	0.000

N o t e . In brackets measurement points are numbered (Fig.1).

All the above facts and the decrease of aerosol specific content by summer 2004 indicate that in the summer period in the region of Norilsk the atmosphere was more clear. The fact that in 2004 a total absence of Ca was detected is difficult to explain.

The relative chemical composition of air in Talnakh and in the periphery of Norilsk in the background conditions almost coincide (Fig. 4) both in the total mass concentration of inorganic components (the difference is in the limits of the quantitative analysis error) and in the main inorganic matrix. The difference is only in microelement composition: their nomenclature and aerosol content slightly differ that, probably, is connected with the peculiarities of productions in the above-mentioned points.

The correspondence of air composition to hygienic standards

Table 3 shows daily mean (dm) and maximal single (ms) values of gas components and the corresponding to them hygienic standards (MPC).[1]
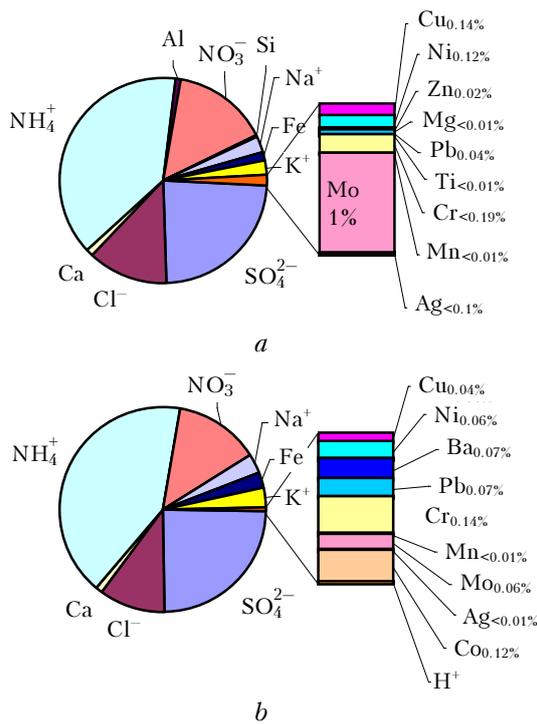
Fig. 4. Mass distribution of chemical elements and ions in the samples of background aerosol; at the measurement point in the vicinity of Talnakh the content of inorganic suspension is 9.8 $\mu g/m^3$ (*a*); at the measurement point in the suburb of Norilsk the content of inorganic suspension is 12.1 $\mu g/m^3$ (*b*).

It follows from Table 3 that in the period under study the excess (20-fold) was mainly observed for sulfur dioxide, which is explained by its no-utilization in the industrial emissions.

Table 3. Maximal and daily mean values of measured gases at the Norilsk hotel

Measured gas	CO_2, mg/m^3	CO, mg/m^3	O_3, $\mu g/m^3$	SO_2, $\mu g/m^3$	NO_2, $\mu g/m^3$	NO, $\mu g/m^3$
Daily mean values	408.5	1.3	36.6	635.7	24.3	14.1
Maximal values	457.0	6.6	127.0	>10000	47.0	112.0
MPC_{dm}		3	30	50	40	60
MPC_{ms}		5	160	500	85	400
MPC_{dm} excess		0.4	1.2	12.7	0.6	0.2
MPC_{ms} excess		1.3	0.8	20.0	0.6	0.3

There was a small excess of carbon monoxide and ozone relative to MPC_{ms} and MPC_{dm}, respectively. Concentrations of other components at that period were below MPC.

Thus, summarizing all results, the following conclusion can be drawn. The air quality in the city in the absence of emission plumes can be considered satisfactory. Contrary to many cities, the transport exhaust pollution in the atmosphere of Norilsk is much less. However, the city and its suburbs are under periodical impacts of the plant emission plumes. Taking into account the aeration peculiarities of the region,

this leads to the increased pollution concentration in the city and adjacent populated areas. Moreover, the data of sub-plume and airborne measurements have shown that Norilsk itself and surrounding settlements are located within the limits of the first zone of fall-out of aerosol from industrial plumes. Therefore, the only way for enterprises to improve the quality of the city air is the reconstruction of air cleaning equipment despite large financial expenses.

Analysis of impurity behavior in the ground air

To better understand interrelations between the measured parameters in the ground atmospheric air, the correlation between eight data series was investigated: six gases, the aerosol number density, and time of day (Table 4).

Table 4. Correlations between data series

	Time	CO_2	CO	O_3	SO_2	NO_2	NO	*NS*
Time	1	−0.183	0.303	0.033	−0.096	0.384	0.114	−0.027
CO_2		1	−0.234	0.056	0.041	−0.085	−0.009	0.004
CO			1	−0.204	0.190	0.609	0.540	0.248
O_3				1	0.001	−0.113	−0.272	0.017
SO_2					1	0.032	0.047	0.802
NO_2						1	0.516	0.136
NO							1	0.163
NS								1

For data series containing no less than 200 values, the correlation coefficients (Table 5) are significant.

Table 5. Significant correlation coefficients for different probabilities of a series containing 200 values

q	0.95	0.975	0.995	0.9995
K	0.1161	0.1381	0.1809	0.2298

The correlation matrix shows two groups of series connected to one another.

First, the connection of the aerosol number density and SO_2, as well as their connection with CO are well seen. This is simply explained by the fact that SO_2 is the main element in the Norilsk plant emissions. At the same time, when the plume passes through the measurement point, the aerosol number density increases sharply. CO is generated during the combustion, which explains its abundance in the plumes of copper and nickel plants crossing the measurement points.

Second, the interrelation of NO_2, NO, CO with time series is well seen. Daily behavior of these gases is clearly characterized by daytime peaks and night minima. It can be assumed with assurance that the main sources of these gas components are exhausts by transport. Table 4 shows that daily behavior of O_3 is lacking and there is a negative correlation with CO and NO.

The correlation matrix is constructed (Table 6) based on the data series of concentration measurements

of some trace gases, ion-element, and dispersion aerosol compositions and meteorological parameters. The data were obtained from July, 31 to August, 14, 2004, with the use of the AN-30 "Optik-E" aircraft–laboratory and the ground-based mobile station in the region of Large Norilsk and adjacent region in the atmospheric layer between 0 and 5500 m. The matrix included 50 parameters and about 48 non-zero integral measurements or group averaging over each parameter.

Table 6

	SO_4^{2-}	Cl^-	Ca	NH_4^+	Al	NO_3^-	Si	Na^+	Fe	Cu	K^+	Ni
$N_{>DL} =$	43	48	42	45	42	48	39	48	43	47	47	40
SO_4^{2-}	1.0000	0.0168	−0.0411	0.5552	0.1137	0.2880	0.8262	0.8311	0.1245	0.0898	0.9310	0.7278
Cl^-		1.0000	0.5261	−0.0885	0.3827	0.6362	−0.0169	0.3110	0.7368	0.6163	−0.0408	0.0208
Ca			1.0000	−0.0972	0.3681	0.2762	0.0213	0.1462	0.5427	0.5809	−0.0328	0.0056
NH_4^+				1.0000	−0.1614	0.4049	0.2493	0.6006	−0.1128	−0.2325	0.4429	0.2277
Al					1.0000	0.1608	0.4078	0.1705	0.4024	0.6288	0.1652	0.1807
NO_3^-						1.0000	0.0449	0.5172	0.4207	0.3802	0.1502	0.0865
Si							1.0000	0.6340	0.2034	0.1720	0.9223	0.7753
Na^+								1.0000	0.4251	0.2591	0.7485	0.5734
Fe									1.0000	0.6595	0.0930	0.1381
Cu										1.0000	0.0756	0.0993
K^+											1.0000	0.8137

	F^-	Zn	Mg	Ba	Pb	Br^-	Ti	Cr	Mn	Mo	Ag	Co
$N_{>DL} =$	22	39	41	42	33	9	40	35	35	30	32	34
SO_4^{2-}	0.1746	−0.0625	0.2440	−0.1445	0.8539	−0.0133	−0.0680	0.0827	0.2638	−0.0435	−0.0626	0.2830
Cl^-	0.4474	0.2267	0.5651	0.2608	0.0509	0.5576	0.2827	0.6921	0.5582	−0.0839	0.5008	−0.0505
Ca	0.2333	−0.1733	0.4762	0.3308	0.1169	0.3123	0.3833	0.5625	0.5802	−0.0189	0.2360	0.0840
NH_4^+	0.3467	−0.2305	−0.0526	−0.2496	0.2559	−0.0301	−0.2035	0.0591	−0.0993	0.1526	−0.1469	0.1856
Al	0.1041	0.2173	0.3704	0.1968	0.3081	0.0310	0.5015	0.2409	0.7023	−0.0585	0.3033	−0.0430
NO_3^-	0.2307	0.0503	0.2393	0.0962	0.1003	0.2755	−0.0424	0.5071	0.2240	0.1055	0.0865	−0.1027
Si	0.0487	0.0242	0.3591	−0.1043	0.9372	−0.0406	0.1620	0.0443	0.4803	−0.0839	0.0282	0.3053
Na^+	0.4792	−0.0391	0.4733	0.0983	0.6728	0.2257	0.0877	0.3774	0.3756	−0.0674	0.1329	0.1791
Fe	0.4011	−0.0289	0.8504	0.3062	0.2308	0.4636	0.5823	0.8164	0.7554	−0.1838	0.4406	−0.0331
Cu	0.2769	0.1212	0.4139	0.2639	0.2490	0.1199	0.4530	0.6003	0.6505	−0.0509	0.3000	−0.1406
K^+	0.1256	−0.0287	0.2228	−0.1362	0.9367	−0.0466	−0.0111	0.0469	0.2645	−0.0393	−0.0877	0.3447
Ni	0.0720	−0.0257	0.2253	−0.1194	0.7890	−0.0158	0.0188	0.0569	0.2688	−0.1125	−0.0631	0.2342
F^-	1.0000	−0.0107	0.3680	0.1831	0.0582	0.4174	0.3144	0.3682	0.2292	−0.1391	0.5649	0.1608
Zn		1.0000	0.0716	0.0790	−0.0169	0.0227	0.0003	−0.1908	0.0158	−0.0725	0.1215	−0.0370
Mg			1.0000	0.3729	0.3751	0.4641	0.5286	0.5561	0.7565	−0.1934	0.4260	0.1728
Ba				1.0000	−0.0517	0.0756	0.2650	0.2086	0.1770	−0.0678	0.1941	0.1816
Pb					1.0000	−0.0156	0.0593	0.1388	0.4888	−0.0774	−0.0528	0.3032
Br^-						1.0000	0.0772	0.4446	0.2425	−0.1605	0.3482	0.1532
Ti							1.0000	0.4405	0.5227	−0.1130	0.3272	−0.0278
Cr								1.0000	0.5784	−0.0614	0.1822	−0.1513
Mn									1.0000	−0.1762	0.3596	−0.0346
Mo										1.0000	−0.1078	0.1000
Ag											1.0000	0.0199

	Be	V	H^+	Sum	Ions	Els	C_v	H, m	t, °C	R, %	O_3	SO_2	aero 0.4−10
1	2	3	4	5	6	7	8	9	10	11	12	13	14
$N_{>DL} =$	32	27	48	48	48	48	48	48	48	48	48	48	48
SO_4^{2-}	−0.0601	−0.0804	0.0490	0.8405	0.8972	0.4979	0.9268	−0.3063	0.2168	0.3450	−0.4657	0.9064	0.6098
Cl^-	0.6858	0.4265	0.5104	0.4894	0.4333	0.4695	−0.0765	−0.1463	0.2458	−0.0286	0.1380	−0.1062	−0.1561
Ca	0.5069	0.3402	0.6617	0.3786	0.1819	0.6721	−0.0639	−0.2817	0.3570	0.0121	0.1845	−0.1077	−0.1020
NH_4^+	−0.1423	−0.2068	0.1513	0.4258	0.5672	0.0253	0.3901	−0.5239	0.4077	0.6254	−0.5068	0.5932	0.0360
Al	0.3536	0.2700	0.1332	0.4311	0.2325	0.7140	0.1731	0.1489	−0.1326	−0.1392	−0.0149	0.0679	0.2546
NO_3^-	0.2399	0.2086	0.4118	0.5338	0.5908	0.2739	0.1012	−0.4577	0.4273	0.4630	−0.2245	0.2759	−0.2171
Si	−0.0171	0.0461	−0.0574	0.7696	0.6984	0.7038	0.9304	−0.0542	0.0044	0.0558	−0.3824	0.7492	0.7484
Na^+	0.2332	0.2234	0.2876	0.8672	0.9103	0.5446	0.7039	−0.4224	0.3854	0.3499	−0.3681	0.7059	0.3490
Fe	0.6999	0.6383	0.4682	0.5335	0.4084	0.6405	0.0671	−0.1766	0.3233	−0.1439	0.1375	0.0118	−0.0248
Cu	0.5304	0.2958	0.5616	0.4676	0.3083	0.6616	0.0662	−0.0180	0.1185	−0.1383	0.2087	−0.0067	0.0914
K^+	−0.0458	−0.0619	0.0350	0.7966	0.8050	0.5632	0.9910	−0.2173	0.1568	0.2399	−0.3934	0.8680	0.6973
Ni	0.0397	−0.0165	0.0158	0.6543	0.6337	0.5180	0.8079	−0.1900	0.1745	0.1610	−0.2376	0.6525	0.5444
F^-	0.5659	0.3017	0.5951	0.3729	0.3901	0.2370	0.0791	−0.2879	0.3802	0.0532	0.1843	0.0898	−0.0725

Table 6 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Zn	0.0588	0.0607	−0.1656	0.0094	0.0113	0.0030	−0.0102	0.4275	−0.4177	−0.3998	0.0429	−0.0778	0.1365
Mg	0.5924	0.6273	0.2593	0.5602	0.4352	0.6597	0.2185	−0.1328	0.2241	−0.1958	0.0002	0.1060	0.1767
Ba	0.3929	0.4934	0.2134	0.0547	−0.0301	0.2107	−0.1257	−0.1543	0.1922	−0.0488	0.1057	−0.1994	−0.1253
Pb	−0.0058	−0.0361	0.0147	0.8077	0.7505	0.7034	0.9465	−0.1609	0.1051	0.1286	−0.3709	0.7575	0.7543
Br⁻	0.4023	0.2552	0.2891	0.2448	0.2311	0.2058	−0.0667	−0.1325	0.1658	0.0395	0.1542	−0.0793	−0.0883
Ti	0.6681	0.6639	0.2778	0.2056	0.0369	0.4896	−0.0188	0.1026	0.0506	−0.3552	0.1822	−0.0817	0.0205
Cr	0.5977	0.5271	0.5057	0.4609	0.3834	0.4917	−0.0018	−0.2654	0.4007	−0.0008	0.1309	0.0188	−0.1202
Mn	0.4329	0.4507	0.2061	0.6258	0.4342	0.8416	0.2704	−0.0292	0.1052	−0.2166	−0.0861	0.1437	0.3043
Mo	−0.1641	−0.1604	0.0343	−0.0695	−0.0445	−0.1008	−0.0518	−0.1344	0.1289	0.1088	−0.1224	−0.0668	−0.1453
Ag	0.5282	0.2871	0.3216	0.2012	0.1377	0.2745	−0.0883	0.0834	0.0600	−0.2728	0.1820	−0.1514	−0.0822
Co	0.1089	−0.0859	0.1578	0.2396	0.2299	0.1941	0.3578	−0.1878	0.1438	0.1309	−0.1503	0.2388	0.3002
Be	1.0000	0.5534	0.5703	0.3287	0.2272	0.4438	−0.0767	−0.1116	0.2912	−0.1741	0.2800	−0.1260	−0.1417
V		1.0000	0.2492	0.2056	0.1024	0.3576	−0.0907	−0.0522	0.1809	−0.2798	0.2027	−0.1344	−0.1077
H⁺			1.0000	0.3629	0.2925	0.4060	−0.0265	−0.4545	0.5378	0.2109	0.3298	0.0048	−0.2510
Sum				1.0000	0.9575	0.8138	0.7706	−0.3514	0.3313	0.2626	−0.3248	0.7135	0.4684
Ions					1.0000	0.6116	0.7756	−0.4014	0.3548	0.3713	−0.3933	0.7782	0.4216
Els						1.0000	0.5510	−0.1549	0.1938	−0.0279	−0.0986	0.3892	0.4354
C_v							1.0000	−0.1748	0.1136	0.2097	−0.4125	0.8773	0.7429
H, m								1.0000	−0.9141	−0.7861	0.2162	−0.2983	0.3738
t, °C									1.0000	0.6001	0.0413	0.1992	−0.4302
R, %										1.0000	−0.3968	0.4222	−0.2130
O_3											1.0000	−0.5392	−0.2880
SO_2												1.0000	0.5589

	aero>0.4	aero>0.5	aero>0.6	aero>0.7	aero>0.8	aero>0.9	aero>1.0	aero>1.5	aero>2	aero>4	aero>7	aero>10	CO_2
$N_{>DL}$ =	48	48	48	48	46	42	45	34	36	27	7	8	48
SO_4^{2-}	0.4334	0.8760	0.8273	0.9408	0.9597	0.9479	0.8193	0.8014	0.7843	0.9051	0.8894	0.1579	0.3960
Cl^-	−0.1602	−0.1213	−0.1162	−0.0753	−0.0653	−0.0826	−0.0291	−0.0930	−0.0892	−0.0809	−0.0620	−0.0406	0.0355
Ca	−0.1011	−0.0794	−0.0335	−0.0492	−0.0726	−0.1121	−0.0665	−0.1552	−0.1371	−0.0421	−0.0456	−0.0199	0.1089
NH_4^+	−0.1147	0.3331	0.3166	0.4596	0.5205	0.5731	0.5801	0.6035	0.5728	0.3966	0.3310	0.0646	0.6988
Al	0.2661	0.1921	0.1781	0.1463	0.1224	0.0939	0.0414	0.0118	0.0090	0.1716	0.1876	0.0120	−0.1809
NO_3^-	−0.3139	0.0154	−0.0085	0.1311	0.1959	0.2515	0.2807	0.3231	0.2850	0.0803	0.0757	−0.0849	0.5168
Si	0.6287	0.8927	0.8311	0.8844	0.8626	0.8002	0.5938	0.5424	0.5064	0.9307	0.9393	0.1450	0.1048
Na^+	0.1943	0.6192	0.5597	0.7012	0.7353	0.7319	0.6279	0.6275	0.6178	0.6990	0.6774	0.0512	0.4656
Fe	−0.0417	0.0187	0.0105	0.0496	0.0564	0.0287	0.0519	−0.0204	−0.0189	0.0738	0.0799	0.0429	0.0626
Cu	0.0964	0.0673	0.0886	0.0600	0.0353	0.0015	0.0058	−0.0454	−0.0204	0.0693	0.0758	0.0357	−0.1012
K^+	0.5374	0.9327	0.8781	0.9698	0.9616	0.9115	0.7100	0.6679	0.6253	0.9899	0.9886	0.1251	0.2928
Ni	0.4191	0.7400	0.6892	0.7666	0.7525	0.6975	0.5048	0.4678	0.4310	0.8094	0.8238	0.0770	0.2018
F^-	−0.1121	0.0138	0.0088	0.0924	0.1140	0.0872	0.1767	0.0597	0.0979	0.1110	0.0682	0.0590	0.1921
Zn	0.1896	−0.0006	−0.0593	−0.0599	−0.0599	−0.0651	−0.1178	−0.0908	−0.1000	−0.0283	0.0101	−0.1083	−0.4035
Mg	0.1621	0.1834	0.1512	0.1775	0.1757	0.1374	0.1245	0.0444	0.0508	0.2203	0.2282	0.2032	0.0232
Ba	−0.0922	−0.1700	−0.1912	−0.1797	−0.1766	−0.1908	−0.1306	−0.1847	−0.1431	−0.1164	−0.1170	0.1641	−0.0093
Pb	0.6274	0.9151	0.8743	0.9098	0.8787	0.8109	0.6126	0.5454	0.5114	0.9472	0.9528	0.2450	0.1840
Br⁻	−0.0853	−0.0858	−0.0643	−0.0464	−0.0392	−0.0698	−0.0054	−0.1031	−0.1029	−0.0446	−0.0585	0.0026	0.0419
Ti	0.0462	−0.0336	−0.0599	−0.0522	−0.0556	−0.0726	−0.0880	−0.0997	−0.0989	−0.0214	−0.0036	0.0492	−0.1732
Cr	−0.1516	−0.0302	0.0031	0.0295	0.0307	0.0154	0.0370	−0.0088	−0.0308	0.0139	0.0050	−0.0090	0.1910
Mn	0.2925	0.2851	0.2868	0.2512	0.2209	0.1794	0.1369	0.0725	0.0702	0.2691	0.2826	0.0947	−0.0515
Mo	−0.1612	−0.0698	−0.0681	−0.0605	−0.0578	−0.0488	−0.0767	−0.0409	−0.0362	−0.0409	−0.0466	−0.0251	0.2266
Ag	−0.0593	−0.1257	−0.1446	−0.1197	−0.1081	−0.1186	−0.0110	−0.0921	−0.0535	−0.1032	−0.0812	−0.0672	−0.1613
Co	0.2606	0.3508	0.3282	0.3253	0.3097	0.2704	0.1833	0.1431	0.1409	0.3754	0.3612	0.2600	0.1257
Be	−0.1359	−0.1222	−0.1318	−0.0951	−0.0915	−0.1102	−0.1060	−0.1284	−0.1309	−0.0841	−0.0549	−0.0009	−0.0152
V	−0.0817	−0.1368	−0.1795	−0.1303	−0.1201	−0.1378	−0.1636	−0.1690	−0.1735	−0.0755	−0.0621	−0.1548	−0.0650
H⁺	−0.2956	−0.1189	−0.0903	0.0012	0.0178	−0.0213	0.0869	−0.0571	−0.0219	0.0191	−0.0224	−0.0300	0.2883
Sum	0.3205	0.7046	0.6670	0.7738	0.7852	0.7546	0.6538	0.5951	0.5766	0.7619	0.7550	0.1114	0.3591
Ions	0.2533	0.7021	0.6597	0.7949	0.8248	0.8161	0.7311	0.6961	0.6763	0.7585	0.7445	0.1090	0.4540
Els	0.3688	0.5182	0.5003	0.5211	0.4920	0.4254	0.3201	0.2297	0.2188	0.5618	0.5709	0.0861	0.0701
C_v	0.5883	0.9552	0.9027	0.9783	0.9682	0.9229	0.7335	0.6935	0.6573	0.9905	0.9906	0.1732	0.2521
H, m	0.5178	0.0099	0.0318	−0.1835	−0.2669	−0.2926	−0.3959	−0.3080	−0.3194	−0.2086	−0.1420	−0.2130	−0.9292
t, °C	−0.5645	−0.0736	−0.0795	0.1240	0.1957	0.2083	0.3300	0.2194	0.2382	0.1442	0.0934	0.1316	0.8191
R, %	−0.3541	0.1005	0.1019	0.2614	0.3395	0.3956	0.5049	0.4711	0.4737	0.2219	0.1475	0.2103	0.8430
O_3	−0.1999	−0.4166	−0.3473	−0.4010	−0.4512	−0.5389	−0.4406	−0.6024	−0.5521	−0.3686	−0.3591	−0.1147	−0.4199
SO_2	0.3766	0.8309	0.7821	0.9051	0.9459	0.9823	0.8768	0.9215	0.8705	0.8424	0.8203	0.0988	0.4677

Table 6 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14
aero 0.4—10	0.9758	0.8894	0.8988	0.7502	0.6634	0.5947	0.3978	0.3825	0.3608	0.7233	0.7418	0.1565	−0.3141
aero >0.4	1.0000	0.7699	0.7898	0.5897	0.4855	0.4088	0.2154	0.2053	0.1897	0.5715	0.5980	0.1350	−0.4830
aero >0.5		1.0000	0.9803	0.9625	0.9210	0.8733	0.6701	0.6552	0.6177	0.9364	0.9415	0.1576	0.0858
aero >0.6			1.0000	0.9417	0.8843	0.8245	0.6665	0.6066	0.5767	0.8896	0.8851	0.1932	0.0527
aero >0.7				1.0000	0.9875	0.9456	0.8021	0.7374	0.7034	0.9682	0.9545	0.1815	0.2764
aero >0.8					1.0000	0.9796	0.8596	0.8091	0.7755	0.9530	0.9336	0.1791	0.3754
aero >0.9						1.0000	0.8882	0.9064	0.8680	0.8891	0.8710	0.1359	0.4451
aero >1.0							1.0000	0.8826	0.8968	0.7050	0.6476	0.2873	0.5101
aero >1.5								1.0000	0.9806	0.6252	0.6016	0.0715	0.5142
aero >2									1.0000	0.5908	0.5560	0.1181	0.4898
aero >4										1.0000	0.9894	0.1886	0.2609
aero >7											1.0000	0.1302	0.2016
aero >10												1.0000	0.1313

The correlation analysis of interrelation of sulfur dioxide, CO_2, ozone, aerosol chemical components, their size distribution, and altitude variation has made it possible to determine the following characteristic groups of gases, elements, and ions in the aerosol composition.

As it was expected, the maximal correlation turned out characteristic for two components dominating in the regional atmosphere due to the specificity of the industrial production in Norilsk. These gases are sulfur dioxide and sulfate anion in the aerosol composition. They form the first group of aerosols correlating with them and to one another, which, evidently, have the same source of origin.

The system of graphs,[2] constructed from the values of the correlation matrix with the confidence limit $q = 0.9995$, this group forms the first cluster of chemical components: the top heptagon with the sulfate-anion in the center (Fig. 5).

High correlation of CO_2 with two components of this cluster — sulfur dioxide and ammonium ion, verifies their joint presence in the industrial emissions of Large Norilsk. The absence in this case of the significant correlation of CO_2 with aerosol elements of this cluster (however, presenting for sulfur dioxide) counts in favor of adsorption of a considerable part of SO_2 molecules on particles of emitted aerosol, since the difference of the diffusion coefficients between gases is much less than between gas molecules and aerosol particles.

Probably, such dry absorption results in the realization of the mechanism of heterogeneous oxidation of SO_2 into SO_3 at the surface of solid aerosols[3] containing oxides of alkali metals, nickel, lead, and silicon, as well as in possible formation of salts of the sulfurous acid and sulfuric acid without participation of water vapor. This conclusion is confirmed both by close to zero correlation of components of this group with the hydrogen ion concentration and high negative correlation with ozone (its depletion near cluster components). Thus, metals of the first cluster are the first contractors of generated sulfites and sulfates. Probably, quartz particles play the role of condensation—coagulation centers.
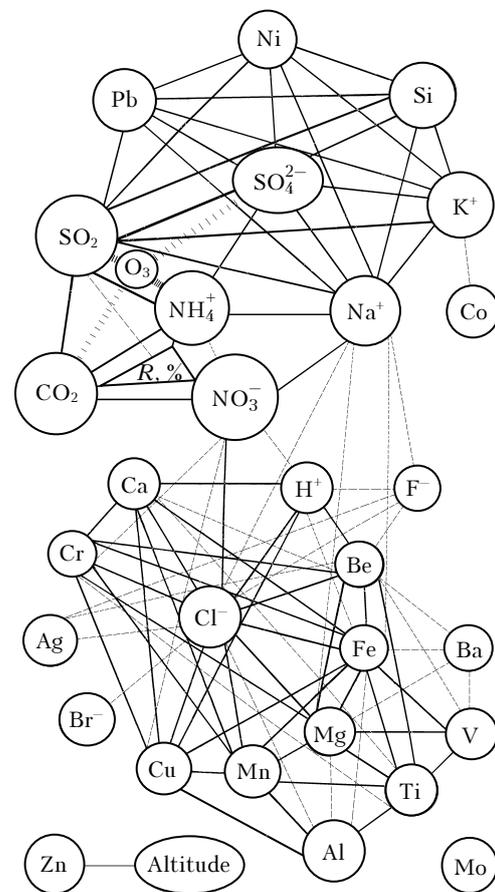
Fig. 5. Graphs of aerosol chemical matrix for the region of Large Norilsk, constructed using the correlation matrix of data for the period of summer measurements (the significance level of solid lines is 0.9995; dashed lines is 0.995−0.975).

Components of the first cluster have the highest correlation coefficients, both with total concentrations of ions and elements separately and with total mass of aerosol components, and overlap the greater part of the number density spectrum (from 0.4−0.5 to 1.5 μm; for lead, potassium, and silicon the second peak in the range of 4−10 μm is observed) determining the volume concentration (C_v) of aerosol of the region as a whole.

The center of the second intercorrelating group of elements is ion of chlorine, which is meant to be of marine origin.[4–6] Sodium and bromine are traditionally attributed to the components of oceanic origin as well. Although there is a correlation with sodium and bromine−ion in our case, its confidence limit q is lower (0.975). Possibly, this is connected with a significant transformation and the processes of fractionation of marine aerosol particles during air transportation in the atmosphere, when, first, they experience deposition of smaller particles of different origin and, second, the chlorine itself is able to participate in the equilibrium transitions accompanied by varying the degree of oxidation, including phase transitions of the type "particle − drop − gas − drop − particle".

As particles become greater, their sedimentation stability decreases strongly, resulting in the particle precipitation from the atmosphere to the underlying surface. Evidently, the industrial emissions favor the strengthening of the condensation−coagulation processes and disturb the stable stratification of aerosol fields in the atmospheric boundary layer, leading to the acceleration of the aerosol transformation and precipitation.

Thus, taking into account the remoteness of other large industrial regions, these aerosol particles reach the Norilsk industrial region saturated by elements and ions, firstly of the sea and soil-erosion origin, and in Norilsk they additionally experience enriching by the components of its industrial emissions.

The enrichment of components of the second cluster inside Norilsk can be estimated by the method of simple approximation based on the following assumptions:

1) all chlorine as a component of aerosol, passed through the region, is not of local industrial origin (due to its non-correlation with SO_2 and other emitted components);

2) relative enrichment by chlorine−ion of the atmospheric boundary layer when passing through the region is only due to the aerosol precipitation from higher altitude layers;

3) the precipitation of chlorine-containing aerosol fraction on the underlying surface of the region should be considered insignificant (if necessary, these losses can be evaluated using the components, highly correlated with chlorine, whose coefficients of relative enrichment became less than unity when air mass passing through the industrial region);

4) based on the above-mentioned, we can consider that the enrichments by other components of this cluster, exceeding the coefficient of chloride−ion enrichment, are due to contribution of the Norilsk industrial region.

Mathematically, such evaluation of the industrial enrichment of element and ion of the second cluster when passing through the region is expressed by:

$$K_E = \frac{[E]_{exit}/[E]_{entr}}{[Cl]_{exit}/[Cl]_{entr}},$$

where *entr* is the windward side (the concentration at the air mass entry in the region); *exit* is the leeward side (at the exit). Results of the estimation are presented in Fig. 6.
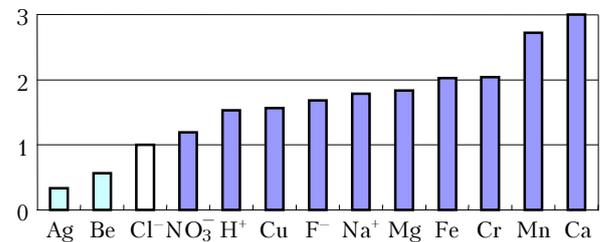
Fig. 6. Evaluation of enrichment of components of the second cluster by chloride−anion. Twelve samples are selected in the layer between 100 and 1500 m on 10−13 August, 2004.

Somewhat isolated diagonal of elements Al−Ti−V is adjacent to the second cluster, which practically does not correlate with the chlorine itself, but has strong relations with the cluster half. Titanium, which has six highly-significant bonds, could be the leader of this group, however, the absence of a closed chain of correlations counts in favor of a complex origin of the group elements. Titanium, as well as iron and aluminum (sometimes manganese) are often reference elements of indication of soil origin. However, the considerable enrichment by Al, Ca, Fe, Mn is indicative of the presence of not only soil-erosion factor at the territory. A possible reason of the considerable increase of their concentrations here can be the periodical rock-blasting in mountains. Titanium, vanadium, partially magnesium, evidently, originate from the underlying surface of oil and gas provinces of Western Siberia.

The nitrate−anion is a connecting link between two main clusters of aerosol under study. It is formed in the atmosphere from nitric oxide photochemically, and, that is evident from its position in the system of graphs, well condenses on any aerosol.

Only two elements − molybdenum and zinc − do not demonstrate any significant bonds. However, it is well-known[6] that the first of these components form a stable highest oxide and highly hydrated oxygen complexes on its basis. This allows one to suppose that it exists in the form of stable aerosol particles of similar composition, which are slowly transforming. Zinc also tends to hydration and formation of complexes. But the fact is of interest that zinc is the only component of all measured aerosol components, which has a high ($r = 0.4275$) and significant ($q = 0.995$) positive correlation with its altitude behavior, possibly, due to long-distance transfer. Some authors believe that zinc emissions exist in atmosphere in the vapor-phase form,[22] i.e., zinc in local emissions does not manifests itself in aerosol form, which is under study.

With more accurate information in hand about the origin, propagation, and lifetime of gas and aerosol-forming matters we could formulate the recommendations about possible ways to decrease the toxicity of individual components and their distant transfer in the atmosphere with aerosol.

Recommendations

To improve the ecological situation in the region, the decrease of sulfur emission is necessary. Apart from the classical desulfurization of fuel, there are three variants of the process with the use of: 1) CuO, which provides about 90% removing NO_x and SO_x[7]; 2) coal fuel with lime additions[8–10] providing from 50 to 80% chemical bonding of SO_x; 3) limestone.[11,12]

Measurements of vertical distribution of admixtures and air temperature have revealed the presence during the whole experiment of permanent inversion at a height of 1 km, preventing the emissions to propagate upward. The climatic data show that such inversion is not destructed even in the day time from September to April all over the region. Even in summer, in the day time, there is a barrier layer at a 900–1000 m altitude. Therefore, the height increase of plant chimneys up to 500 m makes no sense, because all emissions will propagate under the inversion layer.

One of the ways to solve the problem is a change the emission intensity in day and night time. At night the emissions can be accumulated in gasholders, and in day time the gasholders should be released. This will allow using the effect of better scattering of impurities in day time, and, consequently, favor the air cleaning. In the gasholders, the gas condensation will take place and the resulting microdispersion particles will fast coagulate, transforming into the accumulation mode,[13] which is well collected by standard filters. To overcome the inversion layer, the meteotrons should be used instead of standard chimneys.[14,15] The inversion level should be sodar-monitored.[16]

In the city column the impurities are in the form of gases, because the aerosol fraction sediments as coarse particles near the source. The impurities propagate at large distances under the inversion layer; this was found during the experiment inside a layer of 300–400 m. The "gas-particle" transition begins at a distance of 50–100 km. The start of condensation processes depends on the type of the compound. The limited period of the aircraft flight hours hindered us to follow all the transformation process of compounds in the plume. To do this, a specialized experiment in the framework of some research program is needed, the best time for which is any transition season.

The aerosol background in the city is mainly determined by technogenous microdispersion calcium and ash Al, Si, Fe. Therewith, there is a strong dissimilarity in their distribution all over the city, caused by peculiarities of the urban aeration, which is difficult to explain in the framework of commonly accepted ideas. There are zones in the urban territory with weakly changeable background admixtures (stagnation zones).

The aerosol background is improved at the cost of decreasing industrial emissions. To solve the problem of the stagnation zones, a mathematical calculation of the urban air circulation by the Penenko–Aloyan method[17–18] is required, followed by the experimental verification of results, and construction of the control system similar to the described in Ref. 19.

Relatively high ozone concentrations in the Norilsk atmosphere at the period of the above-described experiment says about intense photochemical processes, resulting in formation of the secondary more toxic components, for example, formaldehyde.

To control the photochemical processes in Norilsk, it is necessary to organize the ozone monitoring. For this purpose, an automatic station of a TOR-station type can be used.[20] The use of the foreign UV analyzers is undesirable, because they overestimate the ozone values in the dusty atmosphere.[21]

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