

Chemical composition of industrial aerosol in some regions

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In this paper we discuss the data on chemical composition of aerosol emitted by enterprises in some regions during 1990-2004. The larger half of airborne surveys was carried out in 1990-1992 over largest industrial centers of Russia and Kazakhstan (Nizhshnii Tagil, Khabarovsk, Nizhnevartovsk, Komsomolsk-na-Amure, Ulan-Ude, Pavlodar, Ust-Kamenogorsk, etc.). The data were obtained by collecting air samples from the emission plumes from onboard the Antonov-30 airborne-laboratory "Optik-E". Almost all elements and ions to be determined are found in the plant emissions. Concentrations of one or another component can differ by 5 orders of magnitude, what is probably indicative of the properties of the fuel used or the technological peculiarities. The enhanced content of Si, Ca, Al, Mg, and Zn in ashes fraction is characteristic of the enterprises in Khabarovsk and Pavlodar, which used coal during the period of measurements. In addition, high concentration of the water-soluble fraction of ions NH_4^+ , SO_4^{2-} , and Br^- is observed in the emissions of enterprises in Pavlodar that is indicative of the specific peculiarities of the coal burnt. The concentration of Na^+ , K^+ , and Cl^- is higher in the plumes observed in Khabarovsk. Although the concentrations of aerosol chemical components measured in the plumes are of certain interest, they are not completely informative because the amount of pollutants emitted into the atmosphere depends on the source power, meteorological conditions, solar radiation that favors the transformation of impurities, etc. The air samples were additionally collected at the same heights outside the plume. Hence, one can estimate the enrichment of the ambient air by the emissions. The complex sounding of atmosphere over Norilsk industrial region in 2002 - 2004 allowed to observe the gas-to-particle conversion in the plume emitted from non-ferrous metallurgy enterprises and to evaluate the deposition of aerosol components formed in the plume.

1. Introduction

Concentration of industrial objects on a restricted territory, such as the territory of a modern city, leads to the fact that within the city boundaries there takes place the emission of a large amount of different admixtures that usually are not observed under natural conditions. Studies of the regularities of formation and transformation of air pollution fields in big industrial centers have most rapidly been developed in recent 15-20 years.

The research team of the Antonov-30 airborne-laboratory of IAO SB RAS is engaged in studies industrial emissions during more than 20 years. The original technique was

developed for this purpose and tested in 12 cities, 6 regions, and 2 deposits. Its detailed description is presented earlier (Belan B.D., 1993). Airborne surveys were carried out over largest industrial centres of Russia and Kazakhstan (Nizhnii Tagil, Khabarovsk, Nizhnevartovsk, Komsomolsk-na-Amure, Pavlodar, Ust-Kamenogorsk, Norilsk, etc.).

2. Method and techniques

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.

The aerosol was sampled on the Petryanov filters when the aircraft crossed the emission plume beginning at a distance of 100-200 m from the stack mouth and on remoteness up to 100 km and farther from source. Airflow rate through the filter was controlled by means of the counter SGBd4-1 produced by Signal Company (Engel's, RF) and checked at the plant. Three filters were exposed simultaneously in a flight. For filters exposed in the plume, its geometrical cross section was determined either by means of a lidar or from the data of photoelectric particle counter operating continuously assuming that the section is close to a circular one.

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). The used physico-chemical techniques of analysis are given in table 1.

Table 1 Description of techniques used in analysis of aerosol samples collected on Petryanov filters (AFA-HP/VP-20)

Element or ion component	Method	Detection threshold, $\mu\text{g/sample}$	Error, %
Al, Co, Cr, Mo, Ni, Ti, Zn, B, Si	Atomic-emission	0.02	20
Ag, Ba, Cu, Pb, Sn, V, Mg, Mn	spectroscopy	0.01	20
Ca, Cd; Fe, Ga, W	—" —</td <td>0.2; 0.1</td> <td>20</td>	0.2; 0.1	20
As ⁵⁺ , Zn ²⁺ ; Cd ²⁺	Inverse volt-ammety	0.02; 0.04	15
Na ⁺ , K ⁺	Flame photometry	0.20	10
Br ⁻ , SO ₄ ²⁻ , NO ₃ ⁻	High-effective liquid	0.60	10
Cl ⁻	chromatography	0.20	12
F ⁻ , NH ₄ ⁺ , NO ₃ ⁻	Ionometry	0.20	10

3. Results and Discussion

Almost all elements and ions to be determined are found in the plant emissions (Belan B.D. et al., 1996). Concentrations of one or another component can differ by 5 orders of magnitude, what is probably indicative of the properties of the fuel used or the technological peculiarities. The enhanced content of Si, Ca, Al, Mg, and Zn in ashes fraction is characteristic of the enterprises in Khabarovsk and Pavlodar, which used coal during the period of measurements. The concentration of Na⁺, K⁺, and Cl⁻ is higher in the plumes observed in Khabarovsk. Although the concentrations of aerosol chemical components measured in the plumes are of certain interest, they are not completely informative because the amount of pollutants emitted into the atmosphere depends on the source power, meteorological conditions, solar radiation that favors the transformation of impurities, etc. The air samples were additionally collected at the same heights outside the plume. Hence, one can estimate the enrichment of the ambient air by the emissions. In the majority of events the ratios between the concentrations in plume and background values are within the range from ten to hundred (table 2).

Table 2 Ratios of concentrations of aerosol components in plumes and background conditions at the same height for cases with maximums of relative enrichment (bold)

Com.	City: Khabarovsk			Ermak Pavlodar		Nizhni Tagil			Norilsk	
	Plant Power heat(1) station	Power heat(3) station	Power heat station	Alu-minium plant	Carriage building plant	Ural chemical plastpolymer	Metall urgical works	Coke battery plant	Non-ferrous mining	
F ⁻	-	-	-	-	344	1136	<	21	2	
Na ⁺	133	30	8	<	75	<	<	260	5	
K ⁺	256	99	8	55	132	<	<	<	21	
Cl ⁻	138	92	10	73	2642	282	109	72	1	
Br ⁻	<	<	114	33	288	136	8	12	-	
NH ₄ ⁺	<	1733	49	28	2272	<	<	442	1	
NO ₃ ⁻	<	<	75	<	353	<	55	8	1	
SO ₄ ²⁻	<	<	42	2	66	<	<	23	17	
Hg ²⁺	8	<	32	1	4	18	124	15	-	
As ⁵⁺	<	187	59	2	<	10	<	<	-	
Zn ²⁺	67	45	5	4	<	<	27	<	-	
Cd ²⁺	<	<	1	<	<	<	50	<	-	
Al	248	133	177	147	200	<	211	122	58	
Ca	187	112	319	156	264	87	1	135	16	
Fe	170	59	167	155	39	20	77	51	7	
Mn	37	28	33	97	3	<	<	68	81	
Mg	208	98	4	1	655	95	25	188	256	
Si	634	113	155	198	<	<	<	83	3700	
Pb	<	<	27	180	<	<	500	<	234	
Cr	<	13	125	46	186	66	103	103	1	
Ni	160	27	-	-	1	7	78	10	148	
Cd	<	167	189	172	-	-	-	-	-	
Cu	280	10	22	1	9	12	167	17	39	
V	50	8	67	80	65	43	<	30	3	
Zn	1800	640	390	762	-	-	-	-	28	

Comparison of the results obtained at different enterprises in 1990-1995 has revealed a drawback in the technique of the airborne laboratory use as a complex. The point is that the samples were collected just near the stack mouth in order to catch even giant particles emitted into the atmosphere. Then it occurred that many gaseous substances are not yet condensed at such a short distance, and, hence, they are not settled on the filter. Such substances are NO, NO₂, and SO₂, which have the dew point from 35 to 155°C. Therefore, these substances would condense and transform to aerosol particles at the distances proportional to temperature of the emitted air, depending on the heating of the emission jet from the stack. Thus, one should carry out sounding of a plume at least twice: near the stack mouth, in order to efficiently collect the solid components, and at some distance, in order to collect the condensed ingredients. Evidently, using the difference, one can additionally estimate the contribution of emitted industrial gases in the regional aerosol. However, in 1990-1992 the maps of admixtures were planned and performed immediately over the cities and nearest vicinities. In other case, for example, Baikal'sk Pulp-and-Paper Integrated Plant in 1995 (Ivlev G.A. et al., 1999) the plume propagation conformed to particular wind fields in the region, which in combination with local orography did not allow to perform equidistant tacks experiment and to do a unique conclusion. Nevertheless, these experiments show that one should collect the aerosol fraction generated from gaseous predictors at the distances of no less than 20 km from the source of emission.

The complex sounding of atmosphere over Norilsk industrial region in 2002 - 2004 allowed to observe the gas-to-particle conversion in the plume emitted from non-ferrous metallurgy enterprises and to evaluate the deposition of aerosol components formed in the plume. The main pollutant emitted by Norilsk mining plant is sulfur dioxide. It provided 96% of emissions, and 1 - 1.5% were dust, carbon oxide, and nitrogen oxides. Chemical processes of sulfur transformation occur in the way of its oxidation to the upper valency VI and neutralization: $H_2S \rightarrow SO_2 \rightarrow H_2SO_3 \rightarrow H_2SO_4 \rightarrow M(HSO_4)_m \rightarrow M_2(SO_4)_m$, where Me is any cation. Really the principal part of emission consists of sulfur dioxide. The use of numerical methods (Israel Yu.A. et al., 1989; Ryaboshapko A.G., 1989) 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 (Benkovitz C.M. et al., 2004). The experiments (Park R.J. et al.; Tu F.H. et al., 2004) showed 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. Obviously, such great differences are explained by the prevalence of mechanisms in the plume - chemocondensation, binary or triple nucleation.

The our experimental flight on "equidistant tacks" scheme was carried out on November 10, 2002 in daylight time according to the diagram shown in Fig. 1. Three lower horizontal flight legs were carried out at the distances of 50 to 120 km far from the city.

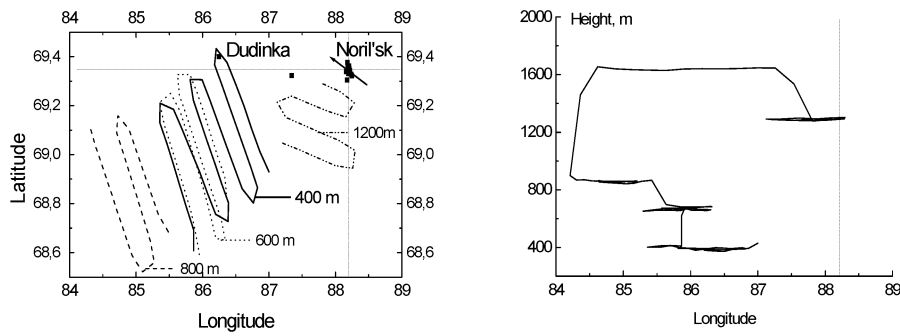


Figure 1. Diagram of flight on "equidistant tacks" scheme on November 10, 2002.

The data collected below the inversion 600 m in the plume of emission is the most effectively representing the subject of analysis. It is seen in Fig. 2 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.

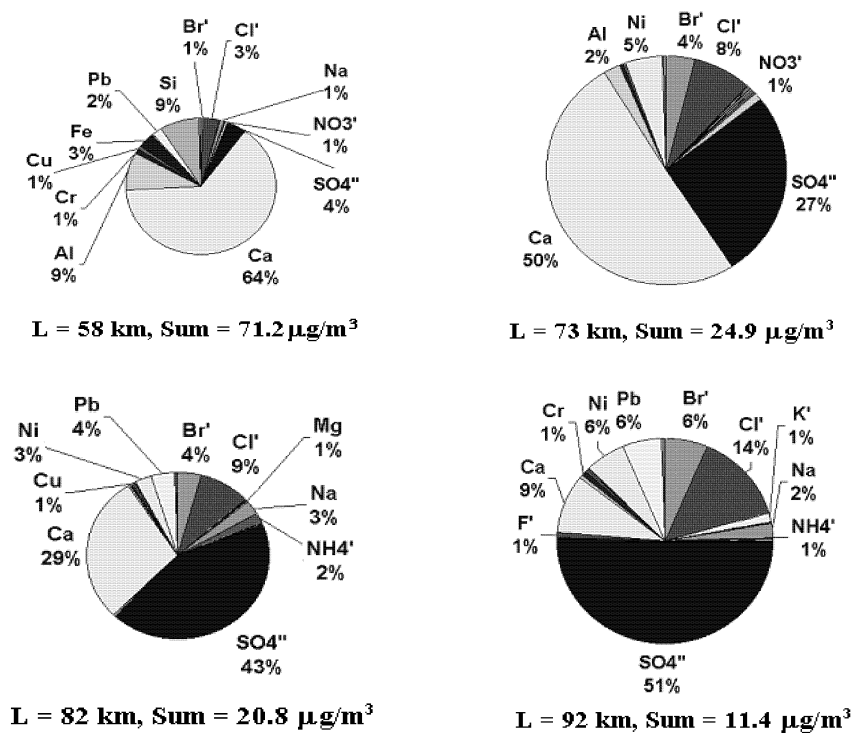


Figure 2. Relative chemical composition of atmospheric aerosol at the height 400 m.

As these measurements have shown, the change of the admixture contents above the inversion (higher 600 m) was inverse: the contribution of calcium is greater, and the portions of others were less as moving from the source. 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.

4. Conclusion

As follow from above, the anthropogenic aerosol includes many toxic components to be regulated in content, the concentrations of which reach high values in plumes, and enrichment relative to the background values can be thousand times, that is indicative of the technologies and fuels used at the enterprises.

The moment of gas-to-particle transformation in the plume of emission of an industrial center was observed in airborne experiment over Noril'sk industrial region. 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.

5. Acknowledgments

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