

Experimental and numerical study of gas-to-particle conversion in an emission plume from mining and metallurgical industry based on airborne sounding in a polar atmosphere

Denis V. Simonenkov¹, Vladimir F. Raputa², Tatyana V. Yaroslavtseva³, Boris D. Belan¹

¹V.E. Zuev Institute of Atmospheric Optics SB RAS (IAO SB RAS). 1, pl. akad. Zueva, Tomsk 634055, Russia

²Institute of Computational Mathematics and Mathematical Geophysics SB RAS. 6, Prosp. Akad. Lavrentyeva, Novosibirsk 630090, Russia

³Novosibirsk Scientific Research Institute of Hygiene of Federal Service for Surveillance on Consumer Rights Protection and Human Wellbeing. 7, ul. Parkhomenko, Novosibirsk 630108, Russia

e-mail: simon@iao.ru

Abstract. The results of an airborne survey of plumes from the Norilsk Mining and Metallurgical Plant by an Optik-É AN-30 aircraft laboratory on November 10, 2002 are discussed. Most pollutants are blown out of the city in the gas phase in the form of acidic oxides (mainly sulfur). Mapping of the substances is performed along the main trajectory of air mass transport at a distance of 20-140 km from the city. Horizontal flights were performed at 400, 600, 800, and 1200 m above sea level at equidistant traverses (from 3 to 6 at each height) normally to the main flow direction. Most pollution was concentrated above the 400-m level. An active gas-to-particle conversion was observed at a distance of 60-100 km from the emission source. In the plume areas distant from the source there was a sulfate anion increase from 4% to 51% in aerosol composition weight and a calcium decrease from 64% to 9%. Under the conditions of low humidity in the polar atmosphere in winter, SO₂ is apparently removed from the air mainly due to dry heterogeneous condensation with calcium oxide as the main counteragent of industrial origin. The concentrations of these active pollutants in the plume are well approximated by a two-parameter transformation model.

1. Introduction

A comprehensive airborne survey of the atmosphere over the Norilsk industrial region was performed by an aircraft laboratory called Optik-É AN-30 [1] in November 2002. The purpose of the complex experimental study was to evaluate the impact of the Norilsk Mining and Metallurgical Plant on air quality of the adjacent and remote areas of this region.

The main source of air pollution is the emission of contaminants from nonferrous metallurgical enterprises. As a result of ore roasting, sulfide sulfur is oxidized to gaseous sulfur dioxide, which accounts for up to 96% of the total emission mass; dust, carbon monoxide, and nitrogen oxides only account for 1-1.5% [2]. Thus, most emissions are blown out of the city in the gas phase in the form of



acidic oxides (mainly sulfur). The chemical processes of sulfur transformation, according to the theory [3, 4], are its oxidation to higher valence, 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 M^{m+} is any metal cation. In fact, the major part of the emissions is sulfur dioxide. In accordance with calculations of [4, 5], the maximum amount of sulfuric acid in the atmosphere during the transport is reached in about 20 hours, and the average life time of sulfur dioxide due to dry deposition and chemical transformations is about 40 hours. The rate of removal of sulfur dioxide abruptly increases by precipitation. In addition, our first experiments [6] showed that the aerosol fraction of the emissions should be sampled at a distance of more than 20 km from the source.

2. Experimental studies

Based on the above information, the mapping of pollutants was performed along the main trajectory of air mass transport at distances of 20-140 km from the city. The flight was carried out on November 10, 2002 in daytime according to the scheme shown in figure 1.

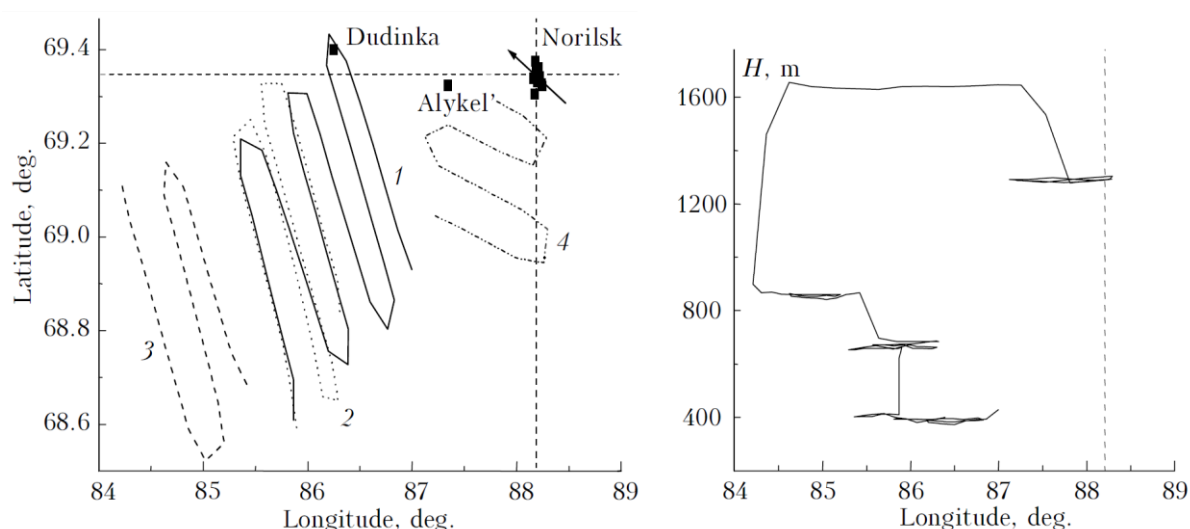


Figure 1. Flight route. November 10, 2002 (1 – 400 m, 2 – 600 m, 3 – 800 m, 4 – 1200 m).

Horizontal flights were performed at heights of 400, 600, 800, and 1200 m above sea level at equidistant traverses, from 3 to 6 at each height. The morning weather in the Norilsk area was determined by the central part of a filling cyclone with surface fronts, and then by a low-gradient field of low pressure. The air mass was of arctic origin.

Maps of horizontal pollutant distributions were constructed with the measurement data at all height levels. Since the profiles of trace gas concentrations from 600 m to 1200 m showed a tendency to decrease with altitude down to the background values, we will focus our attention on the data of the 400-m level (figure 2), where the most part of pollution was concentrated.

The SO_2 concentration in the air from the city reached $450 \mu g/m^3$. The nearest edge of the square was at a distance of 58 km, and the far edge, at 100 km from the city. A significant difference was observed between the urban plume concentrations and the background conditions, where the sulfur dioxide concentration decreased to $50-60 \mu g/m^3$. This confirms the theory of Israel and Ryaboshapko that SO_2 may remain in a plume for tens of hours [4, 5].

Most of the other components of the plume (carbon monoxide, carbon dioxide, and fine aerosol particles) have similar distribution profiles. The data on ultrafine aerosols also confirm that there is an active process of aerosol formation via gas-phase chemical reactions in the plume and at its boundaries.

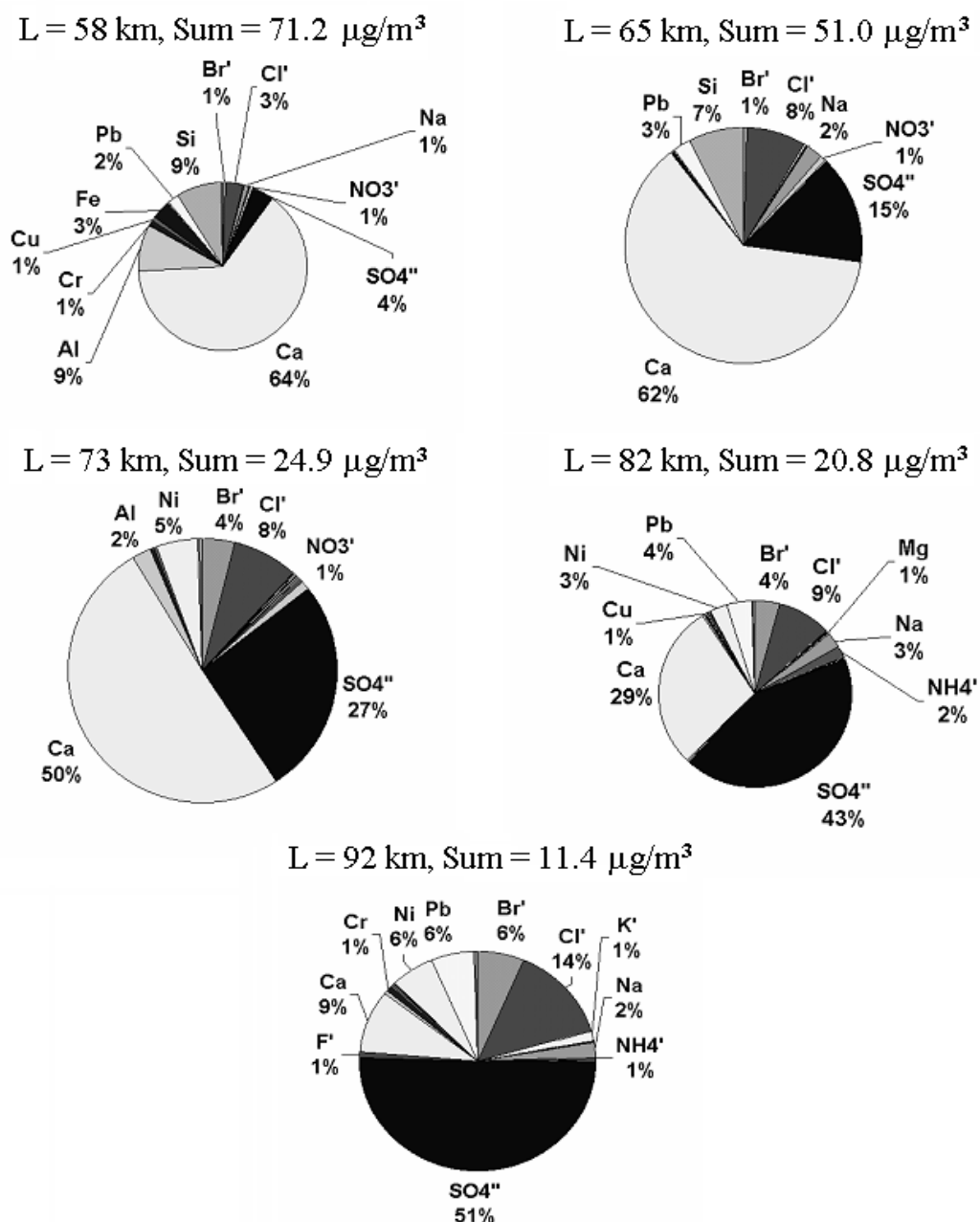


Figure 2. Comparative chemical composition of aerosols sampled at 400-m level at various distances from Norilsk (L; Sum - total concentration of all aerosol elements and ions).

The validity of all these processes is confirmed by the evolution of the chemical composition of the aerosols. Figure 2 shows that in plume areas distant from the source there is a sulfate anion increase from 4% to 51% in aerosol composition weight and a calcium decrease from 64% to 9%.

The source of calcium is, apparently, the lime added during roasting to enrich the copper-nickel ore (separation of iron-bearing pyrite) [7]. The calcium is emitted into the atmosphere during combustion as ultrafine and fine particles of 20-180 nm [8], and apparently reacts directly with sulfur dioxide in such reactions as $\text{CaO} + \text{SO}_2 + 2\text{H}_2\text{O} = \text{CaSO}_3 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_3 \cdot 2\text{H}_2\text{O} + 1/2\text{O}_2 = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [9].

3. Models to reconstruct the concentration fields in the plume

Based on the characteristics of passive substance transport at large distances from a plane source, the following model of reconstruction was used to describe the concentration field along the direction of emission [10]:

$$Q(x, y, \theta) = \theta / \sqrt{(x - \lambda)^2 + (y - \mu)^2} \quad (1)$$

$$\theta = M / 2\pi u H, \quad M = \iint_S m(\xi, \eta) d\xi d\eta, \quad (2)$$

where M is the total mass of pollutants from the territory S . $m(\xi, \eta)$ is the emission of pollutants from a point (ξ, η) belonging to S , and u and H are the average wind speed and height of the mixing layer, respectively. The point (x, y) is assumed to be at a distance of more than 7-10 km from S . The function $m(\xi, \eta)$ is usually unknown.

The following two-parameter relationship was used to estimate the concentration of active pollutants in the plume [5]:

$$C(r, \vec{\theta}) = \theta_1 \exp(\theta_2 r) \quad (3)$$

where r is the distance from the source.

The parameters θ , θ_1 , θ_2 in the relations (1) and (3) are estimated by a least squares method using the observational data.

4. Numerical analysis of the transport processes of passive and active pollutants

The results of numerical reconstruction, using the relation (1), of the concentrations of lead and chlorides in the plume at a reference point located at a distance of 58 km from Norilsk are presented in figure 3. The distribution of the passive pollutants in the atmosphere is consistent with the physical theories.

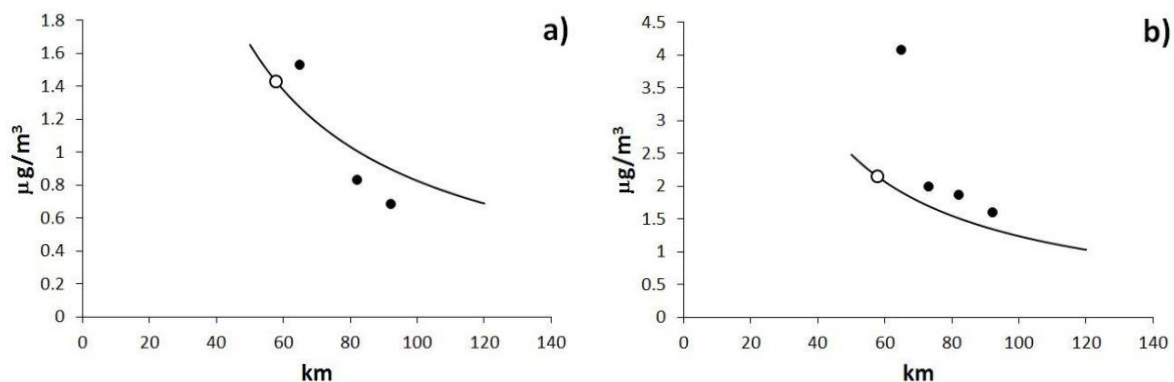


Figure 3. Measured and reconstructed concentrations of lead (a) and chlorides (b) in the plume.

○, ●: Reference and control measurement points.

The results of the estimation of calcium and sulfate concentrations performed with the relation (1) are presented in figures 4a and 4b. It is evident that the passive tracer propagation model is of little use in this case. The model (3) reproduces the transformation process quite adequately in the distance interval under analysis (figure 4c).

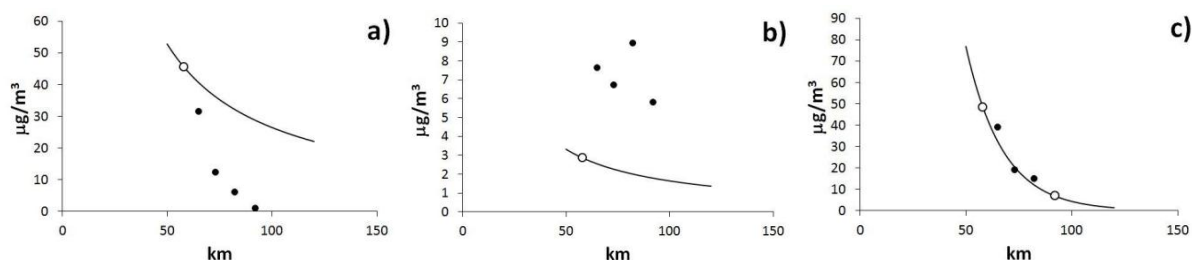


Figure 4. Concentrations of calcium (a) and sulfates (b) measured and reconstructed by model (1). Total concentration of calcium and sulfates in the emission plume (c) estimated by model (3).

5. Conclusions

Talking into account the air transport velocity, an active gas-to-particle conversion was observed at a distance of 60-100 km from the emission source. It confirms the average estimates of the sulfur dioxide lifetime in real atmosphere [4, 5]. Under the conditions of low humidity in the polar atmosphere in winter, SO_2 is apparently removed from the air mainly due to dry heterogeneous condensation, with calcium oxide as the main counteragent of industrial origin. The concentrations of these active pollutants in the plume are well approximated by a two-parameter model of transformation.

Acknowledgments

This work was supported by the Presidium of RAS (program no.15), the Department of Earth Sciences RAS; the Russian Foundation for Basic Research (grants no. 14-05-00526 and 14-05-00590), the Foundation for Global Environmental Research of the National Institutes of the Ministry of Environment of Japan.

References

- [1] Antokhin P N, Arshinov M Yu, Belan B D, Davydov D K, Zhidovkin E V, Ivlev G A, Kozlov A V, Kozlov V S, Panchenko M V, Penner I E, Pestunov D A, Simonenkov D V, Tolmachev G N, Fofonov A V, Shamanaev V S and Shmargunov V P 2012 Optik-É AN-30 aircraft laboratory: 20 years of environmental research *Journal of Atmospheric and Oceanic Technology* vol 29 N 1 pp 64-75
- [2] Bezuglaya E Yu, Rastorgueva G P and Smirnova I V 1991 *By what an Industrial City Breathes* (Leningrad: Gidrometeoizdat) p 256
- [3] Ryaboshapko A G 2002 *Remote atmospheric transfer and atmospheric budgets of sulfur, nitrogen, and mercury compounds* Author's Abstract of Doct. Phys.-Math. Sci. Dissert. (Moscow: IKGE) p 29
- [4] Ryaboshapko A G 1988 *Trudy Instituta Prikladnoy Geofiziki* vol 71 pp 25-32
- [5] Israel Yu A, Nazarov I M, Pressman A Ya, Rovinskii F Ya and Ryaboshapko A G 1989 *Acid Rains* (Leningrad: Gidrometeoizdat) p 269
- [6] Belan B D, Zuev V E and Panchenko M V 1995 Main results of airborne sounding of aerosol conducted at the Institute of Atmospheric Optics from 1981 till 1991 *Atmospheric and oceanic optics* (Tomsk: IAO SB RAS) vol 8 N 1-2 pp 131-156
- [7] *Popular Library of Chemical Elements* 1983 vol 1 (Moscow: Nauka) p 576
- [8] Savenko S V 1991 *Natural and Anthropogenic Sources of Atmospheric Pollution* (Moscow: VINITI) p 212
- [9] Garshin A P 2000 *Inorganic chemistry in schemes, figures, tables...* (St-Peterburg: Lan') p 288
- [10] Raputa V F, Ol'kin S E and Reznikova I K 2008 Numerical analysis of observation data of regional pollution of an area source *Atmospheric and oceanic optics* (Tomsk: IAO SB RAS) vol 21 N 6 pp 486-489