Spatiotemporal variability of the concentration of organic and inorganic carbons in the atmospheric aerosols in Novosibirsk Region

S.A. Popova, V.I. Makarov, and K.P. Koutsenogii

Institute of Chemical Kinetics and Combustion,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk

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We consider the spatiotemporal distributions of the organic (C_{or}) and inorganic (C_e) carbon in the atmospheric aerosols of Novosibirsk Region. The HYSPLIT model was used to demonstrate the possible influence of air mass transport on the increase of the inorganic carbon concentration in the atmospheric aerosols in Novosibirsk, its suburbs, and the Karasuk town.

Introduction

The study of aerosols is needed for understanding many important processes occurring in the atmosphere.

First, the aerosol is the optically active component of the atmosphere, which strongly affects its radiative conditions. The capability of aerosol to absorb, reflect, and scatter sunlight and the thermal radiation from the surface is determined by the physicochemical properties depending on the chemical composition of aerosol particles.

Second, the submicron aerosol particles play the decisive role in condensation of water vapor and in the formation of clouds and hydrological conditions in the atmosphere in general. Thus, the change of the aerosol content, for example, under the anthropogenic impact can affect the global climate through changing the radiative conditions of the atmosphere and influencing the hydrological cycle.

Third, the conversion of gas constituents into particles, different chemical reactions on the surface and in the volume of particles, their following coagulation, and sedimentation are the main ways of self-cleaning of the atmosphere. And, finally, the study of aerosols is important in connection with the fact that they include many harmful organic compounds, in particular, polynuclear aromatic hydrocarbons (PAHs).

The content of organic (C_{or}) and inorganic (C_e) carbon in the atmosphere has been studied earlier, and Refs. 1 and 2 present the results of its determination in some US cities. Regular investigations of the chemical composition and characteristics of the atmospheric aerosol in Siberia have been conducted since 1991 within the framework of the Siberian Aerosols Project, whose objectives, content, and structure are described in Ref. 3.

The data on the chemical composition of aerosol in Siberia are given in Ref. 4, but the information about C_{or} and C_e is quite scanty. A more detailed consideration of the spatiotemporal dynamics of the organic and inorganic carbon concentrations and their contributions to the atmospheric aerosol is presented in Ref. 5.

In this paper we present some results of determination of the organic and inorganic carbon in the atmospheric aerosol, as well as the values of the mass aerosol concentration (C_m) in the city of Novosibirsk and in the Novosibirsk Region in 2001 and 2002.

The atmospheric aerosol was sampled in three sites of Novosibirsk Region: in the city of Novosibirsk, 30 km east from the city in Klyuchi town, and in Karasuk town located 375 km southwest of Novosibirsk. Thus, the investigations were conducted at the regional level, which allowed us to study the spatial distribution of C_{or} and C_e, to carry out simultaneous sampling at the three sites in different seasons, and to reveal the seasonal variability of C_{or} and C_e.

Materials and methods

Samples were collected onto AFA-KhA-20 fine-fiber aerosol filters and GF-92 glass-fiber filters 50 mm in diameter (manufactured by D-3354 Dassel, Germany) with an air filtration unit operated at a rate of 13 and 1.8 m^3/h, respectively. Sampling was carried out simultaneously at all the observation sites round-the-clock for 30 days in winter, spring, summer, and fall. The AFA-KhA-20 filters were weighed before and after sampling upon drying in a desiccator, and the increase in weight was used to calculate the mass aerosol concentration. The GF filter cake was analyzed by the method of reaction gas chromatography. The concentrations $\tilde{N}_{or}$ and $\tilde{N}_e$ and the ratio $\alpha = \tilde{N}_{or}/\tilde{N}_e$ were calculated. The relative fraction of carbon in the total particulate mass φ was calculated as

$$\varphi = (C_{or} + C_e)/C_m.$$

Technique for determination of the organic and inorganic carbon content

The gas chromatography (GC) setup for determination of C_{or} and C_e in aerosol samples is

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described in Refs. 6 and 7. The reactor is made as a glass tubing consisting of three zones for sample injection, pyrolysis, and oxidation. A sample (quarter filter) is injected into the reactor, the carrier gas (argon) is blown through at a rate of 40 ml / min. Then the silica boat with the sample is moved by a magnet from the injection zone into the pyrolysis zone, where the organic matter is evaporated for 30 s at 700°Ñ and transported by the argon flow to the catalyst ($NiO + Al_2O_3$) surface, where it is oxidized to carbon dioxide (CO_2).

The CO_2 gas produced in the oxidation zone passes through the chromatographic column 3 m in length and 3 mm in diameter filled with the activated coal. The analyzed gas from the column is mixed with the hydrogen flow (30 ml / min) and comes to the metanator made as 30-cm long steel tube of 4-mm internal diameter filled by 12% Ni on Al_2O_3. In the metanator, the CO_2 converts into methane ($ÑÍ_4$) at 300°C, that is, the reaction of catalytic hydrogenation occurs. The argon flow with $ÑÍ_4$ comes to the flame ionization detector (FID).

The FID signal is recorded as a peak on the KSP-4 plotter through a low-current meter. The value of $Ñ_{â}$ is determined in a similar way, but the reactor is preliminarily filled with the oxygen. Inorganic carbon is oxidized to $ÑÎ_2$ in the pyrolysis zone. Then the flow of argon with $ÑÎ_2$ through the column comes to the metanator, where $ÑÎ_2$ is converted into methane, and then to the FID.

The standard solution of stearic acid in hexane and the mixture of soot with aluminum oxide were used as references for determination of the C_{or} and C_e.

In Fig. 1 all the points fall on the same straight line, which means the quantitative completion of pyrolysis and catalytic oxidation of the samples under the conditions of our analysis. The multiple injections of the standard have shown that the accuracy of analysis is 5–10%, while for the analyzed sample it is 20–25%. The detection limit is determined by the background of the clean filter and at the signal-to-noise ratio 3:1 it is 2–3 μg of carbon in a sample.

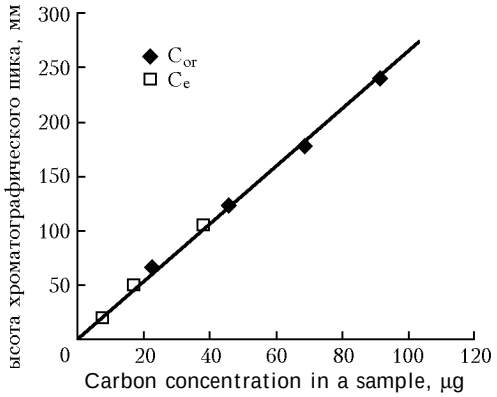


Fig. 1. Chromatographic peak height vs. the amount of carbon in a sample.

Results and discussion

The Table summarizes the geometric mean $\langle \mathbf{x}_i \rangle$ values of the C_m, C_{or}, C_e, α, and φ along with their standard deviations (σ_{gi}).

Concentrations of organic and inorganic carbon and mass aerosol concentration in Novosibirsk Region in 2001 and 2002

Sampling site	Sampling date	C_m		C_{or}		C_e		C_{or} / C_e		$(C_{or}+C_e) / C_m$	
		$\langle \mathbf{x}_i \rangle$, μg / m³	σ_{gi}	$\langle \mathbf{x}_i \rangle$, μg / m³	σ_{gi}	$\langle \mathbf{x}_i \rangle$, μg / m³	σ_{gi}	$\langle \mathbf{x}_i \rangle$	σ_{gi}	$\langle \mathbf{x}_i \rangle$	σ_{gi}
Karasuk	Jan 20–Feb 18 / 01	42.5	1.1	1.4	1.8	2.9	1.7	0.5	1.7	0.1	1.6
	Apr 20–May 19 / 01	31.9	1.8	3.7	1.9	4.7	1.7	0.8	1.3	0.3	1.9
	Jun 20–Jul 08 / 01	24.5	1.4	3.4	1.5	2.8	1.5	1.2	1.3	0.3	1.6
	Sep 20–Oct 19 / 01	20.7	2.1	2.0	1.7	1.2	2.4	1.7	1.7	0.2	1.8
	Jan 24–Feb 22 / 02	18.6	1.6	1.3	1.7	2.8	1.8	0.5	1.6	0.2	1.6
	Apr 20–May 19 / 02	29.3	2.0	5.0	1.8	2.7	2.2	1.9	1.8	0.3	1.7
	Jun 20–Jul 19 / 02	11.3	2.3	2.7	2.0	1.5	1.4	1.8	1.9	0.4	2.3
	Sep 21–Oct 20 / 02	33.4	1.8	3.2	1.8	2.9	2.4	1.1	1.6	0.2	1.3
Klyuchi	Jan 22–Feb 20 / 01	25.0	1.5	2.2	1.7	4.1	1.8	0.5	1.6	0.3	1.5
	Apr 20–May 20 / 01	50.6	1.9	5.4	2.2	7.3	1.9	0.7	1.3	0.3	1.5
	Jun 20–Jul 19 / 01	32.1	1.4	3.6	1.3	3.4	1.3	1.0	1.2	0.2	1.3
	Sep 20–Oct 19 / 01	27.2	1.7	4.5	1.7	2.7	1.9	1.7	1.4	0.3	1.3
	Jan 18–Feb 16 / 02	21.1	1.3	2.1	1.7	4.1	1.6	0.5	1.5	0.3	1.4
	Apr 19–May 19 / 02	40.7	2.1	5.7	2.6	2.5	2.9	2.2	1.9	0.2	1.5
	Jun 20–Jul 19 / 02	25.5	1.4	5.4	1.6	1.5	1.5	3.6	1.6	0.3	1.5
	Sep 20–Oct 19 / 02	34.2	1.6	3.2	1.8	1.3	2.9	2.4	2.1	0.1	1.3
Novosibirsk	Dec 25–Feb 07 / 01	43.6	1.7	6.7	2.2	5.9	2.7	1.1	1.5	0.3	2.0
	Mar 20–Apr 27 / 01	32.5	2.6	8.5	1.7	5.3	1.8	1.6	1.4	0.4	2.1
	Jun 19–Jul 20 / 01	60.9	1.4	8.4	1.6	3.6	1.9	2.4	1.5	0.2	1.7
	Sep 20–Oct 05 / 01	34.7	2.0	9.6	1.8	6.3	2.1	1.5	1.6	0.5	1.4
	Jan 22–Mar 05 / 02	31.5	1.5	5.0	2.0	5.4	2.0	0.9	1.8	0.3	1.6
	Apr 22–May 27 / 02	98.9	1.4	12.6	1.6	11.6	2.2	1.1	1.6	0.3	1.6
	Jun 20–Jul 31 / 02	69.8	1.4	7.6	1.3	4.6	1.4	1.7	1.4	0.2	1.2
	Sep 23–Nov 11 / 02	51.7	1.8	7.8	1.8	6.1	2.1	1.3	1.6	0.3	1.4

It can be seen from the Table that the maximum concentrations C_{or} and C_e are mostly observed in spring. The same trend is seen for the mass aerosol concentration in Novosibirsk and Klyuchi.

Due to high activity of the photochemical processes occurring in the atmosphere and the contribution of particles of soil-erosive origin to atmospheric aerosol, the values of $\tilde{N}_m$ and C_{or} in spring are, on the average, 2 to 3 times higher than in winter. Anthropogenic sources, such as heat electric power production plants and others, whose activity is intensified in winter, emit significant amounts of soot into the atmosphere, and therefore, in contrast to C_{or}, the values of C_e are minimum in summer and fall seasons.

Carbon is one of the basic components of the atmospheric aerosol. Thus, the fraction of total carbon in the aerosol mass is, on the average, 20–30%. In winter, the major fraction accounted for by inorganic carbon, and its concentration is twice as high as that of the organic carbon. In spring of 2001, the ratio C_e / C_{or} was equal, on the average, to 1.3.

The Table demonstrates quite high content of both organic and inorganic carbon in the urban aerosol. If at the rural sites the maximum concentrations for the two years of the study were 5.7 and 7.3 μg/m^3, respectively, then in Novosibirsk $\tilde{N}_{or}$ achieved 12.6 μg/m^3, while $\tilde{N}_{å}$ was as high as 11.6 μg/m^3.

The towns Klyuchi and Karasuk are situated far from intense industrial sources of pollution, and therefore they can be classified as rural regions, because natural atmospheric processes generate the atmospheric aerosol there.

Novosibirsk is a large industrial center with a great number of industrial plants and heavy traffic, which are the main sources of anthropogenic carbon.

The every-day sampling during a month has allowed us to draw and analyze the daily concentrations of organic and inorganic carbon. Figure 2 depicts the daily dynamics of C_e in Novosibirsk, its suburbs, and at the rural site Karasuk in winter of 2002.

It has been found that in some periods C_e sharply increases as compared to the mean value, which can be explained either by single emissions from local sources or by the common regional or, possibly, global source.

Figure 2 shows that in some periods, for example, February 3–6, 13, and 14 of 2002, C_e increased simultaneously at all sampling sites. Using the HYSPLIT model,[8] we have constructed the backward and forward trajectories of air masses at the altitudes of 50, 150, and 250 m.

The back trajectories shown in Figs. 3*a*, and *b* demonstrate that on February 3 and 4 the air masses had the northwestern direction and went from Tyumen and Omsk. On February 13 and 14 the trajectories changed the direction and went from southwest, namely, from Northern Kazakhstan (Figs. 3*c*, and *d*).

From Figs. 3*e*, and *f* it is seen that the forward trajectories drawn from Tyumen and Ekibastuz actually go along the studied observation sites, and on February 3, when the peak of C_e was observed in Karasuk, this site just lied in the zone of the stronger pollution than Klyuchi (Fig. 4*a*).

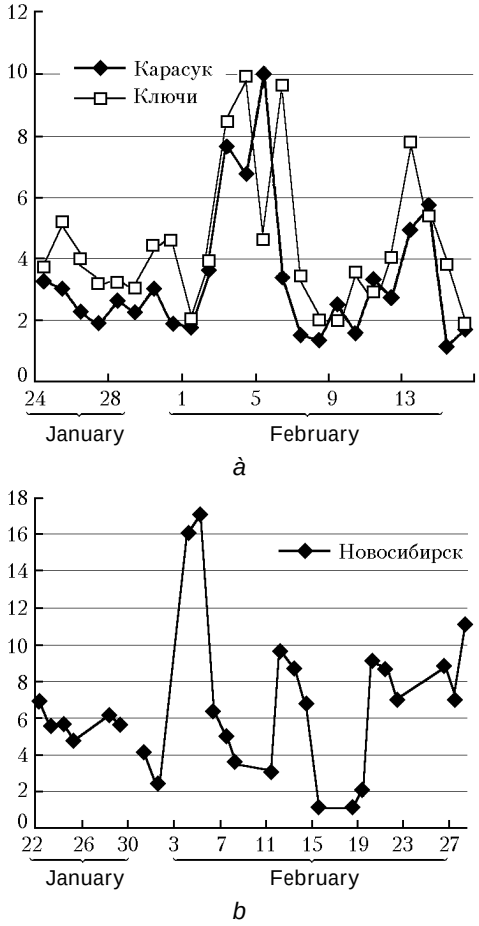


Fig. 2. Inorganic carbon concentration $\tilde{N}_{å}$ (μg/m^3) in 2002: Karasuk and Klyuchi (*a*); Novosibirsk (*b*).

From Fig. 4*b* it is seen that the decrease of C_e on February 4 in Karasuk is explained by its exit from the pollution zone. The suburb remained in the pollution zone, and C_e there was high in this period.

Other periods of high carbon content in the atmospheric aerosol were considered in a similar way. Thus, the Tyumen Region is the oil-and-gas province, and Ekibastuz lies in the coalfield, and the concentration fields shown in Fig. 4 suggest that the emissions from industrial enterprises of Tyumen and Ekibastuz reach the measurement sites and are the pollution sources of regional and global significance.

Note that the HYSPLIT model is used in this paper only to identify the possible source of pollution, and the emission rate of this sources is not considered here.

Conclusions

In this paper we have considered the seasonal and diurnal dynamics of the organic and inorganic carbon concentration on the regional scale.

The contribution of the total carbon to atmospheric aerosol in Novosibirsk Region amounts to 20–30%, while in the city of Novosibirsk it can achieve 50% in some periods.

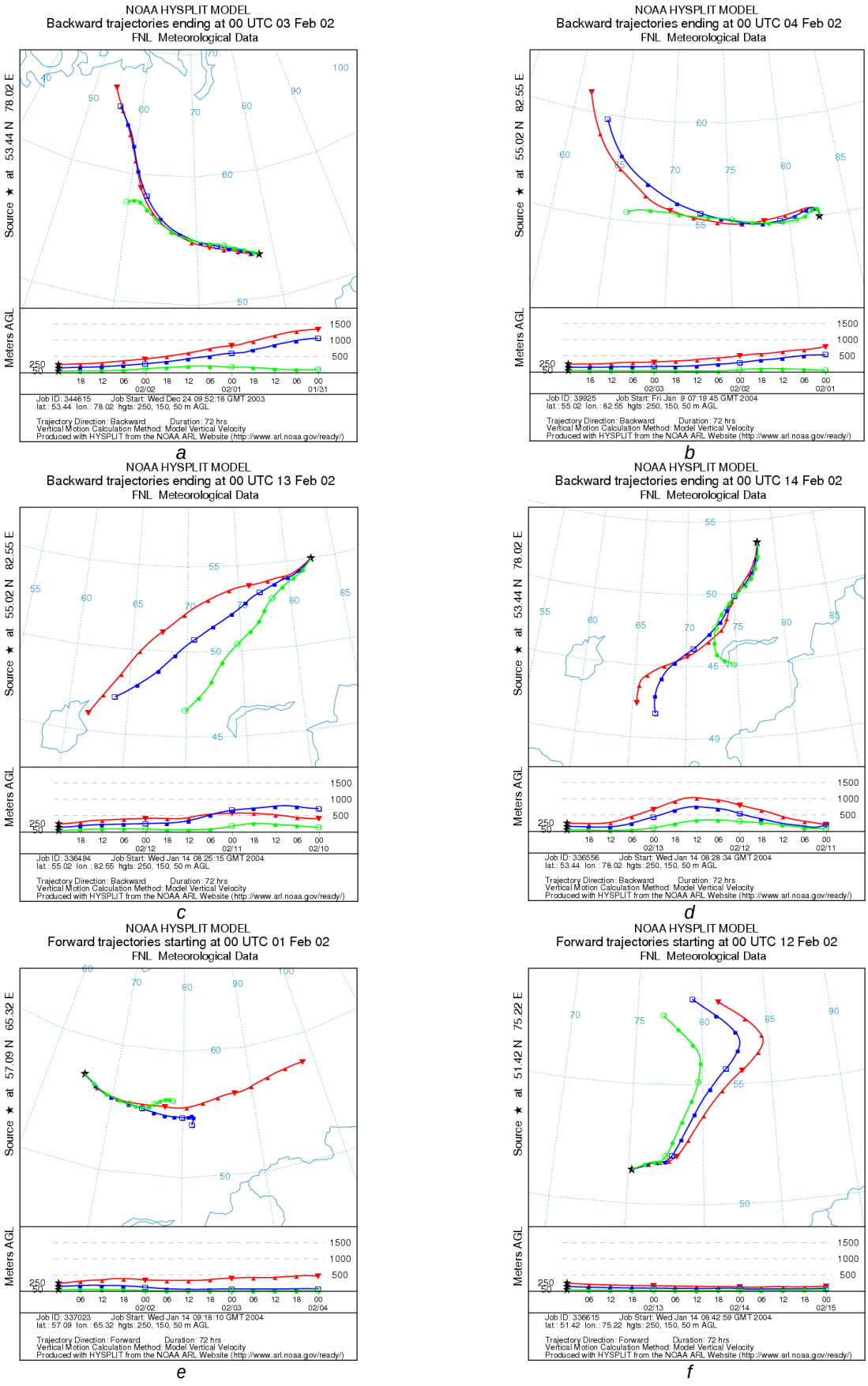
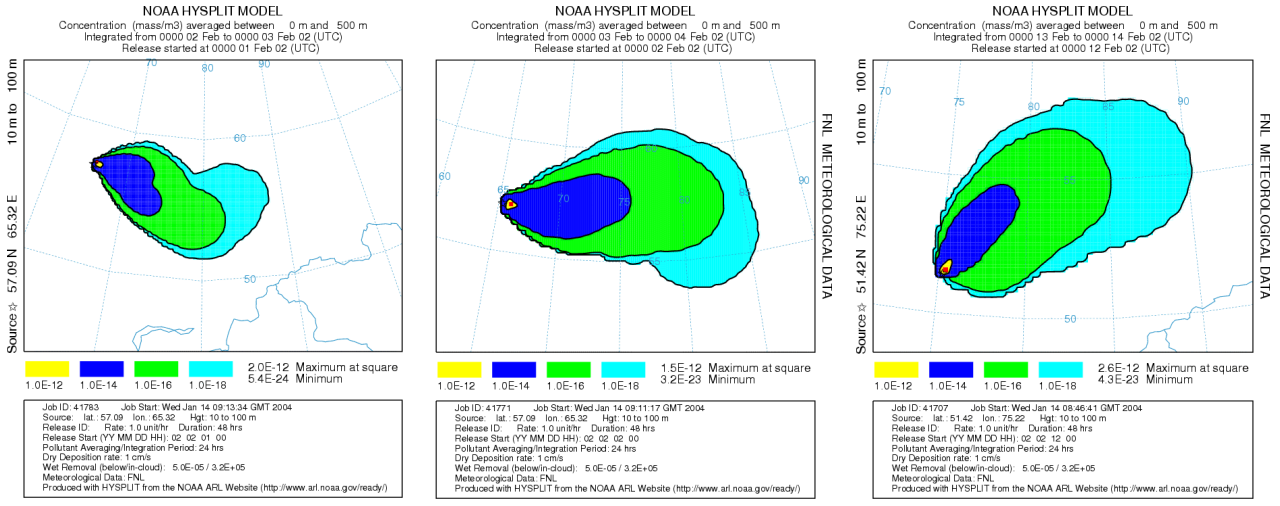


Fig. 3. Backward (*a*–*d*) and forward (*e*, *f*) air mass trajectories.



a *b* *c*

Fig. 4. Areas of spread of industrial pollution: Tyumen (*a*, *b*); Ekibastuz (*c*).

The HYSPLIT has been used to construct the air mass trajectories in order to analyze the effect of air mass transport on C_{or} and C_e in aerosol of the region under study and the concentration field for identification of the possible source of pollution.

It has been found that on February 3–6 and 13–14 of 2002 the possible sources of pollution were industrial enterprises of Tyumen and Ekibastuz.

Acknowledgments

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