Transformation of optical properties and microstructure of aerosol during smog episode in Beijing

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We analyze the optical characteristics and microstructure parameters of the submicron aerosol retrieved from spectronephelometric measurement data acquired during smog episode in Beijing occurred in November 2003. It was shown that the increase of the aerosol volume concentration during smog formation is caused mainly by the growth of particle size rather than number concentration. In the process of aerosol accumulation in the ground layer, its parameters undergo matched variations. Thus, the effective radius increases, while the width of the size spectra, particle refractive index, and relative soot content decrease.

Introduction

Beijing, one of the biggest megalopolises of the world, is characterized by both high level of the mean aerosol concentration and its significant variability. The aerosol content can increase by more than one order of magnitude during several days of smog episodes, which are usually interrupted by the change of air mass.

In recent years, Institute of Atmospheric Physics RAS in cooperation with the Institute of Atmospheric Physics CAS has been carrying out measurements of the aerosol optical characteristics on fall seasons in Beijing.[1] Observations are being carried out with a FAN, the aerosol nephelometer-polarimeter. The optical characteristics measured with a FAN nephelometer enable us to estimate the parameters of microstructure of the submicron aerosol fraction, which is the main constituent of urban smog.[2] In the present study, the peculiarities of the aerosol optical and microphysical characteristics during the smog episode observed in Beijing since November 11 and until November 14, 2003, are analyzed.

In contrast to Ref. 2, the aerosol microstructure in submicron range was determined using the data of spectropolarimetric measurements by solving the inverse problem. Let us note that the range of particle size of the order of some tenth of micrometer, which makes the greatest contribution to scattering, is the boundary for particle counters (upper boundary for mobility analyzers and lower boundary for photoelectric counters). However, it is the range where the particle size distribution is reconstructed most accurately by solving the inverse problem.

Instrumentation and measured characteristics

Aerosol optical properties were measured with a FAN, the nephelometer-polarimeter instrument. The FAN nephelometer is capable of measuring coefficients of directional light scattering D at the scattering angle of 45° and at three wavelengths, 410, 510, and 630 nm, and two its orthogonally polarized components $D_{\parallel}$ and $D_{\perp}$ at the scattering angle of 90° and wavelengths of 450 and 520 nm. The measurements were carried out in two modes. In a routine mode, the directional scattering coefficient $D(45°, 510\ \text{nm})$ was recorded continuously. Several times a day (usually once an hour or two), all seven parameters were measured. These data are analyzed in this paper. The aerosol characteristics measured with a FAN nephelometer are close to those of the aerosol dry fraction. In parallel with the nephelometric measurements, aerosol samples were collected on fiber filters for further analysis of Black Carbon (BC) content using the extinction measurement technique. Measurements were carried out in the building of the Institute of Atmospheric Physics situated in the northern part of the city.

Variations of the optical characteristics in the smog episode

Analysis of the 5-day back trajectories of air masses at the level of 925 mbar shows that on November 10 (before the development of the smog event) and on November 15 (after cleaning of the atmosphere over Beijing) those originated from over Kazakhstan. At the same time, trajectories on November 12 and 13 originated from near the coast of East Chinese and Yellow Seas and passed over densely populated regions of central and western parts of China. Dramatic decrease of the aerosol content in the night from 14 to 15 of November is related to coming of air mass, the 5-day back trajectory of which originated from over the northeastern regions of China.

Let us consider the behavior of the directional scattering coefficients at the angle of 45°, the degree

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of linear polarization P at the angle of 90°, the ratio R of the directional scattering coefficients at the angles of 45 and 90° at green wavelength, as well as the ratio A of the directional scattering coefficients at blue and red wavelengths as the main parameters characterizing the change of quantitative and qualitative aerosol optical properties. Increase of the atmospheric turbidity began in the afternoon on November 11 from the values $D(45°, 510\ \text{nm})$ about 0.02 $\text{km}^{-1} \cdot \text{sr}^{-1}$. The degree of linear polarization at this time was approximately 0.25, and the ratio $D(45°)/D(90°)$ was of the order of 5.5. The directional scattering coefficient in maximum developed smog in the evening on November 14 reached the value of 0.4 $\text{km}^{-1} \cdot \text{sr}^{-1}$. The degree of linear polarization decreased to the value of 0.1, the value R increased up to 7, and A decreased from 1.6–1.7 to 1.2–1.3. Time behavior of the parameters considered is shown in Fig. 1, where the matched time variations of quantitative (D) and qualitative (P, R, A) parameters are seen.

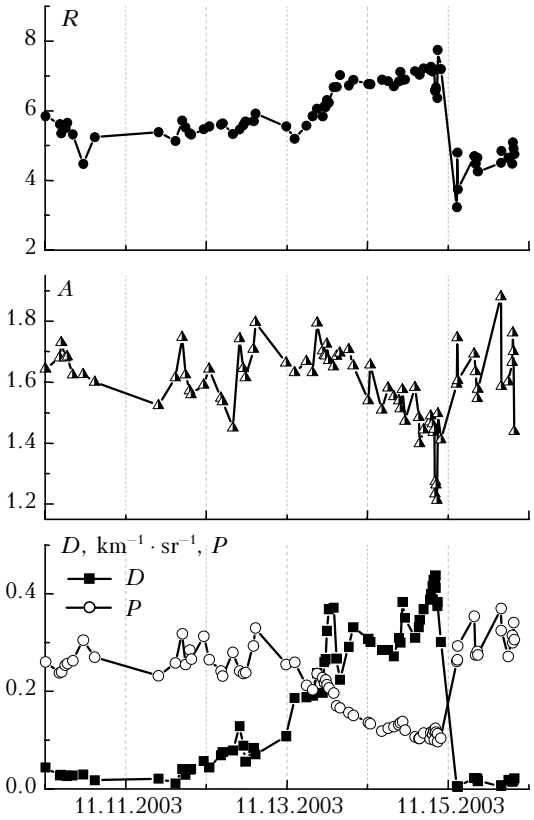

Fig. 1. Time behavior of the aerosol optical characteristics.

The optical characteristics considered well correlate with each other (Fig. 2). The only exception is the absence of noticeable correlation between R and A. Matched variations of the optical parameters are, evidently, the result of transformation of the parameters of aerosol microstructure. In order to reveal the peculiarities in the variations of the aerosol microphysical characteristics at smog formation, the measured optical characteristics were inverted to the aerosol particle size spectrum in the submicron range.

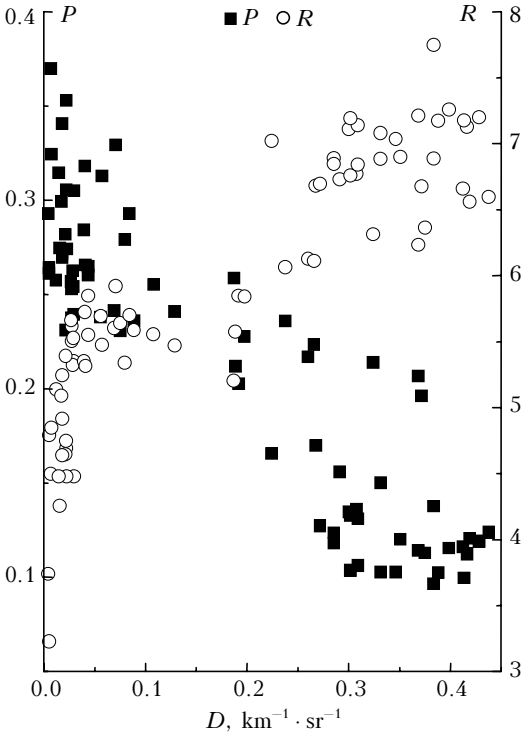

Fig. 2. Correlation between the directional scattering coefficient $D(45°, 510\ \text{nm})$ and the degree of linear polarization P and the ratio $D(45°, 510\ \text{nm})/D(90°, 510\ \text{nm})$.

Technique for solving the inverse problem

The measured aerosol optical characteristics were inverted to aerosol size distributions using the iterative technique, close to that by Twitty.[3,4] Analysis of the structure of the kernels of the integral equations relating the measured and reconstructed characteristics, as well as the numerical experiments with model size distributions showed that the particle size distribution could be retrieved most reliable in the radius range from 0.05 to 0.6 μm.[4] The set of parameters measured with a FAN is insufficient for separate estimation of the real n and imaginary κ parts of the refractive index, so the inverse problem was solved assuming $\kappa = 0$. The real part of the refractive index was chosen using the criterion of the minimum of the norm of the second derivative of the logarithm of the retrieved size distribution with respect to the particle radius.

The rms deviations of the measured optical characteristics from those calculated using the reconstructed size spectrum were usually a few percent. If the rms deviations had exceeded 5%, the measurement was rejected and excluded from further consideration. The following parameters of the reconstructed size distributions were calculated:

total cross section of submicron aerosol particles in a unit volume:

$$S = \int_{0.05}^{0.6} (\mathrm{d}S/\mathrm{d}r)\,\mathrm{d}r, \qquad (1)$$

volume concentration:

$$V = \frac{4}{3}\int_{0.05}^{0.6} r(\mathrm{d}S/\mathrm{d}r)\mathrm{d}r, \quad (2)$$

the effective radius:

$$r_{\mathrm{eff}} = 0.75V/S \quad (3)$$

and the content of BC, normalized to the volume concentration of submicron aerosol:

$$C_{\mathrm{BC}} = V_{\mathrm{BC}}/V,$$

where $\mathrm{d}S(r)/\mathrm{d}r$ is the cross section size distribution, V_{BC} is the volume concentration of BC, recalculated from the data on the mass concentration assuming that the density of the BC component is 1.8 g/cm^3. The use of the integral parameters S, V, r_{eff}, and C_{BC} makes it possible to follow up the variations of both qualitative and quantitative characteristics of the aerosol microstructure.

Transformation of the aerosol microstructure

Time dependences of the refractive index, volume concentration, effective radius and the BC fraction are shown in Fig. 3, and the mean values of these parameters are presented in Table 1.

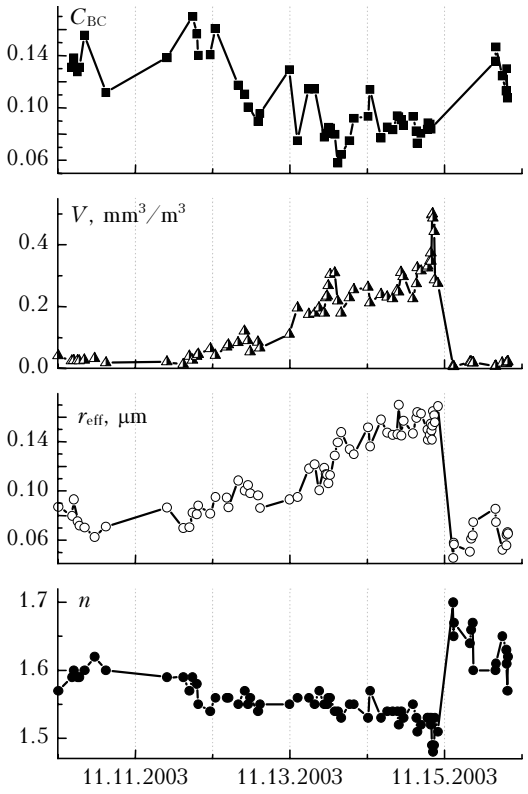

Fig. 3. Temporal behavior of the parameters of aerosol microstructure.

Accumulation of aerosol in the near-ground layer, which began on November 11 and was interrupted by the change of air mass on the night from 14 to 15 of November, was accompanied by matched variations of all microphysical characteristics of the aerosol. Thus the effective radius of particles increased, while the refractive index and the BC fraction decreased. The maximum value of the extinction coefficient calculated by solving the inverse problem reached 3.6 km^{-1} that corresponds to the visibility range close to 1 km. The volume concentration of the submicron aerosol fraction increased since November 10 and until November 14 by more than one order of magnitude. This increase is caused, first of all, by growth of the aerosol particles — the effective particle size increased approximately twofold. The refractive index decreased from 1.6 to 1.52.

Table 1. Daily mean values of the aerosol microphysical parameters

Date, November, 2003	10	11	12	13	14	15
r_{eff}, μm	0.076	0.080	0.096	0.12	0.15	0.062
n	1.6	1.57	1.56	1.55	1.52	1.63
V, mm^3/m^3	0.026	0.035	0.079	0.22	0.32	0.014
C_{BC}	0.13	0.15	0.11	0.083	0.088	0.13

As the turbidity increased, the tendency toward a decrease of the BC fraction was observed. The parameters of microstructure recovered to the background values after the change of air mass. Time variation of the particle size distribution is shown in Fig. 4 where the daily mean distributions $\mathrm{d}V/\mathrm{d}r$ are presented.

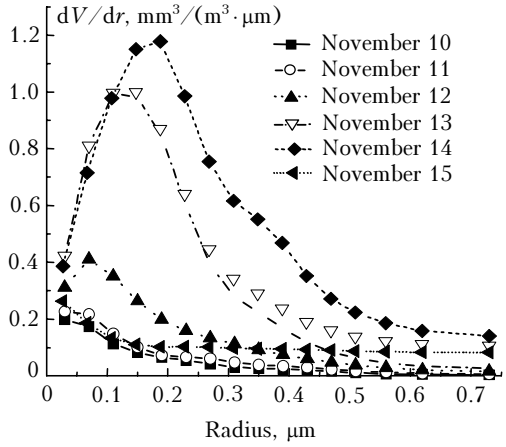

Fig. 4. Daily mean aerosol size spectra.

The distributions observed on November 10–12 and 15 can be approximated by the sum of two lognormal curves, and the only fraction becomes prevalent on November 13 and 14.

Parameters of the lognormal approximation are presented in Table 2, where r_i are the median radii of the number density distributions; N_i are the number densities; ν_i are the standard deviations of the logarithm of radius.

Table 2. Parameters of the approximating lognormal distributions

Date, November, 2003	10	11	12	13	14	15
ν_1	0.8	0.74	0.75	0.63	0.62	0.69
r_1, μm	0.012	0.016	0.021	0.052	0.07	0.013
N_1, 10^3 cm^{-3}	200	145	141	68	40	210
ν_2	0.48	0.47	0.46			0.5
r_2, μm	0.155	0.164	0.19			0.15
N_2, 10^3 cm^{-3}	0.22	0.3	0.3			0.16

Examples of the lognormal approximation are shown in Fig. 5.

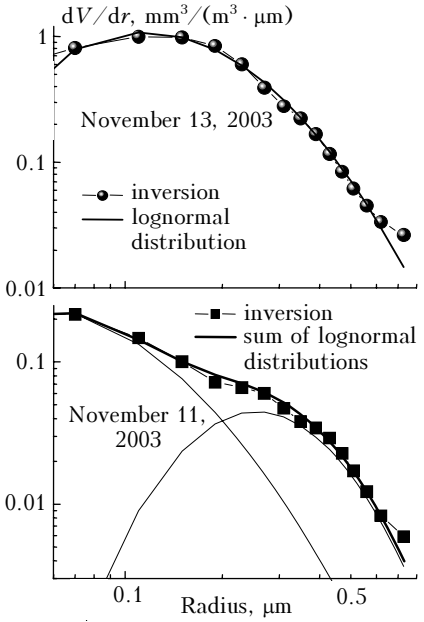

Fig. 5. Lognormal approximation of the particle size distributions.

As follows from Tables 1 and 2, the increase of turbidity is accompanied by a decrease of the parameter of the distribution width and the number density of the approximating distribution. Nevertheless, the number density in the optically active range had the tendency toward increase starting from November 11 until November 13, and decreased only on November 14.

Conclusions

Analysis of transformation of optical and microphysical characteristics of submicron fraction of the near-ground aerosol in the smog episode in Beijing shows that the increase of the aerosol volume concentration was caused first of all by the increase of the effective radius of particles, and not of their number density.

Particle growth was accompanied by narrowing of the particle size distribution, as well as by a decrease of the refractive index and the BC fraction content.

In our opinion, these results are evidence of the important role of the processes of heterogeneous condensation and coagulation in the development of the smog formation.

Acknowledgments

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