

Determination Of Nitrogen Compounds In Atmospheric Air and Aerosol Samples During The First Zvenigorod Winter Cloudiness-Aerosol-Radiation Experiment

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Introduction

Minor nitrogen constituents are chemically active and therefore can indirectly affect atmospheric radiation processes via influence on ozone content and formation of tropospheric aerosols and clouds (Laaksonen et al. 1997; Makar et al. 1998, Brasseur et al. 1999). Furthermore, large NO₂ contents in the lower troposphere observed during thunderstorms or pollution episodes can result in noticeable absorption of downwelling radiation corresponding to estimated local radiative forcing up to 20 W/m² to 30 W/m² (Solomon et al. 1999).

Most intensive and frequent episodes of large lower troposphere NO₂ contents are characteristic of wintertime (Elokhov and Gruzdev 1995). Due to longer nights, winter is also auspicious for heterogeneous chemistry with participation of nitrogen oxides (Makar et al. 1998; Brasseur et al. 1999). During the first winter radiation-aerosol-cloudiness experiment at Zvenigorod Scientific Station (ZSS) of the Institute of Atmospheric Physics in February 1999 and during a month after it, samples of submicron atmospheric aerosols were collected, accompanied by measurements of atmospheric nitrogen oxides contents. The purpose of this work was to search for the relationship of the presence of nitrogen compounds in atmospheric aerosols with pollution of the lower troposphere by nitrogen oxides.

Instruments and Methods of Measurements

Atmospheric aerosols from the near-surface layer (3-m height above the earth surface) were deposited by a cascade impactor on germanium plates transparent in the infrared. At air expenditure through the impactor of 15 l/min, collection of one sample of submicron aerosols took from 16 hours to 30 hours (with interruptions) depending on atmospheric aerosol contents and weather conditions. After aerosol samples had been collected, 8 cm⁻¹ resolution transmittance spectra of the aerosol samples (on the plates) and germanium plates in 500 cm⁻¹ to 5000 cm⁻¹ wave number range were obtained with the use of a two-beam spectrophotometer UR-20, to identify molecular composition of aerosols. Only submicron aerosol samples were analyzed.

Volume mixing ratios of NO and NO₂ at a 10-m height were measured continuously with an analyzer AC-30M having the measuring threshold of 2 ppbv. Despite the fact that only relatively large NO_x

contents in excess of 1 ppbv can be detected, smaller contents could also be obtained from measurements after time averaging due to the small characteristic time of the instrument (50 s).

These measurements were added by measurements of column tropospheric NO₂ contents in daytime with the help of a zenith-viewing grating spectrometer MDR-23 scanning in the 435 nm to 450 nm wavelength range. Twilight NO₂ measurements allow retrieving NO₂ vertical distribution in the stratosphere and estimating NO₂ contents in the near-surface layer, lower and upper troposphere (Elokhov and Gruzdev 1995, 1998). In daytime measurements during the experiment, the tropospheric column NO₂ contents were obtained by subtracting the stratospheric NO₂ content obtained at unpolluted troposphere conditions (on days before and after a pollution episode) from the total column NO₂ contents. Ten years of systematic NO₂ measurements at ZSS show that in pollution episodes the near-surface layer is usually more abundant in NO₂ than the above tropospheric layers.

Results of Measurements

During the two months of measurements (February-March 1999) the NO₂ content in the atmospheric near-surface layer varied from near zero values to values typical for pollution episodes (about 10 ppbv). Figure 1 shows examples of NO₂ vertical profiles obtained from evening twilight measurements on February 5 and 14, representative for the unpolluted and polluted lower troposphere, respectively. NO₂ concentration in the polluted near-surface layer can exceed the NO₂ concentration in the stratospheric NO₂ maximum by as much as an order of magnitude. Even larger (in excess of two orders of magnitude) NO₂ contents are usual (Elokhov and Gruzdev 1995).

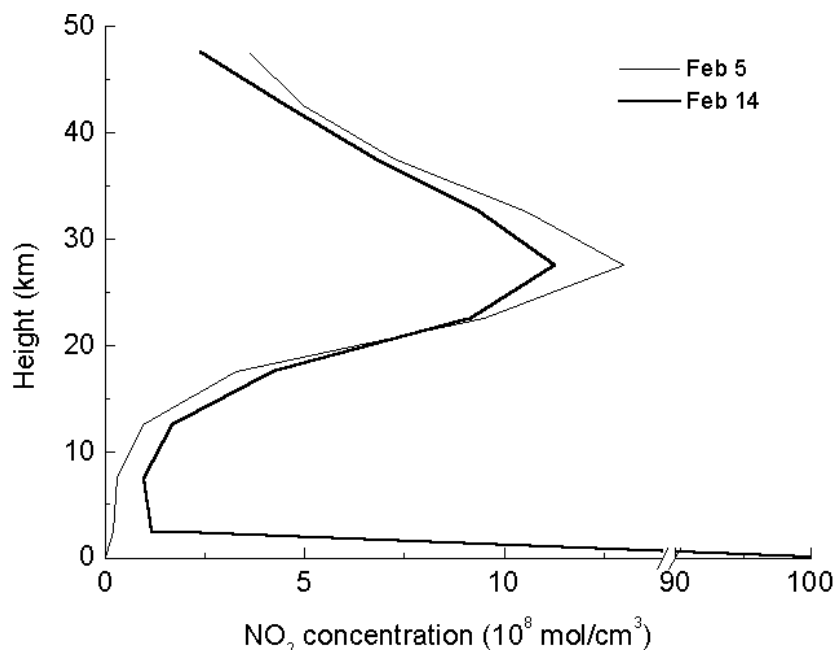


Figure 1. NO₂ vertical profiles obtained from evening twilight spectrometric measurements on February 5 and 14, representative for the unpolluted and polluted lower troposphere, respectively.

Figure 2 shows examples of transmittance spectra of some aerosol samples. All the spectra, including those not shown, exhibit absorption bands, which are characteristic of ammonium NH_4^+ (around 3100 cm^{-1} and 1400 cm^{-1}) and sulfates SO_4^{2-} (near 1080 cm^{-1} and 615 cm^{-1}). Also, some spectra exhibit absorption bands near 1320 cm^{-1} . Absorption near 1320 cm^{-1} can be related to a vibration frequency of chemical bond $\text{HO}-\text{NO}_2$, while for absorption bands of nitrates different authors indicate 1340 cm^{-1} to 1420 cm^{-1} range, with position of centers of the bands depending on nitrate (Nakamoto 1986). We can therefore conclude that the collected aerosol samples are likely to contain nitric acid. In support of this fact, when transmittance spectra were measured repeatedly in ten months after the experiment, they did not contain any sign of 1320 cm^{-1} band.

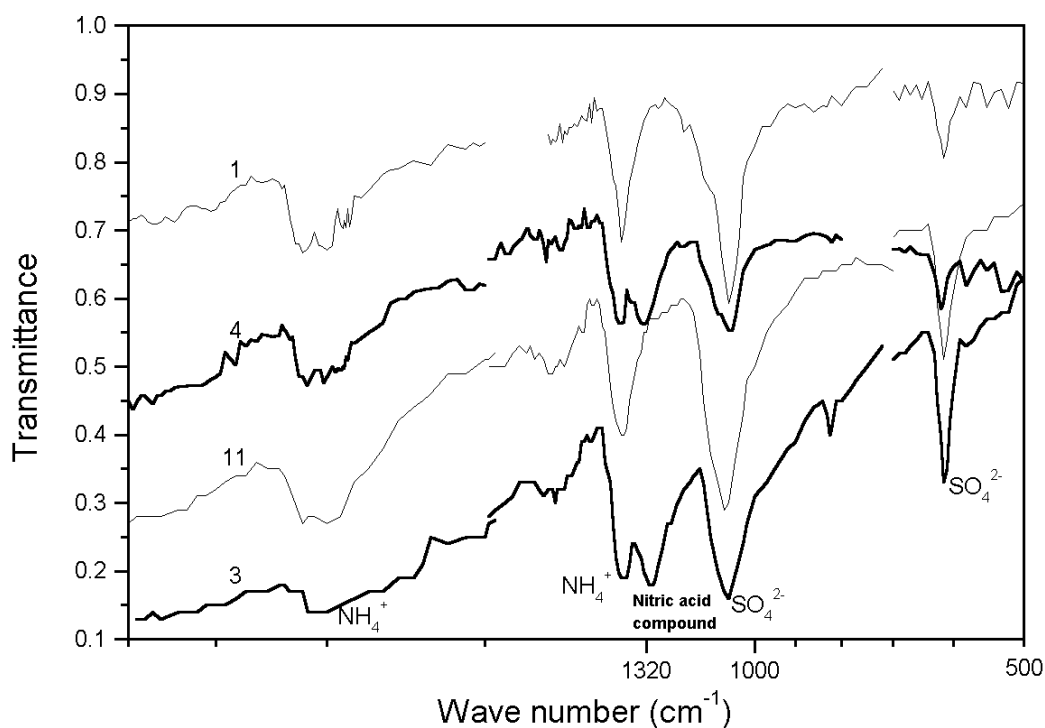


Figure 2. Examples of transmittance spectra of aerosol samples 1, 3, 4, and 11. See Figure 3 to identify time of collecting the samples.

During the two months, 16 aerosol samples were obtained. All the samples contain ammonium sulfate. Six transmittance spectra have a clear 1320 cm^{-1} absorption band, while in seven samples we did not find any sign of nitric acid compounds (NAC). Three of the spectra contain signs of the presence of NAC, but we cannot distinctively distinguish the NAC contribution.

Figure 3 shows results of NO_x measurements for the two months, superimposed in the upper parts of the plots using information from collected submicron aerosol samples. The aerosol samples are successfully numbered and vertical segments show the time of beginning and end of collecting of samples. Samples presumably containing nitric acid are marked by black (samples 3, 4, 6, and 14 through 16), three samples (7, 12, and 13) containing only signs of NAC are marked out by gray, and samples not containing any sign of NAC (1, 2, 5, 6, 8, 10, and 11) are not marked out by any color. Figure 3a presents

hourly mean mixing ratios of NO_2 (solid curve) and NO (dotted curve) in the near-surface air. In Figures 3b-3d, only NO_2 and NO values are retained that correspond to the time intervals when aerosol samples were collected. The values corresponding to aerosol samples without NAC are marked by open squares, while the values corresponding to aerosol samples containing nitric acid or exhibiting signs of NAC are marked by drop lines. Figure 3b shows hourly mean NO_2 mixing ratios, Figure 3c presents 15-min mean column tropospheric NO_2 contents obtained from spectrometric zenith-sky measurements, and Figure 3d shows hourly mean NO mixing ratios.

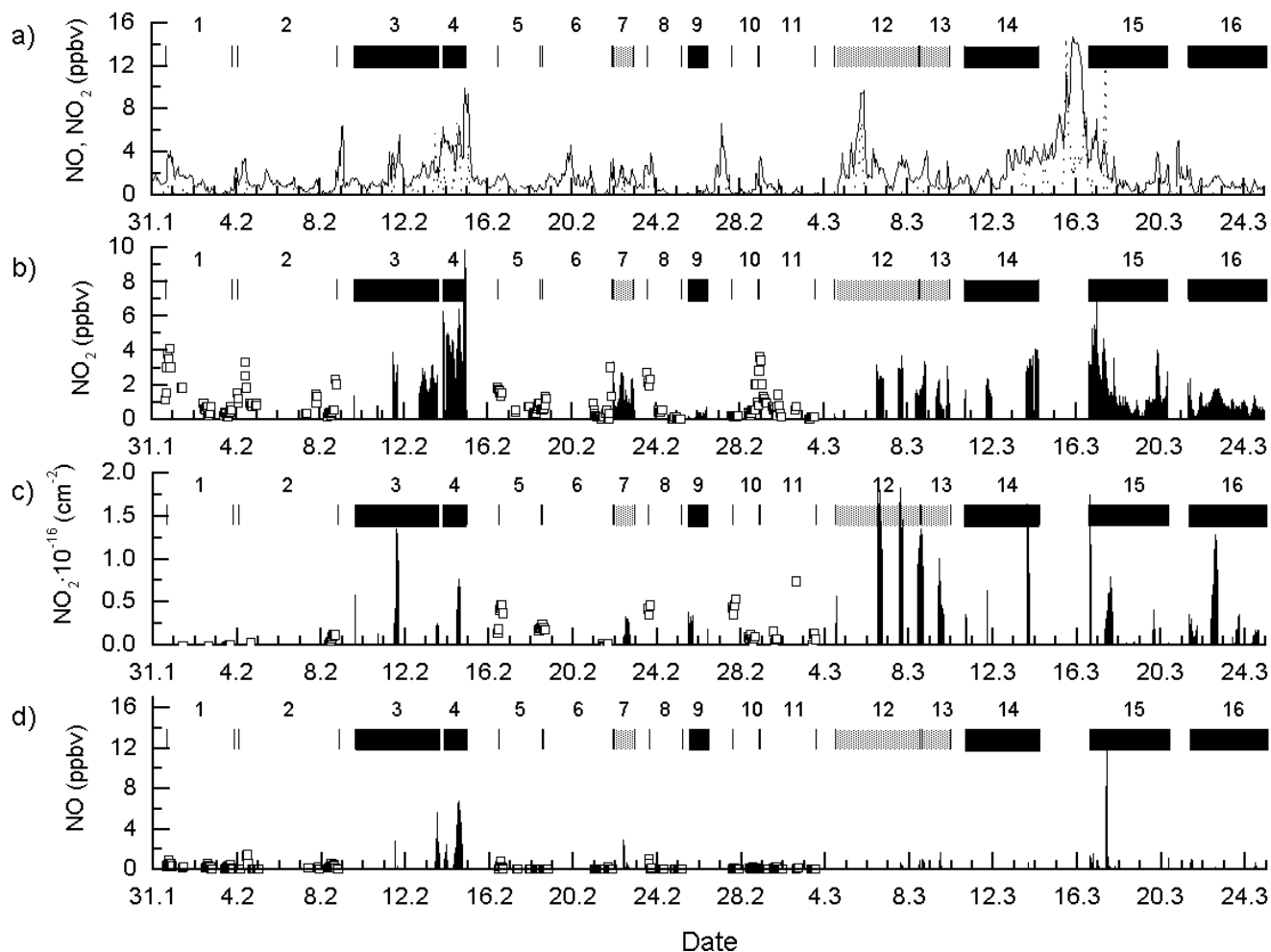


Figure 3. Results of NO_x measurements superimposed by information about collected submicron aerosol samples (numbered; see text for more explanation): a) hourly mean mixing ratios of NO_2 (solid curve) and NO (dotted curve) in the near-surface air; b) hourly mean NO_2 mixing ratios; c) 15-min mean column tropospheric NO_2 ; and d) hourly mean NO mixing ratios. In Figures b-c only NO_x values are retained corresponding to time intervals when aerosol samples were collected. Drop lines and open squares mark out NO_x values corresponding to aerosol samples with and without nitric acid compounds, respectively.

It is worth noting that large near-surface NO₂ mixing ratios always correspond to large column tropospheric NO₂ contents, but the reverse is not true. For example, large NO₂ mixing ratios on February 4 and 28 were observed at near-zero column tropospheric NO₂ abundance and, therefore, were localized near the surface and could be originating from local sources. Therefore, column tropospheric NO₂ is more representative of assumed processes relating chemical composition of aerosols to NO_x pollution.

Analysis of Figure 3 shows that NAC has been found only in aerosol samples collected during periods that include episodes of enhanced column tropospheric NO₂ contents. This implies a possible relation of aerosol NAC to pollution of the atmosphere by nitrogen compounds, more definitely, to large contents of nitrogen dioxide.

Conclusions and Deductions

Large NO_x contents peculiar to pollution episodes can be an important factor influencing composition of atmospheric aerosols, which can result in changes of microphysical and radiative properties of aerosols. Taking into account that lower tropospheric NO₂ in pollution can also contribute to absorbing solar radiation, one could expect additional radiation forcing related to NO₂, at least at regional scales. We can deduce therefore that aerosol, radiation, and climate models should take into account these NO₂ effects.

Acknowledgments

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