Observation of tropospheric NO_2 by airborne multi-axis differential optical absorption spectroscopy in the Pearl River Delta region, south China*

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An airborne multi-axis differential optical absorption spectroscopic (AMAX-DOAS) instrument was developed and applied to measure tropospheric NO_2 in the Pearl River Delta region in the south of China. By combining the measurements in nadir and zenith directions and analyzing the UV and visible spectral region using the DOAS method, information about tropospheric NO_2 vertical columns was obtained. Strong tropospheric NO_2 signals were detected when flying over heavilly polluted regions and point sources like plants. The AMAX-DOAS results were compared with ground-based MAX-DOAS observations in the southwest of Zhuhai city using the same parameters for radiative transport calculations. The difference in vertical column data between the two instruments is about 8%. Our data were also compared with those from OMI and fair agreement was obtained with a correlation coefficient R of 0.61. The difference between the two instruments can be attributed to the different spatial resolution and the temporal mismatch during the measurements.

Keywords: air pollution, tropospheric NO_2, airborne multi-axis differential optical absorption spectroscopy, vertical column

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1. Introduction

Nitrogen dioxide NO_2 is one of the most important trace gases in the atmosphere. In the troposphere, its photolysis leads directly to the formation of ozone. High concentrations of NO_2 are harmful for vegetation and human health. Observing NO_2 in the troposphere is vital for the control of atmospheric pollution.

Differential optical absorption spectroscopy (DOAS)[1,2] of scattered solar radiation is a widely used technique to measure trace gases in the atmosphere, e.g., NO_2 and O_3. By analyzing their unique optical absorption structures, information about atmospheric absorbers along the light path can be retrieved. *In situ* measurements of NO_2 in the troposphere are carried out by means of a variety of detectors, both instruments on the ground and airborne platforms. Ground-based multi-axis DOAS (MAX-DOAS) is a technique that allows us to derive atmospheric NO_2 column densities and profiles.[3–7] Since 1995, detection of tropospheric amounts of NO_2 via GOME satellite measurements have yielded unprecedented information by providing a global view.[8–11] Since August 2002, similar measurements are performed by the scanning imaging absorption spectrometer for atmospheric cartography (SCIAMACHY) instrument on board ENVISAT with improved spatial resolution.[8] The ozone monitor instrument (OMI), operating on board the NASA Earth observing system (EOS) Aura satellite, was launched on 19 June 2004. The spatial resolution of OMI exceeds that of previous instruments. Instruments on board satellites can provide information about atmospheric trace gases on a global or regional scale, but they have difficulties in making out local pollution sources. Airborne UV/visible spectrometers have been used in the past to study stratospheric[12,13] and tropospheric[14–18] trace gases. Several successful attempts have been made to validate tropospheric NO_2 detection results from space borne instruments by comparing those from airborne instruments.[11,19,20] We developed an airborne multi-axis DOAS (AMAX-DOAS) instrument for the observation of tropospheric trace gases, such as NO_2, SO_2, and HCHO in China. Using both spectra from zenith and nadir directions, information on tropospheric trace gases can be retrieved. Combining airborne multi-axis DOAS measurements with radiative transfer calculations, this method has the potential to provide vertical information on trace gases or even their profiles and thus may be used to validate products retrieved from satellite data.

In this study, the AMAX-DOAS instrument was developed and applied to measure tropospheric NO_2 in the Pearl River Delta region of China. AMAX-DOAS measurements taken on 10 December 2008 have been analyzed with respect to NO_2. Combining the DOAS slant column density (SCD) of NO_2 with air mass factors (AMFs) calculated by the ra-

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diative transfer model SCIATRAN,[21] NO_2 tropospheric vertical columns were derived and compared with ground-based observations by a MAX-DOAS instrument located in Zhuhai, and good agreement was found. The airborne results were also compared with those from OMI, and fair agreement was obtained, with a correlation coefficient R of 0.61.

2. Methodology

The retrieval method we used in this study is the well-established differential optical absorption spectroscopy (DOAS) method, a successful spectroscopic technique for the simultaneous detection of trace gases in the atmosphere. The basis of DOAS is the Lambert–Beer law, which here takes the form

$$\ln \frac{I(\lambda,\sigma)}{I_0(\lambda)} = -\sum_i \sigma_i(\lambda,T) \int c_i(l)\,\mathrm{d}l + P(\lambda), \tag{1}$$

where $\sigma_i(\lambda,T)$ is the absorption cross section of the specific trace gas (i) and $c_i(l)$ is the corresponding concentration along the light path. A polynomial $P(\lambda)$ is added to account for slowly varying extinction such as Rayleigh scattering and Mie scattering. The slant column density (SCD) $\int c(l)\,\mathrm{d}l$ represents the mean integrated concentration over all possible lights paths and usually has to be calculated numerically by a radiative transport model. The measured differential optical density is fit to the known differential absorption cross section to obtain the differential SCD (dSCD). The DOAS analysis of our AMAX-DOAS data for the 10th December 2008 was carried out using the WinDOAS software.[23] In the NO_2 fits, the spectral window of 360–387 nm was selected. We took into account the NO_2 cross section at 293 K,[24] the O_3 cross sections at 293 K and 221 K,[25] and the O_4 cross section at 296 K.[26] Furthermore, a Fraunhofer reference spectrum and a Ring spectrum calculated from the Fraunhofer spectrum using the DOASIS-software[27] and the Ring spectrum was included in the fits to account for the "filling in" of the Fraunhofer lines due to rotational Raman scattering.[28] Prior to the fits, all the cross sections used in the fits were convoluted with the instrumental slit functions. For each viewing direction, references were taken for all telescopes of different directions when the solar zenith angle was small and the aircraft was over a clean area. Figure 1 shows an example of a DOAS fit for the spectrum recorded in the nadir direction taken at 12:08 LT on the 10th December 2008. The NO_2 dSCD for this example is about 9.61×10^{16} molec·cm^{-2}, with a residual rms value of 2.57×10^{-3}.

To derive the tropospheric columns, the stratospheric signal has to be subtracted from the total column. In our calculations, Fraunhofer reference spectrums for each direction were taken over a clean air area where we assume that the tropospheric signal in the zenith direction can be neglected, and the tropospheric NO_2 information can be retrieved by subtracting the part in the reference spectrum. The stratospheric NO_2 columns vary slowly with solar zenith angles, so in our calculation, a linear fit to the minima over Zengcheng and northwest of Shenzhen was used to correct the stratospheric variation.

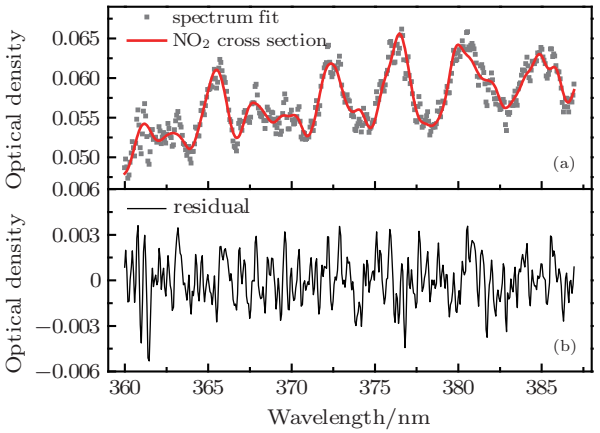


Fig. 1. (color online) Example of a DOAS fit for the spectrum in the nadir direction taken at 12:08 LT on the 10th December. (a) The DOAS fit for NO_2, (b) the residual for NO_2 fit.

The dSCD obviously depends on the light path through the atmosphere to the detector and therefore on such parameters as the solar angles, aerosol load and surface albedo. For a better comparison with other observations, the dSCD is commonly converted to the vertical column density (VCD), which can be expressed as

$$\mathrm{VCD} = \int_0^H c(z)\,\mathrm{d}z, \tag{2}$$

where z stands for the altitude above the ground, and c is the concentration of the trace gas. Furthermore, the so called air mass factor (AMF), which can be expressed as

$$\mathrm{AMF} = \frac{\mathrm{SCD}}{\mathrm{VCD}}, \tag{3}$$

is introduced as the ratio between SCD and VCD and hence contains all the light path dependency. It describes the sensitivity of the instrument for a trace gas under given atmospheric conditions. The tropospheric NO_2 dSCD can be converted to a VCD by dividing through appropriate tropospheric AMF. In this study, the AMF was calculated by the radiative transfer model SCIATRAN.

In order to retrieve the tropospheric NO_2 VCD, we used the following formula and calculated the tropospheric VCD as[22]

$$\begin{aligned}\mathrm{VCD}_{\mathrm{trop}} &= \frac{\mathrm{SCD}_{\mathrm{trop}}(\alpha)}{\mathrm{AMF}_{\mathrm{trop}}(\alpha)} = \frac{\mathrm{dSCD}(\alpha) - \Delta\mathrm{SCD}_{\mathrm{strat}}(\mathrm{SZA})}{\mathrm{AMF}_{\mathrm{trop}}(\alpha)} \\ &= \frac{\mathrm{dSCD}_{\mathrm{trop}}(\alpha)}{\mathrm{dAMF}_{\mathrm{trop}}(\alpha)},\end{aligned} \tag{4}$$

where $\mathrm{SCD}_{\mathrm{trop}}(\alpha)$ is the tropospheric NO_2 SCD, $\mathrm{SCD}_{\mathrm{strat}}(\alpha)$ is the stratospheric NO_2 SCD, $\mathrm{dSCD}(\alpha)$ is the differential SCD for a given viewing direction given at angle α, and $\Delta\mathrm{SCD}_{\mathrm{strat}}(\mathrm{SZA})$ represents the correction for the stratospheric part.

3. Instrument and measurements

Three telescopes were used in our measurement to capture light from the nadir, zenith and 10° below the horizontal plane of the aircraft, as sketched in Fig. 2. Three UV spectrometers, each covering the wavelength range from 290 nm to 420 nm, are separately connected to the three telescopes through quartz fibers. The spectral resolutions of the spectrometers are 0.56 nm. For our calculations, the three directions are defined as 0° for nadir, 180° for zenith, and 80° for the viewing direction of 10° below the horizon (see Fig. 2). Each spectrometer records one spectrum per second, so that, in principle, the signals from different directions can be detected simultaneously. However, in reality, the integration times of the spectrometers are different. For an altitude of about 3 km, the spatial resolution is about 70 m along the flight track and 2.6 m across the flight track.

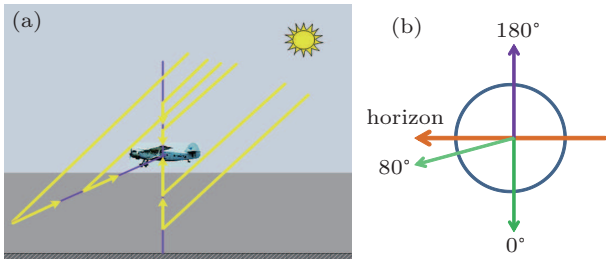


Fig. 2. (color online) Schematic sketch of our air borne MAX-DOAS observation geometry.



Fig. 3. (color online) The flight track on 10th December 2008.

Our airborne MAXDOAS instrument was used for the first time to observe tropospheric NO_2 in the Pearl River Delta region on the 10th, 11th, and 15th December 2008. On the 10th December 2008, the fight track of Y-5 aircraft started from Zhuhai airport (22.0 °N, 113.37 °E, on Sanzao Island) at 11:00 LT, lead to Zhuhai at 11:20 LT, then to Shenzhen at 12:10 LT, to Dongguan at 13:00 LT, to Zengcheng at 14:00 LT, to Humen plant at 15:10 LT, and back to Zhuhai airport at 16:00 LT (see Fig. 3 for a sketch of the flight track). On this day, the sky was generally clear with visibility about 5–18 km and the wind direction was from the North with a speed of about 15 km/h. The temperature was about 12°C. After ascent, the Y-5 aircraft kept cruising at 3 km altitude.

4. Results and discussion

In Fig. 4(a), the NO_2 dSCD retrieved from the nadir and zenith directions for the 10th December are shown. In the nadir viewing direction, increased NO_2 signals were detected over regions indicated by labels I, II, III, and V in Fig. 4(a). Regions I and V can be identified as power plants in Zhuhai and Humen, respectively. The reference spectrum for this day was taken over Zengcheng, where the air seemed to be very clean and NO_2 dSCDs were significantly lower.

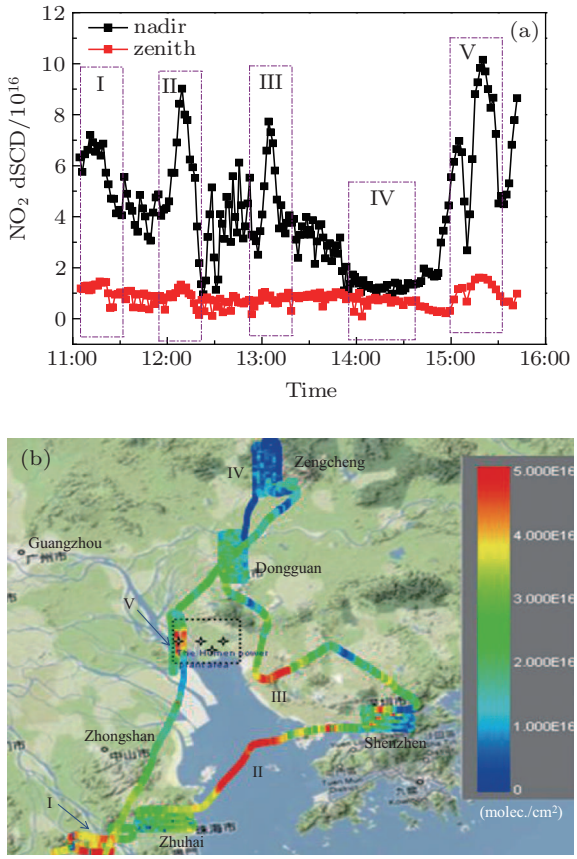


Fig. 4. (color online) (a) Time series of NO_2 slant column densities for AMAX-DOAS on 10 December 2008 in the nadir and zenith directions. Four strong enhancements (I, II, III, and V) and one decrease were detected. (b) NO_2 vertical column density distribution along the flight track. The Humen power plant area is indicated by the black rectangle where stars stand for the location of its chimneys.

Aerosol parameters for the whole flight were chosen according to meteorological data and information from AERONET measurements (http://aeronet.gsfc.nasa.gov). For this day, the wind direction was predominantly from land to sea, so the aerosol type for the radiative transfer model was set to "urban" over the continent and "maritime" over the sea. Since there are no AERONET data available for the PRD region itself, we used the nearest observations in Hong Kong Hong_Kong_PolyU (lsjanet, 2008,

http://aeronet.gsfc.nasa.gov) to set the vertical aerosol optical thickness at 380 nm to a value of 0.5. Other parameters for the radiative transfer were chosen as follows: the surface albedo was set to a value of 0.05 over land and 0.1 over sea, the input profiles (NO_2, temperature, pressure, etc.) were selected from a US standard atmosphere model.

Figure 4(b) shows the tropospheric NO_2 VCD along the flight track. Four regions of high NO_2 can be clarified, part I is near Zhuhai power plant, part III is near Ma Wan and Nanshan power plant, part V is near Humen power plant. In all these areas, high NO_2 concentrations can be expected. While part II with high values, which is over the sea between Zhuhai and Shenzhen, is not near a pollution source. In order to find the pollution source, the HYSPLIT trajectory model (http://www.arl.noaa.gov/) was used to calculate the backward trajectories of airflows, shown in Fig. 5. Three typical back trajectories at 500 m height, 1000 m height, and 2000 m height level were calculated, which together showed that the airflow was mainly from the northeast where the Ma Wan Coal-Fired Power Plant is and some other power plants. So the high concentration of NO_2 can be traced back to the power plants area to the northeast.



Fig. 5. (color online) Backward trajectories ending at 1200 UTC 10 December 2008. Red, blue, and green lines correspond to 500 m, 1000 m, and 2000 m.

The AMAX-DOAS tropospheric VCDs were compared with those from the ground-based MAX-DOAS instrument, which was set up in Doumen, about 30 km from Zhuhai and 50 km from the Zhuhai power plant. The ground-based MAX-DOAS instrument measured five elevations, 5°, 10°, 15°, 20°, 90°, for about 15 min in a circle. The NO_2 VCD was calculated using the dSCDs at 20°. For comparison with the AMAX-DOAS data, the conversion from dSCDs to VCDs for the ground-based instrument was carried out using the same parameters as in the radiative transfer calculations. AMAX-DOAS data for points of the flight track closest to the location of the ground based MAX-DOAS instrument were compared to MAX-DOAS results for the time of the overpass. The resulting average of the AMAX-DOAS VCDs over the area of Zhuhai with a value of 3.15×10^{16} molec·cm^{-2} agreed well with the corresponding MAX-DOAS value, which was 2.9×10^{16} molec·cm^{-2}. The deviation between the two instruments was about 8%.

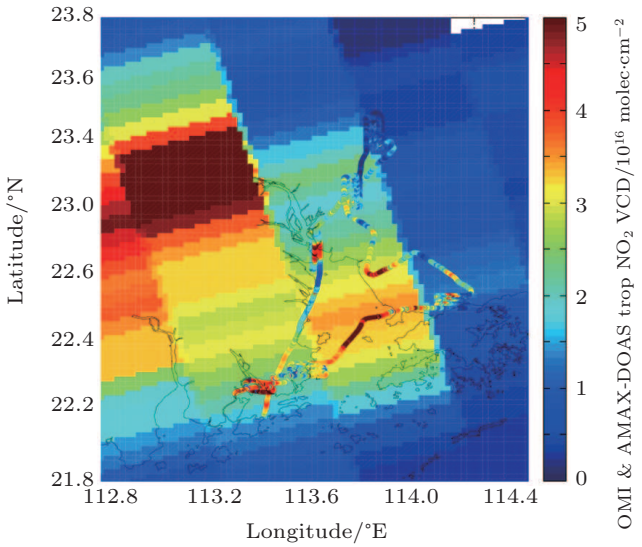


Fig. 6. (color online) Tropospheric NO_2 VCD measured by AMAX-DOAS and OMI. The AMAX-DOAS data were overlaid on OMI's pixels at the same scale using the same colors.

The AMAX-DOAS results were also compared with those from an ozone monitoring instrument (OMI), which has a spatial resolution of 13 km×24 km. In Fig. 6, the NO_2 VCD from the AMAX-DOAS was plotted together with the OMI's pixels. The OMI data were obtained from NASA's official website (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/). The two instruments showed good accordance in regard to the heavily polluted Zhuhai power plant, the sea between Zhuhai and Shenzhen, the sparsely polluted Dongguan and clean Zengcheng, where the reference spectrum was taken. But in heavily polluted regions, the AMAX-DOAS results were much higher than those from OMI. The different spatial resolution might be for one reason: as pointed out above, the AMAX-DOAS pixels (70 m×2.6 m) are much smaller than those of OMI. Therefore, in the comparison, only the OMI data where AMAX-DOAS data are also available were taken into account.

For the correlation analysis between the datasets, the AMAX-DOAS data covered by every pixel was averaged, see Fig. 7. The correlation is quite good: the slope equals 0.41 and the intercept is 1.06×10^{16}. The correlation coefficient R is 0.61. However, in some polluted regions, the AMAX-DOAS values are much higher than those of OMI, which can be explained by the difference of spatial resolution and parameter sets of AMF for the two instruments; the difference in overpass time also influences the results. The results also show that AMAX-DOAS is more sensitive in polluted areas and can validate space borne instruments.

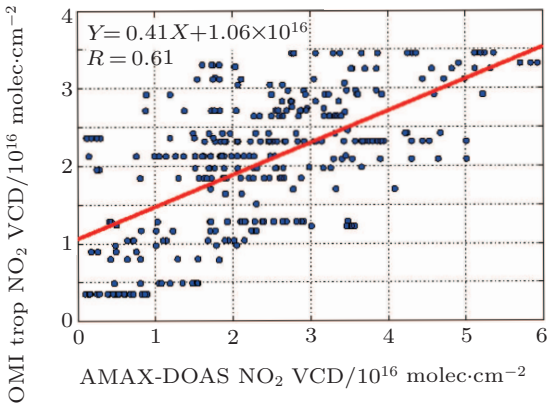


Fig. 7. (color online) Correlation of tropospheric NO_2 VCD between AMAX-DOAS and OMI.

5. Conclusions

Airborne multi-axis DOAS was deployed for the observation of tropospheric NO_2 in the Pearl River Delta region in China. Tropospheric NO_2 columns were retrieved from the measurements, and strongly enhanced values were observed in some heavily polluted regions under clear sky conditions.

In order to convert NO_2 dSCDs to VCDs, air mass factors were calculated using the radiative transfer model SCIATRAN, and sensitivity studies were carried out to investigate the sensitivity of the measurements of NO_2 absorption to several important parameters of the air mass factor calculation. For flight altitudes lower than 2 km in the nadir direction, the deviation from the standard cruising altitude of 3 km is about 20% to 30%. During the flight, the deviation was no more than 3%. The influence of variations of the solar zenith angle during the flight on the air mass factor is estimated to be about 2%. Different surface albedos also have significance, with a difference of air mass factors between loam soil and the ocean of 11%.

The AMAX-DOAS results were compared with those from ground-based MAX-DOAS in Zhuhai, and good accordance was found, with a deviation of 8%. Similar to ground-based MAX-DOAS, AMAX-DOAS can also be used to acquire tropospheric NO_2 VCD more flexibly and quickly in a large region.

The AMAX-DOAS results were also compared with those from OMI, and fair accordance was found, with a correlation coefficient of 0.61. This indicates that the AMAX-DOAS results can be used to validate satellite measurements of tropospheric NO_2, for example OMI, SCIAMACHY and GOME.

The results presented here demonstrate the great potential of airborne UV/VIS absorption measurements for the study of regional tropospheric NO_2 pollution. Such measurements are also suitable for satellite validation and air quality monitoring.

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