Quantification of total emission of air pollutants from Beijing using mobile mini-DOAS

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Abstract
This paper presents a novel method for quantification of the total emission of gases from area sources using the mobile mini-DOAS (Differential Optical Absorption Spectroscopy) instrument, a ground based optical remote sensing technique. The presented method has been applied to measure the emission of SO2 and NO2 from the city of Beijing, P.R. China, on a time scale of approximately 2 h. The measurements have been performed during two field campaigns, in April and in August 2005. The estimated emission of NO2 is roughly the same during the two field campaigns with an average emission of 189 tons day\(^{-1}\) during April and 174 tons day\(^{-1}\) during August. The estimated emission of SO2 varies greatly between the two periods, with an average emission of 293 tons day\(^{-1}\) during April and 52 tons day\(^{-1}\) during August.

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1. Introduction
The world population is expected to grow from 6.3 billion in 2003 to 8.1 billion in 2030, with nearly all the growth in urban areas (UN, 2003). With this increase in population follows increasing problems with urban air pollution in all of the world's major urban centres. The key to alleviating the air pollution problem is knowledge of the sources of the pollutants. Optical remote sensing methods use light with wavelengths ranging from IR to UV to measure the total amount of molecules of a certain gas between a light source and a receiving spectrometer. Optical remote sensing techniques have proven to be important tools (e.g. Heckel et al., 2005; Volkamer et al., 2005) in measuring urban air pollution because of their inherent line-averaging properties, ability of simultaneous measurements of many gases and ease of automation.

In this paper, we present a method of determining the total emission of air pollutants from an area source by use of one very common optical remote sensing technique, the mobile mini-DOAS. We also present measurements where this method has been applied to the city of Beijing, where the total emissions of SO2 and NO2 from the most central part of the urban area have been measured.

2. Method
The mobile mini-DOAS instrument (described by Galle et al., 2002) can be used to measure the flux from a point source by placing it on a moving platform, typically a car, and making a traverse, i.e. recording spectra while passing under the plume. The movement during the traverse is recorded using a small GPS-device. Each measured spectrum is ratioed to a Fraunhofer reference spectrum and the DOAS evaluation yields the difference in total vertical column, the integral over the concentration along a vertical line from the instrument and up, between the measured spectrum and the chosen Fraunhofer reference spectrum.

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The result of one traverse is the total number of molecules in a cross section of the plume. Multiplying with the wind speed and correcting for the angle between the wind direction and the traverse direction gives the total flux of the measured species through this cross section.

This flux measurement can easily be expanded to a measurement of the total emission from an area source by simply encircling the source. This can be understood by thinking of the measurement as two measurements, one upwind of the area that measures the inflow and one downwind of the area that measures the outflow. The difference between the outflow and the inflow is then taken as the production of the pollutant inside the area of interest.

The mobile mini-DOAS technique is inherently a relative measurement technique since every spectrum collected is ratioed to another spectrum, the Fraunhofer reference, collected with the same spectrometer. In a region such as Beijing where the ambient levels of the measured pollutants are high, the mobile mini-DOAS can therefore not yield the absolute inflow or outflow but it can determine the difference between them.

This measurement technique can be performed on large area sources, such as industrial areas or complete cities, as well as on smaller sources, such as individual industries. These measurements can also be performed on isolated distributed sources as well as on area sources inside a larger distributed source since the ambient levels do not affect the result.

One prerequisite for making the flux measurements is that the wind direction is relatively stable for some time before and during the measurement. In the case of a change in the wind field, the pollutants from the area source will not be distributed in accordance with the wind field at the time of the measurement (Fig. 1) and a measurement using the wind field at the time of the measurement will yield an under estimation of the flux. The pollutants will be completely aligned with the wind field when the air from the upwind side of the area source has reached the downwind side. The flux from a measurement during or directly after a minor change in wind field can be calculated by using an interpolation of the wind between the time of the change and the time of the measurement.

Changes in wind field can also result in measurements where the column value in the beginning differs significantly from the column values in the end of the measurement, due to intrusion of unpolluted air in the sampled air mass during the scope of the measurement. Such measurements, where the first and the last few spectra give very different column values, even though they are sampled at the same site, have been rejected in the work of this paper due to the difficulty of interpretation.

The mobile mini-DOAS instrument uses solar radiation, which has been scattered by molecules or particles in the air before reaching the instrument. Normally these scattering events occur at high altitudes, above the boundary layer. However, in the case of high aerosol loads or low clouds the incoming photons might undergo scattering events inside the polluted boundary layer. Such events will yield an over estimation of the vertical column. Full understanding of the number of scattering events occurring and the volume of air probed in each measurement requires computationally expensive radiative transfer modelling of the photons path through the atmosphere. To simplify the calculations, the flux calculations in this paper are made using the assumption that the average path of the incoming light does not significantly differ from the vertical through the boundary layer. This enables the simplification that the measured difference in column throughout the measurements equals the difference in vertical column. To verify that this is a reasonable assumption, the measured spectra have been evaluated for O₄ (Greenblatt et al., 1990), which is a dimer of oxygen and has a concentration distribution proportional to the oxygen concentration squared. A measurement’s O₄ column can therefore be used as a qualitative estimate of the total amount of air that the received light has probed. It can thus be used to indicate whether the assumption of light passing vertically through the boundary layer is justified. Traverses with large rapid variations in the O₄ column cannot be assumed to fulfill this requirement and therefore are not used to calculate the total emission. Since the O₄ column naturally changes over the day due to the changing position of the sun, traverses with low or slow variations in O₄ column are not rejected. The O₄ column is however a blunt tool and does not indicate whether the additional scattering occurs above the

Fig. 1. The effect of changing wind directions. (a) The situation before the wind change; the concentration of the air pollutants is higher downwind of the area source. (b) The situation directly after the wind change. The distribution of the air pollutants is no longer in accordance with the wind field, a measurement at this time will render an under estimation of the total emission.
boundary layer or inside the boundary layer. Furthermore, the detection limit of \( \text{O}_4 \) makes the measurements sensitive only to very large variations in the path length.

### 3. Measurements

The mobile mini-DOAS instrument used in these measurements collects scattered UV and visible sunlight in the zenith position using a telescope with a single quartz lens of 50 mm focal length (Fig. 2). Approximately 2 mm behind the lens is a band pass filter (Hoya U330) which blocks light with wavelengths longer than 360 nm. The lens focuses the scattered light onto the end of an 800 µm quartz fibre that leads the collected light into a S2000 spectrometer (OceanOptics Inc.). The spectrometer detects light in the range from 280 to 420 nm with a resolution of approximately 0.6 nm (FWHM).

In the evaluation of the collected spectra, each measured spectrum is ratioed to another spectrum collected with the same spectrometer, the Fraunhofer spectrum. In these measurements, we have chosen the Fraunhofer spectrum as the average of a number of spectra with good saturation levels and low column values close to the middle of the measurement as this gives the smallest possible variation in temperature and spectral properties between the Fraunhofer reference and the measured spectrum.

The spectra retrieved in these measurements were evaluated using the software WinDOAS (Van Roozendael and Fayt, 2001) in two different wavelength ranges (Table 1). To compensate for the Ring-effect, a Ring spectrum was calculated from the measured Fraunhofer spectrum using the DOASIS software (Kraus) and included in the fit. The cross sections for each gas were collected from literature (Table 2). The 307–320 nm wavelength range gives a value of the differential vertical column of \( \text{SO}_2 \); the 335–365 nm range gives reliable values of \( \text{NO}_2 \) and \( \text{O}_4 \). The retrieved column values of \( \text{HCHO} \) are normally below the detection limit of the instrument.

Notice that the result of evaluating \( \text{O}_4 \) is not the integrated concentration (column) of \( \text{O}_4 \) but rather the once integrated squared concentration of \( \text{O}_2 \), since the equilibrium constant between \( \text{O}_4 \) and \( \text{O}_2 \) is not known (Greenblatt et al., 1990). However, in this paper this will be referred to as the \( \text{O}_4 \) column.

Several measurements using this technique have been performed during two field campaigns in Beijing, Peoples Republic of China. The first campaign took place during two weeks in the beginning of April 2005 and the second took place during the three last weeks of August 2005. The city of Beijing is suitable for this type of measurements as it is surrounded by a series of concentric ring roads (Fig. 3), numbered from two to six, of which the fifth ring road encircles most of the urban area. To encircle the city on the fifth ring road by car takes around two hours. The only major sources of pollutants which are not situated inside the fifth ring road is the Shijingshan industrial area in the western part of the city, and the airport in the north-east.

The city of Beijing is the capital of the Peoples Republic of China and has nearly 11 million permanent residents (2000) plus approximately three million temporary residents (Molina and Molina, 2004).

The main part of the electricity and wintertime heating is generated by coal burning power plants producing emissions of \( \text{SO}_2 \) and particulate matter (approximately 75% of the \( \text{SO}_2 \) emissions in 1999 were from heating and electricity generation (He et al., 2003)). Due to the rapid economic expansion in mainland China, the amount of vehicles in Beijing between 1995 and 2005 increased with an average annual growth rate of 14.5% (Hao et al., 2006). In recent years, the local and central governments have taken strong actions to decrease the levels of especially particulate matter and \( \text{SO}_2 \) (Molina and Molina, 2004; Yi et al., 2007), efforts which decreased the levels of some pollutants (Table 3). However, due to the increasing number of cars, the levels of \( \text{NO}_2 \) have not decreased (road traffic produces 35% of the city’s \( \text{NO}_x \) emissions in 1999 (He et al., 2003)).

### 4. Meteorological modelling

Knowledge of the wind speed and direction during the course of and the hours before the measurements are

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**Table 1**

<table>
<thead>
<tr>
<th>Wavelength range (nm)</th>
<th>Species</th>
</tr>
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<tbody>
<tr>
<td>307–320</td>
<td>( \text{SO}_2, \text{O}_3, \text{ring} )</td>
</tr>
<tr>
<td>335–365</td>
<td>( \text{NO}_2, \text{O}_4, \text{HCHO}, \text{O}_3, \text{ring} )</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Specie</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 )</td>
<td>Vandaele et al. (1994)</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
<td>Voigt et al. (2001)</td>
</tr>
<tr>
<td>( \text{O}_4 )</td>
<td>Hermans et al. (1999)</td>
</tr>
<tr>
<td>\text{HCHO}</td>
<td>Meller and Moortgat (2000)</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>Vandaele et al. (1996)</td>
</tr>
</tbody>
</table>
crucial for estimating the total emission and interpretation of the measurements. For this purpose, the wind field over the urban and rural areas of Beijing has been simulated using The Air Pollution Model (TAPM) v3.0 (Hurley, 2005). The model uses as input terrain height, land use, sea-surface temperature, and synoptic meteorological analyses. The meteorological component of TAPM predicts the local-scale flow, such as sea breezes and terrain-induced circulations, given a larger scale synoptic meteorological field from the Australian Bureau of Meteorology’s Global Analysis and Prediction (GASP) – model. The model was run for the two measurement campaigns in Beijing. The grid centre was set at latitude 39° 43.9’ N and longitude 116° 22.5’ E resulting in that the model covered both the urban and rural areas of Beijing. Three nested domains of 61 × 61 horizontal grid points at 10-, 3-, and 1-km spacing were used for the meteorology and no pollution grids. The lowest ten model levels were at heights of 10, 25, 50, 75, 100, 150, 200, 250, 300 and 350 m, with the model top at 8 km.

5. Experimental results

Figs. 4 and 5 shows the result from one measurement made on ring road five around Beijing on August 15th with start at 14:14 local time. This measurement has been rejected for estimating the calculating flux since the variations in O4 column throughout the measurements are too large.

In the same way as above, Fig. 6a shows the variation of SO2, Fig. 6b shows the variation of NO2, Fig. 6c shows the variation of HCHO and Fig. 6d shows the variation of O4. One striking feature in this traverse is the large peak in O4, HCHO and NO2 at the end of the measurement. However, the large correlation between O4, NO2 and HCHO at the end raises the suspicion that the enhancement in NO2 and HCHO is not due to higher vertical columns in this region, but rather due to longer path length through the lower part of the atmosphere. This is probably also the case since we noted that a large, dark cloud had appeared over the northern part of the city during the course of the measurement. The appearance of this cloud can also be seen in the spectra as a lowering of the spectral intensity towards the end of the measurement.

A lower limit of how much longer the light path is at the end of the measurement can be made by assuming that the extra scattering takes place at ground level, since the O4 concentration varies as the O2 concentration squared. The maximum O4 column in the measurement is approximately \(1.5 \times 10^{13}\) molec cm\(^{-2}\) more than the vertical column in the middle of the measurement, which corresponds to an additional path length of 5.7 km at an air pressure of 1 atm and 25 °C.

The calculated emissions of SO2 and NO2 from four of the measurement days can be seen in Tables 4 and 5. The estimated emission of NO2 is relatively stable between the
two campaigns with average emission rates of 189 tons \( d^{-1} \) in April 2005 and 174 tons \( d^{-1} \) in August. However, the emission rates of \( \text{SO}_2 \) vary strongly between the two campaigns with an average value of 293 tons \( d^{-1} \) in April and 52 tons \( d^{-1} \) in August.

The large difference in estimated emission of \( \text{SO}_2 \) between the two campaigns can be explained by the oxidation of \( \text{SO}_2 \) into \( \text{SO}_4^{2-} \) which occurs at much higher rates during the summer months than during winter. Measurements performed in the winter of 2003 showed an \( \text{SO}_4^{2-} \) to \( \text{SO}_2 \) ratio of 0.27 whereas measurements in the late summer of 2004 showed an \( \text{SO}_4^{2-} \) to \( \text{SO}_2 \) ratio of 5.6, by mass (Yu Tong, personal communication). Using these values for the \( \text{SO}_4^{2-} \) to \( \text{SO}_2 \) ratios, the total emission of \( \text{SO}_2 \) and \( \text{SO}_4^{2-} \) can be estimated to 372 tons \( d^{-1} \) in the April campaign and 343 tons \( d^{-1} \) during the August campaign.

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Fig. 4. Measurement performed on August 18 with start at 14:30 on ring road five around Beijing. The four subfigures show the variation in vertical column of \( \text{SO}_2 \) (a), \( \text{NO}_2 \) (b), \( \text{HCHO} \) (c) and \( \text{O}_4 \) (d) with distance travelled on the ring road. Error bars are the 1 sigma error of the spectral fit.

Fig. 5. The spatial distribution of pollutants during the measurement in Fig. 4. The two subfigures show the variation in vertical column of \( \text{SO}_2 \) (a) and \( \text{NO}_2 \) (b); larger squares correspond to higher differential vertical columns.
6. Discussion

The largest error source is probably the uncertainty in the wind speed and direction. We have used a meteorological model to mitigate this problem. However, one problem persists – the variation of the pollution concentration with altitude. To be accurate, a weighted average of the wind speeds and directions below the boundary layer should be used, where the weighting corresponds to the concentration of the measured air pollutant at that altitude. Since this altitude distribution is usually not known, we have for these calculations assumed the pollutants to be well mixed for altitudes below 400 m, and used the wind speed and wind direction at 200 m. As the comparison in Tables 4 and 5 shows, the variation in flux if using any other altitude as source for wind-data is less than 20%. Due to variations in the wind during the measurements, many

Fig. 6. Measurement performed on August 15 with start at 14:14 on ring road five around Beijing. (a) The variation in the vertical column of SO2 with distance travelled on the ring road. (b) The variation of NO2 with distance. (c) The variation of HCHO with distance. (d) The variation of the vertical column of O4 with distance travelled. Error bars show the 1 sigma error of the spectral fit.

Fig. 7. The spatial distribution of pollutants during the measurement in Fig. 6. The two subfigures show the variation in vertical column of SO2 (a) and NO2 (b); larger squares correspond to higher differential vertical columns.
measurements should be performed and the results averaged to eliminate the errors due to wind fluctuations.

Errors can also be introduced by the experimental setup. The telescope should be mounted in an upright position. A deviation from the exact zenith position will cause the telescope to measure a higher value than the vertical, since the path through the boundary layer will be larger. We estimate the deviation of the telescopes pointing direction to be less than ±5° from zenith during these measurements.

Another source of errors when making measurements in highly polluted areas is the problem with scattering in the lower atmosphere, as discussed earlier. These measurements have been performed under the simplified assumption that all scattering events occur at altitudes above the boundary layer and the evaluated columns of O₄ have been used to verify that this assumption is reasonable. However, due to a high detection limit for O₄ absorption, only measurements with strong light path enhancement in the lower troposphere can be detected and removed.

When performing measurements on large area sources, there is a risk that the amount of aerosols and clouds vary along the measurement path. The risk can be regarded as increasing with the spatial and temporal length of the measurement. The presence of a low cloud or high aerosol load at one region in the measurement can possibly lead to an over estimation of the vertical column in that region, leading to either over- or under estimation of the total emission depending on the direction of the wind.

What one must also bear in mind is that this technique only measures the difference in inflow and outflow. This is of importance for pollutants which are in balance with other, not measurable gases, and where the relative ratios can change over time. The most important example is the balance between NO₂, NO and N₂O₅. With this technique, a measurement around an area source will be affected by two factors, the actual emission from the area to the atmosphere and the conversion in the atmosphere between measurable and not measurable gases.

Finally, there is an error induced by the spectral fit. Since the temperature of the equipment is not controlled, the variations in temperature of the spectrometer will cause shifts in the spectral range and changes in the instrument function during the course of one measurement. The effect of wavelength shifts has been mitigated by fitting the shift between the Fraunhofer reference spectrum and the measured spectrum, while locking the shift of all fitted cross sections to the Fraunhofer reference. Furthermore, the exposure-times of all spectra in one measurement are identical, due to the difficulties of correcting for the dark-current of the detector in spectrometers with varying temperature. Because of this, the saturation ratio of each measured spectrum is not ideal, which decreases the signal to noise ratio.

7. Conclusion

We have presented a measurement technique to derive the total emissions of air pollutants from an area source using the mobile mini-DOAS instrument. Our measurements have resulted in an estimation of the total emissions of SO₂ and NO₂ from the area of Beijing inside the fifth ring road of the city. The measurements were performed during two field campaigns one in April and one in August of 2005. The emission of NO₂ averages to 189 tons d⁻¹ during the April campaign and 174 tons d⁻¹ during the August campaign. The emission of SO₂ averages to 293 tons d⁻¹ during the April campaign and 52 tons d⁻¹ during the August campaign. This technique allows for fast measurements of gas emissions even on large distributed sources and facilitates and increases the accuracy of emission inventories as well as increases the understanding of photo-smog chemistry.

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