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REACTIVE NITROGEN EMISSIONS FROM POINT SOURCES IN HOUSTON USING VISIBLE SPECTROSCOPY MEASUREMENTS FROM AIRCRAFT

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Abstract. Nitrogen dioxide column abundances were measured during the Texas Air Quality Study 2000 using visible absorption spectroscopy from an aircraft. The method allows for quantification of the total number of nitrogen dioxide molecules in the troposphere and is hence a useful tool for measuring the burden of this key trace gas. In particular, we focus here on observations carried out in and around Houston, including focused flights to measure the fluxes of nitrogen dioxide emitted from power plants. This remote sensing technique can be used to infer fluxes irrespective of the aircraft altitude, and the height or uniformity of the boundary layer. We show that our nitrogen dioxide complements in-situ methods and allows for a more comprehensive understanding of point source emissions.

1. Introduction

According to the clean air act of 1970, ozone (O_3) is a criteria pollutant and control strategies for ozone's precursors need to be implemented. Nitrogen dioxide (NO_2) is a key trace element in the formation of photochemical smog or ozone (O_3). Power plants emit nitric oxide (NO) that is readily converted to NO_2. Once the nitrogen is in the form of NO_2, it photolyzes to give an oxygen atom that rapidly reacts with O_2 to form O_3 (Figure 1). The aim of this study is to examine measurements of total column NO_2 in the Houston area and from them estimate NO_X fluxes from power plants.

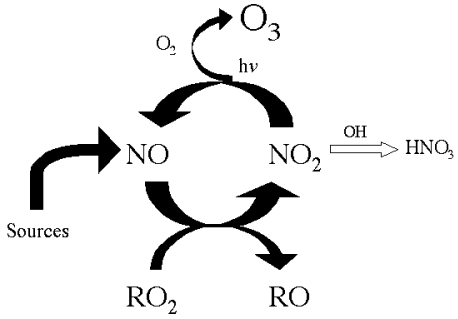

Figure 1. The chemistry cycle of NO, NO_2, hydrocarbons, and O_3 in the formation of photochemical smog.

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During August and September, 2000, the National Oceanic and Atmospheric Administration's (NOAA) Aeronomy Laboratory participated in an airborne and surface measurement campaign referred to as the Texas Air Quality Study 2000 (TexAQS 2000). The study was in Houston, Texas because of the numerous sources of pollution such as oil refineries, power plants, industrial plants, urban sources, and ship channel sources. Houston also has unique meteorology that plays a key role in the high levels of ozone.

In a recent study by Ryerson et al. (1998), in-situ measurements from aircraft have been used to calculate NO_X fluxes from point sources. In this work we use measurements of the total column abundances of NO_2 taken with a miniature differential absorption spectrograph (MIDAS) from aircraft, in conjunction with in-situ measurements taken from the same aircraft to calculate the amount of reactive nitrogen emitted from power plants.

2. Instrumentation and Technique

The measurements were taken using a commercially purchased crossed Czerny-Turner fixed grating spectrograph. The spectrograph, with its 2048 pixel silicon CCD detector and accompanying electronics, is cooled to –20˚C to reduce noise and stabilize the dark current. A slit width of 50 µm in conjunction with a 1200 lines/mm grating produces a full-width-maximum resolution of approximately 1.0 nm over the wavelength range from 425 to 725 nm. The incoming light is collected by downward and upward viewing lenses and directed into the spectrograph using fiber optics. The field of view is approximately 1˚ for the aircraft data.

In the analysis, the differential slant optical depth of the significant atmospheric scattering (e.g., aerosol, Rayleigh) and absorption (e.g., NO_2) processes are linearly fit to the natural logarithm of the ratio of the foreground and background spectra by applying the Beer-Lambert law (*Portmann et al.,* 2001). This can be written as

$$\ln\left[\frac{I(\lambda)}{I_0(\lambda)}\right] = -\sum_m \beta_m Q_m(\lambda) \qquad (1)$$

where $I(\lambda)$ and $I_0(\lambda)$ are the foreground and background spectrums, respectively, β_m are the differential slant columns, and $Q_m(\lambda)$ are the model functions for the absorption and scattering processes included. The background spectrum is measured in clear skies and is assumed to be characterized by the total NO_2 in the non-polluted atmosphere. The foreground spectra contain enhancements in NO_2 absorption in the atmosphere measured during the flights. The model functions included are the cross section for NO_2 by *Harder et al.* (1997) convolved with the instrument function, a constant to account for brightness, and slope (λ^{-1}), and Rayleigh (λ^{-4}) terms. This analysis thus employs the differential optical absorption spectroscopy (DOAS) technique that is extensively discussed in Sanders (1996) and references therein.

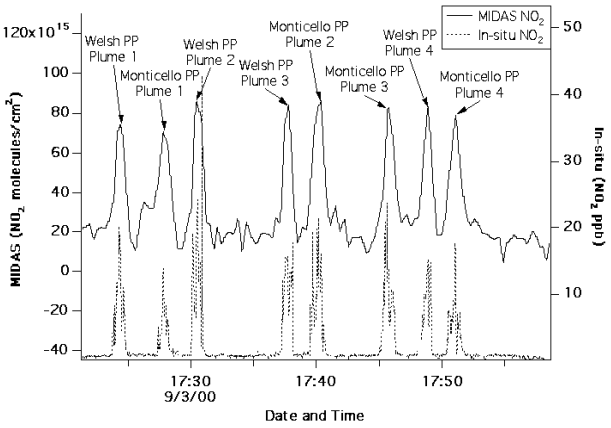

Figure 3. MIDAS NO_2 and in-situ NO_2 measurements are plotted against time from transect 2. MIDAS measurements are in molecules/cm^2 and in-situ measurements are in part per billion by volume.

3. Analysis

We focus on the flight of September 3rd, 2000 in which four multiple passes of plumes from the Welsh and Monticello power plants are made on the same transect. The flight path in figure 2 shows the location of the two power plants and the NO_2 plumes from in-situ measurements taken downwind from the point sources. The enhancement of NO_2 from the power plant plumes is clearly seen when plotted on the flight path and when the NO_2 measurements from MIDAS and from in-situ measurements are plotted versus time (figure 3) for transect 2. The eight plumes in figure 3 represent the four passes of the same two plumes along transect 2.

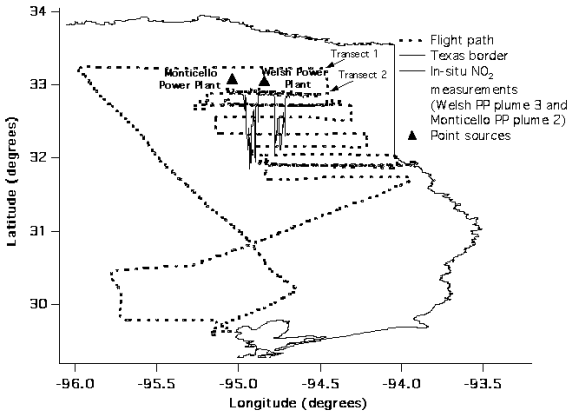

Figure 2. Flight path on September 3rd, 2000. Shows the In-situ NO_2 enhancements downwind from the Monticello and Welsh power plants on transect 2.

The reactive nitrogen fluxes from the Welsh and Monticello power plants are calculated using the following technique. For MIDAS measurements, we calculate the flux of NO_2 using a modified form of the equation presented in Ryerson et al. (1998). MIDAS measures the total column abundance of NO_2 and therefore, the flux is given by

$$MIDAS\_NO_2\_Flux = v(flightspeed)\cos\alpha \int_{t_1}^{t_2} (NO_2 vertical\_column)dt \quad (2)$$

where v is a constant uniform wind speed, α is the angle between the aircraft track and the direction normal to the wind direction, and the integral represents the area under the plumes in figure 3 over the time of the plume transect. Equation (2) assumes the wind speed and direction are constant, plant emissions are constant, and the flight speed is constant. This would suggest that the integrated area of NO_2 plumes would be constant if multiple passes of a plume occurred on the same transect.

Spectrographs are deployed in both the uplooking and downlooking directions, which allows the total path of the enhanced NO_2 column to be measured in these directions (figure 4). In order to convert these measurements to the vertical NO_2 column, the average path length (or air mass factor, AMF) must be known for the look directions and absorber profiles. These AMFs were determined using a plane-parallel calculation based on the DISORT radiative transfer code (*Stamnes et al.,* 1988), which gives an accurate representation of multiple scattering effects (see *Portmann et al.,* 2001, for further details). It was determined that the AMF for the sum of the uplooking and downlooking measurements is approximately

$$AMF = \Gamma + \sec(SZA) \quad (3)$$

where SZA is the solar zenith angle. The factor Γ depends on the surface albedo (A_s) and to a lesser extent on the altitude of the aircraft. It is in the range1.4-2.0 as A_s ranges from 0.05-0.15. Note that Γ=1 in the single scattering approximation if all photons either scatter above the absorbing layer or at the ground. Γ is typically greater than 1 due to multiple scattering effects. It is also possible that three dimensional effects due to the finite horizontal extent of the layer could reduce the Γ compared to plane parallel calculations carried out. We will use a Γ=1.7 to estimate the AMF, which is representative for A_s=0.05 and the aircraft flying in the middle of a 2 km thick boundary layer.

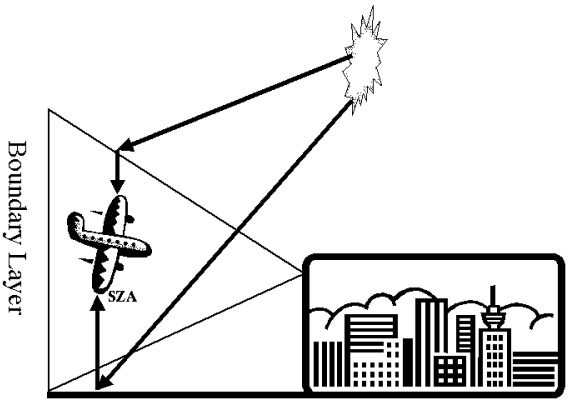

Figure 4. Diagram representing the slant column measurements taken by MIDAS from aircraft.

The Welsh and Monticello power plants report reactive nitrogen fluxes as NO_X emitted in molecules per second. To compare our NO_2 vertical column measurements to the hourly fluxes reported by the power plants, it is assumed that photochemical equilibrium is established between the NO_X species. Therefore, we used in-situ measurements of NO and NO_2 to determine the ratio of NO_X to NO_2. Multiplying our MIDAS NO_2 flux by this ratio results in NO_X emitted from the power plants according to MIDAS measurements.

$$MIDAS\_NO_X\_Flux = (MIDAS\_NO_2\_Flux)\left(\frac{NO_2^{in-situ} + NO^{in-situ}}{NO_2^{in-situ}}\right) \quad (4)$$

4. Results

The average wind speed and direction were calculated from the first and second transects (figure 2) of the flight path, and were assumed to be constant. This average wind speed was 4 m/s with the measured wind speeds varying from 3 to 5 m/s across the plumes in transect 2. Thus, the average wind speed is within 1 m/s of the actual wind speed suggesting up to a 25% uncertainty due to this variability. The wind direction was 337 degrees out of the northwest. The solar zenith angle was 27 degrees. It is assumed that the in-situ NO_2/NO_X ratio is indicative of the ratio throughout the boundary layer.

Calculated net plume NO_X fluxes from equations (2),(3), and (4) for Welsh and Monticello power plants are shown in table 1. Welsh PP plume IV and Monticello PP plume I (figure 3) were not used to calculate a flux because the aircraft did not fly through the entire plume and therefore these plumes had to be omitted in the analysis. Table 1 also shows the hourly reported NO_X emissions from the power plants. The largest uncertainties in our NO_X flux analysis are the wind speed and the AMF variables.

Table 1. Summary of MIDAS NO_X Fluxes

Plume	Reported NO_X fluxes from companies	MIDAS NO_X Flux
Welsh PP I	10.9	5.83
Welsh PP II	10.9	5.71
Welsh PP III	10.9	5.87
Monticello PP II	9.76	6.57
Monticello PP III	9.76	6.08
Monticello PP IV	9.76	6.34

Fluxes are given in units of 10^{25} molecules sec^{-1}

The reported NO_X fluxes from the companies are believed to be accurate to within 30% (Placet *et al.*, 2000; Ryerson *et al.*, 1998). The calculated MIDAS NO_X fluxes are within 48% of the reported fluxes for the Welsh power plant and to within 38% for the Monticello power plant. These differences in NO_X fluxes are within the combined uncertainties in the MIDAS analysis as well as the accuracy of the reported fluxes from the companies. The consistency of the measurements between multiple passes suggests that the assumption of constant wind speed, wind direction, flight speed, and plant emissions is valid.

5. Conclusion

Nitrogen dioxide slant column measurements taken using visible absorption spectroscopy from aircraft in the Houston, Texas area have been used to estimate NO_X fluxes from power plants. The calculated fluxes agree to within 48% of the reported NO_X fluxes from the power plants themselves. The differences in calculated and reported NO_X fluxes are likely within the range of the combined uncertainties in the AMF and the wind speed as well as the accuracy of the companies reported fluxes. The precision of the fluxes calculated using MIDAS is excellent across the three plumes analyzed for each power plant.

We have shown that the in-situ measurements provide the necessary information to convert the MIDAS NO_2 measurements into a NO_X flux. However, we believe that the use of MIDAS measurements can improve the analysis of point source emissions from in-situ measurements because in making MIDAS flux calculations it does not have to be assumed that the boundary layer height and the uniformity of the boundary layer are known. In addition, for in-situ measurements the aircraft must be flying within the boundary layer whereas for MIDAS measurements, the aircraft can fly anywhere in the atmosphere. This is because MIDAS measures the total column abundances of NO_2. Thus, our NO_2 measurements complement in-situ methods and can allow for a more comprehensive understanding of point source emissions.

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