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Date: 29 November 2011

Supplementary Material: Determination of tropospheric vertical columns of NO_2 and aerosol optical properties in a rural setting using MAX-DOAS

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1 Methodology for determining τ and NO_2 VCDs from MAX-DOAS

The result of the MAX-DOAS retrieval (Sect. 2.2) is the DSCD:

$$\mathrm{DSCD}_\alpha = \mathrm{SCD}_\alpha - \mathrm{SCD}_{90} \tag{1}$$

where SCD_α and SCD_{90} are the slant column densities of measurements with $\alpha < 90°$ and $\alpha = 90°$ respectively. The DSCD represents the difference in column amount of the absorber integrated along the light path through the atmosphere and the column amount of the absorber in the SCD_{90}. It depends on the trace gas amount, elevation angle (α), solar zenith angle (SZA), and relative azimuth angle (RAZI) between the sun and the direction the telescope is pointed (β).

The AMF is the average light path enhancement for solar light traveling through the atmosphere compared to a straight vertical path orthogonal to the ground (Perliski and Solomon, 1993; Solomon et al., 1987). It is defined as:

$$\mathrm{AMF} \equiv \frac{\mathrm{SCD}}{\mathrm{VCD}} \tag{2}$$

Similarly, the differential air mass factor (DAMF) is defined as:

$$\mathrm{DAMF} = \frac{\mathrm{DSCD}}{\mathrm{VCD}_{\mathrm{trop}}} \tag{3}$$

Since the DSCD contains only tropospheric trace gas absorptions, for the calculation of the DAMF, only the tropospheric profiles of the trace gases have to be taken into account (Sinreich et al., 2005). Expanding and rearranging Eq. (3) gives:

$$\mathrm{VCD_{trop}} = \frac{\mathrm{DSCD}}{\mathrm{DAMF}} = \frac{\mathrm{SCD}_\alpha - \mathrm{SCD}_{90}}{\mathrm{AMF}_\alpha - \mathrm{AMF}_{90}} \quad (4)$$

Unfortunately the conversion from DSCD to VCD is not easy, because the accurate determination of the DAMF is often difficult.

1.1 Radiative transfer and inversion

In southwestern Ontario, conditions with low aerosol levels are infrequently encountered during the summer and the geometrical approximation often does not hold. Instead, a RTM was used to determine the AMFs (Hendrick et al., 2006; Wagner et al., 2007). McArtim is a backward model that calculates the photon flux at a certain location (latitude, longitude, altitude) in the atmosphere treating multiple scattering with full spherical geometry (Deutschmann et al., 2011). AMFs were calculated for O_4 and NO_2 from McArtim simulated radiances. Input parameters to McArtim include α, SZA, RAZI, altitude, pressure, temperature, surface albedo = 0.05, single scattering albedo (SSA) = 0.95, asymmetry parameter (g, under the Henyey-Greenstein approximation = 0.68), and parameters for the absorbing trace gases.

Wagner et al. (2004) introduced the concept of using the oxygen dimer (O_4) absorption to retrieve aerosol profiles (Frieß et al., 2006; Li et al., 2010; Wittrock et al., 2004). O_4 results from the bimolecular association of O_2:

$$O_2 + O_2 \rightleftharpoons O_4 \quad \text{(R1)}$$

and is temperature and pressure dependent with a scale height of approximately 4 km. An estimated O_4 VCD (expressed as the integrated quadratic O_2 concentration) may be calculated if temperature and pressure vertical profiles are known. This was done for the Ridgetown site using radiosonde data from White Lake, Michigan (UWYO, 2010). The estimated O_4 VCD was 1.28×10^{43} molecules^2 cm^{-5}. This value agrees with other calculated values using similar approaches at similar elevations: 1.30×10^{43} molecules^2 cm^{-5} (Wagner et al., 2009), 1.26×10^{43} molecules^2 cm^{-5} (Wagner et al., 2002). Since O_4 is predominantly in the lowest part of the troposphere, this is the region where O_4 DSCDs are most sensitive to changes in the light path due to varying levels of aerosols. The amount of aerosol present for a given day and location also has a very large effect on the DAMFs.

1.1.1 Aerosol optical depth (τ)

Aerosol optical depth, τ, is the attenuation of light due to aerosol extinction; where I_0 is the original intensity of light, I the intensity after traveling a distance x, and E the aerosol extinction coefficient:

$$\frac{I}{I_0} = e^{-\tau} = e^{-Ex} \quad (5)$$

Typically τ is defined for light traveling through a vertical column of the atmosphere from sea level to infinity (top of the atmosphere), in which E is not constant with height. In order to model conditions with varying degrees of aerosol load, an integrated aerosol optical depth is defined as:

$$\tau = \int_{0\,\mathrm{km}}^{20\,\mathrm{km}} E(z)dz \qquad (6)$$

where z is the height above the ground (km). In the modeling performed here, E was calculated according to the following equation, as developed in Li et al. (2010):

$$E = \frac{\tau_{\mathrm{RTM}}}{H_{\mathrm{aer}}} \qquad (7)$$

where τ_{RTM} is the aerosol optical depth, and $\mathrm{H_{aer}}$ the aerosol layer height, determined by the process described by Eq. (8) below. $\mathrm{H_{aer}}$ is equivalent to the boundary layer if aerosols are 100% confined to the boundary layer (also see Zieger et al., 2011).

Figure 1 provides a complete scheme of the methodology used in this study. The approach used by Li et al. (2010) to determine aerosol optical depths was extended to obtain NO_2 VCDs on a routine basis. A comprehensive description, sensitivity analysis, and further validation may be found in Wagner et al. (2011). McArtim was used to calculate O_4 AMFs at a wavelength of 360 nm, for 50 000 photon paths. A comprehensive set of O_4 DAMFs was catalogued (as a function of input parameters), and used to construct an O_4 DAMF look up table (L_α). A MATLAB routine was used to minimize the difference (measured as the residual sum of squares) between O_4 DAMFS in L_α, as a function of τ and $\mathrm{H_{aer}}$, and O_4 DAMFs found via the measured DSCDs and their corresponding O_4 VCDs (M_α):

$$RSS(\tau, H_{\mathrm{aer}}) = \sum_{\alpha=2^\circ}^{30^\circ} [M_\alpha - L_\alpha(\tau, H_{\mathrm{aer}})]^2 \qquad (8)$$

The results of the minimization yield O_4 DAMF, τ, and $\mathrm{H_{aer}}$ values that may be used to describe the aerosol conditions for each cloud-free measurement series.

1.1.2 NO_2 vertical column densities

In addition to the dependence on the aerosol profile, NO_2 DAMFs are also a function of the vertical concentration profile of NO_2. Under the assumption of a horizontally homogeneous trace gas distribution, the atmosphere may be divided vertically into several layers of height, *h*. Each "box" will have its own DAMF, as follows:

$$\mathrm{DAMF}_{\mathrm{box}_i} = \frac{\mathrm{dDSCD}_i}{\mathrm{dVCD}_i} \qquad (9)$$

where dDSCD_i is the partial DSCD, and dVCD_i is the partial VCD for box_i. Total DAMFs, from 0 m a.g.l. to the top of the atmosphere (TOA) are:

$$\mathrm{DAMF}_{\mathrm{total}} = \frac{\sum_0^{\mathrm{TOA}} \mathrm{DAMF}_{\mathrm{box}_i} \cdot \mathrm{VCD}_i}{\sum_0^{\mathrm{TOA}} \mathrm{VCD}_i} \qquad (10)$$

McArtim was used to calculate NO_2 $DAMF_{box}$ values at 413 nm (within the DOAS fit range) using 50 000 photons for NO_2. These $DAMF_{box}$ values were catalogued in a $DAMF_{box}$ look up table. A MATLAB routine selects the appropriate subset of $DAMF_{box}$ from the look up table, based on the aerosol scenario previously determined (Eq. 8). In order to minimize the effect of stratospheric NO_2, NO_2 $DSCD_{meas}$ ratios were prepared by taking individually measured SCD_α values ($\alpha \leq 30°$) and subtracting from them the SCD_{90} for a given series, then dividing each $DSCD_\alpha$ by the $DSCD_{10}$. These $DSCD_{meas}$ ratios (M_α) were then compared to their corresponding NO_2 $DAMF_{total}$ ratios (L_α). The quality of this fit may again be expressed by the RSS:

$$RSS(H_{\mathrm{gas}}) = \sum_{\alpha=2°}^{30°} [M_\alpha - L_\alpha(H_{\mathrm{gas}})]^2 \tag{11}$$

The "best fit" between the $DSCD_{meas}$ ratios and the $DAMF_{total}$ ratios gives the NO_2 layer height, H_{gas}, and the NO_2 DAMF for a given measurement series as well as the NO_2 VCD_α values via the following equation:

$$\mathrm{VCD}_\alpha = \frac{\mathrm{DSCD_{meas}}}{\mathrm{DAMF_{total}}} = \frac{\mathrm{SCD_{meas}}(\alpha) - \mathrm{SCD_{meas}}(90°)}{\mathrm{AMF_{total}}(H_{\mathrm{gas}},\alpha) - \mathrm{AMF_{total}}(H_{\mathrm{gas}},90°)} \tag{12}$$

Average NO_2 VCDs (henceforth called VCD_{RTM}) were calculated for each series:

$$\mathrm{VCD_{RTM}} = \mathrm{VCD_{avg}} = \overline{\mathrm{VCD}}_{(2°,4°,6°,10°,30°)} \tag{13}$$

This inversion was performed for all complete elevation sequences with SZA<80°. NO_2 sequences with deviations of more than $2\times DSCD_\alpha$ between DSCDs for subsequent elevation angles were skipped. In case of a non-convergent fit, the inversion results were not defined. It should also be noted that the wavelength of the NO_2 inversion differs from that of the aerosol inversion. Thus, the aerosol scenarios determined in the first step of the inversion might not be fully appropriate for the NO_2 measurements. To estimate the systematic error of our procedure, we applied the NO_2 profile retrieval with aerosol profiles scaled to 0.8. These new NO_2 VCDs showed only slight differences (on average $<1\%$) from the original values. Finally, for both aerosol and VCD retrievals, the RSS values determined, as shown in Equations 8 and 11, may be used to assess the quality of the fits. RSS values $<$ 0.25 were deemed good fits for both τ_{RTM} and VCD_{RTM}. RSS values between 0.25 and 2.5 are more uncertain, while RSS values $>$ 2.5 were considered highly uncertain and removed from the data set.

2 The geometrical approximation

Using a simple geometrical consideration, the AMF for an absorbing gas may be approximated if the trace gas layer is located below the scattering altitude:

$$\mathrm{AMF_{GEO}} = \frac{1}{\sin\alpha} \tag{14}$$

Conveniently a DSCD measured at 30° then equals the geometric VCD:

$$\mathrm{VCD_{GEO}}=\frac{\mathrm{DSCD}}{\mathrm{DAMF_{GEO}}}=\frac{\mathrm{DSCD_{30}}}{\frac{1}{\sin(30^\circ)}-\frac{1}{\sin(90^\circ)}}=\frac{\mathrm{DSCD_{30}}}{2-1}=\mathrm{DSCD_{30}} \tag{15}$$

This geometrical approximation assumes that the stratospheric absorption is similar in the horizontal-viewing and zenith directions (essentially canceling each other out). If there is a large amount of aerosol present, and hence a high degree of Mie scattering, this approximation becomes inaccurate. In most cases a RTM must be employed to obtain an accurate AMF (Hendrick et al., 2006; Wagner et al., 2007). In general, this approximation would only hold under clear sky and low aerosol conditions. For this study, geometrically approximated VCDs were determined using NO_2 DSCDs at both 30° and 10°. If a pair of geometric VCDs at these elevation angles in the same measurement series agreed to within 15%, then the $\mathrm{VCD_{GEO}}$, as defined in Eq. (15), was retained. This criterion ensures that the geometrical approximation is valid, and eliminates measurement points greatly affected by horizontal inhomogeneites, aerosols, or clouds (Brinksma et al., 2008; Celarier et al., 2008).

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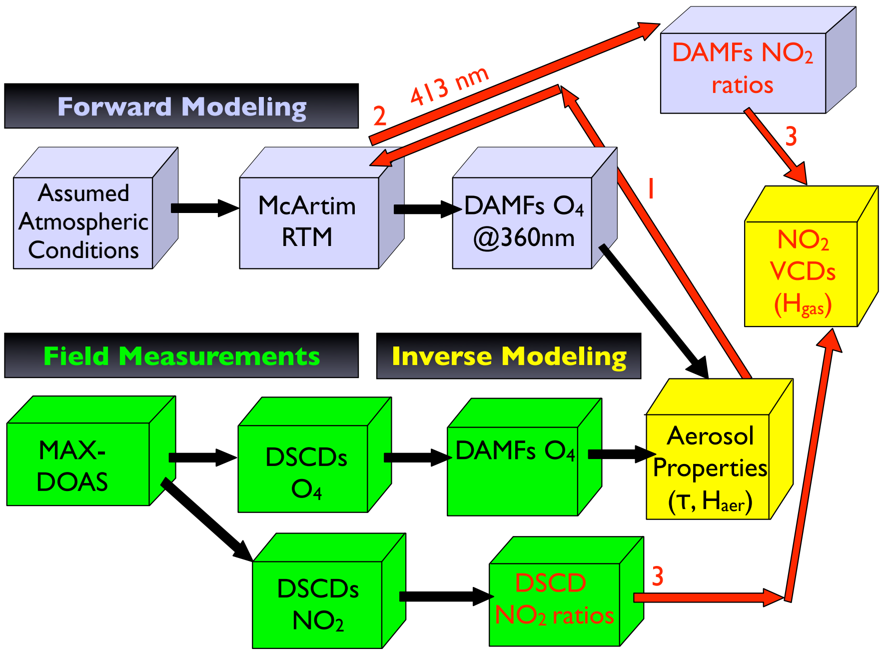

Fig. 1. Flowchart of methodology for determination of NO_2 VCDs and aerosol properties from MAX-DOAS measurements, RTM and inverse modeling. Measurements in green boxes represent products obtained from direct MAX-DOAS measurements in the field, while parameters and products shown in the grey boxes represent modeled quantities and results only. The quantities in the yellow boxes are obtained from inverse modeling.