

# Determination of tropospheric vertical columns of NO<sub>2</sub> and aerosol optical properties in a rural setting using MAX-DOAS

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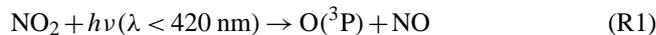
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**Abstract.** Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements were performed in a rural location of southwestern Ontario during the Border Air Quality and Meteorology Study. Slant column densities (SCDs) of NO<sub>2</sub> and O<sub>4</sub> were determined using the standard DOAS technique. Using a radiative transfer model and the O<sub>4</sub> SCDs, aerosol optical depths were determined for clear sky conditions and compared to OMI, MODIS, AERONET, and local PM<sub>2.5</sub> measurements. This aerosol information was input to a radiative transfer model to calculate NO<sub>2</sub> air mass factors, which were fit to the measured NO<sub>2</sub> SCDs to determine tropospheric vertical column densities (VCDs) of NO<sub>2</sub>. The method of determining NO<sub>2</sub> VCDs in this way was validated for the first time by comparison to composite VCDs derived from aircraft and ground-based measurements of NO<sub>2</sub>. The new VCDs were compared to VCDs of NO<sub>2</sub> determined via retrievals from the satellite instruments SCIAMACHY and OMI, for overlapping time periods. The satellite-derived VCDs were higher, with a mean bias of +0.5–0.9 × 10<sup>15</sup> molec cm<sup>-2</sup>. This last finding is different from previous studies whereby MAX-DOAS geometric VCDs were higher than satellite determinations, albeit for urban areas with higher VCDs. An effective boundary layer height, BLH<sub>eff</sub>, is defined as the ratio of the tropospheric VCD and the ground level concentration of NO<sub>2</sub>. Variations of BLH<sub>eff</sub> can be linked to time of day, source region, stability of the atmosphere, and the presence or absence of elevated NO<sub>x</sub> sources. In particular, a case study is shown where a

high VCD and BLH<sub>eff</sub> were observed when an elevated industrial plume of NO<sub>x</sub> and SO<sub>2</sub> was fumigated to the surface as a lake breeze impacted the measurement site. High BLH<sub>eff</sub> values (~1.9 km) were observed during a regional smog event when high winds from the SW and high convection promoted mixing throughout the boundary layer. During this event, the regional line flux of NO<sub>2</sub> through the region was estimated to be greater than 112 kg NO<sub>2</sub> km<sup>-1</sup> h<sup>-1</sup>.

## 1 Introduction

The role of nitrogen oxides in the atmosphere is paramount in atmospheric chemistry due to the deleterious effects they have on the atmosphere and biosphere. Recent estimates of global emissions of NO<sub>x</sub> (NO<sub>2</sub> + NO) to the atmosphere fall in the range of 43–46 Tg N yr<sup>-1</sup> (Jacob, 1999; Martin et al., 2003, 2006) using both bottom up and top down approaches. Approximately 74% of these emissions are attributable to anthropogenic and biomass burning sources. In the troposphere, the main source of ground state oxygen atoms, O(<sup>3</sup>P), is the photolysis of NO<sub>2</sub>, Reaction (R1), which subsequently reacts with molecular oxygen to form ozone, Reaction (R2), collectively the two most important reactions in the photochemical formation of ground level ozone (Finlayson-Pitts and Pitts, 1999).



The main losses of NO<sub>2</sub> in the atmosphere are through the photochemical formation of HNO<sub>3</sub> during the daytime,



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followed by dry and wet deposition, and through the formation of the nitrate radical, NO<sub>3</sub>, and dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, at night. Hydrolysis of N<sub>2</sub>O<sub>5</sub> on aerosols and cloud droplets to form HNO<sub>3</sub> and particle nitrate (McLaren et al., 2004) is thought to be the main removal mechanism for NO<sub>x</sub> in the atmosphere at night (Dentener and Crutzen, 1993). Heterogeneous reaction of NO<sub>2</sub> on surfaces coated with water to form HONO at night is also known to be an important reaction in the atmosphere, as photolysis of HONO is known to be a major source of OH in the morning boundary layer (Platt and Perner, 1980), and has been estimated to contribute up to 30 % of the total OH production integrated over 24 h in polluted environments (Alicke et al., 2003). For these and other reasons, measurement of NO<sub>2</sub> in the troposphere is important.

Concentrations of NO<sub>2</sub> at ground level can be measured via chemiluminescence instruments and through active DOAS (Platt and Stutz, 2008). Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) can also be used for the measurement of certain molecules such as NO<sub>2</sub> and O<sub>4</sub> through the application of the DOAS technique to spectra of sky scattered sunlight to identify and quantify column abundances of trace gases that have narrow band absorption structures in the near UV and Vis wavelength range (Hönninger et al., 2004). In general terms, MAX-DOAS can in principle give more information on the vertical distribution of absorbers than in-situ point source measurements. The measurement requires a less sophisticated optical system, less maintenance, and less power than comparable active DOAS systems. Typical instruments have moving telescopes or mirrors that allow the collection of scattered light from different viewing directions, defined by the elevation angle above the horizon,  $\alpha$ , and the azimuth telescope pointing direction,  $\beta$ . Direct measurements are analyzed to yield slant column densities (SCDs) of trace absorbers integrated along the light path, and differential slant column densities (DSCDs) of trace gas species. DSCDs are determined by fitting all measurements ( $\alpha < 90^\circ$ ) with zenith ( $\alpha = 90^\circ$ ) reference spectra. These spectra, called Fraunhofer references, are used to eliminate strong solar features in the incoming spectrum, and cancel out stratospheric absorptions, allowing DSCDs to contain mainly tropospheric absorptions (Hönninger et al., 2004).

The conversion of DSCDs into vertical column densities (VCDs) is not simple because, unlike for active DOAS, the exact path length for each DSCD is not known and depends on factors such as aerosol levels, clouds, albedo, the profile of the trace gases, and the location of the sun. The air mass factor (AMF) is defined as the ratio of the SCD over the VCD of a trace gas (Solomon et al., 1987; Perliski and Solomon, 1993). Radiative transfer models (RTMs) may be used to obtain AMFs based upon the above parameters. Under conditions with low aerosol, the AMF may be geometrically approximated by  $1/\sin(\alpha)$  for a lower atmospheric absorber and scattering event above the absorbing layer (i.e. troposphere).

However, since aerosols are present in most cases, this approximation is rarely valid, and an RTM should be used.

Spectroscopic instruments aboard satellites allow for the measurement of SCDs of trace gases (Bovensmann et al., 1999; Levelt et al., 2006). Using various algorithms, VCDs of trace gases can be determined after estimation of the AMF through radiative transfer modeling (Martin et al., 2002; Celarier et al., 2008). Satellites have the spatial advantage of obtaining global coverage, but have the temporal disadvantage of only obtaining a daily (OMI) or slightly better than weekly (SCIAMACHY) measurement for a given location on earth. The calculation of appropriate AMFs is a major task in the retrieval of tropospheric VCDs from satellite observations, as it requires a-priori information on clouds, aerosols, ground albedo, and trace gas profile. Satellite measurements of VCDs are also averaged over large pixel sizes and thus are challenged in the detection of changes on small spatial scales.

As MAX-DOAS and satellites yield comparable information on VCDs, intercomparison between the two methods is desirable. Recent studies have attempted to validate satellite measurements with ground-based measurements (Irie et al., 2009; Chen et al., 2009). The Dutch Aerosol and Nitrogen Dioxide Experiments for Validation of OMI and SCIAMACHY (DANDELIONS) study focused on urban areas and used geometrical considerations to convert MAX-DOAS DSCDs into VCDs (Brinksma et al., 2008; Celarier et al., 2008). Results from this study indicated that satellites underpredict NO<sub>2</sub> VCDs. Other studies have used RTMs to determine aerosol conditions and VCDs from MAX-DOAS in both rural and urban areas, using approaches that require a-priori assumptions (Wittrock et al., 2004; Heckel et al., 2005; Irie et al., 2008; Lee et al., 2009; Cl  mer et al., 2010).

In this paper, an original two-step approach to determine NO<sub>2</sub> VCDs from MAX-DOAS measurements is outlined, applied to a data set on a routine basis, and validated with other field measurements. The first step makes use of measured O<sub>4</sub> DSCDs and the RTM McArtim (Monte carlo Atmospheric radiative transfer inversion model) to obtain aerosol conditions for each MAX-DOAS measurement following the approach introduced by Li et al. (2010). This aerosol information is then input to McArtim for the calculation of NO<sub>2</sub> AMFs that are ultimately compared to the measured MAX-DOAS SCDs to obtain NO<sub>2</sub> VCDs. In addition to the NO<sub>2</sub> VCDs, aerosol optical depth ( $\tau$ ) values, aerosol layer heights ( $H_{\text{aer}}$ ), and gas layer heights ( $H_{\text{gas}}$ ) are also determined. A full description and comprehensive analysis of the methodology used is described in Wagner et al. (2011).

Complex meteorological phenomena imposed by lake breezes interacting with anthropogenic sources are known to modify the air quality in southern Ontario (Reid et al., 1996; Hastie et al., 1999; Sills et al., 2011). One goal of the 2007 Border Air Quality and Meteorology Study (BAQS-Met) was to examine such interactions, using a 3-week dataset collected in a rural region of southwestern Ontario,

supported by ground-based and aircraft-based measurements of trace gases and aerosols. The methodology outlined here for the determination of VCDs of NO<sub>2</sub> is validated against experimentally derived composite profiles of NO<sub>2</sub> (aircraft + ground measurements) collected during BAQS-Met, and compared to spatially and temporally coincident NO<sub>2</sub> VCDs determined from the satellite instruments, OMI and SCIAMACHY. The aerosol optical depth values are compared to spatially relevant OMI, MODIS, AERONET, and PM<sub>2.5</sub> measurements. Case studies are presented to demonstrate the ability of MAX-DOAS to detect the complex transport of NO<sub>2</sub> in this region.

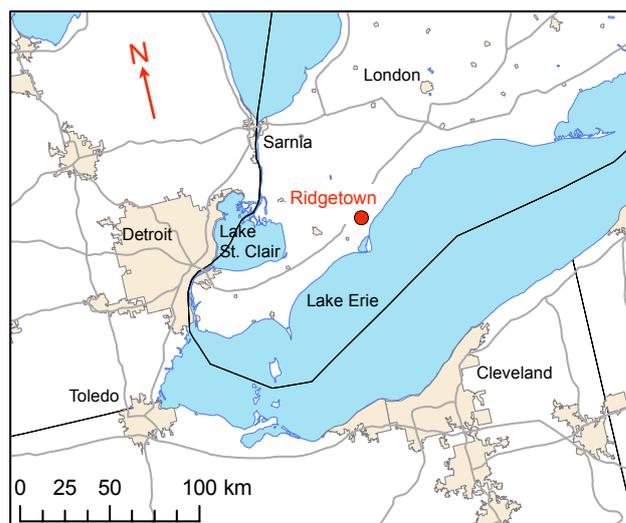
## 2 Experimental

### 2.1 BAQS-Met Ridgetown supersite

Measurements were acquired at the Ridgetown site (Fig. 1), during the BAQS-Met field study, 20 June–10 July 2007. Ridgetown is a rural community with a population of ~3500. The measurement site (42.45° N, 81.89° W), at an elevation of 202 m a.s.l., was located in an agricultural field at the north end of the University of Guelph (Ridgetown campus) away from the town center and direct anthropogenic influences. Surrounding sources (distance and direction) that can influence the site include a major highway, HWY 401 (4 km N), major refineries and chemical industry in Sarnia, ON (70 km NW), 2 major coal-fired power plants (65 km NW), Detroit/Windsor (100 km W), Cleveland, OH (100 km S) and the Golden Horseshoe (Toronto/Hamilton) urban area (200 km NE). Numerous urban areas and coal-fired power plants are also located in the Ohio valley region (100–500 km, S–SW). The site was 10 km from the north shoreline of Lake Erie.

### 2.2 The MAX-DOAS instrument and retrieval

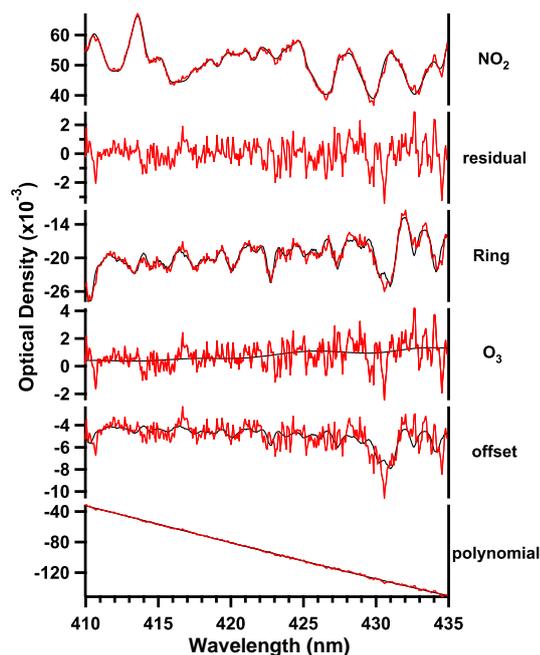
The MAX-DOAS instrument used to measure scattered sunlight included a 1 m focal length Newtonian telescope (Sky Watcher, *f*/5) with a 20 cm primary mirror and a field of view of 0.06°. A stepper motor controlled the elevation angle ( $\alpha$ ), over the range from 0° (horizon) to 90° (zenith) with an error of  $\pm 0.2^\circ$ . A fiber optic coupler in the telescope eyepiece focuses light into the fiber optic (2 m, 1000  $\mu\text{m}$  diameter UV enhanced) that transfers light to a CCD spectrometer (Ocean Optics USB 2000+, 323–471 nm, grating #7, 2400 lines  $\text{mm}^{-1}$ , 50  $\mu\text{m}$  slit, UV4 upgrade, L4 lens), with 0.5 nm resolution. The spectrometer was housed in a Peltier cooling thermoelectric unit (Resonance Inc.) to achieve a stable temperature of  $15 \pm 0.2^\circ\text{C}$ . The spectrometer data was transferred to a PC via USB connection, while a custom LabVIEW program automated the measurement sequence including light level determination, integration times, collection and storage of averaged spectra, and movement of the telescope elevation angle by stepper motor prior to the next



**Fig. 1.** BAQS-Met field study Ridgetown supersite and other areas of interest in southwestern Ontario and adjacent areas in the USA.

measurement. Every measurement began with an automatic determination of light level. This information was used to adjust the integration time of the measurement, ensuring that all measurements had an approximately equal level of signal. One complete cycle lasting approximately 30 min, consisted of a series of measurements with the following elevation angles ( $\alpha$ ): 90°, 30°, 10°, 6°, 4°, 2°. Each measurement typically consisted of 2000 averages with integration times ranging between 30–2000 ms, depending on light conditions. With the rationale of studying the passage of lake breeze fronts at the site, the MAX-DOAS telescope was pointed in the SW direction ( $\beta = 235^\circ$ ), parallel to the shoreline of Lake Erie.

Each spectrum was corrected by subtracting an electronic offset and dark noise spectrum. These corrected spectra were analyzed using the well-known DOAS technique (Plane and Smith, 1995; Platt, 1994; Platt and Stutz, 2008). A wavelength calibration using WinDOAS (Fayt and Roozendael, 2011) was performed by fitting a noon-time zenith spectrum ( $\alpha = 90^\circ$ ) taken on a clean day, henceforth called the Fraunhofer Reference Spectrum (FRS), to a high resolution solar spectrum (Kurucz et al., 1984) that was convolved with the instrument's slit function. A Ring spectrum (Grainger and Ring, 1962) was calculated from the FRS with DOASIS (Kraus, 2006). The NO<sub>2</sub> and O<sub>3</sub> (223 K and 243 K) absorption cross sections (Bogumil et al., 2003; Vandaele et al., 1998) were convolved using WinDOAS to match the instrument's resolution, while the O<sub>4</sub> (Greenblatt et al., 1990) cross section was interpolated. To determine the NO<sub>2</sub> DSCD for each spectrum, a 3rd order polynomial, the logarithm of the FRS, the Ring spectrum, convolved NO<sub>2</sub>, convolved O<sub>3</sub> (223 K) and an additive polynomial (stray light) were fit to the logarithm of the corrected measurement spectrum



**Fig. 2.** NO<sub>2</sub> MAX-DOAS fit retrieval for a measurement with  $\alpha = 4^\circ$  on 20 June 2007, 09:46 EDT. This fit, performed between 410–435 nm, includes the NO<sub>2</sub> and O<sub>3</sub> absorption cross sections, plus a 3rd order polynomial, offset polynomial, FRS, and Ring. The residual of the fit is shown in the second panel. For each remaining panel the black line represents the DOAS fit, and the red line represents the DOAS fit plus the residual of the species examined.

using WinDOAS in the fit range 410–435 nm. All NO<sub>2</sub> fits were performed using a single FRS selected from a clean day during the field study. Figure 2 gives a sample fit for 20 June 2007, 09:46 EDT (Eastern Daylight Time = UTC-4). To determine the O<sub>4</sub> DSCD for each spectrum, a 4th order polynomial, the logarithm of the FRS, the Ring spectrum, interpolated O<sub>4</sub>, convolved NO<sub>2</sub>, convolved O<sub>3</sub> (223 K and 243 K) and an additive polynomial were fit to the logarithm of the corrected measurement spectrum in the fit range 355–385 nm. All O<sub>4</sub> fits were performed using daily FRS spectra selected from time periods closest to solar noon.

### 2.3 The active DOAS instrument and retrieval

Measurements of ground-based NO<sub>2</sub> were made using an active DOAS instrument that has been described in detail previously (McLaren et al., 2010). A retro-reflector was located 1.06 km SW of the site ( $\beta = 235^\circ$ ) at an elevation of 6 m a.g.l., giving a total path length of 2.12 km and an average beam height of 3.5 m a.g.l. The return beam was focused onto a 200  $\mu$ m diameter quartz fiber optic (Ocean Optics), which coupled the light into a miniature spectrometer (Ocean Optics USB2000, Grating #10, 295–492 nm, 1800 lines mm<sup>-1</sup>, 2048 element CCD, 25  $\mu$ m slit, UV2 upgrade, L2 lens, resolution  $\sim 0.5$  nm). Spectra were acquired

with integration times between 150–350 ms and 4000 averages, for a time resolution of 7–13 min. Mercury lamp spectra were collected periodically for wavelength calibration and for convolving molecular reference spectra to the slit function of the spectrometer. Each ambient spectrum was corrected for electronic offset and dark noise. All spectra were fit using DOASIS (Kraus, 2006) in the range of 422–450 nm. The NO<sub>2</sub> fit scenario included a Xe lamp reference spectrum, convolved spectra of NO<sub>2</sub> (Vandaele et al., 1998) and O<sub>3</sub> (223 K) (Bogumil et al., 2003), and a 3rd order polynomial. The detection limit ( $3\sigma$ ) for NO<sub>2</sub> was 1.1 ppb, determined by repetitive determination of a low concentration sample.

### 2.4 SCIAMACHY satellite measurements

The SCanning Imaging Absorption spectroMeter for Atmospheric CHartography (SCIAMACHY) on board the European Space Agency's ENVironmental SATellite (ENVISAT) (Bovensmann et al., 1999) measures Earthshine spectra from the UV to the NIR with a spectral resolution of 0.22–1.48 nm. It is operated in different viewing geometries, including nadir and limb. In nadir geometry (directed vertically down), the footprint of a single pixel is  $\sim 30 \times 60$  km<sup>2</sup>. Global coverage of nadir measurements is achieved every 6 days. In standard operation mode, the measurement state alternates between limb geometry (directed horizontally, tangential to the Earth's surface), and nadir in such a way that limb measurements probe almost the same stratospheric air mass as subsequent nadir measurements.

From the Earthshine spectra measured by SCIAMACHY, total slant column densities of NO<sub>2</sub> are determined using the DOAS fitting technique. For the NO<sub>2</sub> fit in the spectral range 431–460 nm, appropriately convolved absorption cross sections of O<sub>3</sub>, NO<sub>2</sub>, O<sub>4</sub>, H<sub>2</sub>O, H<sub>2</sub>O (liquid), and CHO-CHO, Ring spectra accounting for vibrational and rotational Raman scattering, and a 5th order polynomial are included (Beirle et al., 2010). In order to extract tropospheric column densities, the stratospheric fraction is estimated and subtracted. This was done using the Reference Sector Method (Beirle et al., 2010). Stratospheric column densities are estimated over the remote Pacific and the remaining tropospheric residuals are corrected for longitudinal variations using the limb measurements of SCIAMACHY. For the conversion of tropospheric SCDs into VCDs of NO<sub>2</sub> (VCD<sub>SCIA</sub> values), tropospheric AMFs are calculated via the RTM McArtim (Deuschmann et al., 2011), assuming a fixed tropospheric profile with 80 % of the tropospheric NO<sub>2</sub> within a constant boundary layer with a height of 1 km (Chen et al., 2009).

### 2.5 OMI satellite measurements

Onboard the Aura satellite, the Ozone Monitoring Instrument (OMI) is a nadir-viewing spectroradiometer that uses a 2-D CCD to simultaneously measure the Earthshine spectra in the UV-Vis range from 270–500 nm (Levelt et al., 2006).

Specifically, OMI measures in three broad spectral regions (UV-1, UV-2, Vis) with a spectral resolution between 0.45 and 1.0 nm. It provides global coverage daily with a pixel size of 13 × 24 km<sup>2</sup> at nadir increasing to ~40 × 160 km<sup>2</sup> at the two ends of the scan line.

The present study uses the NASA standard product (overpass version) of the VCD of NO<sub>2</sub> (VCD<sub>OMI</sub>) obtained from the NASA Aura Validation Data Centre (AVDC) website (NASA, 2010b). From the Earthshine spectra measured by OMI, total slant column densities of NO<sub>2</sub> are determined using the DOAS fitting technique. For the NO<sub>2</sub> fit in the spectral range 405–465 nm, appropriately convolved absorption cross sections of O<sub>3</sub> (Burrows et al., 1999), NO<sub>2</sub> (Vandaele et al., 1998), H<sub>2</sub>O (Harder and Brault, 1997), a Ring spectrum (Chance and Spurr, 1997) accounting for vibrational and rotational Raman scattering, and a cubic polynomial are included. To convert these SCDs into VCD<sub>OMI</sub> values, different types of AMFs were calculated using geographically gridded (2.5° × 2.0°) annual mean NO<sub>2</sub> profiles (GEOS-CHEM was used for tropospheric, and the Goddard Chemical Transport model was used for stratospheric profiles (Bucsela et al., 2006)). Details of the algorithm used for the retrieval of the VCD<sub>OMI</sub> may be found in (Boersma et al., 2001; Bucsela et al., 2006; Celarier et al., 2008; Wenig et al., 2008).

## 2.6 MODIS and OMI aerosol products

The MODerate resolution Imaging Spectroradiometer (MODIS) provides the aerosol optical depth over portions of the continents and over oceans, from two satellites (Terra, Aqua). Daily level 2 data products provide a spatial resolution of a 10 × 10 1-km pixel array (nadir). Two MODIS aerosol level 2 data products, collection 5, MOD04\_L2 and MYD04\_L2, from the Terra and Aqua satellites respectively, are available from the Level 1 and Atmospheric Archive and Distribution System (LAADS) website (NASA, 2010a). Only those data products that overlapped Ridgetown were used. All MODIS aerosol optical depth values were found at λ = 550 nm, and had a maximum sensitivity over land of 0.05 ± 15 % (Levy et al., 2007). OMI aerosol optical depth (τ) values were taken from the NASA AVDC (NASA, 2010b). The OMAERUV L2 product was selected (λ = 388 nm) for a satellite overpass of Ridgetown. Information on this OMI near-UV retrieval algorithm may be found in Torres et al. (1998).

## 2.7 AERONET aerosol products

AERosol RObotic NETWORK (AERONET) aerosol optical depth (τ) values were taken from direct solar measurements using CIMEL sun photometers at two measurement sites (Kellogg, Michigan, USA, 42.41° N, 85.37° W, 293 m a.s.l., and Egbert, Ontario, Canada, 44.23° N, 79.75° W, 264 m a.s.l.) (NASA, 2010c). All τ values used

have an uncertainty of ~0.01 to 0.02 (λ = 340 and 380 nm) and were AERONET Version 2.0, Level 2.0 – quality assured data, meaning they were pre- and post-field calibrated, automatically cloud-cleared and manually inspected. Details regarding the AERONET network, and the procedures used to calculate aerosol optical depths may be found in (Dubovik and King, 2000; Holben et al., 1998, 2001).

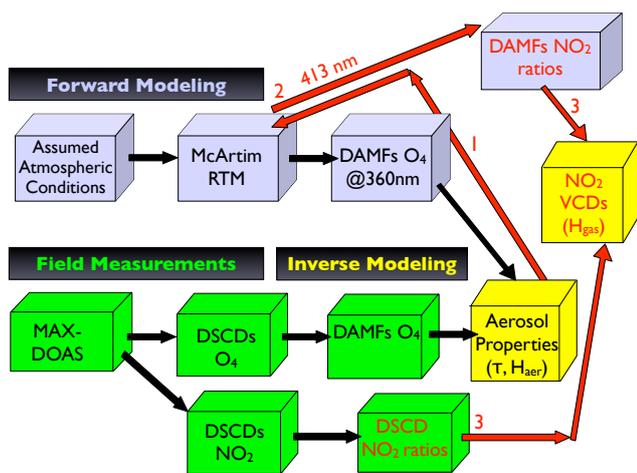
## 2.8 Additional supporting measurements

The NO<sub>2</sub>, SO<sub>2</sub>, and PM<sub>2.5</sub> were measured at ground level using a chemiluminescence NO<sub>x</sub> analyzer with Mo converter (Thermo Model 42C), trace level pulsed fluorescence SO<sub>2</sub> analyzer (Thermo Model 43C-TL), and Tapered Element Oscillating Microbalance (TEOM) ambient PM<sub>2.5</sub> monitor (R & P Model 1400B with sample equilibration system), respectively. These measurement devices were located in the Ontario Ministry of the Environment's mobile particulate laboratory at the Ridgetown site. Measurements of NO<sub>2</sub> and other meteorological measurements were also made on-board the NRC Twin Otter Aircraft that was dedicated to the BAQS-Met field campaign. The NO<sub>2</sub> measurements were performed with a chemiluminescence NO<sub>x</sub> instrument (TECO 42S) retrofit with a photolytic converter, for measurement of “true” NO<sub>2</sub> (±15 %), with a detection limit of 60 pptv (3σ, 1 min). Details on the aircraft campaign measurements are provided in Hayden et al. (2011).

The scanning LIDAR facility (RASCAL – Rapid Acquisition SCanning Aerosol LIDAR), capable of fast azimuth and elevation scanning of the lower troposphere, was present at the Ridgetown site. A full description of its operation is given elsewhere (Strawbridge et al., 2004). It was primarily used for the comparison of boundary layer heights to H<sub>aer</sub> and H<sub>gas</sub>, as described in Sect. 4.3.

## 3 Methodology for determining τ and NO<sub>2</sub> VCDs from MAX-DOAS

A full description of the methodology used for determining aerosol optical depths (τ) and NO<sub>2</sub> VCDs from the MAX-DOAS measurements is included in the Supplemental Material. A short description, summarized in Fig. 3, is given here. The methodology includes experimental retrievals (Fig. 3 – field measurements) of the DSCDs of NO<sub>2</sub> and O<sub>4</sub> from the MAX-DOAS measurements, as described previously. Wagner et al. (2004) introduced the concept of using the O<sub>4</sub> absorption to retrieve aerosol profiles (Frieß et al., 2006; Li et al., 2010; Wittrock et al., 2004). The O<sub>4</sub> species is found in greatest amounts close to ground level, the result being that O<sub>4</sub> DSCDs are very sensitive to changes in light path due to varying levels of aerosols. A radiative transfer model (Fig. 3 – forward modeling), McArtim (Deutschmann et al., 2011), calculated the DAMFs of O<sub>4</sub> at all elevation angles as a function of the solar and experimental conditions at Ridgetown.



**Fig. 3.** Flowchart of methodology for determination of NO<sub>2</sub> 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.

The RTM presumes that the aerosols are confined to a box of height  $H_{\text{aer}}$ .  $H_{\text{aer}}$  is equivalent to the boundary layer height (BLH) if aerosols are 100% confined to the boundary layer (also see (Zieger et al., 2011)), although this is rarely the case. A comprehensive set of O<sub>4</sub> DAMFs was catalogued in a look up table. A MATLAB routine (Fig. 3 – inverse modeling) was used to minimize the difference between O<sub>4</sub> DAMFs in the look-up and O<sub>4</sub> DAMFs calculated by dividing the measured DSCDs by an estimated VCD. This minimization yields  $\tau$ , henceforth named  $\tau_{\text{RTM}}$ , and  $H_{\text{aer}}$ , which describe the aerosol conditions for each cloud-free measurement series.

The aerosol conditions were input to McArtim in the determination of NO<sub>2</sub> VCDs. The NO<sub>2</sub> DAMFs are a function of both the aerosol conditions and the vertical profile of NO<sub>2</sub>. The vertical profile of NO<sub>2</sub> in the troposphere was assumed to be a homogeneous layer of thickness  $H_{\text{gas}}$ . The contribution of stratospheric NO<sub>2</sub> was removed by subtracting the SCD<sub>90</sub> in each measurement series from other SCD <sub>$\alpha$</sub>  values ( $\alpha = 2^\circ, 4^\circ, 6^\circ, 10^\circ, 30^\circ$ ) in the series. McArtim was used to calculate a comprehensive set of “box” NO<sub>2</sub> DAMFs in a lookup table. A minimization of differences between the DSCD<sub>meas</sub> ratios and the DAMF<sub>ratios</sub> in the look-up, yielded the best values of  $H_{\text{gas}}$  and VCD<sub>NO<sub>2</sub></sub>, henceforth known as VCD<sub>RTM</sub>. This inversion was performed for all complete elevation sequences with SZA < 80°. NO<sub>2</sub> sequences with deviations of more than  $2 \times \text{DSCD}_\alpha$  between DSCDs for subsequent elevation angles were eliminated. Results with non-convergent fits were not defined.

Our method assumes that both aerosols and NO<sub>2</sub> are confined to homogeneous layers of height  $H_{\text{aer}}$  and  $H_{\text{gas}}$  respec-

tively. More generally, one may model more complex scenarios in which fractions,  $f_{\text{aer}}$  and  $f_{\text{gas}}$  of total tropospheric aerosols and NO<sub>2</sub> are confined to ground layers, with remaining fractions of aerosols ( $1 - f_{\text{aer}}$ ) and NO<sub>2</sub> ( $1 - f_{\text{gas}}$ ) modeled as exponential decay functions above the homogeneous layer. In this study, a sensitivity analysis showed that the values of  $\tau$  and VCD<sub>RTM</sub> are largely insensitive to the chosen values of  $f$  ( $f \geq 0.5$ ), however the retrieved values of  $H_{\text{aer}}$  and  $H_{\text{gas}}$  are strongly a function of  $f$ . A more comprehensive description, sensitivity analysis, and further validation of the method outlined here may be found in Wagner et al. (2011).

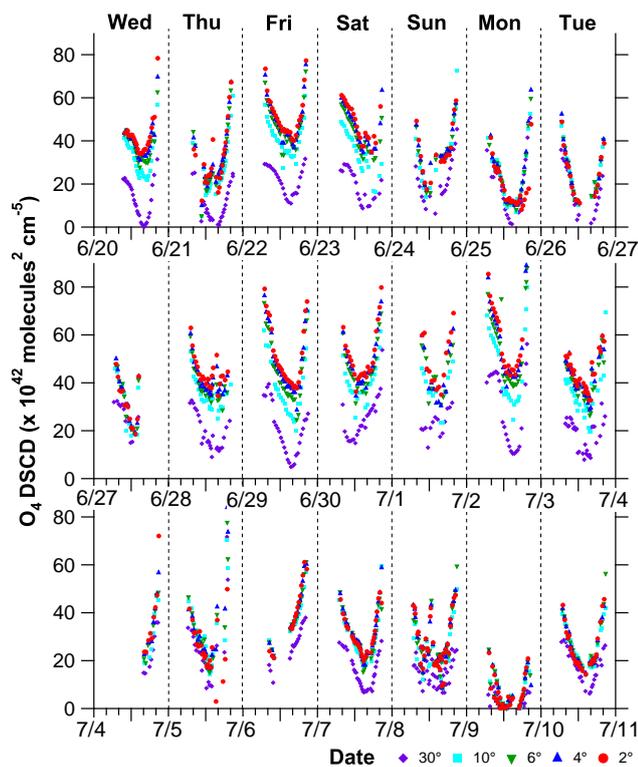
For the sake of comparison, we also present geometrically approximated VCDs of NO<sub>2</sub>, where VCD<sub>GEO</sub> = DSCD<sub>30</sub>, as shown in the Supplemental Material. For the sake of comparing to other measures of VCD in this paper, and to be consistent with other literature, a criterion was applied such that VCD<sub>GEO</sub> ( $\alpha = 30^\circ$ ) and VCD<sub>GEO</sub> ( $\alpha = 10^\circ$ ) must agree to within 15% to be retained, eliminating points affected by horizontal inhomogeneities, aerosols, or clouds (Brinkma et al., 2008; Celarier et al., 2008).

## 4 Results and discussion

### 4.1 Aerosol optical depth/aerosol extinction coefficient

Figure 4 displays the O<sub>4</sub> DSCD values at Ridgetown for the entire field campaign, under cloud-free conditions. The O<sub>4</sub> DSCDs typically increase with decreasing elevation angles, indicative of a tropospheric absorber, such as on 20, 22, 23, 29 June and 2 and 7 July. However, in several cases (parts of 25, 26, 27 June, and 4, 5, 9, and 10 July) there appears to be little dependence of the DSCDs on elevation angle. This phenomenon occurs when high levels of aerosol and/or clouds are present and thus the light path from the last scattering event to the detector becomes effectively equal, regardless of the elevation angle of the observation. As only cloud-free conditions are presented here, the effect is largely due to the presence of aerosols. As such, when qualitatively comparing aerosol levels, days such as 20 June appear to contain low aerosol extinction, while days such as 9 July, contain high aerosol extinction.

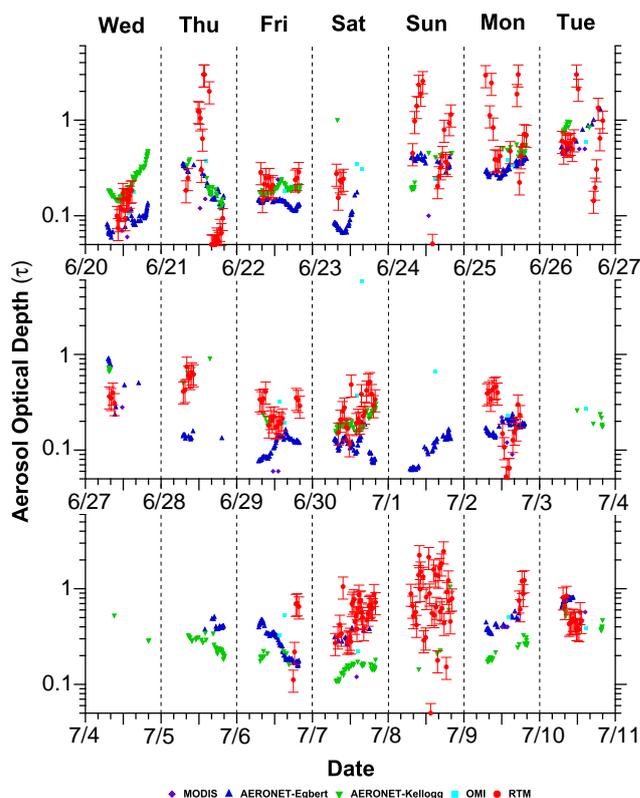
In order to assess conditions on a more quantitative level, the aerosol optical depth ( $\tau_{\text{RTM}}$ ) for each measurement series was determined at 360 nm, as described in Sect. 3 and the Supplemental Material. The  $\tau_{\text{RTM}}$  varied from 0.05 to 2.93, with a mean and a median value of 0.41 and 0.46 respectively (Fig. 5). The average relative error of each  $\tau_{\text{RTM}}$  value was estimated at 26% (Wagner et al., 2011). The  $\tau_{\text{RTM}}$  values were compared to those  $\tau$  values found from satellite measurements ( $\tau_{\text{MODIS}}$ :  $\lambda = 550$  nm,  $\tau_{\text{OMI}}$ :  $\lambda = 388$  nm), and AERONET ground-based measurements at Egbert and Kellogg ( $\tau_{\text{EGB}}$ ,  $\tau_{\text{KEL}}$ ,  $\lambda_{\text{avg}} = 360$  nm for each location). Satellite measurements are only optimally available on a daily basis. The comparison was limited due to the different wavelengths



**Fig. 4.** O<sub>4</sub> DSCDs for cloud-free conditions during the BAQS-Met campaign at the Ridgetown supersite. Major ticks represent 12 midnight and 12 noon EDT, while minor ticks indicate every 4-h increment.

used (particularly for  $\tau_{\text{MODIS}}$ ) and the fact that the satellites only provide 1 or 2 comparison points daily. Although the measurements are made at similar  $\lambda$  for the AERONET locations, they are relatively far from Ridgetown (Egbert  $\sim 320$  km NE, Kellogg  $\sim 330$  km W), yet Ridgetown is approximately central between the two locations. The above factors limit the ability to make direct comparisons of  $\tau_{\text{RTM}}$  at Ridgetown, yet the values of  $\tau_{\text{RTM}}$  do lie within the range of the other measurements, as might be expected during times when the high aerosol loading is associated with regional pollution events that affect eastern North America over large spatial distances. Such regionally polluted conditions were observed from 24–27 June and 8–10 July.

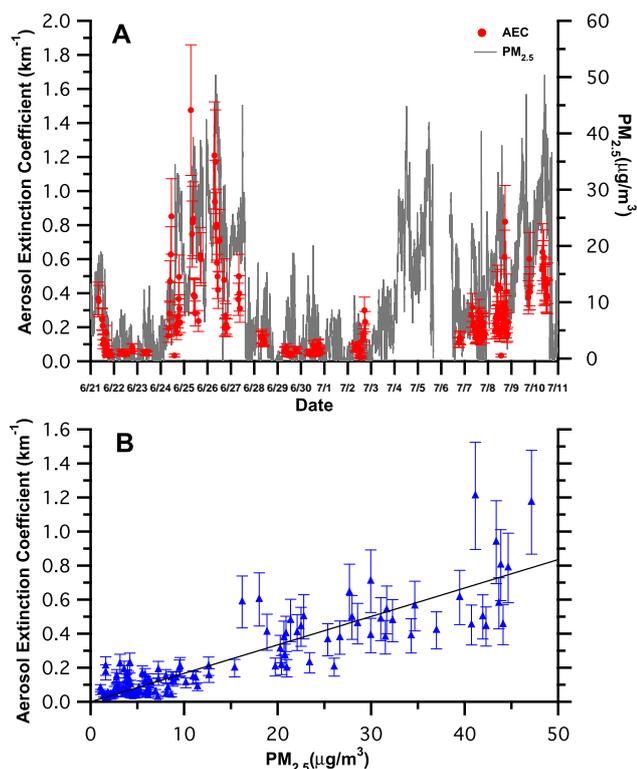
Spatially, it would be better to compare the  $\tau_{\text{RTM}}$  values with aerosol levels measured directly at Ridgetown. Although another measure of  $\tau$  is not available at the site, PM<sub>2.5</sub> mass was measured. When the PM<sub>2.5</sub> was compared to the corresponding  $\tau_{\text{RTM}}$  values, a low level of correlation was found ( $R^2 = 0.068$ ). This is not surprising since PM<sub>2.5</sub> is a ground point-source measurement of particulate mass, while  $\tau_{\text{RTM}}$  represents an integrated column quantity of aerosol extinction. A more appropriate comparison of the aerosol properties may be done by examining the aerosol extinction coefficient ( $E = \tau_{\text{RTM}}/H_{\text{aer}}$ , see Supplement).



**Fig. 5.** Aerosol optical depth for the entire BAQS-Met campaign. For AERONET locations (Egbert, Kellogg)  $\lambda_{\text{avg}} = 360$  nm, for coincident satellite measurements (OMI  $\lambda = 388$  nm, MODIS  $\lambda = 550$  nm), and for the MAX-DOAS-RTM values at Ridgetown,  $\lambda = 360$  nm.

Figure 6a shows the time series comparing the aerosol extinction coefficient and the PM<sub>2.5</sub> measured at Ridgetown. A correlation plot for these two related properties is shown in Fig. 6b using data from the entire study. Both panels show that there is a high degree of correlation between aerosol extinction and PM<sub>2.5</sub> ( $R^2 = 0.75$ ) (also see Zieger et al., 2011). This improved correlation implies that MAX-DOAS observations are sensitive to the total column amount of aerosol, in comparison to the PM<sub>2.5</sub> measurement that is sensitive to the concentration of aerosol. It also implies that temporal variations in the aerosol layer height,  $H_{\text{aer}}$ , are likely significant at Ridgetown.

Recent studies have compared local PM<sub>10</sub> and PM<sub>2.5</sub> measurements to  $\tau$  values determined from MODIS (Chu et al., 2003; Engel-Cox et al., 2004, 2006; Gupta and Christopher, 2008; Kacenenbogen et al., 2006; Pelletier et al., 2007; Schaap et al., 2009; Wang and Christopher, 2003). The extent of correlation they found between  $\tau_{550}$  (MODIS) and PM<sub>2.5</sub> varied, with  $R^2$  values ranging from 0.27 to 0.60. This range is not entirely surprising as variations in local meteorology, differing aerosol composition, and the distribution of the aerosol layer(s) may all play roles in this relationship.



**Fig. 6.** Top panel (A) – aerosol extinction coefficient (red) and PM<sub>2.5</sub> (grey) at Ridgetown. Bottom panel (B) – PM<sub>2.5</sub> vs. aerosol extinction coefficient – Ridgetown. Slope of the trend line (y-intercept zero forced) =  $16 \pm 1 \text{ m}^2 \text{ g}^{-1}$ ,  $R^2 = 0.75$ .

In particular if aerosols are concentrated in the boundary layer, and the boundary layer height is highly variable, a poor relationship between  $\tau$  and PM<sub>2.5</sub> would be expected. If the boundary layer height is known, this correlation may be greatly improved through calculation of  $E$ . For example, Koelemeijer et al. (2006) found that there was a better correlation ( $R^2 = 0.59$ ) between PM<sub>2.5</sub> measurements and the modified aerosol extinction from MODIS,  $E^*$ :

$$E^* = \frac{\tau}{\text{BLH} \cdot f(\text{RH})} \quad (1)$$

with BLH being the boundary layer height, and  $f(\text{RH})$  a factor that takes into account the hygroscopic growth of aerosols, as opposed to directly comparing hourly PM<sub>2.5</sub> and  $\tau$  ( $R^2 = 0.38$ ). Their result implied that most of the aerosol was found within the boundary layer, whose height is variable, preventing an easy direct measurement of aerosol mass through satellite derived quantities.

Further studies have determined aerosol extinction coefficients and aerosol optical depths from MAX-DOAS O<sub>4</sub> measurements and radiative transfer modeling, and compared them to PM<sub>10</sub>, LIDAR calculated extinction coefficients, and aerosol optical depths from sky radiometers. Irie et al. (2008) compared extinction coefficients from MAX-

DOAS-RTM inversions run at 476 nm with LIDAR calculated extinction coefficients (slope = 1.01,  $R^2 = 0.85$ ) and compared  $\tau$  values found from these MAX-DOAS-RTM inversions with  $\tau$  values from a sky radiometer. Both comparisons agreed to within 30 % for values determined from ground level to a height of 1 km. Lee et al. (2009) compared extinction coefficients found from a MAX-DOAS-RTM inversion run at 356 nm to LIDAR calculated extinction coefficients ( $R^2 = 0.70$ ), and they agreed to within 50 %, while a comparison between MAX-DOAS-RTM derived extinction coefficients and PM<sub>10</sub> also showed a relatively good correlation. Our results are consistent with these studies.

#### 4.2 Validation of VCD<sub>RTM</sub> against vertical measurements of NO<sub>2</sub>

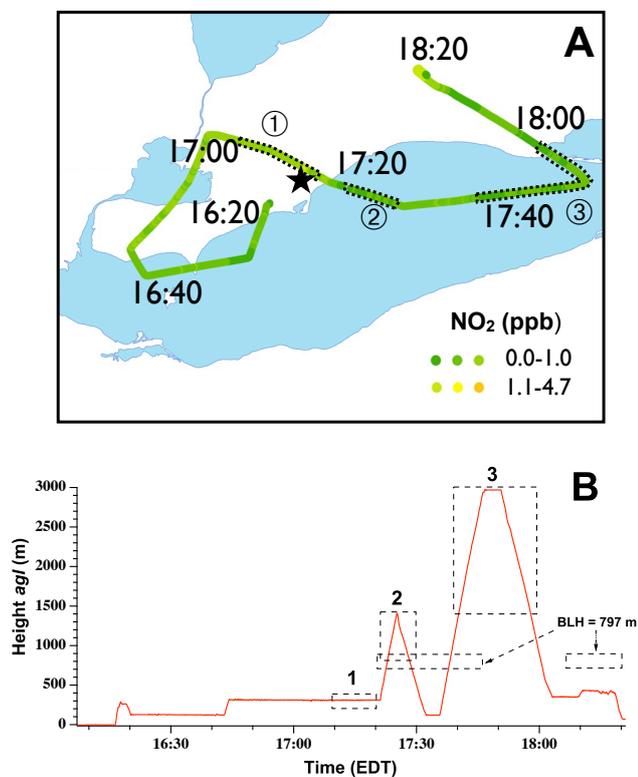
In order to validate our method for deriving NO<sub>2</sub> VCDs using MAX-DOAS and RT calculations, we derived comparative VCDs of NO<sub>2</sub> from a composite profile of ground-based and aircraft-based NO<sub>2</sub> measurements in the vicinity of Ridgetown during the same time frame as the MAX-DOAS measurements. The composite profiles included ground-based NO<sub>2</sub> measurements at Ridgetown via active DOAS, vertical measurements of NO<sub>2</sub> when the aircraft was in the vicinity of Ridgetown, and suitable estimates of NO<sub>2</sub> in the free troposphere above the maximum height of the aircraft. Suitable temporal and spatial overlapping data were found for one day, 26 June 2007. Two composite profiles of NO<sub>2</sub> were derived in the late afternoon on this day, concurrent with two MAX-DOAS measurements and their corresponding VCD<sub>RTM</sub> determinations. The vertical profiles can be split into three sections. Section 1 extends from the ground to the top of the boundary layer, where NO<sub>2</sub> was determined by ground-based and aircraft measurements of NO<sub>2</sub> close to Ridgetown. Section 2 corresponds to the region of the free troposphere from the top of the boundary layer to the maximum height at which aircraft measurements were available. Section 3 corresponds to the free troposphere above the maximum aircraft height, where a constant NO<sub>2</sub> mixing ratio of 50 ppt was assumed (Blond et al., 2007). The boundary layer height in the afternoon,  $797 \pm 45 \text{ m a.g.l.}$ , was determined by potential temperature profiles measured by the aircraft.

Figure 7a shows the flight path on 26 June where the NO<sub>2</sub> mixing ratio is displayed as a function of time and location. The position of the aircraft for every 20 min interval is also shown. Figure 7b shows the altitude profile for the flight including ascending, descending, and stable height time periods. In general, the degree of spatial homogeneity in NO<sub>2</sub> increases with height, in the absence of elevated plumes sources. Our criteria for inclusion of data in the composite profile reflected this; the aircraft had to be within 30 km of Ridgetown over land for boundary layer measurements, within 50 km of the site for heights from the top of the boundary layer to 1400 m a.g.l., and within 140 km of the site for heights between 1400 and 3000 m a.g.l. (Fig. 7). Figure 8

**Table 1.** Comparison of RTM and composite VCDs of NO<sub>2</sub> on 26 June 2007.

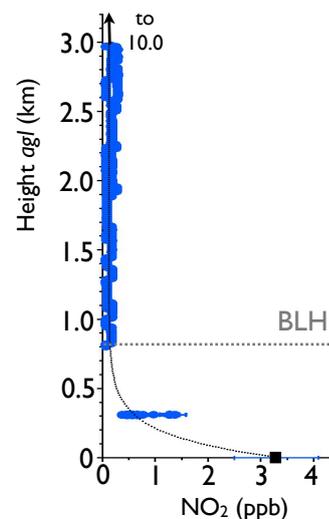
Point	Time (EDT)	VCD <sub>COMP</sub> * (10 <sup>15</sup> molec cm <sup>-2</sup> )	VCD <sub>RTM</sub> * (10 <sup>15</sup> molec cm <sup>-2</sup> )	Error (10 <sup>15</sup> molec cm <sup>-2</sup> )	VCD <sub>RTM</sub> * vs. VCD <sub>COMP</sub>
1	17:25–17:46	3.06 ± 1.22	2.59 ± 0.44	−0.47	
2	17:52–18:15	3.18 ± 1.22	3.50 ± 0.44	0.32	
Mean		3.12 ± 0.86	3.04 ± 0.31	0.40	0.98 ± 0.29
RMSE				0.40	

\* All uncertainties are standard (1σ).



**Fig. 7.** Flight path on 26 June 2007. Panel (A) shows the NO<sub>2</sub> mixing ratios and the aircraft location every 20 minutes. Panel (B) shows the aircraft elevation and BLH (a.g.l.) as a function of time. The numbered sections show the locations, elevations, and approximate mixing ratios used for constructing the composite NO<sub>2</sub> profiles. The Ridgetown supersite location is starred.

displays a sample profile. Error bars in the  $x$  dimension represent uncertainties in the NO<sub>2</sub> mixing ratios. The boundary layer was found to be inhomogeneous on this afternoon. Mixing ratios of NO<sub>2</sub>, measured when the aircraft penetrated into the boundary layer over land close to Ridgetown were much lower than values measured at the ground. For this reason, Sects. 1 and 2 were combined for the purposes of mathematical fitting. The NO<sub>2</sub> profile was assumed to decay exponentially from the ground up through Sects. 1 and 2.



**Fig. 8.** The NO<sub>2</sub> concentration profile used to construct the composite NO<sub>2</sub> VCDs on 26 June 2007. Blue circles represent NO<sub>2</sub> aircraft measurements, while the black square represents the ground-based NO<sub>2</sub> by active DOAS. The boundary layer (BLH) is marked with the horizontal dashed line.

For all sections, number densities of NO<sub>2</sub> were calculated as a function of height accounting for the non-linearity of pressure and temperature. The total tropospheric VCD of NO<sub>2</sub>, henceforth called the composite VCD (VCD<sub>COMP</sub>), is then obtained using Eq. (2):

$$\text{VCD}_{\text{COMP}} = \int_0^{\text{BL}} n_{1,\text{NO}_2} dz + \int_{\text{BL}}^{\text{TOAc}} n_{2,\text{NO}_2} dz + \int_{\text{TOAc}}^{10\text{ km}} n_{3,\text{NO}_2} dz \quad (2)$$

where  $n_{\text{NO}_2}$  is the number density of NO<sub>2</sub> for Sects. 1, 2, 3, and TOAc represents the top of available aircraft measurements.

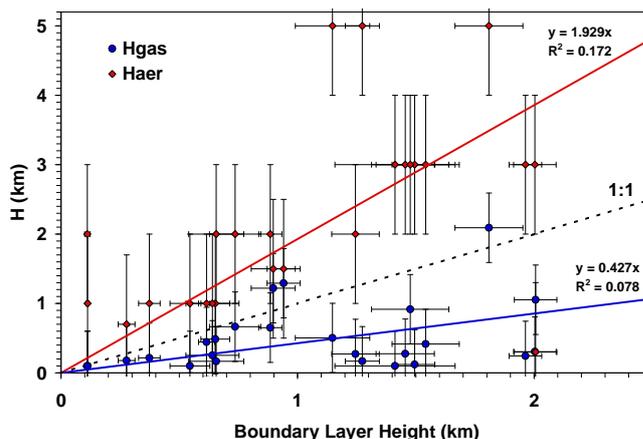
The two VCD<sub>COMP</sub> values determined on this day are compared to the corresponding VCD<sub>RTM</sub> values, coincident in time, in Table 1. The uncertainties in the VCD<sub>COMP</sub> arise from several sources. For Sects. 1 and 2, the uncertainty in the exponential fit of NO<sub>2</sub> vs. height was primary. For Sect. 3 the uncertainty in the NO<sub>2</sub> mixing ratio (50 ppt) was assumed to be ±100%. Uncertainties due to spatial and temporal differences between the aircraft measurements and the

MAX-DOAS column also exist but are not considered here as they cannot be determined. The uncertainty of VCD<sub>RTM</sub> ( $0.44 \times 10^{15}$  molec cm<sup>-2</sup>) was based on the standard deviation of VCD determinations at different elevation angles (see Supplemental Material).

The mean value of VCD<sub>COMP</sub> in Table 1 is  $3.12 \pm 0.86 \times 10^{15}$  molec cm<sup>-2</sup>, which is reasonable for a rural region (Heland et al., 2002; Irie et al., 2009; Ladstätter-Weissenmayer et al., 2003). The mean value of VCD<sub>RTM</sub> was  $3.04 \pm 0.31 \times 10^{15}$  molec cm<sup>-2</sup>. The ratio VCD<sub>RTM</sub>/VCD<sub>COMP</sub>, is  $0.98 \pm 0.29$ , which is not statistically different from 1.0. The mean bias in the comparison is  $-0.08 \times 10^{15}$  molec cm<sup>-2</sup>, again not statistically different from zero. Although we have only compared a limited number of points, this comparison serves as a validation of the method outlined in this paper for the determination of VCDs. There is no evidence of a bias in the determination of VCD using this method at the moderate NO<sub>2</sub> column levels that existed during the comparison.

#### 4.3 Comparison of boundary layer heights and retrievals of H<sub>aer</sub> and H<sub>gas</sub>

Although the focus in this study was not the determination of accurate boundary layer heights (BLHs), it is instructive to compare the retrieved aerosol and gas heights, H<sub>aer</sub> and H<sub>gas</sub>, and BLHs determined by LIDAR backscatter measurements. LIDAR data was available on 6 days (08:00–16:00 EDT), simultaneous with MAX-DOAS-RTM determinations. There were 25 simultaneous determinations of BLH, ranging from 0.1 km–2.0 km a.g.l., from early morning to late afternoon respectively. Figure 9 shows the correlations between the retrieved heights and the BLH, zero-forced since the intercepts were not statistically different from zero. The correlation coefficients are low ( $R^2 = 0.17$  for H<sub>aer</sub>; 0.08 for H<sub>gas</sub>), indicating that the retrievals only capture a small amount of the variance associated with the backscatter BLHs. It is also apparent that the values of H<sub>aer</sub> are significantly higher than the BLHs, by almost a factor of 2, and that the H<sub>gas</sub> values are significantly lower than the BLHs, by a factor of 2. The correlation coefficients are improved by applying a more rigid set of criteria for inclusion of data pairs as shown in Wagner et al. (2011); however the slopes still remain much the same, which requires an explanation. The H<sub>aer</sub> slope of  $1.92 \pm 0.21$  likely results from the fact that aerosols are not exclusively confined to the boundary layer, especially in early morning periods when significant amounts of aerosols left over from the previous day can exist in the residual layer, as was directly observable in LIDAR images. This is partly attributable to the longer lifetime of aerosols in the atmosphere, compared to NO<sub>x</sub>, and partially attributable to the ubiquitous secondary source of aerosols throughout the atmospheric column. On the other hand, the sources of NO<sub>x</sub> are predominantly surface-based within the boundary layer, which combined with its shorter lifetime than aerosols gives

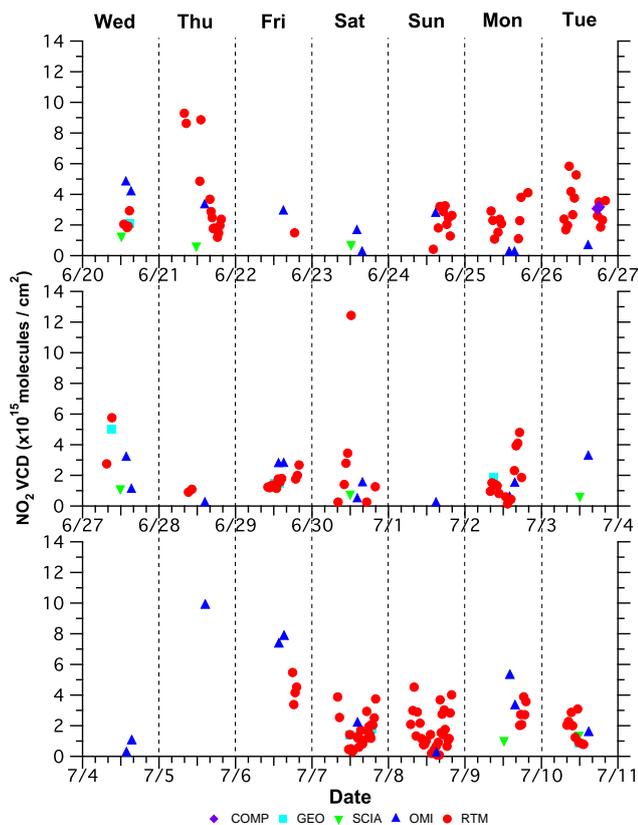


**Fig. 9.** Correlation between MAX-DOAS-RTM retrieved layer heights and boundary layer heights determined by LIDAR backscatter determinations.

rise to a negative gradient of NO<sub>2</sub> in the boundary layer (see Fig. 8). When modeled as a homogeneous layer, the H<sub>gas</sub> height is lower than the BLH (slope =  $0.43 \pm 0.08$ ); however an accurate VCD can still be obtained. A sensitivity analysis was performed in which the fraction of NO<sub>2</sub> ( $f_{\text{gas}}$ ) and aerosols ( $f_{\text{aer}}$ ) confined to the homogeneous layer were allowed to vary from 0.5 to 1.0. The  $\tau_{\text{RTM}}$  values were found to agree quite well ( $\pm 2\%$ ) for moderately and highly polluted days, and less so on low aerosol days with a maximum difference of 21% on a very clean day ( $\tau \sim 0.05$ ). The variance in VCD<sub>RTM</sub> was  $\pm 6\%$  under all aerosol conditions tested in the sensitivity study. Thus accurate values of  $\tau$  and VCD are still obtained using the current methodology. If this method is to be used for accurate determinations of BLH, then time dependent values of  $f_{\text{aer}}$  and  $f_{\text{gas}}$  would be needed. A more thorough discussion of the sensitivity of the retrievals to  $f_{\text{aer}}$  and  $f_{\text{gas}}$  is given elsewhere (Wagner et al., 2011).

#### 4.4 Comparison between VCD<sub>RTM</sub> and satellite VCDs of NO<sub>2</sub>

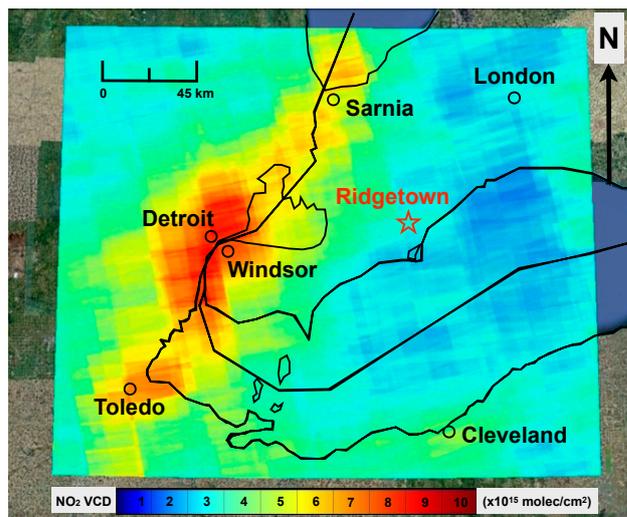
Figure 10 displays all tropospheric VCDs of NO<sub>2</sub> for the Ridgetown site throughout the study. The VCD<sub>RTM</sub>, VCD<sub>GEO</sub>, and VCD<sub>COMP</sub> (26 June) are shown, along with the satellite-derived measures, VCD<sub>OMI</sub> and VCD<sub>SCIA</sub>. Only 9 VCD<sub>SCIA</sub> measurements were available during the study period due to the limited temporal sampling of the ENVISAT satellite. There were 31 measurements from the OMI instrument on the Aura satellite as it provides daily global coverage with successive orbits separated by 100 min providing one or two measurements per day at a specified location. To facilitate comparisons between VCD<sub>RTM</sub> and VCD<sub>satellite</sub>, measurements were paired only when the two measurements were made within one hour of each other. Only one comparison pair was available for SCIAMACHY while 8 comparisons were available for the OMI instrument.



**Fig. 10.** Comparison of all NO<sub>2</sub> tropospheric VCDs at Ridgetown derived from aircraft/ground, satellite, and MAX-DOAS-RTM measurements.

The statistical comparison is provided in Table 2, where all VCDs are compared to VCD<sub>RTM</sub>. The comparison indicates that the VCDs derived by satellite were higher than those of the VCD<sub>RTM</sub>. Presuming a proportionate error, the two satellites determinations are about 50% higher than VCD<sub>RTM</sub>, but only statistically so for the OMI instrument. The proportionate error for OMI was determined in two ways: (i) the ratio of the averages, VCD<sub>OMI</sub>/VCD<sub>RTM</sub>, and (ii) the slope of the regression of VCD<sub>OMI</sub> vs. VCD<sub>RTM</sub>, with the y-intercept forced to zero (intercept was equal to zero within error). If one presumes a constant bias in the satellite retrievals, the mean bias is  $+0.91 \times 10^{15}$  molec cm<sup>-2</sup> for OMI and  $+0.48 \times 10^{15}$  molec cm<sup>-2</sup> for SCIAMACHY. Our results do not provide sufficient statistical evidence as to whether the retrieval error is proportionate or absolute. However, it should be noted that the total VCDs experienced at this rural site are relatively small. Thus the large apparently relative overprediction for the satellite retrievals (+50%) is not necessarily a result that is transferable to more polluted regions with higher VCDs of NO<sub>2</sub>.

Earlier studies (Brinkma et al., 2008; Celarier et al., 2008; Chen et al., 2009; Irie et al., 2009) found various satellite-derived NO<sub>2</sub> VCDs to be substantially lower than



**Fig. 11.** Averaged OMI tropospheric NO<sub>2</sub> VCDs for the intensive field study period (20 June–10 July 2007) in southwestern Ontario. Ridgetown supersite is starred.

MAX-DOAS derived NO<sub>2</sub> VCDs. It should be noted that in those studies the MAX-DOAS VCDs were geometrically approximated (similar to VCD<sub>GEO</sub>), and the distinction from a full MAX-DOAS with radiative transfer derived VCD (VCD<sub>RTM</sub>) should be taken into account in all these studies. Our observation of satellite VCDs with a positive bias compared to VCD<sub>RTM</sub> and VCD<sub>COMP</sub> is in contrast to the earlier studies. One possible explanation for this is that previous comparisons have frequently focused on urban and suburban areas where average NO<sub>2</sub> VCDs were significantly higher. For example, the VCD of NO<sub>2</sub> ranged from  $0.5\text{--}5 \times 10^{16}$  molec cm<sup>-2</sup> during DANDELIONS at Cabauw, Netherlands (Brinkma et al., 2008; Celarier et al., 2008) with a median of  $\sim 1.5 \times 10^{16}$  molec cm<sup>-2</sup>, whereas the VCD range in the current study is  $0.01\text{--}1.25 \times 10^{16}$  molec cm<sup>-2</sup> with a median of  $2.00 \times 10^{15}$  molec cm<sup>-2</sup>. In that study, the MAX-DOAS instruments measured very high NO<sub>2</sub> VCDs in a polluted region, which could not be completely captured by the satellite, due to the regional averaging implicit with a large pixel size. Under such conditions, the satellite will measure lower values than the more localized in situ measurement. The opposite would be true in this study. Being situated in a rural region, the local measurements of NO<sub>2</sub> made by MAX-DOAS and the aircraft are relatively low. In contrast, the large pixel area coverage of the satellite instruments (OMI –  $13 \times 24$  km<sup>2</sup>, SCIAMACHY –  $30 \times 60$  km<sup>2</sup>) will be higher than the local measurement when the pixel is impacted by surrounding urban areas, such as may occur when prevailing westerly winds carry pollutants from Windsor-Detroit towards Ridgetown. If a significant amount of a given pixel lies within a position west of Ridgetown, it may be detecting NO<sub>2</sub> from this urban outflow, and thus overestimate the actual NO<sub>2</sub> present at the site (see Fig. 11).

**Table 2.** Comparison of various NO<sub>2</sub> VCDs to the values of VCD<sub>RTM</sub>.

	OMI AURA*	SCIAMACHY ENVISAT	Geometric Approximation*	Aircraft Composite*
Number of Data Pairs, N	8	1	10	2
$\overline{\text{VCD}}_{\text{measured}} (\times 10^{15} \text{ molec cm}^{-2})$	$2.67 \pm 0.18$	1.39	$1.88 \pm 0.05$	$3.12 \pm 0.86$
$\overline{\text{VCD}}_{\text{RTM}} (\times 10^{15} \text{ molec cm}^{-2})$	$1.76 \pm 0.16$	$0.92 \pm 0.44$	$2.05 \pm 0.14$	$3.04 \pm 0.31$
$\overline{\text{VCD}}_{\text{measured}}/\overline{\text{VCD}}_{\text{RTM}}$	$1.52 \pm 0.17$	1.5	$0.92 \pm 0.07$	$1.02 \pm 0.30$
Slope (forced zero intercept)	$1.47 \pm 0.20$	N/A	$0.88 \pm 0.04$	$1.01 \pm 0.13$
Correlation, <i>R</i>	0.63	N/A	0.97	0.98
Mean Absolute Error ( $\times 10^{15} \text{ molec cm}^{-2}$ )	1.12	0.48	0.30	0.40
RMSE ( $\times 10^{15} \text{ molec cm}^{-2}$ )	1.33	N/A	0.41	0.40
Mean Bias ( $\times 10^{15} \text{ molec cm}^{-2}$ )	+0.91	+0.48	-0.17	+0.08

\* All uncertainties are standard ( $1\sigma$ ).

Additionally, the satellite retrievals used here do not consider aerosol conditions or temporal changes in the NO<sub>2</sub> profile in their fitting routines. Uncertainties in these parameters could lead to uncertainties in the overall satellite-derived VCD, and with low levels of NO<sub>2</sub>, this may lead to large relative uncertainties in these VCDs.

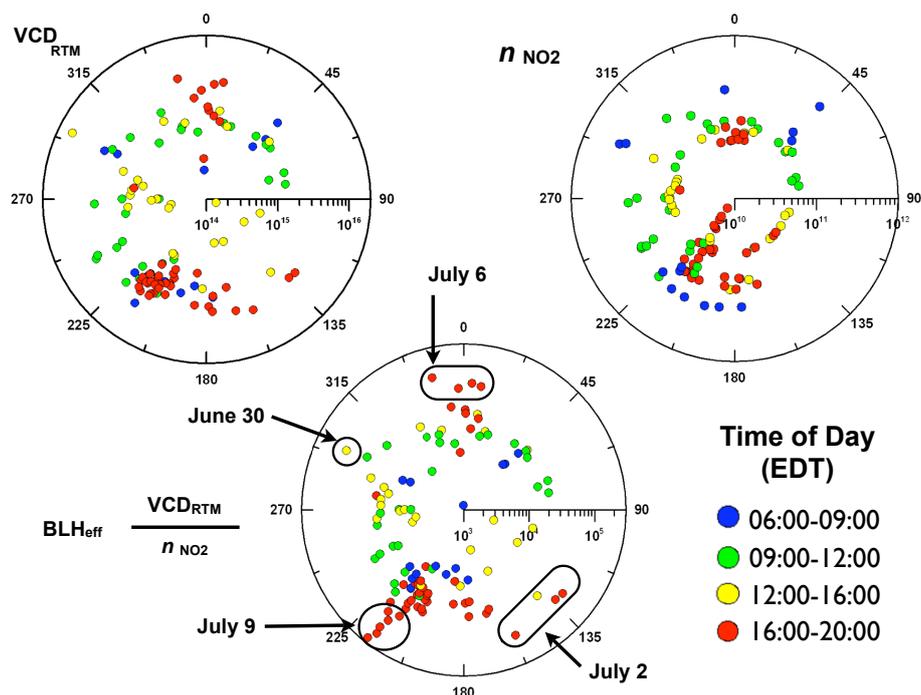
Also included in Table 2 is a statistical comparison of VCD<sub>GEO</sub> to VCD<sub>RTM</sub>, where the conservative selection criteria for inclusion was fulfilled, namely that the values of geometrically approximated VCDs for elevation angles of 10° and 30° in the same measurement series agreed to within 15%. The selection criteria is quite limiting and is fulfilled for 10 data pairs only, as seen in the table. Similar criteria has been used in past studies to ensure that the VCDs determined by the geometric approximation are not heavily influenced by aerosols, thus making them appropriate for comparison to satellite measures (Brinksmas et al., 2008; Celarier et al., 2008). Although our method with full radiative transfer is favored, the VCD<sub>GEO</sub> comparison allows benchmarking to previous literature. The comparison indicates that VCD<sub>GEO</sub> is lower than VCD<sub>RTM</sub> by 8–12%, presuming a proportional error, or with a mean bias of  $-0.17 \times 10^{15} \text{ molec cm}^{-2}$ , presuming an absolute error. Since both of these VCDs are derived either partly or entirely from the same set of MAX-DOAS measurements, they have nearly identical measurement times, and compared pairs show a high correlation between VCD<sub>GEO</sub> and VCD<sub>RTM</sub> ( $R^2 = 0.97$ ).

The average NO<sub>2</sub> VCD retrieved from OMI measurements during the study period (20 June–10 July 2007) for the BAQS-Met study domain is mapped on a  $0.002^\circ \times 0.002^\circ$  grid, as described in Wenig et al. (2008), in Fig. 11. The highest VCDs are seen over the metropolitan area of Detroit/Windsor with average VCDs up to  $\sim 1 \times 10^{16} \text{ molec cm}^{-2}$ . Other areas with enhanced NO<sub>2</sub> columns include the cities of Toledo, Sarnia, and Cleveland. The waterways between Lake Huron and Lake Erie, one of the busiest waterways in the world, (St. Clair River and Detroit River) are also hot spots for enhanced columns of NO<sub>2</sub>, and

likely indicative of the heavy ship traffic and associated industrial activities supported by the presence of the waterway transport. Also visible from the satellite are enhanced NO<sub>2</sub> columns extending well out into the lakes at the ends of these waterways; Lake Erie (south of Detroit) and Lake Huron (north of Sarnia) which are likely indicative of the emissions from underway vessels, anchored vessels awaiting entry into the waterways and recreational boating activities. Considering just the NO<sub>2</sub> VCDs over Lake Erie, the western region of the Lake appears to be the most polluted. In contrast, the measurement site at Ridgetown can be seen to be in a relatively rural area with a study average NO<sub>2</sub> VCD of  $\sim 2\text{--}3 \times 10^{15} \text{ molec cm}^{-2}$ . The lowest VCDs in the domain are seen over Lake Erie, south of London, and in regions surrounding London to the north and west.

#### 4.5 Comparison between VCDs and ground level concentrations of NO<sub>2</sub>

To examine the relationship between NO<sub>2</sub> vertical columns and NO<sub>2</sub> concentrations at ground level, average NO<sub>2</sub> concentrations were calculated for the time periods of all VCD<sub>RTM</sub> determinations. In this analysis and in the case studies to follow, we have used the NO<sub>2</sub> determined from the chemiluminescence instrument (Sect. 2.8) due to the continuous and higher temporal resolution of data available from this instrument compared to the active DOAS instrument. It is well known that the “NO<sub>2</sub>” reported for these instruments may be biased high since they may contain some contribution from NO<sub>z</sub> species ( $\text{NO}_z = \text{NO}_y - \text{NO}_x$ ) due to reduction of NO<sub>z</sub> by the Mo converter. However, for most of the periods of discussion to follow, we generally found good agreement between the NO<sub>2</sub> reported by the chemiluminescence and active DOAS instrument, apart from some early morning periods when we suspect that HONO and HNO<sub>3</sub> accumulated overnight may have contributed to the signal. Figure 12 shows three polar class scatter plots using the various NO<sub>2</sub> measures; where the NO<sub>2</sub> VCD<sub>RTM</sub>, NO<sub>2</sub> number



**Fig. 12.** Polar class scatter plot diagrams for Ridgetown. The NO<sub>2</sub> VCD<sub>RTM</sub> (molec cm<sup>-2</sup>), the NO<sub>2</sub> number density (molec cm<sup>-3</sup>), and the BLH<sub>eff</sub> (cm), are plotted on the radial axis vs. the wind direction, and are color-coded for the time of day of each measurement.

**Table 3.** Average VCD<sub>RTM</sub>, ground NO<sub>2</sub>, and BLH<sub>eff</sub> for selected time periods at Ridgetown.

Time Period (EDT)	VCD <sub>RTM</sub> (×10 <sup>15</sup> molec cm <sup>-2</sup> )	<i>n</i> <sub>NO<sub>2</sub></sub> (×10 <sup>10</sup> molec cm <sup>-3</sup> )	BLH <sub>eff</sub> (m)
06:00–09:00	2.4 ± 0.8	21.4 ± 3.2	119 ± 45
09:00–12:00	2.1 ± 0.7	10.6 ± 1.7	203 ± 77
12:00–16:00	1.5 ± 0.5	6.4 ± 1.0	201 ± 77
16:00–20:00	2.7 ± 0.9	7.1 ± 1.0	521 ± 198

density (*n*<sub>NO<sub>2</sub></sub>), and the ratio VCD<sub>RTM</sub>/*n*<sub>NO<sub>2</sub></sub> are plotted on the radial axis respectively, as a function of the average wind direction and the time of day, color-coded into 4 binned daytime periods. The temporal behavior of the NO<sub>2</sub> measures within each time bin are also tabulated in Table 3, irrespective of wind direction.

Four dominant factors can contribute to the daytime temporal trends in NO<sub>2</sub> observed at the site: (i) temporal changes in emission rates of local NO<sub>x</sub> sources, (ii) changes in dilution effects of boundary layer NO<sub>2</sub> brought about by changes in the boundary layer height, (iii) changes in the Leighton ratio, [NO<sub>2</sub>]/[NO], brought about by changes in the photolysis rate of NO<sub>2</sub>, and (iv) changes in advection patterns. The ground-based NO<sub>2</sub> concentrations show a clear dependence on the time of day, both in Fig. 12 and Table 3. The highest concentrations are seen in the early morning decreasing by a factor of ~3 by the afternoon. The decrease in NO<sub>2</sub> from

early morning to afternoon is likely indicative of a combination of increased dilution in a growing boundary layer, as well as increased photolysis of NO<sub>2</sub>. The photolysis of NO<sub>2</sub> would give highest losses around solar noon (13:31 EDT at this site), and a corresponding minimum in the middle of the day. The lack of a significant minimum in the central bins of *n*<sub>NO<sub>2</sub></sub> in Table 3 indicates that increased dilution in a growing boundary layer is the dominant factor that contributes to the temporal pattern seen for the NO<sub>2</sub> concentration. Conversely, the VCD<sub>RTM</sub> shows less dependence on the time of day (Table 3 and Fig. 12), compared to the NO<sub>2</sub> concentration, and the temporal trend contains a minimum in the middle of the day. This is to be expected, as the column density of a pollutant in the boundary layer should be independent of dilution effects resulting from changes in the boundary layer height. The minimum VCD (1.5 × 10<sup>15</sup> molec cm<sup>-2</sup>) is observed in the bin that contains solar noon (Table 3) when NO<sub>2</sub> photolysis would be at its highest rate, while the highest VCD averages (2.4 and 2.7 × 10<sup>15</sup> molec cm<sup>-2</sup>) were found in the early morning and early evening periods, when the NO<sub>2</sub> photolysis rate is significantly less than solar noon. These observations indicate that the photolysis of NO<sub>2</sub> and consequent lowering of the NO<sub>2</sub>/NO ratio likely play a more dominant role in the temporal behavior of the NO<sub>2</sub> VCD.

To examine the differences between NO<sub>2</sub> vertical columns and NO<sub>2</sub> concentrations measured at ground level, the following ratio was calculated:

$$\text{Ratio} = \frac{\text{VCD}_{\text{RTM}}}{n_{\text{NO}_2}} = \text{BLH}_{\text{eff}} \quad (3)$$

whereby the  $\text{VCD}_{\text{RTM}}$  and  $n_{\text{NO}_2}$  for identical time ranges were compared. In general, one would expect the NO<sub>2</sub> vertical column density and NO<sub>2</sub> concentration at ground level to be correlated with one another. If NO<sub>2</sub> is well mixed within a homogeneous boundary layer, and the vertical column is dominated by NO<sub>2</sub> within the boundary layer, then this ratio will be approximately equal to the boundary layer height. However, as we have already seen (Sect. 4.2), the boundary layer is not always well mixed, and free tropospheric NO<sub>2</sub> can also contribute to the vertical column of NO<sub>2</sub>, creating a deviation of the ratio from the true boundary layer height. For these reasons, we call this ratio the effective boundary layer height,  $\text{BLH}_{\text{eff}}$ . A value of  $\text{BLH}_{\text{eff}}$  higher than the actual boundary layer height would be observed under the following conditions: (i) an elevated plume of NO<sub>2</sub> exists above the surface site or (ii) the column of NO<sub>2</sub> in the free troposphere is a significant fraction of the total tropospheric column (e.g. likely observed under conditions when the boundary layer is relatively unpolluted). Conversely, values of  $\text{BLH}_{\text{eff}}$  lower than the actual boundary layer would be observed when surface sources of NO<sub>2</sub> are not well mixed in the boundary layer, which could occur under conditions of relative atmospheric stability. In addition to these deviations of  $\text{BLH}_{\text{eff}}$ , we also expect that the temporal pattern of  $\text{BLH}_{\text{eff}}$  will generally follow the temporal pattern of the real boundary layer height.

The values of  $\text{BLH}_{\text{eff}}$  observed during this study ranged from 12 m (observed in early morning) to 2.54 km (observed in late afternoon). In general the  $\text{BLH}_{\text{eff}}$  increased from early morning to the end of the day (Table 3, Fig. 12), although the average values observed in the early afternoon (~200 m) are less than one would expect for continental boundary layer heights in midsummer in this region. This likely indicates that NO<sub>2</sub> is not homogeneously mixed in the boundary layer, as we directly observed by the aircraft measurements on 26 June (Sect. 4.2). Instructive here is to identify cases where the VCD measured by MAX-DOAS shows something different than what is measured by the more conventional surface-based point source measurement of NO<sub>2</sub>. These cases would be indicated by the highest and lowest values of  $\text{BLH}_{\text{eff}}$ . The periods of low  $\text{BLH}_{\text{eff}}$  are somewhat trivial and are all isolated to early morning events, when a nocturnal inversion is still intact. During such periods, the NO<sub>2</sub> accumulated throughout the night from regional surface sources are trapped in the low inversion creating relatively high concentrations of NO<sub>2</sub> but only low or moderate tropospheric VCDs. More interesting are periods with high levels of  $\text{BLH}_{\text{eff}}$ , during which a ground-based measurement of NO<sub>2</sub> concentration would underestimate the total amount of NO<sub>2</sub> in the troposphere and transport of NO<sub>2</sub> into the region, with subsequent impacts on regional air quality. In Fig. 12, four such cases are identified as a function of the wind direc-

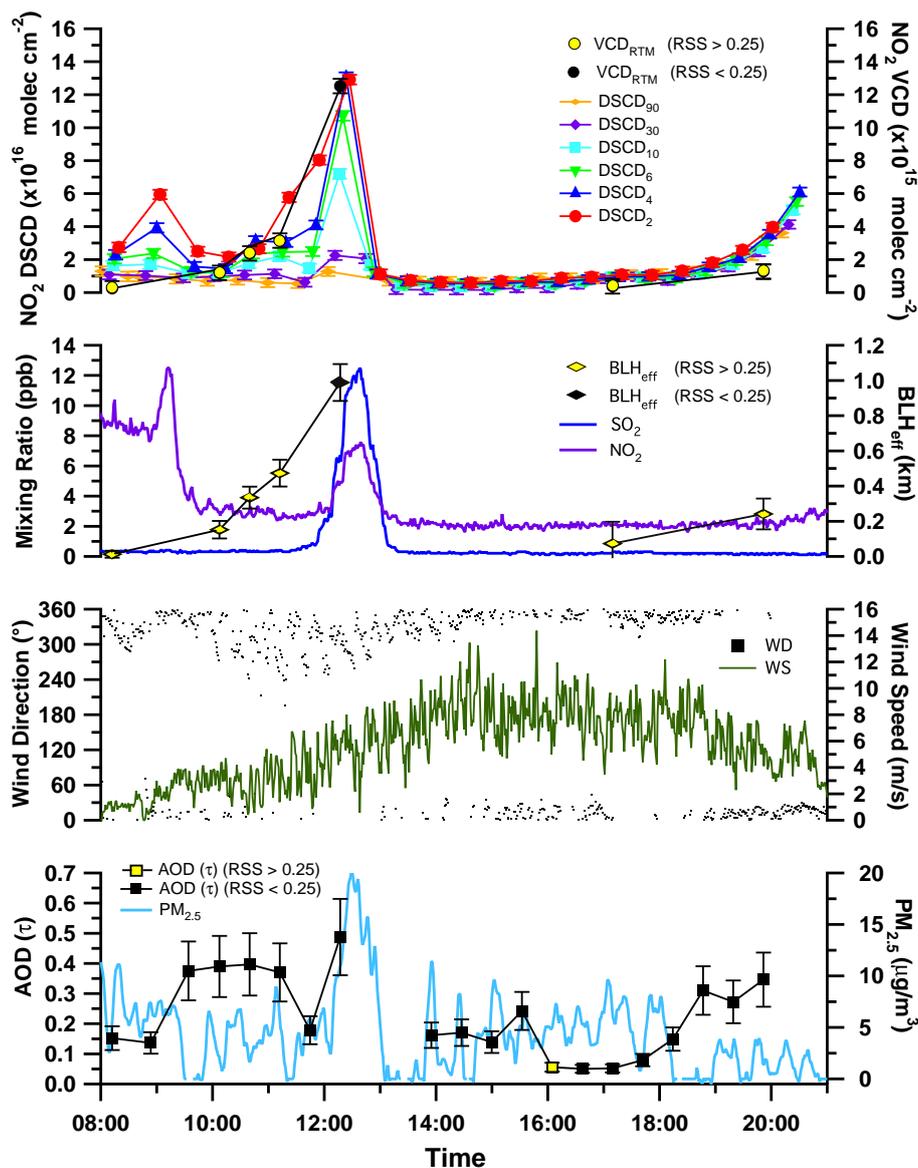
tion measured at ground level. The highest values of  $\text{BLH}_{\text{eff}}$  occurred on 30 June, 2, 6 and 9 July 2007.

On 30 June (between 12:00–12:40 EDT), the highest value of  $\text{VCD}_{\text{RTM}}$  determined in the study was recorded ( $1.25 \times 10^{16}$  molec cm<sup>-2</sup>) and the  $\text{BLH}_{\text{eff}}$  rose to 998 m. During this case, an elevated plume of NO<sub>2</sub> impacted the site from the NW that we attribute to industrial point sources in Sarnia. This case is discussed in further detail in the next section. On 2 July (between 15:00–18:00 EDT), on an otherwise cool, clear and clean day, the  $\text{VCD}_{\text{RTM}}$  increased to  $5 \times 10^{15}$  molec cm<sup>-2</sup> and  $\text{BLH}_{\text{eff}} = 991$  m with virtually no increase in the ground level concentration of NO<sub>2</sub>. We attribute this case to impact by elevated forest fire plumes, originating in northern Ontario that moved southward, while the ground level at Ridgetown experienced a clean lake breeze inflow from the southeast. On 6 July, the  $\text{BLH}_{\text{eff}}$  had a maximum of 1.08 km early in the evening (17:00–19:00 EDT). Winds during this time were from the N–NW and the presence of elevated SO<sub>2</sub> indicates that the site was impacted by a mixture of industrial emissions from Sarnia, and possibly marine vessel emissions from ships on Lake Huron. The high boundary layer height would be typical of a lake breeze layer thermally modified after traveling 70 km inland (Sills et al., 2011). On 9 July late in the afternoon, the highest values of  $\text{BLH}_{\text{eff}}$  (up to 2.5 km) were seen. This case was characterized by strong winds from the SW that is characteristic for southern Ontario, evidence for strong convection and extremely high pollution levels, a classic case of a pollution episode with long-range transport of pollutants from the SW. This case will also be discussed in more detail in the next section.

#### 4.5.1 Case studies

For the case studies that follow, the residual sum of squares (RSS), as described in the Supplemental Material, was used as an indicator of the quality of the fits between measured and modeled  $\tau_{\text{RTM}}$  and  $\text{VCD}_{\text{RTM}}$  values. Values of  $\text{RSS} < 0.25$  were deemed to be good fits, values with  $0.25 < \text{RSS} < 2.5$  are more uncertain. Values of  $\text{RSS} > 2.5$  were very uncertain and were removed from the data set. These thresholds were chosen based on empirical considerations to differentiate between fits with low and high uncertainty. Values with  $0.25 < \text{RSS} < 2.5$  are marked accordingly on Figs. 13, 15, and 16 ( $\text{RSS} > 0.25$ ) as being more uncertain, usually as the atmosphere was not behaving as per the assumption in the RTM (e.g. horizontal homogeneity). Data points with these intermediate RSS values do not necessarily represent poor results, but they indicate values that can have larger uncertainties due to limitations in the forward model, measurement errors, or temporal variations of the atmospheric properties during an elevation sequence.

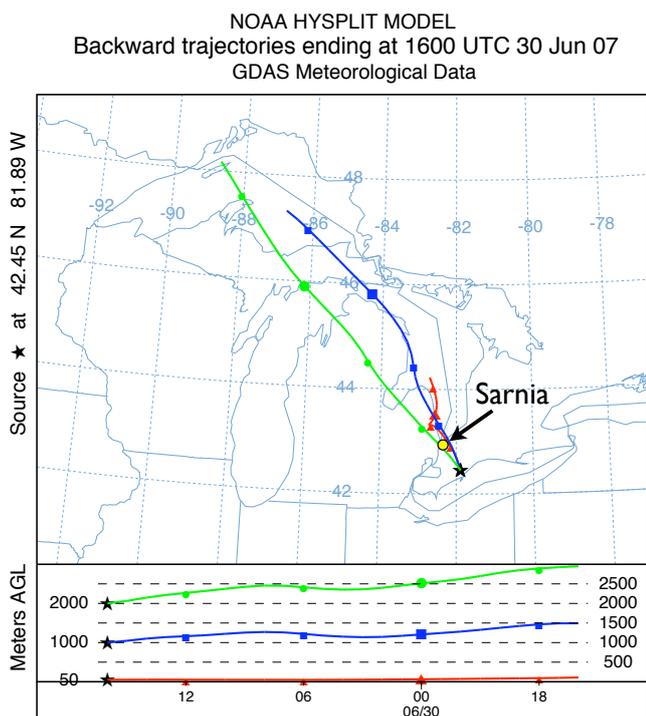
Figure 13 summarizes measurements made on 30 June 2007 at Ridgetown. The synoptic flow was gentle and from the northwest in the morning period.



**Fig. 13.** Measurements at Ridgetown on 30 June 2007. NO<sub>2</sub> MAX-DOAS DSCDs with NO<sub>2</sub> VCD<sub>RTM</sub> values are followed by ground level measurements of SO<sub>2</sub> and NO<sub>2</sub>, BLH<sub>eff</sub>, wind direction, wind speed, PM<sub>2.5</sub>, and AOD ( $\tau_{RTM}$ ).

Relatively high levels of ground level NO<sub>2</sub> (8–12 ppb) but low levels of SO<sub>2</sub> were seen in the morning period 08:00–10:00 EDT. At the same time, the NO<sub>2</sub> VCD<sub>RTM</sub> was quite low ( $<1 \times 10^{15}$  molec cm<sup>-2</sup>), and BLH<sub>eff</sub> was  $\leq 150$  m, indicating a shallow inversion layer. Ground level NO<sub>2</sub> mixing ratios decreased rapidly due to the breakup of the nocturnal inversion at about 09:30 EDT and leveled off for the remainder of the morning at  $\sim 2$  ppb. The characteristic feature on this day was a pollution plume of  $\sim 1$  h duration that impacted the site between 12:00–13:00 EDT. During this short interval, daily maxima were observed for DSCDs ( $\alpha = 2^\circ, 4^\circ, 6^\circ, 10^\circ$ ), VCD<sub>RTM</sub>,  $\tau_{RTM}$ , PM<sub>2.5</sub>, SO<sub>2</sub>, BLH<sub>eff</sub> (Fig. 13), and O<sub>3</sub> (52 ppb, not shown). The

maximum of the pollution plume coincided with the arrival of a meteorological feature that had several characteristics of a lake breeze front arriving from Lake Huron to the north. Evidence for this was an increase in the relative humidity, a slight drop in temperature, and a subtle, gradual but discernible shift in wind direction towards the north. It also coincided with arrival from the north of a thin east-west line of cumulus clouds that moved across Ridgetown between 12:00 and 13:00 EDT. The thin line of clouds provides evidence for enhanced lift along the line of this feature, typical of a lake breeze front (Sills et al., 2011). While final results from an observational analysis by Sills et al. (2011) did not specifically identify a feature with gradients that

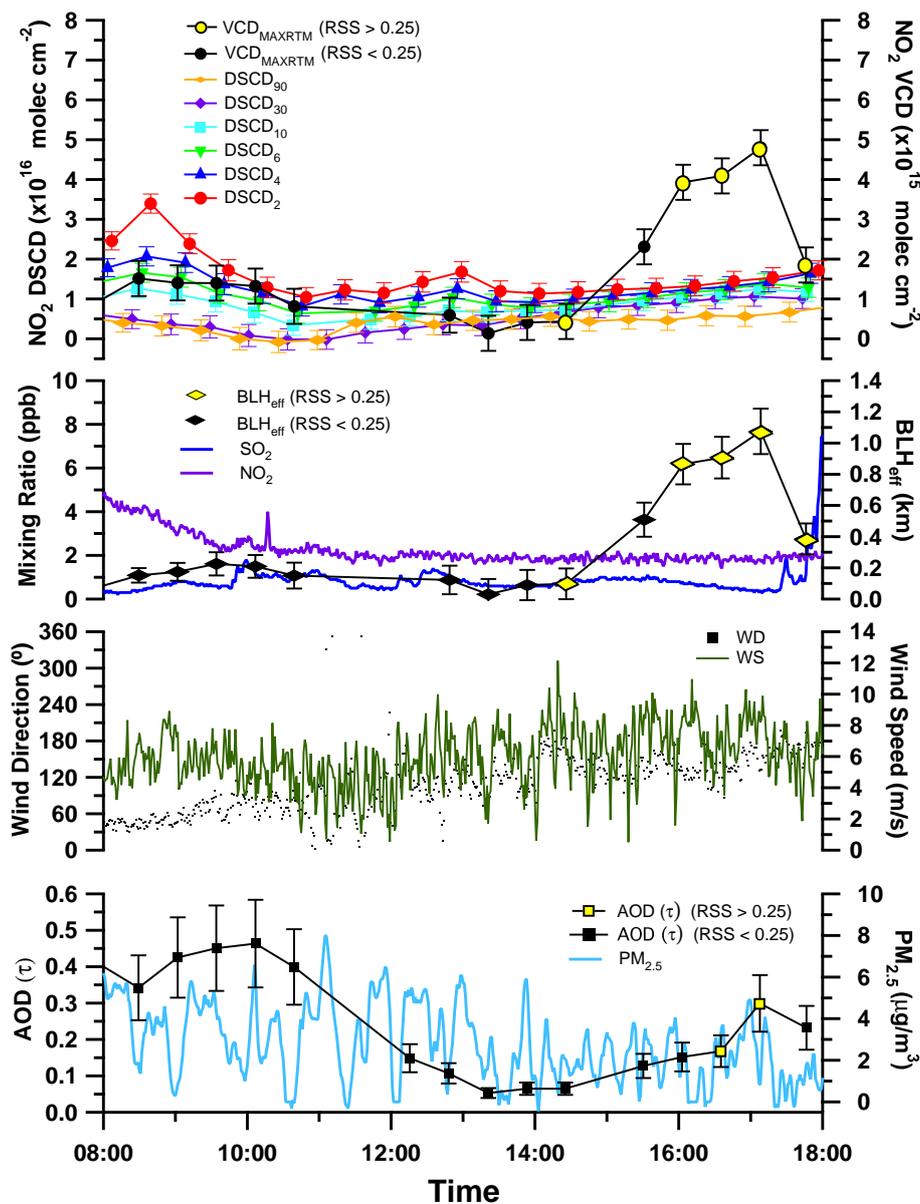


**Fig. 14.** HYSPLIT back trajectory for Ridgetown (starred) on 30 June 2007. Time scale in UTC.

were sharp enough to be called a lake breeze front, there is consensus that the Ridgetown site was experiencing a Lake Huron lake breeze by 14:00 and that this meteorological feature with enhanced lift preceded the arrival of the lake breeze. The results from the MAX-DOAS measurements are particularly informative at this time. In particular, while the DSCDs of NO<sub>2</sub> increased at all elevation angles, the DSCD with  $\alpha = 4^\circ$ , DSCD<sub>4</sub>, was marginally higher than the DSCD<sub>2</sub> (though the difference is not statistically significant). This is an observation that rarely occurs, even under high aerosol conditions when the absorption length through the lower atmosphere becomes similar at all elevation angles, making all DSCDs similar. This result can be contrasted to the result early in the morning when the nocturnal boundary layer was still intact. During that early morning period, we observed the typical situation in which DSCD<sub>2</sub> > DSCD<sub>4</sub> > DSCD<sub>6</sub> > DSCD<sub>10</sub> > DSCD<sub>30</sub>, commonly seen when a polluted layer exists at the surface, where larger DSCDs are observed at lower elevation angles due to the larger effective path length of scattered light through the polluted layer (Hönninger et al., 2004). In addition, it can be observed during the time just preceding the pollution plume peak that the DSCD<sub>2</sub> and DSCD<sub>4</sub> increase before the other DSCDs and well before the ground level in-situ observations of NO<sub>2</sub> and SO<sub>2</sub> show any detectable increase. This points towards a temporal effect whereby an inhomogeneous plume moves into the complex viewing geometry of the MAX-

DOAS. Both effects strongly suggest that the polluted layer was elevated from the surface, or had higher concentrations above the surface than at ground level (Hönninger et al., 2004). Other evidence that the pollution plume was elevated was the rapid increase in the value of BLH<sub>eff</sub>. Despite the presence of an elevated plume, increases in SO<sub>2</sub>, NO<sub>2</sub>, and NO<sub>x</sub> were still seen at ground level during this time period of the plume, which coincided with the arrival of the lake breeze. This suggests that the elevated plume was mixed partially to the surface (but not homogeneously) through a process similar to fumigation, where smokestack effluent brought inland in stable stratified marine air is mixed to the surface when it intersects the convective mixed layer at the lake breeze front (Lyons and Cole, 1973; Sills et al., 2011).

Wind Directions on 30 June 2007 were N–NW (Fig. 13) and the pollutant plume between 12:00–13:00 EDT may be traced back to the region of Sarnia, Ontario ~70 km away, using the NOAA HYSPLIT (Draxler and Rolph, 2011) back trajectory analysis (Fig. 14). Many anthropogenic sources with elevated stack emissions are located close to the Lake Huron shoreline close to Sarnia, including petrochemical refineries, other chemical industries, and a major coal fired electric generation facility in Lambton, Ontario. The excess SO<sub>2</sub>/NO<sub>x</sub> ratio (mole mole<sup>-1</sup>) in the pollution plume at ground level during the pollution event was calculated to be  $2.21 \pm 0.08$  mole mole<sup>-1</sup>. This can be compared to emissions from the largest point sources within a 5 km radius of Sarnia that contain stacks. According to the National Pollutant Release Inventory (EC, 2011), the total emissions of SO<sub>2</sub> and NO<sub>x</sub> from the top 10 point sources in Sarnia are 23.9 kt yr<sup>-1</sup> and 5.82 kt yr<sup>-1</sup> respectively, with a SO<sub>2</sub>/NO<sub>x</sub> ratio of 2.95 mole mole<sup>-1</sup>, dominated by refinery emissions. The corresponding emissions of SO<sub>2</sub> and NO<sub>x</sub> from the stack of the Lambton coal-fired electric utility (~16 km south of the major refineries in Sarnia) are 6.19 kt yr<sup>-1</sup> and 3.96 kt yr<sup>-1</sup>, with a SO<sub>2</sub>/NO<sub>x</sub> ratio of 1.10 mole mole<sup>-1</sup>. Although we cannot identify a single source from this, the evidence suggests that the plume impacting the site during this period was from either one or several elevated fuel combustion sources that fumigated to the surface as the lake breeze front passed Ridgetown. After this time, the winds at the site continued to shift towards a more northerly direction and the site experienced a clean lake breeze from Lake Huron for the rest of the afternoon, devoid of surface or elevated pollution sources of NO<sub>2</sub>. While evidence points to the fact that the plume was elevated, an explanation is still required for the large increase in the VCD and simultaneous arrival with the lake breeze. A lake breeze front is known to be a narrow convergence zone with enhanced lift that can transport pollutants upward (Sills et al., 2011). The front can also result in a region of spatial stagnation, with respect to the inflow layer, if the speed of the front moves slower than the inflow layer. The dynamics of both lift, and recirculation that exist at the front (Lyons and Cole, 1973; Sills et al., 2011) can thus result in a higher concentration of pollutants at the leading

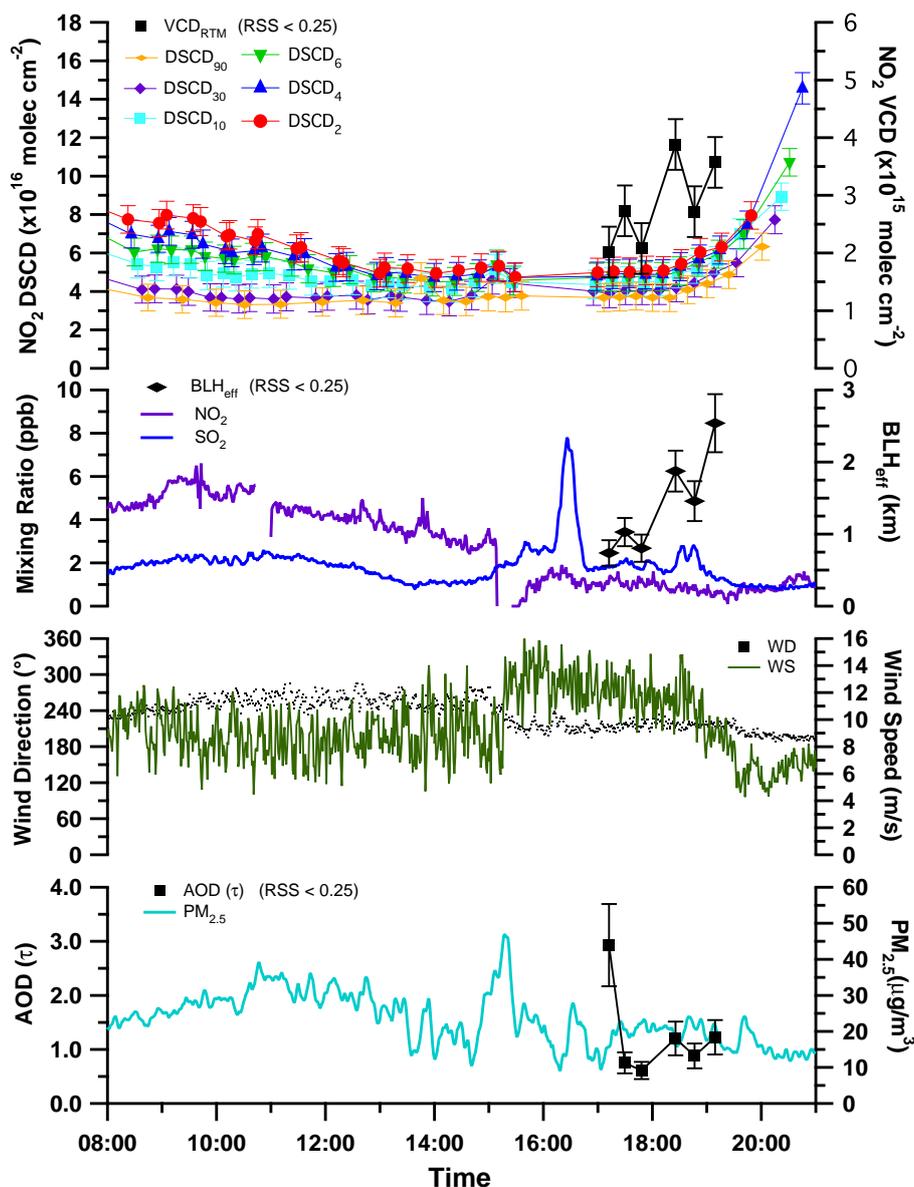


**Fig. 15.** Measurements at Ridgetown on 2 July 2007. NO<sub>2</sub> MAX-DOAS DSCDs with NO<sub>2</sub> VCD<sub>RTM</sub> values are followed by ground level measurements of SO<sub>2</sub> and NO<sub>2</sub>, BLH<sub>eff</sub>, wind direction, wind speed, PM<sub>2.5</sub>, and AOD (τ<sub>RTM</sub>).

edge of a lake breeze, that is still not completely understood. Our result presents evidence (perhaps for the first time) that these dynamics can lead to an overall increase in not only the concentration of pollutants, but also the vertical column of pollutants as well. This is the first demonstration of such an effect using MAX-DOAS, to the best of our knowledge.

Figure 15 summarizes measurements made on 2 July 2007. The area was under the influence of a regional high pressure system on this day with light winds, sunshine, cool temperatures (<21 °C) and low deformation lake breeze conditions (Sills et al., 2011). Ground level pollution (SO<sub>2</sub>, NO<sub>2</sub>, PM<sub>2.5</sub>, O<sub>3</sub>) was low throughout most

of the day, as was O<sub>3</sub> (<35 ppb, not shown). The MAX-DOAS measurements indicated a clean troposphere with VCDs <2 × 10<sup>15</sup> molec cm<sup>-2</sup> and BLH<sub>eff</sub> <200 m prior to 15:00 EDT, indicating either a shallow or inhomogeneously mixed boundary layer with NO<sub>2</sub> confined to the surface. By late morning and throughout the afternoon, the site was experiencing a moderate lake breeze from the S–SE (Lake Erie) although satellite imagery indicates that upper air movement was from the W–NW. After 15:00 EDT, the VCDs of NO<sub>2</sub> showed an appreciable increase from ~5 × 10<sup>14</sup> molec cm<sup>-2</sup> up to 5 × 10<sup>15</sup> molec cm<sup>-2</sup>, while the BLH<sub>eff</sub> increased from less than 100 m to greater than 1 km.



**Fig. 16.** Measurements at Ridgetown on 9 July 2007. NO<sub>2</sub> MAX-DOAS DSCDs with NO<sub>2</sub> VCD<sub>RTM</sub> values are followed by ground level measurements of SO<sub>2</sub> and NO<sub>2</sub>, BLH<sub>eff</sub>, wind direction, wind speed, PM<sub>2.5</sub>, and AOD (τ<sub>RTM</sub>).

A close examination showed that the ground level mixing ratio of NO<sub>2</sub> remained unchanged at ~2 ppb throughout this period, indicating that the increase in vertical column of NO<sub>2</sub> was not due to a surface source of NO<sub>2</sub>. Unlike the elevated plume seen on 30 June, in this case the DSCDs at lower elevation angles (DSCD<sub>2</sub>, DSCD<sub>4</sub>) did not show any appreciable increase. Further examination indicates that the increase in the VCD is being largely driven by the increase in DSCD<sub>30</sub> (VCD<sub>30</sub>). In a qualitative sense, this indicates that the elevated NO<sub>2</sub> must be at very high elevation from the surface, much higher than seen on 30 June. Indeed, elevated forest fire plumes were reported in Southern Ontario on this day. They were clearly visible as brown streaks moving

south in the sky at high altitude, likely in the upper free troposphere. An analysis of satellite imagery and fire occurrences using the Canadian Wildland Fire Information System ([http://cwfis.cfs.nrcan.gc.ca/en\\_CA/index](http://cwfis.cfs.nrcan.gc.ca/en_CA/index)) for several days prior and following this date indicated the most likely source to be an intense line of boreal forest fires that had started on or about 28 June close to the Saskatchewan/Northwest Territories border approximately 2500 km northwest of the site. Although the aerosol optical depth was higher in the morning (τ<sub>RTM</sub>=0.4), likely due to anthropogenic aerosol pollution from urban areas to the northeast, the τ<sub>RTM</sub> also increased marginally (Δτ<sub>RTM</sub>=+0.2) during the biomass burning plume event, while PM<sub>2.5</sub> remained

unchanged. This indicated that only a small amount of aerosol was associated with the plume, perhaps due to sedimentation during the  $\sim 2$  day transport time. Despite this, particle-based receptor modeling of aerosol time of flight mass spectrometry data identified the beginning of an event of aged biomass burning particles at Harrow, ON late in the day or early morning on 2/3 July (McGuire et al., 2011). It is acknowledged that the determination of  $\tau$  using the method outlined here is highly uncertain in a case such as this and would likely benefit from a two level retrieval system, as there are likely two distinct layers of NO<sub>2</sub> and aerosols. As O<sub>4</sub> has a scale height of  $\sim 4$  km in the atmosphere, the use of changes in the O<sub>4</sub> absorption to predict the presence of aerosols will be much less sensitive with aerosol layers in the upper troposphere. Therefore, the value of  $\tau_{\text{RTM}}$  will likely underestimate the true tropospheric AOD in such cases. This could be the situation for the current case study. The VCD<sub>RTM</sub> could also be uncertain due to multiple scattering events in a mixed aerosol-NO<sub>2</sub> plume in the upper troposphere, however it is unlikely to be as sensitive as the AOD, and the prediction of the direction of bias in NO<sub>2</sub> VCD is uncertain without further 2 level radiative transfer modeling. Despite this, the case illustrates a situation where transport of pollution through the region at high altitude was detected by MAX-DOAS, which would be virtually undetected at ground level using standard air quality instrumentation.

Figure 16 summarizes measurements made on 9 July 2007. This day was characterized by warm temperatures (33 °C maximum), hazy conditions with strong W-SW synoptic flow, high deformation lake breeze circulations, and enhanced turbulence (Sills et al., 2011). High pressure existed south east of the Great Lakes, a typical situation for the transport of ozone and aerosol precursors into southern Ontario from the SW (MOE, 2011). Indeed, aerosols were abundant with PM<sub>2.5</sub> levels in the range of 10–50  $\mu\text{g m}^{-3}$ , and  $\tau_{\text{RTM}} \sim 1.0 \pm 0.2$  in late afternoon, apart from a single value of 2.8 at 17:00 EDT. Ozone (not shown) also recorded a maximum of 87 ppb, a few minutes prior to the passage of a lake breeze front. Due to the cumulus clouds in the vicinity for much of the day, VCD<sub>RTM</sub> could not be determined until after 17:00 EDT. Winds that were from the W-SW (260°) at 9 m s<sup>-1</sup>, switched to S-SW (215°) at 13 m s<sup>-1</sup> with gusts up to 17 m s<sup>-1</sup> at 15:10 EDT, indicating the passage of the lake breeze front (Lake Erie), and accompanied with an increase in relative humidity, spikes in PM<sub>2.5</sub>, CO and O<sub>3</sub> (not shown), and a drop in NO<sub>2</sub>. Between 17:00 and 19:15 EDT, conditions were hazy but cloud-free such that estimates of VCD<sub>RTM</sub> were determinable. The NO<sub>2</sub> was relatively low, between 0.5 and 1.5 ppb, while VCDs ranged from  $2\text{--}4 \times 10^{15}$  molec cm<sup>-2</sup>, and BLH<sub>eff</sub> increased from 800 m to 2600 m at 17:10 EDT. The DSCDs do not give any indication of an elevated plume, and a measure of the true boundary layer height was not available at Ridgeway on this day. However, the potential temperature profile measured

by sonde release at White Lake, Michigan, just northwest of Detroit (Station DTX, #72632), indicated a subsidence inversion at 1.90 km at 20:00 EDT (UWYO, 2010), that was comparable to the average BLH<sub>eff</sub> measured between 19:20 and 18:20 EDT (1.93 km). Thus, on this particular day, when strong wind speeds and strong convection would support a well mixed boundary layer, the value of BLH<sub>eff</sub> was comparable to the true boundary layer height measured in a continental region close to the site. This provides an opportunity to further validate our VCD<sub>RTM</sub> determinations during this time period. Between 18:00 and 19:00, the average VCD<sub>RTM</sub> was  $3.4 \pm 0.5 \times 10^{15}$  molec cm<sup>-2</sup>. The tropospheric VCD of NO<sub>2</sub> estimated from the average NO<sub>2</sub> mixing ratio (0.8 ppb) in a homogeneous boundary layer of 1.9 km is  $3.8 \times 10^{15}$  molec cm<sup>-2</sup>. These numbers agree reasonably well. This case, where the boundary layer is relatively homogeneous and well mixed, is one of the few situations during the study where we expect this to be true. In such a case, the mixing ratio of NO<sub>2</sub> measured at ground level is quite low, and may not indicate the total amount of NO<sub>2</sub> being transported into the region in the deep boundary layer. To estimate the total transport of tropospheric NO<sub>2</sub> across a boundary tangential to the wind direction during this pollution event, the flux of tropospheric NO<sub>2</sub> perpendicular to the wind direction,  $F_{\text{NO}_2}$  (molec s<sup>-1</sup>), could be calculated according the following equation:

$$F_{\text{NO}_2} = \text{VCD}_{\text{NO}_2} \times L \times u_{\text{trop}} \quad (4)$$

where  $L$  is the length of a border, and  $u_{\text{trop}}$  is the average flow rate of the troposphere. Using the wind speed at 10 m height (12 m s<sup>-1</sup> in late afternoon) as a lower limit of the flow rate in the lower troposphere, and the average VCD<sub>RTM</sub> in the later afternoon period ( $3.4 \times 10^{15}$  molec cm<sup>-2</sup>), we conservatively estimate the line flux ( $F_{\text{NO}_2}/L$ ) of NO<sub>2</sub> through the region to be greater than  $4.1 \times 10^{18}$  molec cm<sup>-1</sup> s<sup>-1</sup>, or 112 kg NO<sub>2</sub> km<sup>-1</sup> h<sup>-1</sup>, during the pollution event. This may be a useful parameter to compare with model estimates of transport fluxes where they exist.

## 5 Conclusions

We outline an original method for the determination of aerosol optical depths and vertical column densities of NO<sub>2</sub> using a combination of MAX-DOAS measurement of NO<sub>2</sub> and O<sub>4</sub>, radiative transfer, and inversion modeling. The aerosol optical depths ( $\lambda = 360$  nm) determined with this method were compared to other measures of aerosol optical depth regionally available (OMI, MODIS, AERONET) with some qualitative agreement, although differences in the wavelengths used and spatial locations prevented a more direct comparison of these measures. A direct comparison between  $\tau_{\text{RTM}}$  and PM<sub>2.5</sub> measured at the site gave a very low level of correlation, while a direct comparison between the calculated aerosol extinction coefficient ( $\tau_{\text{RTM}}/H_{\text{aer}}$ ) and

PM<sub>2.5</sub> gave a much higher correlation and a mass specific extinction coefficient of  $16 \pm 1 \text{ m}^2 \text{ g}^{-1}$ . While  $H_{\text{aer}}$  is not expected to be equivalent to the true boundary layer height, the improved correlation emphasizes the importance of taking into account boundary layer heights in any attempts to link aerosol optical depths determined by satellite, for example, with human exposure of aerosols at ground level.

The tropospheric VCDs of NO<sub>2</sub> derived this way, VCD<sub>RTM</sub>, were compared to tropospheric VCDs compiled through vertical measurements of NO<sub>2</sub> close to the site, VCD<sub>COMP</sub>. On average, VCD<sub>RTM</sub> was only 2% lower than VCD<sub>COMP</sub>; the difference is not statistically significant. This serves as a validation for the method outlined here for determining NO<sub>2</sub> VCDs. Intercomparison of satellite instrument derived VCDs with a limited number of comparison points from OMI ( $N = 8$ ) and SCIAMACHY ( $N = 1$ ) indicate that the satellite derived measures were  $\sim 50\%$  higher than VCD<sub>RTM</sub> with a mean bias of  $+0.9 \times 10^{15} \text{ molec cm}^{-2}$  for OMI (statistically significant), and  $+0.5 \times 10^{15} \text{ molecules cm}^{-2}$  for SCIAMACHY (not statistically significant). It should be taken in context that the apparently large relative overprediction by the satellites retrievals ( $+50\%$ ) could easily be due to a small constant bias coupled with the overall relatively small tropospheric VCDs of NO<sub>2</sub> that were experienced in this rural region. The relevance of the result to more polluted regions with higher VCDs should be verified.

Previous literature has reported the opposite, namely that satellite derived measures of VCD are on average smaller than VCDs found via MAX-DOAS. The root cause for these differences is probably the different nature of the measurement sites; rural in this study compared to more urban in previous reports, or the overall values of the NO<sub>2</sub> VCDs, which were much lower in this study compared to previous reports. Typically, VCDs derived from MAX-DOAS in previous comparisons with satellite measures of NO<sub>2</sub> have used a geometrical approximation to estimate the air mass factor and VCD, similar to the VCD<sub>GEO</sub> values reported here. Our VCD<sub>GEO</sub> values were marginally lower than our VCD<sub>RTM</sub> values, but only for a small subset of comparisons with a stringent criteria, namely that the VCDs determined using a geometric approximation with elevation angles of 10° and 30° agree to within 15%. The methodology we outlined here to determine VCD<sub>RTM</sub> is not as stringent, and has allowed us to determine VCDs over a much wider range of aerosol conditions than would otherwise be possible using just the geometric approximation.

We define the ratio of the tropospheric VCD and ground level concentration of NO<sub>2</sub> to be the effective boundary layer height, BLH<sub>eff</sub>. The diurnal pattern of BLH<sub>eff</sub> generally follows the expected pattern for the boundary layer height during the day; although we find values of BLH<sub>eff</sub> are generally lower than expected for continental boundary layer heights in late afternoon, likely due to surface sources in a boundary layer that is not well mixed. We illustrate exceptions

to this in three case studies. In two of the cases, we show high values of BLH<sub>eff</sub> are due to elevated plumes of NO<sub>2</sub>, one from elevated stack emissions from industry, and one from biomass burning plumes that were transported through the region. In the third case, we found that BLH<sub>eff</sub> was very high ( $\sim 2 \text{ km}$ ) and similar to the measured continental boundary layer height just northwest of the study region, likely as a result of instability in the atmosphere that promoted convection and efficient mixing throughout the boundary layer. The variations of BLH<sub>eff</sub> with time of day and conditions, should be considered in attempts to determine ground level concentrations of NO<sub>2</sub> from satellite derived measures, or in attempts to validate satellite measurements through use of ground-based measurements.

The case studies examined here also provide some interesting examples of transport of pollutants in this region and the interaction with lake breezes that exist due to the presence of the surrounding lakes. In our first case study, we present an example of suspected fumigation of elevated industrial pollutants brought to the surface at a lake breeze, and an increase in the total NO<sub>2</sub> VCD at the lake breeze. Our last case study occurred during a regional smog event with transport of ozone and aerosol precursors from the southwest. Although ground level concentrations of NO<sub>2</sub> were quite low during this event ( $< 1.5 \text{ ppb}$ ), the column amount of NO<sub>2</sub> was more substantial than otherwise suspected due to a deep and well mixed boundary layer. We have estimated the line flux of NO<sub>2</sub>, at this time, to be greater than  $112 \text{ kg NO}_2 \text{ km}^{-1} \text{ h}^{-1}$ . Multiplication of the line flux by the width of a boundary line perpendicular to the prevailing wind direction would give the total mass transport of tropospheric NO<sub>2</sub> across the boundary line, during the regional pollution event.

**Supplement related to this article is available online at:**  
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