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A comparison of surface NO_2 mixing ratios and total column observations at a South African site*

Micky Josipovic[1*], Debra W. Kollonige[2,3], Roelof P. Burger[1], Anne M.Thompson[1,2,4], Johan P. Beukes[1], Pieter G. van Zyl[1], Andrew D. Venter[1], Kerneels Jaars[1], Douglas K. Martins[2], Ville Vakkari[5], Lauri Laakso[1,5]

1. Unit for Environmental Sciences and Management, North-West University, Potchefstroom Campus, Private Bag X6001, Potchefstroom 2520, South Africa
2. Department of Meteorology, Pennsylvania State University, 503 Walker Building, University Park, PA. 16802-5013, USA
3. University of Maryland – ESSIC, College Park, Md, USA
4. NASA, Goddard Space Flight Center, Greenbelt, Md, USA
5. Finnish Meteorological Institute, Research and Development, P.O. BOX 503, FI-00101, Finland

The total column density nitrogen dioxide (NO_2) retrievals collated by a ground-based sun-tracking spectrometer (Pandora/GSFC) and the satellite-borne (Aura) Ozone Monitoring Instrument (OMI) were compared to the volume mixing ratios measured by a ground-based gas-analyser at Welgegund, North-West University (NWU) atmospheric monitoring station (Potchefstroom, South Africa). An assessment of the comparability between columnar and surface NO_2 measurements was performed. The concurrent ground measurements results over January-March, 2011, were averaged over one hour to correspond to the closest local OMI overpasses (~12:00 UTC).
A novel method for estimating surface mixing ratios from total-column retrievals, via a planetary boundary layer (PBL) height correction factor as tested by Knepp *et al.* (2013) in the USA was applied. This PBL correction factor largely corrects for boundary-layer variability throughout the day, and allows conversion into mixing ratios. The data for the ground instruments were in agreement within the expected uncertainty for each technique and between two remote sensing instruments. However, NO_2 between the ground gas analyser and satellite borne instrument were out of the expected uncertainty limits.

Keywords: NO_2, gas analyser, ground-based spectrometer, boundary layer, total column density, volume mixing ratio, remote sensing.

1. Introduction

Understanding of the column density-to-surface fraction relationship should enable comparisons with surface mixing ratio measurements, which are often compared against numerical units associated with an established ambient air quality (AQ) standard. A significant challenge in this relation is accounting for variability in the planetary (atmospheric) boundary layer (PBL).

Because of NO_2 short photolytic life time outside of the boundary layer and the temperature-dependent partitioning between NO_2 and NO, most of the tropospheric NO_2 column density resides in the PBL (Sluis *et al.*, 2010; Sitnikov *et al.*, 2005; Pisano *et al.*, 1996). However, the height of the PBL is variable throughout the day, responding to local surface heating and other synoptic and meso-scale forcing, emissions being typically well mixed throughout this layer. Therefore, if emissions and removals are constant, it is reasonable to expect pollutant mixing ratios to vary inversely with PBL height while the column density would remain constant (Knepp *et al.*, 2013).

Recently a methodology has been developed for conversion of total-column observations to surface mixing ratio estimations (Knepp *et al.*, 2013). In this study we applied that method and compared column-density measurements derived from two columnar instruments, a ground-based spectrometer and overpassing satellite-borne instrument with the continuous surface-level mixing ratio measurements by a gas analyser.

2. Location

The Welgegund measurement site (26°34'10"S, 26°56'21"E, 1480 m a.s.l.) is located approximately 100 km south-west of the Johannesburg-Pretoria conurbation with a population of over 10 million (Lourens *et al.*, 2012). There is no significant local pollution source close to the measurement site. However, it is frequently impacted by air masses from a number of country's major pollution source regions Importantly, air masses, passing over the regional background from the west of Welgegund where no significant point sources exist, regularly arrive at Welgegund (Beukes *et al.*, 2014).

*Based on the IUAPPA 2013 conference proceedings, Cape Town, 29 September – 4 October 2013, with extra data analysed.

3. Methods and instrumentation

3.1 NO_2 Instrumentation

The surface mixing ratios are measured by a molybdenum-oxide converter with NO detected chemiluminescence after reaction with O_3, (Teledyne AU 200 gas analyser). The instrument records NO and NO_x concentrations from which NO_2 is determined by subtraction of NO from NO_x.

The ground-based spectrometer named "Pandora" used in this study has been validated against similar sun-tracking instruments (Wang *et al.*, 2010), MAX-DOAS and zenith-looking instruments (Pieters *et al.*, 2012) and Aura satellite-borne OMI (Herman *et al.*, 2009). Pandora provides NO_2 vertical-column densities from direct sun observation that serve as a proxy for satellite-derived observations, such as OMI, with 2-minute resolution, thereby allowing direct comparison of *in-situ*/column observations throughout the day as boundary layer dynamics, emissions and atmospheric chemistry change. OMI retrievals were sourced from NASA (Boersma et al., 2002; Bucsela et al., 2006).

3.2 ABL determination

Two methods were used: in first, PBL structure and evolution was modelled using Monin-Obukhov similarity theory. The Hong and Pan (1996) boundary layer parameterization scheme was used for the MM5 model runs using NCEP (NOAA) reanalysis data as input. The hourly boundary layer height was then estimated using a scheme similar to Cimorelli *et al.*, (2004) (Figure 1).

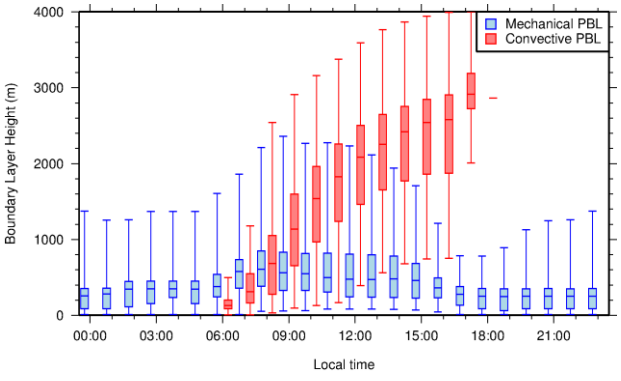

Figure 1: Modelled diurnal planetary boundary leyer (PBL) heights above Welgegund over study period. The box-and-whiskers plot show the minimum, 25 percentile, median, 75 percentile and maximum hourly values.

In second, observed PBL heights were derived from **A**tmospheric **I**nfra-**R**ed **S**ounder (AIRS, Aqua satellite-borne) Level 2 Version 6 temperature and humidity profiles (100 layers, with a nominal grid spacing of about 25 hPa in the PBL). Herein the PBL height can be defined as the height where strong/sharp gradients in both temperature and relative humidity are evidently distinguishable. Thus such AIRS dataset has the potential to provide reliable PBL height information as it contains global observations of the PBL structure that are useful for both spatial and seasonal variability studies (Martins *et al.*, 2010).

3.3 Methods

In this study we applied the methodology developed for the analysis of data collected at NASA's Langley Research Center for the DISCOVER-AQ field campaign in Maryland, USA for conversion of a total-column observation to a surface mixing ratio estimation (Knepp *et al.*, 2013).

Pandora (and similarly OMI) tropospheric NO_2 values were converted to molar ratio values via Equation (1) where $Pandora_{col}$ is the total column density measured by Pandora in molec/cm², OMI_{strat} is the stratospheric component as measured by OMI, PBL is the boundary-layer height in cm, N is the number density of air in molec/cm³, using calculated hourly PBL to properly account for the influence of PBL variability.

$$ppb = \frac{(Pandora_{col} - OMI_{strat}) * 1E9}{PBL * N} \quad (1)$$

The NO_2 surface mixing ratios were obtained from the Teledyne NO & NO_x gas analyser, logging at 1 minute time resolution. These data were subsequently quality-controlled and scientifically flagged per standard procedures and averaged into 15 minutes averages (Vakkari *et al.*, 2011; Laakso *et al.*, 2008).

Pandora's algorithms, which retrieve ground-based total column NO_2 amounts, use direct-sun irradiances between 280 nm and 525 nm at a resolution of approximately 0.5 nm (Brinksma *et al.* 2008; Herman *et al.* 2009; Tzortziou *et al.*, 2012). Pandora has a 1.6-degree field of view (FOV, a circle of ~120 m in diameter at 4 km altitude) and is mounted on a precision pan-tilt tracking device to follow the position of the centre of the sun. Pandora retrieves total columns approximately every 2 minutes. Clouds, ambient temperature, and absorption cross sections all introduce uncertainties into the Pandora total column NO_2 retrieval, and must be corrected in the instrument retrieval algorithm (Herman *et al.*, 2009; Tzortziou *et al.*, 2012). Absolute error in Pandora retrievals is ±0.1 DU, with a precision of about ±0.1 DU in clear skies. This error grows with noise created by clouds in a given retrieval (Reed *et al.*, 2013). The Pandora data were quality-controlled and flagged (mainly for instrument non-functioning periods and cloud cover threshold exceedances). For the purpose of this study, 15 minute averages were created for comparison to the gas analyser.

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OMI Level 2, Version 3 Total and Tropospheric Column NO_2 ($OMNO_2$) data from the NASA GES DISC ("Goddard Earth Sciences Data and Information Services Center") provide (13 x 24 km resolution) total column NO_2 retrievals for direct comparisons. OMI retrievals within 100 km distances to the station were selected and averaged. In addition to the total column amount, OMI data files included quality control flags for conditions that could cause erroneous retrievals. The cloud fraction retrieved by OMI (retrievals with cloud fraction <30 % were selected) and the 'Row Anomaly' flag were used to filter data when Level 1B OMI radiances are compromised by a high signal/noise.

Daily OMI-derived stratospheric column NO_2 data (using the $OMNO_2$ data) were interpolated to the same temporal frequency as the quality-controlled Pandora measurements and subtracted from the Pandora-column observations at the site to yield tropospheric NO_2 column densities applicable to the study period. As a result of poor (cloudy/rainy) weather conditions at the station, 25 days between January 25 and March 15, 2011 could be used for the analysis.

4. Results

4.1 Surface gas analyser vs. Pandora comparison

Preliminary comparisons of the gas analyser surface NO_2 mixing ratios with the Pandora converted surface NO_2 mixing ratios indicate that Pandora was generally underpredicting the surface NO_2 concentration (Figure 2). The mean surface mixing ratio for this study as measured by the gas analyser is ~ 2 ppb as compared to the Pandora converted surface mean of ~ 1 ppb of NO_2. The percent difference between the gas analyser and Pandora is about 50 % when outliers are not included; however, in many instances the Pandora converted surface mixing ratio was within the uncertainty limit of the gas analyser.

4.2 Surface gas analyser-Pandora-OMI inter-comparison

The comparison of all three measurements of NO_2: gas analyser surface mixing ratio, Pandora converted surface mixing ratio, and OMI total column concentration as well as its BL converted VMR indicates that results are sensitive and responsive to evident changes in boundary layer concentrations for both remotely sensed (Pandora and OMI) and surface gas sampling. These results demonstrate the potential application for Pandora to provide surface mixing ratio estimates at similar temporal frequencies as gas analysers. Estimated OMI surface NO_2 is sometimes within the ground/Pandora uncertainty limits when using AIRS-derived PBL heights, but OMI surface NO_2 in clean air remained difficult to capture (Figure 2).

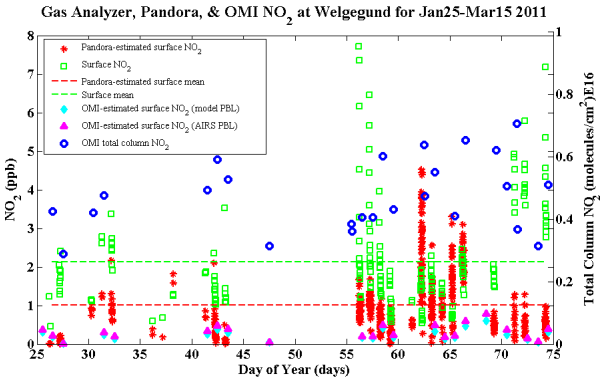

Figure 2: Gas analyser (green circles) vs. Pandora (red stars) vs. Ozone Measuring Instrument (OMI) surface mixing ratios of NO_2 (cyan diamonds) with modelled planetary boundary layer (PBL) and OMI surface mixing ratios of NO_2 (magenta stars) with observed, Atmospheric Infra-red Sounder (AIRS) PBL over Welgegund.

5. Conclusions

For the first time in this region, a quantitative comparison of remotely sensed trace gas columns with gas analyser surface-level NO_2 mixing ratios was undertaken. The data for the ground instruments were in agreement within the expected uncertainty for each technique and between two remote sensing instruments. However, NO_2 between the ground gas analyser and satellite borne instrument were out of the expected uncertainty limits. Both observed and modelled PBL heights were used in the PBL correction, which is likely the greatest uncertainty in the conversion of column to surface NO_2. This study contributes to further exploration of this technique in varied environments as encouraged by the initial study.

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