

Evaluation of OMI NO₂ Data Quality

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Abstract

The two principal quantities calculated by the OMI NO₂ PGEs are the total vertical column density and the tropospheric column density of atmospheric nitrogen dioxide above each location viewed by OMI, at the time of overpass. At this time, the number of experiments that directly measure NO₂—stratospheric, tropospheric, or total—from the ground or from aircraft is somewhat limited, but includes data collected during a few field campaigns, as well as data collected from a geographically distributed network of fixed measuring sites. A number of these measurements can be exploited to at least qualitatively, and in many cases semi-quantitatively, assess the quality of the OMI-retrieved measurements. This document summarizes what has been learned thus far from ground-based measurements collocated with OMI measurements of NO₂.

This document is a supplement to the Readme File included as part of the first public release of the OMI NO₂ data product (OMNO2). The Readme File may be found at http://toms.gsfc.nasa.gov/omi/no2/OMNO2_readme.pdf.

Factors Affecting OMI NO₂ Data Quality

The OMI NO₂ algorithm uses a spectral fitting technique (Differential Optical Absorption Spectroscopy, DOAS) to estimate the NO₂ slant column density (SCD), which is the total NO₂ density along the optical path (*i.e.*, along the solar beam from the top of the atmosphere to the visible surface—cloud or ground—and then along the instrument's line-of-sight, back to the top of the atmosphere). The rest of the algorithm is concerned with the computation of the air mass factor (AMF), which is the number used to convert from the SCD into the vertical column density (VCD), and with the separation of the NO₂ column into stratospheric and tropospheric components.

The determination of the SCD is affected by various types of noise in OMI's detectors. Particular problems arise from the fact that the spectral fitting is applied to the ratio of the (earthshine) radiance and (solar) irradiance spectra, which are not measured simultaneously. In normal operations, the irradiance is measured once per day, and a particular solar measurement is then applied to the subsequent 14-15 orbits. It has been found that the patterns of "hot" pixels, and pixels affected by random telegraph signal (RTS) differ between the measurements of radiance and irradiance, resulting in significant noise in the ratios. This has led, most prominently, to the presence of "stripes" in most of the data products, where values retrieved at some of the 60 cross-track

positions will be persistently higher or lower than the values at adjacent positions. Research groups working with different derived OMI products have taken different approaches to attempt to suppress these stripes. The NO₂ algorithm uses a scheme that adjusts the means of the SCDs for each position, along a single orbital track, to lie on a smooth curve. This *post-hoc* correction has resulted in the suppression of most of the apparent striping in the NO₂ (total and tropospheric), but at the expense of the possible introduction of an unknown bias. In addition, an anomaly occurred on 2006 February 28, which has taken the fold mirror, which switches between earthshine-view and solar-view modes, and since that time no new irradiance measurements have been made. Subsequent processing has proceeded using the last-measured irradiance spectrum, and some degradation has been seen in the retrieved NO₂ data, including an increase in the apparent striping, even after the *post-hoc* correction.

The calculation of the AMF rests on certain assumptions, for example, concerning the overall shape of the NO₂ vertical profile. It also rests on some other data sets, such as the OMI-derived cloud fraction and cloud-top pressure (currently using the oxygen dimer algorithm product), and the surface albedo (currently using the GOME-derived albedo climatology of Koelemeijer).

Finally, the calculation of the AMF is affected by a process that classifies an OMI FoV as having a significant tropospheric pollution component, or not. This classification is performed using an algorithm that constructs an “unpolluted field,” and compares the initial estimate of the VCD to the unpolluted field. To date, this algorithm has only been evaluated against a model-based data set. Though this algorithm is expected to be quite good, it has yet to be critically evaluated using real-world data.

Ground- and Aircraft-based Measurements of NO₂

Ground-based measurements, particularly in regions of moderate-to-intense industrial activity, are subject to variation due to both spatial inhomogeneity of boundary layer NO₂, which can show up as an azimuthal dependence of the measured NO₂, and time-evolution of the NO₂ concentration due to continual variations in NO₂ sources and sinks, wind patterns, and insolation. Such variations undoubtedly account for some of the differences that are seen between the OMI-derived and ground-based measured NO₂ amounts, and must be considered when making such comparisons.

Most current ground-based measurements of NO₂ rely on the absorption of solar irradiance by NO₂ molecules. The **Brewer Method** [Cede and Herman], for example, measures the NO₂ absorption from the direct solar beam using a Brewer spectrophotometer. These measurements may only be made during clear-sky conditions (cloud and aerosol optical thickness less than 1.5). The air mass factors used to transform the measured SCD to the VCD are relatively simple: They are geometric AMFs, modified to account for the absorption by stratospheric ozone.

Besides the simplicity of the AMF calculation and the simplicity of the direct-sun measurement, the Brewer method also has the advantage of requiring a reasonably short measurement time (4 minutes, routinely repeated every half-hour while the solar zenith angle is less than 80°), so measurements made around the OMI overpass time (~13:45 local time) may be isolated for comparison.

The intrinsic variability of the individual measurements, arising ultimately from the fact that the NO₂ optical thickness is small at the wavelengths used, means that a large number of measurements must be made and averaged together to ensure precision. This, of course, means that the measurements are taken over a period of time long enough that the actual atmospheric composition may change, in addition to the optical geometry. Nonetheless, Cede and Herman have collected a large base of data using an instrument located in Greenbelt, Maryland (currently the only station making NO₂ measurements using a Brewer), and Cede et al. have made preliminary comparisons with the OMI total column NO₂ product. The results of those comparisons are presented and discussed in a subsequent section of this document.

Another instrument, the **SAOZ** (*Système d'Analyse par Observations Zénithales*), has a lengthy record of NO₂ measurements, made with a network of instruments, primarily located in the polar latitudes. These instruments measure the zenith-sky radiation (from 400 to 600 nm) during sunrise and sunset (solar zenith angles between 86° and 91°), and perform a DOAS fit to retrieve both O₃ and NO₂. The measurement technique—more specifically, the optical geometry—makes it far more sensitive to NO₂ in the stratosphere than the troposphere, but these instruments are mostly stationed in locations far from sources of anthropogenic NO₂.

While the fact that there are a number of SAOZ instruments distributed over the Earth, regularly measuring NO₂, is an advantage, the fact that these instruments only measure NO₂ at sunrise and sunset, while OMI measures in the middle of the day, means that the measurements are never actually collocated. This is a particular problem, since stratospheric NO₂ varies greatly over the course of the day. Ionov *et al.* have attempted to get around this by using a chemical transport and photochemistry model to adjust the OMI-measured mid-day measurements to the values that obtained at the time of the SAOZ measurement (they chose to compare to the sunrise measurements). The results of the comparison based on these adjusted data are presented in a later section of this document. Actually, because of the orbital inclination of the EOS-AURA satellite (97°), the high-latitude, northern hemisphere sites tend to have their OMI overpasses earlier in the day than the 13:45 equator crossing time, so the adjustment of the OMI-measured stratospheric NO₂ to the sunrise value is not as great as it is in the tropics, or the southern hemisphere stations.

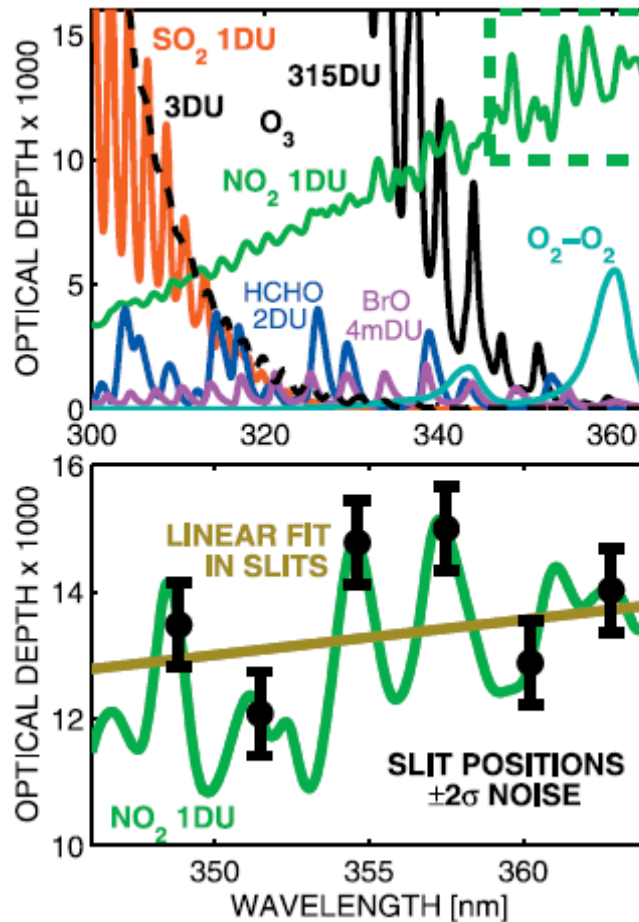
One possible further complication of the SAOZ measurement technique is that, measuring at sunrise and sunset, one is measuring at the very times when the stratospheric NO₂ is changing the most rapidly, due to photochemical destruction.

The Multi-axial DOAS (**MAX-DOAS**) instruments are designed to measure the vertical profile of NO₂ and O₃ in the troposphere. The DANDELIONS (Dutch Aerosol and Nitrogen Dioxide Experiments for validation of OMI and SCIAMACHY) campaign, organized by KNMI (*Koninklijk Nederlands Meteorologisch Instituut*/Royal Dutch Meteorological Institute) during May and June 2005, used three MAX-DOAS instruments to measure NO₂. Preliminary results have been presented by Brinksma *et al.* This campaign was conducted in Cabaw, the Netherlands, and measured a number of air quality-related quantities, but with a primary focus on NO₂. One objective of this field campaign was to intercompare individual MAX-DOAS instruments (and a newer “mini-MAX-DOAS” model). However, the MAX-DOAS results were also compared with collocated OMI tropospheric NO₂ measurements.

We now turn to the results of the validation studies that have been made so far.

Brewer Method

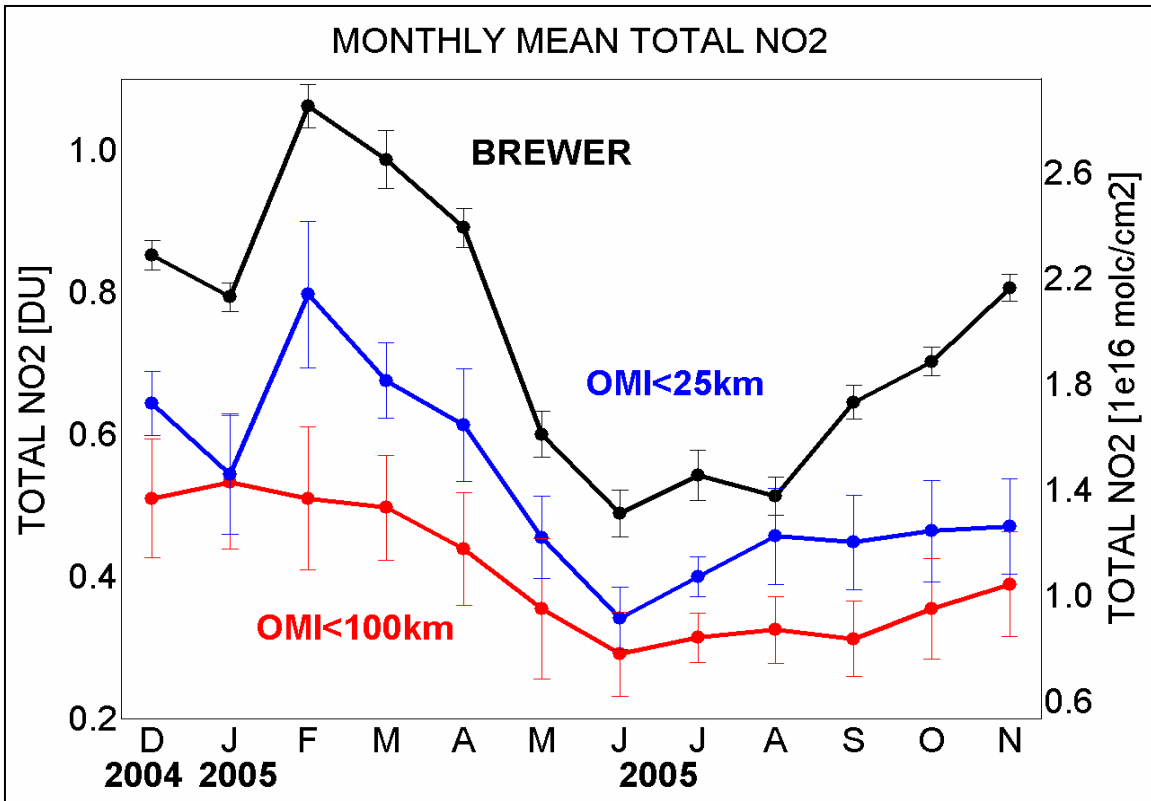
The Brewer Method of NO_2 measurement employs a Brewer Mk-III spectrophotometer with a double-monochromator, operating in direct-sun mode. The instrument has a slit mask that can be inserted into the optical path to allow nearly simultaneous measurements at 6 wavelengths, roughly 3 nm apart. For the NO_2 measurements, the wavelength range measured is 348-363 nm. Typical optical depths of the main trace gases in this wavelength range are shown in the following figure:



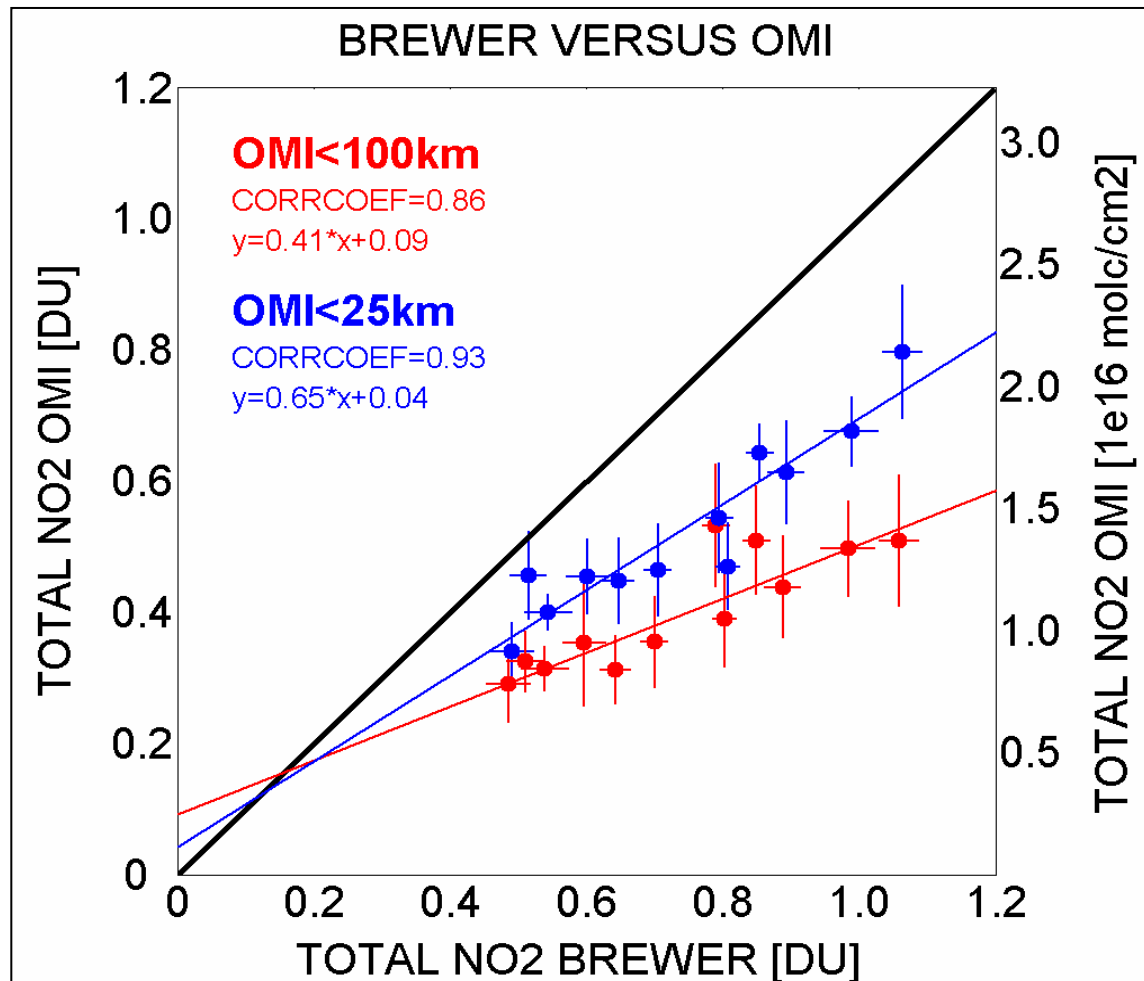
The top panel shows that common trace gases do have some considerable absorption features in the wavelength range measured by the Brewer Method, and these must be taken into account in the retrieval. The principal trace gases with the greatest absorption optical depths in this wavelength range are $\text{O}_2\text{-O}_2$ and O_3 . The ozone concentration, of course, is the primary quantity measured by the Brewer instrument, so is readily accounted for in the data reduction. The $\text{O}_2\text{-O}_2$ concentration can be evaluated for a standard climatological temperature profile. The concentrations of bromine oxide and formaldehyde are assumed to be constant, at climatological values of 0.004 DU and 2

DU, respectively. The aerosol scattering optical depth is co-retrieved with the NO₂ optical depth, assuming a linear wavelength dependence over this small wavelength interval. Cede and Herman estimate the uncertainty in NO₂ of 0.2 to 1.0 DU, with a bias of -0.1 DU, where most of the uncertainty is due to the instrument noise and atmospheric variability over the measurement period.

The measurements were performed at Goddard Space Flight Center (GSFC), Greenbelt, Maryland (38.98°N, 76.83°W, 90 m above sea level). Only clear-sky observations were used. Unfortunately, the location of the instrument is within a few km of several major roadways, including the Capital Beltway. Thus, depending upon the azimuth and altitude of the sun, wind direction, and time-of-day, highly local effects may influence the instrumental measurements. Cede found that the Pearson's coefficient between the OMI overpass NO₂ measurements and the collocated Brewer measurements, as well as the general agreement between the values, increased when the collocation criteria were tightened both in space and time, as shown in the following two figures.



Monthly mean NO₂ total columns. Ground data (black) are temporal averages over a 3 hour window around OMI overpass time (~11:50 to 14:50 local time) and are cloud screened. Satellite data are spatial averages over all pixels, which center within 100km (red) and 25km (blue) around the ground location, and only cloud fractions below 30% are used. Error bars indicate the expanded (=2σ) standard error of the monthly means.



Same data as in previous figure, in a scatter plot including error bars and linear least square fits. Error bars are 2 sigma.

These data, though preliminary, suggest that either the OMI AMF is too large, or that the Brewer AMF is too small. However, there are other possible explanations of the data (particularly in the second figure above), including a possible calibration problem with the Brewer instrument, leading to an over-estimation of the slant column NO_2 . In addition, the graph above shows the effect of tightening the criterion for coincidence: The OMI and Brewer measurements agree much more closely when the criterion is 25 km, than when it is 100 km. It would be difficult, given a data base that spans only one year, to try an even tighter criterion, as the number of collocations would be too small to yield an adequate statistical significance.

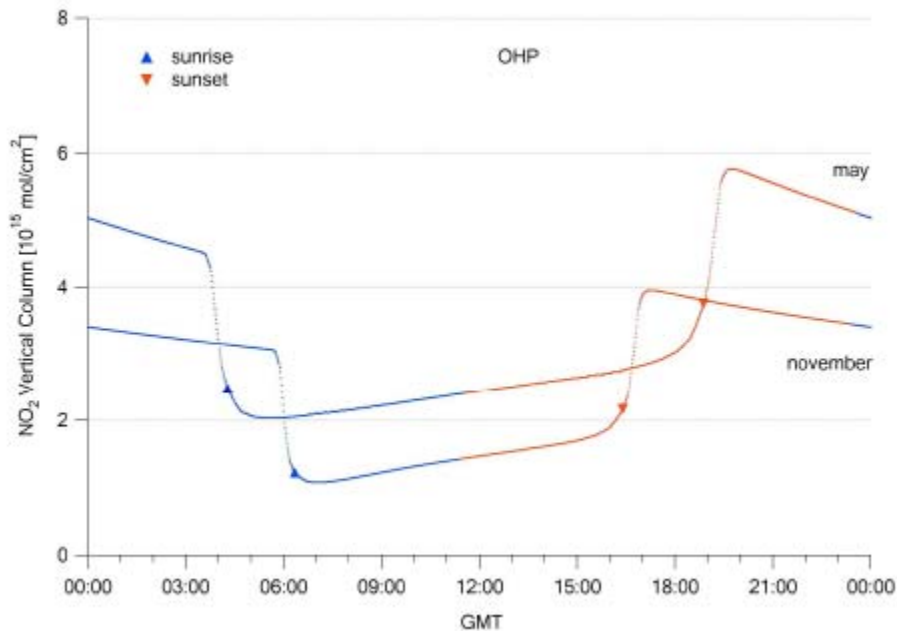
As of this writing, the only Brewer instrument that is being used to make NO_2 measurements is located at the Goddard Space Flight Center, just outside the Capital Beltway. This region can be expected to have tropospheric NO_2 concentrations that vary rapidly, and are spatially highly inhomogeneous. This complicates the question of

collocated measurements. For the purpose of OMI validation, it would be very useful to have measurements made in a location where the NO_2 field is rather more stable.

SAOZ Method

The French CNRS operates a network of SAOZ instruments, which make zenith-sky spectroradiometric measurements, and, using a DOAS retrieval algorithm, retrieve areal column densities of atmospheric trace gases. The measurements are made at sunrise and sunset (SZA from 91° to 86°). With this optical geometry, this method is significantly more sensitive to stratospheric than tropospheric concentrations of absorbing gases. Though SAOZ instruments are stationed at locations well-distributed in latitude, only the station at the Observatoire de Haute-Provence (OHP), in southeastern France, is in an area that experiences any appreciable tropospheric concentrations of NO_2 . As such, the principal value of the SAOZ network to OMI NO_2 validation is to evaluate OMI's retrieval of stratospheric NO_2 .

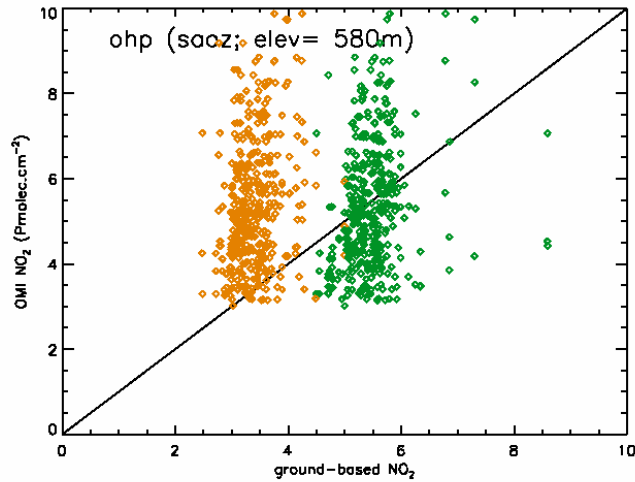
The main challenge in comparing SAOZ data with OMI NO_2 lies in the fact that the SAOZ measurements are made at sunrise and sunset, while the OMI measurements are made in the middle of the day (roughly 13:45 at low- to mid-latitudes). Stratospheric NO_2 builds up at night, but is rapidly photolyzed when the sun comes up, causing a steep drop in concentration just prior to at-surface sunrise. The NO_2 concentration then gradually increases over the course of the day, and then, after the sun sets, again rises sharply. This is illustrated in the following figure (Ionov, *et al.*):



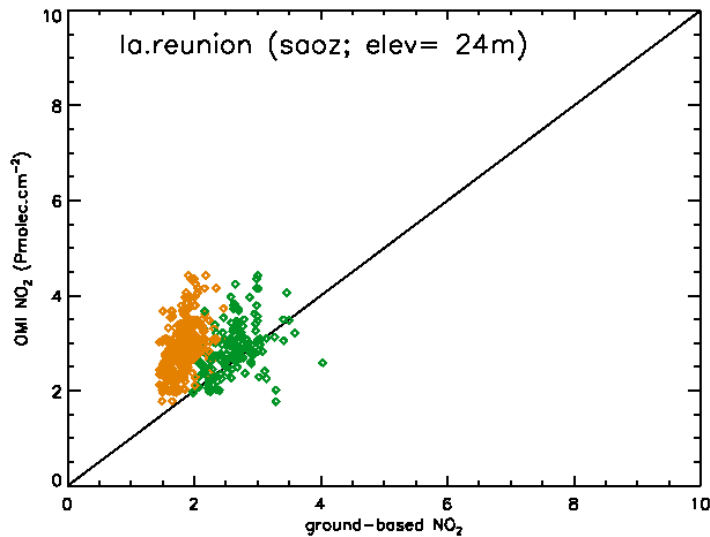
Note that the stratospheric NO_2 concentration rises almost linearly with time over the sunlit portion of the day. Also, the triangles in the figure denote the time at which the SZA is 90° , so the SAOZ measurements are actually being made during a period of time when the stratospheric NO_2 is still changing. Ionov, *et al.* used a photochemical box

model (SLIMCAT 3D chemical transport model) to propagate from the OMI-measured midday NO_2 values to the time of the SAOZ sunrise measurement.

Preliminary examination of the OMI total NO_2 over SAOZ sites by Celarier, et al. showed that, for the small number of sites examined, the OMI NO_2 column amount lay roughly midway between the SAOZ-measured sunrise and sunset values. This is illustrated for the OHP site in the following figure. The orange points represent the sunrise SAOZ measurements, and the green points represent the sunset ones.



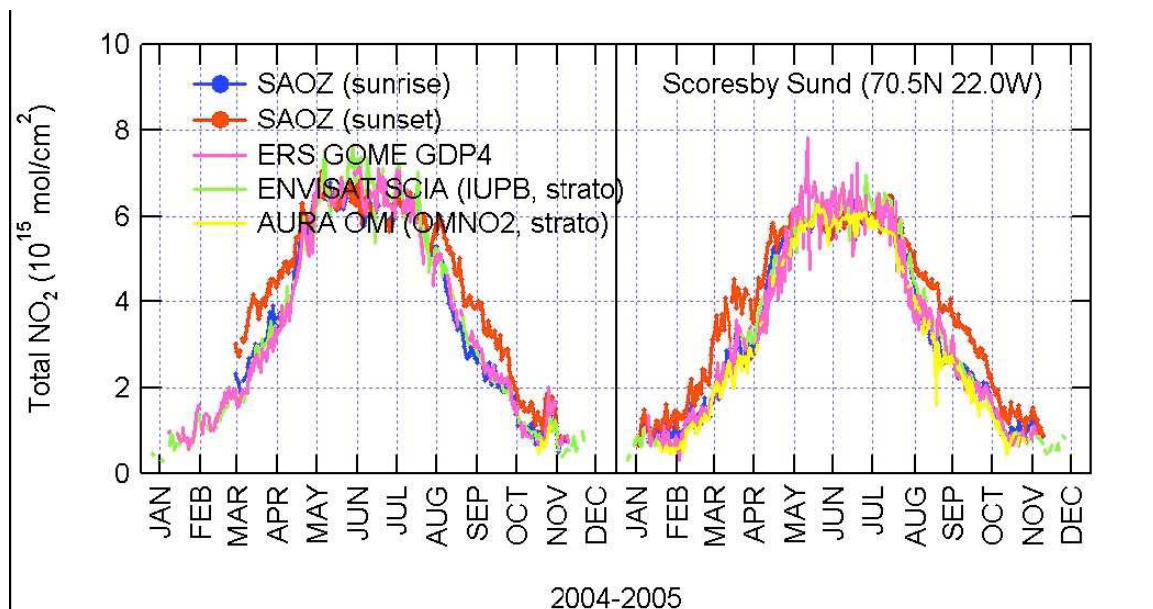
A similar plot for the SAOZ site in La Réunion, shows little of the scatter seen in the OHP data, suggesting that scatter is due to the sensitivity of OMI to tropospheric NO_2 , which is largely absent around La Réunion. A bias (OMI larger) is seen in the La Réunion case.

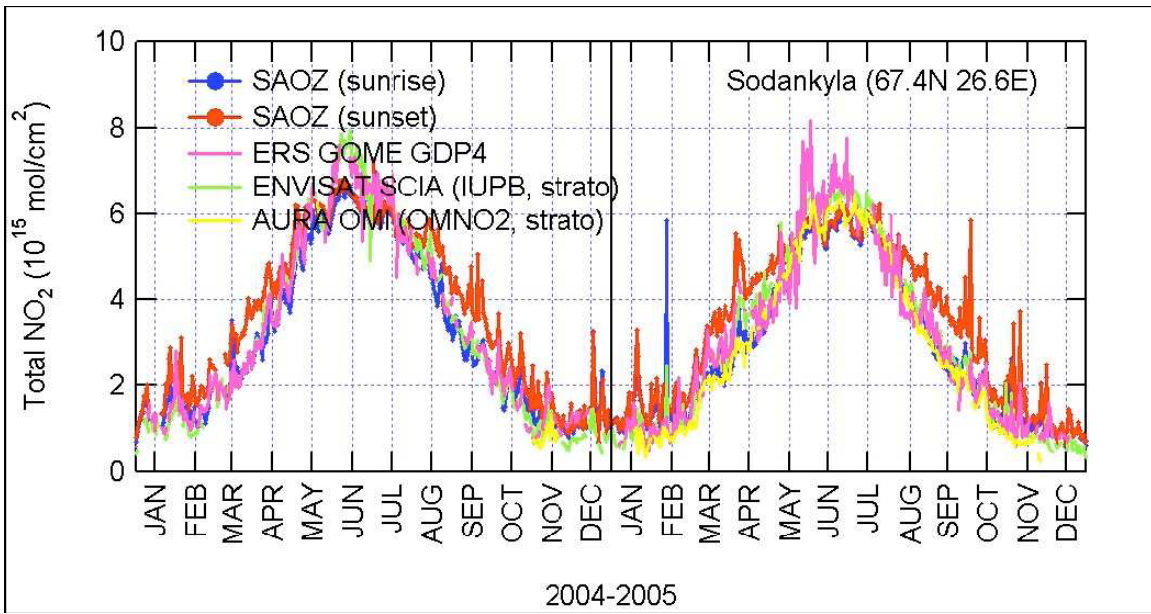
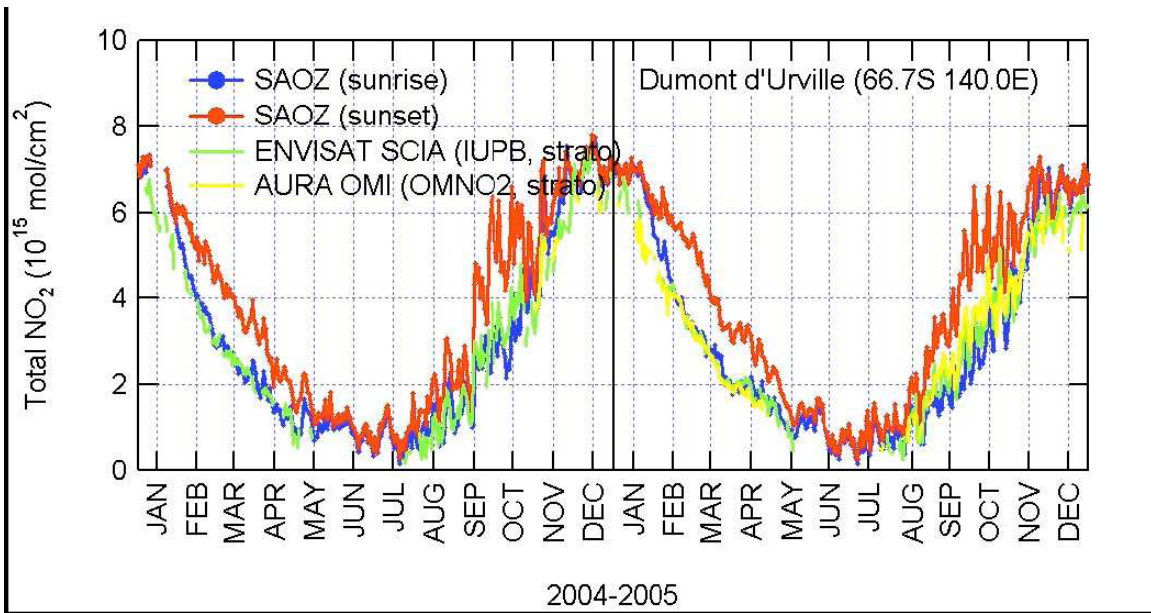


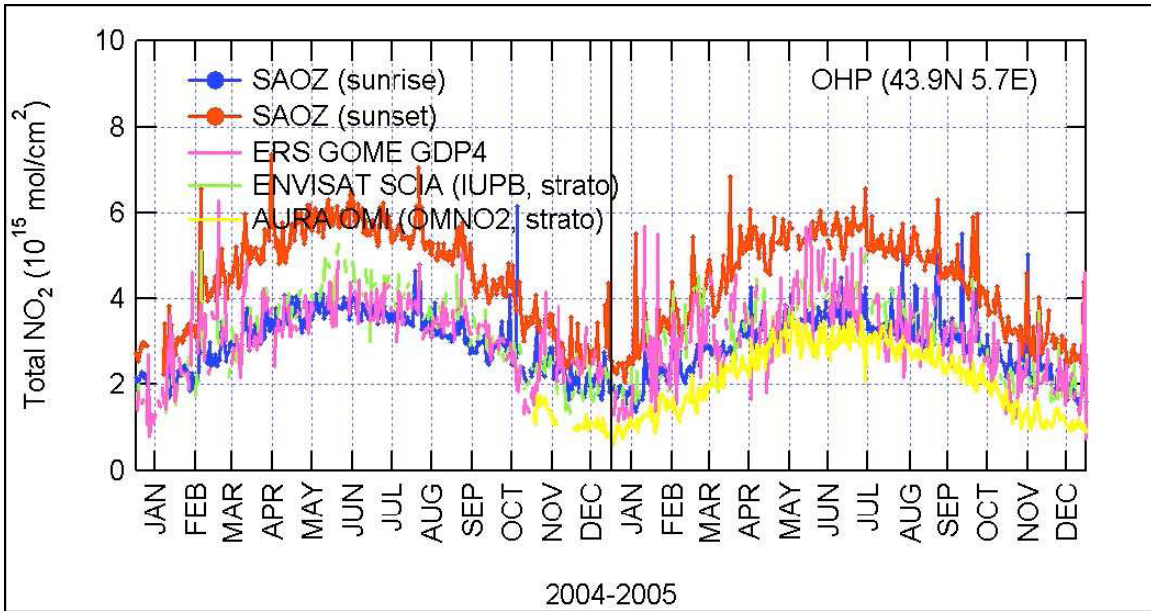
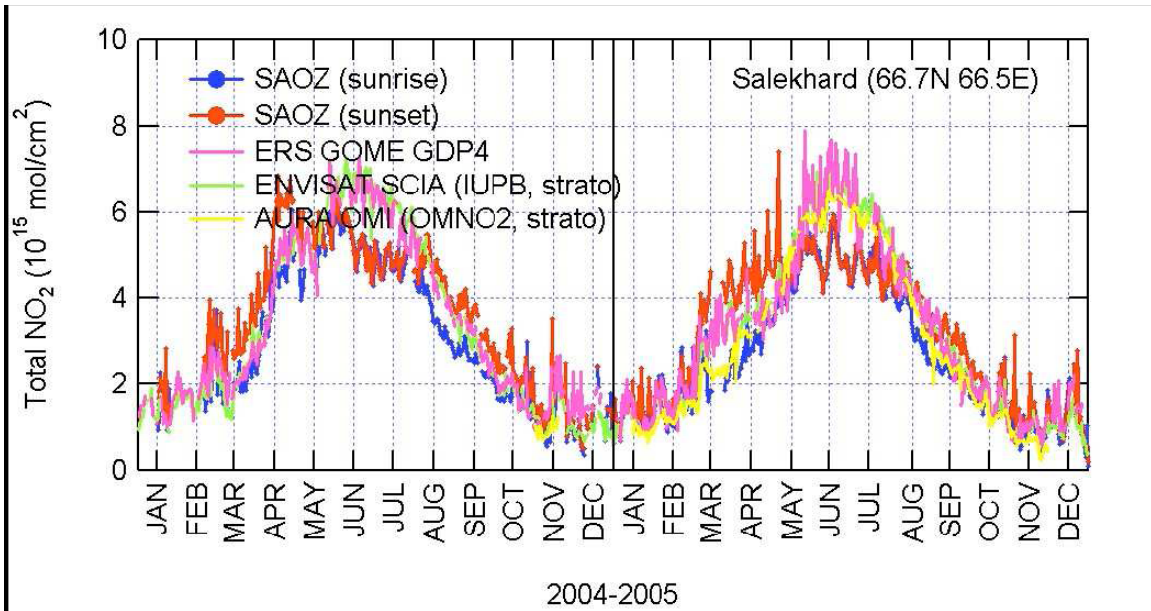
In the study by Ionov, et al., where the midday stratospheric NO₂ (taken to be the total minus tropospheric NO₂ concentrations) is propagated backward in time using their photochemical model, data have been compared over more than a year's time over a small number of sites. The criterion for collocation was that the OMI FoV center should fall within a FoV width of the SAOZ site. In selecting this criterion, one overlooks the fact that most of the stratosphere that is sampled by the SAOZ sunrise measurement is well to the east of the instrument site. Work is currently being undertaken to sample the OMI data in a way that takes account of the SAOZ geometry.

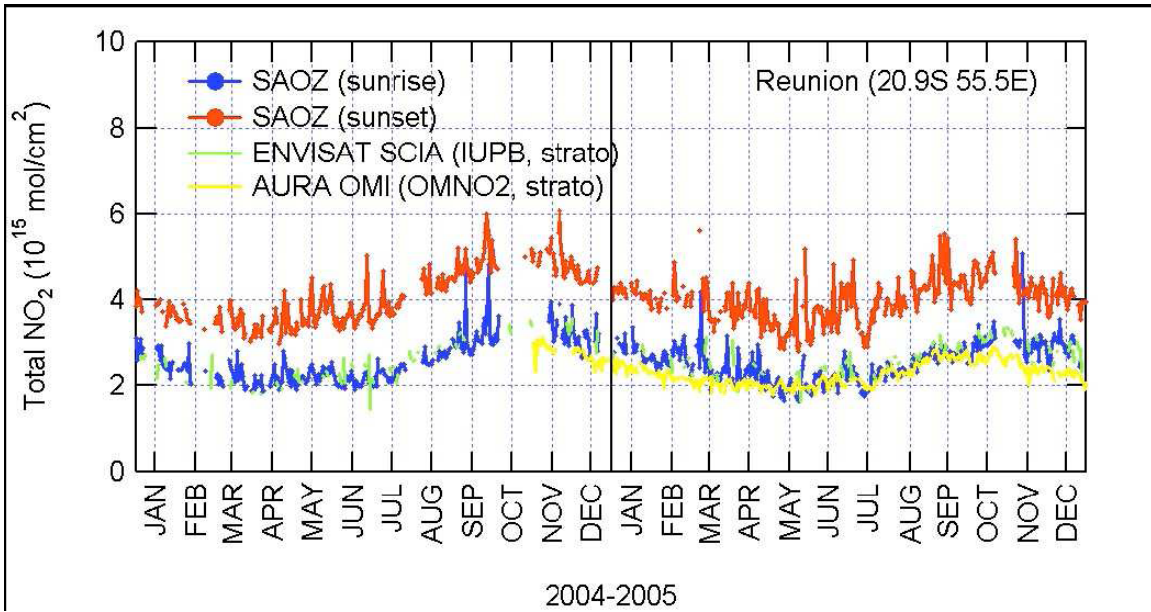
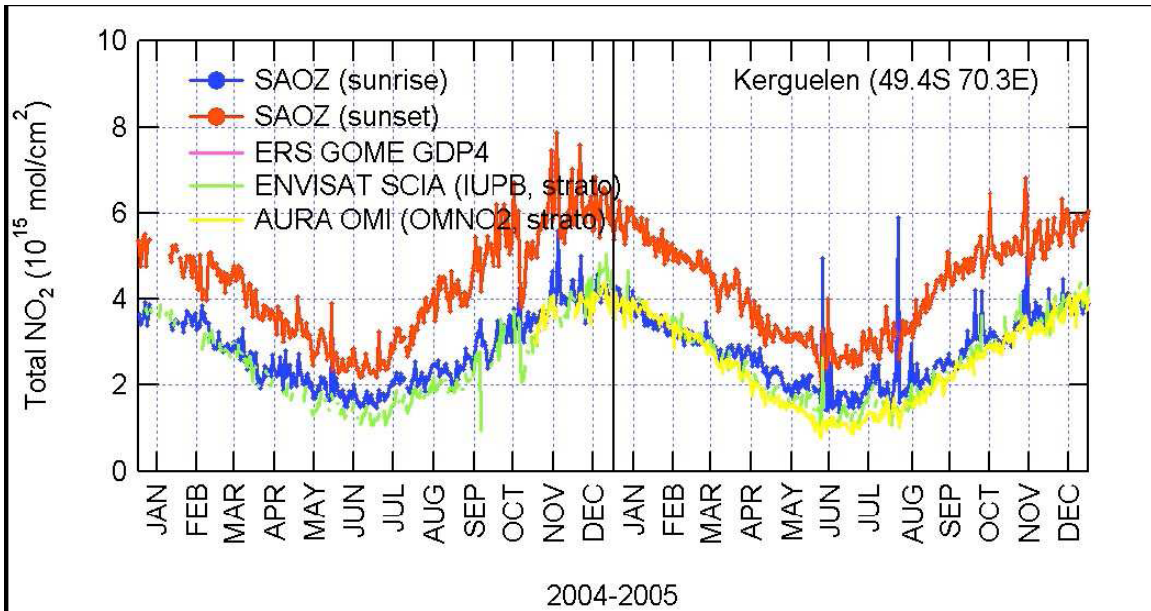
The seasonal SAOZ data may be affected by the fact that the algorithm used uses a single air mass factor for all seasons. This is a concern because the ozone vertical distribution changes over the course of the year.

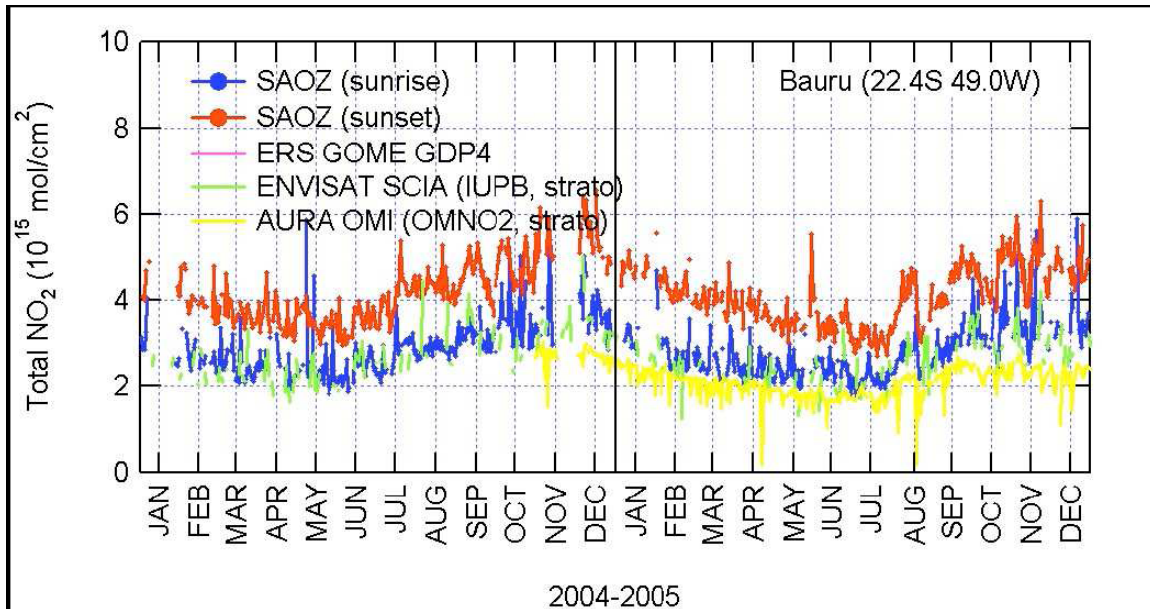
The results of the SAOZ/OMI comparisons are shown in the following figures. Sciamachy and GOME data are also presented. The important comparison is between the SAOZ sunrise measurements (in blue) and the OMI measurements (in yellow).











The fact that the (adjusted) OMI measurements are tracking very well the SAOZ measurements, even when the overall variation is small (as in the case of Bauru) is very encouraging.

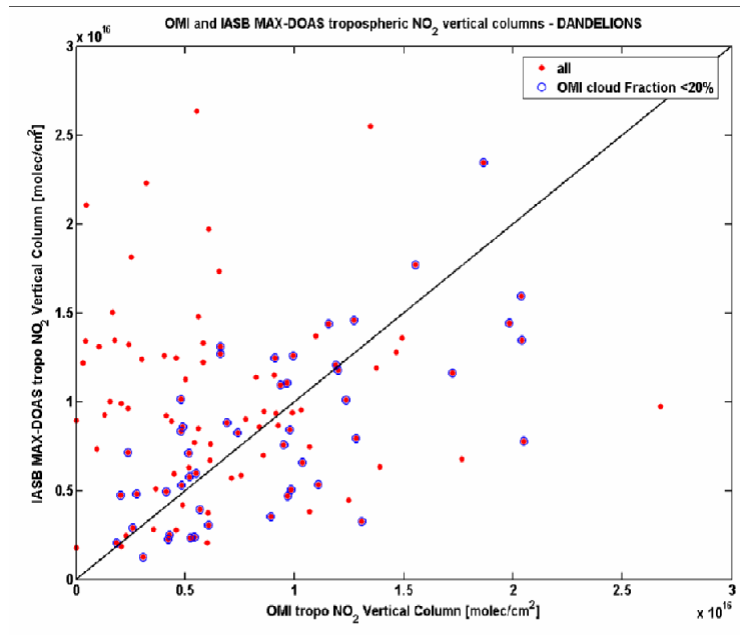
Evaluation of the differences between the OMI and SAOZ measurements show that, for the stations featured in the foregoing plots, the systematic bias ranges from -0.77 Pmolec/cm² (seen at OHP and Bauru), to $+0.22$ Pmolec/cm² (Salekhard), with most of the stations showing a bias of around -0.23 Pmolec/cm². The RMS difference between OMI and SAOZ is around 0.5 ± 0.2 Pmolec/cm². Finally, the Pearson's correlation coefficient calculated for each of the sites is greater than 0.9 except at the low-mid latitude sites (Réunion (0.6), OHP (0.8), and Bauru (0.6)). This is receiving closer study, but is thought to be the result of tropospheric NO₂ variability that is seen by the OMI instrument, but not by the SAOZ instrument, possibly exacerbated by the OMI algorithm's overcorrecting the tropospheric component. It may also be due, in part, to the incomplete removal of OMI's cross-track bias (or "striping"). It will be interesting to re-compare the OMI and SAOZ results, once the algorithm to eliminate the striping is improved—work that is well underway.

In view of the details of the OMI-SAOZ comparisons, it is fair to say that there is good agreement between the two, based both on how closely the OMI data track the SAOZ data. While that is an essentially qualitative judgment, the quantitative measures of comparison that have been examined are also promising. However, we have indicated a number of issues that are known to affect the quantitative comparison. There is an ongoing effort to address those issues.

MAX-DOAS at DANDELIONS

The Multiaxial DOAS (MAX-DOAS) instruments can be used to retrieve daytime tropospheric NO₂ columns, twilight total NO₂ columns, and some vertical profile data. During the DANDELIONS campaign (May 12—June 30, 2005 at Cabauw, the

Netherlands), three MAX-DOAS instruments were deployed, along with a number of other types of instruments. The following figure shows the MAX-DOAS tropospheric vertical column amounts, plotted against the collocated OMI tropospheric NO_2 . The red points indicate all measurements; red points with blue circles indicate only the measurements made when the cloud fraction was below 20%. The Pearson's coefficient for the low cloud fraction points is 0.67.



CONCLUSIONS

Although there are not a lot of ground-based data available for intercomparison studies with the OMI NO_2 product (OMNO2), those that do exist show relatively good agreement.

The Brewer data, collected in a single location, suggest that the OMI total NO_2 column is about 35% too low. The seasonality of the NO_2 columns are very similar.

The SAOZ data, measuring mostly stratospheric NO_2 , collected in eight locations, five of which are at high latitudes, show somewhat different biases at the different stations, but with most biases calculated to be about $-0.2 \text{ Pmolec cm}^{-2}$, on a signal of about 3 Pmolec cm^{-2} , or about 5–10% low. There are some known issues concerning the SAOZ retrievals, such as the fact that the AMF being applied does not take account of the seasonal change in the altitude of the ozone peak; this is manifested in a regular seasonal variation in the difference between SAOZ and OMI (and two other satellite instruments examined by the SAOZ group.) The similarity in the seasonal cycles seen in the SAOZ and OMI data is quite remarkable.

Finally, the MAX-DOAS instrument, deployed on the DANDELIONS campaign at Cabauw, measured tropospheric columns. The correlation between the MAX-DOAS and OMI is quite poor unless nearly cloud-free data are chosen, when the correlation is quite good, about 0.67. However, given the dispersion of the data, and relatively small

number of samples, there are not enough data in the set to make a reliable estimate of any bias that exists between the OMI and MAX-DOAS estimates of tropospheric NO₂ columns.

A small number of *in situ* measurements of NO₂ profiles from aircraft have been made, particularly during the INTEX-B mission. Work is currently underway to evaluate the differences between the measured profiles and the *a priori* profiles, and the sensitivity of the OMI-derived NO₂ columns to those differences. The results of that study will be presented at some time in the future.