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Ground-based validation of EOS-Aura OMI NO_2 vertical column data in the midlatitude mountain ranges of Tien Shan (Kyrgyzstan) and Alps (France)

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[1] Ground-based UV-visible instruments for NO_2 vertical column measurements have been operating at Issyk-Kul station, in Kyrgyzstan, and Observatoire de Haute-Provence (OHP), in France, since 1983 and 1992, respectively. These measurements have already been used for validation of ERS-2 Global Ozone Monitoring Experiment (GOME) and Envisat Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) NO_2 column data. Building upon the successful missions of GOME and SCIAMACHY, the Ozone Monitoring Experiment (OMI) was launched by NASA onboard the EOS Aura satellite in July 2004. Here we present the results of recent comparisons between OMI NO_2 operational data (standard product) and correlative ground-based twilight measurements in midlatitudes, at Issyk-Kul and OHP, in 2004–2006. The stratospheric NO_2 columns, observed by OMI and our ground-based instruments, have been corrected for NO_2 diurnal change and normalized to local noon values using a photochemical box model. According to our comparison, OMI stratospheric NO_2 columns underestimate ground-based measurements by $(0.3 \pm 0.3) \times 10^{15}$ molecules/cm^2 and $(0.7 \pm 0.6) \times 10^{15}$ molecules/cm^2 at Issyk-Kul and OHP, respectively. The effect of tropospheric pollution on the NO_2 measurements in both regions of observations has been identified and discussed.

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1. Introduction

[2] Nitrogen dioxide (NO_2) plays an important role in atmospheric chemistry, both in the stratosphere and in the troposphere. It is one of the key species in the chemistry of ozone, and its tropospheric content is an indicator of poor air quality. Therefore, along with ozone, the global monitoring of NO_2 is a key objective of NASA's Ozone Monitoring Experiment (OMI). In this regard, OMI succeeds two other space experiments: ESA's GOME and SCIAMACHY. GOME (Global Ozone Monitoring Experiment) was launched in April 1995 onboard the ERS-2, into a sun-synchronous polar orbit [*Burrows et al.*, 1999a]. It is a nadir-viewing UV-visible spectrometer that measures the solar irradiance and the solar radiation backscattered from both the atmosphere and the Earth's surface. Besides providing global maps of atmospheric ozone, GOME was also the first spaceborne instrument capable of measuring the total column amount of NO_2. The trace gas column densities given in the GOME data products (ozone and NO_2), are derived by the Differential Optical Absorption Spectroscopy (DOAS) technique [*Platt*, 1994]. GOME was followed by the Scanning Imaging Spectrometer for Atmospheric Cartography (SCIAMACHY) onboard Envisat in 2002, which could also measure NO_2 vertical columns [*Bovensmann et al.*, 1999].

[3] Like the GOME and SCIAMACHY satellite instruments, OMI is a nadir viewing, wide swath UV-visible imaging spectrometer. It was launched on 15 July 2004, onboard NASA's EOS Aura platform, into sun-synchronous near polar orbit [*Levelt et al.*, 2006]. According to numerous validation studies, the overall accuracy of operational GOME and SCIAMACHY NO_2 vertical column data is estimated to fall within $\sim 0.3 \times 10^{15}$ molecules/cm^2 in the areas of low tropospheric NO_2 [*Lambert and Balis*, 2004; *Piters et al.*, 2006]. The scientific requirements for the OMI data products call for an accuracy of $\sim 0.2 \times 10^{15}$ molecules/cm^2, for the same conditions [*Brinksma et al.*, 2003]. The present study contributes to the geophysical validation of operational NO_2 vertical column measurements from Aura OMI (standard product) using collocated ground-based observations at two stations: Issyk-Kul in the central

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Asia and OHP in Europe. Section 2 describes the ground-based UV-visible instruments. Section 3 gives a brief description of the OMI satellite instrument and its operational algorithm to retrieve NO_2 vertical columns. Section 4 presents correlative ground-based and satellite data sets and explains the comparison methodology, going back to the recent validation of GOME NO_2 vertical column data over Issyk-Kul and OHP. Section 5 shows the results and analysis of the comparison with OMI. Finally, the conclusions of our study are given in section 6 and possible future work is discussed.

2. Ground-Based UV-Visible Measurements of NO_2 Vertical Columns

2.1. Issyk-Kul Station

[4] Measurements of NO_2 vertical columns were begun at Issyk-Kul station in 1983 [*Aref'ev et al.*, 1995]. The station is located on the northern coast of Issyk-Kul lake in the Tien Shan mountains, Kyrgyzstan (42.6°N/77.0°E, 1650 m above sea level). The instrument design and retrieval technique is similar to the zenith sky-viewing setup operating at Zvenigorod station in the region of Moscow (Russia), and described in detail in [*Elokhov and Gruzdev*, 1993]. The system uses a Russian manufactured scanning monochromator MDR-23 (LOMO) with 1200 groove/mm grating, providing a spectral sampling of ~0.01 nm. Thus, the measurements are carried out by means of a grating spectrometer operating in ~435–453 nm range with a spectral resolution of ~1.0 nm. The Issyk-Kul instrument was certified by the Network for the Detection of Atmospheric Composition Change (NDACC) (formerly the Network for the Detection of Stratospheric Change, NDSC) as a complementary station, following the results of intercomparison carried out at Zvenigorod, Russia, in 1997 (more information available at http://www.ndsc.ncep.noaa.gov/data/madir).

2.2. Haute-Provence Observatory

[5] Measurements of NO_2 vertical columns were begun at OHP in 1992, when the French Système d'Analyze par Observation Zénithale (SAOZ) UV-visible zenith sky spectrometer was installed. The station is situated in the southeast of France, on a plateau in the Alps (43.9° N/5.7° E, 650 m above sea level). The SAOZ spectrometer was developed in 1988 at Service d'Aéronomie/CNRS [*Pommereau and Goutail*, 1988] and allows measurements of total column ozone and NO_2 from the ground by UV-visible spectrometry of the zenith sky at twilight. Twenty SAOZ instruments have been installed around the globe, creating the SAOZ network, with 10 of them being run by CNRS. This network has been established within international collaborations following the recommendations for long-term monitoring and data quality requirements of NDACC. SAOZ records zenith sky spectra using a wide spectral range (300–620 nm) in the UV-visible, with a spectral resolution of about ~1.0 nm. The instrument is composed of a flat field spectrometer with a concave holographic grating and a 1024 pixel photodiode array. The SAOZ instrument has been qualified for ozone and NO_2 measurements in the NDACC framework during several international intercomparison campaigns [*Vaughan et al.*, 1997; *Roscoe et al.*, 1999; *Vandaele et al.*, 2005].

2.3. NO_2 Vertical Column Retrieval

[6] The NO_2 column amounts at Issyk-Kul and OHP are retrieved using the DOAS technique applied to zenith sky measurements in the 435–453 nm (Issyk-Kul) or 410–530 nm (OHP) spectral range. The measurements are averaged over the solar zenith angle (SZA) range of 85–92° (Issyk-Kul) or 86–91° (OHP), to provide an accurate estimate of NO_2 vertical column at sunrise and sunset. The spectral analysis takes the ratio of the observed spectrum to a reference spectrum, measured at noon under clear sky conditions, and assumed to be less perturbed by molecular absorption. The logarithm of the ratio of twilight to noon spectra is analyzed using a least squares fit to laboratory absorption spectra of ozone and NO_2, along with molecular scattering, aerosol extinction and the Ring effect (inelastic scattering). The resulting NO_2 line-of-sight amounts (or slant columns), corrected for residual absorption in the reference spectra, are then converted to corresponding vertical columns with an air mass factor (AMF) calculated using a radiative transfer model (RTM) for each constituent at each SZA. Both ground-based instruments, Issyk-Kul and OHP, use similar NO_2 absorption cross sections in the DOAS analysis [*Vandaele et al.*, 1998]. A single solar reference spectrum is used for the spectral retrieval of the entire data set at each location. The residual amount of NO_2 present in the reference spectrum was determined by the Langley method, and found to be 4.65×10^{15} molecules/cm^2 and 5.25×10^{15} molecules/cm^2 at Issyk-Kul and OHP, respectively. The AMFs used to convert from the NO_2 slant column to vertical, are different for the retrieval of measurements at Issyk-Kul and OHP. At Issyk-Kul, the seasonal midlatitude AMFs are used on the basis of Air Force Geophysics Laboratory standard atmosphere and calculated using a ray-tracing model for 440 nm, considering multiple scattering in spherical atmosphere. The resulting AMF values at 90° SZA are 18.76, 17.96, 18.17, and 18.19 in March, July, September, and December, respectively (M. Van Roozendael, personal communication, 2003). The SAOZ at OHP uses a midlatitude AMF, calculated by the RTM for 470 nm from the average summer composite evening profiles, measured by the POAM satellite and SAOZ balloon sondes [*Sarkissian et al.*, 1995a]. The resulting AMF value at 90° SZA is 15.65. Generally, the zenith sky UV-visible observations allow measurements even in cloudy conditions, because the stratospheric light path at twilight is large compared to the tropospheric one (roughly 20 times), and multiple scattering in the clouds affects measurements only slightly [*Sarkissian et al.*, 1995b]. However, the studies of NO_2 AMF sensitivity to the tropospheric clouds demonstrate an increase of ~5% at 90° SZA, relative to clear sky RTM calculations [*Pfeilsticker et al.*, 1998; *Bassford et al.*, 2001].

[7] According to conclusions from NDACC intercomparison campaigns [*Vaughan et al.*, 1997; *Roscoe et al.*, 1999; *Vandaele et al.*, 2005], the agreement between NDACC-certified instrument measurements of NO_2 slant column amounts falls within the 5% to 10% range, when common spectral ranges and analysis parameters are imposed. However, the accuracy of NO_2 vertical column retrievals is limited by several uncertainties [*Van Roozendael et al.*, 1994], which contribute to the full error as follows: measurement random error (~4%), the error associated with

NO_2 absorption cross section and its temperature dependence (~15%), the error, associated with the determination of residual amount of NO_2 in the reference spectrum (~10%), and the uncertainty on the AMF calculation (~10%). The total error budget of the ground-based visible NO_2 measurements is a precision of ~11% and an accuracy of ~21%. Assuming the average NO_2 vertical column at midlatitudes is $\sim 3 \times 10^{15}$ molecules/cm^2, this estimate corresponds to $\sim 0.6 \times 10^{15}$ molecules/cm^2 absolute accuracy.

3. Satellite Aura OMI Data on Total NO_2

[8] OMI combines the advantages of its predecessors (GOME and SCIAMACHY), by measuring the complete spectrum in the UV-visible wavelength range (270–500 nm) with a very high spatial resolution (13×24 km^2). It achieves daily global coverage with a 2600 km wide swath. OMI uses 2-D detectors for simultaneous spatial and spectral registration (0.4–0.6 nm spectral resolution). The DOAS technique is applied in the visible to derive the NO_2 vertical column density (VCD).

[9] The operational OMI algorithm improves the accuracy of the NO_2 VCD retrieval (compared to GOME and SCIAMACHY) by discriminating between two components of the column density: an unpolluted component, which includes stratospheric and free tropospheric NO_2, and a polluted component, containing boundary layer NO_2 [*Boersma et al.*, 2002; *Bucsela et al.*, 2006]. The unpolluted component is identified through spatial filtering of the geographic NO_2 field. Small-scale geographical variation of NO_2 is taken to indicate tropospheric NO_2 pollution. In that case, a more appropriate AMF is used to compute more accurate column NO_2 and tropospheric NO_2 concentrations. The AMF is calculated using specific assumed NO_2 profiles for unpolluted (stratospheric and small amount of upper tropospheric) and polluted (lower tropospheric) columns. The amount of tropospheric NO_2 is calculated from these column amounts and the assumed profile shapes.

[10] The DOAS fitting algorithm is applied in the spectral range 405–465 nm to the logarithmic ratio of the measured earthshine radiance spectrum to a solar irradiance spectrum. A much wider fit window (compared to 425–450 nm window, used by GOME and SCIAMACHY) compensates for OMI's lower signal-to-noise ratio in this wavelength region [*Boersma et al.*, 2002]. The functions fitted to the spectral ratio are trace gas cross sections of NO_2 [*Vandaele et al.*, 1998] and O_3 [*Burrows et al.*, 1999b], a reference Ring spectrum [*Chance and Spurr*, 1997] and the coefficients of a polynomial function to model the spectrally slowly varying components of scattering by clouds and aerosols and reflection by the Earth's surface. The nominal fitting temperature of NO_2 absorption cross section is 220 K [*Boersma et al.*, 2002]. Resulting NO_2 slant column densities (SCD) are then converted to VCDs by means of the AMF, which depends upon a number of parameters including viewing geometry, surface albedo and the shape of the NO_2 vertical profile. For each location, the algorithm uses a single mean unpolluted profile derived from a stratospheric model and a geographically gridded set of annual mean polluted profiles obtained from a tropospheric model. An initial estimate of the NO_2 VCD is obtained by dividing the SCD by an unpolluted AMF, which is then geographically gridded using the data acquired within ±12 h from the target orbit. Areas shown by the model to contain climatologically high tropospheric NO_2 amounts are then masked, and the remaining regions are smoothed in latitude bands to construct a global stratospheric field. The smoothing algorithm employs a boxcar smoothing over a 10° latitude band, followed by a zonal planetary wave smoothing. Where the initial VCD exceeds the estimated stratospheric NO_2, the presence of tropospheric NO_2 is inferred, and the VCD is recalculated using an AMF computed from an assumed tropospheric NO_2 profile [*Bucsela et al.*, 2006].

[11] The accuracy of the OMI algorithm for NO_2 vertical columns splits into errors of the slant column retrieval and of the AMF calculation [*Boersma et al.*, 2002]. The slant column errors come from the uncertainty of the NO_2 absorpion cross sections and their temperature dependence, spectral calibration and stability, and measurement noise. AMF errors arise from incorrect day-to-day assumptions regarding the NO_2 profile shape, surface albedo, cloud parameters, and aerosol effects. The estimated accuracy of the OMI NO_2 vertical column under clear sky conditions is ~5% ($\sim 0.2 \times 10^{15}$ molecules/cm^2) and ~20% ($\sim 0.8 \times 10^{15}$ molecules/cm^2) in unpolluted and polluted cases, respectively. In the presence of pollution and clouds, the NO_2 vertical column error can be as large as 50%. The relative errors in the tropospheric NO_2 column estimate are ~30% and ~60% under clear and cloudy conditions, respectively [*Boersma et al.*, 2002].

4. Ground-Based Validation of Satellite NO_2 Data: Comparison Methodology

[12] Satellite total NO_2 vertical columns have been previously compared to ground-based UV-visible measurements at Zvenigorod (Moscow region) and St. Petersburg in Russia. The latter measurements are similar to those carried out at Issyk-Kul station. Correlative data of GOME and SCIAMACHY operational NO_2 products were analyzed. However, these observations were found to be affected by high tropospheric pollution in the region of Moscow [*Timofeev et al.*, 2000] and St. Petersburg [*Poberovsky et al.*, 2007]. The Issyk-Kul station is located in a remote plateau of the Tien Shan mountains in northeast Kyrgyzstan, which is presumed to be a pollution-free area. Operational GOME measurements of NO_2 VCDs (GOME Data Processor 3 (GDP 3)) have been compared with collocated ground-based observations at Issyk-Kul for the period of 1996–2002 [*Ionov et al.*, 2006a]. According to that study, the GOME data are reasonably close to the corresponding ground-based sunrise observations, within $\pm 0.7 \times 10^{15}$ molecules/cm^2, while the agreement with ground-based sunset measurements is not as close, about $\pm 2.2 \times 10^{15}$ molecules/cm^2 (RMS). Some seasonal variation in the absolute difference between GOME and ground-based measurements is present. A number of effects have been proposed to explain and remove that discrepancy, including the use of similar molecular absorption cross sections and seasonal NO_2 AMFs in the processing of Issyk-Kul ground-based data. Also, simulated NO_x photochemistry has been used to adjust sunrise ground-based measurements to the time of GOME overpass, near noon. The GOME data were still found to overestimate twilight

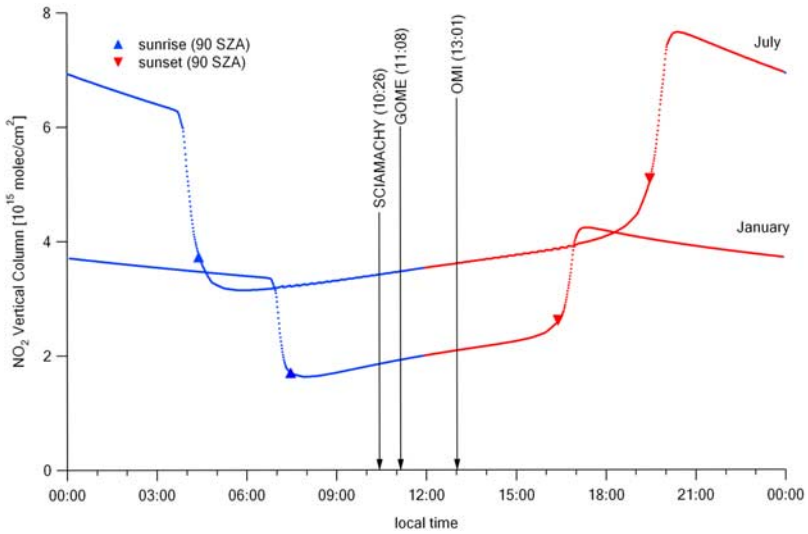

Figure 1. Diurnal cycle of NO_2 vertical column at Issyk-Kul, simulated for January and July. The time of 90° SZA (sunrise and sunset) is shown by markers. The average time of satellite overpass for ERS-2 GOME, Envisat SCIAMACHY, and Aura OMI over Issyk-Kul is indicated by arrows.

ground-based measurements at Issyk-Kul, adjusted to noon, by $(0.6 \pm 0.5) \times 10^{15}$ molecules/cm^2. This may be an indication of some additional source of disagreement, e.g., incorrect treatment of tropospheric NO_2 content in the region of ground-based measurements. Nonetheless, these results are consistent with other GOME validation efforts by NDACC and SAOZ ground-based networks [*Lambert*, 2002; *Lambert and Balis*, 2004].

[13] One difficulty that hampers direct comparison of satellite NO_2 columns measured at nadir and correlative data of ground-based twilight measurements is the diurnal cycle of NO_2, which is season dependent. Atmospheric NO_2 is known to exhibit a strong photochemical cycle throughout the day because of its daytime photolysis into NO and nighttime conversion into N_2O_5, which photolyzes back into NO_2 and NO_3 after sunrise. The typical daily cycle of NO_2 at low and middle latitudes starts with a rapid drop a little after sunrise, followed by a quasi-linear slow increase during the day, then a fast increase at sunset, and finally a slow decrease during night. The diurnal cycle has been simulated with a photochemical box model derived from the SLIMCAT 3-D chemical-transport model [*Denis et al.*, 2005]. It includes 98 chemical and 39 photochemical reactions, including heterogeneous chemistry on liquid and solid particles. Calculations are made at 17 altitude levels with a time step of 1 min. The NO_2 total column is obtained by integrating the profile assuming a constant density in each layer. An example of such a calculation, carried out for the location of Issyk-Kul in January and July, is presented in Figure 1 (the calculation for OHP is quite similar, as it is almost the same latitude). As is also observed in the measurements, the noontime column is relatively close to its sunrise value. However, the ratio between these two changes with season. The noontime column is larger than that of sunrise in the winter and smaller in the summer. In addition, a difference also appears between the satellite measurement times of ~10:30 (SCIAMACHY), ~11:10 (GOME) and ~13:00 (OMI), so the exact satellite overpass time needs to be taken into account. The daily variation of the ratio NO_2(sunrise)/NO_2 has been calculated for each of the 12 months at the location of Issyk-Kul. As we take an average of ground-based measurements between 85 and 92 SZA during twilight, the NO_2 column at 88.5° SZA is considered to be the sunrise reference. All satellite measurements can be normalized to sunrise values using these ratios. (This is different from what was used before by *Ionov et al.* [2006a] for the validation of GOME NO_2 column data at Issyk-Kul, when the ground-based sunrise measurements were adjusted to satellite overpass.) This approach proved to be useful for the comparison of satellite NO_2 data with ground-based SAOZ instruments [*Ionov et al.*, 2006b; *Ionov et al.*, 2007]. We have also tested it for the comparison of GOME NO_2 data with our ground-based measurements at Issyk-Kul in 2001–2003. Unfortunately, there are no GOME data to compare since June 2003 because of the failure of the on-board recorder. Time series of NO_2 VCD ground-based measurements (sunrise, sunset) are compared in Figure 2 (top) with GOME (GDP 4) data in 2001–2003. The average difference between ground-based (GB) and satellite (normalized to sunrise) data ("GOME-GB") is $(0.31 \pm 0.47) \times 10^{15}$ molecules/cm^2, ($R = 0.86$). A similar comparison, but for the measurements of SAOZ instrument at OHP with GOME data in 2004–2006, provides an estimate of average difference GOME-GB as $(0.01 \pm 0.73) \times 10^{15}$ molecules/cm^2 ($R = 0.61$). The time series of NO_2 VCD measurements by SAOZ and collocated GOME (GDP 4) data in 2004–2006 are presented in Figure 2 (bottom). To use both sunrise and sunset ground-based observations for the OMI validation, we apply our simulated NO_2 ratios to adjust both the satellite and ground-based twilight measurements to local noon. The average of the adjusted ground-based sunrise and sunset measurements is then compared with the OMI measured values.

[14] For OMI validation we used the ground-based twilight NO_2 observations at Issyk-Kul and OHP, collected for the period from January 2004 to December 2006. The total

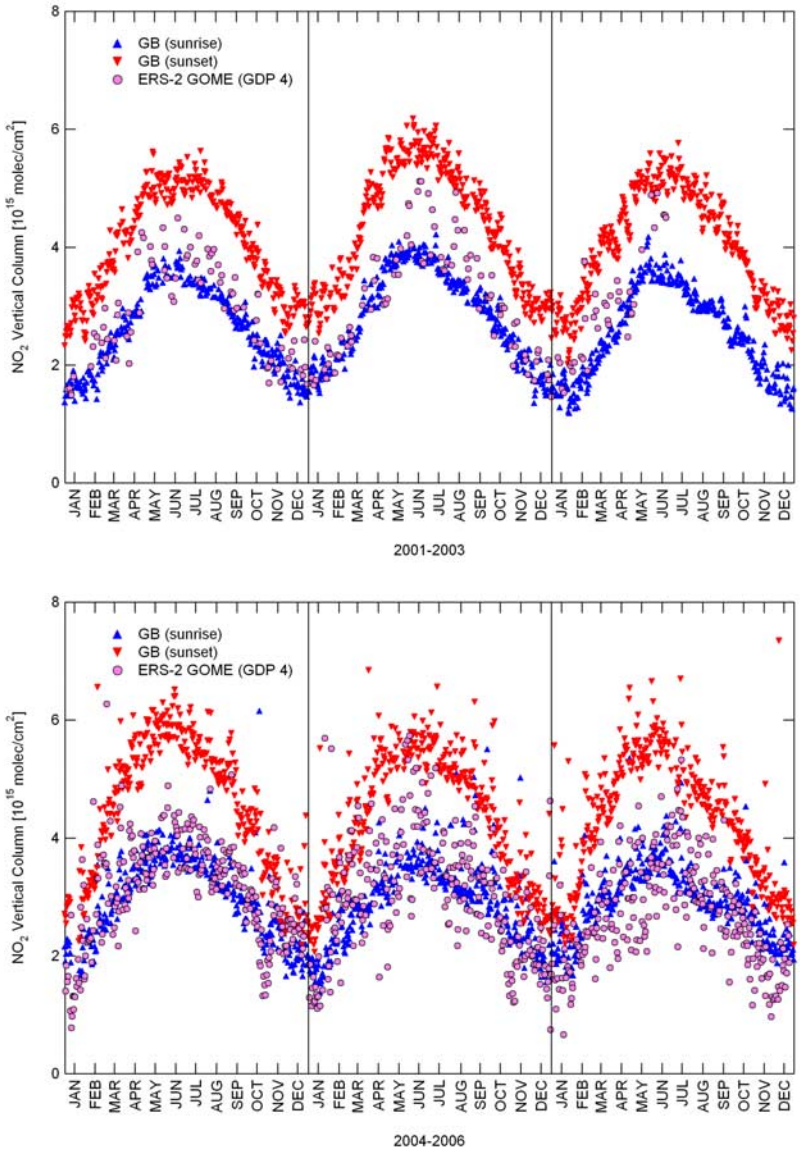

Figure 2. Comparison of GB measurements at (top) Issyk-Kul in 2001–2003 and (bottom) OHP in 2004–2006 with collocated NO_2 vertical column data by ERS-2 GOME (GDP 4.0), normalized to sunrise (SZA $\sim$ 88.5°).

number of data available for comparison amounts to $\sim$1000 sunrise/sunset values at each of the ground sites. For these days the corresponding NO_2 vertical columns have been extracted from the OMI NO_2 station overpass files provided by the Aura Validation Data Center (available at http://avdc.gsfc.nasa.gov). Whenever several OMI overpasses occur during the day, the one that is closer to the ground-based station was selected. Overall, about 1500 pairs of collocated satellite and ground-based measurements were compared ($\sim$700 at Issyk-Kul, and $\sim$800 at OHP). The distance of OMI ground pixel centers from the ground-based instrument location was less than 40 km (average $\sim$10 km). The average cloud fraction of selected OMI pixels was 0.25, indicating clear sky conditions for most observations ($\sim$70% of measurements with cloud fraction < 0.25). The solar zenith angle varied between 20° in summer and 70° in winter (50° on average). The average NO_2 column, measured by the ground-based instrument at Issyk-Kul, was 2.55×10^{15} molecules/cm^2 at sunrise and 3.96×10^{15} molecules/cm^2 at sunset; the average OMI value was 3.21×10^{15} molecules/cm^2. The ground-based SAOZ measurements at OHP provide somewhat higher NO_2 columns: the average is 2.94×10^{15} molecules/cm^2 at sunrise and 4.39×10^{15} molecules/cm^2 at sunset; the average OMI value was 4.91×10^{15} molecules/cm^2. Although at the same latitude, the ground-based data sets at Issyk-Kul and OHP show prominent differences: the time series of NO_2 vertical columns at OHP are noisier, and the sunrise/sunset ratios larger in summer and lower in winter, compared to Issyk-Kul data. This may be attributed to the use of seasonal AMFs at Issyk-Kul, compared to fixed AMFs for OHP, and to the effects of tropospheric pollution,

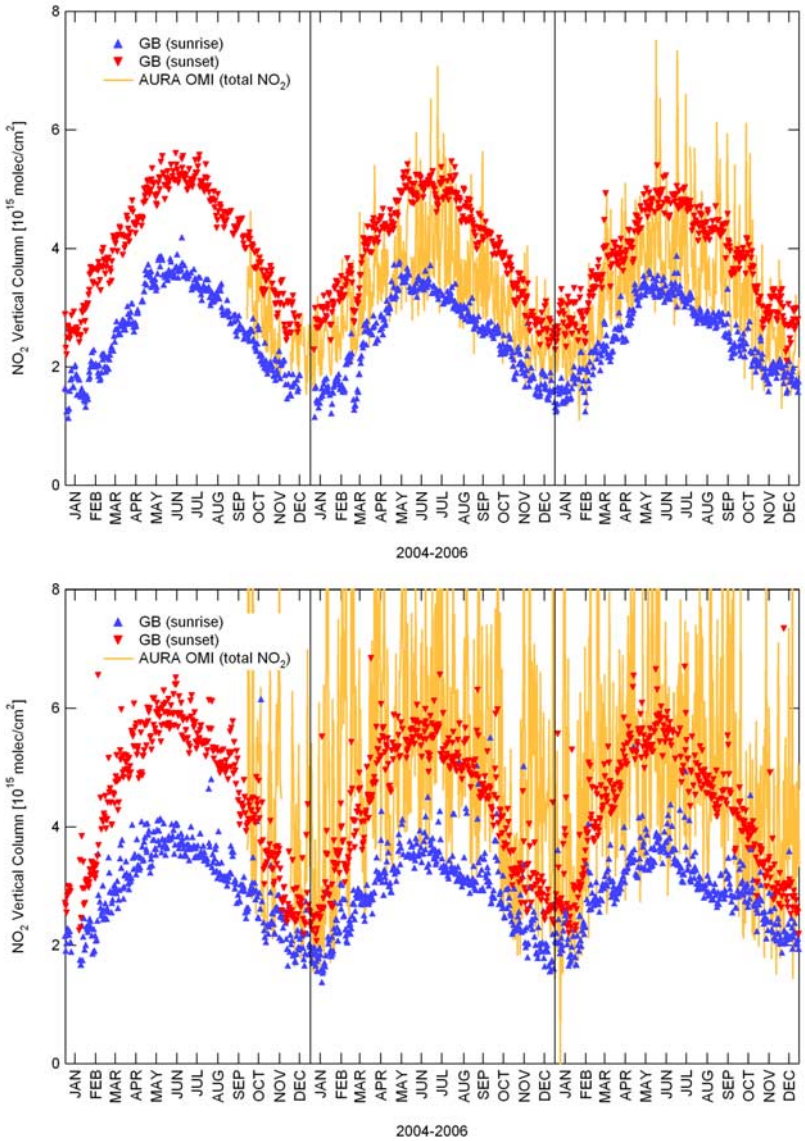

Figure 3. Comparison of Aura OMI NO_2 vertical column data with collocated GB measurements at (top) Issyk-Kul and (bottom) OHP in 2004–2006.

which we assume more likely to occur at OHP than at the remote Issyk-Kul site. This is discussed in section 5.

5. Comparison of OMI NO_2 With Ground-Based Measurements: Results and Analysis

[15] The time series of collocated OMI NO_2 VCDs and ground-based NO_2 measurements at Issyk-Kul and OHP for 2004–2006 are presented in Figure 3. Although both data sets (satellite and ground-based) reproduce the known seasonal variation of NO_2, with maximum values in summer and minimum in winter, OMI VCD data look rather noisy compared to the ground-based measurements, and displays very high day-to-day NO_2 variation (especially at OHP). This may come from tropospheric NO_2 detected by OMI, but not observed in the ground-based measurements, the zenith sky observation mode at twilight being little sensitive to tropospheric NO_2. Therefore it is more appropriate to compare our ground-based measurements with the stratospheric part of OMI NO_2 VCD data. There is no such data field of the OMI NO_2 data product, OMNO2, in the overpass files, but one can obtain it by taking the difference between total (NO_2) and tropospheric ("NO_{2Trop}") NO_2 columns [*Celarier et al.*, 2006]. The resulting estimate of the stratospheric NO_2 column, compared with correlative Issyk-Kul and OHP measurements in 2004–2006, is presented in Figure 4. The stratospheric part of OMNO2 data over Issyk-Kul is rather smooth, compared to total VCD data, and reasonably close to ground-based measurements at sunrise, as expected from NO_2 diurnal cycle simulations (see Figure 4 (top)). However, it looks more noisy at OHP and systematically lower than SAOZ sunrise measurements (see Figure 4 (bottom)). The absolute difference between ground-based NO_2 data and OMI stratospheric columns, adjusted to local noon, is plotted in Figure 5, as a function of month. As is seen in the plot, the satellite and ground-based data over Issyk-Kul agree within ($\sim$0.26 ± 0.28) × 10^{15} molecules/cm^2 ("OMI-GB"), with a correlation coef-

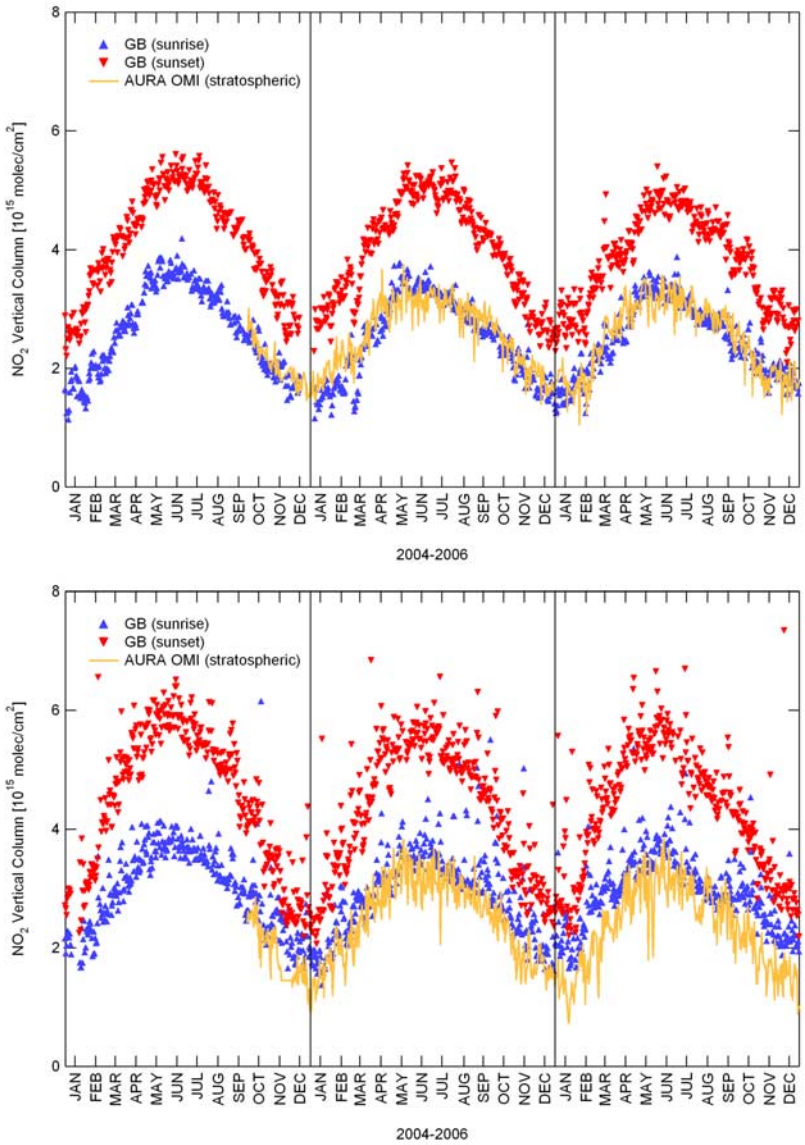

Figure 4. Comparison of GB measurements at (top) Issyk-Kul and (bottom) OHP with collocated NO_2 data by Aura OMI (stratospheric vertical column) in 2004–2006.

ficient of 0.87. This kind of agreement is somewhat better than that achieved in similar comparisons between Issyk-Kul measurements and GOME data in 1996–2002 (GDP 3) and 2001–2003 (GDP 4): $(+0.61 \pm 0.53) \times 10^{15}$ and $(+0.31 \pm 0.47) \times 10^{15}$ molecules/cm^2 (GOME-GB), respectively. The correlation coefficient is 0.73 in comparison with GDP3, and 0.86 with GDP4. The SAOZ observations at OHP agree with stratospheric OMNO2 data within $(\sim 0.71 \pm 0.58) \times 10^{15}$ molecules/cm^2 (OMI-GB), with a correlation coefficient of 0.62. In addition, there is a clear seasonal dependence of OMI-GB absolute difference at OHP, larger in winter, smaller in summer.

[16] Remaining systematic differences between OMI and ground-based stratospheric NO_2 columns may be attributed to the estimation of the tropospheric NO_2 column, which has different impact on the ground-based measurements and observations from the space. The time series of the relevant data field (NO_{2Trop}) from the OMNO2 overpass file over Issyk-Kul and OHP are presented in Figure 6. At first glance, the episodes of anthropogenic pollution are surprisingly intense and frequent in the remote and mountainous area of Issyk-Kul lake. However, satellite global mapping of NO_2 tropospheric columns reveals a number of NO_x sources near Issyk-Kul station. Thus, we have computed a map of the annual tropospheric NO_2 in the region of Kyrgyzstan on the basis of the global data of SCIAMACHY monthly mean tropospheric NO_2 in 2003–2006, available at the Tropospheric Emission Monitoring Internet Service (TEMIS, http://www.temis.nl) [*Boersma et al.*, 2004], and presented in Figure 7 (top). Locations of the main anthropogenic pollution sources, as revealed from the map, are presented in Table 1, with an estimation of the annual tropospheric NO_2 column. According to the OMI overpass OMNO2 data set, the average value of the tropospheric NO_2 column is 0.72×10^{15} molecules/cm^2. That is even less than the estimation from SCIAMACHY tropospheric NO_2 mapping

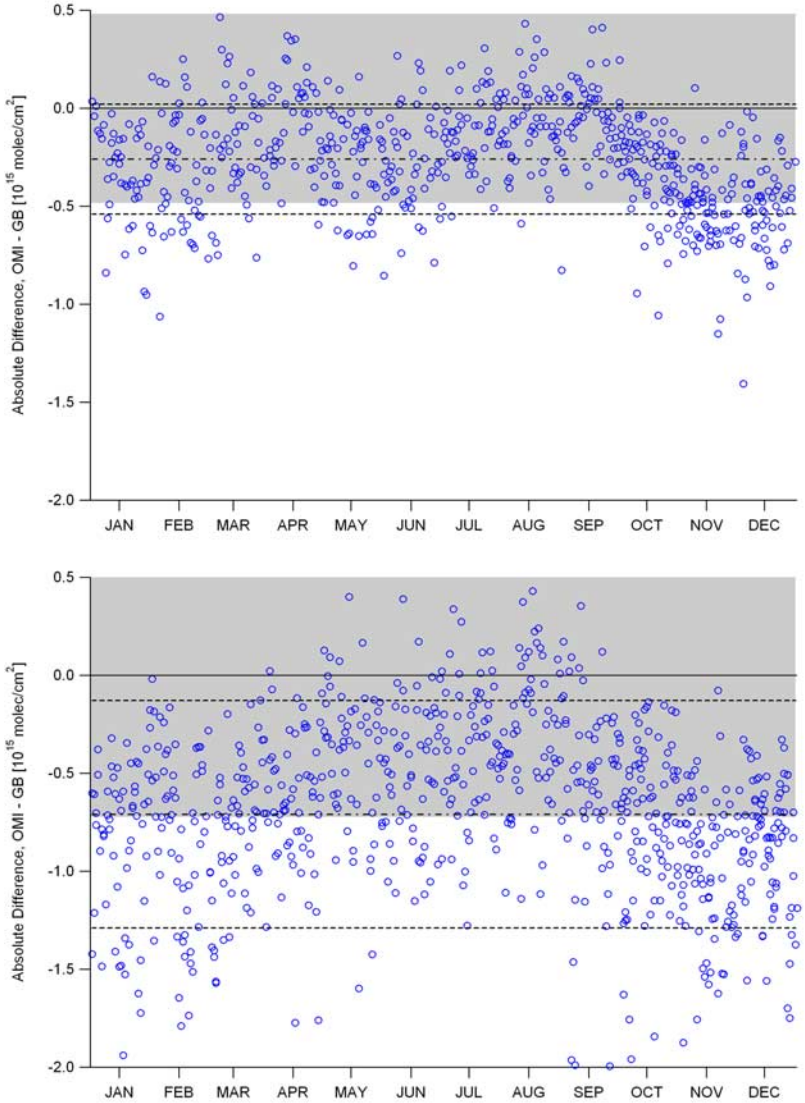

Figure 5. Absolute difference in NO_2 vertical column between Aura OMI (stratospheric) and GB measurements at (top) Issyk-Kul and (bottom) OHP, plotted as a function of month. The average difference and standard deviation are indicated with dotted-dashed and dashed lines, respectively. The grey area indicates expected RMS difference OMI-GB.

at Issyk-Kul, $\sim 1.19 \times 10^{15}$ molecules/cm^2 (Figure 7 (top), Table 1). The most intense NO_x source near the Issyk-Kul station is the city of Alma-Ata, Kazakhstan, ~60 km to the north (NO_2 tropospheric column $\sim 3.96 \times 10^{15}$ molecules/cm^2). There are two more distant sources, which may also affect Issyk-Kul observations in case of extended air transport: the city of Tashkent, Uzbekistan (~700 km to the southwest, $\sim 5.29 \times 10^{15}$ molecules/cm^2), and Urumqi, China (~900 km to the east, $\sim 10.47 \times 10^{15}$ molecules/cm^2). By considering only the OMI stratospheric NO_2 column, we may lose a portion of tropospheric NO_2 that may still be detectable with the ground-based instrument. Tropospheric pollution is much higher over OHP than over Issyk-Kul, according to the OMI overpass OMNO2 data set, with an average tropospheric NO_2 column of 2.56×10^{15} molecules/cm^2. The SCIAMACHY data provides an estimate of the mean annual tropospheric NO_2 column at OHP as 3.14×10^{15} molecules/cm^2 (Figure 7 (bottom), Table 1). As is seen from the map, there are numerous NO_x pollution sources near OHP station, including the cities of Marseille and Toulon (France), ~60 km to the south (NO_2 tropospheric column up to 8.80×10^{15} molecules/cm^2) and the Po river valley in northern Italy, ~600 km to the northeast (NO_2 tropospheric column up to 20.26×10^{15} molecules/cm^2).

[17] In addition to proper treatment of the tropospheric contribution to satellite and ground-based NO_2 VCD measurements, there are a number of uncertainties (as mentioned in section 3), that may also introduce disagreements: NO_2 absorption cross sections and their temperature dependence, AMF changes associated with seasonal variations of NO_2 profile shape and different effects linked to the presence of clouds in the ground-based and/or satellite field of view. However, both ground-based and OMI retrievals use the same NO_2 absorption cross sections, [*Vandaele et al.*, 1998] and fitting temperature, 220 K. The SAOZ measurements at OHP are processed with a fixed AMF, as are the OMI stratospheric

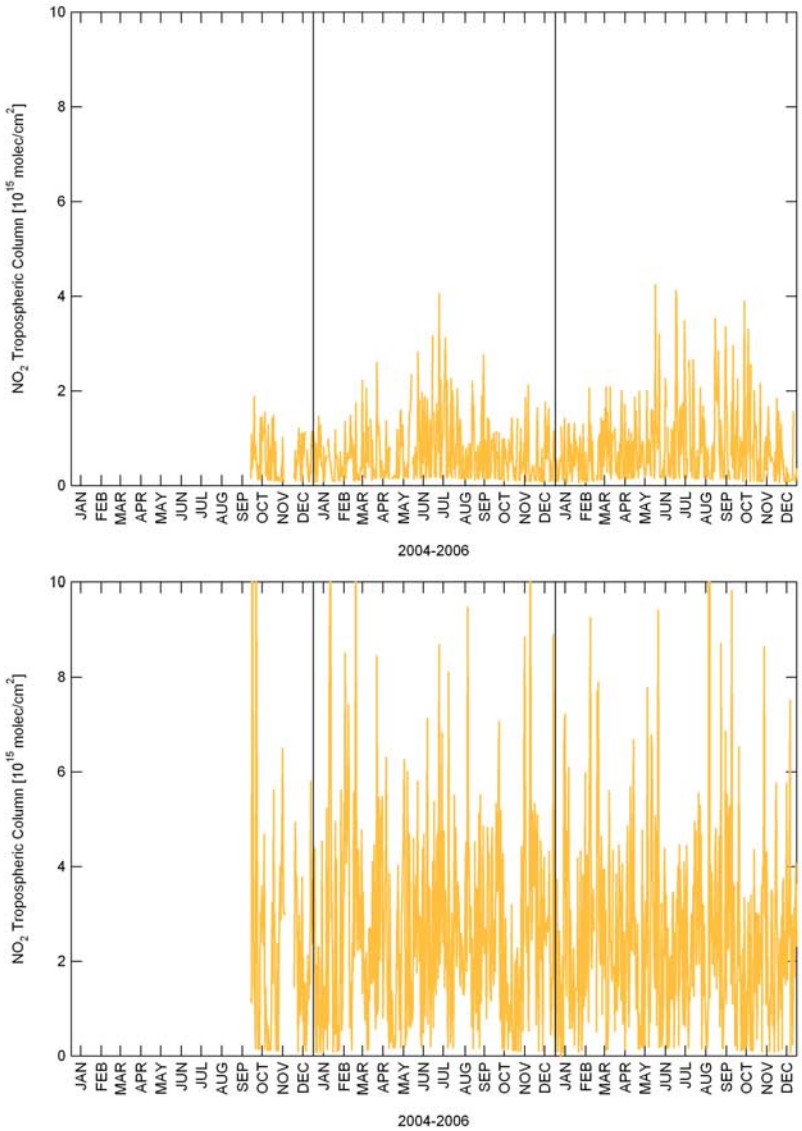

Figure 6. Time series of tropospheric NO_2 vertical column over (top) Issyk-Kul and (bottom) OHP, as measured by Aura OMI in 2004–2006.

NO_2 columns. This may introduce a systematic bias between OMI and SAOZ at OHP, but not the seasonal difference we observe. Clouds have a small effect on the ground-based AMF, and a larger effect on the satellite AMF. Clouds obscure NO_2 below them and increase the sensitivity to NO_2 above clouds because of the relatively high cloud albedo [*Boersma et al.*, 2002]. However, ~70% of OMI NO_2 data selected for comparison have a cloud fraction less than 0.25, which is almost cloud free. The level of agreement depends also on the accuracy of the photochemical model correction for the NO_2 diurnal cycle, which we apply to the OMI data. The error arising from the uncertainties in model initialization data (ozone, temperature, aerosol distribution and the main reaction and photolysis rates) may be as large as 8–14% [*Bracher et al.*, 2005].

[18] To estimate the potential difference between the twilight ground-based and daytime satellite NO_2 vertical column measurements, the results of sunrise and sunset ground-based observations, both adjusted to local noon, were compared to each other. Resulting RMS difference is 0.29×10^{15} molecules/cm^2 (~12%) and 0.72×10^{15} molecules/cm^2 (~22%) for the measurements at Issyk-Kul and OHP, respectively. According to the ground-based measurement error budget (see section 2.3), this difference includes the measurement random error, the uncertainty of the AMF calculation, and the error due to mismatch of air masses, in addition to the uncertainty of the photochemical model calculation. The difference is higher at OHP than at Issyk-Kul, as the tropospheric pollution is more frequent and intense near OHP. Obviously, the systematic errors related to NO_2 absorption cross section and residual NO_2 amount in the reference spectrum, does not contribute to these differences. Considering the same NO_2 absorption cross section used by OMI, and same photochemical model used to adjust its measurements to local noon, potential OMI-GB RMS difference may be characterized by these

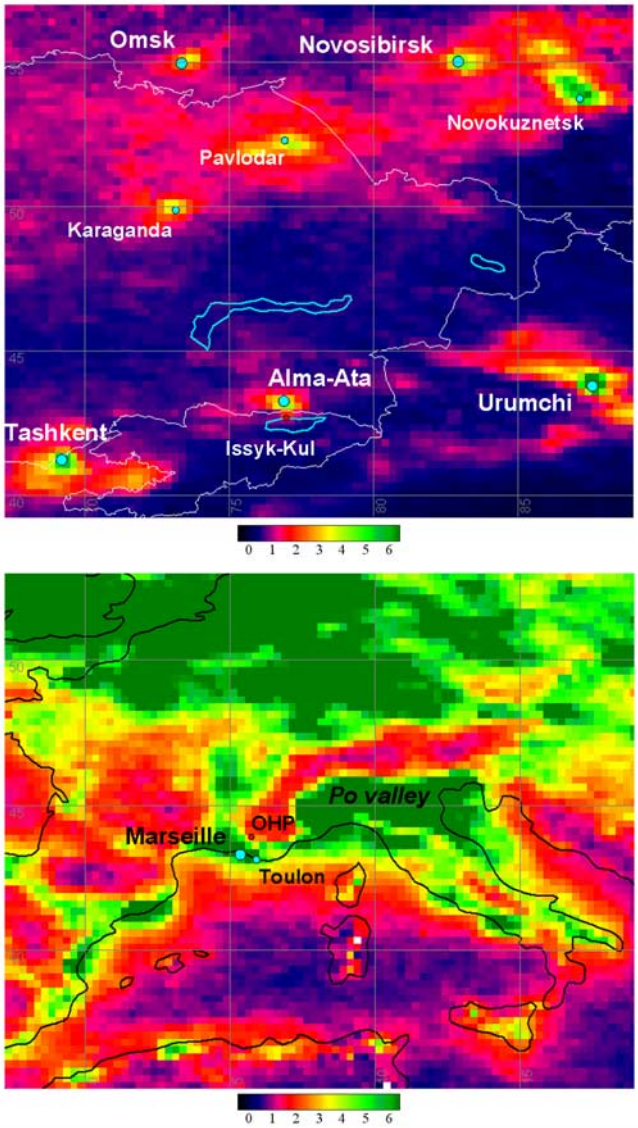

Figure 7. Annual maps of tropospheric NO_2 vertical column over (top) central Asia and (bottom) central Europe, produced from the global data of Envisat SCIAMACHY monthly mean tropospheric NO_2 in 2003–2006, given in 10^{15} molecules/cm^2 (available at http://www.temis.nl).

estimates (increased by the error of residual NO_2 in the ground-based reference spectrum, ~10%): ~16% at Issyk-Kul and ~24% at OHP. The resulting comparison error bars are presented in Figure 5 (grey area).

[19] Basically, the total error of remote sensing is a sum of three components [*Rodgers*, 2000]: the smoothing error, the measurement error and the forward model error. The last two components have been discussed above. The smoothing error may also be important, especially in the intercomparison of different remote sensing instruments [*Rodgers and Connor*, 2003]. To account for smoothing error, the averaging kernel concept, providing the relation between the retrieved quantities and the true trace gas spatial distribution, is by now well established in remote sensing (also for DOAS total column retrievals [*Eskes and Boersma*, 2003]). The difference between the averaging kernels of ground-based UV-visible and satellite OMI NO_2 vertical column measurements may introduce certain disagreements in their comparison, especially in the presence of tropospheric pollution. The problem is not only the difference in vertical sensitivity, but also the horizontal smoothing; thus, for the ground-based zenith sky twilight measurements the horizontal projection of the probed air mass is estimated to extend from nearby the station to the distance of few hundred kilometers toward the sun [*Lambert and Balis*, 2004]. Although detailed investigation of satellite and ground-based retrieval averaging kernels is outside the scope of the present study, additional tests were run to analyze the influence of some intercomparison parameters on the agreement between the two data sets. Statistical characteristics of OMI-GB differences for the subsets of OMI data, selected by the pixel distance, cloud fraction, and cross track position, are presented in Table 2. A threshold of 10 km was used for the distance of OMI pixel from the ground-based instrument. We selected OMI pixels with cloud fraction <0.25. The OMI cross track position was selected either in the middle of the scan (cross track pixel numbers 15–35), or at the edges, to account for the OMI spatial resolution change (from ~13 × 24 km^2 in the nadir to ~78 × 128 km^2 at the edges) and known OMI cross-track anomaly [*Celarier et al.*, 2006]. According to the estimates provided in Table 2, the difference between OMI stratospheric NO_2 column and correlative ground-based measurements at Issyk-Kul does not depend much on any of these selection criteria. However, this is not the case for the measurements at OHP station. For example, selecting OMI pixels more than 10 km distance from OHP increases the scatter (standard deviation) from ± 0.43

Table 1. Anthropogenic NO_x Pollution Sources Near Issyk-Kul and OHP Stations[a]

Ground-Based Station	Antropogenic Pollution Source: Location Name	Distance From the Station, km	Direction From the Station	Tropospheric NO_2, 10^{15} molecules/cm^2
Issyk-Kul	-	-	-	1.19
Issyk-Kul	Alma-Ata	60	north	3.96
Issyk-Kul	Tashkent	700	southwest	5.29
Issyk-Kul	Urumchi	900	east	10.47
OHP	-	-	-	3.14
OHP	Marseille, Toulon	60	south	8.80
OHP	Po Valley	600	northeast	20.26

[a]Revealed from the annual tropospheric NO_2 mapping of SCIAMACHY monthly mean tropospheric NO_2 data in 2003–2006 (available at http://www.temis.nl).

Table 2. Statistical Difference Between Ground-Based UV-Visible and Satellite OMI Stratospheric NO_2 Column Measurements at Issyk-Kul and OHP in 2004–2006[a]

	OMI Pixel Distance		OMI Pixel Cloud Fraction		OMI Pixel Cross-Track Number	
Station	<10 km	>10 km	<0.25	>0.25	15–35	<15, >35
Issyk-Kul	−0.27 ± 0.28	−0.25 ± 0.29	−0.26 ± 0.29	−0.28 ± 0.28	−0.30 ± 0.27	−0.26 ± 0.28
	0.88	0.86	0.87	0.88	0.89	0.87
OHP	−0.71 ± 0.43	−0.70 ± 0.76	−0.63 ± 0.46	−0.88 ± 0.76	−0.70 ± 0.49	−0.71 ± 0.60
	0.78	0.43	0.75	0.44	0.71	0.61

[a]With respect to OMI pixel distance, cloud fraction, and cross-track pixel number (the average OMI-GB difference ± standard deviation, given in 10^{15} molecules/cm^2, and correlation coefficient).

to ± 0.76 × 10^{15} molecules/cm^2, and decreases the correlation with ground-based measurements from 0.78 to 0.43. A similar effect is observed when going from the middle of the OMI cross scan to the edges – the standard deviation of OMI-GB difference is increased from ± 0.49 to ± 0.60 × 10^{15} molecules/cm^2, and the correlation decreased from 0.71 to 0.61. The major change in the level of agreement between OMI and OHP measurements is obtained when the cloud fraction selection criteria are applied. Both the average OMI-GB difference and its standard deviation increase for OMI pixels with cloud fraction larger than 0.25, from −0.63 ± 0.46 to −0.88 ± 0.76 × 10^{15} molecules/cm^2; the correlation is reduced from 0.75 to 0.44.

[20] Considering the fact that both Issyk-Kul and OHP instruments are at the same latitude, applying a similar measurement technique and comparison methodology, such a sensitivity of the OMI-GB difference to pixel distance, spatial resolution, and cloud fraction is likely to indicate the influence of tropospheric pollution on the agreement between OMI data and ground-based measurements at OHP (in contrast to the similar comparison at Issyk-Kul). In the presence of tropospheric NO_2 pollution, comparison of OHP measurements with the data of more distant and larger OMI pixels is affected by a possible mismatch of air masses actually probed by correlative ground-based and satellite observations. Normally, the air mass may travel for hundred kilometers during the hours between daytime satellite and twilight ground-based observation. However, the most marked episodes of NO_x pollution, detectable from the ground and space, are likely to coincide with the thermal inversion and stable air mass. Further, the presence of clouds in OMI's field of view will hide a part of the NO_2 tropospheric column below the cloud cover, while the ground-based measurements will overestimate the NO_2 column because of the increase of light path by multiple scattering inside the cloud. The effects of tropospheric pollution on the processing of OMI NO_2 measurements are likely to be responsible for most of the difference we observe between the satellite and ground-based NO_2 data. An operational stratosphere-troposphere separation of satellite NO_2 measurements was first implemented with the OMI processing algorithm. Similar comparisons of ground-based NO_2 measurements with correlative satellite data from GOME and SCIAMACHY do not reveal such systematic differences as those observed here between the OMI data and SAOZ measurements at OHP [*Ionov et al.*, 2006b]. On the other hand, the measurements at seven more SAOZ stations in the tropics and polar regions were found to agree with OMI NO_2 data within −0.3 × 10^{15} molecules/cm^2 (OMI-GB), except Bauru, Brazil (22.4°S/49.0°W), which is also exposed to tropospheric pollution [*Ionov et al.*, 2006b].

[21] The zonal distribution of NO_2 vertical columns (total, stratospheric, and tropospheric) over a 0.25°-wide latitude belt centered at 43.25°N (the mean of the Issyk-Kul and OHP latitudes) is presented in Figure 8. The OMI total and stratospheric NO_2 columns were taken from OMNO2 Level2G daily gridded data, available at Goddard Earth Sciences Distributed Active Archive Center (GES DAAC, http://disc.sci.gsfc.nasa.gov). Average NO_2 total and tropospheric columns were computed from the OMI measurements within each 0.25° × 0.25° grid cell, and the stratospheric column was, as before, estimated as the difference between total and tropospheric columns. SCIAMACHY tropospheric NO_2 columns were calculated from the monthly mean tropospheric NO_2 mapping in 2003–2006, provided by TEMIS (http://www.temis.nl). Although not usable for the direct comparison with OMI daily NO_2 data, the annual tropospheric NO_2 columns from SCIAMACHY are a good global reference for the regions of permanent pollution. Thus, highly increased NO_2 total columns in the OMI daily data mostly correlate with high tropospheric NO_2 values of the annual SCIAMACHY data (e.g., over the known polluted regions of USA, Europe and Asia, see Figure 8). According to the plot, the OMI stratospheric NO_2 column is rather smooth over some parts of the globe, suggesting that it represents the zonal wave fit used in the OMI algorithm, rather than true values (see section 3). Thus, the daily stratospheric NO_2 column determined by OMI is unlikely slowly varying with longitude in the range of 10°W–70°E in March and September (Figure 8). Most of that midlatitude region belongs to the densely populated Europe (10°W–30°E), providing a considerable tropospheric pollution, indicated also by the annual tropospheric NO_2 from SCIAMACHY (Figure 8, gray values). Hence, a large polluted area around OHP station at 44°E is presumed to be masked out of the stratospheric field smoothing within the standard OMI processing [*Bucsela et al.*, 2006; *Celarier et al.*, 2006]. Since the true OMI measurements do not contribute to the resulting stratospheric NO_2 column in that region, such estimation is likely to be inaccurate over OHP. This is not the case for Issyk-Kul, because of the large area of relatively clean troposphere found to the east and west of the station.

6. Conclusions and Further Work

[22] Operational Aura OMI measurements of the NO_2 vertical column have been compared with collocated UV-Visible ground-based observations in midlatitudes, at

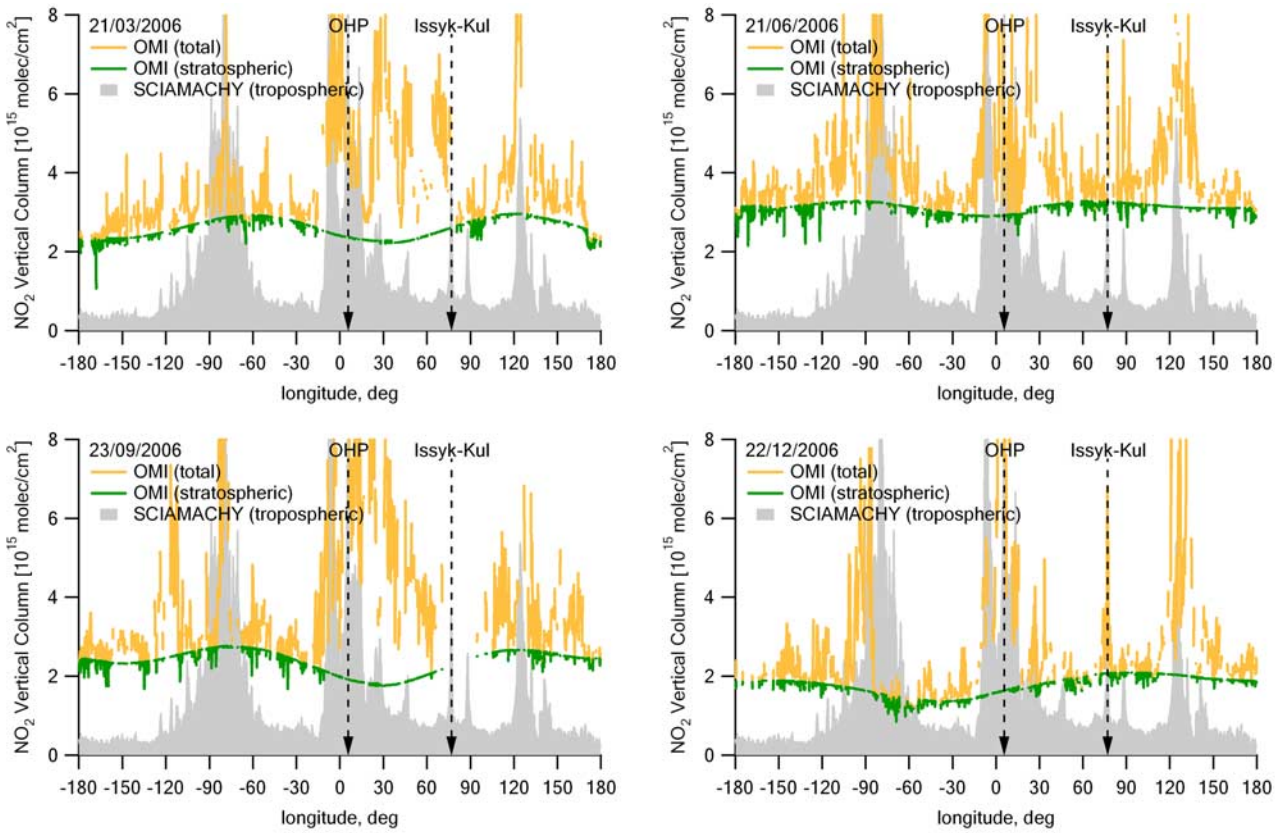

Figure 8. Longitudinal distribution of Aura OMI total and stratospheric NO_2 vertical column (Level2G) over a 0.25°-wide latitude belt at 43.25°N for the different seasons (spring, summer, autumn, and winter) of 2006. Grey values represent annual tropospheric NO_2 vertical column for the same latitude, calculated from the global data of Envisat SCIAMACHY monthly mean tropospheric NO_2 in 2003–2006 (available at http://www.temis.nl).

Issyk-Kul station in Kyrgyzstan and Observatoire de Haute-Provence in France for the period 2004–2006. Although located in remote mountainous sites, both stations were found to be exposed to local pollution sources. Considerable tropospheric pollution in the region of Issyk-Kul and OHP was detected by OMI, and also observed by SCIAMACHY. The annual tropospheric NO_2 column over Issyk-Kul is estimated to be 0.72×10^{15} molecules/cm^2 and 1.19×10^{15} molecules/cm^2, as measured by OMI and SCIAMACHY, respectively. At OHP, the annual tropospheric NO_2 column is estimated to be even much higher: 2.56×10^{15} molecules/cm^2 and 3.14×10^{15} molecules/cm^2, as measured by OMI and SCIAMACHY. Therefore, direct comparison between OMI and ground-based measurements of the NO_2 total column is impossible, as the ground-based twilight measurements are much less sensitive to tropospheric NO_2, than satellite nadir measurements. Consequently, the stratospheric NO_2 column was calculated as a difference between OMI total and tropospheric column [*Celarier et al.*, 2006], and compared with ground-based measurements at Issyk-Kul and OHP. All OMI data and ground-based measurements have been compensated for NO_2 diurnal photochemical change and normalized to local noon values using a photochemical box model. According to the comparison results, midlatitude OMI stratospheric NO_2 column data underestimates ground-based measurements by $(0.26 \pm 0.28) \times 10^{15}$ molecules/cm^2 and $(0.71 \pm 0.58) \times 10^{15}$ molecules/cm^2 at Issyk-Kul and OHP, respectively. These differences are at the limit of the comparison error derived from estimates of measurement absolute accuracy and photochemical model uncertainty: $\sim 0.5 \times 10^{15}$ molecules/cm^2 and $\sim 0.7 \times 10^{15}$ molecules/cm^2, for the measurements at Issyk-Kul and OHP, respectively. The present study shows better agreement, compared to similar validation of GOME data over Issyk-Kul in 1996–2003, but worse agreement, compared to validation of GOME data over OHP in 2004–2006 and SCIAMACHY in 2004–2005. The latter may be partly attributed to the difficulties of stratosphere-troposphere separation within the OMI processing algorithm in the presence of heavy NO_x pollution at OHP.

[23] For the accurate validation of satellite OMI NO_2 data, the effects of tropospheric pollution should be further studied in detail. The smoothing errors, arising from the difference in spatial sensitivity (both vertical and horizontal) of both ground-based and space-based remote sensing measurements, can be evaluated by means of the careful investigation of corresponding averaging kernels [*Rodgers and Connor*, 2003; *Eskes and Boersma*, 2003; *Lambert and Balis*, 2004]. Comparison of UV-visible ground-based measurements with the initial OMI NO_2 data (assuming a stratospheric AMF, and without stratospheric/tropospheric

separation) may be useful as well, as it will be more consistent with similar validation studies of GOME and SCIAMACHY satellite instruments.

[24] **Acknowledgments.** We acknowledge A. Elokhov and A. Gruzdev (Institute of Atmospheric Physics, Moscow) for the development of operational DOAS algorithm, software, and instrument interface installed at the Issyk-Kul ground-based station. We also thank H. K. Roscoe (British Antarctic Survey) for providing an operational software suite for the retrieval of NO_2 vertical profile, including chemical box model to calculate the NO_2 diurnal variation by M.P. Chipperfield (University of Leeds). The Dutch-Finnish built OMI is part of the NASA EOS Aura satellite payload. The OMI project is managed by NIVR and KNMI in the Netherlands. We thank the OMI International Science Team for the satellite data used in this study. OMI NO_2 data were obtained from the NASA Aura Validation Data Center (AVDC) and Goddard Earth Sciences (GES) Data and Information Services Center (DISC), home of the GES Distributed Active Archive Center (DAAC). This work was performed in the framework of the International ESA/KNMI/NIVR OMI "Announcement of Opportunity for Calibration and Validation of the Ozone Monitoring Instrument," providing early access to provisional OMI data sets and guidance to the public OMI data. SCIAMACHY tropospheric NO_2 data were obtained from the KNMI TEMIS website. GOME level 2 data was provided by ESA within "Announcement of Opportunity" project (ERS AO3–174). GOME data search and extraction was carried out with a software tool, developed by K. Bramstedt (University of Bremen). This work was partly supported by Russian Ministry of Education and Science (MK-5390.2006.5), International Science and Technology Center (ISTC Kr-763, Kr-1371), and the Administration of St. Petersburg (PD06–1.5–5).

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