Evaluation of stratospheric NO\textsubscript{2} retrieved from the Ozone Monitoring Instrument: Intercomparison, diurnal cycle, and trending

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[1] A 5+ year record of satellite measurements of nitrogen dioxide columns from the Ozone Monitoring Instrument (OMI) is evaluated to establish the quality of the OMI retrievals and to test our understanding of stratospheric NO\textsubscript{2}. The use of assimilation techniques to retrieve stratospheric vertical columns of NO\textsubscript{2} from OMI slant column observations is described in detail. Over remote areas the forecast model state is generally within 0.15 × 10\textsuperscript{15} molecules/cm\textsuperscript{2} of the analysis. Dutch OMI NO\textsubscript{2} (DOMINO) and Standard Product (SP) stratospheric NO\textsubscript{2} columns agree within 0.3 × 10\textsuperscript{15} molecules/cm\textsuperscript{2} (13\%) with independent, ground-based measurements. This is comparable to the level of consistency (15–20\%) among ground-based techniques. On average, DOMINO stratospheric NO\textsubscript{2} is higher than SP by 0.2 × 10\textsuperscript{15} molecules/cm\textsuperscript{2}, but larger differences occur on the synoptic scale. Overlapping OMI orbits poleward of 30° enabled us to extract information on the diurnal variation in stratospheric NO\textsubscript{2}. We find that in the Arctic, the daytime increase of NO\textsubscript{2} has a distinct seasonal dependence that peaks in spring and fall. Daytime increase rates inside the denoxified Arctic polar vortex are low, but we find high rates (>0.4 × 10\textsuperscript{15} molecules/cm\textsuperscript{2}/h) outside the vortex. A multilinear regression to the DOMINO record shows a distinct quasi-biennial oscillation (QBO) signal in stratospheric NO\textsubscript{2} columns over the tropics. The QBO’s amplitude is comparable to the annual cycle and stronger over the Southern Hemisphere than over the Northern Hemisphere. We infer near-identical trends from DOMINO observations (+0.4%/decade) as from ground-based instrumentation over Lauder (+0.6%/decade) in the 2004–2010 period.


1. Introduction

[2] Nitrogen dioxide (NO\textsubscript{2}) is an important trace gas in the atmosphere because of its role in the photochemistry of ozone in the stratosphere and in the troposphere. NO + NO\textsubscript{2} (NO\textsubscript{3}) in the stratosphere originates from the oxidation of N\textsubscript{2}O in the middle stratosphere. NO + NO\textsubscript{2} destroy ozone catalytically, but they can also suppress ozone depletion by converting reactive chlorine and hydrogen compounds into unreactive reservoirs such as ClONO\textsubscript{2} and HNO\textsubscript{3}. Monitoring of stratospheric NO\textsubscript{2} thus provides important support to monitoring of the ozone layer. Furthermore, outstanding questions exist about long-term changes in stratospheric NO\textsubscript{2} reported for instance from New Zealand [Liley et al., 2000] and northern Russia [Gruszdev, 2008]. In the troposphere, NO\textsubscript{2} is mainly produced by combustion, emission by soils, and lightning. Tropospheric NO\textsubscript{2} oxidizes rapidly, leading to the formation of ozone and aerosols. These secondary pollutants have highly uncertain effects on climate [Intergovernmental Panel on Climate Change, 2007], influence the oxidizing capacity of the troposphere, and affect human health. Global mapping of tropospheric NO\textsubscript{2} concentrations provides important constraints on the temporal behavior of NO\textsubscript{2} emissions.

[3] Satellite remote sensing is used for measuring stratospheric as well as tropospheric NO\textsubscript{2} amounts. Stratospheric NO\textsubscript{2} has been measured by a number of satellites since the 1980s, e.g., SME (Solar Mesosphere Explorer) [Mount et al., 1984], which first used the DOAS approach, SAGE-II/III...
(Stratospheric Gas and Aerosol Experiment) [Chu and McCormick, 1986], HALOE (Halogen Occultation Experiment) [Gordley et al., 1996], and POAM (Polar Ozone and Aerosol Measurement) [Randall et al., 1998]. More recently, retrievals from the nadir-viewing UV-Vis spectrometers GOME (Global Ozone Monitoring Experiment) [Burrows et al., 1999] and its successor GOME-2 [Munro et al., 2006], SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY) [Bovensmann et al., 1999], and OMI (Ozone Monitoring Instrument) [Levelt et al., 2006a] have provided information on both stratospheric and tropospheric NO$_2$. Over unpolluted regions typically more than 90% of the observed NO$_2$ resides in the stratosphere, but over industrialized continental regions this fraction can range from 10 to 50%, depending on the degree of pollution. A challenge for the retrieval algorithms is the separation of the stratospheric and tropospheric contribution to the total NO$_2$ absorption inferred from the spectral measurements. Inaccuracies in this separation not only affect the stratospheric measurements themselves, but also the tropospheric retrievals that rely on residual techniques. Current methods to estimate stratospheric NO$_2$ use chemistry-transport models [Boersma et al., 2004; Richter et al., 2005], filtering techniques based on subsets of satellite measurements [Bucsela et al., 2006], or independent measurements of stratospheric NO$_2$ [Beirle et al., 2010]. These techniques need to be thoroughly tested against independent observations, which is one of the goals of this study.

In this work we focus on OMI stratospheric NO$_2$. The OMI retrievals start with total NO$_2$ slant column densities (SCDs), inferred from the instrument’s spectrally resolved measurements in the visible. The total slant columns represent the integrated concentration of NO$_2$ along the effective light path through the atmosphere. Since photons in the visible traverse the lower atmosphere, there can be a significant contribution from tropospheric NO$_2$ to the total slant column. In the Dutch OMI NO$_2$ retrieval (DOMINO) Boersma et al. [2007], the stratospheric component of the NO$_2$ slant column is estimated by data assimilation of OMI slant columns in the TM4 chemistry-transport model. In the NASA/KNMI retrieval (Standard Product, Bucsela et al. [2006]), the stratospheric component is estimated by fitting a second-order Fourier function in the zonal direction to a 24 h composite of OMI observations. Both methods use air mass factors (AMFs) to convert stratospheric slant columns into vertical columns, but the AMFs are calculated with different radiative transfer models, and use different a priori information on the vertical distribution of stratospheric NO$_2$.

In order to test and improve the stratospheric NO$_2$ information derived from OMI, the present work evaluates the two different OMI retrievals. We compare OMI stratospheric NO$_2$ from both retrievals with independent measurements taken at 14 remote NDACC (Network for the Detection of Atmospheric Composition Change) stations around the world. Doing so, we used UV-Vis measurements from the SAOZ (Système d’Analyse par Observations Zénithal) network, a collection of near-identical collectively operated instruments that is part of NDACC, UV-Vis measurements from other NDACC stations as well as FTIR observations.

We subsequently evaluate the ability of the retrieval algorithms to observe spatial and temporal variability in stratospheric NO$_2$. We will show that the Dutch OMI NO$_2$ retrieval captures spatial and temporal variations in stratospheric NO$_2$ induced by planetary waves, and also the daytime buildup of stratospheric NO$_2$ resulting from the photolysis of N$_2$O$_5$. Furthermore, we will analyze the 5 year record of OMI stratospheric NO$_2$ columns and discuss signatures of the quasi-biennial oscillation apparent over tropical and midlatitudes.

## 2. OMI Stratospheric NO$_2$ Data

### 2.1. OMI

The Dutch-Finnish Ozone Monitoring Instrument (OMI) is a UV-Vis imaging spectrometer that records the backscattered radiances from the Earth’s atmosphere in three spectral channels between 264 and 504 nm at an average spectral resolution of 0.5 nm. It combines a wide longitudinal swath (2600 km) with high spatial resolution (24 x 13 km$^2$) at nadir. OMI is part of the NASA EOS-Aura mission (launched July 2004) which is in a Sun-synchronous ascending node orbit that crosses the equator at 1340 local time (LT). In sections 2.2 and 2.3 we describe the algorithms of the DOMINO and the Standard Product. The DOMINO product is available at http://www.temis.nl/airpollution/no2.html, the Standard Product is available at http://daac.gsfc.nasa.gov/Aura/data-holdings/OMI/index.shtml. Both products use OMI NO$_2$ slant columns as input, and these are also included in the final product. A detailed description of OMI’s scientific objectives is given by Levelt et al. [2006b], instrument details are available from Dobber et al. [2006].

### 2.2. Dutch OMI NO$_2$ (DOMINO) Retrieval

The retrieval of the stratospheric and tropospheric NO$_2$ vertical columns by the DOMINO algorithm is the result of a multistep process. In the first step, slant columns of NO$_2$ are retrieved with the DOAS (Differential Optical Absorption Spectroscopy) [Platt and Stutz, 2008] method, by minimizing the differences between modeled and observed Earth reflectance spectra. The minimization is performed in the 405–465 nm spectral window, taking into account absorption by NO$_2$, ozone, and water vapor, the Ring effect and a third-order polynomial that describes the background of the reflectance spectrum. The NO$_2$ cross section spectrum for 220 K is taken from Vandoest et al. [1998]. The retrieval method accounts for the temperature sensitivity of the NO$_2$ spectrum by applying a correction for the difference between the effective temperature of NO$_2$ along the light path derived from ECMWF meteorological analyses and modeled profiles, and the 220 K of the NO$_2$ absorption cross-section spectrum [Boersma et al., 2004]. Earth reflectance spectra follow from dividing the Earth radiance measurements by the OMI-measured solar irradiance. For signal-to-noise considerations a fixed solar irradiance spectrum has been constructed from daily irradiance measurements taken in 2005. Calibration errors resulting from, amongst others, the limited signal-to-noise of the solar irradiance measurements cause systematic enhancements of NO$_2$ slant columns at specific viewing angles, that show up as stripes along the orbit [Boersma et al., 2007].
improved calibration approach, with a better correction of the CCD detector’s dark current, significantly reduced these stripes [Dobber et al., 2008]. The data used in this study have been processed with this improved dark current calibration. The precision of the retrieved NO$_2$ slant columns has been estimated to be $0.7 \times 10^{15}$ molecules/cm$^2$ [Boersma et al., 2007], which corresponds to approximately 10% of the unpolluted, and <5% of the polluted, slant column.

[9] In the second step, OMI NO$_2$ slant columns are assimilated in the TM4 chemistry transport model [Dentener et al., 2003]. The assimilation procedure is described in section 2.2.1. In the third and final step the assimilated stratospheric slant column is subtracted from the total slant column and the remaining tropospheric slant column is converted into a vertical column by dividing by the tropospheric air mass factor (AMF). The AMF is defined as the ratio of slant column density of the absorber along the (slant) optical path to the vertical column density. The AMF is calculated using the DAK [de Haan et al., 1987; Stammes, 2001] radiative transfer model that takes into account viewing geometry, the absorber’s vertical profile shape, terrain height, surface albedo, clouds, and Rayleigh scattering (including multiple scattering effects). The AMF depends on the tropospheric NO$_2$ profile, which is taken from space-time collocated TM4 model results. The spectral fitting and the tropospheric AMF have been studied in detail elsewhere [Boersma et al., 2002, 2004, 2007] and we will now focus on the assimilation procedure to estimate stratospheric NO$_2$.

2.2.1. Estimation of the Stratospheric NO$_2$ Column

2.2.1.1. TM4

[10] We use the TM4 chemistry transport model (CTM) for the assimilation of OMI NO$_2$ slant columns. The assimilation system operates at a resolution of $3^\circ \times 2^\circ$ (longitude $\times$ latitude), with 35 sigma pressure levels up to 0.38 hPa in the vertical direction. After 1 February 2006 the model configuration was changed to 34 pressure levels, driven by a change in the sigma levels of the meteorological input. TM4 uses forecasted and analyzed 6-hourly meteorological fields, (3-hourly for boundary layer fields) from the European Centre for Medium Range Weather Forecast (ECMWF) operational model. These fields include global distributions of wind, temperature, surface pressure, humidity, cloud cover and (liquid and ice) water content, and precipitation. Mass conserving preprocessing of the meteorological input is performed as described by Bregman et al. [2003]. The physical processes included in determining tracer evolution are mass conserved advection, convective transport, boundary layer diffusion, photolysis and dry and wet deposition. NO$_x$ emissions are based on the EU POET (Precursors of Ozone and their Effects on the Troposphere) database for 1997 [Olivier et al., 2003], yielding a global total of 46 Tg N/yr. Chemical processes in the troposphere are governed by the Carbon Bond Mechanism 4 (CBM-4) scheme that includes non-methane hydrocarbons to account for loss by reaction with OH [Horwell et al., 1998].

[11] The CBM-4 scheme accounts for O$_3$-NO$_2$-HO$_x$ chemical reactions in the stratosphere, including the conversion of NO and NO$_2$ to N$_2$O$_5$ and HNO$_3$. Other chemical aspects, such as the photolysis of N$_2$O$_5$ and reactions with halogens such as bromine and chlorine are missing. Some effects of the simplified chemistry in the stratosphere are compensated for by constraining the modeled concentrations to observed climatological values in the middle/upper stratosphere. Above 50 hPa in the tropics and above 100 hPa in the extratropics, ozone concentrations are nudged to mean observed values taken from the Fortuin-Kelder climatology [Fortuin and Kelder, 1998] (scaled with the TOMS total O$_3$ column for 1997) with a relaxation time of 2–5 days, depending on latitude. At 10 hPa, stratospheric HNO$_3$ is nudged to the UARS-derived O$_3$/HNO$_3$ ratios for 1992 (B. Bregman, personal communication, 1997), with a characteristic relaxation time of 2 months. This is a modification of the original TM4 code, where the UARS O$_3$/HNO$_3$ ratio is simply prescribed. The long relaxation time prevents the nudging from strongly interfering with the NO$_x$ analysis resulting from the data assimilation discussed below. Above 10 hPa, the NO$_x$ volume mixing ratio is nudged to its modeled value at 10 hPa, again with characteristic relaxation time of 2 months. The prescribed 10 hPa HNO$_3$ mixing ratio constitutes the effective source of stratospheric NO$_x$ in TM4.

2.2.1.2. Data Assimilation

[12] The purpose of the assimilation is to regularly update the TM4 simulation of the three-dimensional NO$_2$ distribution with available measurement data in such a way that the model simulation of the stratospheric NO$_2$ column is in close agreement with the OMI measurements. The assimilation also provides a realistic error estimate for the stratospheric NO$_2$ column (see below). The assimilation scheme is based on the Kalman filter technique, with a prescribed parameterization of the horizontal correlations between forecast errors to reduce computational effort. A schematic layout of the assimilation procedure is presented in Figure 1. The upper loop in Figure 1 illustrates the TM4 simulation of the three-dimensional NO$_2$ field with a time step $\Delta t$ (30 min in TM4). If NO$_2$ slant columns are available with a measurement time within 15 min of the model time, the model field is updated by the Kalman filter. In the Kalman filter update, the forecast model state is adjusted toward the observations, replacing the forecast with the analysis. This analyzed profile field $x_a$ includes NO$_2$ in both troposphere and stratosphere, and is calculated from the forecast $x_f$ and the 2-D field of superobservations $y$ (explained below) by

$$ x_a = x_f + P(HPH_f + R)^{-1}(y - y_m), $$

with matrix $H$ the observation operator, $P$ the forecast error covariance matrix, and $R$ the combined observation and representativeness error covariance [Eskes et al., 2003]. The role of $H$, $P$ and $R$ will be discussed in more detail below. The term $PH_f(HPH_f + R)^{-1}$ determines the most likely adjustment of the model state, given the difference between observed and forecast model column ($y - y_m$, observation minus forecast, O–F). Note that the total slant column $y$ includes the NO$_2$ present in both troposphere and stratosphere. The relative size of the adjustment depends on the ratio between the uncertainties in the model forecast and observations, and the model analysis will closely follow the observations when this ratio is large.

[13] The observation operator $H$ is proportional to the averaging kernel [Eskes and Boersma, 2003], a 35-element vector that contains the sensitivity of OMI to NO$_2$ in each model layer. The scalar product of the observation operator
vector and the TM4 NO\textsubscript{2} profile at the location of the individual OMI observations yields the slant column that would be observed by OMI given the modeled profile \(\tilde{x}_f\). The average of all OMI observations (and model equivalents) with center coordinates inside a 3° × 2° TM4 grid cell is treated as a single measurement, dubbed superobservation (and model equivalent). \(\tilde{y}_m\) is the model forecast of the superobservations, given by \(\mathbf{H}\tilde{x}_f\). In order to reduce the computational effort, the Kalman filter is applied for these superobservations.

The diagonal elements of the observation error covariance matrix \(\mathbf{R}\) equal the square of the observation error \(\mathbf{R}_{ii} = \sigma_i^2\), where \(\sigma_i\) is chosen to depend explicitly on the modeled profile shape,

\[
\sigma_i = \frac{(A_{\text{trop}} + BS_{\text{strat}})/S}{S},
\]

with \(S_{\text{trop}}\) the tropospheric contribution to the total slant column \(S\), and \(S_{\text{strat}}\) the stratospheric contribution to the slant column taken from the TM4 forecast. The unknown true \(S_{\text{trop}}\) and \(S_{\text{strat}}\) are approximated by the model estimates. The values assigned to the coefficients \(A\) and \(B\) are 4.0 and 0.25 \((\times 10^{15}\,\text{molecules/cm}^2)\), respectively. This implies that the observation error rapidly increases for modeled tropospheric vertical columns larger than approximately 0.5 \(\times 10^{15}\) molecules/cm\(^2\). Furthermore, the small value of the stratospheric observation error \(B\) reflects the relatively accurate measurement of stratospheric NO\textsubscript{2}; radiative transfer calculations have small errors for NO\textsubscript{2} in the middle and higher atmosphere. Because of averaging of OMI observations into superobservations, much of the noise in the OMI observations cancels out, consistent with our small value for \(B\). The value of \(B\) is furthermore consistent with the standard deviation of the observed O − F value. The large value of \(A\) reflects the large retrieval uncertainty for tropospheric NO\textsubscript{2}, which is very sensitive to assumptions on cloud modeling, surface reflectivity, profile shape or aerosol concentration [Boersma et al., 2004]. In the stratosphere total reactive nitrogen (NO\textsubscript{2}) is a well-conserved quantity, with relatively small source and sink contributions. This implies that the information from the observations can be stored in the model over long time periods. Furthermore, experiences with ozone assimilation have shown that modern weather prediction models are well capable of describing the dynamical variability of stratospheric tracer concentrations [Eskes et al., 2003]. A successful stratospheric assimilation can therefore be expected. In contrast, the tropospheric NO\textsubscript{2} budget is characterized by strong sources and sinks, resulting in short NO\textsubscript{2} lifetimes of 5–20 h in the lower troposphere. Updates brought to the simulated tropospheric NO\textsubscript{2} concentration field are therefore rapidly lost, typically within 1 day. The observation error covariance matrix \(\mathbf{R}\) defined in this way effectively filters out OMI observations with increased tropospheric NO\textsubscript{2} columns by attributing less weight to OMI observations over (known) polluted areas. This filtering leads to a strong forcing of the simulated stratospheric NO\textsubscript{2} concentrations toward the OMI observations, and will result in only a marginal adjustment of the simulated tropospheric NO\textsubscript{2} field.

The covariance matrix \(\mathbf{P}\) accounts for the forecast error due to model imperfections. The diagonal or variance is set to a fixed value \(\mathbf{P}_{ii} = \sigma_i^2\), where \(\sigma_i = 0.15 \times 10^{15}\) molecules/cm\(^2\). This value is consistent with the variance of O − F values apparent over remote areas. A
second-order autoregressive (Thieaux) function with a characteristic length of 600 km (hereafter called correlation length) describes the correlation between the errors of neighboring grid cells. This correlation length transforms a local O − F difference into a spatially extended, smeared forcing in model space. Consequently, the correlation length filters out structures smaller than 600 km in the O − F, reducing the local impact of small-scale structures (partly from tropospheric origin) on the assimilated stratospheric NO₂ field. This implies that small-scale variations in the OMI observations, such as the stripes [Boersma et al., 2007], are dampened and have only minor implications for the (stratospheric) analysis. Strong gradients in stratospheric NO₂ are occasionally found, in particular related to the Noxon cliff [Noxon, 1979]. Such sharp drops in NO₂ concentrations indicate that air masses on either side of the cliff have a very different chemical history. Error correlations are assumed to be small in such cases. To account for this we introduce an NO₂ concentration gradient dependence in the correlation,

\[ C_{ij} = \begin{cases} e^{-\left(\frac{\Delta \rho_{ij}}{\sigma}\right)^2} & \Delta \rho_{ij} < 0.9 \\ 0 & \Delta \rho_{ij} > 0.9 \end{cases} \]

with \( c_i \) and \( c_j \) the concentrations in grid cells \( i \) and \( j \), \( \sigma \) the characteristic concentration length, which is set to 30%. Such a term is effective in preventing the occurrence of negative analyzed NO₂ values within the vortex. The off-diagonal elements \( P_{ij} \) are the product of \( C_{ij} \) and the correlation length.

[16] All the model NOₓ species (NO, NO₂, NO₃, N₂O₅, HNO₄) are assumed to be fully correlated. Hence the forcing of the modeled NO₂ field is also directly applied to the other four nitrogen oxides. The (3° × 2°) forecast NO₂ field is spatially interpolated to the location of the OMI pixel center, and the stratospheric vertical column is calculated by summing all layers above the tropopause. In the calculation of the stratospheric slant column, the NO₂ amount in each layer is multiplied by the corresponding element from the observation operator before summation. This is represented by the lower branch in the scheme shown in Figure 1. The TM4 tropopause level follows from applying the WMO 1985 definition (lowest level where the lapse rate is smaller than 2°C/km) to the ECMWF temperature profiles. The forecast stratospheric NO₂ slant columns are used in the retrieval of the tropospheric vertical column, and they are stored in the DOMINO data file (as data field “AssimilatedStratosphericSlantColumn”). The forecast stratospheric NO₂ vertical columns (data field “AssimilatedStratosphericVerticalColumn”) are used in the remainder of this study. The forecast columns in regions with negligible overlap between consecutive OMI orbits, have evolved freely for about 24 model hours since previous OMI overpass and model forcing. Using forecast columns instead of the analyzed columns has the advantage of reducing attribution errors for localized tropospheric contributions to the NO₂ slant column that are not simulated by the model, for instance from boreal fires. Such events may be partly attributed to the stratosphere in the analysis, which would lead to a local underestimation of the tropospheric column.

2.2.2. Assimilation Results

[17] Figure 2 shows the global distribution of monthly mean observation minus forecast (O − F) and the model forcing (analysis minus forecast, A − F) for March 2005. The difference between Figure 2 (left) and Figure 2 (right) illustrates the effect of the assimilation: considerable O − F differences, resulting mostly from (anthropogenic) tropospheric NO₂ sources, have only a minor influence on the analysis. On the other hand, synoptic-scale structures in
O – F persist in the A – F differences. That the A – F differences are much smaller (generally less than \( \pm 0.15 \times 10^{15} \) molecules/cm\(^2\)) than the O – F differences (up to \( \pm 0.4 \times 10^{15} \) molecules/cm\(^2\)) demonstrates that most tropospheric contributions are effectively discounted by the assimilation procedure in combination with equation (2). The persistent synoptic-scale structures in the A – F differences indicate a slight tendency in TM4 to deviate from the observed fields. The absence of land–sea transitions in the A – F differences illustrates that the strength of the forcing is comparable over land and over sea. This reflects that the stratospheric NO\(_2\) field is largely decoupled from the troposphere in the analysis, and as such is not bound to the geographical distribution of land–sea masses.

[18] We evaluate the impact of the assimilation by comparing a 12 month TM4 free run to the assimilation run. Both runs were initialized with the same model start field for 1 January 2005. In the tropics (30°S–30°N) the difference assimilation minus free model run increases by approximately \( +0.5 \times 10^{15} \) molecules/cm\(^2\) per month and stabilizes at \( +1.3 \times 10^{15} \) molecules/cm\(^2\), which implies that TM4 in the free-running mode underestimates the stratospheric NO\(_2\) vertical column in the tropics by 50%. For midlatitudes the difference between TM4 and assimilation varies with season, with an amplitude comparable to the value in the tropics. The main source of stratospheric NO\(_2\), nitrous oxide (N\(_2\)O), is not modeled by TM4, which may explain part of the biases in TM4 NO\(_2\). Stratospheric NO\(_2\) is effectively driven by the UARS ratio of HNO\(_3\):O\(_3\) in combination with the Fortuin & Kelder O\(_3\) climatology. Since the nudging is relatively slow (the relaxation time is 2 months, comparable with the time scale of poleward transport) stratospheric NO\(_2\) concentrations in TM4 follow the climatologies with significant delay. Imposing the HNO\(_3\):O\(_3\) ratio, such as applied in the original TM4 model, is likely to reduce the bias.

[19] Up to now, no validation studies of TM4 stratospheric tracers have been reported, but TM4 stratospheric ozone columns are consistent with the 30 year data record of total column ozone observations by TOMS, SBUV, GOME, SCIAMACHY, OMI and GOME-2 that is presented by van der A et al. [2010]. The significant differences between TM4 and assimilated stratospheric NO\(_2\) that we find here, illustrate that the absolute values of the DOMINO stratospheric NO\(_2\) columns are strongly driven by the OMI NO\(_2\) observations and that the model input is limited to providing a forecast from observation–based analyzed fields.

2.3. NASA GSFC (Standard Product) Retrieval

[20] The Standard Product (SP) is an operational algorithm for the retrieval of tropospheric NO\(_2\) vertical column densities for OMI. Analogously to the DOMINO product, the SP algorithm starts with DOAS fitted slant column densities of the OMI L2 data. The basic algorithm for the retrieval of total vertical column and tropospheric NO\(_2\) is described by Boersma et al. [2002] and Bucsela et al. [2006]. The Standard Product identifies the stratospheric NO\(_2\) vertical columns as the slowly varying part of the total vertical column NO\(_2\) field, which implies that medium–scale variations up to several 100 km in the total column NO\(_2\) field are attributed to tropospheric signals.

[21] In the first step, NO\(_2\) slant columns are converted into initial vertical columns (VCD\(_{\text{init,SP}}\)) by dividing by an (unpolluted) air mass factor (AMF\(_{\text{init,SP}}\)). These air mass factors are derived from radiative transfer calculations with the TOMRAD radiative transfer model [Dave, 1965] with annually averaged simulated NO\(_2\) profile shapes. These profiles are constructed by merging the GSFC CTM [Douglass et al., 2003] 3-D profiles for the stratosphere with 3-D tropospheric profiles from the GEOS-Chem model [Martin et al., 2002a].

[22] In essence the Standard Product builds on the reference sector method [Martin et al., 2002b] and on the method reported by Wenig et al. [2003], who assumed GOME observations over unpolluted regions (oceans) to represent the stratospheric NO\(_2\) field for these latitudes, and interpolated to fill the gaps over the continents. The Standard Product applies a second-order Fourier (wave-2) fit in 1°-wide latitude bands in the zonal direction to all data collected within \( \pm 12\) h of the target orbit [Bucsela et al., 2008]. Prior to the wave-2 fit, regions with known high-tropospheric NO\(_2\) abundances (identified using GEOS-Chem) are masked and a 9° wide boxcar running average is applied in the meridional direction. Areas with strong deviations from the wave-2 fit are identified as contaminated by tropospheric NO\(_2\) pollution and also masked. Then, the wave-2 fit is performed for the second time. The local stratospheric NO\(_2\) column is thus based on a spatial fit to a 24 h ensemble of OMI observations, and is subtracted from the OMI observations to produce the tropospheric slant column field. The stratospheric NO\(_2\) columns used in this study are calculated by evaluating the wave-2 polynomial, using the coefficients that are stored in the SP data file. A detailed discussion of the Standard Product algorithm can be found elsewhere [Bucsela et al., 2006; Celarier et al., 2008].

3. Data Sets

[23] OMI stratospheric NO\(_2\) columns are compared to ground-based UV-Vis and FTIR measurements taken at various NDACC (Network for the Detection of Atmospheric Composition Change) stations. Part of the NDACC UV-Vis instruments belong to the SAOZ network. The nearly identical SAOZ instruments all are operated by CNRS. In this study we make a distinction between the SAOZ instruments and the other NDACC-certified UV-Vis instruments that are operated by individual institutes.

3.1. SAOZ

[24] The SAOZ (Système d’Analyse par Observations Zénithal) system constitutes a network of ground-based UV-Vis spectrometers to measure stratospheric ozone and NO\(_x\). SAOZ spectrometers [Pommereau and Goutail, 1988] record the zenith sky spectrum between 300 and 620 nm at 1 nm resolution. Currently, the SAOZ network consists of 10 instruments located at various latitudes between 70°S and 70°N, and their locations are shown in Figure 3. In general, the SAOZ instruments are situated at pristine or elevated locations, far away from significant sources of tropospheric NO\(_2\).

[25] Measurements are performed around twilight (solar zenith angles between 86° and 91°). The long light path through the stratosphere, and the relatively short vertical light path through the troposphere make the measured slant
column roughly 18 times more sensitive to stratospheric NO$_2$ than to NO$_3$ in the troposphere.

[26] NO$_2$ slant columns are retrieved by a DOAS fit in the 410–530 nm wavelength range to the ratio of the twilight spectrum and a reference spectrum, typically taken at noon under cloud free conditions. Different SAOZ groups take different approaches for the reference spectrum. For instance, Vaughan et al. [2006] use a new reference spectrum for each month, whereas Ionov et al. [2008] employ a fixed reference spectrum for the entire measurement series at a measurement site. Slant columns are converted to vertical columns by the air mass factor (AMF) which is calculated with a radiative transfer model developed by CNRS [Sarkissian et al., 1995]. The air mass factors are calculated at 470 nm taking into account solar zenith angle and NO$_2$ profile shape. SAOZ uses fixed AMFs for three different geographical regions: midlatitude (OHP and Kerguelen), tropics (Reunion and Bauru) and polar (Dumont d’Urville, Sodankyla, Scoresby). These AMFs have been calculated for summer sunset conditions using composite NO$_2$ profiles from SAGE-II, POAM-III and SAOZ balloon observations.

[27] Intercomparisons of NDACC-certified UV-Vis instruments show that retrieved NO$_2$ slant columns agree within 5–10% for common spectral ranges and analysis parameters, [e.g., Vaughan et al.; 1997; Roscoe et al., 1999; Vandaele et al., 2005]. However, the accuracy of the stratospheric NO$_2$ vertical column is limited by errors in the AMF calculation, errors in the residual NO$_2$ amount in the reference spectrum, and errors resulting from not accounting for the temperature dependence of the NO$_2$ absorption cross section. This yields an overall accuracy of 21% of stratospheric NO$_2$ vertical columns retrieved with ground-based UV-Vis instruments [Ionov et al., 2008].

[28] In order to compare stratospheric NO$_2$ observations from SAOZ (sunrise, sunset) and OMI (approximately 1340 LT), we need to account for the considerable time difference between the two measurement methods. A chemical box model [Denis et al., 2005; Ionov et al., 2008], based on chemistry from the SLIMCAT 3-D CTM [Chipperfield et al., 1996], is used to calculate representative overhead columns at 1200 LT from the SAOZ twilight measurements. This model simulates the diurnal variation of stratospheric NO$_2$ with 1 min time steps, and it includes 98 chemical and 39 photochemical reactions, including heterogeneous chemistry on liquid and solid aerosols. The error associated with this model-based adjustment is not included in the above quoted 21% accuracy. OMI stratospheric NO$_2$ data are also adjusted to local noon with the same model. The magnitude of the adjustment depends, apart from time of overpass, on season and latitude. For the SAOZ sunrise to noon correction the adjustment ranges from <0.1 × 10$^{15}$ molecules/cm$^2$ (5%) in the tropics to >2 × 10$^{15}$ molecules/cm$^2$ (30%) for the high-latitude stations in summer. For DOMINO the adjustment to local noon is typically smaller (up to 0.4 × 10$^{15}$ molecules/cm$^2$, or 12%).

3.2. NDACC UV-Vis Zenith Sky Data

[29] In addition to the SAOZ stations several independently operated SAOZ-like instruments contribute to the NDACC network (http://www.ndsc.ncep.noaa.gov/). Similar to the SAOZ stations these instruments record the UV-Vis zenith sky spectrum at sunrise and sunset. NDACC and SAOZ instruments are comparable, but not identical. The operational wavelength range or the employed fitting window for NO$_2$ retrieval is different for some of the NDACC instruments. Furthermore, different radiative transfer codes are used to determine the AMFs. The resulting error budget has been reported to be similar to the SAOZ instruments, with a 21% accuracy of the stratospheric vertical NO$_2$ column [Ionov et al., 2008]. The twilight NO$_2$ columns retrieved by the NDACC instruments are adjusted to local noon columns by the same model that was used to adjust the SAOZ and OMI measurements.

3.3. Ground-Based FTIR Stations

[30] The NDACC network also contains several NO$_2$ observing Fourier Transform Infra-Red (FTIR) instruments. The direct Sun measurement from FTIR is only possible at daytime under clear sky conditions. Owing to its wavelength range and high spectral resolution the FTIR method is sensitive to the pressure and temperature dependence of the NO$_2$ cross-section spectrum. Camy-Peyret et al. [1983] and Flaud et al. [1983] presented error estimates of FTIR NO$_2$ column retrievals, showing accuracies of approximately 10%. However, the dominant error source in FTIR are inaccuracies in the a priori NO$_2$ profile assumed in the retrieval and these can result in errors of approximately 30% [Rinsland et al., 2003] as we will discuss later. Other sources of error are the assumed temperature profile, signal to noise, and the accuracy of the absorption cross section.

4. Evaluation of OMI Stratospheric NO$_2$

4.1. Evaluation of Ground-Based Techniques

[31] First we investigate the consistency between the FTIR and UV-Vis measurements of stratospheric NO$_2$. This is motivated by an earlier study by Vaughan et al. [1997]
that reported discrepancies of up to 30% in the NO$_2$ column between different UV-Vis instruments. At the NDACC stations Jungfraujoch and Izaña, FTIR instruments are collocated with zenith sky observing instruments, which enables the evaluation of both techniques against each other. The Kiruna station is located 300 km west of Sodankyla, close enough to compare the Kiruna FTIR to the Sodankyla SAOZ instrument in absence of strong gradients in stratospheric NO$_2$. Figure 4 shows a comparison of stratospheric NO$_2$ columns inferred from ground-based FTIR and UV-Vis instruments with those retrieved from OMI for Sodankyla, Jungfraujoch and Izaña. The FTIR measurement closest in time to the OMI overpass was used, with a typical time difference between OMI overpass and FTIR measurement of 30 min to 2 h. (top) The grey bands represent the range covered by the SAOZ sunrise and sunset measurements. (bottom) The solid line in the scatterplots denotes unity, and the dashed lines represent a reduced major axis fit [Clarke, 1980] to the data.

Figure 4. Comparison between SAOZ, FTIR, and DOMINO stratospheric NO$_2$ columns for (left) Sodankyla/Kiruna, (middle) Jungfraujoch, and (right) Izaña. OMI pixels within 10 km of the measurement station have been used. SAOZ and OMI data have been adjusted to local noon using a SLIMCAT-based chemical box model. For days with multiple FTIR measurements, the data closest in time to OMI overpass are taken, with a typical time difference between OMI overpass and FTIR measurement of 30 min to 2 h. (top) The grey bands represent the range covered by the SAOZ sunrise and sunset measurements. (bottom) The solid line in the scatterplots denotes unity, and the dashed lines represent a reduced major axis fit [Clarke, 1980] to the data.
values with poorer correlation ($r = 0.69$, slope = $+1.26$, offset = $-0.14 \times 10^{15}$ molecules/cm$^2$). Recently, a thorough inspection of the UV-Vis instrument at Izaña revealed improper illumination of the detector and issues with the stray light correction resulting in a 15% underestimation of the UV-Vis stratospheric NO$_2$ columns (M. Gil, personal communication, 2010). Correcting for these inaccuracies would bring UV-Vis more in line with FTIR and OMI. We conclude that the ground-based techniques are mutually consistent within 15–20%, which is consistent with accuracies reported in other studies. De Mazière et al. [1998] found a $+5\%$ offset between the ground-based FTIR and zenith sky measured vertical NO$_2$ columns at Jungfraujoch. Kerzenmacher et al. [2008] performed a comprehensive validation study of ACE-FTS (a spaceborne FTIR recording solar occultation spectra) versus ground-based FTIR and UV-Vis (SAOZ) instruments and found a $+15\%$ offset between the spaceborne FTIR and SAOZ techniques.

4.2. Evaluation of OMI Stratospheric NO$_2$ With Ground-Based Measurements

[33] DOMINO and ground-based observations of stratospheric NO$_2$ over Sodankyla agree very well, as shown in Figure 4. Figure 5 shows the seasonal variation in stratospheric NO$_2$ columns measured by DOMINO, the Standard Product (SP) and ground-based instruments from the NDACC network, with high-NO$_2$ columns in summer and smaller columns in winter. DOMINO and SP both show reasonable agreement with the ground-based data. The bias between the latitude and seasonally averaged OMI products and ground-based data is generally within $1 \times 10^{15}$ molecules/cm$^2$, and as shown in Figure 6, the stations do not share a clear persistent bias pattern. Figure 6 shows the differences between OMI and ground-based measurements of stratospheric NO$_2$ at individual stations. Figure 6 does not reveal a consistent seasonal cycle in the bias among the stations. Table 1 shows that, with the exception of Dumont d’Urville, the average bias for a given station for both retrievals is smaller than $0.3 \times 10^{15}$ molecules/cm$^2$, with an RMS error of approximately $0.2 \times 10^{15}$ molecules/cm$^2$. The agreement between OMI and ground-based stratospheric NO$_2$ is on average within 13%. We consider this agreement optimal, given the estimated accuracy of the ground-based techniques of 21% and the precision of the OMI retrievals of approximately $0.2 \times 10^{15}$ molecules/cm$^2$. Over the SAOZ and NDACC stations, DOMINO exceeds ground-based stratospheric NO$_2$ by $+0.23 \times 10^{15}$ molecules/cm$^2$ and SP by $+0.06 \times 10^{15}$ molecules/cm$^2$ which implies that DOMINO is
Figure 6. Differences between OMI stratospheric \( \text{NO}_2 \) columns and ground-based observations for various stations in 2005. Blue dots indicate the differences between DOMINO and ground-based stratospheric \( \text{NO}_2 \), and red dots represent SP minus ground-based. Only satellite observations within 10 km of the ground-based station have been selected, and ground-based and satellite data have been adjusted to 1200 local time (LT). In case of multiple OMI overpasses per day, the overpass closest to local noon was selected.

Table 1. Statistical Summary of Comparison DOMINO and SP Versus Ground-Based Observations

<table>
<thead>
<tr>
<th>Station</th>
<th>Absolute Difference</th>
<th>Relative Difference (%)</th>
<th>RMS</th>
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Other NDACC

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FTIR

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<td>SP</td>
<td>DOMINO</td>
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on average approximately $0.2 \times 10^{15}$ molecules/cm$^2$ higher than SP over these stations.

5. Detailed Comparison of Stratospheric NO$_2$ From DOMINO and SP

Figures 5 and 6 show that the DOMINO stratospheric columns are higher than those from SP. This is confirmed by Table 1, which summarizes the annual mean bias between the OMI retrievals and the ground-based measurements. Figure 7 shows a comparison for DOMINO and SP stratospheric NO$_2$ retrievals for January and July 2005. The left panel confirms that DOMINO is generally higher than SP, more so in January than in July 2005. Figure 7 also shows that the bias between the two retrievals is not uniform, but reveals large, synoptic-scale spatial features. Such differences have been reported earlier by Lamsal et al. [2010], who found DOMINO and SP stratospheric slant columns to agree within $\pm 1 \times 10^{15}$ molecules/cm$^2$. The stratospheric NO$_2$ field retrieved from SCIAMACHY limb measurements [Beirle et al., 2010] shows considerable longitudinal variation at midlatitudes, that is similar to the zonal variations in DOMINO stratospheric NO$_2$. This indicates that the synoptic-scale spatial features in the difference between DOMINO and SP stratospheric NO$_2$ result from the SP not properly capturing the longitudinal variation in the stratospheric NO$_2$ field. Here we examine the origin of the differences further, by comparing the stratospheric AMFs of both algorithms. Figure 7 (middle) clearly shows that DOMINO AMFs are smaller than those from the SP, especially at large solar zenith angles. This is supported by the comparison between stratospheric AMFs near the equator shown in Figure 8. For this particular part of the orbit, we find discrepancies between DOMINO and SP AMFs on the order of 5% with a notable increase around viewing zenith angles of 45°. Investigation of the look-up tables of the DOMINO and SP revealed that the latter has reference points for VZA = 0°, 30°, 45° & 70°, indicating that the large discrepancy for VZAs between 45° and 70° is most likely due to interpolation errors in the SP look-up table. In future versions, the SP look-up table will use more reference points to resolve this issue. The systematic discrepancy of approximately 5% between the AMFs for VZA < 45° result from differences in the AMF calculation between the DOMINO and SP algorithms. Table 2 gives an overview of all differences between both algorithms. Different NO$_2$ profile shapes (DOMINO profiles are taken from TM4 assimilation whereas Standard Product profiles are derived from merged GSFC CTM and GEOS-Chem simulations) accounts for a 1–2% difference between the DOMINO stratospheric AMF and AMF$_{init,SP}$. Similarly, the correction for the temperature sensitivity of the NO$_2$ spectrum discussed in section 2.2 will introduce differences as DOMINO uses ECMWF temperature profiles whereas SP uses climatological profiles. The different radiative transfer models used for the AMF calculation (DAK in case of DOMINO and TOMRAD for SP) account for another 1–2% difference in the AMFs. Both models assume plane-parallel atmospheres, however TOMRAD includes a correction for atmospheric sphericity while DAK includes polarization [Stamnes et al., 1989].

Figure 7 (right) shows the impact of the AMF differences alone. The DOMINO stratospheric columns deviate more strongly from the SP initial vertical columns (VCD$_{init,SP}$) than the ultimately reported (wave-2 processed) SP stratospheric columns. Apparently, masking out polluted areas, accounting for tropospheric contributions to VCD$_{init,SP}$, and the wave-2 processing itself, compensate to
some extent for the higher SP AMFs, as indicated by the smaller differences between DOMINO and SP stratospheric NO$_2$ columns than between DOMINO VCD$_{\text{strat}}$ and SP VCD$_{\text{init}}$ in Figure 7 (left).

6. Day-to-Day Dynamical Effects

[36] The Arctic polar vortex of the 2004–2005 winter was dynamically active with various excursions to lower latitudes between January and March [Singleton et al., 2007]. A major stratospheric warming in mid-March caused the final breakup of the vortex [Manney et al., 2006; Singleton et al., 2007].

[37] Figure 9 shows the dynamic behavior of the polar vortex in the period from 9 to 21 March 2005. The PV and temperature at 50 hPa (third and fourth columns, respectively, of Figure 9) show that until 14 March the polar vortex appears stationary over the North Atlantic. On 17 March the vortex has tilted in east-west direction, after which it collapsed and broke up as seen on 21 March.

[38] The stratospheric NO$_2$ profile peaks between 30 and 50 hPa, and therefore we expect good spatial correlation between the DOMINO stratospheric NO$_2$ field (Figure 9, first column) and the temperature distribution at 50 hPa (Figure 9, third column). During 9–14 March OMI observes reduced stratospheric NO$_2$ columns inside the vortex over the North Atlantic and Greenland as compared to air masses outside the vortex, and enhanced NO$_2$ outside the vortex over Siberia and southern Europe. The boundary between reduced and enhanced stratospheric NO$_2$ roughly coincides with the $-65^\circ$C contour at 50 hPa. On 17 March, the reduced NO$_2$ columns over Great Britain coincide with the low temperatures inside the tilted and weakening vortex.

[39] The synoptic-scale variations in the stratospheric NO$_2$ field around the vortex are not observed by the Standard Product (second column of Figure 9), but are smoothed by the wave-2 fitting instead. Actually, the enhanced stratospheric NO$_2$ at the vortex edge shows up as a reduction in the SP NO$_2$, probably resulting from the masking of polluted areas.

[40] We now focus on the effect of the movement of the vortex edge on stratospheric NO$_2$ over Sodankyla. Temperature and PV at 50 hPa on 9 March show that the vortex lies over Sodankyla, that is skirted by the vortex edge and the warmer air mass with enhanced stratospheric NO$_2$ outside the vortex. The westward displacement of the vortex on 12 March moves NO$_2$-rich air over Sodankyla, which results in an episodic enhancement of the stratospheric NO$_2$ columns of more than $1 \times 10^{15}$ molecules/cm$^2$. Figure 10 shows DOMINO and FTIR observations over Sodankyla and Jungfraujoch of this episodic enhancement, that peaks on 14 March and lasts approximately 7 days.

[41] Figure 10 shows that the stratospheric NO$_2$ column over Sodankyla is coupled to the temperature at 30 hPa. The persistent low temperatures ($T \approx -80^\circ$C) at 30 hPa in the first half of February coincide with low and unchanging FTIR-observed NO$_2$ columns (approximately $1 \times 10^{15}$ molecules/cm$^2$). After 21 February the stratospheric NO$_2$ column increases steadily in accordance with the increasing temperature, and the episodic enhancement of stratospheric NO$_2$ around 15 March correlates with a

| Table 2. Overview of Algorithm Differences Between OMI DOMINO and OMI SP |
|-----------------------------|-------------------|-----------------|-------------------|-----------------|-----------------------|
| Algorithm       | Stripe Correction | Radiative Transfer Model | $\lambda$ (nm) | Source          | Stratospheric Column Shape |
| DOMINO         | no                | DAK              | 440              | TOMS-GOME       | TM4 assimilation       |
| SP             | yes               | TOMRAD           | 440              | GOME            | TM4 climatology of GEOS-Chem and GSFC CTM |

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Figure 8. Comparison between stratospheric air mass factors (AMF) between DOMINO and Standard Product (SP) retrievals of stratospheric NO$_2$ on 23 January 2005. (a) AMF$_{\text{strat,D}}$ − AMF$_{\text{init,SP}}$ for OMI orbit 2806 over the Pacific. The inset shows, for a single OMI measurement, the variation of AMF$_{\text{strat,D}}$ and AMF$_{\text{init,SP}}$ as a function of viewing zenith angle (VZA). The red line marks the location of the selected OMI measurement. (b) AMF$_{\text{strat,D}}$/AMF$_{\text{init,SP}}$ as a function of VZA. The negative viewing zenith angles correspond to the western part of the swath.
sudden increase in the 30 hPa temperature over Sodankyla. Such positive correlations between short-term changes and local stratospheric temperature have been observed before [Mount et al., 1987; Pommereau and Goutail, 1988]. We find a temperature dependence of $d\text{NO}_2/dT = 7 \times 10^{13}$ molecules/cm$^2$/K ($r = 0.95$), which is consistent with the $6 \times 10^{13}$ molecules/cm$^2$/K over Kiruna reported by Pommereau and Goutail [1988]. It is unlikely that the observed temperature dependence of the stratospheric NO$_2$ column results from the temperature sensitivity of the NO$_2$ absorption cross section in the spectral fitting. First of all, the DOMINO retrieval takes this sensitivity into account (see section 2.2). Furthermore, if this sensitivity were to be neglected, it is much weaker and different in sign ($-0.3\%$/K) than the effect we find here ($+3.5\%$/K over Kiruna). We attribute the coupling between temperature and stratospheric NO$_2$ to the temperature dependence of the N$_2$O$_5$ (photo)dissociation rate and the NO$_x$ partitioning, as proposed by Van Roozendael et al. [1994]. The weaker correlation between temperature and stratospheric NO$_2$ column over Jungfraujoch (Figure 10, top) most likely results from stronger stratospheric dynamics at this location.

[42] During the cold winter of 2004–2005, over a large area the stratospheric temperatures fell below the formation temperature of polar stratospheric clouds (PSC), resulting in increased ozone loss in the Arctic stratosphere [Singleton et al., 2007]. Until 11 March the air over Sodankyla is inside the polar vortex, however after 21 February the stratospheric NO$_2$ column over Sodankyla increases steadily with the rising temperature at 30 hPa. This implies that the N$_2$O$_5$ and HNO$_3$ reservoirs in the vortex air over Sodankyla are not depleted by denitrification and subsequent sedimentation, but are still present to be (photolytically) converted into NO$_x$. 

**Figure 9.** Time series (9, 12, 14, 17, and 21 March 2005) of polar vortex dynamics. First and second columns represent stratospheric NO$_2$ fields from DOMINO and SP, respectively, at local time of approximately 1330 LT. Third and fourth columns indicate the temperature and potential vorticity, respectively, at 50 hPa (1200 UTC) from ECWMF (ERA interim model version 1, analysis data).
Figure 10 shows that the Standard Product reproduces the seasonal trend of the stratospheric NO\textsubscript{2} but does not capture the short-term increases associated with the vortex displacement. This is also shown by the sequence of SP stratospheric NO\textsubscript{2} plots in Figure 9 (second column). Figure 10 (bottom) shows that the discrepancy between DOMINO and SP stratospheric NO\textsubscript{2} in case of large gradients in the stratospheric NO\textsubscript{2} field can be as large as $1 \times 10^{15}$ molecules/cm\textsuperscript{2}.

7. OMI Observations of the Diurnal Variation of Stratospheric NO\textsubscript{2}

As a result of OMI’s 2600 km wide swath, consecutive orbits start to overlap poleward of 30° latitude. The overlap increases with increasing latitude and results in up to 4 OMI overpasses per day at the same ground location near the Arctic circle. The number of overpasses is even higher for regions in midnight sun when OMI observations are possible during the descending part (“night-side”) of the orbit. For instance, Scoresby (70.5°N) can have as much as 7 OMI overpasses in summer. Therefore, OMI is able to sample the diurnal variation of stratospheric NO\textsubscript{2} from space with an interval of 100 min. Initial attempts to observing the diurnal variation of stratospheric NO\textsubscript{2} from space made use of climatological data [Sassi and Salby, 1999; Brohede et al., 2007]. Here we report for the first time on the direct observation of the diurnal variation in stratospheric NO\textsubscript{2} columns. Figure 11a shows the diurnal variation of DOMINO stratospheric NO\textsubscript{2} over Scoresby on individual days between 9 March and 8 October 2005. With the exception of very early measurements in June and July, stratospheric NO\textsubscript{2} increases quasi-linearly during the day. The number of daily overpasses increases from winter to summer as a result of the increasing number of sunlit hours with season. The slope of the curves in Figure 11a indicates that the increase rate of stratospheric NO\textsubscript{2} is larger in spring and fall than during summer. The low increase rate in summer results from the depletion of the N\textsubscript{2}O\textsubscript{5} reservoir by photodissociation during the long sunlit hours, while the nights are too short to replenish the reservoir. The DOMINO stratospheric NO\textsubscript{2} column over Scoresby in June–July (represented by the light and dark green lines in Figure 11a) decreases before 1000 LT (OMI measurements from the descending part of the orbit), and increases quasi-linearly after 1000 LT (OMI measurements from the ascending part of the orbit). We hypothesize that the early morning decrease is caused by the rising Sun, shifting the NO\textsubscript{x} partitioning toward NO. The observed early morning decrease and consecutive increase after 1000 LT (OMI measurements from the ascending part of the orbit) is consistent with SLIMCAT-based box model simulations [see, e.g., Celarier et al., 2008, Figure 2]. For comparison, Figure 11b shows the diurnal variation of DOMINO stratospheric NO\textsubscript{2} over Jungfraujoch. Because of its lower latitude (46.5°N), Jungfraujoch has at most two OMI overpasses per day. Apart from the seasonal increase in stratospheric NO\textsubscript{2}, we find that the increase rate is more constant throughout the year compared to the high-latitude sites. The weaker seasonal dependence of the increase rate is caused by the longer nights that allow for the replenishing of N\textsubscript{2}O\textsubscript{5}.
spheric NO$_2$ for Scoresby and other high-latitude SAOZ stations. The linear increase rates of stratospheric NO$_2$ for these high-latitude sites both show a distinct seasonal dependence, with stronger increases in spring and fall, reflecting the formation of N$_2$O$_5$ during the night in those seasons.

The increase rate is determined by a linear fit to OMI stratospheric NO$_2$ (forecast based on assimilation) of consecutive overpasses after 1000 LT. We also determined the increase rate using the measured slant columns divided by the geometric air mass factor. The resulting increase rates were very similar to the results presented in Figure 12a as is illustrated by the coplotted slant column-based increase rates for Kiruna (solid black boxes), showing that the increase rates reported here do not follow from the assimilation, but are actually observed.

At high latitudes, in spring and fall the increase rate is approximately $0.2 \times 10^{15}$ molecules/cm$^2$/h and drops to $0.05-0.1 \times 10^{15}$ molecules/cm$^2$/h in summer. For Salekhard and Zhigansk (orange and red data points in Figure 12a) the OMI-inferred increase rate in spring ($0.4 \times 10^{15}$ molecules/cm$^2$/h) is considerably higher than in fall ($0.15 \times 10^{15}$ molecules/cm$^2$/h). This asymmetry between spring and fall is likely caused by the collar of NO$_x$-rich (and warmer) air, which girds the Arctic polar vortex, that lies over Salekhard and Zhigansk in spring. In fall, the vortex and its surrounding collar are absent. The position and movement of the Arctic polar vortex in spring 2005 was discussed in section 6. The seasonal dependence of the increase rate derived from SAOZ measurements (Figure 12b) is similar to DOMINO, with a maximum in spring and fall, and a minimum in summer. SAOZ-inferred increase rates over Salekhard also indicate a higher increase rate in spring than in fall. During summer, SAOZ-derived increase rates for high-latitude sites are close to 0, which is consistent with the identical morning and evening SAOZ NO$_2$ columns over Sodankyla in summer reported by Goutail et al. [1994]. For midlatitudes, the OMI-derived increase rates (Figure 12c) are similar to those derived from SAOZ (Figure 12d), with weak seasonal dependence. The OMI and SAOZ-inferred increase rates over Jungfraujoch are comparable to the annual mean increase rate of $0.1 \times 10^{15}$ molecules/cm$^2$/h reported for Zugspitze [Süssmann et al., 2005]. For comparison, Gil et al. [2008] reported an annual mean increase of $0.06 \times 10^{15}$ molecules/cm$^2$/h over Izaña (28.3°N).

Figure 13 shows a map of the mean linear increase rate of OMI stratospheric NO$_2$ for the Northern Hemisphere, derived for the first (Figure 13, top) and second half (Figure 13, bottom) of March 2005. The geographical distribution of the increase rate closely resembles the morphology of the stratospheric NO$_2$ that was presented in Figure 9: the region with low increase rates coincides with the low NO$_2$ values inside the denoxified polar vortex and we find high increase rates for the air outside the vortex that is rich in reactive nitrogen. The mid-March break-up of the polar vortex is reflected in the geographical distribution and the values of the increase rate for the second half of March (Figure 13, bottom): the area with low increase rates has shrunk, and the value of the increase rates themselves has grown.

8. OMI Observed Trends Stratospheric NO$_2$

The DOMINO data set covers more than 5 years (October 2004 to May 2010) of global stratospheric and tropospheric NO$_2$ observations, which allows for the study of temporal variability on various time scales in stratospheric NO$_2$.

8.1. Seasonal Variation and QBO

Figure 14 shows a multiyear time series of zonally averaged DOMINO stratospheric NO$_2$ columns. Over the polar and midlatitudes, stratospheric NO$_2$ shows a distinct annual cycle that is related to the number of sunlit hours and peaks in summer. The annual cycle is strongest over the polar regions, because of wintertime denitriﬁcation in the polar night when stratospheric NO$_2$ is converted into the long-lived HNO$_3$ and N$_2$O$_5$ reservoirs. The latitudes between 60°-90°S show reduced NO$_2$ columns in Antarctic spring (OND) as a result of denitriﬁcation inside the polar vortex during winter and early spring.

Figure 14 shows consistently higher summertime values of stratospheric NO$_2$ over the Antarctic in comparison to the Arctic. This interhemispheric asymmetry in the summertime stratospheric NO$_2$ columns has also been observed in GOME [Wenig et al., 2004] and in Odin/OSIRIS measurements [Brohede et al., 2007]. Solomon et al. [1984] attribute this interhemispheric asymmetry to differences in the meridional circulation as the Southern Hemisphere exhibits much less planetary wave activity than the Northern Hemisphere. The weaker planetary wave activity in the Southern Hemisphere should result in less efficient transport away from the pole. Naudet et al. [1987] suggested that the lower albedo (more ocean) at visible wavelengths and larger solar zenith angles in the Southern Hemisphere (resulting from the smaller Earth-Sun distance in Southern Hemisphere summer) lead to less photodissociation and thus higher concentrations of NO$_2$ in the stratosphere. Model calculations by Cook and Roscoe [2009] show that the NO$_2$ partitioning depends on temperature, with an increase of the modeled NO$_2$ vertical column of
Therefore, it is likely that the higher summertime stratospheric NO$_2$ over Antarctica is also related to the Antarctic summer stratosphere being up to 8 K warmer than over the Arctic, owing to radiative (shorter Earth-Sun distance in January) and to dynamical effects [Rosenlof, 1996; Siskind et al., 2003].

For midlatitudes, we see a clear annual cycle in stratospheric NO$_2$, with an amplitude of approximately $1 \times 10^{15}$ molecules/cm$^2$. At higher latitudes the seasonal cycle is stronger as a result of the denoxification in winter. In the tropics the amplitude of the seasonal cycle is comparable to the amplitude of semiannual harmonics that, as we will show later, results from the quasi-biennial oscillation (QBO) [Reed et al., 1961]. The weaker seasonal cycle in the tropics reflects the weak seasonal variation in the solar irradiation and the lower stratospheric NO$_2$ concentration. In the tropics, tropospheric air enters the stratosphere. During the poleward transport by the Brewer-Dobson circulation, N$_2$O in this imported air is converted into NO$_y$ by the reaction with atomic oxygen. This leads to an increase of stratospheric NO$_2$ concentration with latitude and a build up of NO$_2$ in the polar regions.

The QBO is an oscillation in the equatorial zonal winds between 20 and 35 km altitude. The period of the oscillation ranges between 23 and 34 months, with a mean period of 28 months, hence the name quasi-biennial. The QBO in stratospheric ozone has been observed for many years [Funk and Garnham, 1962], but its effect was
observed for the first time in stratospheric NO$_2$ by analysis of altitude-resolved SAGE II measurements [Zawodny and McCormick, 1991]. They attribute the NO$_2$-QBO mainly to QBO-induced modulations in the vertical transport of NO$_x$ in the equatorial region, because changes in the NO$_x$ partitioning due to changes in observed temperature and ozone concentrations are insufficient to explain the NO$_2$-QBO. Ground-based observations at midlatitudes and high latitudes suggest that the NO$_2$-QBO is not confined to the tropics: analysis of long-term measurement series reveals a correlation between the QBO cycle and variations in the overhead stratospheric NO$_2$ column at Lauder [Liley et al., 2000] and over Antarctica [Cook and Roscoe, 2009]. Liley et al. [2000] propose that the QBO affects stratospheric NO$_2$ outside the tropics “dynamically,” by changing transport rates of relevant chemical species.

[54] We now analyze the OMI NO$_2$ time series with the multilinear regression methods described by Zawodny and McCormick [1991], Liley et al. [2000] and Gruev and Elokhov [2009] in search of the QBO. The employed fitting model

\[ y(t) = A_0 + \sum_{i=1}^{3} \Gamma_i + A_d t + A_{\text{QBO}}(t + \phi_{\text{QBO}}) + A_I(I_{\text{QBO}}) + A_I(I_{\text{ENSO}}) + X(t) \]

(4)

(with $\Gamma_i = A_i \sin(\frac{2\pi i}{365.25}) + B_i \cos(\frac{2\pi i}{365.25})$ harmonic terms with 12, 6 and 4 month periodicity) contains background ($A_0$) and linear trend ($A_d t$). The harmonic terms with 12 and 6 months periodicity describe the annual cycle and the asymmetry between the equinoctial periods, respectively. Additional index terms describe the QBO ($I_{\text{QBO}}$), Solar Index ($I_S$) and El Niño–Southern Oscillation ($I_{\text{ENSO}}$); $\phi_{\text{QBO}}$ and $\phi_{\text{ENSO}}$ represent the phase (lag) of the QBO and of the ENSO terms, respectively. The QBO index is given by the monthly mean of the zonally averaged equatorial winds at 30 hPa calculated by the NCEP/NCAR Climate Data Assimilation System (http://www.cpc.ncep.noaa.gov/data/indices/qbo.u30.index). The Solar Index $I_S$ is parameterized by the monthly means of the solar radio flux density at 10.7 cm (ftp://ftp.ngdc.noaa.gov/STP/SOLAR_DATA/SOLAR_RADIO/FLUX/Penticton_Absolute/monthly). The ENSO index $I_{\text{ENSO}}$ is based on the monthly mean sea level pressure difference between Tahiti and Darwin (http://www.bom.gov.au/climate/current/soihtm1.shtml). $I_{\text{QBO}}$, $I_S$ and $I_{\text{ENSO}}$ are scaled to $[-1, 1]$. Prior to applying the fitting model to the OMI data series, we tested our fitting procedure by reproducing the coefficients reported by Liley et al. [2000] for stratospheric NO$_2$ observed at NDACC station Lauder between 1981 and 1999. As shown in Table 3 we found a trend of +5.2(±0.5)% per decade, which is consistent with the +5% per decade reported by Liley. Similar to their approach we fixed the lag of the QBO and ENSO terms of 140 days and 13 months, respectively. Additional terms were used to account for the El Chichón (April 1982) and Pinatubo (June 1991) eruptions (see Liley et al. [2000] for details). The amplitude and lag of the QBO index are free parameters in the fit to the global OMI data set. The SI and ENSO terms were not fitted because these parameters affect the fitting stability at certain latitudes, resulting in an irregular latitudinal dependence of...
the background term, furthermore their contribution to the resulting fit is relatively small.

[55] As a confidence check we also employed the fitting model of Zawodny and McCormick [1991], who parameterize the QBO by harmonics with 18, 24 and 30 month periodicity. These harmonic functions adequately parameterize the QBO index for the limited time range of the OMI data set, and this parameterization yields more stable fits than the tabulated monthly mean QBO index. The harmonic fitting model produces the same results as the fitting model based on work by Liley et al. [2000]. The fitting model, whose results are presented in Figure 15, shows that the ratio of the NO$_2$-QBO and the annual term (green trace in Figure 15f) peaks in the tropics with maxima located around 15°S and 5°N. The amplitude of the NO$_2$-QBO in the tropics is comparable to the annual term, which is illustrated by Figures 15a, 15b and 15e and by Figure 14. The OMI time series show a clear interhemispheric asymmetry in the NO$_2$-QBO: its peak value is nearly 2 times larger in the Southern Hemisphere than in the Northern Hemisphere. Furthermore the NO$_2$-QBO peaks at 15°S in the Southern Hemisphere versus 5° in the Northern Hemisphere. This is illustrated by Figures 15a, 15b, 15d and 15e, showing the OMI time series for 5°S, 15°S, 5°N, and 15°N, respectively.

Other studies into the QBO such as those of Zawodny and McCormick [1991], Dunkerton [2001], Randel and Wu [1996], usually report QBO anomalies that are equatorially symmetric in the tropics. However, these studies involve

Table 3. Fitted Trends in Ground-Based (Lauder) and Ozone Monitoring Instrument (OMI) Stratospheric NO$_2$ Over Lauder

<table>
<thead>
<tr>
<th>Period</th>
<th>Trend (%/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981–1999</td>
<td>5.2(±0.5)</td>
</tr>
<tr>
<td>1981–2010</td>
<td>5.2(±0.5)</td>
</tr>
<tr>
<td>2004–2010</td>
<td>0.4(±2)</td>
</tr>
<tr>
<td>2004–2010</td>
<td>0.6(±2)</td>
</tr>
</tbody>
</table>

*The errors are estimated by varying the length of the fitting window with ±1 year.

The background term corresponds to $A_0$ in equation (4). The harmonic term $a_1$ in equation (4) yields the annual term via the following trigonometry relations: $a_1 \sin(2\pi t/25) + \phi = a_1 \cos(\phi)\sin(2\pi t/25) + a_1 \sin(\phi) \cos(2\pi t/25)$, where $a_1 \cos(\phi)$ and $a_1 \sin(\phi)$ equal the parameters $A_1$ and $B_1$, respectively. Then $\phi = \arctan(B_1/A_1)$, and the annual term corresponds to $A_1/\cos(\phi)$.
Figure 16. Time series of sunrise stratospheric NO\textsubscript{2} columns measured at Lauder (black line) and collocated DOMINO stratospheric NO\textsubscript{2} columns (red diamonds). Data were averaged in 7 day bins and a three point wide running average filter was applied to remove outliers that occasionally occur in the Lauder series in winter. The Lauder data was downloaded from ftp://ftp.cpc.ncep.noaa.gov/ndacc/station/lauder/ames/uvvis/.

8.2. Long-Term Trends in Stratospheric NO\textsubscript{2}

[57] Figure 16 shows the agreement between collocated OMI stratospheric NO\textsubscript{2} data and the 1981–2010 time series of ground-based stratospheric NO\textsubscript{2} columns measured at Lauder at sunrise. OMI generally reproduces the values of the summer maxima and their year-to-year variability. This shows the potential of instruments such as OMI, and presumably also GOME and SCIAMACHY, to contribute to observing trends in stratospheric NO\textsubscript{2} from space, provided that the data record is of sufficient length.

[58] For the 1981–1999 period Liley et al. [2000] report a 5.3% per decade increase in stratospheric NO\textsubscript{2}, which is twice the well-known 2.5% per decade increase rate of tropospheric N\textsubscript{2}O [World Meteorological Organization, 2007]. This increase remains unchanged when the Lauder data record is extended to 2010. (As shown in Table 3, this trend in stratospheric NO\textsubscript{2} over Lauder cannot be reproduced by OMI because of the short time period with measurements.) For the time span of the OMI mission (2004–2010) the Lauder data yields an increase of 0.4(±2)% per decade, which is similar to the 0.6(±2)% per decade increase of stratospheric NO\textsubscript{2} derived from the OMI data over Lauder. For instance, for 1995–2010 we find a trend of +3.0 (±1)% per decade, showing that a 15 year period is also too short to reproduce the trend observed in Lauder between 1981 and 1999 (and 1981–2010).

9. Summary and Conclusions

[59] We have presented stratospheric NO\textsubscript{2} columns obtained from OMI with a data assimilation approach that makes use of the TM4 chemistry transport model. For each OMI observation, we calculate the stratospheric NO\textsubscript{2} column from the TM4 forecast that is based on the analyzed model state. The assimilation of OMI NO\textsubscript{2} total columns in TM4 corrects the tendency of the stratospheric part of the model to diverge from the observations. The scheme is insensitive to tropospheric contributions, and results in a forecast model state that is generally within 0.15 × 10\textsuperscript{15} molecules/cm\textsuperscript{2} of the analysis over remote areas where stratospheric NO\textsubscript{2} dominates the total column.

[60] The evaluation of ground-based techniques for measuring stratospheric NO\textsubscript{2} shows that UV-Vis and FTIR retrievals are only consistent within 15–20% due to inaccuracies in, e.g., the assumed profile and air mass factor, casting some doubt on their usefulness as “ground-truthing” for satellite retrievals. Lacking an alternative, we used ground-based UV-Vis and FTIR measurements from 14 mostly pristine locations in the world to validate the Dutch OMI NO\textsubscript{2} (DOMINO) retrieval (based on data assimilation) and the NASA GSFC Standard Product. OMI retrievals and ground-based estimates of stratospheric NO\textsubscript{2} columns agree on average within 0.3 × 10\textsuperscript{15} molecules/cm\textsuperscript{2} (13%), comparable to the accuracy of the ground-based instruments.

[61] Stratospheric NO\textsubscript{2} retrieved from the DOMINO retrieval on average exceeds the Standard Product by 0.2 × 10\textsuperscript{15} molecules/cm\textsuperscript{2}, but on short spatial and time scales, larger biases occur (up to 1 × 10\textsuperscript{15} molecules/cm\textsuperscript{2}). Synoptic-scale differences between the two retrievals are explained by differences in the stratospheric air mass factors, and by the spatial smoothing technique used in the Standard Product algorithm. Differences between stratospheric air mass factors can be as high as 8% for specific satellite viewing angles, partly because of interpolation errors in the Standard Product air mass factor look-up table that has only few reference viewing angles. The considerable differences resulting from the air mass factors are dampened by the spatial smoothing (wave-2 fit) in the Standard Product.

[62] The OMI data record runs from October 2004 onward and covers more than 5 years. This allows for the study of temporal variability in stratospheric NO\textsubscript{2} columns on various time scales. During Arctic winter, DOMINO retrievals show low stratospheric NO\textsubscript{2} concentrations within the Arctic polar vortex and higher NO\textsubscript{2} in adjacent regions. The morphology of the stratospheric NO\textsubscript{2} field in the wider vortex area closely resembles the temperature distribution at 50 hPa. A study of day-to-day variability in stratospheric NO\textsubscript{2} shows that DOMINO captures the collapse of the polar vortex during late winter, corroborated by ground-based NO\textsubscript{2} observations over Sodankylä and Jungfraujoch. The early springtime stratospheric NO\textsubscript{2} columns correlate strongly with stratospheric (30–50 hPa) temperatures, reflecting the temperature dependence of the N\textsubscript{2}O\textsubscript{5} (photo) dissociation rate and of the NO\textsubscript{2} partitioning.
[64] Using the overlapping orbits poleward of 30° latitude, we find that it is possible to observe the diurnal variation in stratospheric NO$_2$ columns with OMI. At high latitudes (>60°), the diurnal increase rate has a distinct seasonal dependence with a maximum in spring and fall, which is consistent with increase rates inferred from SAOZ measurements at sunrise and sunset. The low increase rates at high latitudes in summer are attributed to the near-depletion of stratospheric N$_2$O$_5$, resulting from the long sunlight hours. A map of OMI-derived increase rates shows that in late winter its geographical distribution follows the morphology of the stratospheric NO$_2$ field with low increase rates inside the denoxified Arctic polar vortex and high increase rates in the NO$_2$-rich air outside the vortex.

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