

1 **Reply to reviewers**

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3 Reviewer #1:

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5 During discussion, I brought up only one major concern, which I however consider to be
6 crucial:

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8 My main concern is that the study does not at all account for seasonality, while all involved
9 components (NO_x emissions (heating, lightning, biomass burning), NO_x lifetime, convection
10 patterns, NO_x profiles, and cloud characteristics) can vary strongly over the year. The value
11 of an annual mean pseudoprofile is thus questionable, as the different cloud pressure levels
12 and the corresponding NO₂ columns are not at all equally distributed over the year.

13

14 That is correct.

15

16 Previous cloud slicing studies have considered seasonality (e.g. Liu et al. for CO and Choi et
17 al. for NO₂), and I see no reason why this study does not. Thus, I recommend to perform the
18 cloud slicing on a seasonal basis. If statistics is too low for 3 months, the seasons from several
19 years can be merged. This requires major revisions, but will yield better interpretable
20 pseudoprofile and very likely strengthen the discussion of the model comparison."

21

22 We have introduced a new section (Section 3.6) titled "Seasonal Analysis", showing what
23 results from applying the cloud slicing technique on a seasonal basis over the year 2006.
24 Statistics from 3 months of data were strong enough to obtain results that are meaningful,
25 consistent with available climatologies, and in line with the conclusions that we drew from
26 the annual means.

27

28 The authors refuse to deal with this concern, not for scientific reasons, but to limit the paper
29 range. I can understand this point, as the paper is indeed not short. But still, I am convinced

1 that a seasonal analysis would strengthen the message of the study significantly (a seasonal
2 mean NO_x profile makes sense, while an annual mean NO_x profile derived from cloud slicing
3 can actually entangle a summer profile at high altitudes (lightning, convection) with a winter
4 profile at low altitudes), and I would definitely prefer a discussion of meaningful (seasonal
5 mean) pseudoprofiles over a discussion of something hard to assess (annual mean
6 pseudoprofile).

7
8 The possibility of entangling a profile from one period (e.g. summer) at high altitudes with a
9 profile from a different period (e.g. winter) at low altitudes is inherent to cloud slicing. This
10 possibility constitutes part of the pseudoprofile error: "... called representation error, because
11 a profile measured under high cloud conditions is not representative of a profile under low
12 cloud conditions, nor in general representative of an average cloudy state". For annual as
13 well as seasonal means, this type of error may be corrected using a model-based
14 pseudoprofile-to-profile ratio. A more explicit mention to the entanglement of seasonal
15 features in annual mean pseudoprofiles has been inserted in Section 2.1.3 ("Error Analysis")

16
17 In Section 4 ("Summary and conclusions"), we added the following paragraph:

18 "Handling pseudoprofile errors is another matter. The presence of systematic pseudoprofile
19 error in cloud-slicing estimates and its general predominance over instrumental error suggest
20 that the vertical information contained in cloudy pixels may be extracted optimally by an
21 assimilation procedure that improves the atmospheric state (i.e. the model profile shape) at the
22 right time and location using the averaging kernel of the observation."

23
24 I propose to focus the discussions and figures to one season in the paper and provide the other
25 seasons in a supplement, which could help to limit the amount of extra work, as the overall
26 structure of the paper would remain unchanged.

27
28 We opted to keep the discussion on annual means, since they support our main conclusion
29 (that they provide an observational constraint with the capability to resolve tropospheric

1 processes vertically as well as geographically), and to include the seasonal analysis as a
2 complementary result.

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4 The revised manuscript does hardly mention the aspect of seasonality and does not discuss its
5 impact at all. I can not recommend publication in ACP before this is revised.

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1 Reviewer #2:

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3 1) A priori discussion

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5 I appreciate that the authors discuss the effects of a priori profile in the response. I think the
6 authors need to include the entire discussion, not just the sentence, in the manuscript in a
7 separate section, so the discussion will be available for readers in the manuscript.

8

9 Thank you. We have included a separate section titled "On the influence of a priori
10 information" as Supplementary Material.

11

12 2) Error discussion

13

14 First, I suggest the subsection heading "Retrieval error" instead of "Retrieval (random) error"
15 since the retrieval error is not random in reality.

16

17 We removed the word "random" from the section header.

18

19 And again, I would like the authors to add the discussion of the retrieval error in the response
20 to the "Retrieval error" subsection in the manuscript.

21

22 Done. We justified the derivation of retrieval error and put it in relation to pseudoprofile
23 error.

24

25 3) Regarding the model usage in this study

26

27 Overall, authors utilize the model in many ways in this study, e.g., determining the below-
28 cloud column (as a priori), and prescribing the difference in the "true" profiles and the
29 pseudoprofiles, both of them are impossible without trust in the model.

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On the other hand, authors discuss the differences in cloud slicing results and the model and mention a number of model shortcomings. This seems a bit ironic, regarding the cloud slicing study would be impossible without trust in the model.

I understand that the model is the only resource that can be utilized to apply the cloud slicing technique over the global atmosphere, at the same time, however, model DOES have uncertainties, due to the limited human knowledge of atmospheric chemistry. I would like authors to note this in the manuscript, possibly in the subsection to introduce the model.

We introduced the following sentence in Section 4 (“Summary and conclusions”):

Note that support from a CTM model (the TM4 in our case) is required to make provision for the cloud-slicing technique (in order to determine a priori corrections for undercloud leakage), so that a level of trust must initially be placed in the model. When comparing the resulting pseudoprofiles against those of the model, a number of potential model shortcomings are found which work against our initial trust in the model corrections. This conflicting outcome should be understood and justified to the extent that a priori corrections have a limited impact on the resulting cloud slicing profiles.

OMI tropospheric NO₂ profiles from cloud slicing: constraints on surface emissions, convective transport and lightning NO_x

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Abstract

We derive a global annual and seasonal climatology of tropospheric NO₂ profiles from OMI cloudy observations for the year 2006 using the cloud slicing method on six pressure levels centered about 280, 380, 500, 620, 720 and 820 hPa. A comparison between OMI and the TM4 model tropospheric NO₂ profiles reveals striking overall similarities, which confer great confidence to the cloud-slicing approach to provide details that pertain to annual as well as to seasonal means, along with localized discrepancies that seem to probe into particular model processes. Anomalies detected at the lowest levels can be traced to deficiencies in the model surface emission inventory, at mid tropospheric levels to convective transport and horizontal advective diffusion, and at the upper tropospheric levels to model lightning NO_x production and the placement of deeply transported NO₂ plumes such as from the Asian summer monsoon. The vertical information contained in the OMI cloud-sliced NO₂ profiles provides a global observational constraint that can be used to evaluate chemistry transport models (CTMs) and guide the development of key parameterization schemes.

1 Introduction

Global maps of tropospheric NO₂ vertical column densities (VCDs) derived from satellite UV/Vis nadir sounders such as OMI, GOME and SCIAMACHY have contributed to the development of a variety of applications. Clear sky observations of tropospheric NO₂ VCDs, those with cloud fractions typically below 25%, have been used to constrain surface NO_x

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1 emission inventories (Martin et al., 2003) (Mijling and Van der A, 2012) (Miyazaki et al.,
2 2012), detect and monitor point source emission trends (Richter et al., 2005) (Van der A et al.,
3 2008) and constrain surface NO₂ lifetimes (Beirle et al., 2011) to cite a few examples. Still
4 cloudy conditions predominate, which prevent the detection of NO₂ concentrations at the
5 surface. For OMI, more than 70% of the measurements collected in the extratropics is
6 affected by clouds and typically discarded, with the consequent loss of information. The
7 utilization of cloudy data from satellite IR and UV/Vis nadir sounders provides access to a
8 large repository of observations with potential to reveal information about trace gas
9 concentrations at different altitudes and to constrain the parameterizations of a number of
10 cloud related processes.

11 Clouds are introduced in general circulation models (GCMs) because of their broadband
12 radiative effects and direct relation with the water vapour feedbacks and precipitation (Jakob,
13 2003). Clouds also affect the redistribution of trace gases via convection and interaction with
14 chemistry, which are essential elements in chemistry transport models (CTMs). Convective
15 transport of polluted plumes (including NO_x, but also HO_x, CO and non-methane
16 hydrocarbons NMHC) from the boundary layer can cause substantial enhancement of upper
17 tropospheric ozone, an important anthropogenic greenhouse gas (Pickering et al., 1992). At
18 high altitudes, enhanced chemical lifetimes and stronger winds are also responsible for the
19 long-range transport of pollutants. Still the exchange between environment and cloud air that
20 determines the way that convective columns evolve (i.e. the entrainment and detrainment
21 rates in mass flux schemes) remains uncertain. The presence of convective clouds not only
22 transports pollutants vertically, it also removes soluble species (like HNO₃) by precipitation,
23 and modulates photolysis rates by altering the actinic fluxes above and below the cloud (Tie
24 et al., JGR, 2003). Associated with the deepest convective clouds, the production of NO_x by
25 lightning is a key component of the NO₂ budget in the upper troposphere, not only because of
26 its relation with O₃ production, but because it affects the general oxidizing capacity of the
27 atmosphere and the lifetimes of tracers destroyed by reactions with OH - like CO, SO₂ and
28 CH₄. Yet the source strength and spatial distribution of lightning NO_x emissions remain
29 uncertain – with a global best estimate of 5±3 Tg a⁻¹ (Schumann and Huntrieser, 2007).

30 In large scale global CTMs, convection and other cloud related processes such as scavenging
31 and lightning NO_x production are represented by sub-grid parameterizations. Most convective
32 parameterizations are tested against temperature and humidity profiles from radiosondes

1 (Folkens et al., 2006), but chemical tracers provide additional constraints. A number of studies
2 have tried to quantify the effect of different convective schemes on tropospheric CO and O₃
3 profiles using satellite based climatologies for comparison with model data (Mahowald et al.,
4 1995) (Barret et al., 2010) (Hoyle et al., 2011) finding the largest discrepancies in the tropical
5 middle and upper troposphere. Even though NO₂ may appear unsuitable as a tracer of air
6 motion because of its high reactivity with other NO_y members (such as N₂O₅, HNO₃, PAN,
7 NO₃⁻ and HNO₄) and the presence of time-varying sources (mainly surface emissions and
8 lightning NO_x, but also aircraft and stratospheric inflows), its short lifetime makes it attractive
9 to study very fast transport mechanisms like convection. A number of studies have
10 demonstrated the capabilities of satellite UV/Vis sounders to estimate the source strength and
11 3D distribution of lightning NO_x over cloudy scenes [(Boersma et al, 2005), (Beirle et al,
12 2006), (Martin et al. 2007) and (Miyazaki et al., 2014)]. These studies have found good
13 agreement between modeled and observed lightning NO₂ over the tropical continents – albeit
14 with discrepancies in the geographical and vertical distributions. Other studies have compared
15 the performance of lightning parameterizations against satellite lightning flash densities, like
16 (Tost et al., 2007) and (Murray et al., 2012), to conclude that it is difficult to find a good
17 combination of convective and lightning scheme that accurately reproduces the observed
18 lightning distributions - leaving the problem of the NO_x yield per flash aside. So there is a
19 clear need for measurements with which the development of model parameterizations of
20 convective transport and lightning NO_x schemes can be guided.

21 In this paper, we use a variation of the cloud slicing technique first developed by (Ziemke
22 et al., 2001) for tropospheric ozone, and later exploited by (Liu et al., 2014) for tropospheric CO
23 and (Choi et al., 2014) for tropospheric NO₂, based on the increments of gas vertical column
24 density above cloud as a function of cloud pressure within a certain longitude/latitude/time
25 cell. Obviously, large cloud fractions and some degree of cloud height diversity within the
26 cell are conditions required for this technique to produce useful results. The cloud slicing
27 approach applied by (Choi et al., 2014) on OMI NO₂ data was able to find signatures of
28 uplifted anthropogenic and lightning NO₂ in their global free-tropospheric NO₂
29 concentrations, as well as in a number of tropospheric NO₂ profiles over selected regions. In
30 this work, global annual NO₂ VMR profiles are generated at a spatial resolution of 2°x2° on
31 pressure levels centered about 280, 380, 500, 620, 720 and 820 hPa. We give particular
32 consideration to the scattering sensitivity of the OMI measurements above the cloud, as well
33 as to the representativity of the cloud-sliced profiles with regard to a cloudy atmosphere. We

report on results from this methodology as well as its direct applicability as observational constraint using a state-of-the art chemical transport model.

2 Methodology

The methodology to produce observed and modeled annual climatologies of tropospheric NO₂ VMR profiles under cloudy scenes starts with a description of the OMI and TM4 datasets involved. We introduce the pre-processing steps required to estimate NO₂ VCDs above cloud from OMI slant column measurements, followed by the upscaling steps required to bring the spatial resolution of the satellite observations in line with the TM4 model grid for comparison.

OMI NO₂ products

The NO₂ slant columns used in this work are retrieved by the UV/Vis spectrometer OMI [Ozone Monitoring Instrument, (Levelt et al., 2006)] according to the KNMI DOMINO version 2.0 (Boersma et al., 2007) (Boersma et al., 2011). The data files, which include total and stratospheric slant columns, averaging kernel information, cloud fraction, cloud pressure and assimilated trace gas profiles from the TM4 model, are available at <http://www.temis.nl/airpollution/no2.html>.

Of particular importance to this study are the cloud pressures and fractions retrieved by the OMI O₂-O₂ cloud algorithm (Acarreta et al, 2004). The OMI O₂-O₂ cloud algorithm uses an optically thick lambertian cloud model with a fixed albedo of 0.8; the fraction of this lambertian cloud model covering the pixel is called effective cloud fraction [$c_{\text{eff}} = (R_{\text{obs}} - R_{\text{clear}})/(R_{\text{cloudy}} - R_{\text{clear}})$], where R_{cloudy} and R_{clear} are modeled clear and cloudy sky reflectances, and R_{obs} is the observed continuum reflectance – i.e. the reflectance with the O₂-O₂ absorption line removed], which is not the same as the geometric cloud fraction but an equivalent amount that yields the same top of atmosphere (TOA) reflectance as observations; the altitude level of the lambertian cloud model is then adjusted so that it results in the same amount of O₂-O₂ absorption as in observations [Stammes et al., 2008]. The OMI O₂-O₂ cloud pressure refers to the optical radiative cloud pressure near the midlevel of the cloud and below the MODIS infrared-based cloud top, which is about 250 hPa higher than OMI for deep convective clouds or about 50-70 hPa higher for extratropical midlevel clouds. The OMI O₂-O₂ cloud pressure has been validated against PARASOL with a mean difference below 50 hPa and a standard deviation below 100 hPa (Stammes et al., 2008). The OMI O₂-O₂ cloud fraction has been validated against MODIS with a mean difference of 0.01 and standard deviation of 0.12 over

cloudy scenes (effective cloud fractions larger than 50% without surface snow or ice) (Sneep et al., 2008). In this paper, we use the cloud radiance fraction defined as $CRF = c_{eff} R_{cloudy}/R_{obs}$ – which represents the weight of the air mass factor of the cloudy part.

TM4 model

The TM4 chemistry transport model has a spatial resolution of $2^\circ \times 3^\circ$ with 35 sigma pressure levels up to 0.38 hPa (and approximately 15 levels in the troposphere) driven by temperature and winds from ECMWF reanalyses and assimilated OMI stratospheric NO_2 information from previous orbits. The tropospheric chemistry scheme is based on (Houweling et al., 1998) using the POET emissions (Olivier et al., 2003) database based on the EDGAR inventory for anthropogenic sources, which are typical of years 1990-1995, with biomass emissions of NO_x based on ATSR fire counts over 1997-2003 and released in the lowest model layers. The photolysis rates are calculated as in (Landgraf and Crutzen, 1998) and modified as in (Krol and van Weele, 1997). In the TM4 model, the physical parameterization for convective tracer transport is calculated with a mass flux scheme that accounts for shallow, mid-level and deep convection (Tiedtke, 1989). Large scale advection of tracers is performed by using the slopes scheme of (Russell and Lerner, 1981). The lightning NO_x production is parameterized according to (Meijer et al., 2001) using a linear relationship between lightning intensity and convective precipitation, with marine lightning 10 times less active than continental lightning and scaled to a total annual of 5 TgN/yr (Boersma et al., 2005). The vertical lightning NO_x profile for injection into the model is an approximation of the outflow profile suggested by (Pickering et al., 1998). Including free-tropospheric emissions from air-traffic and lightning, the total NO_x emissions for 1997 amount to 46 TgN/yr. More about this model may be found in (Boersma et al., 2011) and references therein.

2.1 Cloud slicing

A technique initially developed for estimating upper tropospheric ozone using nadir sounders (Ziemke et al., 2001), cloud slicing consists in arranging collections of trace gas VCDs measured above clouds against cloud pressure over a certain area and time period in order to estimate a gas volume mixing ratio (VMR) via the pressure derivative as:

$$VMR = 0.1 \cdot g \cdot M_{air}/N_A \cdot \frac{\partial VCD}{\partial p} \quad (1)$$

where $g = 9.8 \text{ m/s}^2$, $M_{air} = 28.97 \text{ g/mol}$ and $N_A = 6.022 \times 10^{23} \text{ molec/mol}$ with VCD expressed in molec/cm^2 and cloud pressure expressed in hPa. The method determines an average trace gas

volume mixing ratio over a certain area, time period and cloud pressure interval (Choi et al., 2014). In this paper, annual average tropospheric NO₂ VCD lat/lon grids from OMI and TM4 are produced for six tropospheric layers with bottom cloud pressures located within pressure intervals centered at about 330, 450, 570, 670, 770 and 870 hPa. The cloud pressure intervals used for cloud slicing were chosen after several trial runs and are laid out in Table 1 and Fig. 1. An annual climatology of NO₂ VMR profiles is then estimated after differencing the annual tropospheric VCD arrays above cloud with respect to pressure.

Figure 1 shows the latitude-height section of annual zonal mean OMI cloud frequency for the year 2006, showing that cloud slicing does not provide uniform global sampling. Most high clouds (mainly deep cumulus, since cirrus pass generally undetected by OMI) occur along the intertropical convergence zone (ITCZ) near the equator and over tropical continents, but can also be seen in the mid-latitude storm track regions and over mid-latitude continents in the summer; mid-level clouds are prominent in the midlatitude storm tracks, usually guided by the tropospheric westerly jets, and some occur in the ITCZ; low clouds, including shallow cumulus and stratiform clouds, occur essentially over the oceans but are most prevalent over cooler subtropical oceans and in polar regions (Boucher et al, 2013). In summary, cloud sampling proves best at low to mid altitudes in the extratropics and mid to high altitudes in the deep tropics. On the contrary, cloud sampling is typically poor off the west coasts of subtropical (Pacific, Atlantic and Indian) landmasses at high altitudes - which are areas of large-scale subsidence with persistent low stratocumulus, and at low altitudes over the tropical landmasses, particularly the Amazon basin and Central Africa.

2.1.1 NO₂ above cloud

The tropospheric NO₂ vertical column density above the cloud VCD_{above} for an instrument like OMI is defined here as a function of the total slant column SCD as:

$$VCD_{above} = (SCD - SCD_{strat} - SCD_{below})/AMF_{above} \quad (2)$$

Where SCD_{strat} is the stratospheric slant column, SCD_{below} accounts for the slant surface component leaked from below the cloud (i.e. the amount of surface signal that seeps through the cloud for partially cloudy conditions), and AMF_{above} denotes the scattering sensitivity above the cloud. The stratospheric slant column arises from TM4 model stratospheric profiles assimilated to OMI observations over unpolluted areas (Belmonte Rivas et al., 2014). The undercloud leaked component is defined as:

$$SCD_{below} = (1 - CRF) \cdot \sum_{ground}^{CLP} m_{clear}(p) \cdot n(p) \cdot T_{corr}(p) \quad (3)$$

Where CRF is the cloud radiance fraction, m_{clear} is the clear sky component of the scattering sensitivity (purely dependent on Rayleigh scattering and surface albedo), $n(p)$ is the a priori trace gas profile (i.e. the TM4 model), and T_{corr} is the OMI temperature correction defined below. Note that the summation goes from the ground to the cloud level pressure CLP (see Fig. 2), where the cloud level is given by the OMI O₂-O₂ cloud pressure. The scattering sensitivity above the cloud AMF_{above} is defined as (see appendix A):

$$AMF_{above} = \sum_{CLP}^{tropopause} m(p) \cdot n(p) \cdot T_{corr}(p) / \sum_{CLP}^{tropopause} n(p) \quad (4)$$

Where m is the total scattering sensitivity [usually defined as $(1-CRF) m_{clear} + CRF m_{cloudy}$ as in (Boersma et al., 2004)]. Note that the summation in this case goes from cloud level to the tropopause (see Fig. 2). The total scattering sensitivity m has been derived from the averaging kernel $AK(p)$ as:

$$m(p) = AK(p) \cdot AMF / T_{corr}(p) \quad (5)$$

Where AMF is the total airmass factor (used to compute the total vertical column $VCD = SCD/AMF$ from the total slant column SCD , and different from the tropospheric airmass factor AMF_{trop} used to compute $VCD_{trop} = SCD_{trop}/AMF_{trop}$). The temperature correction is defined as in (Boersma et al., 2004) and accounts for the temperature dependence of the NO₂ absorption cross-section and its influence on the retrieved slant column using ECMWF temperatures:

$$T_{corr}(p) = (220 - 11.4) / [T(p) - 11.4] \quad (6)$$

The elements of the averaging kernel contain the height dependent sensitivity of the satellite observation to changes in tracer concentrations and they are calculated with a version of the Doubling Adding KNMI (DAK) radiative transfer model in combination with TM4 simulated tropospheric NO₂ profiles. Of central importance to our cloud slicing approach is that an undercloud leaked component (SCD_{below}) is removed from the tropospheric slant column, and a scattering sensitivity above the cloud (AMF_{above}) is used to estimate the vertical column density above the cloud VCD_{above} . This is in contrast with the methodology applied in (Choi et al., 2014), where undercloud leakages are neglected (making tropospheric estimates more sensitive to surface contamination, particularly at low cloud fractions), and the scattering sensitivity above the cloud assumed equal to the geometric airmass factor.

As far as model quantities are concerned, the NO₂ column above the cloud in TM4 is simply calculated as:

$$VCD_{above} = \sum_{CLP}^{tropopause} n(p) \quad (7)$$

Where $n(p)$ is the a priori trace gas profile (i.e. the TM4 model). Note that the a priori gas profiles, originally reported on hybrid sigma pressure grids, have been resampled onto a uniform pressure grid with steps of 23.75 hPa to simplify averaging operations. The cloud level pressure that defines the model above-cloud NO₂ columns in Eq. (7) is the same OMI O₂-O₂ cloud pressure used for cloud slicing. Using OMI's cloud information to sample the TM4 model amounts to assuming that cloud altitudes and fractions in the model are identical to those observed by OMI. We know that differences between instantaneous model and observed cloud fields can be notable, but we also know that current model cloud fields are able to reproduce the average geographical and vertical distribution of observed cloud amounts reasonably well (Boersma et al., 2015), albeit with reports of underestimation of the low cloud fractions in the marine stratocumulus regions, underestimation of the midlevel cloud fractions everywhere, and slight overestimation of the high cloud fraction over the deep tropics (Nam et al., 2014) - errors that are likely related to the microphysical cloud and convection parameterizations. Therefore, using an observed cloud field to probe into model cloud processes, though probably suboptimal in case by case studies, is likely to be fine in an annual average sense.

2.1.2 Spatial averaging

A comparison of OMI observations with a model such as TM4 should also take into account the inhomogeneity of the tropospheric NO₂ field, which is usually large due to the presence of strong point sources and weather-scale variability. The model NO₂ columns should be viewed as areal averages, given that the limit of scales represented in the model is given by its resolution. Thus it is important to aggregate OMI observations to attain the same spatial resolution used by the model. The OMI NO₂ VCD above cloud observations (with a nominal spatial resolution of 13x24 km at the swath center) are aggregated onto daily 1°x1° longitude-latitude bins – later spatially smoothed to 2°x2° – before comparison with the afternoon TM4 model outputs defined on a 2°x3° grid on a daily basis as in Eq. (7). The aggregated OMI product collects all VCDs observed within a specified period (1 day) with solar zenith angle less than 70°, surface albedo less than 30% and CRF larger than 20% at the OMI pixel level

(roughly equivalent to an effective cloud fraction of 10%, which is a minimum condition for cloud fraction and pressure to be properly reported by OMI). No weighting is applied. At this point, populating the grid bins with as many OMI measurements as possible is important in order to avoid spatial representation errors between the two records (a partially filled bin may not be representative of what occurs over the entire cell, which is what the model represents). The aggregated CRF (and all other OMI and model quantities) are then evaluated at grid resolution, and a CRF threshold of 50% at cell level is applied to both observations and model data. The annual mean tropospheric VCD above cloud is then calculated per pressure layer using the CLP thresholds specified in Table 1 on daily gridded OMI and TM4 NO₂ VCD outputs, provided there are at least 30 measurements in a bin.

2.1.3 Error analysis

In the cloud slicing method, the derivation of annual mean VMR profiles from annual layered VCD amounts above cloud follows as:

$$\langle \text{VMR}_i \rangle = C \cdot (\langle \text{VCD}_{i+1} \rangle - \langle \text{VCD}_i \rangle) / (\langle p_{i+1} \rangle - \langle p_i \rangle) \quad (8)$$

where C is defined as $0.1 \times g \times M_{\text{air}} / N_A$ as in Eq. (1) and the index i refers to the cloud level. We term these objects VMR pseudoprofiles because they are constructed on the conditional provision of cloud presence, and the presence of cloud modifies the underlying NO₂ profile: either directly, via chemical or dynamical processes such as lightning NO_x production, advection of (clean/polluted) air from below, suppression of biomass burning or decreased photolysis under the cloud, or more indirectly via selective sampling of seasonal features, such as entangling a wet season column of enhanced lightning at high altitude with a dry season column of enhanced biomass burning at low altitude. One can appreciate that the effect of cloud presence on the profile varies with cloud altitude, which is unfortunate, because we use changes in cloud altitude to sample the underlying profile. This state of affairs introduces a source of systematic error between the cloud-slicing estimate (i.e. the pseudoprofile) and the actual underlying profile, which we term pseudoprofile error. One may evaluate (and further compensate for) the pseudoprofile error associated to conditional cloud sampling by comparing the model VMR profile estimated using the cloud-slicing technique against the underlying "true" mean NO₂ VMR profile from the same model, as described below. Other sources of systematic error may also intervene, including uncertainties in the a priori corrections and errors in the stratospheric column. The effect of uncertainties in the a priori corrections is limited by the impact that a priori corrections have on pseudoprofiles,

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which is itself limited (see Supplement). The effect of errors in the stratospheric column are expected to be small, since stratospheric columns only show a small additive bias (Belmonte Rivas et al., 2014) that is bound to cancel via the pressure difference. One could also include temporal representativity errors from mismatched collocations between model and OMI clouds in this category, which (Boersma et al., 2015) estimate to lie around 10%. In this section we provide a brief description of the retrieval error that may be expected from instrumental random noise properties alone, followed by an estimate of pseudoprofile error based on model behavior.

Retrieval error

The retrieval error in the annual mean cloud-slicing profiles is calculated by standard error propagation of Eq. (1). Note that we do not compute VMRs on daily or orbital basis (since one does not achieve the necessary cloud height diversity but in exceptional circumstances), but from the difference of annual mean VCDs. The derivation follows as:

$$\begin{aligned}\delta VMR &= 0.1 \cdot g \cdot \frac{M_{air}}{N_A} \cdot \delta \left(\frac{\partial VCD_{annual}}{\partial p_{annual}} \right) \\ &= 0.1 \cdot g \cdot \frac{M_{air}}{N_A} \cdot \left(\frac{\delta(VCD_1 - VCD_2)}{p_1 - p_2} + \frac{(VCD_1 - VCD_2)}{(p_1 - p_2)^2} \delta(p_1 - p_2) \right) \\ &= 0.1 \cdot g \cdot \frac{M_{air}}{N_A} \cdot \left(2 \cdot \frac{\delta VCD_{annual}}{p_1 - p_2} + \frac{(VCD_1 - VCD_2)}{(p_1 - p_2)^2} \cdot 2 \cdot \delta p_{annual} \right)\end{aligned}$$

Where VCD_1 , VCD_2 , p_1 and p_2 are all mean annual quantities estimated for contiguous pressure levels. Assuming random Gaussian errors in the determination of single OMI observations with an uncertainty δVCD of 50% in the OMI vertical column density (Boersma, 2004) and an uncertainty δp of 100 hPa in O_2 - O_2 cloud pressure (Stammes et al. 2008), the standard error of the mean annual quantity (VCD or pressure) is the standard error of the single retrieval divided by the square root of the number of OMI measurements collected per grid cell N_{grid} in a year:

$$\begin{aligned}\delta VCD_{annual} &= \delta VCD / \sqrt{N_{grid}} \\ \delta p_{annual} &= \delta p / \sqrt{N_{grid}}\end{aligned}$$

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So that we obtain:

$$\delta VMR = 0.1 \cdot g \cdot \frac{M_{air}}{N_A} \cdot \left(2 \frac{\delta VCD}{\Delta p} + 2 \frac{\Delta VCD}{\Delta p} \cdot \frac{\delta p}{\Delta p} \right) \cdot \frac{1}{\sqrt{N_{grid}}} \quad (9)$$

Pseudoprofile (systematic) error

The extent to which cloud-slicing profiles remain physical and accurate representations of an average cloudy atmosphere is limited by the assumptions that underlie the cloud slicing difference, which goes as:

$$VMR(p_{mid}) \propto VCD(p < p_{dn} | p_{cloud} = p_{dn}) - VCD(p < p_{up} | p_{cloud} = p_{up}) \quad (10)$$

In cloud-slicing, the mean VMR between the pressure levels p_{up} and p_{dn} is given by the difference between the VCD above cloud pressure p_{dn} , provided there is cloud at p_{dn} , and the VCD above cloud pressure p_{up} , provided there is cloud at p_{up} too. The problem is that the presence of cloud modifies the profile. One may think that the column difference in Eq. (10) is an approximation to what happens when clouds are located at p_{mid} , somewhere between p_{up} and p_{dn} . But assuming that the trace gas concentration profile does not change with small changes in cloud altitude (which are otherwise necessary to estimate the VMR slope) entails some error. Ideally, we would like to calculate:

$$VMR_{true}(p_{mid}) \propto VCD(p < p_{dn} | p_{cloud} = p_{mid}) - VCD(p < p_{up} | p_{cloud} = p_{mid}) \quad (11)$$

Now we have a unique (and physically plausible) cloud condition behind the difference, $p_{cloud} = p_{mid}$, and a VMR estimate that is representative of gas concentration provided that there are clouds at the p_{mid} level. Yet if we would like to obtain a VMR estimate that is representative of trace gas concentration in a general cloudy atmosphere, then we would calculate:

$$VMR_{ref}(p_{mid}) \propto VCD(p < p_{dn} | \forall p_{cloud}) - VCD(p < p_{up} | \forall p_{cloud}) \quad (12)$$

That is, VMR_{ref} represents a mean VMR profile provided that there are clouds anywhere in the column, i.e. regardless of cloud altitude. We call the difference between VMR and VMR_{true} sampling error, because the cloud diversity necessary to estimate the trace gas concentration is distorting the underlying profile. We call the difference between VMR_{true} and VMR_{ref} representation error, because a profile measured under high cloud conditions is not representative of a profile under low cloud conditions, nor in general representative of an average cloudy state. The sum of the sampling and representation errors, that is the difference

between the cloud-sliced VMR pseudoprofile and the average profile in a cloudy atmosphere
 VMR_{ref} is what we call pseudoprofile error. All VMR, VMR_{true} and VMR_{ref} profiles can be
 calculated on account of the TM4 CTM, so that a model based estimation of the sampling and
 representation (pseudoprofile) systematic error becomes available. The general pattern of
 pseudoprofile errors (see Sect. 3.3) indicates that biases are small in the upper three levels,
 largely positive (100-200%) over tropical and extratropical outflows in the lower two levels,
 and negative (up to 100%) over the continents for the lower three levels (particularly over
 central and South America, Australia, Canada and Siberia). One way to bypass this systematic
 error is to scale the observed VMR pseudoprofiles by the model profile-to-pseudoprofile ratio
 as:

$$VMR_{ref,OMI} = VMR_{OMI} \cdot (VMR_{ref,TM4}/VMR_{TM4}) \quad (13)$$

This model-based pseudoprofile correction (applied in Sect. 3.4) remains subject to the
 accuracy with which the model represents its own profiles, and should be treated with caution.

3 Results and discussion

3.1 NO₂ VCD above cloud

Figure 3a shows the annual mean tropospheric NO₂ VCD aggregates on 1°x1° grids observed
 by OMI for the year 2006 above clouds with mean pressures centered around 330, 450, 570,
 670, 770 and 870 hPa – see Fig. 1 and Table 1. A similar set of annual mean NO₂ VCDs
 above cloud has been extracted from the TM4 model using identical cloud sampling (i.e.
 using the cloud fraction and cloud pressure from OMI) for comparison (see Fig. 3b).

Most of the lightning NO₂ emissions are expected above clouds higher than 450 hPa (i.e. the
 upper two levels in Fig. 3a) although some deep convection may also be present over strong
 industrial sources (like northeast US, Europe, China, and the Johannesburg area) or biomass
 burning sources in central Africa, the Amazon basin or northeast India, complicating the
 problem of process attribution.

The two middle levels in Fig. 3a are expected to carry, along with the NO₂ burden inherited
 from the upper levels, additional signatures from frontal uplifting into the mid-troposphere by
 conveyor belts over major industrial sources in northeast US, central Europe and China, as
 well as convective transport of biomass burning sources over central Africa, South America,
 Indonesia and northern Australia. The strong convective signatures of surface industrial and

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1 biomass burning sources, along with their low tropospheric outflows, dominate the two lowest
2 levels in Fig. 3a. Note the extensive lack of data over the tropical continents at low altitudes, a
3 region where persistent high cloud precludes penetration into the lowest levels, and over the
4 subtropical subsidence areas.

5 By differencing the annual average VCD arrays with respect to pressure, we expect to
6 separate the contributions from different altitudes to the total tropospheric VCD column. But
7 before that, let us take a look at the scattering sensitivities above cloud and the effects of
8 correcting for undercloud leakage in these results. Fig. 4 shows the annual mean tropospheric
9 scattering sensitivity above cloud level [AMF_{above} in Eq. (4)] applied to generate the OMI
10 NO_2 VCDs shown in Fig. 3a. Globally, the tropospheric scattering sensitivity above the cloud
11 does not deviate more than a 10% from the geometric airmass factor at most cloud altitudes,
12 except at the lowest levels, where it suffers reductions of up to 30%. This reduction in
13 scattering sensitivity at the lowest cloud levels may come as a surprise, particularly when
14 clouds are known to boost the scattering sensitivity just above the cloud top. However, the
15 pronounced decrease in scattering sensitivity at the lowest cloud levels is related to
16 penetration of substantial amounts of NO_2 (from strong or elevated surface sources) into the
17 cloud mid-level, where extinction acts to reduce the scattering sensitivity. Other than the
18 extinction effect, the variability in scattering sensitivity is governed by changes in the
19 observation geometry (AMF_{above} decreases as the sun angle increases) and the temperature
20 correction introduced in Eq. (6), which is responsible for the subtropical bands and the
21 variability at high southern latitudes.

22 The corrections for the surface leaked component introduced in Eq. (3) are largest (see
23 [Supplement](#)) over polluted regions for the highest clouds (up to 50-66%) and smallest over
24 clean areas like the oceans. In order to verify that the model-based undercloud leak
25 corrections do not appreciably change the OMI NO_2 VCDs arrays, we have performed a
26 separate trial run where the CRF threshold (at grid level) is increased from 50% to 80% (see
27 [Supplement](#)) to conclude that none of the prominent VCD signatures seen in Fig. 3a (or none
28 of the VMR features that we will see later) changes appreciably in the restricted CRF>80%
29 case. Results from the CRF>80% trial run include notably diminished cloud frequencies and
30 spatial coverage, seriously thinning the population that produces the annual averages and
31 generally damaging their representativity. This effect is particularly notable in the upper two
32 levels (280 and 380 hPa) and to lesser extent over the large-scale subsidence area in the

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lowest level, since deep convective and low marine stratocumulus clouds are not particularly extensive but have a preference for low effective cloud fractions. Excluding the contributions from these cloud types in the CRF>80% case does not change the mid-tropospheric NO₂ patterns relative to the CRF>50% case, but it is biasing the OMI aggregates in the upper troposphere low relative to the modeled average, which is not particularly sensitive to this change. In summary, the CRF>80% trial run does not show any clear signs of a priori information constraining the results, but it provides hints of results being influenced detrimentally by the lower sampling densities afforded by a higher CRF threshold.

3.2 NO₂ VMR pseudoprofiles

The annual mean tropospheric NO₂ VMR pseudoprofiles observed by OMI for the year 2006 are compared against their TM4 model counterparts in Figs. 5a-c. Note that pseudoprofile errors do not affect this comparison, since both observed and modeled pseudoprofiles are observing identical (if somewhat unphysical, because of sampling and representation issues) atmospheric states. After the pressure difference, there remain some instances where negative VMRs are found, but these are mainly associated to poorly populated cells (such as at high latitudes, near the tropics at low altitudes, or around subsidence regions). These instances are identified and dealt with by recourse to information from nearby cells, when available, or otherwise ignored.

Many of the cloud slicing features observed at the upper two levels (280 and 380 hPa) in Fig. 5a can be attributed to actual biomass burning, lightning and deep convection. It may be difficult to separate these components clearly without a proper seasonal analysis (deferred to Section 3.6), although one can identify areas of predominant lightning production as those regions that do not seem connected via convection to surface sources underneath and use the OTD-LIS flash rate climatology and the ATSR fire counts (see Fig. 6 below) as interpretation aids for attribution. Positive anomalies (observations larger than modeled amounts) are detected in Fig. 5a over all major industrial areas (eastern US, central Europe and eastern China) both at 280 and 380 hPa levels, suggesting that deep transport of boundary layer NO₂ may be too weak in the model. On the contrary, there are extensive negative anomalies (meaning observations lower than modeled amounts) in background upper tropospheric NO₂ both at 280 and 380 hPa, which is consistent with reports of model overestimation of the amount of NO₂ attributed to lightning over the tropical oceans in (Boersma, 2005).

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1 Negative anomalies in Fig. 5a are particularly large over Siberia, Amazonia and the Bengal
2 Bay. The negative anomaly over eastern Siberia, an area of predominant biomass burning,
3 could be related to excessive fire-induced NO₂ emission over boreal forests in the model
4 (Huijnen et al., 2012). In South America, lightning NO₂ contributions seen by OMI appear
5 confined mostly to the western equatorial coast (Peru, Ecuador and Colombia) on one side,
6 and southern Brasil and off the east coast of Uruguay on the other hand (more in line with the
7 OTD-LIS flash climatology shown in Fig. 6) - in stark contrast with model amounts, which
8 locate the lightning maximum further to the north over the brasilian Matto Grosso, where the
9 maxima in precipitation related to the South American monsoon system usually takes place. It
10 is worth noting that the lightning intensity in the TM4 model is solely driven by convective
11 precipitation, although [Albrecht et al, 2011] report that convective precipitation is not always
12 well correlated with lightning in this area, showing that the most efficient storms in producing
13 lightning per rainfall are located in the south regions of Brazil. The negative anomaly over
14 Amazonia is therefore very likely related to problems with the TM4 lightning scheme. The
15 negative anomaly over the Bengal Bay, an area of maxima in precipitation related to the
16 Indian monsoon, could also be a reflection of excess model lightning linked to convection.

17 Other notable discrepancies in Fig. 5a include positive anomalies over central Africa and
18 northeast India at 280 hpa. Over central Africa, the pattern of positive anomalies bears only
19 partial resemblance with the pattern of biomass burning emission underneath (see midlevel
20 OMI VMRs in Fig. 5b) – suggesting that upper level positive anomalies in central Africa may
21 be related more to deficiencies in the lighting scheme than to convective transport. Actually,
22 (Barret et al., 2010) report that lightning flash frequencies simulated by TM4 are lower than
23 measured by the LIS climatology over the Southern Sahel, which is consistent with our
24 observations. On the other hand, the large positive anomaly observed over the Tibetan plateau
25 at 280 hPa, which significantly deviates from the OTD-LIS flash rate climatology in the area
26 (confined to the Himalayan foothills only), is likely an effect of deep transport associated with
27 the Asian monsoon. The model does show an enhacement in upper tropospheric NO₂ over
28 India, but not moving far enough north into the Tibetan plateau and failing to reproduce the
29 strong enhancements in upper tropospheric NO₂ over northeast India and Southern China
30 related to the Asian summer monsoon plume – which (Kar et al., 2004) also detected in the
31 MOPITT CO profiles.

1 The cloud slicing features observed at the mid-tropospheric levels (500 and 620 hPa) in Fig.
2 5b may be mostly attributed to mid-tropospheric convection of strong surface sources and
3 their associated outflows. We observe a remarkable agreement between model and
4 observations on the localization and intensity of major convective signals over industrial
5 sources (eastern US, central Europe, China and India) as well as over typical biomass burning
6 sources in central Africa, Indonesia and South America. Contrary to what is observed in the
7 upper levels (see prevalent negative anomalies in Fig. 5a), there are extensive positive
8 anomalies (meaning observations larger than modeled amounts) in background middle
9 tropospheric NO₂ both at 500 and 620 hPa in Fig. 5b, particularly over the tropics and
10 subtropics – which is indicative of deficient model mid-tropospheric outflows at these levels.
11 Positive anomalies over the continents are particularly large over China (with an outflow
12 related positive anomaly downwind over the Pacific), central US, and the biomass burning
13 regions in central Africa and South America. While it may be more or less clear that enhanced
14 mid-tropospheric NO₂ concentrations observed over the oceans are related to enhanced
15 convective inflows into this level (without definitely discarding a problem with NO₂ lifetime),
16 the origin of the convective anomalies remains ambiguous. A cursory look at the NO₂
17 concentrations observed at lower levels might help discriminate whether flux anomalies into
18 the mid-troposphere are related to deficiencies in model prescribed surface emissions or
19 problems with the convective transport scheme, or both.

20 For example, the pattern of anomalies over China at lowest levels (see Fig. 5c) is prominently
21 positive, but it carries a dipolar positive (China) - negative (Japan) pattern that is no longer
22 observed at higher levels. So, while it is possible that some of the mid-tropospheric
23 convective anomalies are a response to flux anomalies carried from underneath (i.e. a
24 deficiency in the originally prescribed surface emission), as it happens over eastern US and
25 Europe, where negative anomalies are carried upwards (see Fig. 5b), the overall effect does
26 not exclude net deficiencies in model convective transport. As far a biomass burning is
27 concerned, the pattern of anomalies over central Africa and South America in the lowest
28 tropospheric levels (see Fig. 5c) is unfortunately not as evident (given the lack of low cloud
29 detections) as over China but mostly neutral or slightly negative, indicating that mid-
30 tropospheric positive anomalies in this area respond to either a convective transport scheme
31 that is too weak or a model injection height that is too low.

1 The lower tropospheric levels (720 and 820 hPa) in NO₂ sampled by the cloud slicing
2 technique are shown in Fig. 5c. These levels sustain the highest NO₂ concentrations in the
3 vicinity of major industrial hubs (eastern US, central Europe and China) and the strongest
4 anomalies as well, which in this case can be linked directly to deficiencies in prescribed
5 surface emissions. All major features in the anomaly patterns at these levels can be matched
6 unambiguously to the pattern of OMI to TM4 total tropospheric NO₂ column differences for
7 clear sky-conditions shown later in Fig. 12, characterized by positive anomalies over
8 northeast US, central Europe and Japan, and negative anomalies over China. These low level
9 signatures are consistent with NO₂ increases over China, India and the Middle East, and NO₂
10 decreases over eastern US and central Europe, which are not reflected in the model emission
11 inventory. Other salient features at these levels include an interesting band of negative
12 anomalies along the ITCZ (perhaps related to rapid convective mixing of relative “clean” air
13 from the boundary layer) and extensive positive anomalies over the oceans (more so at 720
14 than at 820 hPa) – revealing deficient model outflows at high latitudes and suggesting that
15 poleward transport of NO₂ in the model may not be vigorous enough (a problem likely related
16 with horizontal diffusion in the model).

17 In summary, there is remarkable agreement between observed and modeled
18 upper/middle/lower tropospheric NO₂ amounts, their main distributions resembling each other
19 at continental scale, with localized differences suggesting that the cloud slicing technique
20 holds promise for testing model features related to anthropogenic emission, convection and
21 uplift, horizontal advection and lightning NO_x production. ▼

22 3.3 Classification

23 In the previous section, we studied the geographical distribution of observed and modeled
24 NO₂ amounts on different pressure layers. In this section, we focus on the vertical dimension
25 by looking at NO₂ VMR amounts across pressure layers. In order to simplify the analysis, we
26 have defined a set of geographical classes based on the amount of variance contained in the
27 TM4 model NO₂ profiles. These classes characterize how much of the NO₂ content in the
28 profile can be apportioned to surface sources and how much to outflows – further subdivided
29 into outflows with low, mid or high altitude components. Annual mean NO₂ VMR profiles are
30 plotted for each class, along with reference to pseudoprofile error. A standard empirical
31 orthogonal function (EOF) decomposition of the reference TM4 profiles [VMR_{ref} in Eq. (12)]
32 is employed to characterize the geographical variance of NO₂ vertical profiles under cloudy

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1 conditions and identify major spatial patterns. The first four EOF eigenvectors (out of a total
2 of six) are shown in Fig. 7a. The first EOF represents profiles with higher concentrations near
3 the surface – a profile over a surface source. The second EOF represents profiles with
4 concentrations uniformly distributed across the column – a profile for a generic outflow type.
5 The third and fourth EOF eigenvectors divide the generic outflow type into subtypes with
6 stronger high altitude (EOF3>0), low altitude (EOF3<0) or mid-tropospheric (EOF4>0)
7 components. The classes that result from applying masks based on the conditions defined in
8 Table 2 are shown in Fig. 7b. According to the TM4 model, the classes containing all primary
9 and secondary industrial sources (i.e. strong projections on EOF1) are mainly confined to the
10 US, Europe and China. Other secondary industrial sources relate to India, the Middle East and
11 the Baykal Highway (a major road connecting Moskow to Irkutsk, passing through
12 Chelyabinsk, Omsk and Novosibirsk). Major biomass burning sources include large sectors in
13 Africa and South America, Indonesia, New Guinea, and northern Australia. NO₂ outflows
14 over the tropics (i.e. strong projections on EOF2) are subdivided into generic tropical
15 outflows (with strong upper and mid-tropospheric components, or larger projections on EOF3
16 and EOF4) and outflows over large-scale subsidence areas (with stronger lower tropospheric
17 components, or negative projections on EOF3). The extratropical outflows differ from the
18 tropical outflows in that the sign of the mid-tropospheric projection is reversed, so that
19 extratropical profiles are more C-shaped (according to the model). The boreal outflow differs
20 from the extratropical outflow in that it has an extremely large upper tropospheric component
21 (i.e. a very large projection on EOF3). Finally, we have defined a separate class, labeled clean
22 background, including all those areas without significant projections on either source or
23 outflow eigenvectors.

24 The average tropospheric NO₂ profiles estimated using the cloud slicing method on OMI and
25 TM4 datasets for all the 11 classes (15 classes when primary and secondary industrial regions
26 are subdivided geographically into China, USA and Europa subclasses) defined in Table 2
27 and Fig. 7b are shown next in Figs. 8 and 9. These plots compare the OMI and TM4 VMR
28 pseudoprofile estimates calculated in a cloud slicing fashion as in Eq. (10), along with the
29 reference TM4 VMR_{ref} profile calculated as in Eq. (12) for an average cloudy atmosphere.
30 Recall that the difference between the TM4 VMR and VMR_{ref} profiles gives an indication of
31 pseudoprofile error – or the representativity of the cloud-slicing estimate relative to a general
32 cloudy situation. The OMI VMR cloud slicing estimate is bounded by error bars calculated

from standard error propagation as in Eq. (9), and scaling by the square root of the number of profiles collected per grid cell – also shown in right subpanels in Figs. 8 and 9.

The cloud-slicing estimate for the annual tropospheric NO₂ profiles over primary industrial centers in eastern US, Europe and China are shown in the first row in Fig. 8. There is a remarkably good correspondence between observed and modeled tropospheric NO₂ profiles over these strongly emitting areas, particularly over central Europe, attesting to the accuracy and representativity of the cloud-slicing estimates for yearly means. Pseudoprofile errors are small in these areas, so that cloud-slicing estimates remain a good representation of average cloudy conditions. The OMI to TM4 VMR differences at the lowest levels are consistent with known deficiencies in model prescribed surface emissions (OMI smaller than the TM4 over eastern US and central Europe, but larger over China). These low level anomalies are carried upwards to a level of 500-600 hPa, above which the effects of enhanced convective mid-tropospheric and deep transport start to dominate regardless of the signature of the surface difference. The second row in Fig. 8 show the annual tropospheric NO₂ profiles over secondary industrial centers around eastern US, Europe and China. The low level features related to surface emission are identical to those of the primary centers, but the signature of enhanced mid-tropospheric convection is clearer - indicating that vertical transport in the model is too weak or lifetime too short, regardless of the sign of the surface anomaly. The sign of the OMI to TM4 difference is reversed in the upper two levels, in line with the generalized model overestimation of NO₂ in the upper troposphere. The third row in Fig. 8 shows the cloud-slicing estimate for the annual tropospheric NO₂ profiles over secondary industrial pollution centers in India, the Middle East and the Baykal Highway - note that pseudoprofile errors are larger in this case. For India, the differences between OMI and TM4 profiles at low levels point at a large underestimation of model surface emissions, and model overestimation of upper tropospheric NO₂ amounts – this upper level anomaly related to the misplaced Asian summer monsoon signal, which in observations appears located over the Tibetan plateau. For the Middle East, the difference between OMI and TM4 profiles points at large differences at mid-tropospheric level (OMI larger than TM4). The agreement between OMI and TM4 profiles for the Baykal Highway class is reasonably good – allowing for a small underestimation of model surface emissions. After deep transport in China, this is the class with higher upper level NO₂ amounts, most likely related to fire-induced convection from boreal fires. The left panel in the fourth row in Fig. 8 shows the cloud slicing estimate for the annual tropospheric NO₂ profile over tropical biomass burning regions, featuring

1 positive anomalies at middle levels and negative anomalies at lower and upper levels, again
2 pointing at defective model convective transport into the mid-troposphere (or issues with the
3 pyro-convection height). The cloud-slicing estimates for annual tropospheric NO₂ profiles
4 over typical outflow regions are shown in the middle and right panels in the fourth row
5 (tropical and tropical subsidence outflows) and left and middle panels in the fifth row
6 (extratropical and boreal outflows) in Fig. 8. As a salient feature, all of the outflow profiles
7 share a prominent mid-tropospheric plume centered around 620 hPa in the tropics and a little
8 lower in the extratropics, around 720 hPa, with NO₂ amounts much smaller than the model in
9 the upper troposphere and general agreement at the lowest level, producing profiles which are
10 generally S-shaped (instead of C-shaped as in the model). The mid-tropospheric plume is
11 likely related to enhanced convective fluxes of NO₂ over industrial and biomass burning areas
12 (but definitely not discarding issues with NO₂ lifetime or substantial chemical NO_x recycling
13 from HNO₃ and PAN sources at this level). Note also the generalized model overestimation of
14 NO₂ in the upper levels (tropical and extratropical), which is consistent with reports of excess
15 lightning NO_x production over the tropical oceans in (Boersma et al., 2005). The upper level
16 overestimation is particularly large for the boreal outflow class, which we also mentioned
17 could be related to the excess fire-induced convection over Siberia or too large NO_x emission
18 factors. Finally, the cloud-slicing estimate for the annual tropospheric NO₂ profile over the
19 clean Southern Ocean is shown on the right panel of the last row in Fig. 8, with good
20 agreement at the top levels and gradually increasing model underestimation towards the
21 surface, suggesting enhanced lateral contributions at high latitudes from horizontal eddy
22 diffusion.

23 The left panel in Fig. 9 shows the annual tropospheric NO₂ profile for all the primary surface
24 sources together (eastern US, central Europe and China), indicating that differences at surface
25 level average out globally, leaving the effects of enhanced observed mid-tropospheric
26 convection and deep transport to stand out. The signature of enhanced mid-tropospheric
27 convection becomes even clearer in the mid panel in Fig. 9, which shows the annual
28 tropospheric NO₂ profile for all secondary surface sources together (around primary sources,
29 plus India, the Middle East, the Baykal Highway and the biomass burning areas), where the
30 signature of enhanced deep transport is in this case replaced by model overestimation of upper
31 tropospheric NO₂. The model overestimation of upper level NO₂ appears clearly on the right
32 panel in Fig. 9, which shows the annual tropospheric NO₂ profile for all the outflow classes,
33 along with a prominent model underestimation of mid-tropospheric NO₂ levels. In summary,

and consistent with our comments on Figs. 5a-c, the average profiles that result from applying the cloud slicing technique on observed OMI and modeled TM4 datasets show striking overall similarities, which confer great confidence to the cloud-slicing approach, along with more localized differences that probe into particular model processes and parameterization schemes.

3.4 Cross-sections

We would like to wrap up our results in the form of observed and modeled annual zonal mean and longitudinal NO₂ cross-sections along the tropics (Figs. 10a-b and 11). Note that in order to bypass pseudoprofile errors, the observed NO₂ pseudoprofiles are scaled in this section by the model profile-to-pseudoprofile ratio as in Eq. (13) to form what is called the observation update.

For the annual zonal mean tropospheric NO₂, the left-to-right panel comparison in Fig. 10a shows that although the observation update does not change the strength of major industrial emission over the northern midlatitudes at the lowest levels, the associated convective cloud is reaching higher in altitude. In the tropics and southern latitudes, vertical transport of the combination of biomass burning and industrial emissions is stronger and reaching higher - with a prominent high plume originating from the Johannesburg area. The observation update does bring notably stronger midtropospheric outflows distributed over a broader latitude band and weaker NO₂ signatures at high altitude. The enhanced midtropospheric plume is best appreciated in Fig. 10b, which shows the annual zonal mean tropospheric NO₂ averaged over the Pacific Ocean sector (180W-135W) – the dominant sources of NO₂ over the oceans are thought to include the long-range transport from continental source regions, as well as chemical recycling of HNO₃ and PAN sources [Staudt et al., 2003]. [Schultz et al., 1999] actually shows that the decomposition of PAN originating from biomass burning actually accounts for most of the midtropospheric NO_x in the remote Southern Pacific, suggesting that enhanced convective flux from surface sources may not be the only agent responsible for the enhanced midtropospheric outflows observed by OMI.

Figure 11 shows a picture for the annual longitudinal NO₂ cross-section for tropical latitudes between 10N and 20S, where the observation update raises the convective plumes from major biomass burning areas in South America, central Africa and Indonesia/Northern Australia to higher altitude, between 500 and 600 hPa, with a slight westward tilt and longer downstream

transport of cloud outflow at upper levels caused by the tropical easterly jet, and generally weaker NO₂ signatures at high altitude.

In summary, the OMI cloud-slicing NO₂ profiles seem to suggest that raising the polluted plumes to higher altitudes allows for much longer residence and chemical lifetimes, and longer and more widely distributed horizontal transport of NO₂ (following poleward advection and dispersion by the subtropical jet and by baroclinic waves at lower levels) in the mid-troposphere. These observations are in line with reports in (Williams et al, 2010) showing that the underestimation of upper tropospheric O₃ in TM4 relative to observations over Africa may be linked to a too weak convective uplift using the Tiedtke scheme. The studies of (Tost et al., 2007), (Barret et al., 2010) and (Hoyle et al., 2011) corroborate this finding, indicating that the vertical extent of tropical convection and associated transport of CO and O₃ in the middle and upper troposphere is underestimated in Tiedtke based models. Accurately constraining the convective transport in CTMs should contribute to the determination of the vertical distribution of lightning NO_x, since knowledge of the extent of mixing of air into the cloud as a function of altitude is required to separate the NO_x produced by lightning from that produced by upward transport (Dickerson, 1984).

3.5 Consistency check

Because of their annual and global character, we do not have any direct means to validate the OMI annual tropospheric NO₂ profile climatology estimates in the same way that it has been done, for example, in [Choi et al., 2014]. But we can check their consistency by demanding that the total tropospheric NO₂ column from the cloud-slicing technique does not deviate significantly from the total tropospheric NO₂ column observed in clear sky conditions (see Fig. 12). The total tropospheric NO₂ column VCD_{slicing} from the cloud slicing technique is calculated as the sum of partial vertical column densities obtained from the annual mean pseudoprofile VMR as:

$$VCD_{slicing}(lat, lon) = \sum_{i=1, \dots, 6} VMR_i(lat, lon) \cdot (\langle p_{i+1} \rangle - \langle p_i \rangle) / C \quad [14]$$

Where C is the same constant defined in Eq.(8). Note that absent VMR grid values (such as at high altitude over subsidence regions, or at low altitude over the tropical continents) are ignored without provision of a priori information.

1 We do know that there are some basic differences between NO₂ profiles observed under clear
2 and cloudy conditions though. In the TM4 model, the differences between cloudy
3 (CRF>50%) and clear (CRF<25%) profile climatologies (see left panel in Fig. 13 below),
4 show strong negative anomalies over the biomass burning areas (central Africa, southern
5 America, northern Australia, southern India, but also in the Persian Gulf and Turkestan) most
6 likely related to fire suppression during the wet/cloudy season. Over industrial areas (USA,
7 Europe and China) a more complex pattern of anomalies arises that likely results from the
8 competing effects of suppressed photolysis under clouds (small positive anomaly), venting by
9 passing fronts (large negative anomalies) and accumulation patterns dependent on a
10 predominant synoptic weather type [cyclonic or anticyclonic, (Pope et al., 2014)]. This pattern
11 of differences between cloudy and clear annual NO₂ profile climatologies is well reproduced
12 by OMI observations (see right panel in Fig. 13 below). The sole difference is that OMI sees
13 larger outflows at higher latitudes in the cloudy case – perhaps a deficiency of the model in
14 redistributing its horizontal flows under frontal conditions.

15 Another more direct way to perform this consistency check is to look at the differences in
16 total NO₂ columns between model (TM4) and observations (OMI) for the clear and cloudy
17 cases separately, as shown in Fig. 14. For the clear sky case (see left panel in Fig. 14) the
18 pattern of anomalies that arises is consistent with existing long-term satellite NO₂ trend
19 studies [(van der A. et al., 2008) and (Richter et al., 2005)] that report significant reductions
20 in NO₂ in Europe and eastern parts of the United States, strong increases in China, along with
21 evidence of decreasing NO₂ in Japan, increasing NO₂ in India, Middle East, and middle
22 Russia - and some spots in central United States and South Africa. The differences between
23 model and clear-sky OMI NO₂ total columns are being used to update the surface emission
24 inventories (Mijling & van der A, 2012) (Ding et al., 2015). What is comforting is that a
25 similar pattern of differences arises in the cloudy case (using the cloud-slicing TM4 and OMI
26 profiles), and with a similar amplitude, verifying that the OMI cloud slicing columns are
27 internally consistent with the clear sky OMI observations in detecting anomalies that can be
28 ultimately related to outdated model emission inventories.

29 In Figure 14, note that the model total tropospheric NO₂ columns over clean remote areas (i.e.
30 tropical and extratropical outflow regions over the oceans) in the cloudy case do not deviate
31 in general by more than 0.1xE-15 molec/cm² from observations This is a good result,
32 showing that the estimate of the stratospheric column (by data assimilation) does not produce

significant cloud-cover dependent biases in the tropospheric column. If we recall that the observed cloud-slicing NO₂ profile over clean remote areas is S-shaped, with a much stronger mid-tropospheric component and a much reduced upper tropospheric load than in the model, then we can infer that there has been as much gain in the mid-tropospheric component as there has been loss at high altitude, which is another form of closure.

3.6 Seasonal analysis

The seasonal mean tropospheric NO₂ VMR pseudoprofiles for the DJF, MAM, JJA and SON periods observed by OMI over the year 2006 compared against their TM4 model counterparts are shown next. These plots have been generated using the same cloud slicing gridding and threshold configurations applied for the annual means, with a required minimum of 7 measurements collected per bin during each season (instead of 30 for the annual means). This section is not intended to provide a thorough analysis of seasonal variability in (observed or modeled) tropospheric NO₂ profiles, but to reveal the potential of the cloud slicing technique to provide details that pertain to seasonal as well as to annual means.

The largest signatures of seasonal variability expected to arise in these figures will be a) a seasonal cycle in lightning activity in the upper levels (280-380 hPa); b) a seasonal cycle of biomass burning in the mid levels (500-620 hPa); and c) a seasonal cycle over industrial areas at lower levels (720-820 hPa), featuring minimum NO₂ levels in the summer months due to changes in the lifetime of NO_x [van der A. et al., 2008]. The seasonal cycle in lightning NO_x emissions may be verified against the climatology of lightning flashes observed by LIS/OTD (data set available online [<ftp://ghrc.nsstc.nasa.gov/pub/lis/climatology>], see [Cecil et al., 2014]). The seasonal cycle in biomass burning may be verified against the climatology of ATSR and AVHRR fire counts [(Dwyer et al., 2000) and (Schultz, 2008)].

Africa

Over Africa, persistent lightning activity at upper levels is expected to take place about the Equator (the Congo Basin) all year long, shifting southward towards South Africa in SON and DJF, and northward towards the Gulf of Guinea, the Sahel and Sudan in MAM and JJA, features which are all captured by OMI in Fig. 15 (in reasonable agreement with TM4, though some discrepancies are apparent too). These lightning signatures are not to be confused with traces of NO₂ lifted from biomass burning underneath, which feature a precisely opposite phase. Remarkable biomass burning signatures can be appreciated throughout the entire

1 tropospheric column in Figures 15-18 as NO₂ enhancements north of Equator (Sahel) in DJF,
2 and south of Equator (Angola and Zambia) in JJA, shifting eastward towards Mozambique
3 and Madagascar in SON (best seen at 500 and 620 hPa in Figs. 17-18). We note that the
4 penetration of seasonal biomass burning signatures into 280-380-500 hPa is stronger in OMI
5 than in TM4. In addition, note the strong enhancement in lightning activity seen by OMI off
6 the Southeast coast of Africa in MAM and JJA at 380 hPa in Fig.16, in connection with the
7 confluence of the warm Agulhas and the cold Antarctic Circumpolar Current, which is
8 virtually missed by TM4.

9 South America

10 Over South America, a maximum in lightning activity is expected to occur over central Brazil
11 in SON, as captured by OMI in Figs. 19-20 (in agreement with TM4, though some
12 discrepancies persist relative to the location of the lightning maximum, as we mentioned
13 when describing the annual means), migrating towards the southeast in DJF. Lightning and
14 precipitation are persistent in the northwest (Colombia, Venezuela and Central America) all
15 year-round, intensifying in MAM and JJA, as reasonably captured by OMI in Fig. 15, along
16 with some persistent NO₂ enhancements over la Plata Basin and off into the Brazil-Malvinas
17 Confluence Zone. The lightning signatures at upper levels may be partly overlapped by those
18 from biomass burning lifted from underneath, but their separation is more difficult in this
19 case. For instance, the NO₂ enhancements detected by OMI at 500 hPa over Brazil in SON and
20 DJF in Fig. 21 correlate well with the lightning signatures at 380 hPa, but they also correlate
21 with the biomass burning signals at 620 hPa, indicating that both processes may be occurring
22 at the same time in separate but nearby locations (e.g. combining the start of the wet season in
23 the Amazon Basin in DJF, with the end of the burning season in eastern Brazil). The cycle of
24 biomass burning in South America, which takes place over the dry season, starts in southern
25 Brazil in JJA, to find a maximum in SON eastward towards the coastal states, as OMI
26 captures in Figs. 21-23 (in reasonable agreement with TM4). In DJF, some activity may
27 persist in eastern Brazil and new activity develop over the lower slopes of the Argentinian
28 Andes during the austral summer, generally complicating attribution. Finally, it is interesting
29 to note in Fig. 23 the remarkable decrease in NO₂ levels at 720 hPa over the Amazon Basin
30 during the rainy season in DJF and MAM, as if in connection with an efficient NO₂ removal
31 mechanism.

32 Southeast Asia and Australia

At upper levels, one should expect to see persistent lightning activity over Indonesia all year round, as qualitatively observed by OMI in Fig. 24 (and in agreement with TM4), migrating northward towards South Asia in MAM and JJA, and southward towards Australia in SON and DJF. These lightning signatures may be mixed to greater or lesser degree with NO₂ lifted from biomass burning and/or anthropogenic sources underneath. Over South Asia, biomass burning is expected to find its maximum in MAM, as OMI captures in Figs. 26-28 particularly over north India and Myanmar. These emissions are likely responsible for a large part of the NO₂ enhancement observed around India at upper levels in MAM. The very strong NO₂ enhancement observed over South Asia at upper levels in JJA (Figs. 24-25) is likely related to deep transport of surface emissions (biomass and industrial) during the monsoon season, which TM4 locates over the Indo-Gangetic area and OMI locates over the Tibetan Plateau. Over Indonesia and Northern Australia, a maximum in biomass burning activity is expected be reached in SON, as OMI captures reasonably well in Figs. 26-28, indicating that the strong NO₂ enhancement seen by OMI over Northern Australia at 280 hPa in SON may well be tainted by deep transport of biomass burning.

Over a major industrial source like China, near-surface concentrations of NO₂ around 720 to 820 hPa are expected to reach minimum/maximum levels in JJA/DJF, just on account of increased/reduced exposure to sunlight (i.e. reduced/increased NO_x lifetime), as shown by both OMI and TM4 in Fig. 28. At mid-tropospheric levels though, other effects such as vertical transport intervene. Note in Figs. 26-27 that the TM4 model registers maximum mid-tropospheric NO₂ levels over China in JJA, and minimum in DJF. However, OMI observes stronger mid-tropospheric NO₂ levels in DJF than in JJA. According to OMI, surface emissions from China (and also from Europe and the US, as well shall see next) are being transported in larger quantities and to higher altitudes than in the model, particularly during the winter months.

Europe and North America

In connection with summer convection, lightning activity at northern midlatitudes is expected to be strongest in JJA. Enhancements in upper tropospheric NO₂ are observed by OMI (and TM4) in Fig. 29 over the eastern Mediterranean in JJA and SON. Enhanced NO₂ levels over Siberia in JJA may also be related to summer convection and increased biomass burning. In the US, lightning activity is expected to reach a maximum in JJA and shift southward towards the Gulf of Mexico in SON and DJF, features which are all registered by OMI in Fig. 29 (in

reasonable agreement with TM4, though some discrepancies are apparent in DJF). Figures 30-31 reveal an interesting discrepancy between the OMI and TM4 pseudoprofiles regarding the intensity and reach of convective penetration at 500 hPa of anthropogenic NO₂ above major industrial areas. As already noted for China, the TM4 model is placing enhancements of mid-tropospheric NO₂ over central Europe and eastern US in MAM and JJA, whereas OMI registers a more uniform distribution of mid-tropospheric signatures across the year, showing maxima in DJF and SON. This disagreement is suggestive of problems with the model convective scheme, possibly related to frontal uplift by conveyor belts in the wintertime. At levels closest to the surface, the variation in NO₂ concentration over major industrial areas (Europe and US, but also China, India and the Middle East) registered by OMI in Figs. 19-20 shows minima in JJA and maxima in DJF, just as expected and in agreement with TM4.

In summary, both the OMI and TM4 model pseudoprofiles show seasonal features that are consistent with the available lightning flash and fire count climatologies, and complementary to the results obtained for the annual means. On a finer scale, we observe some significant differences – on lightning distribution, or the intensity and reach of convective transport over strong biomass or industrial sources - whose detailed examination deserves future work.

4 Summary and conclusions

In this paper, we derive a global annual and seasonal climatology of tropospheric NO₂ profiles from OMI cloudy measurements for the year 2006 using the cloud slicing method on six pressure levels centered at about 280, 380, 500, 620, 720 and 820 hPa. The cloud-slicing profiles have been estimated after differencing annual and seasonal tropospheric NO₂ columns above cloud with respect to pressure, using mean cloud pressures located at about 330, 450, 570, 670, 770 and 870 hPa. We term these objects pseudoprofiles, since the required presence of a probing cloud necessarily draws the cloud-slicing estimate away from the underlying NO₂ profile. The systematic error between the cloud-sliced NO₂ pseudoprofile and the actual average NO₂ profile in a cloudy atmosphere is called pseudoprofile error, which can be evaluated (and possibly corrected) using a CTM model.

The total tropospheric NO₂ content in the cloud slicing profiles is consistent with the OMI clear sky total tropospheric column for the same year, after making allowance for a natural

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1 change in the global NO₂ distribution that occurs in passing from clear to cloudy conditions.
2 This change includes suppression of biomass burning during the wet/cloudy season,
3 suppressed NO₂ photolysis under clouds, venting by weather fronts and accumulation patterns
4 dependent on the predominant (clear or cloudy sky) synoptic weather type. The internal
5 consistency between OMI clear-sky and cloud slicing tropospheric NO₂ columns confirms the
6 capability of cloud slicing profiles to detect CTM model anomalies that can be ultimately
7 related to problems in model emission inventories, but with additional vertical information
8 that allows distinction between surface, mid-tropospheric and upper-tropospheric processes.

9 The vertical information contained in OMI tropospheric NO₂ profiles derived from the cloud
10 slicing technique provides a wealth of information that can be used to evaluate global
11 chemistry models and provide guidance in the development of sub-grid model
12 parameterizations of convective transport, fire-induced injection, horizontal advective
13 diffusion and lightning NO_x production. Overlapping processes (i.e. the effects of deep
14 convection and lightning NO_x in the upper troposphere, the effects of midtropospheric
15 convection and anomalies in surface emissions in the mid-troposphere) as well as
16 uncertainties in the chemical degradation and NO_x recycling rates currently limit the degree to
17 which discrepancies between observations and simulations can be unambiguously attributed
18 to a single process, although the availability of observational constraints definitely constitutes
19 an improvement.

20 As an example of such an application, we have performed a comparison between cloud
21 slicing tropospheric NO₂ profiles from OMI and the TM4 model. In the upper troposphere
22 (280 and 380 hPa levels), observed NO₂ concentration anomalies reveal excessive model
23 background NO₂ amounts which are consistent with too strong model lightning emissions
24 over the oceans (and/or too long lifetimes) combined with misplaced lightning NO₂ over
25 central Africa and South America, which is indicative of limitations in the convectively
26 driven model lightning NO_x scheme of (Meijer et al., 2001). Other anomalies suggest
27 observed enhanced deep transport of NO₂ from major industrial centers relative to TM4,
28 including a prominent signal from the Asian summer monsoon plume that the model fails to
29 place accurately, and [probable](#) excess model fire-induced convection over Siberia.

30 In the mid troposphere (500 and 620 hPa levels), observed NO₂ concentration anomalies
31 reveal deficient model background NO₂ amounts suggestive of too small model convective
32 inflows into this level, with deficits particularly large over China, central US, [and Europe](#)

during the boreal winter, and the biomass burning regions in central Africa and South America, combined with extensive outflows over the oceans that are stronger and more widely distributed in latitude than in the model. This is consistent with independent reports of underestimation of vertical transport by convective clouds in Tiedtke based models. Raising the NO₂ plumes to higher altitudes allows for much longer residence and chemical lifetimes, and longer and more widely distributed horizontal transport of NO₂ following poleward advection and dispersion by the subtropical jet in the mid-troposphere, all of which end up producing typical outflow profiles over the oceans that are generally S-shaped with a prominent mid-tropospheric plume centered around 620 hPa in the tropics and around 720 hPa in the extratropics. The role that the recycled NO_x component may play in the enhanced mid-tropospheric outflows observed by OMI over remote ocean regions is unclear at this stage, but the cloud slicing technique shows promise to study such effects.

In the lower troposphere (720 and 820 hPa), observed NO₂ concentration anomalies show a pattern that is consistent with deficiencies in model surface emissions related to known NO₂ trends characterized by NO₂ increases over China, India and the Middle East, and NO₂ decreases over eastern US, central Europe and Japan. The lower levels also show extensive positive anomalies over the oceans (particularly at 720 hPa), which are indicative of deficient model outflows at low altitudes (and/or too short model lifetimes) with deficient poleward diffusion of NO₂ at low to mid-tropospheric levels, and an interesting band of negative anomalies along the ITCZ.

Note that support from a CTM model (the TM4 in our case) is required to make provision for the cloud-slicing technique (in order to determine a priori corrections for undercloud leakage), so that a level of trust must initially be placed in the model. When comparing the resulting pseudoprofiles against those of the model, a number of potential model shortcomings are found which work against our initial trust in the model corrections. This conflicting outcome should be understood and justified to the extent that a priori corrections have a limited impact on the resulting cloud slicing profiles.

Handling pseudoprofile error using model-based profile-to-pseudoprofile ratios is another matter. The presence of systematic pseudoprofile errors in cloud-slicing estimates and their general predominance over random instrumental error suggest that the vertical information contained in cloudy pixels may be extracted optimally by an assimilation procedure that improves the atmospheric state (i.e. the model profile shape) at the right time and location

using the averaging kernel of the observation. To date, most data assimilation experiments using OMI NO₂ observations have focused on clear-sky measurements. The current results provide strong motivation to use both clear and cloudy pixels in assimilation experiments, as in e.g. (Miyazaki et al., 2014).

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Appendix A: Gas columns above and below cloud

If the tropospheric AMF_{trop} is defined as:

$$AMF_{trop} = CRF \cdot AMF_{cloud} + (1 - CRF) \cdot AMF_{clear} \quad (A1)$$

Where the clear AMF can be expressed as:

$$\begin{aligned} AMF_{clear} &= \frac{\sum_0^{tropopause} m_{clear}(z) \cdot n(z)}{\sum_0^{tropopause} n(z)} \\ &= \frac{\sum_0^{CLP} m_{clear}(z) \cdot n(z) + \sum_{CLP}^{tropopause} m_{clear}(z) \cdot n(z)}{\sum_0^{tropopause} n(z)} \\ &= \frac{\sum_0^{CLP} m_{clear}(z) \cdot n(z)}{\sum_0^{CLP} n(z)} \cdot \frac{\sum_0^{CLP} n(z)}{\sum_0^{trop} n(z)} + \frac{\sum_{CLP}^{trop} m_{clear}(z) \cdot n(z)}{\sum_{CLP}^{trop} n(z)} \cdot \frac{\sum_{CLP}^{trop} n(z)}{\sum_0^{trop} n(z)} \\ &= AMF_{below}^{clear} \cdot \frac{VCD_{below}}{VCD_{trop}} + AMF_{above}^{clear} \cdot \frac{VCD_{above}}{VCD_{trop}} \end{aligned} \quad (A2)$$

Where m_{clear} is the clear-sky scattering sensitivity and n(z) is the model a priori trace gas profile. Similarly, the cloudy AMF can be expressed as:

$$\begin{aligned} AMF_{cloud} &= \frac{\sum_0^{tropopause} m_{cloud}(z) \cdot n(z)}{\sum_0^{tropopause} n(z)} \\ &= \frac{\sum_0^{CLP} m_{cloud}(z) \cdot n(z) + \sum_{CLP}^{tropopause} m_{cloud}(z) \cdot n(z)}{\sum_0^{tropopause} n(z)} \\ &= \frac{\sum_{CLP}^{trop} m_{cloud}(z) \cdot n(z)}{\sum_{CLP}^{trop} n(z)} \cdot \frac{\sum_{CLP}^{trop} n(z)}{\sum_0^{trop} n(z)} = AMF_{above}^{cloud} \cdot \frac{VCD_{above}}{VCD_{trop}} \end{aligned} \quad (A3)$$

Where m_{cloudy} is the cloudy-sky scattering sensitivity. Note that by construction:

$$VCD_{trop} = \sum_0^{tropopause} n(z) = VCD_{above} + VCD_{below} \quad (A4)$$

Then the tropospheric AMF can be written, after inserting Equations (A2) and (A3) into Eq.

(A1), and rearranging terms relating to above and below components separately as:

$$AMF_{trop} = \frac{VCD_{above}}{VCD_{trop}} \left(CRF \cdot AMF_{cloud\ above} + (1 - CRF) \cdot AMF_{clear\ above} \right) + \frac{VCD_{below}}{VCD_{trop}} (1 - CRF) \cdot AMF_{clear\ below}$$

$$= \frac{VCD_{above}}{VCD_{trop}} AMF_{above} + \frac{VCD_{below}}{VCD_{trop}} AMF_{below}$$

$$(A5)$$

From this formulation arise definitions for AMF_{above} and AMF_{below} :

$$AMF_{above} \equiv \frac{\sum_{CLP}^{trop} (CRF \cdot m_{cloud}(z) + (1 - CRF) \cdot m_{clear}(z)) \cdot n(z)}{\sum_{CLP}^{trop} n(z)} \quad (A6)$$

$$AMF_{below} \equiv \frac{\sum_0^{CLP} (1 - CRF) \cdot m_{clear}(z) \cdot n(z)}{\sum_0^{CLP} n(z)} \quad (A7)$$

Now it is straightforward to write:

$$SCD_{trop} = AMF_{trop} \cdot VCD_{trop}$$

Which after substitution of Eq. (A5) becomes

$$SCD_{trop} = \left(\frac{VCD_{above}}{VCD_{trop}} \cdot AMF_{above} + \frac{VCD_{below}}{VCD_{trop}} \cdot AMF_{below} \right) \cdot VCD_{trop}$$

$$= VCD_{above} \cdot AMF_{above} + VCD_{below} \cdot AMF_{below} = SCD_{above} + SCD_{below} \quad (A8)$$

Allowing the separation of the slant components above and below the cloud as:

$$VCD_{above} = (SCD_{trop} - SCD_{below}) / AMF_{above} \quad (A9)$$

Now, in [Boersma, ACP, 2005] the above-cloud part of the NO_2 column is retrieved by removing the model predicted ghost column (integrated from the ground to the cloud level pressure, identical to VCD_{below}) that is implicitly added via the tropospheric airmass factor as:

$$VCD_{above} = SCD_{trop} / AMF_{trop} - CRF \cdot VCD_{below} \quad (A10)$$

However, by virtue of Eq. (A4), formulation in Eq. (A10) in [Boersma, ACP, 2005] should be changed to:

$$VCD_{above} = SCD_{trop} / AMF_{trop} - VCD_{below} \quad (A11)$$

1 Which is equivalent to Eq. (A9).

2

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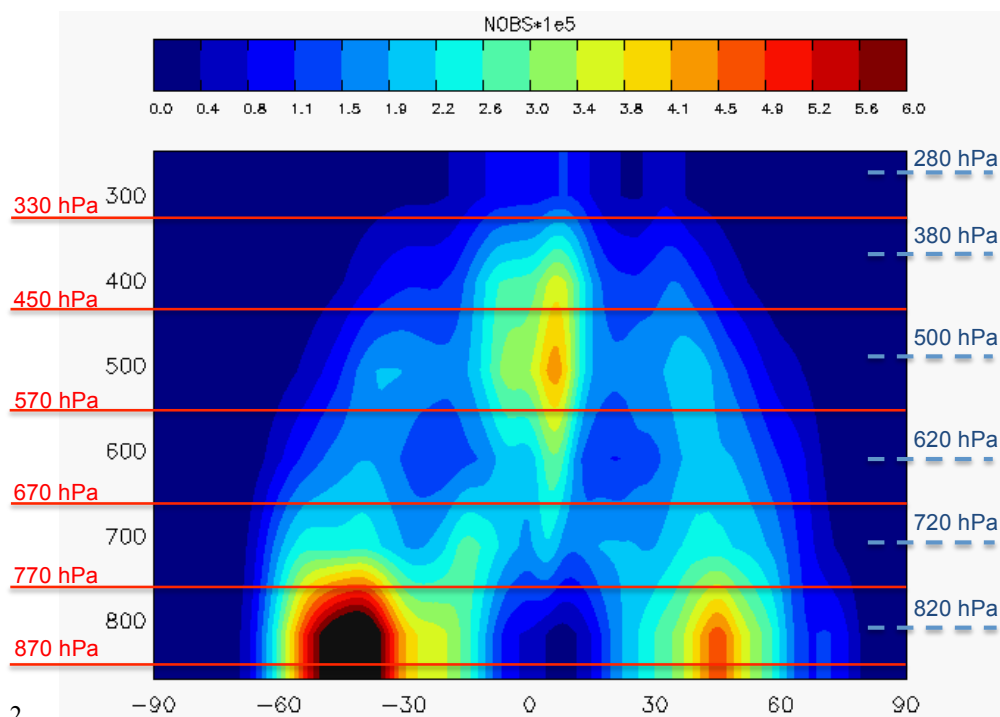
Table 1. Cloud pressure intervals and mean cloud pressure levels used for cloud slicing (hPa):
the VCD pressure interval gives the boundaries of the cloud pressure bin. The VMR pressure
interval refers to where the VMR is assumed constant after the pressure difference.

	VCD Pressure Interval	<VCD pressure>	VMR Pressure Interval	<VMR pressure>
Level 1	Tropopause - 380	330	Tropopause - 330	280
Level 2	380 - 500	450	330 - 450	380
Level 3	500 - 620	570	450 - 570	500
Level 4	620 - 720	670	570 - 670	620
Level 5	720 - 820	770	670 - 770	720
Level 6	820 - 1000	870	770 - 870	820

1 Table 2. Model based source and outflow class definitions based on EOF decomposition.

2

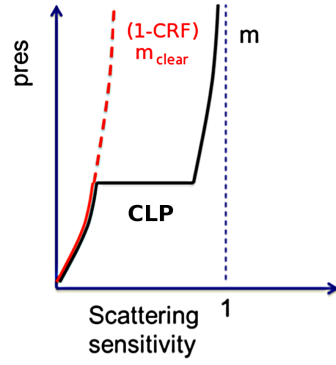
Class label	Main condition	Extra condition
Primary industrial	EOF1 > 400 pptv	US, Europe, China
Secondary industrial	100 pptv < EOF1 < 400 pptv	US, Europe, China
Biomass burning	100 pptv < EOF1 < 400 pptv	geographic
Baykal highway	100 pptv < EOF1 < 400 pptv	geographic
Indostan	100 pptv < EOF1 < 400 pptv	geographic
Middle East	100 pptv < EOF1 < 400 pptv	geographic
Tropical outflow	EOF1<50 pptv, EOF2>15 pptv	EOF3>0, EOF4>0
Tropical subsidence	EOF1<50 pptv, EOF2>15 pptv	EOF3<0
Extratropical outflow	EOF1<50 pptv, EOF2>15 pptv	EOF3>0, EOF4<0
Boreal Outflow	EOF1<50 pptv, EOF2>15 pptv	EOF3 >>0
Clean background	EOF1<15 pptv, EOF2<15 pptv	



2

3 Figure 1. Latitude-height section of annual zonal mean OMI cloud frequencies (CRF>50%) -
 4 observed during daytime around 13.45 LST. On the left in red, the bottom pressure
 5 boundaries for the calculation of annual mean NO₂ VCDs above cloud (after Table 1). On the
 6 right in blue, the approximate pressure for the resulting NO₂ VMR after differentiation of
 7 VCDs (also after Table 1).

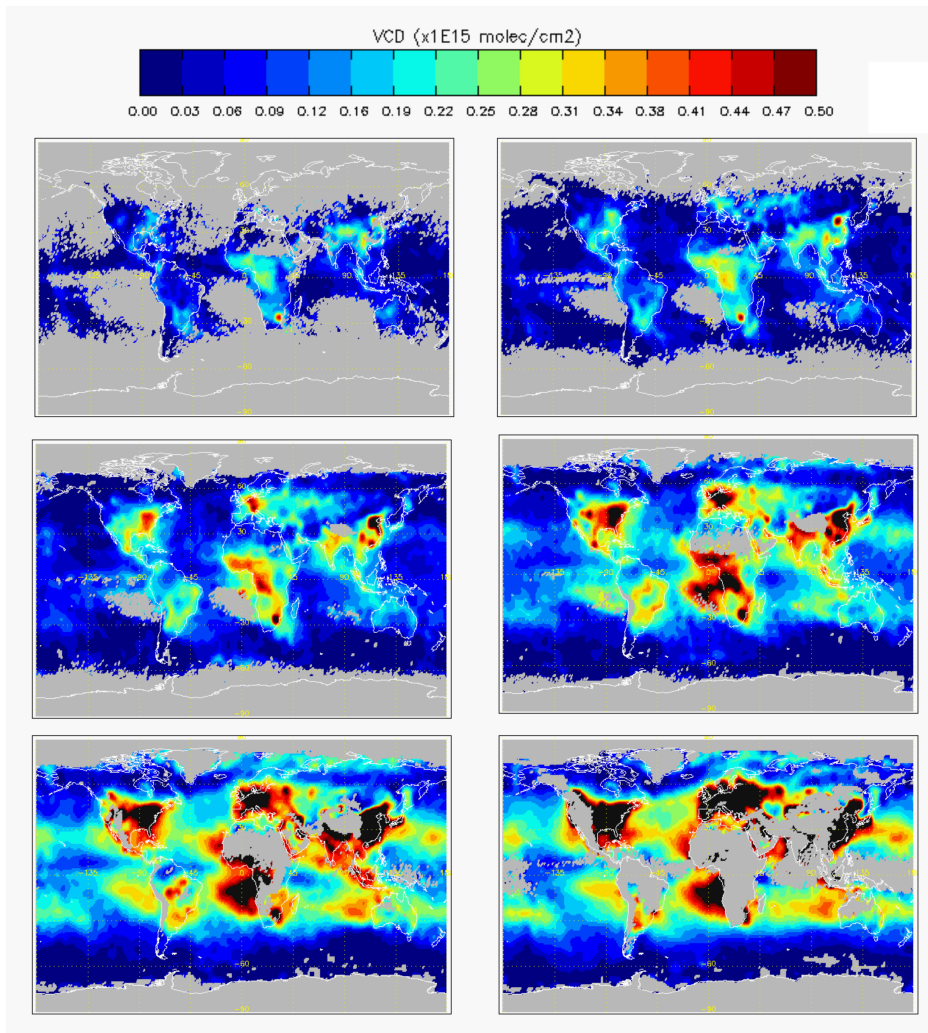
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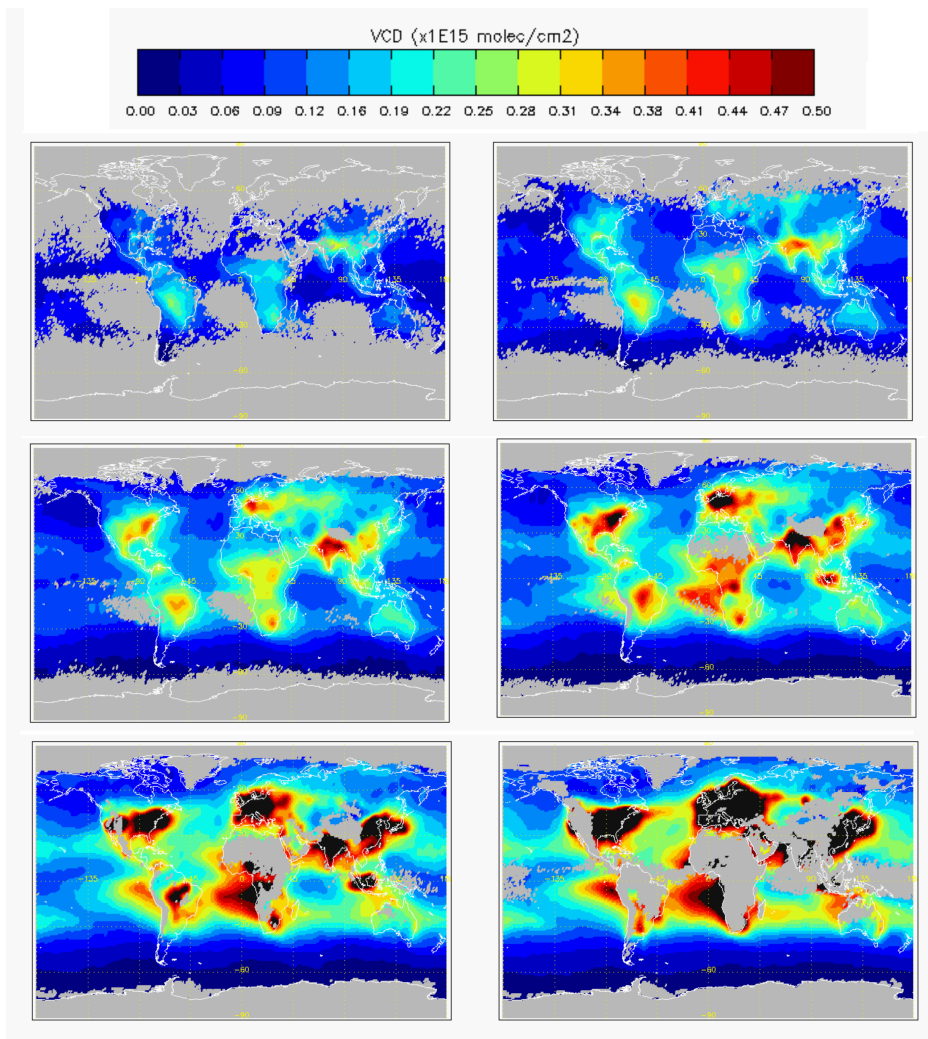
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2 Figure 2. Schematic diagram of the scattering sensitivity above and below the cloud
 3 (normalized by the geometric air mass factor): CLP is the cloud level pressure, and m is the
 4 total scattering sensitivity, usually defined as $(1-CRF) m_{clear} + CRF m_{cloudy}$. The red curve
 5 illustrates a residual sensitivity to NO₂ contents below the cloud when conditions are partially
 6 cloudy.

7



1
2 Figure 3a. OMI NO₂ VCDs above cloud - average quantities for the year 2006: for high
3 altitude clouds (top row, 330 and 450 hPa), mid altitude clouds (middle row, 570 and 670
4 hPa) and low clouds (bottom row, 770 and 870 hPa). Grey means no data available (i.e.
5 insufficient number of cloud detections in the cell).
6



1
2 Figure 3b. TM4 NO₂ VCDs above cloud - average quantities for the year 2006: for high
3 altitude clouds (top row, 330 and 450 hPa), mid altitude clouds (middle row, 570 and 670
4 hPa) and low clouds (bottom row, 770 and 870 hPa). Grey means no data available (i.e.
5 insufficient number of cloud detections in the cell).
6

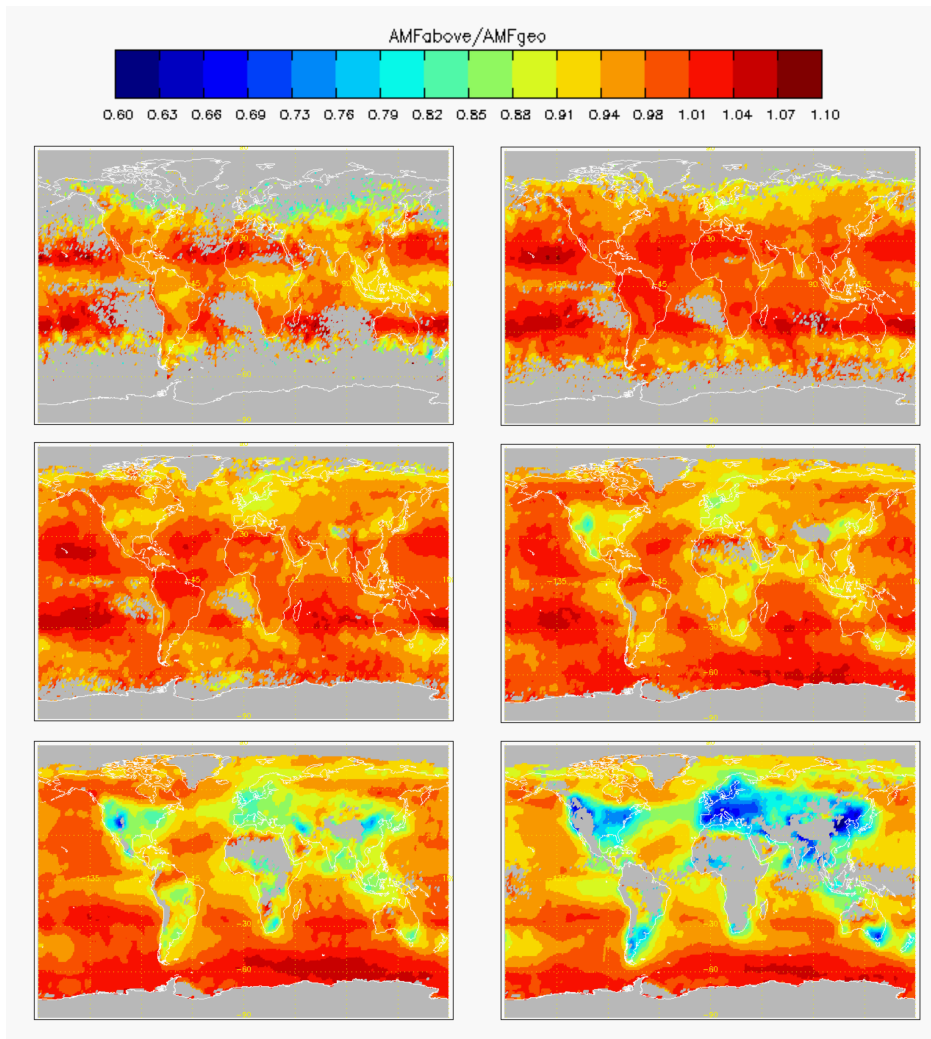


Figure 4. Tropospheric scattering sensitivities above cloud level [AMF_{above}/AMF_{geo} in Eq. (4)]: for high altitude clouds (top row, 330 and 450 hPa), mid altitude clouds (middle row, 570 and 670 hPa) and low clouds (bottom row, 770 and 870 hPa).

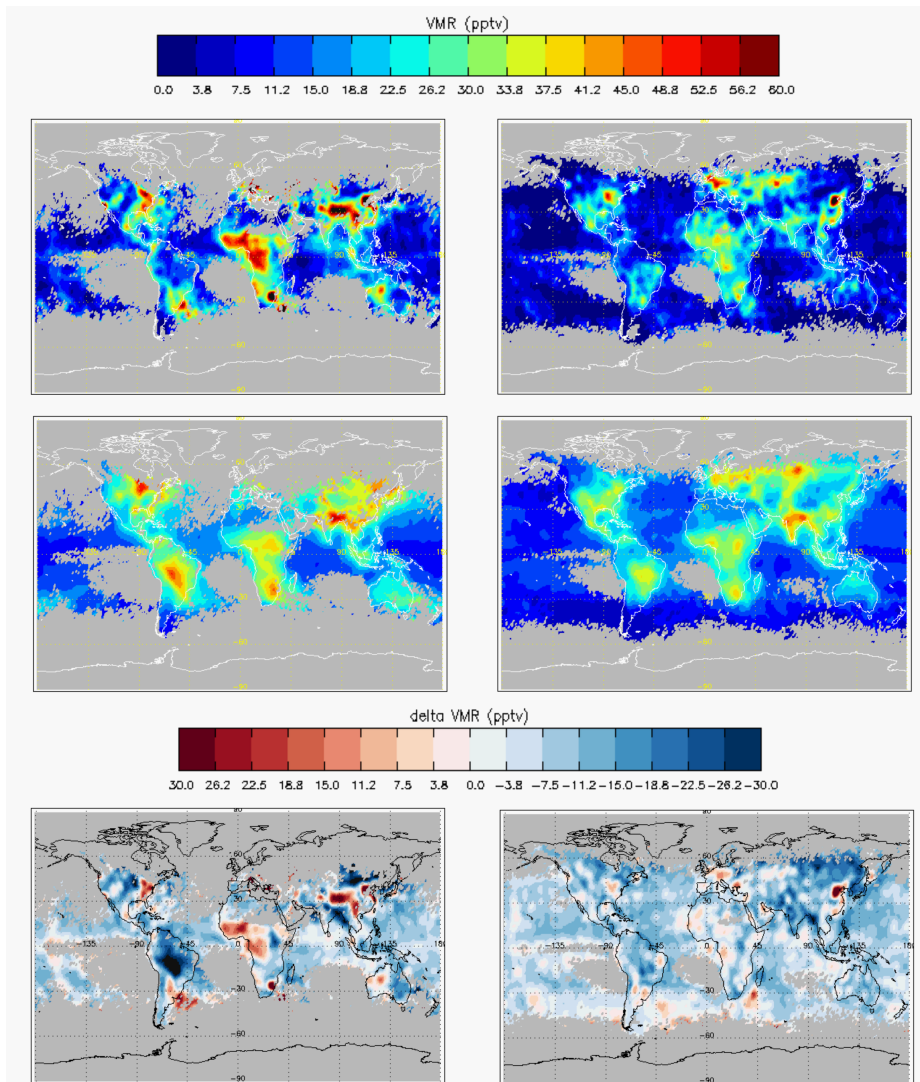


Figure 5a. Upper cloud levels (280 hPa left, 380 hPa right): OMI versus TM4 model NO₂ VMRs (OMI top, TM4 middle, difference bottom) average quantities for the year 2006.

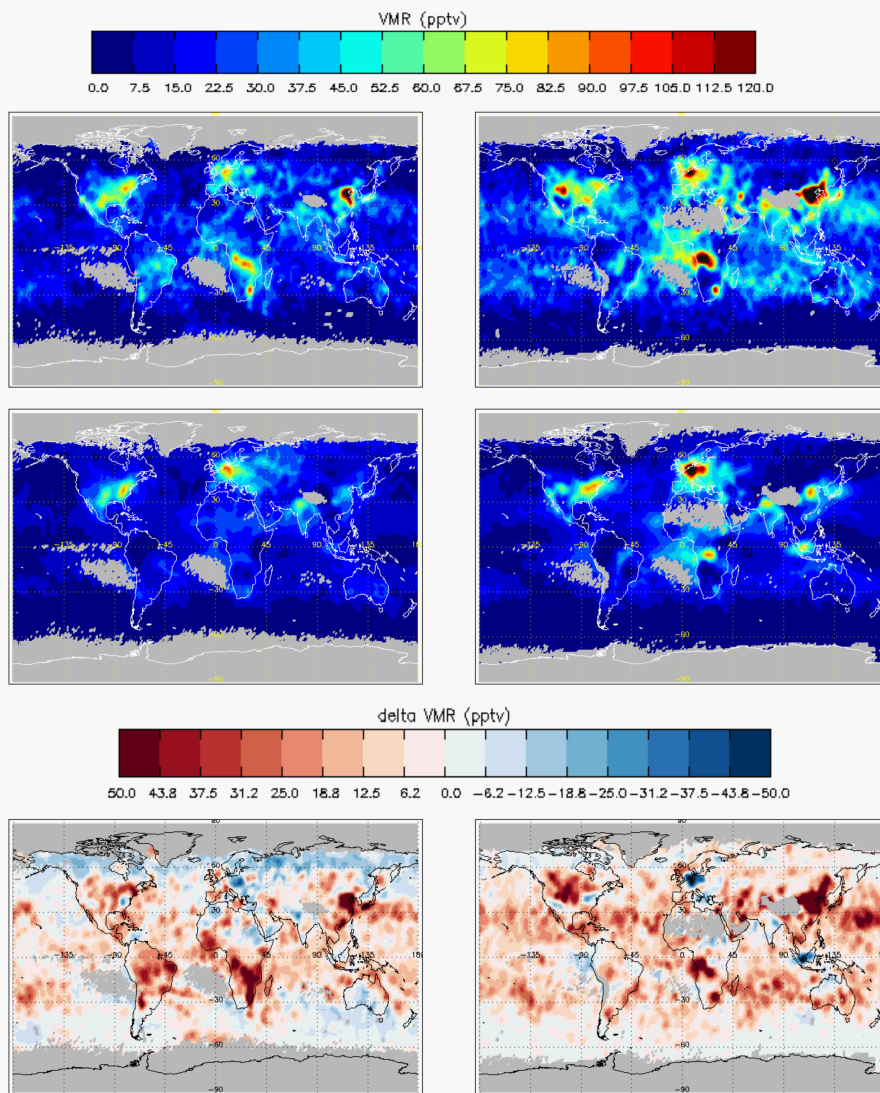


Figure 5b. Middle cloud levels (500 hPa left and 620 hPa right): OMI versus TM4 model NO₂ VMRs (OMI top, TM4 middle, difference bottom) average quantities for the year 2006.

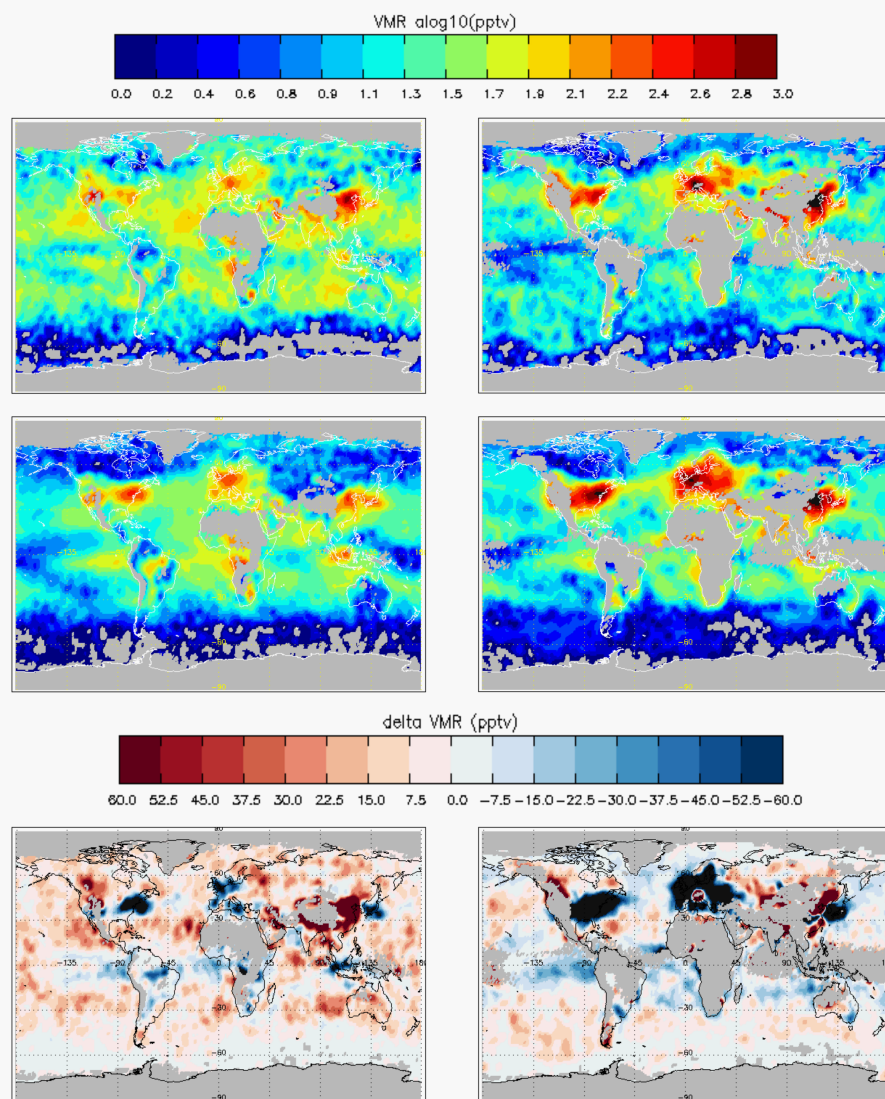
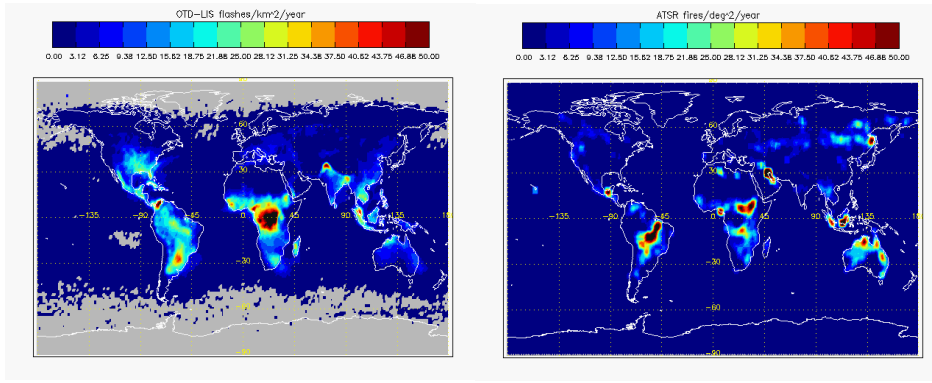


Figure 5c. Lower cloud levels (720 hPa left and 820 hPa right): OMI versus TM4 model NO₂ VMRs (OMI top, TM4 middle, difference bottom) average quantities for the year 2006.



1
2 Figure 6. Interpretation aids for process attribution: mean flash rate climatology (1998-2010)
3 from the LIS-OTD sensor (left, [Cecil et al., 2014]) and fire count climatology (1997-2003)
4 from the ATSR sensor (right, [Arino et al., 2012]).
5

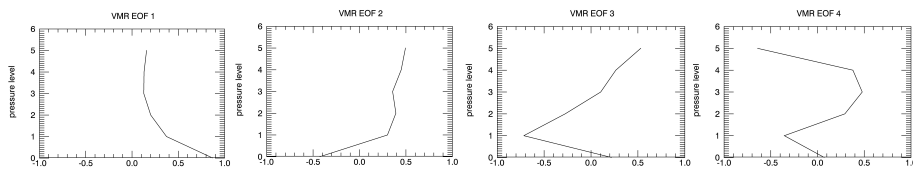


Figure 7a. Classification EOFs: surface source, outflow, high/low outflow, middle outflow.

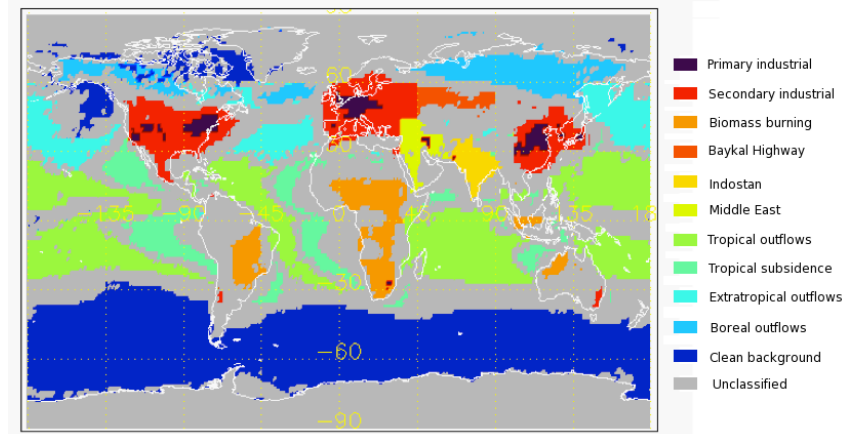
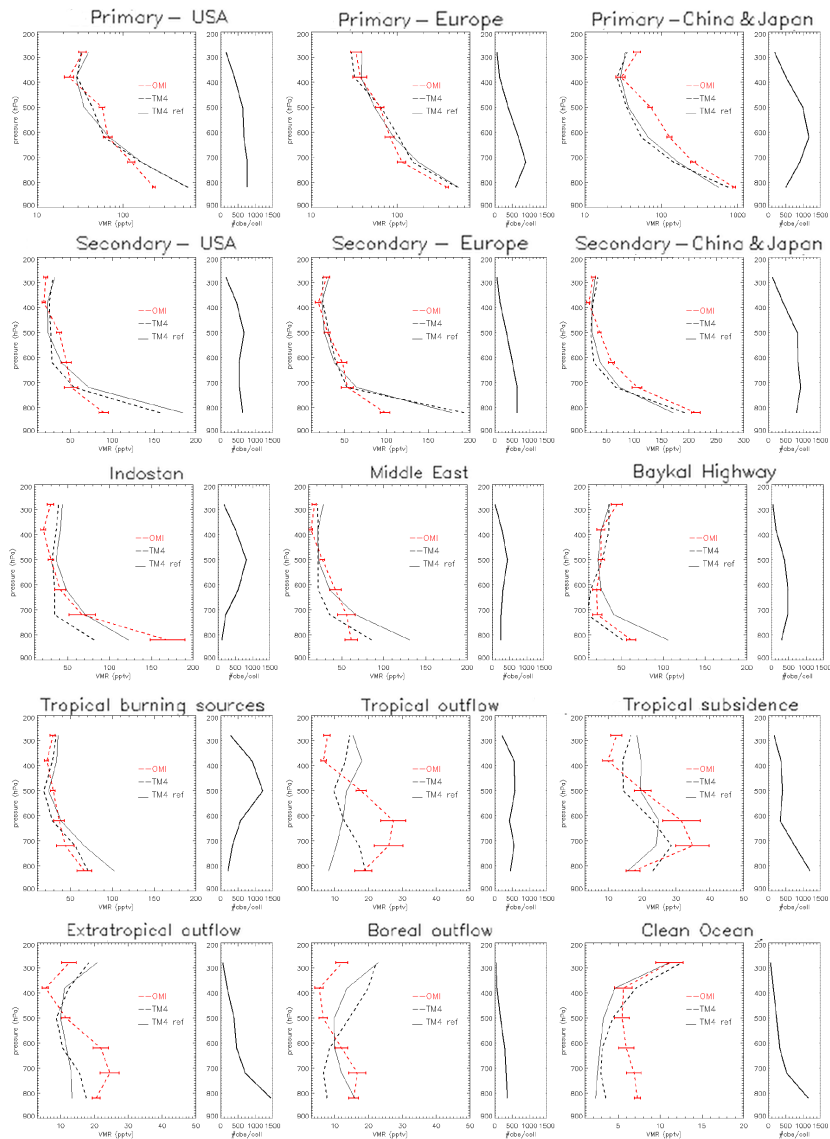


Figure 7b. Model based classes based on EOF decomposition of model NO_2 profiles under cloudy conditions: black (primary industrial), red (secondary industrial), orange (biomass burning), ochre (Baykal Highway), yellow (Indostan), light green (Middle East), green (tropical outflow), turquoise (tropical subsidence), cyan (extratropical outflow), blue (boreal outflow), dark blue (clear background). Gray for unclassified.



1

2 Figure 8. Cloud-slicing NO₂ VMR profiles for the year 2006 by class (OMI pseudoprofile,
3 dashed red line; TM4 pseudoprofile, dashed black line; TM4 profile for cloudy conditions,
4 continuous black line). The error bars show random retrieval errors. The differences between
5 continuous and dashed black lines show systematic pseudoprofile errors. The subpanels on
6 the right show the average number of OMI observations collected per grid cell per year for
7 that class.

1

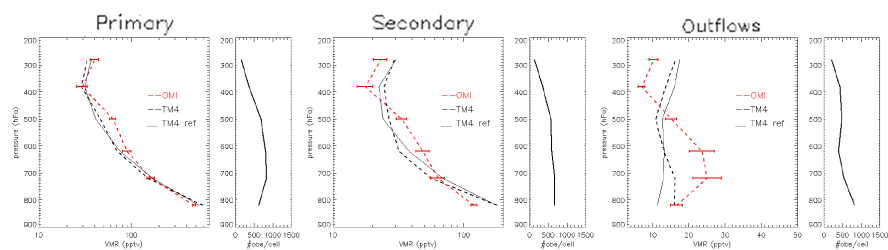


Figure 9. Cloud slicing NO_2 VMR profiles for year 2006 by class: all primary sources (left), all secondary sources (middle) and all outflow classes (right). (OMI pseudoprofile, dashed red line; TM4 pseudoprofile, dashed black line; TM4 profile for cloudy conditions, continuous black line). The error bars show random retrieval errors. The differences between continuous and dashed black lines show systematic pseudoprofile errors.

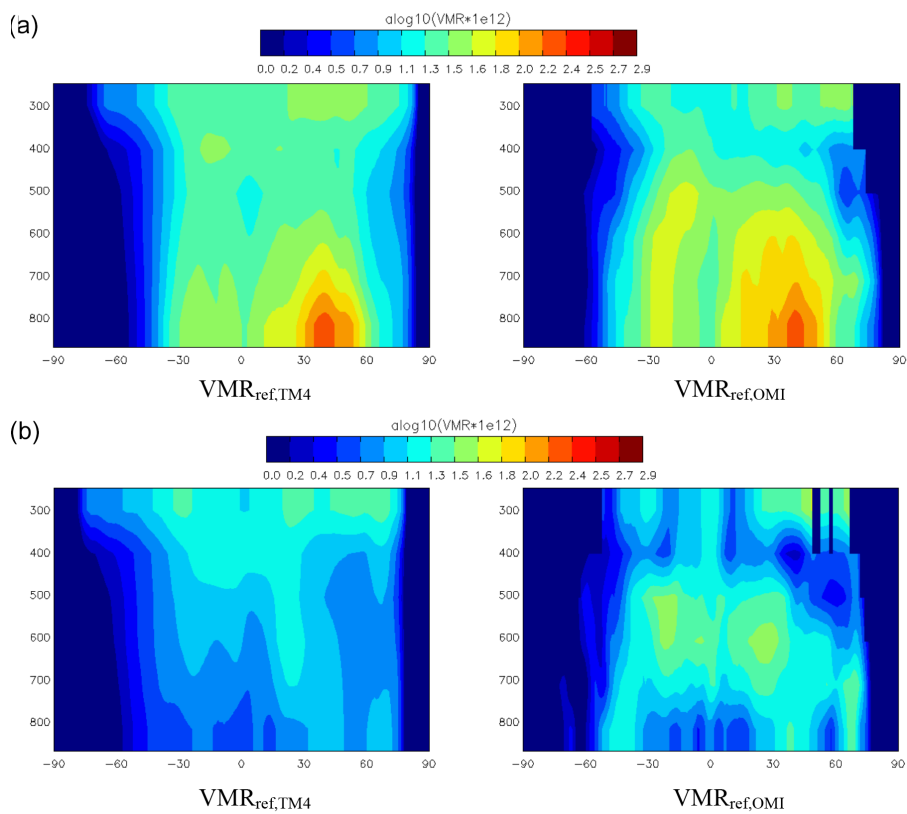
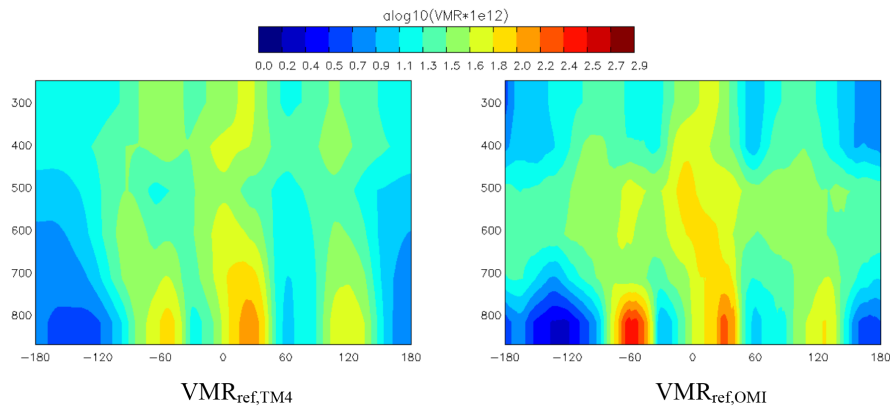
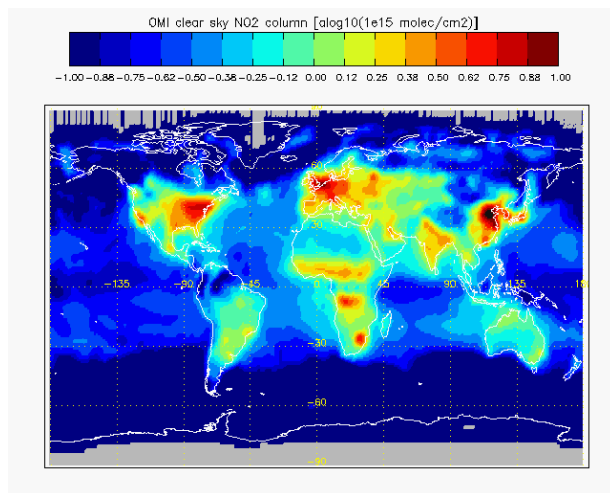


Figure 10a. Latitude-height cross-section of annual zonal mean tropospheric NO_2 from TM4 (left) and OMI (right) with $\text{CRF} > 50\%$.
 Figure 10b. Latitude-height cross-section of annual zonal mean tropospheric NO_2 from TM4 (left) and OMI (right) with $\text{CRF} > 50\%$ over the remote Pacific sector (180W-135W).



1
2 Figure 11. Longitudinal cross-section of annual mean tropospheric NO₂ from TM4 (left) and
3 OMI (right) with CRF > 50% over the tropics (10N-20S).



5
6 Figure 12. Annual clear sky OMI tropospheric NO₂ total columns for the year 2006.

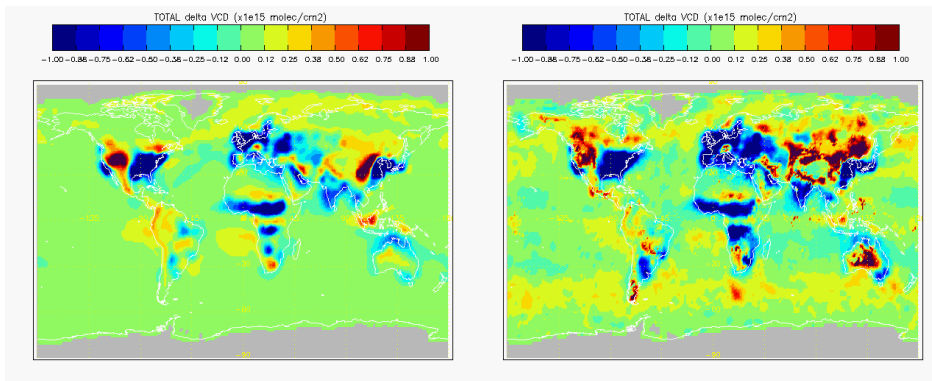


Figure 13. Total tropospheric NO₂ columns differences between cloudy (CRF>50%) and clear (CRF<25%) conditions for TM4 (left) and OMI (right).

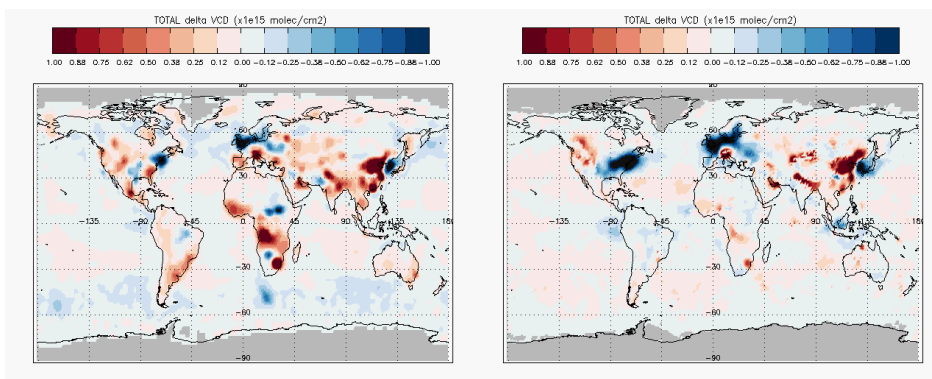


Figure 14. Total tropospheric NO₂ column differences (OMI-TM4) in clear (left) and cloudy (right) conditions for the year 2006.

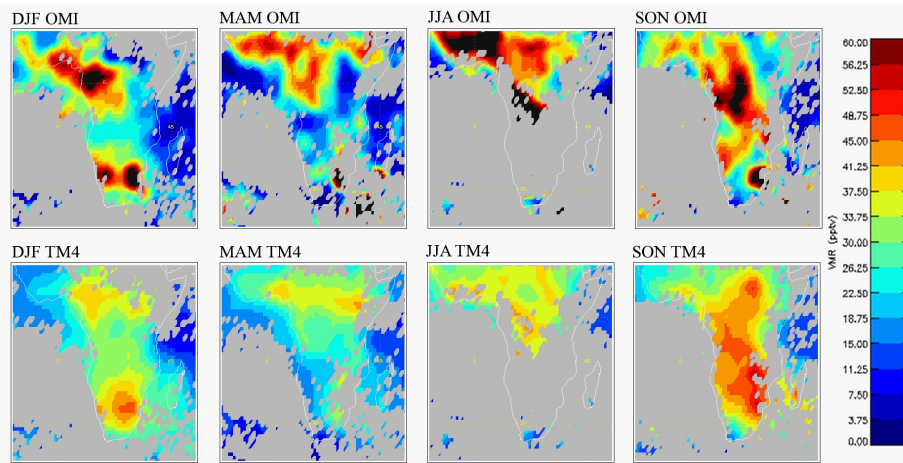


Figure 15. African sector at 280 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO₂ VMRs pseudoprofiles for the year 2006.

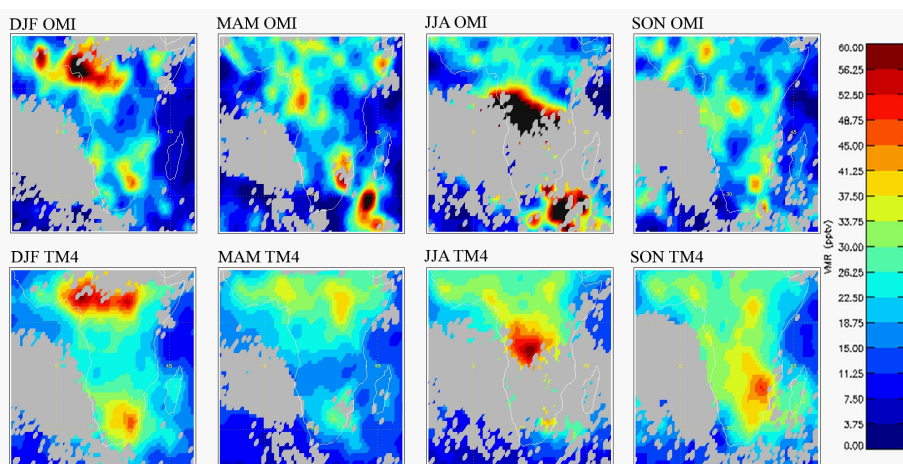


Figure 16. African sector at 380 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO₂ VMRs pseudoprofiles for the year 2006.

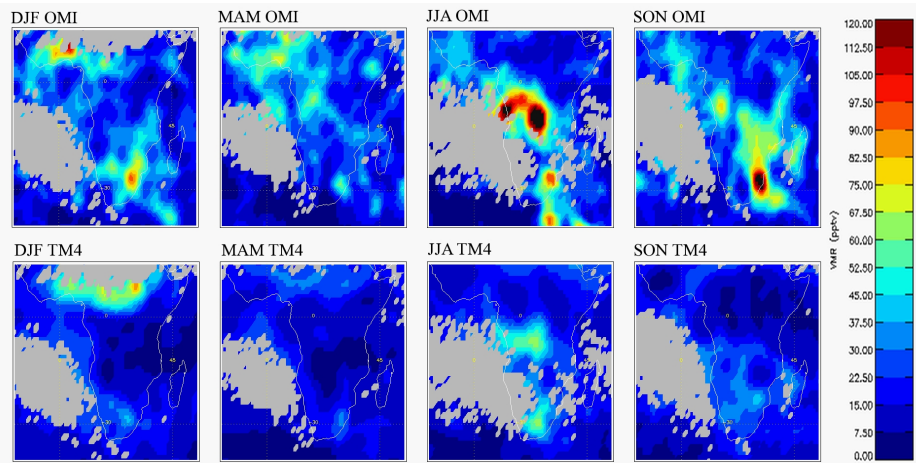


Figure 17. African sector at 500 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO₂ VMRs pseudoprofiles for the year 2006.

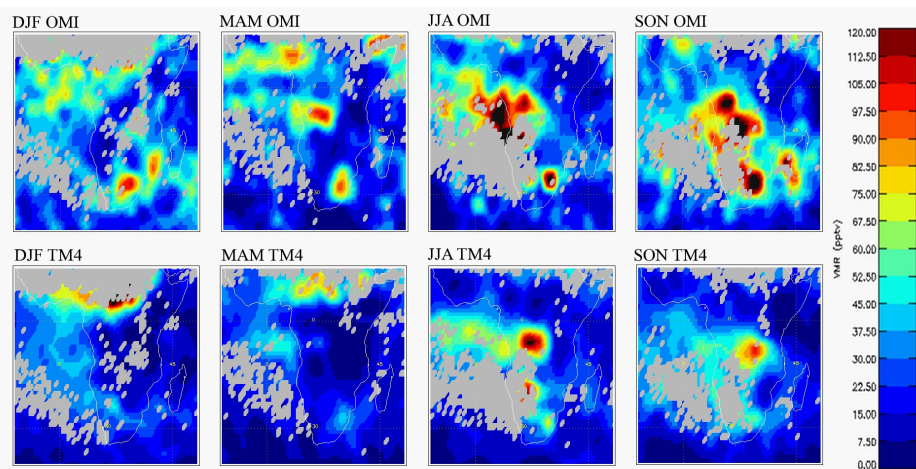


Figure 18. African sector at 620 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO₂ VMRs pseudoprofiles for the year 2006.

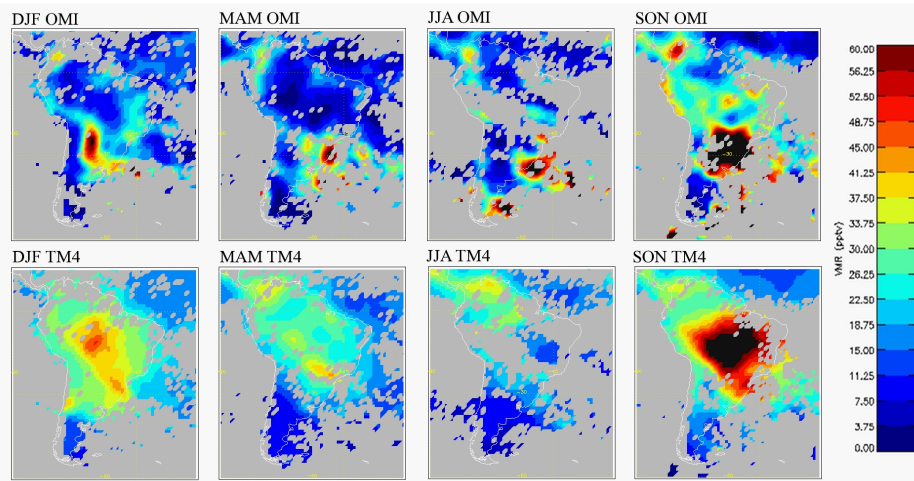


Figure 19. South American sector at 280 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO₂ VMRs pseudoprofiles for the year 2006.

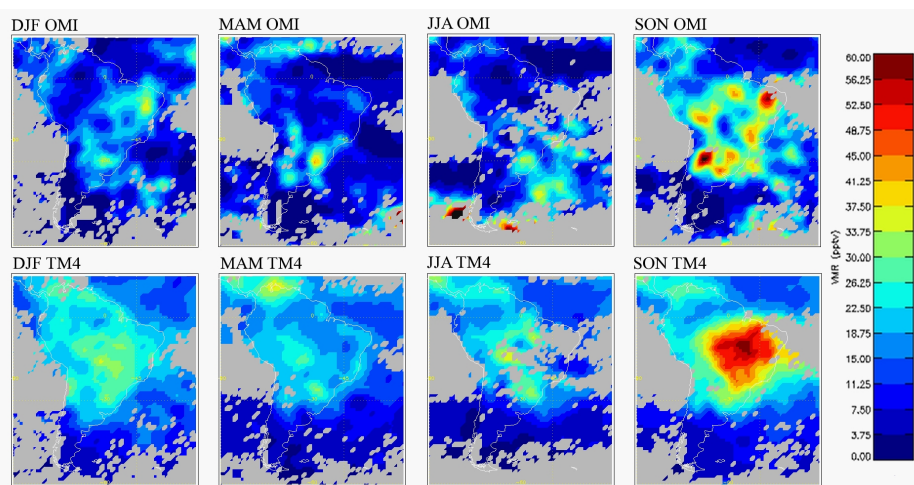


Figure 20. South American sector at 380 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO₂ VMRs pseudoprofiles for the year 2006.

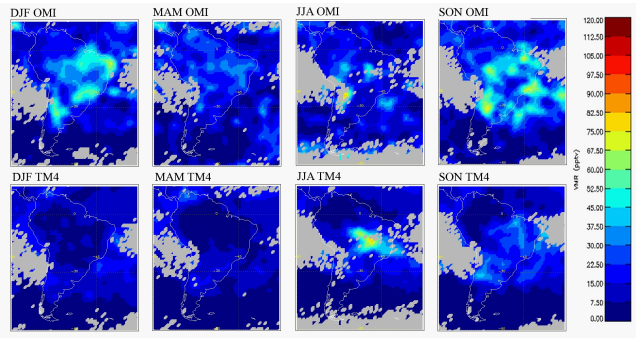


Figure 21. South American sector at 500 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

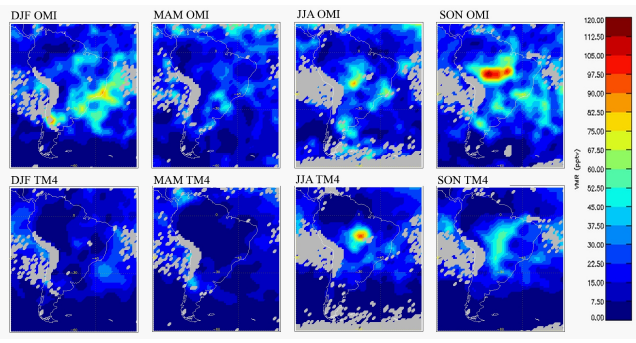


Figure 22. South American sector at 620 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

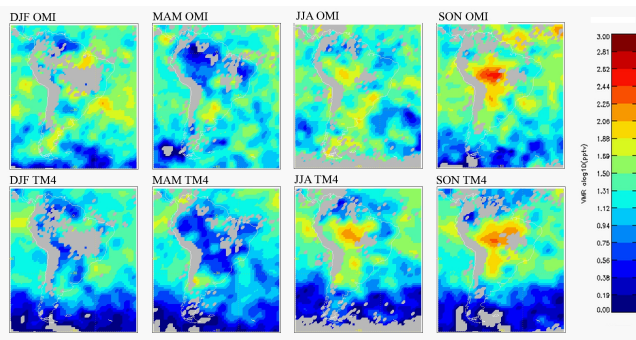


Figure 23. South American sector at 720 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

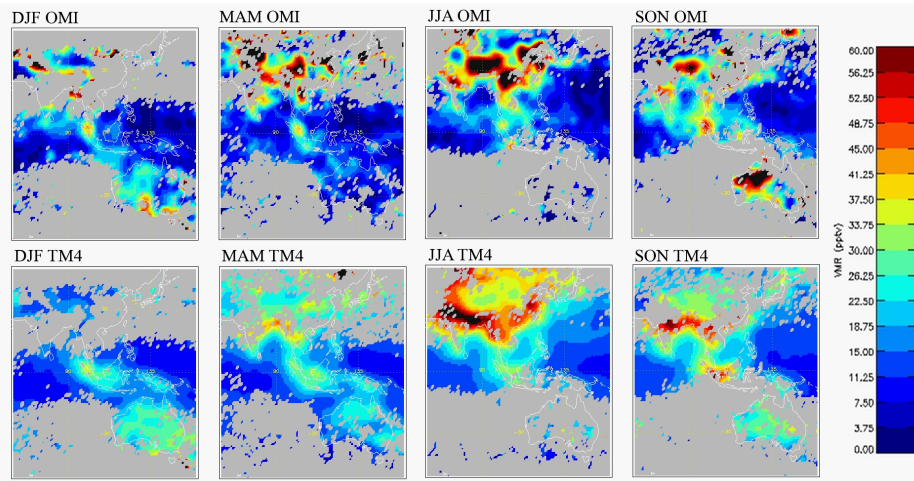


Figure 24. Asian sector at 280 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

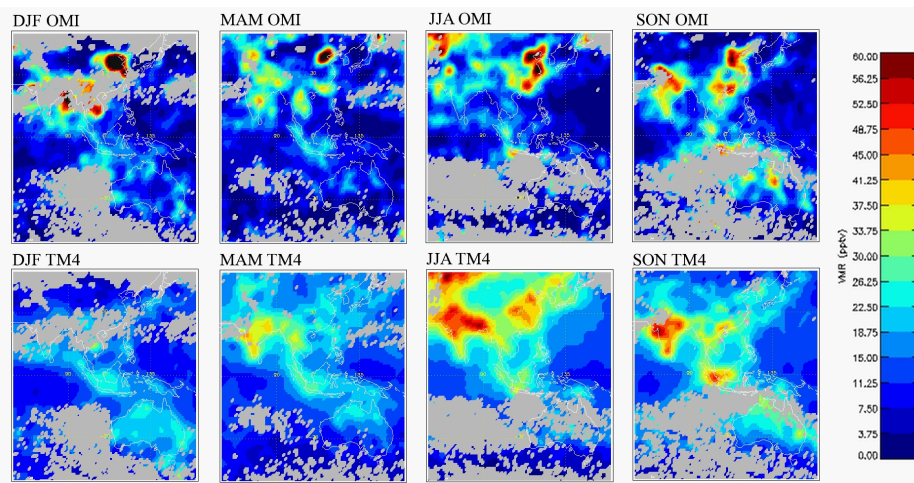


Figure 25. Asian sector at 380 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

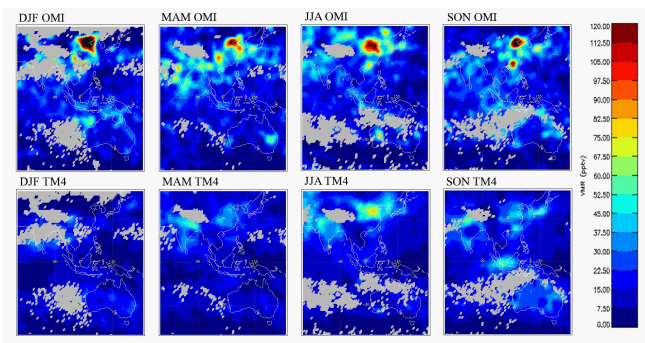


Figure 26. Asian sector at 500 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

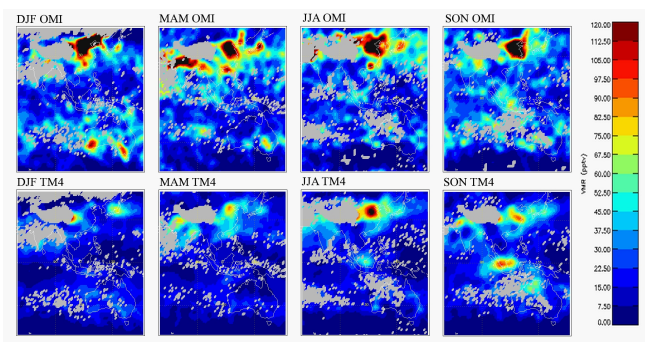


Figure 27. Asian sector at 620 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

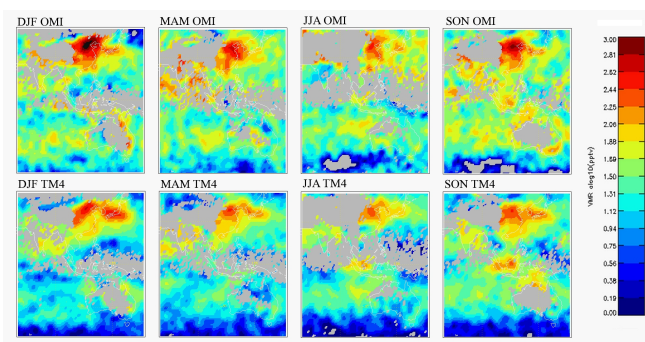


Figure 28. Asian sector at 720 hPa: Seasonal variability in OMI (top row) versus TM4 model (bottom row) average NO_2 VMRs pseudoprofiles for the year 2006.

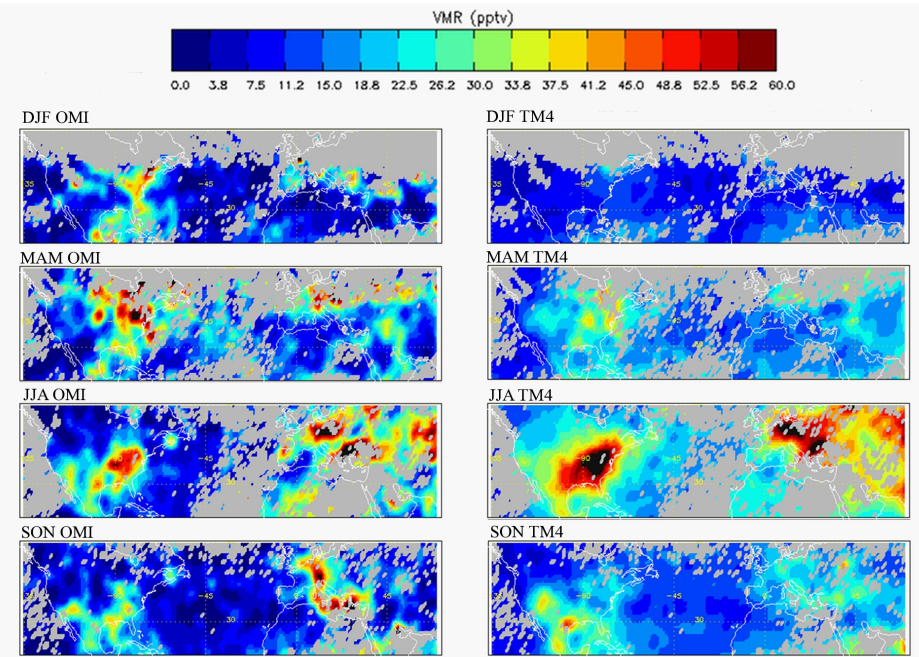


Figure 29. North American and European sector at 380 hPa: Seasonal variability in OMI (left column) versus TM4 model (right column) average NO₂ VMRs pseudoprofiles for 2006.

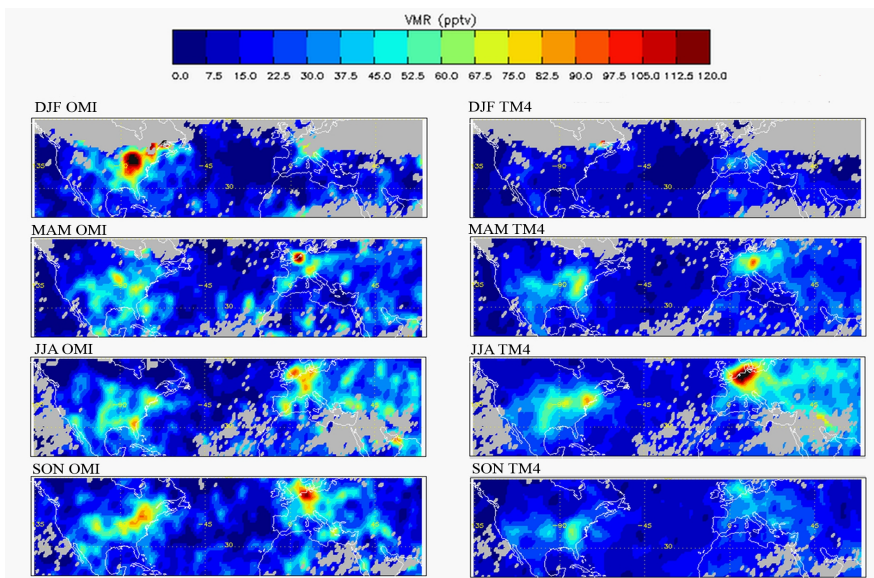


Figure 30. North American and European sector at 500 hPa: Seasonal variability in OMI (left column) versus TM4 model (right column) average NO₂ VMRs pseudoprofiles for 2006.

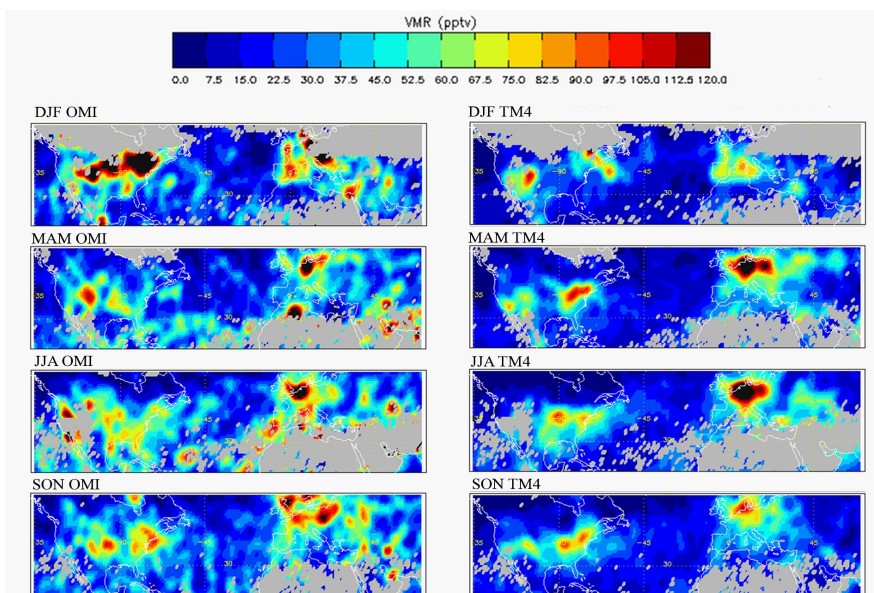


Figure 31. North American and European sector at 620 hPa: Seasonal variability in OMI (left column) versus TM4 model (right column) average NO₂ VMRs pseudoprofiles for 2006.

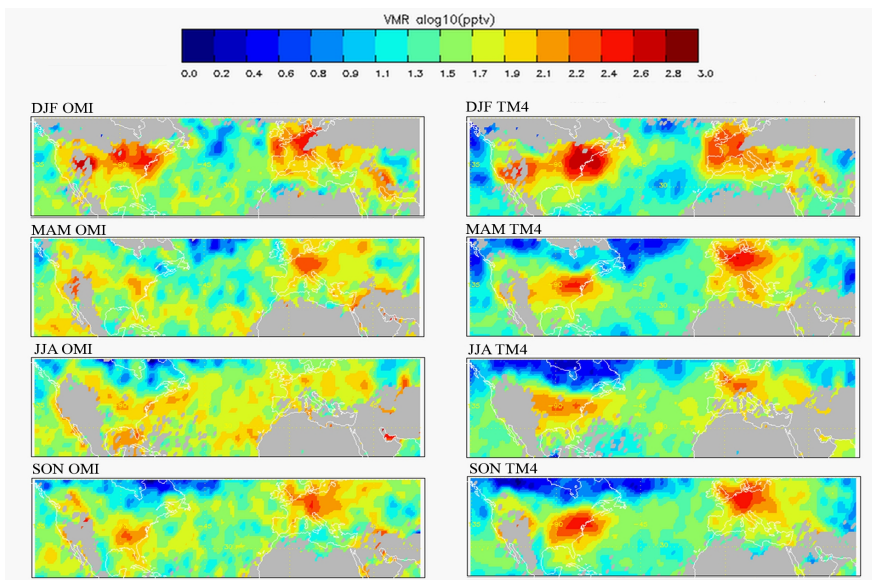


Figure 32. North American and European sector at 720 hPa: Seasonal variability in OMI (left column) versus TM4 model (right column) average NO₂ VMRs pseudoprofiles for 2006.

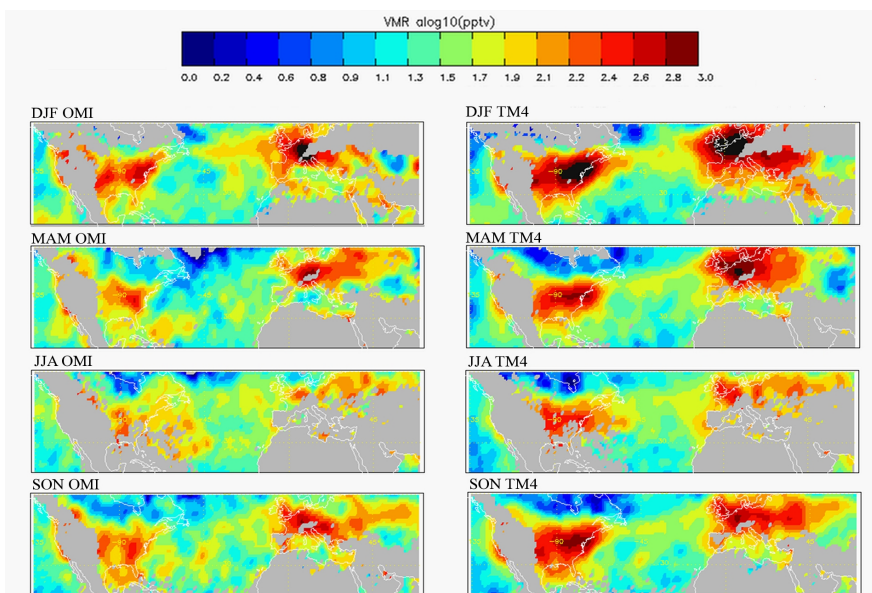


Figure 33. North American and European sector at 820 hPa: Seasonal variability in OMI (left column) versus TM4 model (right column) average NO₂ VMRs pseudoprofiles for 2006.