FOLLOW-UP RESPONSES TO REVIEWER #2

Ms. Ref. No.: Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2018-556.

Title: Nitrogen oxides in the global upper troposphere: interpreting cloud-sliced NO_2 observations from the OMI satellite instrument

Journal: Atmos. Chem. Phys. Discuss.

Reviewer comments are in blue. Responses are in black and include line numbers consistent with the updated manuscript with changes tracked (response to reviewer #2 and minor editorial updates). The manuscript starts on the 4th page of this pdf.

Responses to Anonymous Referee #1:

We would like to thank reviewer #2 for their second meticulous review of the paper. Their comments and careful thought of the paper are incredibly helpful and will no doubt improve the quality of the publication.

1. line 60: Bucsela et al. (2010) should appear on the previous line.

Updated.

2. lines 99 -100: I still do not understand how taking the difference between the column covering 380 hPa and the tropopause and that covering 380 to 500 hPa yields the column centered at 380 hPa (330 - 450 hPa).

We now clarify that UT NO_2 is obtained as the difference between two neighboring partial tropospheric columns retrieved above clouds that are at a mean pressure range of 330-450 hPa and 380-500 hPa (lines 99-100).

3. line 107: The criterion of cloud radiance fraction > 0.7 allows some amount of signal from the lower troposphere to enter the cloud-sliced data set. Both Choi et al. (2014) and Pickering et al. (2016) favored CRF > 0.9 for this reason. Pickering et al. (2016) report a 5% high bias when using CRF >0.7 compared with CRF > 0.9. A paragraph is needed discussing all of the uncertainties involved in the OMI cloud-sliced NO2 product including this possible bias.

Thank you for highlighting the sensitivity test by Pickering et al. (2016). Their results clearly demonstrate that the effect of different CRF thresholds of 0.9 and 0.7 is small (<5%) and not significant (derived NO_x yields have large variability: 117 ± 94 mol fl^{-1} using a CRF>70% and 112 ± 67 mol fl^{-1}). We now state this in the paper (lines 117 and 128-127).

4. lines 257 - 262: The production rate derived here is very model dependent. The authors need to state this fact and that the values derived here are influenced by any error that exists in the UT NOy chemistry that may be in GEOS-Chem. Such possible errors have recently been discussed by Travis et al. (2016) and Silvern et al. (2018).

We now state that the modelled and observed NO_2 are consistent over the pressure range of the OMI UT NO_2 product (6-9 km). The comparison between modelled and observed NO_2 by Silvern et al. (2018) is adapted in Figure 1 below and shows that the model reproduces the observed NO_2 across the altitude range of the OMI UT NO_2 product (lines 225-227). The bias reported by Travis and Silvern is for higher altitudes.

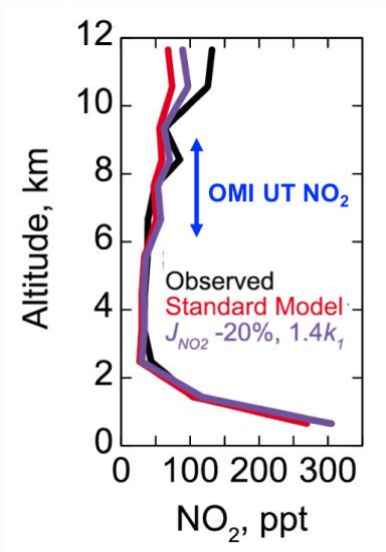

Figure 1. Comparison of TD-LIF and GEOS-Chem NO_2 during SEAC^{4}RS (adapted from Silvern et al., 2018). Two versions of GEOS-Chem are shown that test sensitivity of NO_2 vertical distribution to uncertainties in reaction kinetics and photolysis. Blue arrow shows the altitude range of the NASA OMI UT NO_2 product.

5. page 3, line 97: Is aerosol really accounted for in the NO2 air mass factors, and if so, how?

Yes. We now reference Boersma et al. (2004) (line 122) that is in turn referenced by Belmonte-Rivas et al. (2015) when describing the air mass factor calculation.

I disagree. Please have another look at Boersma et al., 2004 last sentence of section 3.2. Aerosols are not explicitly taken into account in the DOMINO NO2 data product, only implicitly in partially cloudy scenes through the cloud correction applied. However, this correction has no effect on the cloudy scenes discussed here.

Thank you for pointing us to the appropriate location in Boersma et al. (2004) that makes clear that aerosols are not directly accounted for in the DOMINO NO_2 AMF calculation. We have updated the text to reflect this (line 95).

6. page 7, line 199: I understand that aircraft measurements are screened for stratospheric air masses in tropospheric applications. However, here data are compared to satellite retrievals, and these will -- as far as I understand – include such stratospheric air masses if they are in the right pressure range above a cloud. I therefore wonder if this screening really makes sense here.

Both the aircraft and satellite products exclude stratospheric contributions, and so the comparison is consistent. We now clarify that the OMI satellite product is tropospheric NO2 only (line 74). We already state that the KNMI product removes stratospheric NO2 by subtracting the stratospheric contribution in the retrieval (lines 121-122). We now elaborate that the stratospheric contribution in the NASA product is removed when differencing two nearby partial columns, as NO2 aloft is assumed uniform (lines 134-135 and lines 141-142).

This is not the point. The NASA product takes the difference in NO2 columns over neighbouring clouds having different cloud top. Any NO2 in between these altitudes will contribute to the retrieved UT mixing ratio, regardless of its origin. If stratospheric NO2 is brought down to the UT, the cloud slicing method will detect it as UT NO2 (as it should).

The retrieval approach of Choi et al. (2014) only considers scenes with well-mixed NO_2, diagnosed with a vertical gradient threshold of 0.33 pptv hPa^{-1} from the GMI chemical transport model. We also only consider scenes with more than 50 measurements at coarse resolution (5° × 8°), so downwelling from the stratosphere that concerns the reviewer would have to persist throughout the gridsquare and over the whole season for multiple years (2005-2007) to bias the OMI UT NO_2. We also now state that the contribution of stratospheric injection, as estimated by Murray et al. (2012) using GEOS-Chem, is small (lines 240-242).

7. Please add the uncertainty estimates for the NOx yield and global lightning NOx source given in the text also to the abstract and conclusions.

The error in the NO_x yield and global lightning NO_x source is now stated in the Abstract and Conclusions. We have also included the estimate of global lightning NO_x with the size of the uncertainty inferred from the relative size of the uncertainty in the NO_x production rate (lines 286-289).

References:

Murray et al. (2012), doi:10.1029/2012jd017934.

Nitrogen oxides in the global upper troposphere: interpreting cloud-sliced NO_2 observations from the OMI satellite instrument

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Abstract. Nitrogen oxides ($NO_x \equiv NO + NO_2$) in the upper troposphere (UT) have a large impact on global tropospheric ozone and OH (the main atmospheric oxidant). New cloud-sliced observations of UT NO_2 at 450-280 hPa (~6-9 km) from the OMI satellite instrument produced by NASA and KNMI provide global coverage to test our understanding of the factors controlling UT NO_x. We find that these products offer useful information when averaged over coarse scales (20° × 32°, seasonal), and that the NASA product is more consistent with aircraft observations of UT NO_2. Correlation with LIS/OTD satellite observations of lightning flash frequencies suggests that lightning is the dominant source of NO_x to the upper troposphere except for extratropical latitudes in winter. The NO_2 background in the absence of lightning is 10-20 pptv. We infer a global mean NO_x yield of 280 ± 80 moles per lightning flash, with no significant difference between the tropics and mid-latitudes, and a global lightning NO_x source of 5.9 ± 1.7 Tg N a^{-1}. There is indication that the NO_x yield per flash increases with lightning flash footprint and with flash energy.

1. Introduction

Nitrogen oxides ($NO_x \equiv NO + NO_2$) in the upper troposphere (UT) have profound effects on the oxidizing capacity of the atmosphere and on climate, but the factors controlling their concentrations are poorly understood. NO_x in the UT impacts climate by efficiently producing ozone where it is a potent greenhouse gas (Dahlmann et al., 2011; Worden et al., 2011; Rap et al., 2015) and by increasing the concentration of OH (the main tropospheric oxidant) (Murray et al., 2012; Murray et al., 2014). Primary NO_x sources in the UT include lightning, aircraft, convective injection, and downwelling from the stratosphere (Ehhalt et al., 1992; Jaeglé et al., 1998; Bertram et al., 2007). NO_x cycles chemically with reservoir species including nitric acid (HNO_3), pernitric acid (HNO_4), dinitrogen pentoxide (N_2O_5), peroxyacetylnitrate (PAN), and other organic nitrates, thus defining the NO_y chemical family ($NO_y \equiv NO_x$ + reservoirs). Effective loss of NO_x from the UT is through subsidence of NO_y to lower altitudes where deposition of HNO_3 provides the ultimate sink. The residence time of NO_y in the UT is 10-20 days (Prather and Jacob, 1997). The lifetime of

NO_x against conversion to short-lived reservoirs varies from ~3 hours in the convective outflow of thunderstorms to 0.5-1.5 days in background air (Nault et al., 2016). Chemical recycling from these reservoirs maintains relatively high UT NO_x background concentrations (Bradshaw et al., 2000; Baehr et al., 2003; Nault et al., 2016).

Representation of lightning NO_x in chemical transport models (CTMs) is particularly uncertain. Physically-based parameterizations relating lightning frequency to deep convective cloud tops, convective mass flux, convective precipitation, or high-cloud ice content have poor predictive capability (Tost et al., 2007; Allen et al., 2010; Murray et al., 2012; Finney et al., 2014), limiting our ability to estimate the response of lightning NO_x to future climate (Finney et al., 2016; 2018). An alternative is to prescribe flash densities from space-based observations and static NO_x production rates per flash (Sauvage et al., 2007; Allen et al., 2010; Murray et al., 2012). NO_x production efficiencies per flash in the literature vary from <10 to 5000 moles nitrogen per flash (mol N fl^{-1}) (Schumann and Huntrieser, 2007; Murray, 2016). Global chemical transport models (CTMs) typically use 100-500 mol N fl^{-1}, sometimes assuming higher production rates at mid-latitudes than in the tropics (Hudman et al., 2007; Ott et al., 2010), and a global lightning NO_x source of 3-7 Tg N a^{-1} to match observations of tropospheric ozone and NO_y species (Sauvage et al., 2007).

Our understanding of UT NO_x has so far been evaluated with observations from aircraft campaigns (Drummond et al., 1988; Jacob et al., 1996; Crawford et al., 1997; Jaeglé et al., 1998; Bradshaw et al., 2000; Hudman et al., 2007; Stratmann et al., 2016). There are also long-term NO_x measurements from instruments onboard commercial aircraft dating back to the 1990s, but these are mostly over the north Atlantic and the NO_2 measurements have low precision and interference from thermally unstable NO_x reservoir compounds (Brunner et al., 2001). A number of studies have used satellite observations of tropospheric NO_2 columns from solar backscatter to infer lightning NO_x emissions (Beirle et al., 2010; Pickering et al., 2016; Bucsela et al., 2010), including in combination with global models (Boersma et al., 2005; Martin et al., 2007; Miyazaki et al., 2014). These studies estimate global lightning NO_x emission of 1 to 8 Tg N a^{-1}.

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New cloud-sliced satellite products of tropospheric NO_2 mixing ratios at 280-450 hPa (~6-9 km) offer additional vertical resolution by retrieving partial NO_2 columns above clouds and exploiting differences in heights of neighboring clouds to calculate NO_2 mixing ratios (Choi et al., 2014; Belmonte-Rivas et al., 2015). There are two new products of seasonal mean UT NO_2 mixing ratios retrieved from Ozone Monitoring Instrument (OMI) partial NO_2 columns by research groups at KNMI and NASA. The KNMI product has been evaluated against UT NO_2 from the Tracer Model version 4 (TM4) CTM. Large regional differences between OMI and TM4 are attributed to model deficiencies in lightning NO_x and uplift of anthropogenic pollution (Belmonte-Rivas et al., 2015). The NASA UT product is new to this work and follows a similar retrieval approach to the mid-tropospheric (900-650 hPa) product of Choi et al. (2014). That product was evaluated with aircraft observations of NO_2 and interpreted with the Global Modeling Initiative (GMI) CTM (Choi et al., 2014). Choi et al. (2014) identified large discrepancies between modeled and observed NO_2 seasonality over regions influenced by pollution and lightning.

Here we compare the two UT NO_2 products, obtained with distinct retrieval methods, and use aircraft observations of NO_2 from multiple NASA DC8 aircraft campaigns to arbitrate and evaluate the information that can be derived from the satellite datasets. We go on to test current understanding of UT NO_x and the implications for lightning emissions using the GEOS-Chem CTM.

2. OMI observations of upper troposphere NO_2

OMI is onboard the NASA Aura satellite launched into sun-synchronous orbit in July 2004. It has an overpass time of about 13h30 local time (LT), a swath width of 2600 km, and a horizontal resolution of 13 km × 24 km at nadir (Levelt et al., 2006). Columns of NO_2 along the instrument viewing path (slant columns) are obtained by spectral fitting of solar backscattered radiation in the 405-465 nm window (Boersma et al., 2011). Standard products of total and tropospheric column NO_2 are screened for cloudy scenes using a cloud radiance fraction threshold of 0.5. Partial columns of NO_2 above cloudy scenes can be used to estimate vertically resolved NO_2 mixing ratios, as was first demonstrated with satellite observations of ozone (Ziemke et al., 2001). This approach, so-called cloud slicing, assumes a uniform trace gas concentration between two horizontally nearby clouds at different altitudes, so that the UT NO_2 mixing ratio is proportional to the slope of the partial columns versus the corresponding cloud pressures at the optical centre of the cloud. Two products of seasonal mean UT NO_2 have been retrieved from OMI following distinct retrieval steps detailed below: a product from KNMI at 330-450 hPa for 2006 (Belmonte-Rivas et al., 2015) and from NASA at 280-450 hPa for 2005-2007 following an approach similar to that used to retrieve mid-tropospheric NO_2 (Choi et al., 2014). In what follows we distinguish the two OMI NO_2 products as KNMI and NASA.

The KNMI product uses DOMINO v2.0 slant columns (Boersma et al., 2011) and OMCLDO2 cloud fractions and altitudes (Acarreta et al., 2004) over partially to very cloudy scenes (cloud radiance fraction > 0.5). Contamination due to NO_2 from below (up to 66% over polluted land masses) is estimated using the TM4 model and removed. Stratospheric NO_2 from an assimilated product (Belmonte-Rivas et al., 2014) is also removed. An air mass factor (AMF) (detailed in Boersma et al. (2004)) that accounts for viewing geometry, surface albedo, light attenuation by gases along the viewing path, and sensitivity to NO_2 vertical distribution is applied to the resultant partial slant columns to convert to vertical columns. Additional data filtering removes scenes with solar zenith angle (SZA) ≥ 70° and surface albedo ≥ 30%. Resultant daily vertical partial columns are aggregated on consistent pressure and horizontal (1° × 1°) grids and used to determine seasonal mean UT NO_2 mixing ratios for gridsquares with at least 30 measurements. UT NO_2 centred at 380 hPa (range 330-450 hPa) is estimated as the difference between partial tropospheric columns retrieved above two neighboring clouds with cloud pressures in the ranges 330-450 hPa and 380-500 hPa, respectively. Biases from sampling cloudy scenes, such as the effect of clouds on photochemistry, are corrected using TM4. These are small (typically <20%) in the UT (Belmonte-Rivas et al., 2015).

The NASA UT NO_2 product for 2005-2007, centred at 350 hPa (~280-450 hPa), uses updated version 3 slant columns (OMNO2 v3.0) (Krotkov et al., 2017) that correct for a positive bias in the DOMINO v2.0 product with improved spectral fitting (Marchenko et al., 2015; van Geffen et al., 2015). Partial columns from the cloud height to the top of the atmosphere are retrieved for individual OMI pixels above very cloudy scenes (cloud radiance fraction > 0.7) to minimize contamination from below. Cloud fraction and height is from the OMCLDO2 product (Acarreta et al., 2004). The AMF accounts for viewing path geometry and light scattering by clouds with uniform scatter that are optically thick and geometrically thin (near-Lambertian clouds). Data filtering is applied to remove scenes with SZA > 80°, snow/ice cover, and severe aerosol pollution that could be misclassified as clouds. Daily UT NO_2 is estimated for neighboring partial columns with sufficient cloud variability (cloud pressure distance > 160 hPa) and well-mixed NO_2 (NO_2 vertical gradient < 0.33 pptv hPa^{-1} diagnosed with the GMI CTM). The stratospheric column is assumed uniform above neighboring clouds and so is removed when differencing two nearby partial columns. Daily values of UT NO_2 are gridded to obtain seasonal means at 5° × 8° (latitude × longitude) for scenes with at least 50 measurements. Gaussian weighting is applied to assign higher weighting to UT NO_2 closest to 350 hPa. Choi et al. (2014) used a similar approach to retrieve mid-tropospheric NO_2, except that cloud fraction and height were from the OMCLDRR product, and successful retrieval required a stricter cloud radiance fraction of 0.9, a minimum of 30 measurements, and a wider minimum cloud pressure distance of 200 hPa. A shift in cloud radiance fraction

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threshold from 0.9 (Choi et al., 2014) to 0.7 (this work) only introduces a small (<5%) difference in the retrieved partial columns due to contamination from below, as estimated by Pickering et al. (2016) for OMI scenes over the Gulf of Mexico.

Figure 1 compares seasonal mean UT NO_2 from the two satellite products in December-February and June-August. KNMI NO_2 is gridded to the NASA coarse grid. Data for March-May and September-November are in the Supplement (Figure S1). KNMI NO_2 has greater coverage than the NASA product, due to a lower cloud fraction threshold in the retrieval. The two products exhibit very different spatial features. Spatial correlation between the two products (Pearson's correlation coefficient between coincident gridsquares) is R = 0.41 in December-February and R = 0.38 in June-August. There is marginal improvement in the correlation with further spatial averaging. At 20° × 32° we find R = 0.50 in December-February and R = 0.45 in June-August. The correlation only increases substantially in September-November from R = 0.49 at 5° × 8° (Figure S1) to R = 0.66 at 20° × 32°. KNMI is systematically lower than NASA in all seasons for coincident gridsquares, varying from 16% lower in June-August to 48% lower in December-February at 20° × 32°.

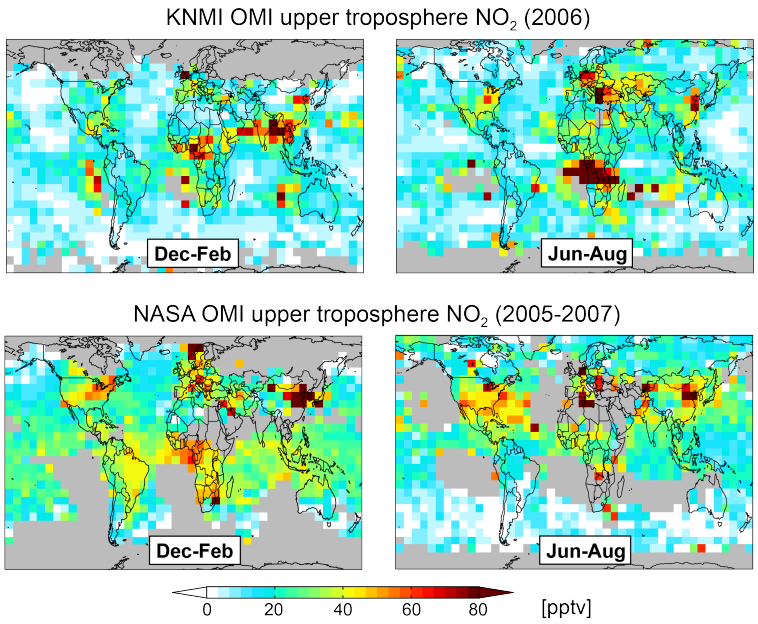

Figure 1. Upper troposphere (UT) NO_2 from the OMI satellite instrument. Seasonal mean UT NO_2 from KNMI in 2006 at 330-450 hPa (top) is compared to NASA in 2005-2007 at 280-450 hPa (bottom). Data are at 5° × 8° horizontal resolution for December-February (left) and June-August (right). Grey areas indicate no data and, for NASA, scenes with fewer than 50 measurements.

Contamination of UT NO_2 from below the cloud may still be present in the datasets despite attempts to correct for this using the TM4 model in the case of KNMI and by only considering very cloudy scenes in the case of NASA. These include a large enhancement in KNMI NO_2 (> 90 pptv) over southern Africa in June-August when there is intense biomass burning, and the NO_2 hotspot over northeast China in all seasons in both products (Figures 1, S1). Belmonte-Rivas et al. (2015) caution that the contamination correction in the KNMI product relies on accurate simulation of NO_2 vertical distribution.

3. Evaluation of OMI upper troposphere NO_2 with aircraft observations

We evaluate the OMI UT NO_2 products with observations from NASA DC8 aircraft campaigns over North America and Greenland in spring-summer, for which dense coverage is available (Figure 2). These include the INTEX-A, INTEX-B, ARCTAS, DC3, and SEAC^{4}RS campaigns. Only INTEX-B is in the same year as the OMI products but we consider interannual variability to be only a small source of error. All NO_2 measurements are from thermal-dissociation laser-induced fluorescence (TD-LIF) instruments (Day et al., 2002). These are susceptible to interference from decomposition of thermally unstable reservoir compounds including methyl peroxy nitrate ($CH_3O_2NO_2$) and HNO_4 (Browne et al., 2011). Publicly available DC3 and SEAC^{4}RS TD-LIF NO_2 are already corrected for this interference. We apply a correction for the other campaigns using the relationship between temperature and percentage interference from Browne et al. (2011). Observed mean ambient air temperature in the UT during INTEX-A was 246 K, corresponding to 20% interference. That for INTEX-B was 241 K (30% interference) and 236 K for ARCTAS (38% interference).

There are also NO_2 observations from the recent NASA ATom campaign, and from the In-service Aircraft for a Global Observing System (IAGOS) commercial aircraft campaign (Berkes et al., 2017). These use chemiluminescence instruments that are also susceptible to interference. Chemiluminescence and TD-LIF NO_2 are consistent during the SEAC^{4}RS campaign for the altitude range considered in this work (6-9 km) (Travis et al., 2016), but the interference from chemiluminescence is challenging to quantify, due to dependence on the operator and instrument design that varies across campaigns (Reed et al., 2016).

Figure 2 shows the sampling extent of TD-LIF UT NO_2 over North America and Greenland in spring-summer at 450-280 hPa around the satellite overpass (11h00-16h00 LT) for scenes not influenced by the stratosphere (diagnosed with collocated ozone/CO > 1.25 mol mol^{-1} (Hudman et al., 2007)). Concentrations of UT NO_2 exceed 80 pptv over the eastern US due to lightning NO_x emissions and convective transport of boundary layer pollution, and are < 30 pptv over the rest of the domain.

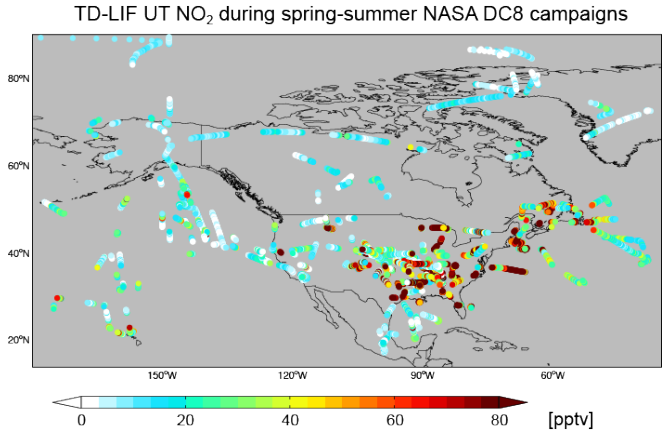

Figure 2. NASA DC8 upper troposphere NO_2 over North America in spring-summer (March-August). Observations are from the TD-LIF instrument at 450-280 hPa, 11h00-16h00 local time, and without stratospheric influence. Campaigns include INTEX-A in June-August 2004 (Singh et al., 2006), INTEX-B in March-May 2006 (Singh et al., 2009), ARCTAS in March-April and June-July 2008 (Jacob et al., 2010), DC3 in May-June 2012 (Barth et al., 2015), and SEAC^{4}RS in August 2013 (Toon et al., 2016).

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Figure 3 shows the spatial correlation between the March-August mean gridded aircraft data and the OMI UT NO_2 from the KNMI and NASA products as a function of horizontal resolution. There is no significant spatial correlation between the OMI products and aircraft NO_2 at 5° × 8° (R < 0.1) and 10° × 16° (R < 0.2). The correlation improves with further spatial averaging, peaking at 20° × 32° (R = 0.56 for KNMI, R = 0.64 for NASA). The satellite products are also spatially consistent at this resolution (R = 0.89), but KNMI is 43% lower than NASA.

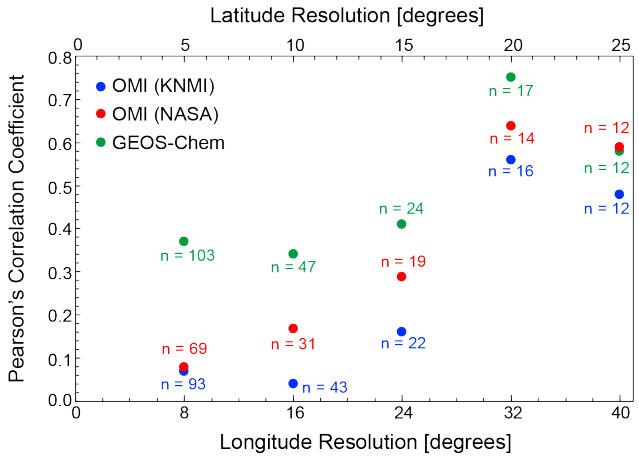

Figure 3. Evaluation of OMI and GEOS-Chem upper troposphere NO_2 with aircraft observations. Individual points are Pearson's correlation coefficients between gridded March-August mean UT NO_2 measured from the aircraft and OMI KNMI in 2006 (blue), OMI NASA in 2005-2007 (red), and GEOS-Chem in 2006 (green), for grid averaging domains of 5° × 8° (latitude × longitude), 10° × 16°, 15° × 24°, 20° × 32°, and 25° × 40°. Values inset are the number of points at each resolution. The domain sampled is shown in Figure 2.

Figure 4 compares the spatial distrbution of OMI and aircraft UT NO_2 at 20° × 32° over North America. Domain mean KNMI UT NO_2 is 38% lower than the aircraft observations, compared to 2.2% higher for NASA UT NO_2. Both products exhibit less variability (reduced major axis, RMA, regression slopes < 1) and high bias in background NO_2 compared to the aircraft observations (positive RMA intercepts of 5.9 ± 1.4 pptv for KNMI and 9.2 ± 2.7 pptv for NASA). We proceed with the NASA UT NO_2 product at 20° × 32°, as correlation peaks at this resolution and the NASA product is more consistent with domain mean aircraft UT NO_2 than the KNMI product.

4. Constraints on upper tropospheric NO_x

The NASA product provides near-global coverage of UT NO_2 to assess current understanding of regional UT NO_x sources and dynamics by comparing to UT NO_2 from the GEOS-Chem CTM (version 10-01; http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_v10-01) driven with NASA MERRA-2 reanalysis meteorology. The model horizontal resolution is 2° × 2.5° and the output is regridded to 20° × 32° for comparison with OMI. GEOS-Chem is sampled under all-sky conditions in the satellite overpass window (12h00-15h00 local time). We find that the effect on NO_2 of sampling the model under cloudy conditions is small. Isolating NO_2 under very cloudy conditions using MERRA-2 cloud fractions decreases modeled UT NO_2 by no more than 5 pptv in the tropics/subtropics and less at higher latitudes. We use output from the model for 2006 following a one-

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year spin-up for chemical initialization. Interannual variability in UT NO_2, determined as the difference between modeled 2006 and multi-year mean (2005-2007) UT NO_2, is small (< 4 pptv) everywhere except central Africa year-round (4-12 pptv), the Arctic north of 60°N (up to 25 pptv), and the Middle East in June-August and northern India in March-May (both 10-20 pptv). Recent evaluation of model NO_2 with observed vertical profiles from the SEAC^{4}RS aircraft campaign show no significant bias in the 6-9 km range of the OMI product (Travis et al., 2016; Silvern et al., 2018).

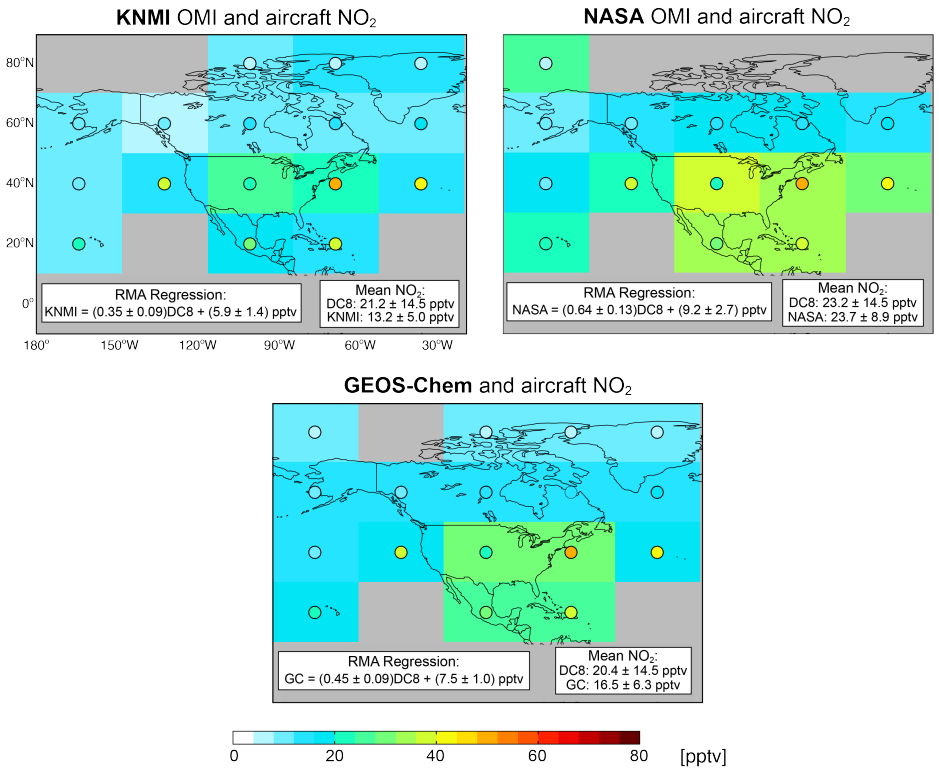

Figure 4. March-August upper troposphere NO_2 over North America. All data are at 20° × 32°. Background colors in the different panels show concentrations from KNMI, NASA, and GEOS-Chem (GC). Circles show the aircraft observations (same in all panels). Aircraft observations are for 11h00-16h00 local time (LT). The model is sampled in the satellite overpass time window (12h00-15h00 LT). Model and aircraft data are at 280-450 hPa and screened for stratospheric influence using ozone/CO > 1.25 mol mol^{-1}. Inset boxes show reduced major axis (RMA) regression statistics and mean NO_2 for coincident gridsquares. Grey gridsquares indicate no observations.

Local GEOS-Chem emissions of NO_x in the UT include aircraft and lightning. Aircraft emissions from the AEIC inventory (Stettler et al., 2011) total 0.82 Tg N in 2006; much less than lightning in the same year (6.5 Tg N). Transport from the stratosphere is simulated using a climatology of NO_y species concentrations from the GMI model above the tropopause (Murray et al., 2012) and is very small (0.4 Tg N a^{-1} as total NO_y). Lightning in the model is estimated using the parameterization implemented by Murray et al. (2012). This includes an initial estimate of lightning flashes using the Price and Rind (1992, 1993, 1994) relationship between cloud-top height and lightning flashes. These are then scaled to the same annual global flash frequency (46 fl s^{-1}) and regional

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distribution as the climatology from the combined Lightning Imaging Sensor (LIS) and Optical Transient Detector (OTD) high-resolution monthly climatology (LIS/OTD HRMC) (Cecil et al., 2014). The standard GEOS-Chem model has higher NO_x yields per flash at northern mid-latitudes (north of 35°N) than in the tropics (500 mol N fl^{-1} versus 260 mol N fl^{-1}), but we find that this overestimates observed OMI UT NO_2 by 10-20 pptv (20-40%) at northern mid-latitudes in summer when the lightning source is dominant. Here we address this overestimate by assuming a NO_x yield of 260 mol N fl^{-1} everywhere. This decreases global lightning NO_x emissions by 15% from 6.5 to 5.5 Tg N a^{-1}. The lightning parameterization in GEOS-Chem does not distinguish lightning NO_x production from flashes within or between clouds (intra- or inter-cloud) or from the cloud to the Earth's surface (cloud-to-ground).

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Figure 3 shows the spatial correlation between the model and aircraft observations. The model is more consistent with the aircraft observations than OMI at fine spatial resolution. Like OMI, GEOS-Chem correlation with the aircraft observations improves with spatial averaging, peaking at 20° × 32° (R = 0.75). Figure 4 also shows comparison of March-August GEOS-Chem UT NO_2 with the aircraft observations at 20° × 32°. The model is sampled over the same pressure range as NASA (280-450 hPa) around the OMI overpass (12h00-15h00 LT) and is filtered for stratospheric influence using model ozone/CO > 1.25 mol mol^{-1}. Domain average UT NO_2 from the model is 19% lower than the aircraft measurements and the model also overestimates background UT NO_2 (intercept = 7.5 ± 1.0 pptv) and underestimates the variability (slope = 0.45 ± 0.09).

Figure 5 compares seasonal mean OMI and GEOS-Chem UT NO_2 in December-February and June-August. The other seasons are shown in the Supplement (Figure S2). Formation of PAN, HNO_4 and $CH_3O_2NO_2$ accounts for over 75% of NO_x loss in the model in all seasons. Lower concentrations of UT NO_2 in the northern hemisphere winter compared to summer in the model is mostly because lightning activity is at a minimum. The model underestimates UT NO_2 in the northern mid-latitudes in winter by 20-40 pptv, suggesting misrepresentation of another process in the model, such as excessive NO_x loss by N_2O_5 hydrolysis in aerosols (Kenagy et al., 2018). The particularly large bias over polluted regions in winter could also be due to contamination of the UT NO_2 retrievals by enhanced boundary layer NO_2.

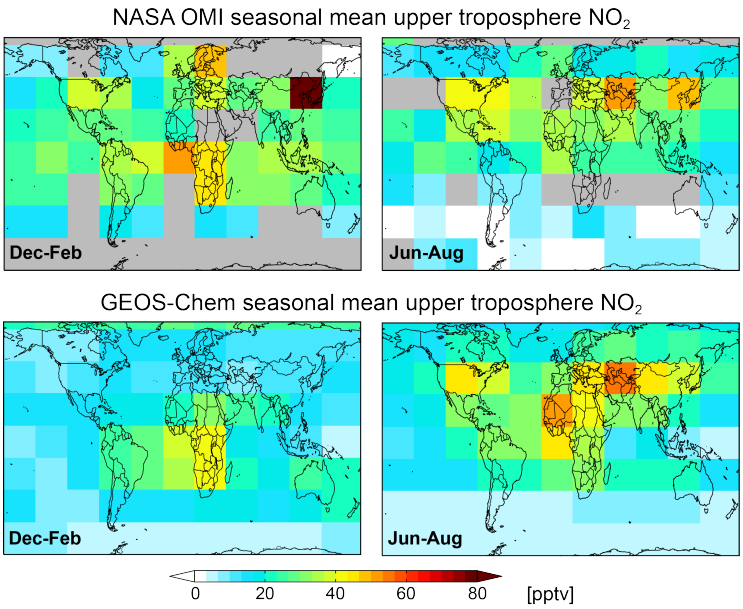

Figure 5. Observed and modelled upper troposphere NO_2. The figure shows NASA OMI seasonal mean UT NO_2 for 2005-2007 (top) and corresponding GEOS-Chem model values (bottom). The model is sampled at 280-450 hPa during the satellite overpass (12h00-15h00 LT), and filtered for stratospheric influence. Data are at 20° × 32° horizontal resolution for December-February (left) and June-August (right). Grey gridsquares in the top panel indicate no OMI data.

Figure 6 shows the log-log relationship between seasonal mean LIS/OTD lightning flash climatology and seasonal mean UT NO_2 from OMI and GEOS-Chem, and the corresponding reduced major axis linear regression fits. Data are divided into northern mid-latitudes and tropics. We exclude the contaminated observations over northeast China and the wintertime northern mid-latitude gridsquares that show no correlation with lightning flashes ($R < 0.1$). Results from multi-model sensitivity studies indicate that UT NO_x in winter is predominantly from surface sources, with a smaller contribution from extra-tropical lightning (Grewe et al., 2001). Background concentration of UT NO_2 (intercepts in Figure 6) from non-lightning sources is 10-20 pptv and is 3-5 pptv higher in the northern mid-latitudes than the tropics. The slopes for the linear fits to lightning flash frequency are consistent between the OMI observations and GEOS-Chem, and show similar slopes for northern mid-latitudes and the tropics. Fitting the ratio between OMI observations and GEOS-Chem on the 20° × 32° grid implies a NO_x yield per flash of 280 ± 80 mol N fl^{-1} with no significant difference between mid-latitudes and the tropics, and no significant difference with the GEOS-Chem prior estimate of 260 mol N fl^{-1}. Out prior estimate of global lightning source was 5.5 Tg N a^{-1}, and the improved estimate is 5.9 ± 1.7 Tg N a^{-1}.

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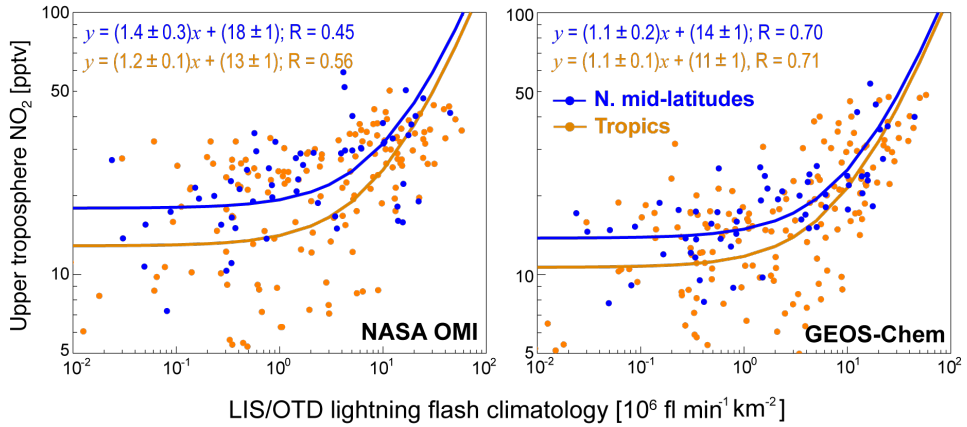

Figure 6. Log-log relationship between upper troposphere NO_2 and lightning flash frequencies, and linear regression fits between the two. Individual points are coincident seasonal mean UT NO_2 from OMI (left) and GEOS-Chem (right) versus seasonal mean LIS/OTD lightning flash climatologies for coincident 20° × 32° gridsquares in the northern mid-latitudes (> 30°N; blue) and tropics (< 30°N; orange). Northern mid-latitude points exclude December-February that show poor correlation with lightning flashes (see text for details). Lines and legends show reduced major axis linear regression fits to the data with corresponding Pearson's correlation coefficients. The regression lines plot as curves on the log-log scale, highlighting the NO_2 background at low lightning flash rates and the correlation of NO_2 with lightning at high flash rates.

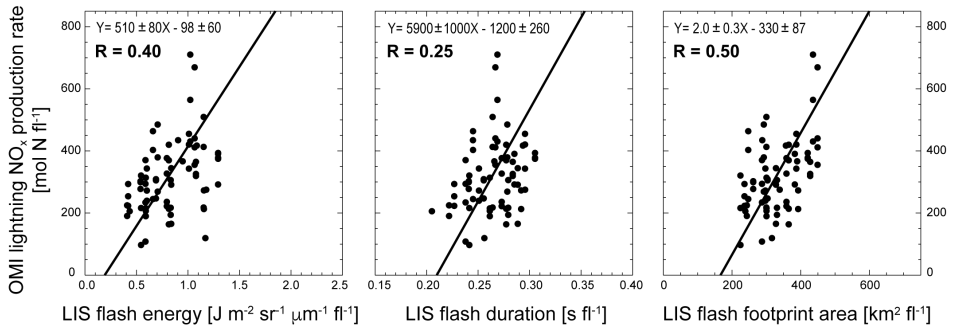

Figure 7. Relationship between OMI and GEOS-Chem derived lightning NO_x production rates and LIS lightning properties: energy (radiance), duration, and footprint area. Individual points are seasonal mean 20° × 32° gridsquares at 40°N-40°S.

Properties of lightning flashes including energy, duration, and footprint area, have been retrieved from the OTD and LIS sensors (Beirle et al., 2014). The flash footprint area is the spatial extent of lightning detection events contributing to the flash (collection of local events) diagnosed by the satellite data. Figure 7 shows the relationship between OMI and GEOS-Chem derived lightning NO_x production rates and LIS lightning properties from Beirle et al. (2014). The strongest correlation is with lightning extent (R = 0.50), followed by energy (R = 0.40). The correlation with flash duration is weak (R = 0.25). The relationships in Figure 7 suggest a dependence of lightning NO_x production rates on lightning flash energy of 510 ± 80 mol N (J m^{-2} sr^{-1} μm^{-1})$^{-1}$ and on flash footprint

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area of 2.0 ± 0.3 mol N km^{-2}, possibly offering guidance for relating NO_x yields to physical properties in global models rather than the current approach of assigning static values.

5. Conclusions

Measurements of NO_x in the upper troposphere (UT) have mainly been from aircraft campaigns that are limited in space and time. Two new cloud-slicing UT NO_2 products from the Ozone Monitoring Instrument (OMI) produced by KNMI and NASA offer the potential to address uncertainties in our understanding of UT NO_x sources. Here we intercompared these products, evaluated them with aircraft observations, and used them together with GEOS-Chem model simulations to demonstrate a dominance of lightning as a source of UT NO_x.

The KNMI and NASA UT NO_2 products use very different retrieval methods. Seasonal mean concentrations from the two products show weak global correlation at the 5° × 8° (latitude × longitude) resolution of the NASA retrieval, with some improvement when the data are further averaged to 20° × 32° (R = 0.5-0.7). At that resolution they show correlation with in situ aircraft observations of UT NO_2 over North America for different years (R = 0.56-0.64). The KNMI product is biased low by 38% relative to the aircraft observations while the NASA product has no significant bias.

We find from the relationship of OMI UT NO_2 with LIS/OTD flash rates that most NO_x in the upper troposphere is from lightning, except in the mid-latitudes in winter. The background NO_2 concentration in the absence of lightning is 10-20 pptv. The relationship suggests no difference in NO_x yields per flash between the mid-latitudes and the tropics, in contrast to the higher yields at mid-latitudes often assumed in models. We derive a global mean lightning NO_x production rate per flash of 280 ± 80 mol N fl^{-1}, from which we infer a best estimate for the global lightning NO_x emission of 5.9 ± 1.7 Tg N a^{-1}.

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Data Availability

Data from this work can be made available upon request: E. A. Marais for GEOS-Chem output, M. Belmonte-Rivas for KNMI OMI UT NO_2, S. Choi and J. Joiner for NASA OMI UT NO_2, and S. Beirle for LIS lightning properties.

Competing Interests

The authors declare that they have no conflicts of interest.

Author Contributions

EAM conducted model simulations, analysed and interpreted satellite, model, and aircraft data, and prepared the manuscript, DJJ provided supervisory guidance and assisted in the writing. SC, JJ, and MR-B retrieved the OMI UT NO_2 products, RCC aided in interpreting aircraft observations., LTM contributed LIS/OTD lightning flash observations, SB contributed lightning flash properties, LS, VS, and LJ contributed updated GEOS-Chem code.

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