Using satellite observations of tropospheric NO_2 columns to infer long-term trends in US NO_x emissions: the importance of accounting for the free tropospheric NO_2 background

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Abstract. The National Emission Inventory (NEI) of the US Environmental Protection Agency (EPA) reports a steady decrease of US NO_x emissions over the 2005-2017 period at a rate of 0.1 Tg N a^{-1} (53% decrease over the period), reflecting sustained efforts to improve air quality. Tropospheric NO_2 columns observed by the satellite-based Ozone Monitoring Instrument (OMI) over the US show a steady decrease until 2009 but a flattening afterward, which has been attributed to a flattening of NO_x emissions in contradiction with the NEI. We show here that the steady 2005-2017 decrease of NO_x emissions reported by the NEI is in fact largely consistent with observed network trends of surface NO_2 and ozone concentrations. The OMI NO_2 trend is instead similar to that observed for nitrate wet deposition fluxes, which is weaker than that for anthropogenic NO_x emissions, due to a large and increasing relative contribution of non-anthropogenic background sources of NO_x (mainly lightning and soils). This is confirmed by contrasting OMI NO_2 trends in urban winter, where the background is low and OMI NO_2 shows a 2005-2017 decrease consistent with the NEI, and rural summer, where the background is high and OMI NO_2 shows no significant 2005-2017 trend. A GEOS-Chem model simulation driven by NEI emission trends for the 2005-2017 period reproduces these different trends except for the post-2009 flattening of OMI NO_2, which we attribute to a model underestimate of free tropospheric NO_2. Better understanding is needed of the factors controlling free tropospheric NO_2 in order to relate satellite observations of tropospheric NO_2 columns to the underlying NO_x emissions and their trends. Focusing on urban winter conditions in the satellite data minimizes the effect of this free tropospheric background.

1. Introduction

Nitrogen oxide radicals ($NO_x \equiv NO + NO_2$) emitted by fuel combustion harm air quality by catalyzing ozone production and by producing nitrate particulate matter. They also contribute to acid and nitrogen deposition. Starting in the early 2000s, the US Environmental Protection Agency (EPA) implemented increasingly stringent NO_x emission controls targeted principally at improving ozone air quality. The EPA National Emission Inventory (NEI) reports a steady decrease of US NO_x emissions over the 2005-2017 period at a rate of 0.10 Tg N a^{-1} or 53% overall (EPA, 2018). However, Jiang et al. (2018) showed that tropospheric NO_2 columns observed by the OMI satellite instrument over the US stopped decreasing after 2009, and they concluded that NO_x emissions have been decreasing much less than reported by the NEI. Here we show that the flattening of the OMI NO_2 trend is in fact not inconsistent with the sustained decrease of NO_x emissions reported by the NEI, and that the NEI emission trend is consistent with other atmospheric observations of NO_x and ozone trends. Our results demonstrate the importance of accounting for the free tropospheric NO_2 background when using satellite observations of NO_2 columns to infer NO_x emissions and their trends.

The Ozone Monitoring Instrument (OMI) aboard the US National Aeronautics and Space Administration (NASA) Aura satellite has been making continuous daily global observations of NO_2 since late 2004 (Levelt et al., 2006; 2018). The NO_2 retrieval (Boersma et al., 2011; Bucsela et al., 2013) involves spectral fitting of measured nadir solar backscatter at 400-500 nm, yielding "slant" NO_2 columns along the line of sight from which the contribution from the stratosphere is removed (Martin et al., 2002; Richter and Burrows, 2002; Bucsela et al., 2013). The slant tropospheric columns are then converted to actual tropospheric NO_2 columns by accounting for surface and atmospheric scattering, and assuming a vertical distribution of NO_2 within the column ("shape factor"). In polluted regions with high NO_x emissions, most of the information in the NO_2 tropospheric column is presumed to originate from the boundary layer. Thus the column is commonly viewed as a proxy for NO_x emissions.

Satellite observations of tropospheric NO_2 columns have been used extensively to infer NO_x emissions and their trends (Leue et al., 2001; Martin et al., 2003; Richter et al., 2005; Boersma et al., 2008). OMI NO_2 observations from the early part of the record showed decreasing trends over the US consistent with the decreases in NO_x emissions reported by the NEI (Russell et al., 2012; Duncan et al., 2013; Streets et al., 2013; de Foy et al., 2015; Duncan et al., 2016; Krotkov et al., 2016), and consistent also with trends in NO_2 concentrations observed from surface networks (Kharol et al., 2015; Lamsal et al., 2015; Lu et al., 2015; Tong et al., 2015; Zhang et al., 2018). Several studies reported a steepening of the OMI NO_2 decrease during the Great Recession of 2007-2009 and a subsequent flattening attributed to economic recovery (Russell et al., 2012; Tong et al., 2015; de Foy et al., 2016). However, the analysis of the 2005-

2015 record by Jiang et al. (2018) shows that the post-2009 flattening of the NO_2 trend extends well beyond the initial economic recovery period.

The NEI is a 'bottom-up' national inventory compiled by the EPA every three years using continuous emission monitoring systems (CEMS) for large point sources, and estimates derived from activity data and emission factors (NO_x emitted per unit of activity) for smaller and distributed sources. Emissions in 2017 estimated by EPA (2018) included 35% from on-road mobile sources, 25% from off-road mobile sources, 12% from industrial point sources, and 27% from electricity generating units (EGUs). Mobile emissions are estimated with the Motor Vehicle Emission Simulator (MOVES) model using as inputs vehicle population, vehicle miles traveled (VMT), and operating modes. Long-term trends in NO_x emissions are re-computed with each new NEI release using updated emission models so that national trends are self-consistent for a given NEI version.

Many recent studies using near-source, urban, and regional observations of atmospheric NO_x have found that the NEI greatly overestimates US NO_x emissions (Castellanos et al., 2011; Brioude et al., 2013; Anderson et al., 2014; Goldberg et al., 2016; Souri et al., 2016; Travis et al., 2016). CEMS measurements of point sources are considered reliable but tunnel and roadside measurements show that the MOVES inventory for mobile sources may be too high (Fujita et al., 2012). Fuel-based approaches for estimating emissions from mobile sources appear to be more reliable than the MOVES VMT approach (Dallmann and Harley, 2010; McDonald et al., 2012; Kim et al., 2016). McDonald et al. (2018) showed that on-road gasoline NO_x emission factors used by NEI are a factor of 2 too high compared to roadside observations and their fuel-based inventory. All these studies were conducted under summertime or warm conditions. By contrast, atmospheric observations of NO_x and related species during the WINTER campaign over the Northeast US during February-March 2015 showed good agreement with the NEI (Jaeglé et al., 2018; Salmon et al., 2018).

The uncertainty regarding NEI NO_x emissions suggests that the trend in these emissions could be uncertain as well. However, a flattening out of US NO_x emissions over the past decade as inferred by Jiang et al. (2018) from the OMI data would be difficult to reconcile with observations of steady improvement in ozone air quality (Astitha et al., 2017; Chang et al., 2017), which has been attributed specifically to NO_x emission controls (Hidy and Blanchard, 2015; Simon et al., 2015; Strode et al., 2015; Xing et al., 2015; Blanchard and Hidy, 2018; Li et al., 2018). Here we conduct a more comprehensive analysis of 2005-2017 trends in US NO_x emissions by using the GEOS-Chem chemical transport model (Travis et al., 2016) to interpret concurrently the trends observed in OMI NO_2 columns, nitrogen wet deposition fluxes, and surface observations of NO_2 and ozone.

2. 2005-2017 trends of OMI tropospheric NO_2 columns

Figure 1 shows the 2005-2017 trends of OMI tropospheric NO_2 columns averaged spatially and annually over the contiguous US. The observations are from the NASA operational retrieval (Level 2, v3.0; Krotkov et al., 2017) after removing cloudy scenes (cloud radiance fraction > 0.5), bright surfaces (surface reflectivity > 0.3), and observations affected by the so-called row anomaly (Dobber et al., 2008). OMI is in a sun-synchronous orbit with overpass at 13:30 local time. It measures back-scattered solar radiation in the nadir and off-track, with 13×24 km^2 nadir pixel resolution and global daily coverage. The retrieval fits the backscattered radiance spectrum to obtain the total slant NO_2 column along the line of sight from the Sun to the satellite. The stratospheric contribution to the total slant column is estimated using OMI observations over clean background and cloudy areas and applying an interpolating-filtering-smoothing algorithm (Bucsela et al., 2013). The remaining tropospheric slant column is then converted to a vertical column with an air mass factor (AMF; Palmer et al., 2001) that convolves the altitude-dependent sensitivity from atmospheric scattering (scattering weights) with the local relative vertical distribution of NO_2 from the Global Modeling Initiative (GMI) model (shape factor). Over continental source regions, the AMF dominates the overall retrieval error due to uncertainties in a priori NO_2 profiles, surface albedo, and aerosol/cloud parameters (Kleipool et al., 2008; Boersma et al., 2011; Lamsal et al., 2014; Lorente et al., 2017). We re-computed the AMFs using GEOS-Chem rather than GMI shape factors and found little difference in the mean (Figure 1).

The OMI data show an evident flattening of NO_2 columns after 2009, as pointed out by Jiang et al. (2018) who also find the same flattening in alternative OMI NO_2 retrievals produced by KNMI (Boersma et al., 2011) and UC Berkeley (Laughner et al., 2018). NO_2 tropospheric columns decrease at a mean rate of 6±0.5% a^{-1} over the 2005-2009 period but then do not change significantly post-2009. We find that data for the western, central, northeastern, and southeastern US all show similar trends. Hence we focus our analysis on the mean trends over the contiguous US, following Jiang et al. (2018).

Also shown in Figure 1 are trends from a 13-year simulation (2005-2017) with the GEOS-Chem global chemical transport model at 0.5^o×0.625^o nested horizontal resolution over North America. The model is driven by NEI NO_x emissions for fuel combustion, decreased by 60% for non-EGU sources following Travis et al. (2016). It also includes NO_x emissions from background (non-fuel combustion) sources including open fires (Darmenov and da Silva, 2013), lightning (Murray et al., 2012), and soil and fertilizer (Hudman et al., 2012). Further details on the model are in the Appendix. The model NO_2 column averages 28% lower than observed, due to both an underestimate in background NO_2, discussed below, and because the Travis et al. (2016) correction to the NEI is excessive, which we will address in a separate paper. More to the point here, the model shows a sustained decrease averaging 3.3±0.1% a^{-1} over the 2005-2017 period, at odds with the OMI observations, though lower than the NEI reported decrease of 5.9% a^{-1} over the same period. Here and throughout this paper we derive linear trends by ordinary regression and

express them in units of [% a^{-1}] relative to the mean over the data period, following Jiang et al. (2018). We compute uncertainty using the bootstrapping method as the error standard deviation of the linear trend.

The weaker relative trend in the model compared to the NEI is because of the contribution from background NO_x sources. The right panel of Figure 1 shows the annual total US NO_x emissions for 2005-2017 in the GEOS-Chem simulation. Anthropogenic emissions from fuel combustion decrease at a rate of 5.9% a^{-1}, following the NEI trend. But these emissions account for only 61% of total US emissions in 2005 and 42% in 2017. Natural emissions from lighting and soils play a relatively increasing role as anthropogenic emissions decrease. They have interannual variability but no significant 2005-2017 trend. The trend of total US NO_x emissions for 2005-2017 in GEOS-Chem is -3.5% a^{-1}, closely matching the simulated NO_2 column trend.

Trends in the NO_x chemical lifetime over the 2005-2017 period would affect the relationship between trends in NO_x emissions and atmospheric NO_2. Many factors could contribute to a trend in NO_x lifetime (Laughner, 2018; Laughner and Cohen, 2018). We find in GEOS-Chem that the daily tropospheric NO_2 column lifetime over the contiguous US is 8.1 h in 2005 (annual mean) and 7.7 h in 2017. In the model at least, the trend in NO_x lifetime is much weaker than the trend in emissions, so that the trend in concentrations mainly follows that of emissions.

3. 2005-2017 trends of surface observations

Long-term records of surface NO_2 concentrations over the US are available at a large number of monitoring sites from the US EPA Air Quality System (AQS) (https://www.epa.gov/aqs; Demerjian et al., 2000) and at additional sites in the Southeast from the Southeastern Aerosol Research and Characterization Study (SEARCH) network (https://www.dropbox.com/sh/o9hxoa4wlo97zpe/AACbm6LetQowrpUgX4vUxnoDa?dl=0; Hansen et al., 2003; Edgerton et al., 2006). AQS sites are mainly urban and measure NO_2 with a chemiluminescence analyzer equipped with a molybdenum converter, known to have positive interferences from NO_x oxidation products including peroxyacetylnitrate (PAN) and nitric acid (HNO_3; Dunlea et al., 2007; Steinbacher et al., 2007; Reed et al., 2016). SEARCH sites are both urban and rural and use a more specific photolytic converter instrument in which broadband photolysis of NO_2 is followed by chemiluminescence detection of the NO product with accuracy better than 10% (Ryerson et al., 2000; Pollack et al., 2010).

The top and middle rows of Figure 2 show annual average trends in daily surface NO_2 concentrations at the 132 AQS sites with continuous yearlong records for 2005-2017 and the 2 rural SEARCH sites (Centreville, AL and Yorkville, GA) with continuous records for 2005-2016 (SEARCH was discontinued in 2017). Also shown for the AQS sites are the values corrected for interferences based on local GEOS-Chem monthly mean NO_2, alkyl nitrate, PAN, and HNO_3 concentrations and following the

correction factor in Lamsal et al. (2008). The AQS data show decreasing trends throughout the 2005-2017 period, generally consistent with the NEI. The rural SEARCH sites also show a steady decrease but are more noisy (only 2 sites). One would expect the trend in the urban AQS data to be most indicative of the trend in anthropogenic NO_x emissions from fuel combustion. GEOS-Chem underestimates the AQS observations because of the urban nature of the sites, but the model relative decreases agree closely with observations for both the AQS and the SEARCH data. This is in sharp contrast to the OMI NO_2 data.

Jiang et al. (2018) reported AQS surface NO_2 trends of -6.6±1.4% a^{-1} for 2005-2009 and -2.6±1.5% a^{-1} for 2011-2015, indicating a significant weakening of the trend with time. But they used all AQS sites in that analysis including those with incomplete records. We find that when using only sites with continuous records, the slope is steeper for the latter time period. Specifically, we find the AQS trend to be -6.6±1.2% a^{-1} for 2005-2009 and -4.5±1.7% a^{-1} for 2011-2015. In comparison, the NEI emission trend is -6.4% a^{-1} for 2005-2009 and -5.3% a^{-1} for 2011-2015. Thus the surface data suggest a slight weakening of the NO_x emission trend relative to the NEI but not the flattening implied by the OMI data. Jiang et al. (2018) presented an alternative fuel-based NO_x emission inventory to the NEI featuring a slowdown in the trend of US NO_x emissions after 2009 due to a slower rate of reduction for industrial, off-road mobile, and on-road diesel sources as well as a smaller relative contribution of on-road gasoline. That inventory shows a -2.9% a^{-1} trend for 2011-2015. The AQS trend is in somewhat better agreement with the NEI inventory but could accommodate either inventory within its error standard deviation.

The bottom row of Figure 2 shows observed and simulated trends in nitrate (NO_3^-) wet deposition fluxes for the 138 National Acid Deposition Program (NADP; https://nadp.slh.wisc.edu/data/NTN/) sites with continuous yearlong records for 2005-2017. Nitric acid gas and nitrate aerosol are both efficiently scavenged by precipitation and the lifetime of NO_x is sufficiently short that nitrate wet deposition fluxes should relate to total NO_x emissions. The relationship is not one-to-one because of competition from dry deposition but one would not expect a long-term trend in the wet/dry deposition ratio. GEOS-Chem model values for individual years are corrected for precipitation bias using the high-resolution PRISM precipitation data (http://prism.oregonstate.edu; Di Luzio et al., 2008) as described by Paulot et al. (2014) and Travis et al. (2016). Model values average 17% lower than observed, again because the model may underestimate emissions, but the trends are consistent. The fluxes show a decrease over the 2005-2017 time period (averaging 2.7±0.3% a^{-1} observed, 2.9±0.3% a^{-1} modeled), weaker than for surface NO_2 concentrations. After 2012, there is still a significant decrease in nitrate wet deposition, though it is less than during the earlier time period (averaging 1.3±0.9% a^{-1} observed, 1.7±0.7% a^{-1} modeled).

Nitrate wet deposition is more sensitive to background (non-fuel combustion) influences than NO_2 concentrations because (1) the wet deposition sites are prevailingly rural; (2) precipitation scavenges a deeper column. Indeed, in GEOS-Chem, the mean nitrate wet deposition trend is more consistent with the -

3.5% a^{-1} trend of total NO_x emissions (including lightning and soils) than that of emissions from fuel combustion (-5.9% a^{-1}).

The relative contribution from background sources to nitrate wet deposition would be expected to increase over time as fuel combustion emissions decrease. In order to quantify this, we performed GEOS-Chem sensitivity simulations for 2005 and 2017 with only background NO_x emissions (shutting off NO_x emissions from US fuel combustion). We find that background contributes 50% of nitrate wet deposition at NADP sites in 2005 but 69% in 2017. In contrast, background only contributes 5% to surface NO_2 at AQS sites in 2005 and 10% in 2017.

Figure 3 shows summertime ozone trends for 2005-2017 as further evidence of a sustained decrease in anthropogenic NO_x emissions. Data are from the AQS and Clean Air Status and Trends Network (CASTNET; https://www.epa.gov/castnet) networks. We show records for the 47 CASTNET and 427 AQS sites with continuous summertime records for 2005-2017. The trends are for the 95th percentiles in the maximum daily 8-h average (MDA8) values determined at individual sites and then averaged across all sites for each summer. We excluded high elevation (> 1.5 km) CASTNET sites in the western US because they have different trends driven in part by the larger influence from background ozone (Cooper et al., 2011; Lin et al., 2017; Jaffe et al., 2018). Much of the interannual variability in ozone concentrations in Figure 3 can be explained by surface temperatures, including the 2012 peak in ozone in the observations and captured by GEOS-Chem, which is due to anomalously high temperatures (Fiore et al., 2015; Jia et al., 2016; Lin et al., 2017). Nonetheless, the surface observations do show overall decreases over the 2005-2017 time period. On a national scale, the observations show declines of 1.11±0.08 ppb a^{-1} (CASTNET) and 1.04±0.03 ppb a^{-1} (AQS) with no indication of a post-2009 flattening. The GEOS-Chem model shows similar trends. The sustained (post-2009) decrease of ozone pollution over the past decade provides additional evidence of a continued decrease in anthropogenic NO_x emissions.

4. Comparative analysis of trends

Figure 4 combines into a single plot the relative trends since 2005 of NEI NO_x emissions, OMI tropospheric NO_2 columns, surface NO_2 concentrations, and nitrate wet deposition fluxes. Observed surface NO_2 concentrations follow the NEI emissions trend, showing consistency with a sustained decline of emissions over the 2005-2017 time period. This behavior is well captured by GEOS-Chem, which confirms the 1:1 relationship expected between surface NO_2 concentrations and NO_x emissions. Nitrate wet deposition observations show a much weaker trend, which we attributed in Section 3 to a larger contribution of the background. The GEOS-Chem trend for nitrate wet deposition and tropospheric NO_2 columns is similarly weaker than for surface NO_2, reflecting the influence of the background, but shows a

steeper decrease than observed after 2009. This suggests that GEOS-Chem may underestimate the background contribution.

Satellite-based tropospheric NO_2 columns show trends remarkably similar to those of nitrate wet deposition fluxes, both in the OMI observations and in GEOS-Chem, suggesting that the post-2009 flattening of the OMI trend is due to a large and increasing relative influence of the background rather than to a leveling of US NO_x emissions.

5. Background contribution to OMI NO_2 trends

We showed in Section 4 that the 2005-2017 trend of OMI NO_2 columns over the US is similar to that of nitrate wet deposition, and much weaker than that of surface NO_2 concentrations, pointing to the importance of background in affecting the NO_2 column. To further examine this effect, we segregated the OMI observations by winter/summer and urban/rural. Urban conditions are defined as the top 10% NO_x-emitting 0.5°×0.625° grid squares in the US according to the NEI. We expect background influences to be relatively higher at rural than urban sites, and higher in summer (lightning, soil, intercontinental transport; Fischer et al., 2014) than in winter. Thus background influences should be minimum in winter urban conditions and maximum under summer rural conditions.

Figure 5 shows the results. OMI NO_2 observations in urban winter show a steady decline at a mean rate of 3.3±0.5% a^{-1}, with no post-2009 flattening, though there is some suggestion of a slightly weaker trend after 2009 when compared to GEOS-Chem driven by NEI. By contrast, the OMI NO_2 observations in rural summer show no significant trend over the 2005-2017 period. GEOS-Chem for rural summer shows a significant decreasing trend for 2005-2017 but weaker than for urban winter and becoming insignificant for the 2009-2017 period. The winter rural and summer urban conditions in Figure 5 show trends intermediate between these two limiting cases. The ability of GEOS-Chem to capture the observed post-2009 weakening of the trend in the summer urban case argues against a seasonal flattening of emissions that would affect summer but not winter.

It thus appears that the post-2009 flattening of the OMI NO_2 trend over the US is due to increasing relative importance of the NO_2 background, rather than to flattening of US NO_x emissions. Satellite observations of tropospheric NO_2 columns are more sensitive to the free troposphere than to the boundary layer because of atmospheric scattering; the sensitivity increases by a factor of 3 from the surface to the upper troposphere for clear sky and by much more for a cloudy atmosphere (Martin et al., 2002). For the OMI NO_2 data set used here the sensitivity increases on average by over a factor of 4 from the surface to the upper troposphere, as given by the scattering weights (Krotkov et al., 2017). The AMF is intended to correct for this effect but relies on an assumed model vertical distribution of NO_2 that may not correctly

account for free tropospheric levels or for the changing ratio between the free troposphere and the boundary layer as anthropogenic NO_x emissions decrease.

There is indeed evidence that free tropospheric NO_2 makes a large contribution to OMI NO_2 columns and that models underestimate this contribution. Measurements of NO_2 vertical profiles during the SEAC^{4}RS aircraft campaign over the Southeast US in August-September 2013 showed a median concentration of 300 ppt near the surface dropping to a 50 ppt background in the free troposphere at 2-10 km and rising back to 130 ppt at the 12 km aircraft ceiling (Silvern et al., 2018). By applying OMI scattering weights to this median vertical profile, most representative of a rural profile, Travis et al. (2016) found that the boundary layer below 1.5 km contributed only 19-28% of the OMI NO_2 tropospheric column. A GEOS-Chem simulation of the SEAC^{4}RS conditions matched the observed 50 ppt background (mostly from lightning) but could not reproduce the enhancement above 10 km (Travis et al., 2016; Silvern et al., 2018). The GMI model used to compute AMFs in the NASA OMI NO_2 retrievals also has little NO_2 in the upper troposphere (Lamsal et al., 2014). Measurements of NO_2 in the upper troposphere are prone to positive interferences because of inlet decomposition of labile reservoirs (Reed et al., 2016) but the measurements in SEAC^{4}RS were designed to minimize and correct for these interferences (Thornton et al., 2000; Day et al., 2002; Wooldridge et al., 2010; Nault et al., 2015). Silvern et al. (2018) suggested that errors in the kinetics of NO-NO_2-O_3 cycling reactions could explain model underestimates of NO_2 concentrations in the upper troposphere.

Choi et al. (2014) and Belmonte Rivas et al. (2015) used the so-called cloud-slicing method to isolate the upper tropospheric contribution to the OMI NO_2 observations by comparing neighboring cloudy scenes with cloud tops at different altitudes. They report in this manner partial NO_2 columns at 6-10 km altitude. Marais et al. (2018) evaluated these data in comparison with aircraft observations and found large uncertainties, but concluded that GEOS-Chem underestimates NO_2 at 6-10 km over North America by 20-30 ppt in winter with no significant bias in summer. The good agreement in summer is consistent with the comparison to SEAC^{4}RS observations, which shows however a low model bias above 10 km.

We conducted a sensitivity test adding 50 ppt of background NO_2 to the GEOS-Chem vertical profiles above 5 km altitude in winter and above 10 km in summer, up to the local tropopause. The resulting normalized vertical profiles (shape factors) were convolved with the vertical distribution of sensitivities (scattering weights) provided by the NASA retrieval to re-compute the AMFs. The implications for the model trends are shown in Figure 5 as the blue lines. The effect is large for winter rural conditions, where the added free tropospheric background is particularly important and largely reconciles the model trend with the OMI observations. It is much less in summer, where the addition is only above 10 km and there is already substantial background NO_2 present. The discrepancy between model and

observations in summer is though largely driven by the uptick in the summer rural observations for 2016-2017.

It is possible that additional background NO_2 missing from the model in summer could be present in the tropopause region and lower stratosphere. The deepest convection in summertime over the US can reach 17 km in the lowermost stratosphere (Randel et al., 2012; Huntrieser et al., 2016b; Anderson et al., 2017; Herman et al., 2017; Smith et al., 2017). Such deep convective injection could conceivably deliver substantial lightning NO_2 above the tropopause. Although delivered above the tropopause, this NO_2 would be counted as tropospheric in retrievals because it would represent an enhancement above background NO_2 columns in the stratospheric separation. It could have a particularly important effect on the AMF by being delivered above clouds. High NO_x mixing ratios in the lowermost stratosphere were observed over the Central and Southeast US during the DC3 aircraft campaign in May-June 2012 and attributed to lightning (Huntrieser et al., 2016a; Huntrieser et al., 2016b), and higher lightning flash rates have been observed in tropopause-penetrating above-anvil cirrus plumes (Bedka et al., 2018). There is suggestive evidence that convective injection into the lowermost stratosphere over the US may have increased during the 2004-2013 period (Cooney et al., 2018), which could further affect the OMI NO_2 column trend, although the Lightning Imaging Sensor (LIS) satellite data do not show a 2003-2012 trend in total lightning over the US (Koshak et al., 2015). While tropopause heights in the GEOS MERRA-2 meteorological data driving GEOS-Chem agree well with SEAC^{4}RS observations of water vapor and ozone (Kuang et al., 2017; Smith et al., 2017), models in general do not properly capture the observed convective injections into the lowermost stratosphere (Smith et al., 2017; Anderson et al., 2019). The 0.5°×0.625° resolution of the MERRA-2 meterological data would be too coarse to resolve convective overshoots.

6. Conclusions

US emissions of nitrogen oxides ($NO_x \equiv NO + NO_2$) from fuel combustion have been steadily declining over 2005-2017 at a mean rate of 5.9% a^{-1} according to the National Emission Inventory (NEI) of the US EPA. Tropospheric NO_2 columns over the US observed by OMI on board the Aura satellite show instead a leveling off after 2009, leading to the suggestion that the NEI emission trend is in error and that related air quality gains have halted. Here we re-examined this issue by using trends in surface observations together with a 2005-2017 GEOS-Chem chemical transport model simulation to better understand the relationship between satellite NO_2 observations, NO_x emissions, and their trends.

We started by comparing the 2005-2017 GEOS-Chem simulation driven by NEI emission trends to the OMI observations. The model shows a sustained decrease in the tropospheric NO_2 column at a mean rate of 3.3±0.1% a^{-1} over the period. The rate is less than the NEI trend because of natural NO_x emissions (mainly from lightning and soils) that account in GEOS-Chem for 58% of total NO_x emissions over the US

by 2017. Nevertheless, the GEOS-Chem simulation cannot capture the post-2009 flattening in the OMI observations.

We then examined 2005-2017 US trends in surface observations of NO_2 concentrations and nitrate wet deposition fluxes from surface networks (AQS, SEARCH, NADP). Surface NO_2 concentrations measured by the AQS (urban) and SEARCH (rural) surface networks show a decline over the 2005-2017 time period that closely follows the NEI emissions trend, and the same is found in GEOS-Chem. Some deviation between AQS NO_2 and the NEI towards the later part of the time period suggests that the rate of decrease in emissions may have slowed slightly. Nitrate wet deposition shows a much weaker 2005-2017 trend than surface NO_2 and NEI emissions, both in the observations and the model, reflecting a large and increasing relative contribution from background sources (69% in the model in 2017) as anthropogenic emissions decrease. Surface ozone concentrations from the CASTNET and AQS networks show sustained 2005-2017 decreases, consistent with the model; such sustained decreases would be hard to reconcile with a flattening of NO_x emissions.

Bringing together these observed trends, we see two different patterns: (1) a 2005-2017 decrease in surface NO_2 that supports the steady decrease in NO_x emissions reported by the EPA NEI; (2) a weaker trend and post-2009 flattening of OMI NO_2 and nitrate wet deposition that reflects a growing influence from the background, rather than large error in NEI NO_x emissions.

We confirmed the importance of background NO_2 in driving the post-2009 flattening of OMI NO_2 trends over the US by segregating the OMI observations into urban/rural and winter/summer. There is a steady 2005-2017 decrease in the urban winter data where background influence is lowest. By contrast, there is no significant 2005-2017 trend in rural summer (where background influence is highest). The failure of GEOS-Chem to reproduce the observed post-2009 flattening then points to a model underestimate of the NO_2 background. Cloud-sliced OMI NO_2 data indicate a GEOS-Chem underestimate of the upper tropospheric background in winter. Deep convective injections of lightning NO_x above the tropopause might add to the NO_2 background in summer. Observations from the NASA SEAC^{4}RS aircraft campaigns show higher NO/NO_2 ratios than simulated by GEOS-Chem, which could reflect errors in the kinetics of NO-NO_2-O_3 chemical cycling (Silvern et al., 2018). While such errors would be most important in summertime, chemistry important for wintertime NO_x not comprehensively included in models may help to explain the winter background NO_2 underestimate. Observations of short-chained alkyl nitrates show higher concentrations in the northern extratropical free troposphere in winter than captured by GEOS-Chem, and may represent an increasing reservoir of background NO_x (Fisher et al., 2018). Measurements from the WINTER campaign suggest models may also overestimate NO_x loss via N_2O_5 hydrolysis (Jaeglé et al., 2018; Kenagy et al., 2018; McDuffie et al. 2018), and recent laboratory data suggest that models

using the recommended NASA-JPL kinetics for the NO_2+OH reaction may overestimate NO_x loss at cold temperatures (Amedro et al., 2019).

We conclude that the sustained 2005-2017 decrease in US NO_x emissions reported by the EPA is supported by observations, and that better understanding of the free tropospheric background is needed to interpret satellite observations of NO_2 tropospheric columns in terms of their implications for NO_x emissions and their trends. The concern is minor in highly polluted areas where NO_x emissions are sufficiently high to dominate over the background influence. In the US, however, NO_x emissions have now decreased to the point that NO_2 columns over non-urban areas are mostly contributed by the free tropospheric background. Accounting for this poorly understood background will become increasingly important as NO_x emissions continue to decrease in the developed world, and in tropical regions that are undergoing rapid development but have a deep troposphere and intense lightning.

Appendix: the GEOS-Chem model

We conducted a 13-year simulation (2005-2017) with the GEOS-Chem global 3D chemical transport model version 11-02c (http://www.geos-chem.org) using NASA MERRA-2 assimilated meteorological data (Gelaro et al., 2017). We use the nested North America version of GEOS-Chem at the native MERRA-2 0.5°×0.625° horizontal resolution over North America and adjacent oceans (140-40°W, 10-70°N) with dynamic boundary conditions from a global simulation with 4°×5° horizontal resolution. The simulation includes detailed NO_x-hydrocarbon-aerosol chemistry as described in Travis et al. (2016), Fisher et al. (2016) and Marais et al. (2016). US anthropogenic emissions are distributed spatially following the NEI2011 inventory (EPA, 2018). NEI2011 is scaled for individual years using national annual totals (EPA, 2018), and we decrease non-EGU NO_x emissions by 60% as in Travis et al. (2016) for all years. Open fire emissions are from the daily Quick Fire Emissions Database (QFED; Darmenov and da Silva, 2013) with diurnal variability from the Western Regional Air Partnership (Air Sciences, 2005). Soil NO_x emissions, including emissions from fertilizer application, are computed according to Hudman et al. (2012), with a 50% reduction in the Midwestern US for summertime based on a previous comparison with OMI NO_2 observations (Vinken et al., 2014). Lightning NO_x emissions are described by Murray et al. (2012) with a horizontal distribution matching climatological observations of lightning flashes, interannual variability driven by MERRA-2 convection, and most of the release at the top of convective updrafts (Ott et al., 2010). The NO_x yield per flash is 260 mol to the south of 35°N and 500 mol to the north (Hudman et al., 2007; Huntrieser et al., 2008; 2009; Ott et al., 2010; Travis et al., 2016).

The GEOS-Chem simulation of NO_x and related species over the US has been evaluated in a number of recent papers including Zhang et al. (2012), Ellis et al. (2013), and Lee et al. (2016) for nitrogen deposition, Travis et al. (2016) for NO_x concentrations over the Southeast US during the SEAC^{4}RS

campaign, Fisher et al. (2016) for organic nitrates during that same campaign, Jaeglé et al. (2018) for the WINTER campaign, and Fischer et al. (2014) for the ensemble of PAN observations. These evaluations find that the model is overall successful with no indication of systematic bias.

Data availability.

OMI NO_2 observations are available from https://mirador.gsfc.nasa.gov/.

AQS NO_2 and ozone observations are available from https://www.epa.gov/aqs.

SEARCH NO_2 observations are available from https://www.dropbox.com/sh/o9hxoa4wlo97zpe/AACbm6LetQowrpUgX4vUxnoDa?dl=0.

NADP nitrate wet deposition observations are available from https://nadp.slh.wisc.edu/data/NTN/.

CASNTET ozone observations are available from https://www.epa.gov/castnet.

GEOS-Chem output from this work is available upon request.

Author contributions. DJJ, LJM, and RFS designed the study. RFS and MPS conducted model simulations. RFS analyzed satellite, surface, and model data. KRT contributed NEI emissions in GEOS-Chem and supported data analysis. LJM, EAM, RCC, and JLL helped with scientific interpretation and discussion. SC, JJ, and LNL provided OMI data and supporting guidance. RFS and DJJ wrote the manuscript and all authors provided input on the paper for revision before submission.

Competing interests. The authors declare that they have no conflict of interest.

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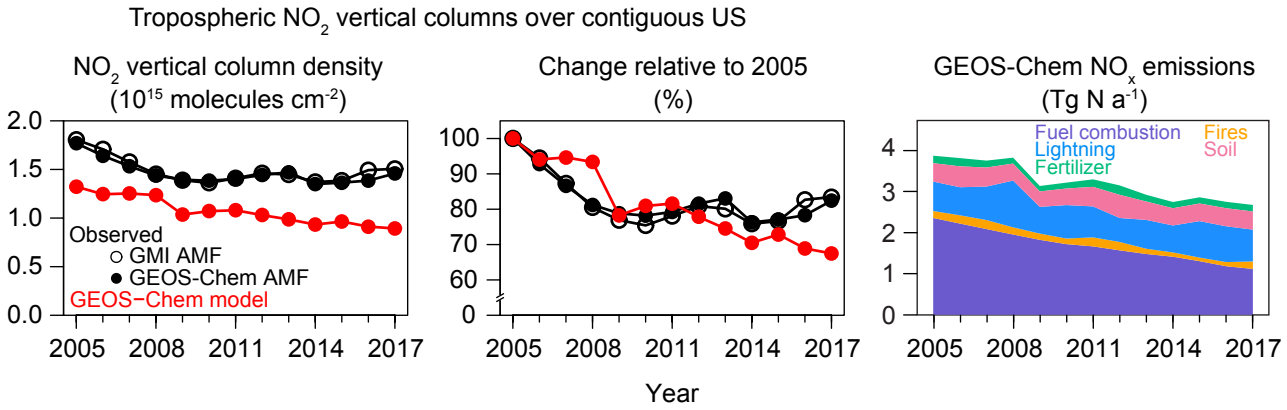

Figure 1. 2005-2017 trends in tropospheric NO_2 columns and NO_x emissions over the contiguous US. The left panel shows OMI observations averaged over the contiguous US and the corresponding GEOS-Chem simulation. The OMI observations are from the NASA retrieval (Krotkov et al., 2017) with air mass factors (AMFs) computed from the original GMI model NO_2 vertical profiles or GEOS-Chem vertical profiles. The middle panel shows percent changes in tropospheric NO_2 columns relative to 2005. The right panel shows 2005-2017 annual total NO_x emissions from the GEOS-Chem model, including anthropogenic fuel combustion emissions from the National Emission Inventory (NEI) with a 60% decrease for non-EGU sources (see text and Appendix).

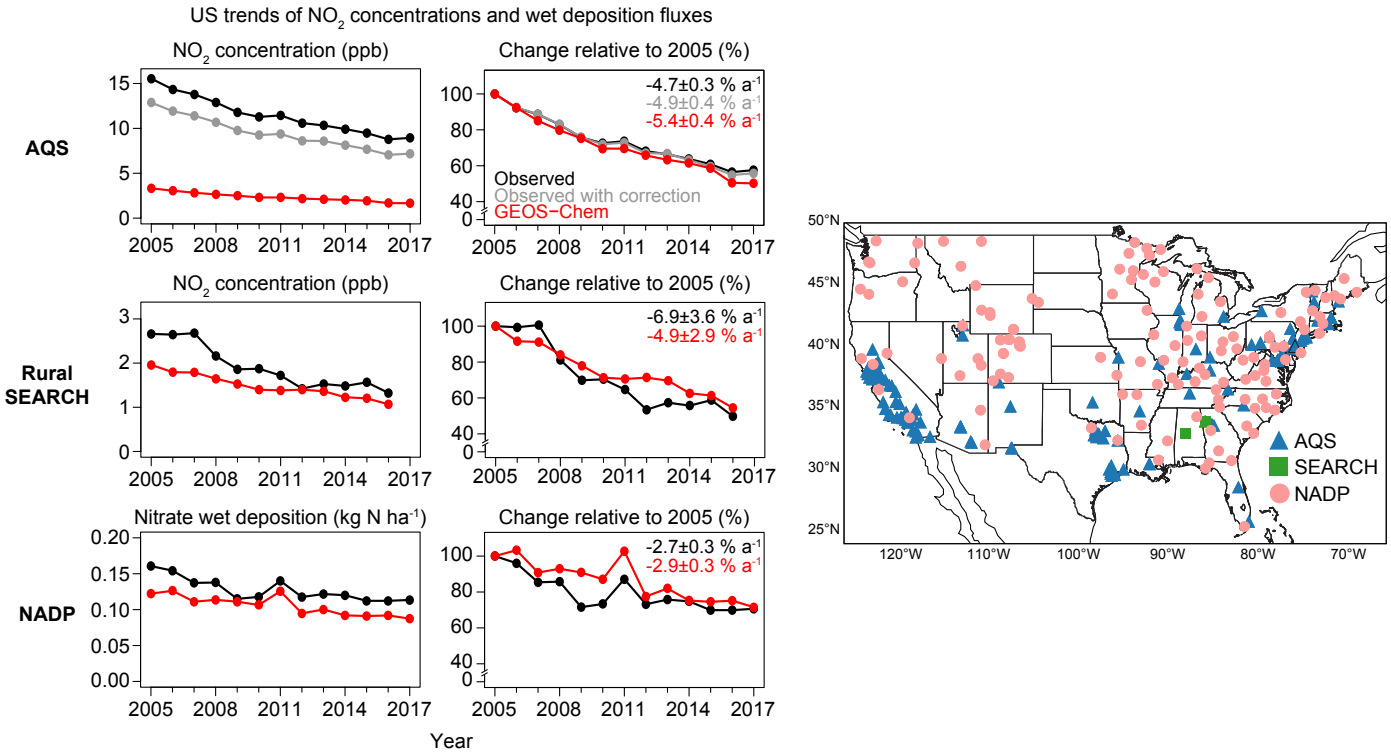

Figure 2. 2005-2017 trends in annual mean surface NO_2 concentrations and nitrate wet deposition fluxes over the contiguous US. Observations are compared to GEOS-Chem model values sampled at the corresponding sites. The map at the right shows the observation sites for the AQS, SEARCH, and NADP measurements networks with continuous annual records for 2005-2017 (2016 for SEARCH). The top row shows surface NO_2 observed at AQS sites (mainly urban). The measurements are affected by positive interference from NO_x oxidation products and the gray line shows the data corrected as in Lamsal et al. (2008). The middle row shows surface NO_2 at the 2 rural SEARCH sites in the Southeast US. The bottom row shows nitrate wet deposition fluxes at NADP sites. The right panels show trends relative to 2005 values and the mean ± standard deviation percent change per year is shown inset. All trends shown are statistically significant.

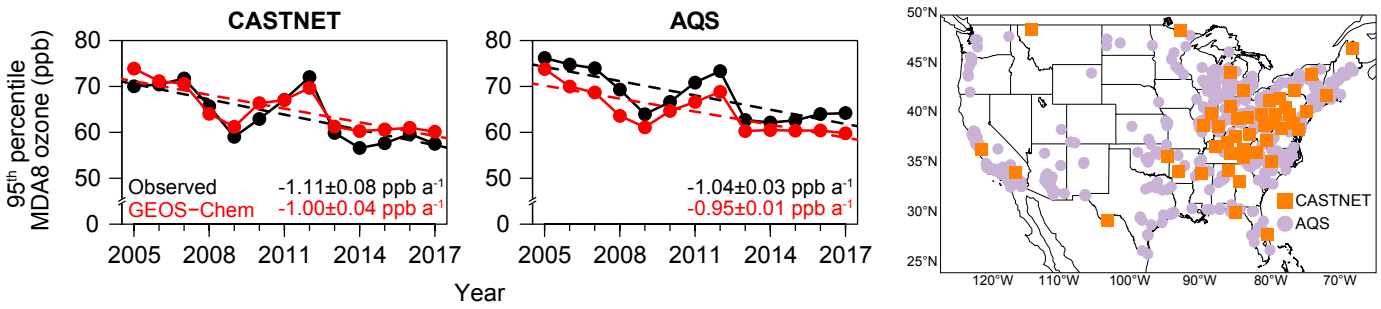

Figure 3. Summertime surface ozone trends for 2005-2017 at the CASTNET and AQS networks in the contiguous US. The trends are for the 95th percentile of the maximum daily 8-hour average (MDA8) ozone concentrations computed for individual sites (shown in the map on the right) and then averaged over all sites from the network. High elevation (> 1.5 km) CASTNET sites in the western US are excluded. The slope and standard deviation of the linear regressions are shown inset, and all trends shown are statistically significant.

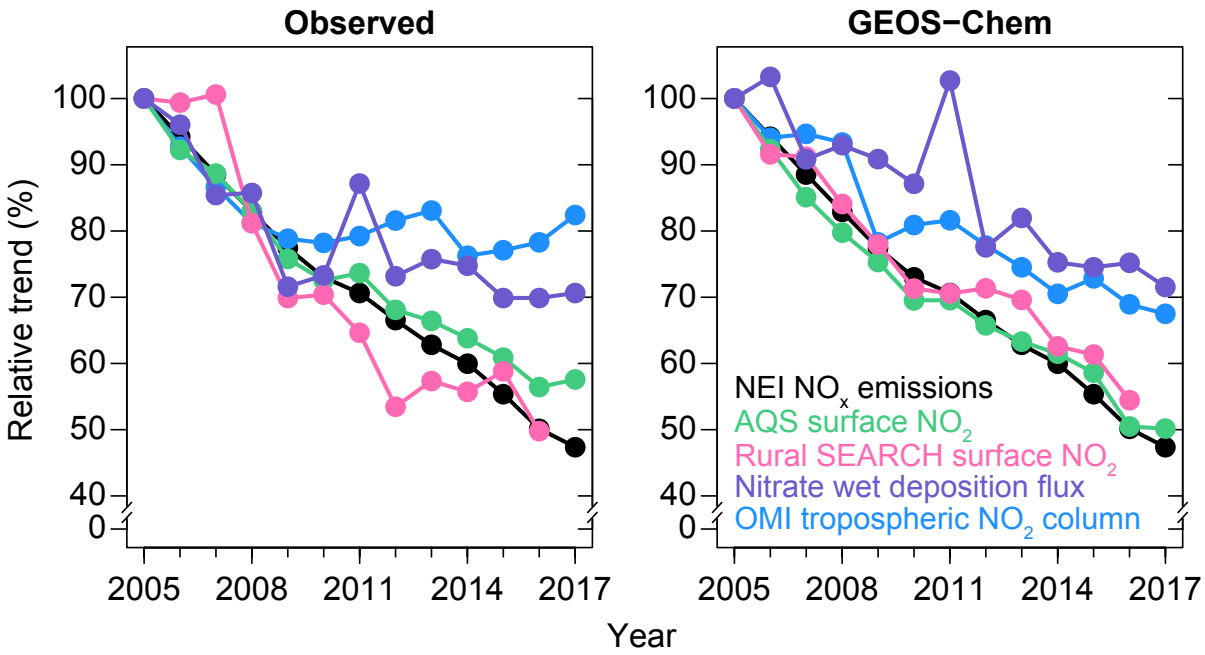

Figure 4. Relative trends since 2005 of NEI NO_x emissions and relevant atmospheric quantities averaged over the contiguous US. The left panel shows observations and the right panel shows the GEOS-Chem simulation. NEI NO_x emissions are the same in both panels. The SEARCH network was discontinued in 2016.

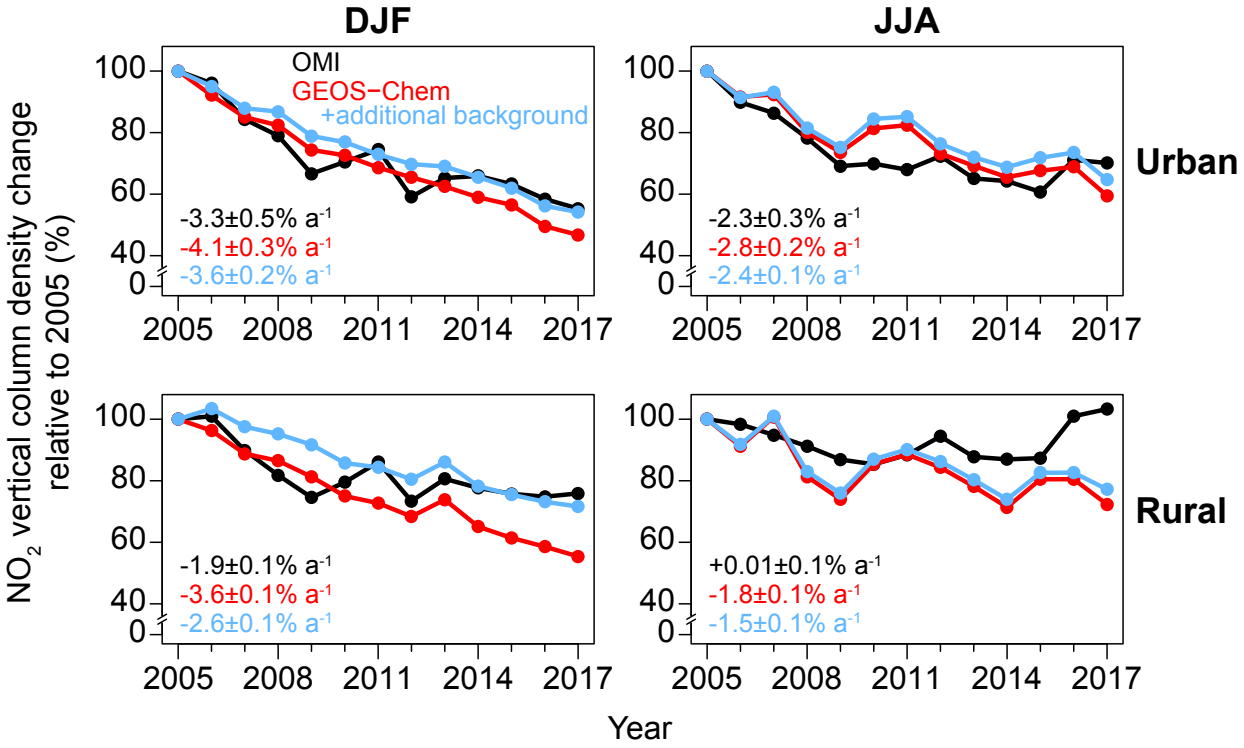

Figure 5. OMI tropospheric NO_2 column trends over the contiguous US relative to 2005, separated by urban/rural and summer (JJA)/winter (DJF). OMI observations are shown in black, the standard GEOS-Chem model simulation with EPA National Emission Inventory (NEI) trends (EPA, 2018) is in red, and the GEOS-Chem sensitivity simulation with additional NO_2 background (50 ppt above 5 km in winter and above 10 km in summer, up to the local tropopause) is shown in blue. Slopes and standard deviation of the linear regressions are shown inset. Urban conditions are defined as the top 10% NO_x-emitting 0.5°×0.625° grid squares in the NEI.