We thank the referees for their insightful comments. Our point-by-point responses to the referee comments and the revisions to the manuscript are as follows:

Response to Referee # 2

General Comments: Shah et al present a combined model, satellite, and ground-based approach to disentangle the effects of changing NOx emissions and NOx lifetime on observed column NO2. The results of this study, and studies like this, are of great importance to the community seeking to utilize remote sensing approaches to infer trends in emissions. It has been well established that NOx lifetime is dependent on NOx concentration (due to the feedback on HOx) especially in the extremes of high and low [NOx] leading to strong spatial variability in NOx lifetime. There has been less focus on variability in tau(NOx) at a fixed location can impact calculated NOx emissions and the impact of NOx on tau(NOx) beyond its control on HOx. The manuscript is well written and within the scope of ACP. I recommend that it be published following the authors attention to the following comments.

Specific Comments:

1. Model resolution: To what extent does model spatial resolution impact the results? If I am not mistaken, the model resolution is approximately 50 x 50 km in the study region. I would expect that O3 titration would display significant variability on this scale and that the mean modeled P(NO3) = k[NO2][O3], which is driving the nocturnal NOx lifetime, may not correspond to that calculated at smaller spatial scales? It would be helpful for the authors to comment on the extent to which model resolution is important and what direction the effects of resolution may have on calculations in NOx lifetime.

Following the referee's suggestion, we have added a discussion about this in the manuscript.

Added text:

Line 210 - Sub-grid scale variability in NO_x and oxidant concentrations can also affect the modeled NO_x lifetimes because of the non-linearity of NO_x chemistry. For example, NO_x lifetime within a concentrated NO_x plume at night can be long because of oxidant depletion, and assuming that the plume is instantaneously diluted within the model grid cell can result in a shorter NO_x lifetime (Brown et al., 2012). However, studies that explicitly treat sub-grid scale plumes suggest that this effect can be important locally near large sources but is small at the regional scale (Karamchandani et al., 2011).

2. N2O5 to NO3 ratio: The N2O5 / NO3 ratio also scales with [NOx]. With decreasing NOx, this ratio decreases and L(NO3) becomes more important than L(N2O5). To what extent is this important here, or is the nocturnal NOx lifetimes essentially all limited by P(NO3) and L(N2O5 + NO3) >> P(NO3)? While this may not impact the retrieval of NOx emissions trends, it could have a sizeable effect on nitrate aerosol formation rates.

We do see an increase in NO_x loss via the NO_3+VOC reactions at lower NO_x emissions. However, the contribution of $L(NO_3)$ to the total NO_x loss is less than 5% (higher in summer than in winter) because of high NO_2 concentrations and the effect of the change in $L(NO_3)$ on the overall NO_x lifetime is small. We have added the following text to the manuscript:

Added text:

Line 246 - At lower NO_x emissions, NO_x loss by NO_3+VOC reactions also increased relative to NO_x loss by N_2O_5 hydrolysis, because of an increase in the ratio of NO_3 to N_2O_5 concentrations. However, the contribution of NO_3+VOC reactions to the total NO_x loss remains less than 5% because of high NO_2.

3. ClNO2 branching fraction: What is the mechanism for ClNO2 in the model? What is the distribution of ClNO2 branching fractions? Does this change in time? If 30-50% of NOx is lost to N2O5, ClNO2 has the potential to return half of this. A short section on the parameterization used and the uncertainty in this (most measurements show that parameterizations of ClNO2 branching fractions are much larger than observations) should be included. I appreciate that NOx lifetime may not be that dependent on aerosol surface area, but the net NOx removal is certainly dependent on the ClNO2 branching fraction.

In the model, $ClNO_2$ forms by N_2O_5 hydrolysis only on sea-salt aerosols, with a fixed branching ratio of 1. When we calculate the NO_x lifetime, we include $ClNO_2$ in the NO_x burden and do not consider $N_2O_5+H_2O/Cl^- \rightarrow ClNO_2$ as a NO_x loss process. We have clarified these two points in the revised manuscript and added a discussion on the effect of this model assumption on the NO_x lifetime.

Added text:

Line 137 - N_2O_5 hydrolysis produces HNO_3 and $ClNO_2$ on sea-salt aerosols with a 1:1 branching ratio (reaction R8) and only HNO_3 on other aerosol types (reaction R7).

Line 205 - We assume that the yield of $ClNO_2$ from N_2O_5 hydrolysis for all aerosols other than sea-salt is 0, which is lower than the average value of ~0.3 estimated by field studies in China (McDuffie et al., 2018a; Tham et al., 2018). If we had assumed a higher $ClNO_2$ yield in the model, the loss of NO_x by N_2O_5 hydrolysis would be slower, particularly in winter when it is limited by ozone and the HNO_3 and $ClNO_2$ branches compete for the limited N_2O_5, and the daytime NO_x loss would increase because of the additional daytime NO_2 from $ClNO_2$ photolysis.

Caption of Fig. 3: The sink from $N_2O_5+H_2O$ excludes the fraction that forms $ClNO_2$.

Response to Referee # 3

The study examines and compares the trends of spaceborne NO2 columns and bottom-up NOx emissions (MEIC) over Eastern China. The observed NO2 trends between 2012 and 2017 appear consistent with the emission trends in summer as well as in winter, when taking into account changes in the NOx lifetimes during that period. GEOS-Chem simulations for the years 2012 and 2017 indicate very little change in the summertime NOx lifetime, due to the compensation of higher daytime OH and lower nighttime aerosol loss; in winter, however, the increasing trend in nighttime ozone appears to drive a decreasing trend of the NOx lifetime, due to the large share of the overall NOx sink being due to N2O5 hydrolysis on aerosols. These model findings appear consistent with the comparison of MEIC emissions and OMI columns.

The topic of the paper is very significant since the community and policy-makers will be interested by further information on NOx emission trends and how they relate to NO2 data. The paper is clear and well written. However, I am not entirely convinced by the robustness of the conclusions.

Major comments

For one thing, uncertainties should be better acknowledged and (wherever possible) evaluated. Given the importance of the aerosol sink in the discussion of the trends, sensitivity studies are necessary to demonstrate that the conclusion holds despite uncertainties in aerosol surface densities and especially in the N2O5 uptake coefficient. I understand that the NO2+O3 reaction might be the main limiting factor to N2O5 loss, at least during the winter, but it might not be the case during summer, and in any case it requires more than just qualitative arguments. It is worth noting that campaign data (e.g. Brown et al., JGR 114, D00F10, doi:10.1029/2008JD011679, 2009) suggested much lower N2O5 uptake coefficients than those (Bertram and Thornton) used in GEOS-Chem.

Following the referee's suggestion, we now include a discussion of the uncertainties and the results of a new sensitivity simulation that we conducted to evaluate the effects of the main uncertainties. The following text was added to the modified manuscript:

Added text:

Line 200 - The modeled NO_x lifetimes can be affected by uncertainties in the modeled aerosol surface area, γ_{N2O5}, and the yield of $ClNO_2$. We find that the GEOS-Chem aerosol concentrations at the surface are about 30% higher than observations from the MEE network. On the other hand, GEOS-Chem's γ_{N2O5} values are 25% lower on average than the observation-based estimates from the WINTER campaign (Jaeglé et al., 2018; McDuffie et al., 2018b). We tested the sensitivity of the modeled NO_x lifetime to the aerosol surface area and γ_{N2O5} with a separate simulation and find that a 30% change in either quantity changes the NO_x loss by N_2O_5 hydrolysis by only 8% in summer and less than 2% in winter. We assume that the yield of $ClNO_2$ from N_2O_5 hydrolysis for all aerosols other than sea-salt is 0, which is lower than the average value of ~0.3 estimated by field studies in China (McDuffie et al., 2018a; Tham et al., 2018). If we had assumed a higher $ClNO_2$ yield in the model, the loss of NO_x by N_2O_5 hydrolysis would be slower, particularly in winter when it is limited by ozone and the HNO_3 and $ClNO_2$ branches compete for the limited N_2O_5, and the daytime NO_x loss would increase because of the additional daytime NO_2 from $ClNO_2$ photolysis. Sub-grid scale variability in NO_x and oxidant concentrations can also affect the modeled NO_x lifetimes because of the non-linearity of NO_x chemistry. For example, NO_x

lifetime within a concentrated NO_x plume at night can be long because of oxidant depletion, and assuming that the plume is instantaneously diluted within the model grid cell can result in a shorter NO_x lifetime (Brown et al., 2012). However, studies that explicitly treat sub-grid scale plumes suggest that this effect can be important locally near large sources but is small at the regional scale (Karamchandani et al., 2011).

A second major comment is related to the calculation of NOx lifetimes (Figure 3), which are averages for the bottom 0-2 km of the atmosphere. I assume that the values given (about 6 hours in the summer and 21-27 hours in winter) are 24-hour averages. Two issues arise: 1) in summer, the relevant lifetime for OMI NO2 columns is the average NOx lifetime during the few (~6) hours preceding the satellite overpass time (13:30 LT); and 2) the vertical profile of the OMI sensor sensitivity should be taken into account. I know that at least 70% of the columns lies below 2 km altitude, but the sensitivity profile is very steep and very anti-correlated with the NO2 vmr profile, even below 2 km. Furthermore, the part of the column lying above 2 km altitude is non-negligible and might have very different trends from the lowermost part. I suspect that taking these effects into account will increase the relative importance of NO2+OH to the total loss, with possibly significant consequences for the trend and for the seasonal evolution.

The seasonal NOx lifetimes are 24-hour mean values. We have clarified this in text manuscript. We also agree that because of the shorter summer lifetime the daytime loss processes affect OMI NO_2 columns much more than those at night. We have now stated this this in the revised manuscript.
To test how sensitive the lifetime is to the column height, we recalculated the NO_x lifetime for the full tropospheric NO_2 column and took into account the vertical sensitivity of the retrieval. We find minor differences compared to the 0–2 km mean NO_x lifetimes and loss pathways (NO_2+OH does increase a little), because bulk of the NO_x column is located below 2 km. We have included the figure showing the tropospheric column NO_x lifetime and loss pathways in the Supplement and have referenced it in the main text.

Added text (underlined):
Line 186 - We find in GEOS-Chem that the seasonal variation in NO_2 columns is mainly driven by the NO_x lifetime in the boundary layer, which increases from 5.9 h in summer to 21 h in winter (24-h mean lifetimes for 2017, Fig. 3). We find little difference between the boundary layer and the tropospheric column NO_x lifetimes (Supplement Fig. S2) since most of the column is in the boundary layer. In summer, NO_x is lost mostly through oxidation by OH in daytime (43%) and through N_2O_5 hydrolysis forming HNO_3 at night (33%). The daytime oxidation processes have a larger effect on the afternoon NO_2 columns because of the short NO_x lifetime in summer.

Added supplemental figure:

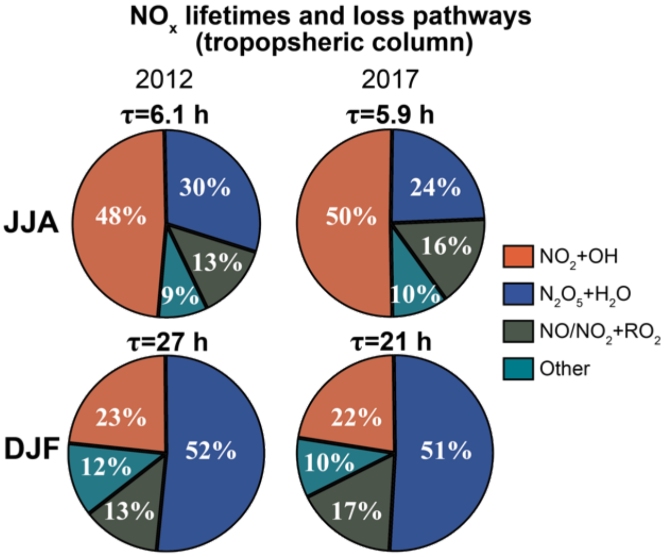

Figure S2: NO$_x$ lifetime (τ) and loss pathways for the tropospheric column over central-eastern China. The lifetimes are the GEOS-Chem averages for the tropospheric column weighted by the OMI averaging kernel over the domain delineated in Figure 1, and the pie charts show the relative contributions of the different NO$_x$ sinks. For the lifetime calculation we define NO$_x$ as NO+NO$_2$+NO$_3$+2N$_2$O$_5$+HONO+HNO$_4$+ ClNO$_2$. Values are given for summer (JJA) and winter (DJF) of 2012 and 2017. The sink from NO/NO$_2$ + RO$_2$ is the net flux, accounting for partial recycling of the organic nitrates, and includes the contributions from peroxyacyl nitrates (PANs). The 'Other' sinks include NO$_3$ + VOC reactions, NO$_2$ and NO$_3$ hydrolysis in aerosols, and NO$_x$ deposition.

Minor comments:

- line 112 how important is the correction using GEOS-Chem simulated concentrations of HNO3 and organic nitrates?

The correction for HNO$_3$ and organic nitrates decreases the seasonal-mean NO$_2$ concentrations over eastern China by 25% in summer and 6% in winter. We have specified this in the revised manuscript.

Added text:

Line 116 - The correction for HNO$_3$ and organic nitrates decreases the seasonal-mean NO$_2$ concentrations over eastern China by 25% in summer and 6% in winter.

- why not use the ground-based NO2 measurements to evaluate the trends?

We did not use the ground-based NO$_2$ measurements to evaluate the trends because the stations are located in dense urban areas and are more sensitive to trends of vehicular NO$_x$ emissions than trends in NOx emissions from industries and power plants. Indeed, Zheng et al. (2018) showed that trends the surface NO$_2$ concentrations were flatter than trends in OMI NO$_2$ columns. We have cited this result from Zheng et al. (2018) in the revised text.

Added text:

Line 224 - Zheng et al. (2018) also showed consistency in the trends of OMI NO_2 columns and the MEIC NO_x emissions, but found that the NO_2 trends at the MEE surface sites are flatter because the sites are urban and more sensitive to vehicular NO_x emissions.

- l. 135 the NO2 hydrolysis coefficient is said to be decreased from 10^{-4} to 10^{-5}. Relative to what study or what model version? Is this value used for all RH and all aerosol types? Jaeglé et al. (JGR 2018) use 10^{-4} and assume that the reaction makes only HONO (i.e. no HNO3), which would lead to very high HONO/NO2 ratios over China. A comment on this would be appreciated.

We have added the reference for the original γ values, and have added a comment regarding the difference of the γ and products of NO_2 hydrolysis with those in Jaeglé et al. (2018). Please see the modified text below.

- l.136-138 This gives the impression that the well-known issue of the HONO missing sources has been solved, which is not the case, since many other sources have been proposed to explain the observations.

We agree with the reviewer that the issue of missing HONO sources is an open question. We have revised the text to reflect this better. Please see the modified text below.

What is the contribution of NO2 hydrolysis to the NOx sink in the simulations?

NO_2 hydrolysis is a minor sink of NO_x, contributing between 1% (2011 summer) and 7% (2011 winter).

Added text (underlined):

Line 138 - Uniform values of γ_{NO_3} and γ_{NO_2} are used for all aerosol types and all RH conditions. γ_{NO_3} is taken to be 1×10^{-3} following Jacob (2000). γ_{NO_2} for the hydrolysis reaction (R11) is decreased from 1×10^{-4} (Jacob, 2000) to 1×10^{-5} on the basis of laboratory measurements (Bröske et al., 2003; Stemmler et al., 2007; Tan et al., 2016). This decrease of γ_{NO_2} yields a 24 h mean wintertime HONO/NO_2 molar concentration ratio of 0.035 over eastern China in GEOS-Chem, consistent with the observed range of 0.015–0.071 (Hendrick et al., 2014; Spataro et al., 2013; Wang et al., 2017, 2013). The GEOS-Chem HONO/NO_2 ratio is likely low because of unknown sources of HONO particularly during the day (Kleffmann, 2007; Spataro and Ianniello, 2014). For the WINTER campaign, Jaeglé et al. (2018) used a γ_{NO_2} of 1×10^{-4} but assumed that the reaction produces only HONO. Using this γ_{NO_2} for eastern China would lead to a significant overestimate of the observed HONO/NO_2 ratio.

- what is the model performance for aerosol surface density over China?

GEOS-Chem overestimated aerosol surface area by 30% compared to ground-level measurements at the MEE sites. Specified this on Line 201.

- l.172-174 The NO2 column measurement and the surface NO2 measurement represent different times, therefore the similar winter-summer ratios are not necessarily expected.

We agree that the winter-summer ratios of NO_2 columns and surface NO_2 need not be similar as the measurement times differ. We have modified the text to reflect that the similarity exists despite the different measurement times.

Revised text:

Line 180 - ~~GEOS-Chem shows similar ratios for NO_2 columns and surface NO_2, as would be expected since most of the tropospheric NO_2 column is in the boundary layer.~~

GEOS-Chem shows similar ratios for the afternoon NO_2 columns and 24-h mean surface NO_2, despite different averaging times.

- l.186 Regarding the aerosol loss, a discussion of the uptake coefficient is required (see above, major comment)
We have added a discussion of the uptake coefficient in the revised manuscript as described in the response to major comment #1 (above).

- l.187-190 and Figure 4: not useful for the discussion, could possibly be dropped.
We have moved Fig. 4 to the Supplement, following the referee's suggestion. We have retained the text on lines 187-190, because it clarifies why the NO_x lifetime derived from the decay of NO_2 concentrations away from a source cannot be used to verify the simulated NO_x chemical lifetime for our study region.

- Figure 1: I suggest to indicate on each plot, the domain-averaged NO2 column
Following the referee's suggestion, we have added the domain-averaged NO_2 column in the figure.

Technical comments:
- the reference Manders et al. (2017) is missing
The Manders et al. (2017) reference is on Line 461.
- the reference Bertram and Thornton (2009) is missing
We have now added the reference for Bertram & Thornton (2009)
- references: use journal abbreviations
We have edited the References and use journal abbreviations.

Effect of changing NO_x lifetime on the seasonality and long-term trends of satellite-observed tropospheric NO_2 columns over China

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Abstract. Satellite observations of tropospheric NO_2 columns are extensively used to infer trends in anthropogenic emissions of nitrogen oxides ($NO_x \equiv NO + NO_2$), but this may be complicated by trends in NO_x lifetime. Here we use 2004–2018 observations from the OMI satellite-based instrument (QA4ECV and POMINO v2 retrievals) to examine the seasonality and trends of tropospheric NO_2 columns over central-eastern China, and we interpret the results with the GEOS-Chem chemical transport model. The observations show a factor of 3 increase in NO_2 columns from summer to winter, which we explain in GEOS-Chem as reflecting a longer NO_x lifetime in winter than in summer (21 h versus 5.9 h in 2017). The 2005–2018 summer trends of OMI NO_2 closely follow the trends in the Multi-resolution Emission Inventory for China (MEIC), with a rise over the 2005–2011 period and a 25% decrease since. We find in GEOS-Chem no significant trend of the NO_x lifetime in summer, supporting the emission trend reported by MEIC. The winter trend of OMI NO_2 is steeper than in summer over the entire period, which we attribute to a decrease in NO_x lifetime at lower NO_x emissions. Half of the NO_x sink in winter is from N_2O_5 hydrolysis, which counterintuitively becomes more efficient as NO_x emissions decrease due to less titration of ozone at night. Formation of organic nitrates also becomes an increasing sink of NO_x as NO_x emissions decrease but emissions of volatile organic compounds (VOCs) do not.

1 Introduction

Emissions of nitrogen oxides ($NO_x \equiv NO+NO_2$) from fossil fuel combustion in China have been changing fast in the past few decades, due to rapid economic expansion on the one hand and strengthening environmental regulations on the other hand. Growing fossil fuel use with weak pollution controls resulted in almost three-fold increase in China's NO_x emissions between 1990 and 2010, according to bottom-up inventories based on activity data and emission factors (Granier et al., 2011; Zhang et al., 2012b). Since then, China has adopted strong measures to decrease air pollution by setting stringent emissions standards, capping coal use, increasing vehicle fuel efficiency, closing outdated facilities, and growing renewable energy (Liu et al., 2016; Zheng et al., 2018). Bottom-up inventories estimate that China's NO_x emissions decreased by 20% between 2011 and 2017, despite continuing economic expansion (Sun et al., 2018; Zheng et al., 2018). There is a strong need to evaluate these emission inventories and their trends for air quality management.

Satellite-based observations of tropospheric NO_2 columns by solar backscatter have been used extensively as a proxy for NO_x emissions and their trends (Martin, 2008; Streets et al., 2013). These observations have been qualitatively consistent with the trends in Chinese NO_x emission inventories, showing an increasing trend of NO_2 columns over China between 1994 and 2011, and a sharp reversal in eastern China since 2011 (Richter et al., 2005; van der A et al., 2006, 2008; Lin et al., 2010; Krotkov et al., 2016; Schneider et al., 2015; Duncan et al., 2016; Cui et al., 2016; Georgoulias et al., 2019; Wang et al., 2019). However, the trends in the NO_2 columns are steeper than in the emission inventories (Zhang et al., 2007; Stavrakou et al., 2008; Zhang et al., 2012b; Hilboll et al., 2013; Liu et al., 2017; Zheng et al., 2018). For example, Zhang et al. (2007) found that NO_2 columns over China increased two-fold from 1996 to 2004 while their emission inventory reported a 60% increase. For 2010–2015, the Multi-resolution Emission Inventory for China (MEIC) estimates a 14% decrease in NO_x emissions but NO_2 columns from the OMI satellite instrument indicate a 22% decrease (Zheng et al., 2018).

Differences in the trends between NO_2 columns and NO_x emission inventories could reflect errors in the inventories (Saikawa et al., 2017) and satellite retrievals (Lin et al., 2014; Lorente et al., 2017), but also trends in the lifetime of NO_x against atmospheric oxidation. This lifetime is of the order of hours and may change with the chemical environment, including the NO_x concentration itself (Stavrakou et al., 2008; Lamsal et al., 2011; Valin et al., 2011; Lu and Streets, 2012; Duncan et al., 2013; Gu et al., 2016; Cooper et al., 2017; Laughner and Cohen, 2019). NO_x is oxidized to nitric acid (HNO_3) and organic nitrates ($RONO_2$), including peroxyacyl nitrates ($RC(O)OONO_2$). There is also a minor sink from NO_2 dry deposition (Zhang et al., 2012a). Oxidation in the daytime is driven by photochemically produced hydrogen oxide ($HO_x \equiv OH+HO_2+RO_2$) radicals:

$$\mathrm{NO_2 + OH \xrightarrow{M} HNO_3} \qquad \text{(R1)}$$

$$\mathrm{NO + RO_2 \xrightarrow{\alpha\ M} (1-\alpha)NO_2 + (1-\alpha)RO + \alpha RONO_2} \qquad \text{(R2)}$$

$$\mathrm{NO_2 + RC(O)OO \overset{M}{\longleftrightarrow} RC(O)OONO_2} \qquad \text{(R3)}$$

where α in reaction R2 is the branching ratio for organic nitrate formation. NO_x and HO_x concentrations are tightly interlinked (Kleinman, 1994; Laughner and Cohen, 2019). When NO_x levels are sufficiently low (the so-called NO_x-limited conditions), an increase in NO_x drives an increase in HO_x, particularly OH through the $\mathrm{NO + HO_2 \rightarrow NO_2 + OH}$ reaction. When NO_x levels are high (the so-called NO_x-saturated conditions), reaction R1 becomes the dominant HO_x sink and an increase in NO_x causes a decrease in HO_x.

At night, the chemical loss of NO_x proceeds through a series of reactions (R4–R10) beginning with the oxidation of NO and NO_2 by O_3 to form nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5). N_2O_5 and NO_3 react in aerosols to produce HNO_3, and NO_3 additionally reacts with volatile organic compounds (VOCs) to form either HNO_3 or $RONO_2$:

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2} \tag{R4}$$

$$\mathrm{NO_2} + \mathrm{O_3} \longrightarrow \mathrm{NO_3} + \mathrm{O_2} \tag{R5}$$

$$\mathrm{NO_3} + \mathrm{NO_2} \overset{\mathrm{M}}{\longleftrightarrow} \mathrm{N_2O_5} \tag{R6}$$

$$\mathrm{N_2O_5} \xrightarrow{\mathrm{H_2O}(l),\ \text{aerosols}} 2\mathrm{HNO_3} \tag{R7}$$

$$\mathrm{N_2O_5} + \mathrm{Cl^-} \xrightarrow{\mathrm{H_2O}(l),\ \text{aerosols}} \mathrm{HNO_3} + \mathrm{ClNO_2} \tag{R8}$$

$$\mathrm{NO_3} \xrightarrow{\mathrm{H_2O}(l),\ \text{aerosols}} \mathrm{HNO_3} + \mathrm{OH} \tag{R9}$$

$$\mathrm{NO_3} + \mathrm{VOC} \longrightarrow \mathrm{HNO_3}, \mathrm{RONO_2}, \text{other products} \tag{R10}$$

A change in NO_x emissions can change the nighttime levels of ozone and reaction (R6) is quadratic in NO_x concentrations, leading to nonlinearity between NO_x emissions and NO_2 concentrations. In addition, aerosol concentrations in China have decreased by about 30% since 2013 (Lin et al., 2018; Zheng et al., 2018; Zhai et al., 2019; Ma et al., 2019), which would decrease the rate of nighttime NO_x loss (R7–R9). A decrease in aerosol concentrations will also slow the NO_x loss by hydrolysis of NO_2 in aerosols:

$$\mathrm{NO_2} \xrightarrow{\mathrm{H_2O}(l),\ \text{aerosols}} 0.5\ \mathrm{HONO} + 0.5\ \mathrm{HNO_3} \tag{R11}$$

Here we present trends in tropospheric NO_2 columns over China from 2004 to 2018 observed by the Ozone Monitoring Instrument (OMI) satellite instrument, showing a peak in 2011. We use the GEOS-Chem chemical transport model applied to the MEIC inventory (Zheng et al., 2018) to investigate how changes in NO_x lifetimes have affected the relationship between tropospheric NO_2 columns and NO_x emissions, and whether this can reconcile the differences in trends between the two quantities. Results have important implications for the use of satellite NO_2 retrievals to infer trends in NO_x emissions.

2 Observations and model

2.1 OMI NO_2 column retrievals

We use 2004–2018 tropospheric NO_2 column data retrieved from the OMI instrument aboard the NASA Aura satellite. Aura is in sun-synchronous polar orbit satellite with daytime equator crossing at 13:45 local solar time (LST). OMI measures backscattered solar radiation from the Earth in the ultraviolet and visible wavelength range (270–504 nm). It has a swath width of 2600 km and a ground pixel size of 13 km × 24 km at nadir (Levelt et al., 2006, 2018). Several OMI pixels are affected by the so-called row anomaly possibly from an obstruction in their field of view (Dobber et al., 2008). Pixels not affected by the row anomaly have no significant calibration drift over the length of the record (Boersma et al., 2018).

We use tropospheric NO_2 columns from two retrievals: the European Quality Assurance for Essential Climate Variables (QA4ECV) project's NO_2 ECV precursor product (Boersma et al., 2018) and the Peking University POMINO product, version 2 (Lin et al., 2015; Liu et al., 2019). NO_2 tropospheric column retrieval in the ECV product involves (1) spectral fit of the backscattered solar radiation in the 405–465 nm window to obtain the total NO_2 slant column (SC), (2) removal of the stratospheric component by data assimilation with the TM5-MP chemical transport model, and (3) conversion of the tropospheric SC to a tropospheric vertical column (VC) with an air mass factor (AMF = SC/VC) that depends on viewing geometry, surface albedo, retrieved cloud properties, and the NO_2 vertical profile (taken from the TM5-MP model).

The POMINO v2 product starts with the tropospheric NO_2 slant columns from the ECV retrieval but uses different methods and data sources for the AMF calculation. The main difference is the treatment of aerosols. ECV assumes that aerosol effects are implicitly accounted for in the independent retrieval of cloud pressure and cloud fraction, which are prerequisites for NO_2 retrievals. POMINO explicitly accounts for aerosols in the radiative transfer calculations with aerosol optical properties and vertical profiles from the GEOS-Chem model corrected with satellite observations from the MODIS and CALIOP instruments. In polluted areas (aerosol optical depth greater than 0.5), the choice of aerosol correction method can affect the AMF by 45% (Lorente et al., 2017) and the sign of the correction depends on the vertical distribution of aerosols relative to NO_2 (Palmer et al., 2001; Martin et al., 2003; Liu et al., 2019). POMINO also includes angular dependence of surface reflectance, online radiative transfer calculation, and consistency in retrievals of cloud properties and NO_2 (Lin et al., 2015; Liu et al., 2019).

We create monthly mean gridded (0.5º latitude × 0.625º longitude) datasets of ECV and POMINO NO_2 columns over China for June-July-August (JJA) 2005–2018 and December-January-February (DJF) 2004–2018. We exclude pixels with snow-covered surfaces and cloud fraction greater than 30%. We use cloud fraction data from the corresponding retrievals. We include only cross-track viewing positions of 5 through 22 to exclude data affected by the row anomaly (Boersma et al., 2018) and swath edges. For comparison with GEOS-Chem, the POMINO and ECV NO_2 columns are recalculated with modified air mass factors using the pixel-specific GEOS-Chem NO_2 vertical profiles (Palmer et al., 2001).

2.2 Ground-based observations

We use hourly measurements of NO_2 and O_3 concentrations from the network of ~1000 sites operated by the China Ministry of Ecology and Environment (MEE) since 2013 (http://beijingair.sinaapp.com). We correct the known interference of organic nitrates and HNO_3 in the NO_2 measurements by using the GEOS-Chem simulated concentrations for those species following Lamsal et al. (2008)~~. We~~ and then grid (0.5º×0.625º grid) and seasonally average the data, discarding sites with less than 50% coverage in a season. The correction for HNO_3 and organic nitrates decreases the reported seasonal-mean NO_2 concentrations over eastern China by 25% in summer and 6% in winter.

2.3 GEOS-Chem model

We use the GEOS-Chem chemical transport model version 12.1.0 (www.geos-chem.org) driven by assimilated meteorological fields from the NASA Global Modeling and Assimilation Office's Modern-Era Retrospective analysis for Research and Applications, version 2 (MERRA-2) system (Gelaro et al., 2017). GEOS-Chem simulates the chemistry of major gas- and aerosol-phase species in the troposphere (Pye et al., 2009; Kim et al., 2015; Travis et al., 2016; Fisher et al., 2016; Sherwen et al., 2016). We use the GEOS-Chem Classic nested-grid configuration over East Asia (11ºS–55ºN, 60–150ºE) at 0.5º×0.625º resolution (Wang et al., 2004; Chen et al., 2009), with lateral chemical boundary conditions from a 4º×5º global simulation. Anthropogenic emissions over China are from the MEIC inventory updated annually for 2000–2017 (www.meicmodel.org; Zheng et al., 2018). MEIC includes monthly emission profiles for each sector (Li et al., 2017a) and hourly profiles developed at Tsinghua University. We vertically resolve emissions from point sources (power plants and industries) following profiles used in the LOTOS-EUROS model (Manders et al., 2017), and speciate anthropogenic NO_x emissions as NO (90%), NO_2 (9.2%) and HONO (0.8%) following Menut et al. (2013). GEOS-Chem includes additional NO_x emissions from soil and fertilizer use (Hudman et al., 2012), lightning (Murray et al., 2012), shipping (Vinken et al., 2011; Holmes et al., 2014) and aircraft (Stettler et al., 2011). Vertical mixing in the planetary boundary layer is simulated using a non-local mixing scheme (Lin and McElroy, 2010).

We modified the standard GEOS-Chem version 12.1.0 chemistry to update the reactive uptake coefficients (γ) of N_2O_5, NO_3, and NO_2 on aerosols (Jacob, 2000) based on recent comparison of GEOS-Chem to observations from the Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) aircraft campaign over the eastern United States (Jaeglé et al., 2018; Shah et al., 2018). $\gamma_{N_2O_5}$ is computed following Bertram and Thornton (2009) for sulfate-nitrate-ammonium aerosols, and is taken to be 1×10^{-4} (RH < 50%) or 1×10^{-3} (RH > 50%) for organic aerosols. N_2O_5 hydrolysis produces HNO_3 and $ClNO_2$ on sea-salt aerosols with a 1:1 branching ratio (reaction R8) and only HNO_3 on other aerosol types (reaction R7). Uniform values of $\gamma_{N_2O_5}$ and γ_{NO_2} are used for all aerosol types and all RH conditions. γ_{NO_3} is taken to be 1×10^{-3} following Jacob (2000). γ_{NO_2} for the hydrolysis reaction (R11) is decreased from 1×10^{-4} (Jacob, 2000) to 1×10^{-5} on the basis of laboratory measurements

(Bröske et al., 2003; Stemmler et al., 2007; Tan et al., 2016). This decrease of γ_{NO_2} yields a 24 h mean wintertime HONO/NO_2 molar concentration ratio of 0.035 over eastern China in GEOS-Chem, consistent with the observed range of 0.015–0.071 (Hendrick et al., 2014; Spataro et al., 2013; Wang et al., 2017, 2013). The GEOS-Chem HONO/NO_2 ratio is likely low because of unknown sources of HONO particularly during the day (Kleffmann, 2007; Spataro and Ianniello, 2014). For the WINTER campaign, Jaeglé et al. (2018) used a γ_{NO_2} of 1×10^{-4} but assumed that the reaction produces only HONO. Using this γ_{NO_2} for eastern China would lead to a significant overestimate of the observed HONO/NO_2 ratio.

We evaluate the model with the spatial and seasonal distributions of OMI NO_2 observations for 2016/17 DJF and 2017 JJA (the latest year with MEIC data) and use these two periods to analyze the seasonality of NO_x lifetime and loss pathways in the model. To calculate the emission-driven changes in NO_x lifetimes, we conduct a sensitivity simulation in which we set anthropogenic emissions over China to 2012 levels but use the 2016/17 meteorology and NO_x emissions from soils, lightning, ships, and aircraft. Chinese NO_x emissions decreased by 25% from 2012 to 2017 according to MEIC (Supplement Fig. S1). For comparison with OMI observations, we sample the model at 13–14 LST and exclude model columns with surface snow cover or with model cloud fraction greater than 30%. We focus on the large polluted region of central-eastern China (30–41ºN, 112–122ºE; ~~rectangle~~rectangles in ~~left panels of~~ Fig. 1), where we may expect tropospheric NO_2 columns to be most sensitive to Chinese NO_x emissions, and where the relatively narrow latitude range leads to consistent seasonal variations. This region accounted for 50% of anthropogenic Chinese emissions in 2017 according to MEIC.

3 Results and discussion

3.1 Seasonal variation of NO_2 columns and NO_x lifetimes

Figure 1 shows the NO_2 columns from the POMINO and ECV retrievals, and from the GEOS-Chem model, for JJA 2017 and DJF 2016/17. In central-eastern China, we find that in both seasons over 70% of the GEOS-Chem tropospheric NO_2 column as would be observed by OMI is in the boundary layer below 2 km altitude. Thus we expect the NO_2 column to reflect mostly the local NO_x emissions rather than the free tropospheric background (Silvern et al., 2019). In summer, average GEOS-Chem NO_2 columns over central-eastern China are within 10% of the POMINO and ECV NO_2 columns. There is scatter in the spatial relationship ($r \approx 0.5$) that could be due to a combination of model and retrieval errors. In winter, however, POMINO is 42% higher than GEOS-Chem while ECV is 16% lower. The difference in aerosol correction between POMINO and ECV is largest in winter, due to high aerosol concentrations and high solar zenith angles. In ECV, polluted scenes with high aerosol optical depths (and likely high NO_2) can be misclassified as cloudy and excluded from the seasonal-mean, which leads to a negative sampling bias (Lin et al., 2014, 2015; Liu et al., 2019). On the other hand, retrieving NO_2 columns under high-aerosol conditions can be uncertain because of the strong sensitivity to the vertical distribution of NO_2 relative to that of aerosols, although this is less of a problem in POMINO as it uses the CALIOP-observed aerosol vertical profiles (Lin et al., 2014, 2015; Liu et al., 2019).

Liu et al. (2019) compared the ECV and POMINO retrievals to ground-based Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) NO_2 column observations on 49 days in 3 Chinese cities. POMINO was on average closer to the MAX-DOAS NO_2 than ECV (-3% versus -22% bias) and on hazy days (+4% versus -26% bias), but on clear (cloud fraction=0) days ECV performed better (-6% bias) than POMINO (+30% bias). These biases were slightly larger in fall and winter, although sampling in individual seasons was sparse. There is uncertainty in the comparison as the column observed by MAX-DOAS may not be representative of the satellite pixel, and aerosol vertical profiles used in the satellite and MAX-DOAS retrievals may be inconsistent (Lin et al., 2014).

Figure 2 compares the mean winter-summer ratios of NO_2 columns from the ECV and POMINO retrievals over central-eastern China with GEOS-Chem and with the ratios of 24-h mean surface NO_2 concentrations at the MEE sites. GEOS-Chem shows similar ratios for the afternoon NO_2 columns and 24-h mean surface NO_2, ~~as would be expected since most of the tropospheric NO_2 column is in the boundary layer.~~despite different averaging times. We find that the seasonal amplitude in the ~~MEE~~surface NO_2 data is most consistent with the ECV NO_2 columns, whereas the seasonal amplitude of POMINO NO_2 is larger. Winter-summer ratios of NO_2 columns are 2.6 in the ECV retrieval, 3.5 in POMINO, and 2.7 in GEOS-Chem. Winter-summer ratios of surface NO_2 concentrations are 2.3 in the MEE data and 2.5 in GEOS-Chem. Anthropogenic NO_x emissions in the MEIC inventory ~~peak in winter but the~~show little seasonality, with a winter-summer ratio is only 1.15 (Li et al., 2017b). We find in GEOS-Chem that the seasonal variation in NO_2 columns is mainly driven by the NO_x lifetime in the boundary layer, which increases from 5.9 h in summer to 21 h in winter (24-h mean lifetimes for 2017~~(~~, Fig. 3). We find little difference between the boundary layer and the tropospheric column NO_x lifetimes (Supplement Fig. S2) since most of the column is in the boundary layer.

In summer, NO_x is lost mostly through oxidation by OH in daytime (43%) and through N_2O_5 hydrolysis forming HNO_3 at night (33%). The daytime oxidation processes have a larger effect on the afternoon NO_2 columns because of the short NO_x lifetime, particularly in summer. In winter, the NO_x lifetime is much longer because of the lower concentrations of OH and RO_2 radicals. N_2O_5 hydrolysis accounts for 51% of NO_x loss in winter. Remarkably, the loss of NO_x from N_2O_5 hydrolysis is a factor of 2 slower in winter than in summer, despite the longer nights and higher aerosol concentrations (Zhai et al., 2019), because of the low nighttime ozone concentrations. The overall NO_x lifetime in winter and the contribution from N_2O_5 hydrolysis are similar to values inferred over the eastern US during the WINTER campaign (Jaeglé et al., 2018), despite a factor of ~5 difference in aerosol concentrations between the two regions. Loss of NO_x by N_2O_5 hydrolysis in China in winter is limited by the supply of ozone, not the supply of aerosol.

The modeled NO_x lifetimes can be affected by uncertainties in the modeled aerosol surface area, $\gamma_{N_2O_5}$, and the yield of $ClNO_2$. We find that the GEOS-Chem aerosol concentrations at the surface are about 30% higher than observations from the MEE network. On the other hand, GEOS-Chem's $\gamma_{N_2O_5}$ values are 25% lower on average than the observation-based estimates from the WINTER campaign (Jaeglé et al., 2018; McDuffie et al., 2018b). We tested the sensitivity of the modeled NO_x lifetime to the aerosol surface area and $\gamma_{N_2O_5}$ with a separate simulation and find that a 30% change in either quantity changes the NO_x loss by N_2O_5 hydrolysis by only 8% in summer and less than 2% in winter. We assume that the yield of $ClNO_2$ from N_2O_5 hydrolysis for all aerosols other than sea-salt is 0, which is lower than the average value of ~0.3 estimated by field studies in China (McDuffie et al., 2018a; Tham et al., 2018). If we had assumed a higher $ClNO_2$ yield in the model, the loss of NO_x by N_2O_5 hydrolysis would be slower, particularly in winter when it is limited by ozone and the HNO_3 and $ClNO_2$ branches compete for the limited N_2O_5, and the daytime NO_x loss would increase because of the additional daytime NO_2 from $ClNO_2$ photolysis. Sub-grid scale variability in NO_x and oxidant concentrations can also affect the modeled NO_x lifetimes because of the non-linearity of NO_x chemistry. For example, NO_x lifetime within a concentrated NO_x plume at night can be long because of oxidant depletion, and assuming that the plume is instantaneously diluted within the model grid cell can result in a shorter NO_x lifetime (Brown et al., 2012). However, studies that explicitly treat sub-grid scale plumes suggest that this effect can be important locally near large sources but is small at the regional scale (Karamchandani et al., 2011).

Leue et al. (2001) previously estimated the NO_x lifetime in the eastern US by using the offshore gradient of satellite-observed NO_2 columns. We tried this approach and found that the offshore gradients of NO_2 columns perpendicular to the east coast of China are consistent between model and observations (Supplement Fig. ~~4~~S3). However, there is little seasonal difference in the gradients, suggesting that their magnitudes are determined by dilution more than chemical decay.

3.2 2004–2018 trends in NO_2 columns and lifetimes

Figure ~~5~~4 shows the trends in the summer and winter NO_2 columns from the ECV retrieval, and in anthropogenic NO_x emissions from MEIC, over central-eastern China for the 2004–2018 extent of the OMI record. According to MEIC, NO_x emissions increased at 5–6% a^{-1} in 2005–2011 and decreased at the same pace after 2011. OMI NO_2 columns mirror the trajectory of the MEIC NO_x emissions: rising between 2005 and 2011, reversing direction in 2011/12, and falling back to around 2005 levels by 2018. Zheng et al. (2018) also showed consistency in the trends of OMI NO_2 columns and the MEIC NO_x emissions, but found that the NO_2 trends at the MEE surface sites are flatter because the sites are urban and more sensitive to vehicular NO_x emissions. The summer trends in OMI NO_2 closely track the MEIC emissions but the winter trends are steeper. The same summer-winter differences in NO_2 column trends over China are seen in the POMINO retrieval (Supplement Fig. ~~S2~~S4) and in retrievals from the Ozone Mapping Profiler Suite (OMPS) instrument (Lin et al., 2019). Previous studies also reported such a seasonal difference between summer and winter NO_2 column trends (Uno et al., 2007; Zhang et al., 2007; Stavrakou et al., 2008; Gu et al., 2013).

The steeper slopes in winter could reflect a trend in NO_x lifetime as NO_x and other emissions change. A few modeling studies have previously explored this dependence for China. Uno et al. (2007) found no significant change in the annual mean NO_x lifetime over 1996–2004. Stavrakou et al. (2008) found that the increase in NO_x emissions over 1997–2006 drove a 25% decrease in summer NO_x lifetime, due to higher OH from faster $NO+HO_2$ reaction, and a 10% increase in winter NO_x lifetime, due to lower OH from faster NO_2+OH reaction.

We examined the effect of 2012–2017 changes in MEIC emissions for NO_x and other species on the lifetime of NO_x simulated by GEOS-Chem (Fig. 3). During that period, NO_x emissions in central-eastern China decreased by 25% and boundary layer aerosol concentrations in GEOS-Chem decreased by 20%. Observed aerosol concentrations from the MEE network decreased by 30% over the 2013–2017 period (Zhai et al., 2019). We find no significant change in the summer NO_x lifetime between 2012 and 2017. The NO_x lifetime during the day shortened slightly, as summertime OH concentrations increased by 6% and RO_2 concentrations increased by 13%. However, the NO_x lifetime during the night increased as aerosol concentrations dropped, canceling the overall effect.

In contrast, the winter NO_x lifetime decreased by 22% (from 27 h to 21 h) between 2012 and 2017 (Fig. 3), driven mostly by faster loss by N_2O_5 hydrolysis in aerosols, and also by faster loss from reactions with OH and RO_2. The loss rate from RO_2 + NO/NO_2 is largely determined by the emission rate of VOCs, which changed by less than 3% over 2012–2017 (Zheng et al., 2018), effectively decreasing the NO_x lifetime as NO_x emissions dropped. ~~The faster loss by N_2O_5 hydrolysis~~At lower NO_x emissions, NO_x loss by NO_3+VOC reactions also increased relative to NO_x loss by N_2O_5 hydrolysis, because of an increase in the ratio of NO_3 to N_2O_5 concentrations. However, the contribution of NO_3+VOC reactions to the total NO_x loss remains less than 5% because of high NO_2. The faster loss by N_2O_5 hydrolysis in 2017 relative to 2012 might seem counterintuitive since both aerosols and NO_x dropped over the period. However, winter aerosol levels for converting N_2O_5 to HNO_3 remain in excess even in 2017. Instead, we find that the driving factor behind the increase in N_2O_5 hydrolysis is a rise in nighttime ozone concentrations. At night, fast titration by NO (reaction R4) is an important sink of ozone close to NO_x sources. As NO_x emissions decrease, less ozone is titrated, which then enables the formation of NO_3 by reaction (R5) and subsequent formation of N_2O_5. The simulated NO_x lifetime against loss by N_2O_5 hydrolysis decreases by 26% from 54 h in the winter 2011/12 to 40 h in the winter 2016/17. Ground-based observations at the MEE sites show an increase in winter nighttime ozone consistent with the model (Fig. ~~6~~5).

Figure ~~5~~4 shows the implications of these changes in seasonal NO_x lifetime on the 2012–2017 NO_2 column trends simulated by GEOS-Chem. ~~There is no significant change in~~Neither the 24-h mean nor the daytime NO_x lifetime changes significantly in summer and therefore the NO_2 columns track the MEIC emission trends, consistent with observations. In winter, the shortening of the NO_x lifetime steepens the trends of NO_2 columns relative to NO_x emissions. Wintertime GEOS-Chem NO_2 columns decrease by 35% between 2011/12 and 2016/17, faster than the 25% decrease in the MEIC NO_x emissions. The NO_x

lifetime in winter is about one day, long enough for faster NO_x loss at night to affect NO_2 columns in the afternoon when OMI makes its observations. Comparison to the observed wintertime trend suggests that the GEOS-Chem decrease in NO_x lifetime over 2012–2017 may not be steep enough. There is substantial uncertainty in the factors controlling wintertime OH concentrations (Tan et al., 2018; Miao et al., 2018) and these might also affect the model trend. Meteorological variability can also cause interannual changes in wintertime NO_2 of ~20% (Lin and McElroy, 2011), but the effect on longer-term trends will be smaller. GEOS-Chem trends for 2005–2012 should be symmetric to those for 2012–2017, since NO_x emissions in 2005 are similar to those in 2017 (Fig. ~~5~~4).

The use of satellite-based NO_2 column observations to evaluate trends in NO_x emission inventories in China can be compared to similar work previously done for the US. Jiang et al. (2018) found that OMI NO_2 columns over the US during 2009–2015 decreased slower than NO_x emissions in the US Environment Protection Agency's (EPA) National Emissions Inventory (NEI), suggesting that NO_x emission controls were not as effective as reported by the NEI. However, Silvern et al. (2019) explained this discrepancy by a large relative contribution of the free tropospheric background to the NO_2 column over the US, weakening the relationship between NO_2 columns and US anthropogenic NO_x emissions. This is not a major concern over central-eastern China, where the contribution of the free troposphere above 2 km to the tropospheric NO_2 column as sensed by OMI is less than 30%. Laughner & Cohen (2019) find an increase in summer NO_x lifetime over 2010–2013 in OMI observations of isolated urban plumes over the US, reflecting NO_x-limited conditions where OH concentrations decrease as NO_x decreases. This would dampen the response of NO_2 columns to emission reductions. Such an effect is not apparent in central-eastern China, which is prevailingly in the so-called transition regime between NO_x-saturated and NO_x-limited conditions (Jin and Holloway, 2015; Li et al., 2019).

4 Conclusions

We examined the seasonality and trends of satellite-derived tropospheric NO_2 columns over China and their relation to NO_x emissions. Observations from the satellite-based OMI instrument show a factor of 3 increase in tropospheric NO_2 columns from summer to winter, and we show that this can be explained by the seasonal variation in NO_x lifetime against oxidation. NO_2 columns for the 2004–2018 duration of the OMI record peak in 2011 and subsequently decrease, consistent with the Multi-resolution Emission Inventory for China (MEIC). The summer trends in OMI NO_2 columns match closely the MEIC emission trends, but the winter trends are steeper than MEIC. We attribute the steeper winter trends to a decrease in the NO_x lifetime, mostly by faster N_2O_5 hydrolysis in aerosols, as NO_x emissions decrease. Lower NO_x emissions lead to an increase in nighttime ozone in winter, promoting N_2O_5 formation. Our analysis of the OMI NO_2 column observations thus supports the magnitude and trends of NO_x emissions in the MEIC inventory, while emphasizing the need to account for changes in NO_x lifetime when interpreting trends in satellite NO_2 columns in terms of trends in NO_x emissions.

Data availability. The QA4ECV data is available at http://www.qa4ecv.eu, POMINO v2 at http://www.phy.pku.edu.cn/~acm/acmProduct.php#POMINO, the MEE surface data at http://beijingair.sinaapp.com and the MEIC inventory data at http://www.meicmodel.org. GEOS-Chem results are available on request from the corresponding author.

Author contributions. VS and DJJ designed the study. VS performed the model simulations and data analysis. KL and SZ processed the ground-based observations. RFS contributed analysis software. ML and JL provided the POMINO data. QZ provided the MEIC data. VS and DJJ wrote the paper with contributions from all co-authors.

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

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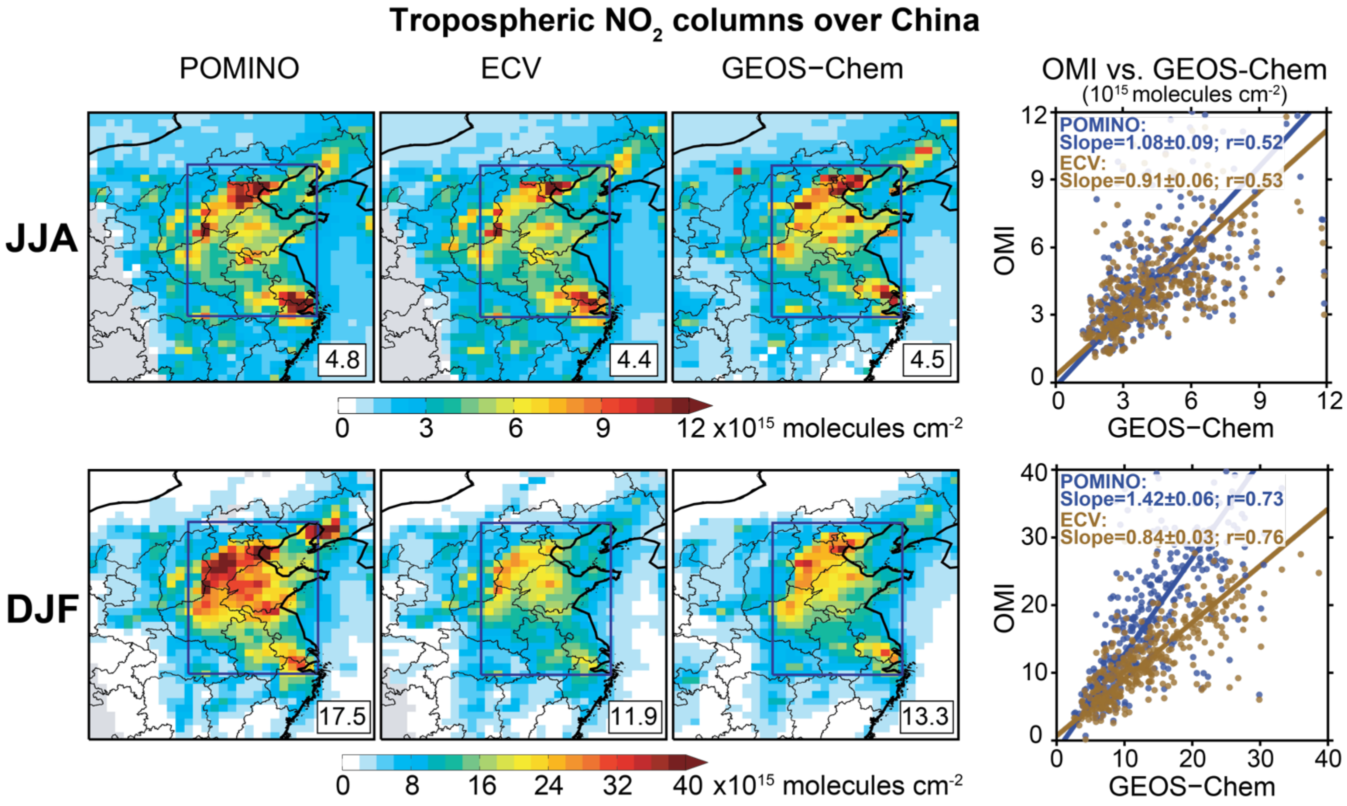

Figure 1: Tropospheric NO$_2$ columns over China. Values are 3-month means for June-July-August (JJA) 2017 and December-January-February (DJF) 2016/17 on the 0.5°×0.625° GEOS-Chem grid. OMI retrievals from POMINO (Liu et al., 2019) and ECV (Boersma et al., 2018) are compared with the GEOS-Chem model. The JJA and DJF panels have different color scales. Locations where none of the OMI data met our selection criteria are in grey. The mean NO$_2$ columns over central-eastern China (blue rectangle) are given inset in units of [10^{15} molecules cm^{-2}], e.g., 4.8×10^{15} molecules cm^{-2} for the top left panel. The scatterplots show the spatial correlations between the OMI retrievals and GEOS-Chem on the 0.5°×0.625° grid for central-eastern China ~~(delineated box in left panels),~~, along with the Pearson's correlation coefficient (*r*), reduced-major-axis linear regressions, and regression slopes. Error standard deviations on the slopes were derived by the bootstrap method.

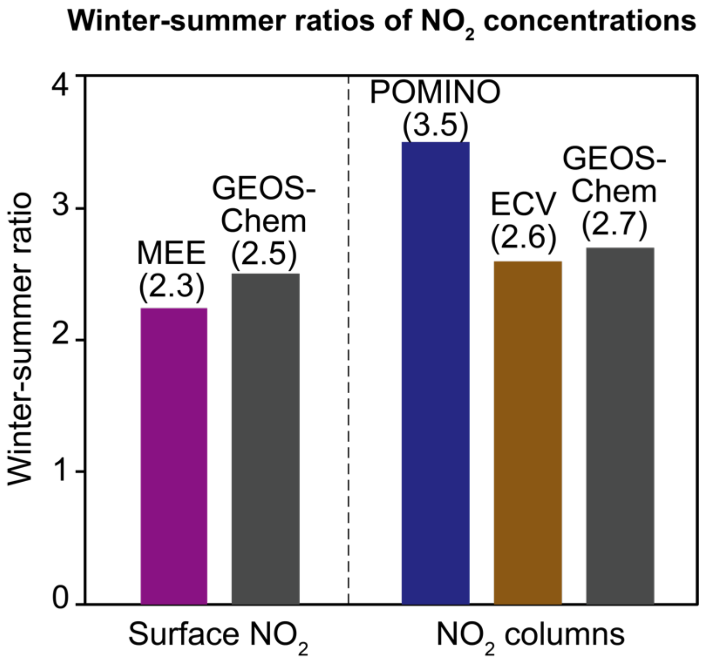

Figure 2: Mean winter-summer ratios of NO_2 concentrations over central-eastern China. The values are ratios of the seasonal mean NO_2 surface concentrations observed at the ensemble of MEE sites in central-eastern China, and of the mean POMINO and ECV tropospheric NO_2 columns (recalculated using the GEOS-Chem NO_2 profiles) at the MEE station locations. Central-eastern China is as defined by the rectangle in Figure 1. GEOS-Chem values sampled at the measurement locations are also shown. Observations and model results are for JJA 2017 (summer) and DJF 2016/17 (winter).

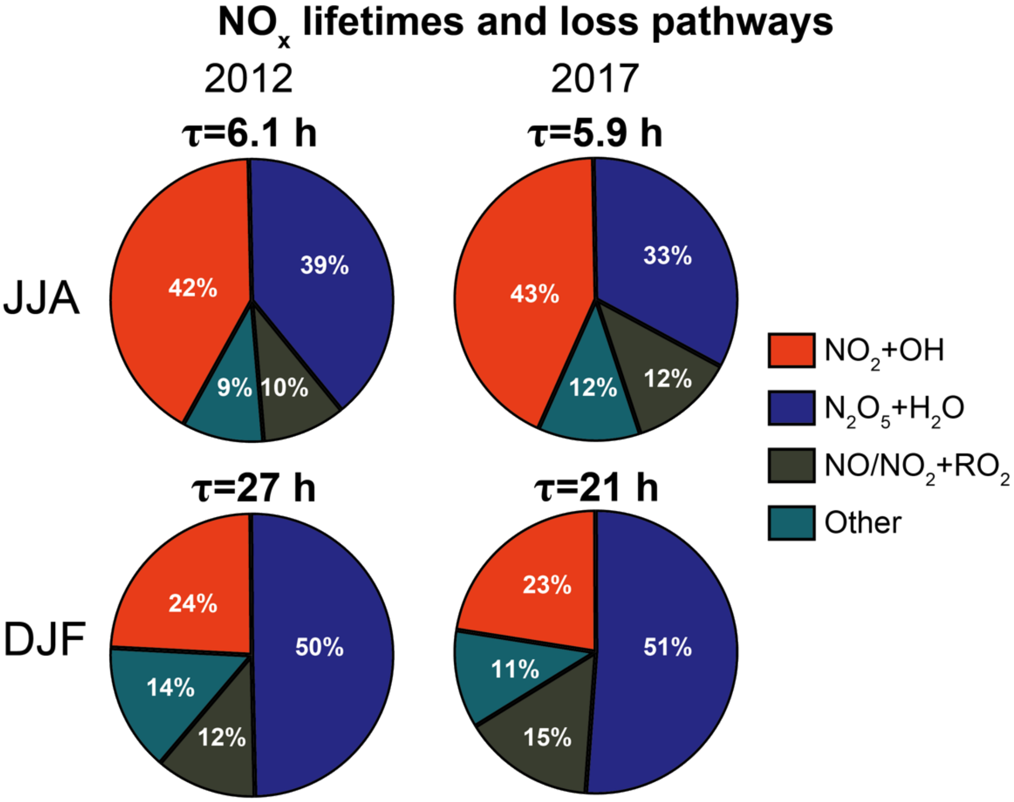

Figure 3: NO_x lifetime (τ) and loss pathways in the boundary layer over central-eastern China. The lifetimes are the GEOS-Chem averages for the bottom 0-2 km of atmosphere over the domain delineated in Figure 1, and the pie charts show the relative contributions of the different NO_x sinks. For the lifetime calculation we define NO_x as $NO+NO_2+NO_3+2N_2O_5+HONO+HNO_4+ClNO_2$. Values are given for summer (JJA) and winter (DJF) of 2012 and 2017. The sink from $N_2O_5+H_2O$ excludes the fraction that forms $ClNO_2$. The sink from $NO/NO_2 + RO_2$ is the net flux, accounting for partial recycling of the organic nitrates, and includes the contributions from peroxyacyl nitrates (PANs). The 'Other' sinks include NO_3 + VOC reactions, NO_2 and NO_3 hydrolysis in aerosols, and NO_x deposition.

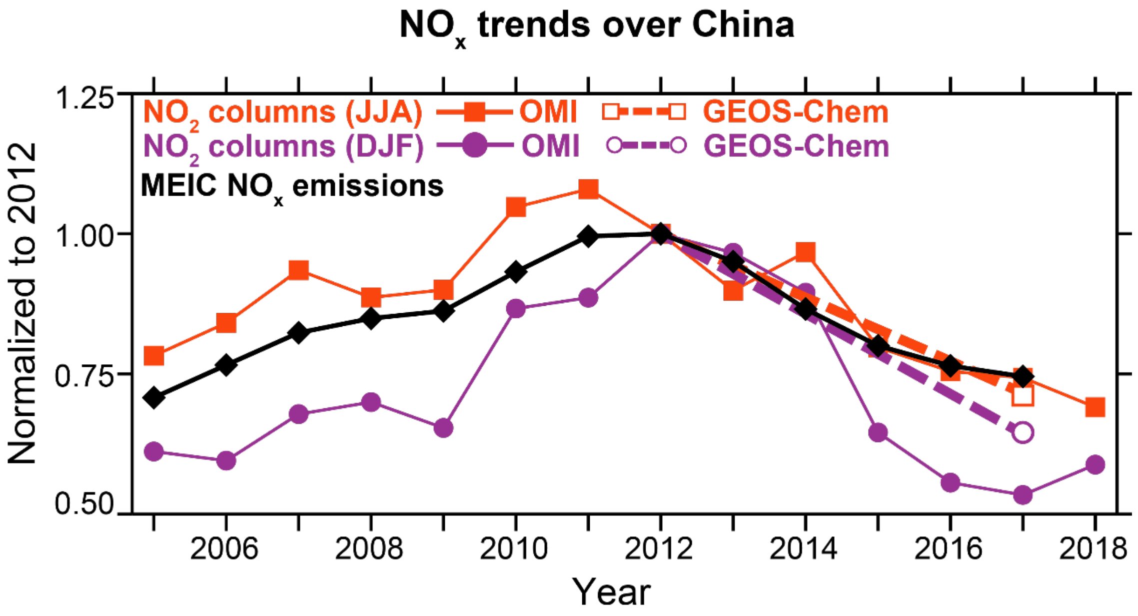

Figure ~~5~~4: Trends in NO_x emissions and NO_2 concentrations over central-eastern China. The figure shows the JJA and DJF relative trends in the OMI (ECV) tropospheric NO_2 columns averaged over central-eastern China (domain delineated in Figure 1) for the 2004–2018 duration of the OMI record, and the corresponding trends in annual NO_x emissions estimated by the MEIC inventory. GEOS-Chem 2012–2017 trends in NO_2 columns are also shown. All quantities are normalized to a value of 1 in 2012.

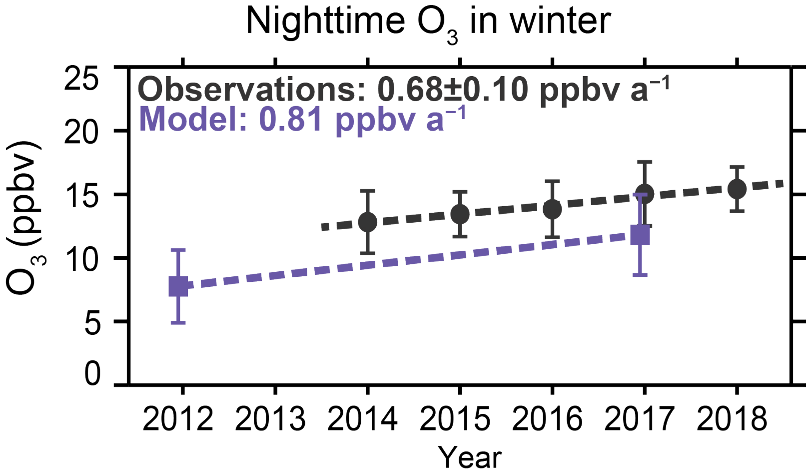

Figure ~~6~~5: Trend in nighttime surface ozone in China in winter. Values are DJF means over 21:00–5:00 local time for the network of sites in central-eastern China operated since 2013 by the China Ministry of Ecology and Environment (MEE). The sites are gridded on the $0.5^{o}\times0.625^{o}$ GEOS-Chem grid. The symbols are averages for all grid cells containing sites and vertical bars are the standard deviation of the spatial distribution. Model values are similarly sampled and gridded over the ensemble of MEE sites operating since 2013. Trends are from an ordinary least squares regression.