Effect of changing NO\textsubscript{x} lifetime on the seasonality and long-term trends of satellite-observed tropospheric NO\textsubscript{2} columns over China

Viral Shah\textsuperscript{1}, Daniel J. Jacob\textsuperscript{1,2}, Ke Li\textsuperscript{1}, Rachel F. Silvern\textsuperscript{2}, Shixian Zhai\textsuperscript{1}, Mengyao Liu\textsuperscript{1}, Jintai Lin\textsuperscript{3}, and Qiang Zhang\textsuperscript{4}

\textsuperscript{1}Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA
\textsuperscript{2}Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
\textsuperscript{3}Laboratory for Climate and Ocean-Atmosphere Studies, Department of Atmospheric & Oceanic Sciences, School of Physics, Peking University, Beijing, China
\textsuperscript{4}Department of Earth System Science, Tsinghua University, Beijing, China

Correspondence: Viral Shah (vshah@seas.harvard.edu)

Received: 23 July 2019 – Discussion started: 19 August 2019
Revised: 6 November 2019 – Accepted: 3 December 2019 – Published: 7 February 2020

Abstract. Satellite observations of tropospheric NO\textsubscript{2} columns are extensively used to infer trends in anthropogenic emissions of nitrogen oxides (NO\textsubscript{x} ≡ NO + NO\textsubscript{2}), but this may be complicated by trends in NO\textsubscript{x} lifetime. Here we use 2004–2018 observations from the Ozone Monitoring Instrument (OMI) satellite-based instrument (QA4ECV and POMINO v2 retrievals) to examine the seasonality and trends of tropospheric NO\textsubscript{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\textsubscript{2} columns from summer to winter, which we explain in GEOS-Chem as reflecting a longer NO\textsubscript{x} lifetime in winter than in summer (21 h versus 5.9 h in 2017). The 2005–2018 summer trends of OMI NO\textsubscript{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\textsubscript{x} lifetime in summer, supporting the emission trend reported by the MEIC. The winter trend of OMI NO\textsubscript{2} is steeper than in summer, supporting the emission trend reported by the MEIC. The winter trend of OMI NO\textsubscript{2} is steeper than in summer, supporting the emission trend reported by the MEIC. The winter trend of OMI NO\textsubscript{2} is steeper than in summer, supporting the emission trend reported by the MEIC. The winter trend of OMI NO\textsubscript{2} is steeper than in summer, supporting the emission trend reported by the MEIC.

1 Introduction

Emissions of nitrogen oxides (NO\textsubscript{x} ≡ NO + NO\textsubscript{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 an almost threefold increase in China’s NO\textsubscript{x} emissions between 1990 and 2010, according to bottom-up inventories based on activity data and emission factors (Granier et al., 2011; Q. Zhang et al., 2012). 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 use (Liu et al., 2016; Zheng et al., 2018). Bottom-up inventories estimate that China’s NO\textsubscript{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\textsubscript{2} columns by solar backscatter have been used extensively as a proxy for NO\textsubscript{x} emissions and their trends (Martin, 2008; Streets et al., 2013). These observations have been qualitatively consistent with the trends in Chinese NO\textsubscript{x} emission inventories, showing an increasing trend of NO\textsubscript{2} columns over China between 1994 and 2011, with 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; Q. Zhang et al., 2012; Stavrakou et al., 2008; 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 twofold 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$_4$ emissions, but NO$_2$ columns from the Ozone Monitoring Instrument (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 (L. Zhang et al., 2012). Oxidation in the daytime is driven by photochemically produced hydrogen oxide (HO$_x$ = OH + HO$_2$ + RO$_2$) radicals:

$$\text{NO}_2 + \text{OH} \xrightarrow{M} \text{HNO}_3,$$  \hspace{1cm} (R1)

$$\text{NO} + \text{RO}_2 \xrightarrow{\alpha M} (1 - \alpha) \text{NO}_2 + (1 - \alpha) \text{RO} + \alpha \text{RONO}_2,$$  \hspace{1cm} (R2)

$$\text{NO}_2 + \text{RC(O)OO} \xrightarrow{M} \text{RC(O)OONO}_2,$$  \hspace{1cm} (R3)

where $\alpha$ in Reaction (R2) is the branching ratio for organic nitrates formation. NO$_x$ and HO$_x$ concentrations are tightly interlinked (Kleinman, 1994; Laughner and Cohen, 2019). When NO$_x$ levels are sufficiently low (so-called NO$_x$-limited conditions), an increase in NO$_x$ drives an increase in HO$_x$ particularly OH through the NO + HO$_2$ $\rightarrow$ NO$_2$ + OH reaction. When NO$_x$ levels are high (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$_3$ proceeds through a series of steps in Reactions (R4)–(R10) beginning with the oxidation of NO and NO$_2$ by ozone to form the nitrate radical (NO$_3$) and dinitrogen pentoxide (N$_2$O$_5$). N$_2$O$_5$ 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$_2$.

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$ \hspace{1cm} (R4)

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$ \hspace{1cm} (R5)

$$\text{NO}_3 + \text{NO}_2 \xrightarrow{M} \text{N}_2\text{O}_5$$ \hspace{1cm} (R6)

$$\text{N}_2\text{O}_5 + \text{H}_2\text{O}(l) \xrightarrow{\text{aerosols}} 2\text{HNO}_3$$ \hspace{1cm} (R7)

$$\text{N}_2\text{O}_5 + \text{Cl}^- + \text{H}_2\text{O}(l) \xrightarrow{\text{aerosols}} \text{HNO}_3 + \text{ClNO}_2 + \text{OH}^-$$ \hspace{1cm} (R8)

$$\text{NO}_3 + \text{H}_2\text{O}(l) \xrightarrow{\text{aerosols}} \text{HNO}_3 + \text{OH}$$ \hspace{1cm} (R9)

$$\text{NO}_3 + \text{VOC} \rightarrow \text{HNO}_3, \text{RONO}_2, \text{other products}$$ \hspace{1cm} (R10)

A change in NO$_3$ 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$_3$ loss (Reactions R7–R9). A decrease in aerosol concentrations will also slow the NO$_3$ loss by the hydrolysis of NO$_2$ in aerosols.

$$\text{NO}_2 + \text{H}_2\text{O}(l), \text{aerosols} \rightarrow 0.5\text{HONO} + 0.5\text{HNO}_3$$ \hspace{1cm} (R11)

Here we present trends in tropospheric NO$_2$ columns over China from 2004 to 2018 observed by the OMI satellite instrument, showing a peak in 2011. We use the GEOS-Chem chemical transport model applied to the MEIC (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. The 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 with a 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 (Levett 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
simulated concentrations for those species following Lamsal et al. (2008) and then grid (0.5° × 0.625° grid) and seasonally average the data, discarding sites with less than 50% coverage in a season. The correction for HNO3 and organic nitrates decreases the reported seasonal mean NO2 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 (https://doi.org/10.5281/zenodo.1553349) 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; 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 (11° S–55° N, 60–150° E) at 0.5° × 0.625° resolution (Wang et al., 2004; Chen et al., 2009), with lateral chemical boundary conditions from a 4° × 5° global simulation. Anthropogenic emissions over China are from the MEIC updated annually for 2000–2017 (http://www.meicmodel.org/, last access: 30 June 2018; Zheng et al., 2018). The 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 NOx emissions as NO (90%), NO2 (9.2%), and HONO (0.8%) following Menut et al. (2013). GEOS-Chem includes additional NOx 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 (Settler et al., 2011). Vertical mixing in the planetary boundary layer is simulated using a nonlocal 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 N2O5, NO3, and NO2 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). γN2O5 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. N2O5 hydrolysis produces HNO3 and CINO2 on sea salt aerosols with a 1:1 branching ratio (Reaction R8) and only HNO3 on other aerosol types (Reaction R7). Uniform values of γNO3 and γNO2 are used for all aerosol types and all RH conditions. γNO3 is taken to be 1 × 10−3 following Jacob (2000). γNO2 for the hydrolysis Reaction (R11) is de-
1486 V. Shah et al.: Effect of changing NO$_x$ lifetime

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$^\circ$ × 0.625$^\circ$ 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 in the inset (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$^\circ$ × 0.625$^\circ$ grid for central–eastern China, 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.

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 the MEIC (Fig. S1 in the Supplement). For comparison with OMI observations, we sample the model at 13:00–14:00 LST and exclude model columns with surface snow cover or with a model cloud fraction greater than 30 %.

We focus on the large polluted region of central–eastern China (30–41$^\circ$ N, 112–122$^\circ$ E; rectangles in 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 NO$_x$ emissions in 2017 according to the 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, as well as 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 of altitude. Thus, we expect the NO$_2$ column to reflect mostly the NO$_x$ emissions from soils, lightning, ships, and aircraft. 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 ($r$ ≈ 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 \( \text{NO}_2 \)) 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 \( \text{NO}_2 \) columns under high aerosol conditions can be uncertain because of the strong sensitivity to the vertical distribution of \( \text{NO}_2 \) 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) \( \text{NO}_2 \) column observations on 49 d in three Chinese cities. POMINO was on average closer to the MAX-DOAS \( \text{NO}_2 \) than ECV (−3 % vs. −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 the 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 \( \text{NO}_2 \) columns from the ECV and POMINO retrievals over central–eastern China with GEOS-Chem and with the ratios of 24 h mean surface \( \text{NO}_2 \) concentrations at the MEE sites. GEOS-Chem shows similar ratios for the afternoon \( \text{NO}_2 \) columns and 24 h mean surface \( \text{NO}_2 \), despite different averaging times. We find that the seasonal amplitude in the surface \( \text{NO}_2 \) data is most consistent with the ECV \( \text{NO}_2 \) columns, whereas the seasonal amplitude of POMINO \( \text{NO}_2 \) is larger. The winter–summer ratios of \( \text{NO}_2 \) columns are 2.6 in the ECV retrieval, 3.5 in POMINO, and 2.7 in GEOS-Chem. The winter–summer ratios of surface \( \text{NO}_2 \) concentrations are 2.3 in the MEE data and 2.5 in GEOS-Chem. Anthropogenic \( \text{NO}_x \) emissions in the MEIC show little seasonality, with a winter–summer ratio of only 1.15 (Li et al., 2017b). We find in GEOS-Chem that the seasonal variation in \( \text{NO}_x \) columns is mainly driven by the \( \text{NO}_x \) 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 \( \text{NO}_x \) lifetimes (Fig. S2) since most of the column is in the boundary layer.

In summer, \( \text{NO}_x \) is lost mostly through oxidation by OH in daytime (43 %) and through \( \text{N}_2\text{O}_5 \) hydrolysis forming \( \text{HONO} \) at night (33 %). The daytime oxidation processes have a larger effect on the afternoon \( \text{NO}_2 \) columns because of the short \( \text{NO}_x \) lifetime, particularly in summer. In winter, the \( \text{NO}_x \) lifetime is much longer because of the lower concentrations of \( \text{OH} \) and \( \text{RO}_2 \) radicals. \( \text{N}_2\text{O}_5 \) hydrolysis accounts for 51 % of \( \text{NO}_x \) loss in winter. Remarkably, the loss of \( \text{NO}_x \) from \( \text{N}_2\text{O}_5 \) hydrolysis is a factor of 2 slower in winter than in summer, despite the longer nights and higher aerosol con-
centrations (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 CINO\(_2\). 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 CINO\(_2\) 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 CINO\(_2\) 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\(_x\) and CINO\(_2\) branches compete for the limited \(N_2O_5\), and the daytime \(NO_x\) loss would increase because of the additional daytime \(NO_x\) from CINO\(_2\) photolysis.

Sub-grid-scale variability in \(NO_x\) and oxidant concentrations can also affect the modeled \(NO_x\) lifetimes because of the nonlinearity 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 \(NO_x\) columns. We tried this approach and found that the offshore gradients of \(NO_x\) columns perpendicular to the east coast of China are consistent between the model and observations (Fig. 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 \(NO_x\) columns and lifetimes

Figure 4 shows the trends in the summer and winter \(NO_x\) columns from the ECV retrieval, as well as in anthropogenic \(NO_x\) emissions from the MEIC, over central–eastern China for the 2004–2018 extent of the OMI record. According to the MEIC, \(NO_x\) emissions increased by 5\%–6\% a\(^{-1}\) in 2005–2011 and decreased at the same pace after 2011. OMI \(NO_x\) 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 \(NO_x\) columns and the MEIC \(NO_x\) emissions but found that the \(NO_x\) 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 \(NO_x\) closely track the MEIC emissions, but the winter trends are steeper. The same summer–winter differences in \(NO_x\) column trends over China are seen in the POMINO retrieval (Fig. 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 \(NO_x\) 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 + 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.
We find no significant change in the summer NO\textsubscript{x} lifetime between 2012 and 2017. The NO\textsubscript{x} lifetime during the day shortened slightly, as summertime OH concentrations increased by 6% and RO\textsubscript{2} concentrations increased by 13%. However, the NO\textsubscript{x} lifetime during the night increased as aerosol concentrations dropped, canceling the overall effect.

In contrast, the winter NO\textsubscript{x} lifetime decreased by 22\% (from 27 to 21 h) between 2012 and 2017 (Fig. 3), driven mostly by faster loss by N\textsubscript{2}O\textsubscript{5} hydrolysis in aerosols and also by faster loss from reactions with OH and RO\textsubscript{2}. The loss rate from RO\textsubscript{2} + NO/NO\textsubscript{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\textsubscript{x} lifetime as NO\textsubscript{3} emissions dropped. At lower NO\textsubscript{x} emissions, NO\textsubscript{3} loss by NO\textsubscript{3} + VOC reactions also increased relative to NO\textsubscript{3} loss by N\textsubscript{2}O\textsubscript{5} hydrolysis because of an increase in the ratio of NO\textsubscript{3} to N\textsubscript{2}O\textsubscript{5} concentrations. However, the contribution of NO\textsubscript{3} + VOC reactions to the total NO\textsubscript{x} loss remained less than 5\% because of high NO\textsubscript{2}. The faster loss by N\textsubscript{2}O\textsubscript{5} hydrolysis in 2017 relative to 2012 might seem counterintuitive since both aerosols and NO\textsubscript{x} dropped over the period. However, winter aerosol levels for converting N\textsubscript{2}O\textsubscript{5} to HNO\textsubscript{3} remain in excess even in 2017. Instead, we find that the driving factor behind the increase in N\textsubscript{2}O\textsubscript{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\textsubscript{x} sources. As NO\textsubscript{x} emissions decrease, less ozone is titrated, which then enables the formation of NO\textsubscript{3} by Reaction (R5) and the subsequent formation of N\textsubscript{2}O\textsubscript{5}. The simulated NO\textsubscript{3} lifetime against loss by N\textsubscript{2}O\textsubscript{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. 5).

Figure 4 shows the implications of these changes in seasonal NO\textsubscript{x} lifetime for the 2012–2017 NO\textsubscript{2} column trends simulated by GEOS-Chem. Neither the 24 h mean nor the daytime NO\textsubscript{x} lifetime changes significantly in summer, and therefore the NO\textsubscript{2} columns track the MEIC emission trends, consistent with observations. In winter, the shortening of the NO\textsubscript{x} lifetime steepens the trends of NO\textsubscript{2} columns relative to NO\textsubscript{x} emissions. Wintertime GEOS-Chem NO\textsubscript{2} column decreases by 35\% between 2011/12 and 2016/17, faster than the 25\% decrease in the MEIC NO\textsubscript{x} emissions. The NO\textsubscript{2} lifetime in winter is about 1 d, long enough for faster NO\textsubscript{x} loss at night to affect NO\textsubscript{2} columns in the afternoon when the OMI makes its observations. Comparison to the observed wintertime trend suggests that the GEOS-Chem decrease in NO\textsubscript{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\textsubscript{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 symmetrical with those for 2012–2017, since NO\textsubscript{x} emissions in 2005 are similar to those in 2017 (Fig. 4).

The use of satellite-based NO\textsubscript{2} column observations to evaluate trends in NO\textsubscript{x} emission inventories in China can be compared to similar work previously done for the US. Jiang et al. (2018) found that OMI NO\textsubscript{2} columns over the US during 2009–2015 decreased slower than NO\textsubscript{x} emissions in the US Environmental Protection Agency (EPA) National Emissions Inventory (NEI), suggesting that NO\textsubscript{x} emission controls were not as effective as reported by the NEI. However, Silvern et al. (2019) explained this discrepancy with a large relative contribution of the free tropospheric background to the NO\textsubscript{2} column over the US, weakening the relationship between NO\textsubscript{2} columns and US anthropogenic NO\textsubscript{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\textsubscript{2} column as sensed by the OMI is less than 30\%. Laughner and Cohen (2019) find an increase in summer NO\textsubscript{x} lifetime over 2010–2013 in OMI observations of isolated urban plumes over the US, reflecting NO\textsubscript{x}-limited conditions in which OH concentrations decrease as NO\textsubscript{x} decreases. This would dampen the response of NO\textsubscript{2} columns to emission reductions. Such an effect is not apparent in central–eastern China, which is prevailing in the so-called transition regime between NO\textsubscript{x}-saturated and NO\textsubscript{x}-limited conditions (Jin and Holloway, 2015; Li et al., 2019).

4 Conclusions

We examined the seasonality and trends of satellite-derived tropospheric NO\textsubscript{2} columns over China and their relation to NO\textsubscript{x} emissions. Observations from the satellite-based OMI instrument show a factor of 3 increase in tropospheric NO\textsubscript{2}
columns from summer to winter, and we show that this can be explained by the seasonal variation in NOx lifetime against oxidation. NO2 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 NO2 columns closely match the MEIC emission trends, but the winter trends are steeper than the MEIC. We attribute the steeper winter trends to a decrease in the NOx lifetime, mostly by faster N2O5 hydrolysis in aerosols, as NOx emissions decrease. Lower NOx emissions lead to an increase in nighttime ozone in winter, promoting N2O5 formation. Our analysis of the OMI NO2 column observations thus supports the magnitude and trends of NOx emissions in the MEIC, while emphasizing the need to account for changes in NOx lifetime when interpreting trends in satellite NO2 columns in terms of trends in NOx emissions.

Data availability. The QA4ECV data are available at https://doi.org/10.21944/qa4ecv-no2-omi-v1.1 (last access: 15 January 2019; Boersma et al., 2019). POMINO v2 at https://www.amazon.com/clouddrive/share/zyC4mNEyRfRk0IX114sR511WTMpcP1d4SwLVrW55iFG/folder/S71R7WSLSPikdLT_jsNX8g (last access: 23 January 2019; ACM group, 2019). MEE surface data at http://beijingair.sinaapp.com (last access: 10 March 2019; China National Environmental Monitoring Center, 2019), and MEIC data at http://www.meicmodel.org (last access: 30 June 2018; MEIC team, 2018). To access the MEIC data, contact Qiang Zhang (qiangzhang@tsinghua.edu.cn). GEOS-Chem results are available on request from the corresponding author.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-20-1483-2020-supplement.

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 coauthors.

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

Acknowledgements. The development of the POMINO product was funded by the National Natural Science Foundation of China (41775115). We acknowledge the QA4ECV project for the NO2 data.

Financial support. This research has been supported by the National Aeronautics and Space Administration Earth Science Division (grant no. NNX17AI67G).

Review statement. This paper was edited by Chul Han Song and reviewed by four anonymous referees.

References

ACM group: POMINO v2 NO2 Level-2 data, Peking University, available at: https://www.amazon.com/clouddrive/share/zyC4mNEyRfRk0IX114sR511WTMpcP1d4SwLVrW55iFG/folder/S71R7WSLSPikdLT_jsNX8g, last access: 23 January 2019.

Boersma, K. F., Eskes, H. J., Richter, A., De Smedt, I., Lorente, A., Beirle, S., van Geffen, J. H. G. M., Zara, M., Peters, E., Van Roozendael, M., Wagner, T., Maasakkers, J. D., van der A, R. J., Nightingale, J., De Rudder, A., Irie, H., Pinardi, G., Lambert, J.-C., and Compernolle, S. C.: Improving algorithms and uncertainty estimates for satellite NO2 retrievals: results from the quality assurance for the essential climate variables (QA4ECV) project, Atmos. Meas. Tech., 11, 6651–6678, https://doi.org/10.5194/amt-11-6651-2018, 2018.

Boersma, K. F., Eskes, H., Richter, A., De Smedt, I., Lorente, A., Beirle, S., Van Geffen, J., Peters, E., Van Roozendael, M., and Wagner, T.: QA4ECV NO2 tropospheric and stratospheric vertical column data from OMI (Version 1.1), Royal Netherlands Meteorological Institute (KNMI), https://doi.org/10.21944/qa4ecv-no2-v1.1, 2019.

Bröské, R., Kleffmann, J., and Wiesen, P.: Heterogeneous conversion of NO2 on secondary organic aerosol surfaces: A possible source of nitrous acid (HONO) in the atmosphere?, Atmos. Chem. Phys., 3, 469–474, https://doi.org/10.5194/acp-3-469-2003, 2003.

Brown, S. S., Dubé, W. P., Karamchandi, P., Yarwood, G., Peischl, J., Ryerson, T. B., Neuman, J. A., Nowak, J. B., Holloway, J. S., Washenfelder, R. A., Brock, C. A., Frost, G. J., Trainer, M., Parrish, D. D., Fehsenfeld, F. C., and Ravishankara, A. R.: Effects of NOx control and plume mixing on nighttime chemical processing of plumes from coal-fired power plants, J. Geophys. Res., 117, D07304, https://doi.org/10.1029/2011JD016954, 2012.

Chen, D., Wang, Y., McElroy, M. B., He, K., Yantosca, R. M., and Le Sager, P.: Regional CO pollution and export in China simulated by the high-resolution nested-grid GEOS-Chem model, Atmos. Chem. Phys., 9, 3825–3839, https://doi.org/10.5194/acp-9-3825-2009, 2009.

China National Environmental Monitoring Center (CNEMC): China National Environmental Monitoring NO2 and ozone data archive, available at: http://beijingair.sinaapp.com, last access: 10 March, 2019.
McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Martin, R. V., Jacob, D. J., Chance, K., Kurosu, T. P., Ma, Z., Liu, R., Liu, Y., and Bi, J.: Effects of air pollution control policies on PM$_{2.5}$ pollution improvement in China from 2005 to 2017: a satellite-based perspective, Atmos. Chem. Phys., 19, 6861–6877, https://doi.org/10.5194/acp-19-6861-2019, 2019.

Lammers, A. M. M., Builjtes, P. J. H., Currier, L., Denier van der Gon, H. A. C., Hendriks, C., Jonkers, S., Kranenburg, R., Kuenen, J. J. P., Segers, A. J., Timmermans, R. M. A., Visschedijk, A. J. H., Wichink Kruijt, R. J., van Pul, W. A. J., Sauter, F. J., van der Swaluw, E., Swaluw, T. D., Dörner, S., Hilboll, A., Mann, K., Roberts, J. M., Thornton, J. A., and Brown, S. S.: Chemical feedbacks weaken the wintertime response of particulate sulfate and nitrate to emissions reductions inventories of anthropogenic air pollutants and greenhouse gases in China, Atmos. Chem. Phys., 17, 9261–9275, https://doi.org/10.5194/acp-17-9261-2017, 2017.

Martin, R. V.: Satellite remote sensing of surface air quality, Atmos. Environ., 42, 7823–7843, https://doi.org/10.1016/j.atmosenv.2008.07.018, 2008.

Martin, R. V., Jacob, D. J., Chance, K., Kurosu, T. P., Palmer, P. I., and Evans, M. J.: Global inventory of nitrogen oxide emissions constrained by space-based observations of NO$_2$ columns, J. Geophys. Res.-Atmos., 108, 4537, https://doi.org/10.1029/2003JD003453, 2003.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Jaegel, L., Guo, H., Weber, R. J., Reeves, J. M., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Dibb, J. E., Veres, P., Ebben, C., Sparks, T. L., Wooldridge, P. J., Cohen, R. C., Hornbrook, R. S., Apel, E. C., Campos, T., Hall, S. R., Ullmann, K., Roberts, J. M., Thornton, J. A., and Brown, S. S.: CINO$_2$ Yields From Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of the Current Parameterization, J. Geophys. Res.-Atmos., 123, 13094–131015, https://doi.org/10.1002/2018JD029938, 2018a.

McDuffie, E. E., Fibiger, D. L., Dubé, W. P., Lopez-Hilfiker, F., Lee, B. H., Thornton, J. A., Shah, V., Jaegel, L., Guo, H., Weber, R. J., Michael Reeves, J., Weinheimer, A. J., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Dibb, J. E., Veres, P., Ebben, C., Sparks, T. L., Wooldridge, P. J., Cohen, R. C., Hornbrook, R. S., Apel, E. C., Campos, T., Hall, S. R., Ullmann, K., and Brown, S. S.: Heterogeneous N$_2$O$_5$ uptake During Winter: Aircraft Measurements During the 2015 WINTER Campaign and Critical Evaluation of Current Parameterizations, J. Geophys. Res.-Atmos., 123, 4345–4372, https://doi.org/10.1002/2018JD028336, 2018b.
emissions and meteorology, Atmos. Chem. Phys., 19, 11031–11041, https://doi.org/10.5194/acp-19-11031-2019, 2019.
Zhang, L., Jacob, D. J., Knipping, E. M., Kumar, N., Munger, J. W., Carouge, C. C., van Donkelaar, A., Wang, Y. X., and Chen, D.: Nitrogen deposition to the United States: distribution, sources, and processes, Atmos. Chem. Phys., 12, 4539–4554, https://doi.org/10.5194/acp-12-4539-2012, 2012.
Zhang, Q., Streets, D. G., He, K., Wang, Y., Richter, A., Burrows, J. P., Uno, I., Jang, C. J., Chen, D., Yao, Z. and Lei, Y.: NOx emission trends for China, 1995–2004: The view from the ground and the view from space, J. Geophys. Res.-Atmos., 112, D22306, https://doi.org/10.1029/2007JD008684, 2007.
Zhang, Q., Geng, G., Wang, S., Richter, A., and He, K.: Satellite remote sensing of changes in NOx emissions over China during 1996–2010, Chinese Sci. Bull., 57, 2857–2864, https://doi.org/10.1007/s11434-012-5015-4, 2012.
Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China’s anthropogenic emissions since 2010 as the consequence of clean air actions, Atmos. Chem. Phys., 18, 14095–14111, https://doi.org/10.5194/acp-18-14095-2018, 2018.