Nitrogen oxides emissions, chemistry, deposition, and export over the Northeast United States during the WINTER aircraft campaign

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Key Points:

- Existing anthropogenic NOₓ inventory consistent with aircraft and ground-based observations over NE United States during winter.
- Slow rate of NOₓ chemistry (22-hour NOₓ lifetime), with half of NOᵧ present as NOₓ, 37% as HNO₃ and pNO₃⁻ and remaining 13% mostly as PAN.
- Model reproduces NOᵧ partitioning and predicts a 42% NOₓ export efficiency in winter, with a 55-45% split between wet and dry deposition.
Abstract. We examine the distribution and fate of nitrogen oxides (NOx) in the lower troposphere over the Northeast United States (NE US) using aircraft observations from the Wintertime INVestigation of Transport, Emissions, and Reactivity (WINTER) campaign in February-March 2015, as well as the GEOS-Chem chemical transport model and concurrent ground-based observations. We find that the National Emission Inventory (NEI) from the US Environmental Protection Agency (EPA) is consistent with WINTER observations of total reactive nitrogen (\(^{1}\text{NO}_x\)) to within 10% on average, in contrast to the significant overestimate reported in past studies under warmer conditions. Updates to the dry deposition scheme and dinitrogen pentoxide (N\(_2\)O\(_5\)) reactive uptake probability, \(\gamma(N_2O_3)\), result in an improved simulation of gas-phase nitric acid (HNO\(_3\)) and submicron particulate nitrate (pNO\(_3^-\)), reducing the longstanding factor of 2-3 overestimate in wintertime HNO\(_3\)+pNO\(_3^-\) to a 50% positive bias. We find a NO\(_x\) lifetime against chemical loss and deposition of 22 hours in the lower troposphere over the NE US. Chemical loss of NO\(_x\) is dominated by N\(_2\)O\(_5\) hydrolysis (58% of loss) and reaction with OH (33%), while 7% of NO\(_x\) leads to the production of organic nitrates. Wet and dry deposition account for 55% and 45% of \(^{1}\text{NO}_x\) deposition over land, respectively. We estimate that 42% of the NO\(_x\) emitted is exported from the NE US boundary layer during winter, mostly in the form of HNO\(_3\)+pNO\(_3^-\) (40%) and NO\(_x\) (38%).

Plain Language Summary

Nitrogen oxides are a key family of pollutants emitted by cars, electric utilities, and industry. The fate of nitrogen oxides remains poorly understood especially during the winter season, when low sunlight leads to their persistence in the atmosphere. We analyze comprehensive aircraft observations of nitrogen oxides and their atmospheric products over the Northeast United States during winter 2015. This detailed chemical information allows to resolve a long-standing overestimate of the oxidation products of nitrogen oxides, and place new constraints on their deposition to land ecosystems and export to the global atmosphere.

1 Introduction

Understanding the chemical evolution of nitrogen oxides (NO\(_x\)=NO+NO\(_2\)) anthropogenic emissions is critical to constraining their regional and global effects on oxidants, ozone (O\(_3\)) chemistry, inorganic and organic aerosol formation, and nitrogen deposition to ecosystems. As the seasons change from summer to winter in the midlatitudes, the lifetime of NO\(_x\) in the lower troposphere increases from 3-6 hours to more than a day because of the photochemical decrease in hydroxyl radical (OH) concentrations (Martin et al., 2003). The main oxidation product of NO\(_x\) is generally nitric acid (HNO\(_3\)), but in the presence of volatile organic compounds (VOCs) significant amounts of peroxyl acyl nitrates (PNs) and alkyl nitrates (ANs) can be produced. The transition from summer to winter is accompanied by a near cessation of biogenic emissions of VOCs in temperate continental regions. These much lower biogenic VOC emissions together with reduced OH lead to a decrease in the wintertime production of PNs and ANs, and thus an increase in the relative importance of HNO\(_3\) as a NO\(_x\) sink. At the same time, the pathway for HNO\(_3\) chemical production shifts from the daytime reaction of NO\(_2\) with OH to a more dominant role for nocturnal chemistry via dinitrogen pentoxide (N\(_2\)O\(_5\)) hydrolysis (Dentener & Crutzen, 1993; Evans & Jacob, 2005; Tie et al., 2001), which can also produce nitryl chloride (CINO\(_2\)) on chloride-containing aerosols (Behnke et al., 1997; Finlayson-Pitts et al., 1989). Colder
temperatures favor the partitioning of HNO$_3$ into particulate inorganic nitrate (pNO$_3^-$), a major component of submicron aerosol mass during winter.

The Wintertime INvestigation of Transport, Emissions, and Reactivity (WINTER) aircraft campaign in February-March 2015 presents a unique opportunity to examine these poorly understood wintertime processes near polluted regions in the Northeast United States (NE US). Here, we analyze WINTER observations of NO$_x$ and its oxidation products (N$_2$O$_5$, HNO$_3$, pNO$_3^-$, ClNO$_2$, HONO, PNs, ANs) with the GEOS-Chem chemical transport model (CTM).

Given the paucity of field experiments during winter, we will use these aircraft observations to re-examine some challenges that have faced CTMs in past studies: constraining anthropogenic NO$_x$ emissions, improving the representation of N$_2$O$_5$ hydrolysis, addressing the persistent bias in HNO$_3$ and pNO$_3^-$ during winter, and assessing the relative importance of continental deposition versus export of NO$_x$ and its oxidation products.

Anthropogenic NO$_x$ emissions over the United States have been rapidly decreasing since 2000 due to emission control programs on point sources, stricter vehicle emissions standards, and changes in energy consumption driven by the economy. The U.S. Environmental Protection Agency (EPA) National Emission Inventory (NEI) reports national emissions by sector and year. The EPA estimates a 43% decrease in annual total NO$_x$ emissions between 2005 and 2015, mostly driven by large decreases in NO$_x$ emitted by electric utilities (-62%), industrial fuel combustion (-35%) and transportation (-47%) (EPA, 2017). This decreasing trend is broadly consistent with both ground-based observations of NO$_2$ and satellite observations of tropospheric NO$_2$ columns (Duncan et al., 2016; Krotkov et al., 2016; Lamsal et al., 2015; Lu et al., 2015; Russell et al., 2012; Tong et al., 2015). For example, Krotkov et al. (2016) analyzed the 2005-2015 trends in tropospheric NO$_2$ columns measured by the Ozone Monitoring Instrument (OMI) onboard NASA’s Aura satellite, finding a 40% decrease over the Ohio River Valley and the I-95 megapolisis extending from Washington D.C. to New York City (DC-NYC). Similarly, Lu et al. (2015) reported a 49% decrease in OMI-derived NO$_x$ emissions over 35 U.S. urban areas between 2005 and 2014.

Despite the broad consistency of EPA’s NEI trends and observations, recent reports suggest that the magnitude of NO$_x$ emissions from the NEI inventory, in particular motor vehicle emissions, might be overestimated by up to a factor of 2 (Anderson et al., 2014; Canty et al., 2015; Goldberg et al., 2014; Travis et al., 2016). Comparing DISCOVER-AQ aircraft observations obtained over the Baltimore/Washington region to the CMAQ model, Anderson et al. (2014) and Goldberg et al. (2014) reported a factor of 2 overestimate in NO$_x$, which they attribute to a combination of overestimate in mobile emissions and errors in ANs and PNs chemistry. Travis et al. (2016) used aircraft observations of NO$_x$ and its oxidation products over the Southeast U.S. to infer that NEI NO$_x$ emissions are too high by 40%, likely due to an overestimate in mobile and industrial emissions. The above studies took place during summer months in the Eastern U.S., and other studies with similar conclusions took place under warm conditions in California (Brioude et al., 2013; Fujita et al., 2012; McDonald et al., 2012) and Texas (Souri et al., 2016). In contrast to these past studies, we will show that the NEI NO$_x$ emissions inventory captures observations over the NE US during winter, pointing to potential issues with the seasonal dependence of anthropogenic NO$_x$ emissions as represented within the NEI inventory and/or to issues with CTM’s representations of boundary layer mixing and/or NO$_x$ chemistry during summer.
During winter at midlatitudes, N$_2$O$_5$ hydrolysis on aerosols (R3) has an outsized influence on NO$_x$ and O$_3$ chemistry, because of lower OH concentrations and longer nights (e.g., Alexander et al., 2009; Dentener & Crutzen, 1993; Mcintyre & Evans, 2010). At night, the following sequence of reactions lead to the formation of HNO$_3$:

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (\text{R1})$$
$$\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5 \quad (\text{R2})$$
$$\text{N}_2\text{O}_5 + \text{aerosol} \rightarrow (2-\phi) \text{HNO}_3 + \phi \text{ClNO}_2 \quad (\text{R3})$$

By producing ClNO$_2$ at night, R3 can also lead to halogen activation the next morning as ClNO$_2$ photolyses thereby influencing daytime oxidants, NO$_x$ recycling, and O$_3$ production (Thornton et al., 2010). The rate of (R3) depends on aerosol surface area and on the uptake coefficient for N$_2$O$_5$, $\gamma$(N$_2$O$_5$) which represents the probability that a N$_2$O$_5$ molecule is lost from the gas phase upon collision with a surface. Laboratory studies have demonstrated that $\gamma$(N$_2$O$_5$) varies by several orders of magnitude depending on aerosol composition as well as phase state, temperature and liquid water content (LWC) (Abbatt et al., 2012 and references therein). Field determinations of $\gamma$(N$_2$O$_5$) on ambient atmospheric aerosol have reported values between 2×10$^{-5}$ and 0.175 (McDuffie et al., 2018 and references therein), with higher values on sulfate-rich aerosol and lower values for aerosol with large organic and/or nitrate content. This large variability makes model representations of $\gamma$(N$_2$O$_5$) challenging (e.g., Davis et al., 2008; Evans & Jacob, 2000), especially as the impacts of R3 on the concentrations of NO$_x$, O$_3$, and OH in the northern extratropics are very sensitive to $\gamma$(N$_2$O$_5$) values between 0.001 and 0.02 (Mcintyre and Evans, 2010). Laboratory experiments show that the yield for ClNO$_2$ formation, $\phi$, is a strong function of particulate chloride (pCl$^-$) concentrations and LWC (Bertram & Thornton, 2009).

Direct atmospheric observations of ClNO$_2$ demonstrate a large variability for $\phi$(ClNO$_2$), spanning between 0.014 and 1 (e.g. Mielke et al., 2011; Osthoff et al., 2008; Phillips et al., 2016; Thornton et al., 2010; Wang et al. 2017). The regional impacts of ClNO$_2$ formation on the NO$_x$ and oxidant budgets remain poorly understood as only recently have models begun to implement this reaction in their chemical mechanism (e.g., Li et al., 2016; Riedel et al., 2014; Sarwar et al., 2012, 2014).

A number of studies with the GEOS-Chem model have noted a factor of 2-3 overestimate in pNO$_3^-$ and HNO$_3$ relative to surface observations over the U.S. during winter months (Heald et al., 2012; Walker et al., 2012; Zhang et al., 2012). This bias also exists, albeit to a somewhat smaller extent in other models and leads to a systematic overestimate of PM$_{2.5}$ concentrations over the U.S. and Canada during winter (Simon et al., 2012 and references therein). In an intercomparison of regional and global CTMs to surface concentrations of pNO$_3^-$ over western Europe, Collette et al. (2011) found that 4 out of 6 models over predicted pNO$_3^-$ concentrations by factors of 1.5-4 during winter. The causes for this bias are unclear, but several potential explanations have been proposed: overestimate in NO$_x$ and/or ammonia (NH$_3$) emissions, excessive HNO$_3$ production via gas-phase and heterogeneous reactions, underestimate in the dry deposition velocity of HNO$_3$, incorrect predictions of aerosol pH leading to incorrect HNO$_3$/pNO$_3^-$ partitioning (e.g., Heald et al., 2012; Pye et al., 2018; Vasilakos et al., 2018, under review; Zhang et al., 2012). This persistent bias calls into question the accuracy of models in predicting the response of wintertime aerosol concentrations and nitrogen deposition fluxes to reductions in anthropogenic emissions (Ellis et al., 2013; Holt et al., 2015; Lamarque et al., 2013; Pye et al., 2009; Simpson et al., 2014).
Here, we use the GEOS-Chem model to show that the WINTER observations provide critical insights to these questions related to NOx and its oxidation products. Our work complements the observationally-based WINTER analyses of HNO3/pNO2− partitioning by Guo et al. (2016), $\gamma$(N2O5) by McDuffie et al. (2018) and of the NOy lifetime by Kenagy et al. (2018). A number of companion papers interpret the WINTER observations with the GEOS-Chem model to examine the dominant pathways and trends in SO42−-NO3-NH4+ aerosol formation (Shah et al., 2018), the distribution, emissions and production of primary and secondary organic aerosol (Schroder et al., 2018), and the role of residential burning as a source of organic aerosol over the NE US (Schroder et al., 2018; Sullivan et al., 2018, under review).

2 WINTER aircraft campaign and surface observations

The WINTER aircraft campaign took place between February 1 and March 15, 2015 out of Hampton, Virginia (https://www.eol.ucar.edu/field_projects/winter). We conducted 13 flights with the NCAR/NSF C-130 aircraft over the NE US (Figure 1). Flights were designed to sample the lower troposphere over and downwind of major pollution regions along the Eastern Seaboard and Ohio River Valley, with 71% of the flight hours taking place within 1 km of the surface, and 85% within 2 km. As nocturnal chemistry was an important focus of WINTER, and due to the longer duration of night in winter, 58% of the flight hours were conducted at night (solar zenith angle>90°).

Table 1 summarizes the main aircraft measurements used in this study. Details on specific instruments are available in other WINTER papers (Fibiger et al., 2018; Guo et al., 2016; Lee et al., 2018; McDuffie et al., 2018; Schroder et al., 2018). Of relevance to this study, the C-130 payload included a detailed characterization of not only NOx and total reactive nitrogen (NOy, defined as NOy = NO+NO2+HNO3+HONO+2N2O5+CINO2+PNs+ANs), but also of the individual species composing NOy. Furthermore, NO, NO2, N2O5, and NOy were each measured using two different techniques (Table 1). Duplicate measurements of the same species agreed to within 1-19% during WINTER and the sum of individual NOy species ($\sum$NOy) were consistent with NOy measurements to within 20-30% (Lee et al., 2018; McDuffie et al., 2018). Note that we assume that the NOy measurements only include gas-phase reactive nitrogen species and do not sample particulate nitrate (pNO2−). pNO2− was measured separately for PM1 (particulate matter with an aerodynamic diameter < 1 μm) and PM4. Guo et al. (2016) showed that nearly all pNO2− occurred as PM1 during WINTER, and in our analysis we only use the two PM1 pNO2− measurements, which agreed to within 30% (Guo et al., 2016; Schroder et al., 2018). In this paper, we will refer to NOy as the sum of NO2 and pNO2− ($^1$NO2=NOy+pNO2−).

For comparison to the GEOS-Chem model, we average these observations on a uniform 1-minute interval along the flight tracks. For species measured by two instruments, we take the arithmetic average of these measurements when both are available or use only the available measurement. We calculate the dry aerosol surface area by combining dry aerosol size distribution observations from the Passive Cavity Aerosol Spectrometer Probe (PCASP, 0.1-3 μm) and Ultra-High Sensitivity Aerosol Spectrometer (UHSAS, 0.06-1 μm) instruments onboard the aircraft. The RH-dependent aerosol growth factors are calculated as described in McDuffie et al. (2018): for <1 μm, growth factors are derived from the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) observations of aerosol dry mass and estimates of aerosol liquid water, for 1-3 μm aerosol growth factors are calculated with the Extended-AIM

We complement these aircraft observations with measurements from several surface networks in February-March 2015. We use surface observations of NO$_2$ and HCHO from the EPA Air Quality System (AQS) monitoring network (https://www.epa.gov/outdoor-air-quality-data). Hourly NO$_2$ concentrations are measured with standard chemiluminescence monitors equipped with molybdenum oxide converters (Demerjian, 2000). Daily averages of ambient HCHO concentrations are measured every 6 days using an adsorbent cartridge followed by analysis using High Performance Liquid Chromatography (HPLC). The Clean Air Status and Trends Network (CASTNET, http://epa.gov/castnet) measures ambient concentrations of HNO$_3$ and PM$_{2.5}$ pNO$_3^-$ integrated over a week. We also use measurements from the Chemical Speciation Network (CSN, https://www3.epa.gov/ttnamti1/speciepg.html) and the Interagency Monitoring of Protected Visual Environments (IMPROVE, http://vista.cira.colostate.edu/improve/) networks, which report 24-hour mean concentrations of PM$_{2.5}$ pNO$_3^-$ every third or sixth day. Note that the IMPROVE and CASTNET pNO$_3^-$ measurements can be biased low due to volatilization of ammonium nitrate from the filters during sampling, storage, or shipping prior to analysis (Hand et al., 2011). Weekly wet deposition of nitrate are reported by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN, https://nadp.isws.illinois.edu/). For comparison to the GEOS-Chem model, we only select sites with more than 75% temporal coverage over the February 1-March 15, 2015 period and sample the model on the days of observations.

### 3 The GEOS-Chem chemical transport model

#### 3.1 General description

We use the GEOS-Chem chemical transport model (Bey et al., 2001) driven by assimilated meteorological fields from NASA’s GEOS-FP system (Goddard Earth Observation System-Forward Processing, Lucchesi, 2013) at 3-hour temporal resolution for 3-D fields and 1-hour resolution for 2-D fields. The original spatial resolution of GEOS-FP fields is 0.25° latitude by 0.3125° longitude and 72 vertical levels. For this study, we use a one-way nested configuration of GEOS-Chem over North America (Kim et al., 2015) with 0.5°×0.625° resolution over North America and dynamic boundary conditions from a 4°×5° global simulation. Initial simulations were at the native 0.25°×0.3125° resolution, but as multiple sensitivity studies were conducted we switched to using a 0.5°×0.625° resolution to save computational time. We found that the degraded horizontal resolution did not affect our results, confirming previous work over the southeast U.S. (Yu et al., 2016). The global simulation is run for 14 months (July 2014-March 2015) to provide initial and boundary conditions. The nested simulation is initialized on January 16, 2015 and run until March 31, 2015. Unless otherwise noted, the results presented here are for the WINTER period (February 1-March 15, 2015). For comparison to the aircraft observations, we sample the model in time and space corresponding to the location of the aircraft. We eliminate measurement time points in concentrated pollution plumes with NO$_2$> 10 ppbv or SO$_2$> 10 ppbv, which are not resolved by the ~50 km horizontal resolution of the model. This removes 3% of the 1-minute time averaged observations.

#### 3.2 Reference simulation
The Reference simulation is based on the public release version 10-01 of GEOS-Chem (http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_v10-01). Boundary layer mixing uses the nonlocal scheme of Holtslag and Boville (1993) as implemented in GEOS-Chem by Lin and McElroy (2010). This scheme uses the planetary boundary layer (PBL) depth diagnosed within the GEOS-FP fields using a 2 m² s⁻¹ threshold on the total eddy diffusion coefficient of heat. During WINTER, the GEOS-FP daytime (10 am – 4 pm local time) mean PBL depth along the flight tracks was 830±360 m over land and 1,150±340 m over the ocean. We compare the monthly mean daytime maximum PBL depth observed at the Micropulse Lidar Network (MPLNET) site in Greenbelt, Maryland for 2001-2008 (Lewis et al., 2013) with the GEOS-FP PBL depth at that location for 2013-2016 (Figure S1), finding good agreement between observed (February 1,380±210 m; March 1,700±160 m) and modeled (February 1,370±240 m; March 1,520±310 m) PBL depth. In addition, the GEOS-Chem model reproduces the vertical profiles of trace gases and aerosols observed during WINTER (Section 4.1), a further indication that the PBL depth and associated mixing are simulated reasonably well during February and March.

The HOx-NOx-VOC-O₃-BrO₃ tropospheric chemistry chemical mechanism is described in Mao et al. (2010, 2013) with recent updates for biogenic VOC chemistry (Fisher et al., 2016; Travis et al., 2016). We use γ(N₂O₅) from Evans & Jacob (2005), which assumes aerosol-specific parameterizations for sulfate-nitrate-ammonium (SNA: SO₄^{2-}-NO₃⁻-NH₄⁺), organic aerosol (OA), black carbon, dust and sea-salt. The aerosol multi-component system for SNA, OA, black carbon, dust and sea-salt was most recently described in Kim et al. (2015). To simulate secondary OA, we use the SIMPLE parameterization of Hodzic and Jimenez (2011), which has been shown to perform well during WINTER (Schroder et al., 2018). The particle pH dependent gas-particle partitioning of HNO₃ and NH₃ is computed with the ISORROPIA II thermodynamic module (Fontoukis and Nenes, 2007), as implemented by Pye et al. (2009). We assume bulk metastable equilibrium of the gas-phase with liquid SO₄^{2-}-NO₃⁻-NH₄⁺ PM₁ aerosol. The public release version of GEOS-Chem includes Na⁺ and Cl⁻ from submicron sea-salt in the gas-aerosol equilibrium. In our Reference simulation, we assume that submicron sea-salt is externally mixed, such that Na⁺ and Cl⁻ ions do not participate in the HNO₃ and NH₃ gas-particle partitioning as discussed in Guo et al. (2016) and Shah et al. (2018). In addition to the aqueous phase oxidation of sulfur dioxide (SO₂) via hydrogen peroxide (H₂O₂) and O₃, included in the public release version of GEOS-Chem, we have added metal-catalyzed SO₂ oxidation following Alexander et al. (2009) as described in Shah et al. (2018).

Anthropogenic emissions over the U.S. are from the 2011 EPA National Emissions Inventory (NEI11v6.1) at a horizontal resolution of 0.1°×0.1°, as implemented in GEOS-Chem by Travis et al. (2016). These emissions are adjusted to 2015 using the EPA’s national annual trend report (EPA, 2017), with scaling factors of 0.8 for NOₓ, 0.72 for SO₂, 0.83 for carbon monoxide (CO), 0.93 for VOCs. The emissions are hourly and day-specific (including day-of-week variations). As surface temperatures in February 2015 were 6°C colder compared to the 2001 temperatures used in Gilliland et al. (2006), we adjusted hourly NH₃ emissions from livestock to 2015 temperatures following Aneja et al. (2000). This temperature adjustment resulted in a factor of 2 reduction in livestock NH₃ emissions for the WINTER period and improved agreement with WINTER observations of NH₄⁺ and pNO₃⁻ (Shah et al., 2018). Based on tall tower and aircraft measurements, Lu et al. (2015) found that the NEI emission inventory
overestimated toluene emissions by a factor of 2.5. In our reference simulation, we reduce the NEI toluene emissions by this factor, leading to a significant reduction in the GEOS-Chem overestimate in toluene compared to WINTER aircraft observations, with a 50% overestimate instead of a factor of 3 overestimate prior to the adjustment (not shown). For shipping emissions, we replace the NEI emission inventory with the International Comprehensive Ocean-Atmosphere Data Set (ICOADS) (Wang et al., 2008; Lee et al., 2011). The emissions are distributed based on reported monthly ship locations and are released at the surface. Shipping emissions of NOx are processed by the PARANOX module (Vinken et al., 2012; Holmes et al., 2014) to account for O3 and HNO3 production in the plume. Open biomass burning emissions (wildfires and agricultural fires) are from the year-specific Global Fire Emissions Database (GFED) v4 (van der Werf et al., 2017) and biogenic emissions from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) v2.1 (Guenther et al., 2012).

Wet deposition includes the processes of rainout and washout of gases and aerosols based on Liu et al. (2001) with updates from Wang et al. (2011) and Amos et al. (2012). Croft et al. (2016) found that cloud water content of precipitating clouds in GEOS-Chem’s wet deposition scheme is an order of magnitude higher than observations in cold regions, which affects rainout scavenging. To address this, we modify the wet deposition scheme as described in Shah et al. (2018), by assuming a linearly decreasing value of cloud water content from 1 g m\(^{-3}\) for liquid clouds (T≥268 K) to a minimum of 0.1 g m\(^{-3}\) for ice clouds (T≤258 K). This modification increases wet deposition fluxes by about 20% during the WINTER period.

### 3.3 Updates to GEOS-Chem for this study: Improved simulation

In addition to the Reference GEOS-Chem simulation described in section 3.2, we conduct a second simulation, referred to as “Improved” simulation, with the following modifications (summarized in Table S1).

#### 3.3.1 Wintertime sources of HCHO

Formaldehyde (HCHO) is a key indicator of photochemistry as it is an intermediate in VOC oxidation, provides a source of HO\(_x\) radicals, and thus affects both O3 and NOx photochemistry. Photolysis of HCHO can be a dominant source of HO\(_x\) radicals during midlatitude winters, when low H\(_2\)O and high SZA lead to weak OH production from O(\(^1\)D)+H\(_2\)O (e.g., Snow et al., 2003). Comparisons of the mean observed HCHO vertical profile during WINTER and the Reference GEOS-Chem simulation show a systematic model underestimate in the boundary layer (Figure 2d). Below 1 km altitude, the Reference simulation has a -46% normalized mean bias (NMB = 100×∑(M\(_i\)-O\(_i\))/∑O\(_i\), with observations O\(_i\) and model M\(_i\) summed along the flight tracks). In addition, the Reference simulation underestimates EPA surface observations of HCHO by a factor of 2.5, with a NMB of -63% (Figure 2ac). Zhu et al. (2017) report a similar model bias during winter months in their evaluation of GEOS-Chem against 9 years of EPA HCHO surface observations. Lueken et al. (2012) show that CMAQ has a -69% bias compared to EPA HCHO observations for January 2002. The state-of-the-art WINTER aircraft HCHO measurements confirm the model bias found in these previous studies and demonstrate that the high HCHO concentrations are present throughout the lower troposphere. This persistent bias is unlikely due to an overestimate in HCHO sinks, which are dominated by
photolysis. Thus, the systematic model underestimate of HCHO points to missing primary emissions and/or secondary photochemical production of HCHO during winter.

In the Reference simulation over the NE US lower troposphere (defined as 35-45°N; 89-64°W; 0-1.7 km, blue box on Figure 1) we find that primary emissions of HCHO account for 10% of the HCHO source, with the remaining 90% due to secondary production, which is dominated by methane (CH₄) oxidation. In the NEI inventory the two dominant sources of HCHO over the NE US during winter are mobile emissions and residential wood combustion (RWC), accounting for 47% and 42% of primary emissions, respectively. Point sources account for 9.3% of HCHO emissions and less than 2% are from other sources such as solvent use and waste disposal. Based on cold-start exhaust measurements of the HCHO-to-toluene emission ratio from cars at different temperatures, Jobson & Huangfu (2016) and Jobson et al. (2017) have suggested that wintertime cold temperature vehicle start emissions are underestimated by a factor of 5 in the NEI inventory. Furthermore, VanderSchelden et al. (2017) found that RWC accounted for 73% of the HCHO observed over Yakima, Washington during winter, a much larger fraction than expected based on the NEI inventory.

To examine whether a potential underestimate in RWC and mobile emissions could explain the observed HCHO, we increase the NEI HCHO emissions for these two sources by a factor of 5 in the Improved simulation (resulting in a factor of 4.6 increase in total primary emissions of HCHO). As shown in Figure 2, the resulting HCHO in the Improved simulation is in better agreement with both aircraft and surface observations (NMB=+14% for surface observations; NMB=−6% for aircraft observations below 1 km). In this simulation, primary emissions account for 30% of the HCHO source, with 70% due to secondary production. Overall, this leads to a 20% increase in OH over the NE US in the Improved simulation.

Observed WINTER concentrations of C₃ alkenes, which can be an important secondary source of HCHO, are overestimated in GEOS-Chem by 50-100% (not shown), so they cannot explain the missing HCHO. Another possible explanation to reconcile model and observations would be the rapid oxidation of larger VOCs, which are not represented in GEOS-Chem. A more in-depth analysis of whether the missing wintertime sources of HCHO are primary or secondary will be presented in a forthcoming study. For the purpose of this paper, we make the simplifying assumption that all missing HCHO is due to an underestimate of primary emissions, which we increase to match the observed HCHO mixing ratios during WINTER.

3.3.2 Simple ClNO₂ chemistry

We add ClNO₂ as a new chemical species in the chemical mechanism. We include a simplified treatment of its chemistry, assuming that its only production is via R3 and its only loss is via photolysis, neglecting ClNO₂ deposition, which is expected to be small (Kim et al., 2014). We use ClNO₂ cross sections from Ghosh et al. (2012). Upon photolysis of ClNO₂, NO₂ and Cl are produced. We do not track the Cl radical as chlorine chemistry is not included in this version of the model. The main concern herein is the impact of ClNO₂ as a NO₂ reservoir, which is captured by this approach. The impact of ClNO₂ on the oxidant budget will be examined in a separate study, in which we consider the reactions of Cl radicals with CH₄ and VOCs.

3.3.3 Heterogeneous chemistry
The Evans & Jacob (2005) $\gamma$(N$_2$O$_5$) parameterization was found to overpredict direct
observations of $\gamma$(N$_2$O$_5$) on ambient aerosols (Bertram et al., 2009), as well as $\gamma$(N$_2$O$_5$) derived
from in situ observations of NO$_3$ and N$_2$O$_5$ (Brown et al., 2009). For SNA aerosol, we replace
the Evans & Jacob (2005) $\gamma$(N$_2$O$_5$) parameterization with the Bertram & Thornton (2009)
parameterization, which considers the competing effects of pNO$_5^-$, pCl$^-$ and LWC. The LWC is
calculated within ISORROPIA II based on SNA aerosol composition, relative humidity and
temperature. As the version of GEOS-Chem we are using does not include full chlorine
chemistry, we make the simplifying assumption that 10% of pCl$^-$ from submicron sea salt is
discharged onto SNA aerosol. This is likely an underestimate of pCl$^-$ present during WINTER, as
we neglect anthropogenic sources, which accounted for up to half the HCl observed during
WINTER (Haskins et al., 2018, under review). We calculate the ClNO$_2$ yield, $\phi$(ClNO$_2$), on
SNA aerosol using the Bertram & Thornton (2009) parameterization as a function of LWC and
pCl$^-$ concentrations. For all other aerosol we assume $\phi$(ClNO$_2$)=0, except for sea salt aerosol for
which we assume $\phi$(ClNO$_2$)=1.

Evans & Jacob (2005) parameterized $\gamma$(N$_2$O$_5$) on OA using the laboratory measurements
of Thornton et al. (2003) on malonic acid. However malonic acid represents very hygroscopic
organic aerosol, which accounts for a small fraction of OA in the atmosphere. Field
measurements indicate that humic-like substances are more representative of the broader
composition of water-soluble organic compounds in the atmosphere (e.g. Fuzzi et al., 2001,
Zhang et al., 2007). We thus update $\gamma$(N$_2$O$_5$) on OA to use the laboratory measurements of
Badger et al. (2006) on humic acid, with $\gamma$(N$_2$O$_5$)$=10^{-4}$ for RH<50% and $10^{-3}$ for RH≥50%. This
choice is also supported by $\gamma$(N$_2$O$_5$) measured on mixed organic-inorganic aerosol systems
(Gaston et al., 2014). These values are 1-2 orders of magnitude lower than what was previously
assumed in GEOS-Chem for the OA component. For all other aerosol, we keep the same
formulation as in Evans & Jacob (2005). The resulting $\gamma$(N$_2$O$_5$) calculated at 0.6 km altitude
during the WINTER campaign is shown in Figure 3b. The large pNO$_5^-$ concentrations over the
Midwest and NE US lead to a decrease in $\gamma$(N$_2$O$_5$) from 0.02 (Reference simulation, Figure 3a)
0.01 (Improved simulation). In coastal areas of the Eastern U.S., the pCl$^-$ dependence of
$\gamma$(N$_2$O$_5$) on SNA aerosol results in a strong $\gamma$(N$_2$O$_5$) gradient from 0.01 to 0.03. McDuffie et al.
(2018) conducted an iterative box modeling analysis fit to 10-second averages of WINTER
observations of NO$_2$, O$_3$, N$_2$O$_5$, and ClNO$_2$ to infer 2876 individual determinations of $\gamma$(N$_2$O$_5$)
from all WINTER night (SZA > 90º) flights. They found a median value of $\gamma$(N$_2$O$_5$)=0.0143,
consistent with our median Improved simulation value of 0.011. McDuffie et al. (2018) also
found a strong gradient in $\gamma$(N$_2$O$_5$) over coastal areas of the NE U.S. (see their Figure 3b). We
calculate that $\phi$(ClNO$_2$) is lowest (0.1-0.3) in the continental eastern U.S. with low RH and pCl$^-$
concentrations, increasing rapidly to 0.5-0.8 over the ocean off the US East Coast (Figure 3c).

Laboratory studies have reported values of $\gamma$(NO$_3$) between 1.5×10$^{-4}$ to 0.72, depending
on aerosol type, with most of the values in the 10$^{-4}$-10$^{-3}$ range for water with dissolved ions and
for OA (e.g. Brown and Stutz, 2012 and references therein). Some of the high values measured
correspond to fast initial uptake on the surface of the aerosol, after which $\gamma$(NO$_3$) decays to a
steady-state value 1-2 orders of magnitude lower (e.g., Mak et al., 2007). The original $\gamma$(NO$_3$)
value assumed in GEOS-Chem was 10$^{-3}$ based on the recommendation of Jacob (2000). Mao et
al. (2013) increased $\gamma$(NO$_3$) to 0.1 on all aerosol in GEOS-Chem. We decrease it back to 10$^{-3}$, to
be consistent with the laboratory measurements summarized in Brown and Stutz (2012).

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In the reference GEOS-Chem model, the products of NO₂ heterogeneous uptake on aerosol are assumed to be \( \frac{1}{2} \text{HNO}_3 + \frac{1}{2} \text{HONO} \) \( (\gamma(\text{NO}_2) = 10^{-4}) \), based on the recommendation of Jacob (2000). As summarized in the recent review by Sparato and Ianniello (2014), laboratory studies of the heterogeneous uptake of NO₂ show that the kinetics of this reaction are first order in NO₂, and that the main observed gas-phase product is nitrous acid (HONO), with some formation of adsorbed HNO₃. However, the detailed reaction mechanisms for heterogeneous NO₂ hydrolysis remain debated and some of the adsorbed HNO₃ could be released back as NO₂ or NO (Finlayson-Pitts et al., 2003; Gustafsson et al., 2009; Jenkin, 1988; Ramazan et al., 2004).

Furthermore, several studies show that this reaction could be photo-enhanced on various aerosol surfaces, producing mainly HONO (e.g., Sparato and Ianniello, 2014 and references therein). In the Improved simulation, we assume that HONO is the only product of NO₂ heterogeneous uptake \( (\text{NO}_2 \rightarrow \text{HONO}) \) and keep \( \gamma(\text{NO}_2) = 10^{-4} \).

### 3.3.4 Dry deposition

Dry deposition velocities, \( v_d \), are simulated in GEOS-Chem using the resistance-in-series scheme of Wesely (1989) as implemented by Wang et al. (1998). The total resistance to dry deposition (which is the inverse of \( v_d \)) is calculated as the sum of the aerodynamic resistance, \( R_a \), the quasi-laminar boundary layer resistance, \( R_s \), and the surface resistance, \( R_c \). \( R_c \) includes the influence of leaves, lower canopy, and ground. Based on early observations of increasing \( R_f \) for SO₂, NO₂, and HNO₃ on snow surfaces below 0°C (Johansson and Granat, 1986; Valdez, 1987), Wesely (1989) added a temperature dependent function, \( 1000 \exp(-T_s - 4) \) (in units of s m⁻¹, with surface temperature, \( T_s \), in °C) to all surface resistance terms. This results in unrealistically low \( v_d \) values for \( T_s < -2°C \), in particular near-zero values for \( v_d(\text{HNO}_3) \). Following more recent parameterizations, we limit the increase in \( R_c \) at low temperatures to no more than a factor of 2 (Erisman et al., 1994; Zhang et al., 2003). Furthermore, as HNO₃ has a high affinity for all natural surfaces, a common assumption is that its surface resistance is negligible (Hertel et al., 2012; Seinfeld & Pandis, 2006; Wesely & Hicks, 2000). Accordingly, we update GEOS-Chem to impose \( R_c(\text{HNO}_3) = 1 \) s cm⁻¹.

Over much of the NE US during the campaign, \( T_s \) ranged between 0°C and -15°C. Our updates increase \( v_d \) by 10-50% for most species, with a particularly large increase for \( v_d(\text{HNO}_3) \) from mean values of 0.6 cm s⁻¹ to 2.1 cm s⁻¹. These updated values are consistent with measurements of \( v_d(\text{HNO}_3) \) reported in the literature (e.g., Janson and Granat, 1999; Pryor et al., 2002; Sievering et al., 2001), with little seasonal difference between summer and winter at sites with cold wintertime temperatures (Munger et al., 1996; Zimmerman et al., 2006).

### 4 Results

#### 4.1 Vertical distribution of trace gases and aerosols during WINTER

Figure 4 displays the WINTER campaign mean observed profiles of O₃, CO, and aerosol surface area, as well as profiles of \( ^1\text{NO}_x \) \( (^1\text{NO}_x = \text{NO}_x + p\text{NO}_3^-) \), \( \text{NO}_3 \) \( (\text{NO}_3 = \text{NO} + \text{NO}_2) \), HNO₃, pNO₃⁻, and \( \Sigma\text{PNs} \). We also show nighttime vertical profiles of N₂O₅, CINO₂, and HONO. Background O₃ in the free troposphere is ~50 ppbv, decreasing to ~40 ppbv near the surface where high NOₓ emissions lead to net O₃ loss. The GEOS-Chem model captures this gradient and is generally within 2-5 ppbv of observations at all altitudes. The mixing ratios of O₃ increase
by 2 ppbv on average in the Improved simulation relative to the Reference simulation, due to the decrease in γ(N$_2$O$_3$) and in the associated O$_3$ loss via R1-R3. The GEOS-Chem model underestimates CO observations throughout the troposphere by 10-20 ppbv. This appears to be related to an underestimate of background CO in the free troposphere. Such a low bias in northern hemisphere mid- and high-latitudes is a common feature in many CTMs (Monks et al., 2015; Naik et al., 2013; Shindell et al., 2006) and could indicate an overestimate of global OH concentrations in models (Strode et al., 2015 and references therein).

The model simulation reproduces the vertical profile of median aerosol surface area (Figure 4). Shah et al. (2018) provide a detailed evaluation of aerosol composition simulated in GEOS-Chem against both WINTER aircraft and ground-based observations. They find that the model reproduces the observed concentrations of SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and OA particulates to within 15-20%. Shah et al. (2018) showed that the median PM$_1$ pH calculated by GEOS-Chem along the WINTER flight tracks below 1 km altitude over land was 1.29, in good agreement with the pH of 1.34 inferred from thermodynamic analysis of observed PM$_1$ composition (Guo et al., 2016). This consistency between modeled and observed aerosol surface area, composition (affecting γ(N$_2$O$_3$)), and particle pH is particularly important to our estimates of NO$_x$ loss via N$_2$O$_3$ hydrolysis, as well as to the gas/aerosol partitioning of HNO$_3$ which is a strong function of particulate pH (Guo et al., 2016; Shah et al., 2018).

There is a remarkable agreement between observed and modeled profiles of TNO$_3^-$, with mean values of 5 ppbv near the surface decreasing to less than 1 ppbv above 2 km altitude (Figure 4). The model also reproduces the vertical distribution of NO$_x$, HNO$_3$, pNO$_3^-$, and ∑PNs, with the Improved simulation being within 20-40% of observations. Relative to the Reference simulation, the Improved simulation results in closer agreement with observed HNO$_3$ and pNO$_3^-$, because of our updated γ(N$_2$O$_3$) and $\gamma_0$(HNO$_3$) (section 3.3). Furthermore, the Improved simulation predicts higher concentrations of ∑PNs (taken as the sum of peroxyacetyl nitrate, peroxyacryloyl nitrate, and peroxypropionyl nitrate in GEOS-Chem), in better agreement with observations. This is mostly due to higher HCHO concentrations (section 3.3.1), leading to more OH, enhanced RO and RO$_2$ production from VOC oxidation and thus enhanced PNs production in the Improved simulation compared to the Reference simulation.

Because of the lower γ(N$_2$O$_3$) and γ(NO$_3$) assumed in the Improved simulation, GEOS-Chem predicts a doubling of nighttime N$_2$O$_3$ mixing ratios from mean values of ~100 pptv to ~200 pptv below 1 km altitude (Figure 4). While in better agreement with observations (mean of ~300 pptv), the Improved simulation is 30-40% too low. The Improved simulation qualitatively reproduces the observed CINO$_2$ profile, but tends to underestimate observations below 500 m, which were mostly taken over water. This suggests that $\phi$(ClNO$_2$) is underestimated in our simulation as discussed in more detail in Section 4.3.

WINTER observations show highly variable HONO mixing ratios with mean values of 59±115 pptv at night and 24±45 pptv during the day (< 1 km altitude). The Improved simulation predicts mean HONO of 59±90 pptv at night and 16±37 pptv during the day. These values are nearly a factor of two higher than those predicted in the Reference simulation (Figure 4), as a result of the combined effects of changing NO$_2$ heterogeneous uptake to produce only HONO (section 3.3.3) and enhanced HCHO primary emissions, which increase OH and the gas-phase HONO production via NO+OH.
In the next two sections, we examine in more detail the spatial distribution of NO$_x$ and its oxidation products.

### 4.2. Anthropogenic NO$_x$ emissions during winter

Figure 5, panels a and b, shows that the magnitude and spatial distribution of observed $^7$NO$_y$ below 1 km altitude is reproduced by GEOS-Chem, with the highest $^7$NO$_y$ mixing ratios (>6 ppbv) concentrated over the Ohio River Valley and downwind of the DC-NYC megalopolis. The model displays a small negative bias (-6%) and high correlation coefficient (r=0.81).

Simulations with the FLEXPART particle dispersion model indicate that the WINTER campaign sampled air that was influenced by emissions 6-24 hours back. Because of the short time between emissions and sampling and the long lifetime of NO$_x$ during winter, most of $^7$NO$_y$ is in the form of NO$_x$ over the NE US. The observed NO$_x$/$^7$NO$_y$ ratio varies from ~70-90% over source regions with the highest NO$_x$, decreasing to 20-25% off the coast. The model reproduces this general pattern (Figure 5, panels e and f). The simulated NO$_x$ mixing ratios display a ~25% underestimate relative to the aircraft observations below 1 km altitude. We hypothesize that this underestimate is due to a small overestimate of the NO$_x$ oxidation rate and to an underestimate in $\phi$(ClNO$_2$) (see section 4.3).

We also compare the Improved GEOS-Chem simulation to surface hourly NO$_2$ measurements from the EPA AQS monitoring network obtained at 93 sites in the eastern U.S. between 1 February-15 March 2015 (Figure 6). Most of these sites are in urban (39 sites) and suburban (38 sites) environments and display very strong diurnal variations with the highest NO$_2$ concentrations observed during the early morning rush hour, when the shallow PBL traps pollutants near the surface. As the spatial heterogeneity of NO$_2$ near localized sources is not resolved by the ~50 km horizontal resolution of GEOS-Chem, we focus on NO$_2$ observations in the afternoon (14:00-18:00 hours local time), when the PBL is deepest and mixing will lead to more homogeneity. The commercial instruments used to measure NO$_2$ have known interferences to NO$_x$ oxidation products, in particular ANs, PAN, and HNO$_3$ (e.g., Dunlea et al., 2007; Steinbacher et al., 2007). We correct for these interferences by applying the correction factor developed by Lamsal et al. (2008), using the GEOS-Chem hourly NO$_2$ and its oxidation products for each site. This correction is minimal for winter months (<10%). We find that GEOS-Chem underestimates afternoon AQS NO$_2$ observations by 35%, slightly larger than the underestimate we found relative to aircraft NO$_x$ observations. Restricting our comparison to rural EPA sites, the model bias is lower (NMB=+5%, Figure 6).

Overall, our comparison between the GEOS-Chem simulation and WINTER observations of $^7$NO$_y$ suggests that NO$_x$ emissions in the NEI inventory over the NE US are consistent with aircraft observations in the bottom 1 km of the atmosphere to within 10% on average. Salmon et al. (2018) find a similar agreement between the 2011 NEI NO$_x$ emission inventory and top-down NO$_x$ emissions from airborne mass balance experiments conducted around the Washington D.C.-Baltimore region during WINTER. These findings are in contrast with previous studies suggesting that NEI NO$_x$ emissions, in particular motor vehicle emissions, might be overestimated by a factor of 2 (Section 1). These previous studies were focused on summer months in the Eastern U.S. or under warm conditions in California and Texas.
These diverging findings suggest potential issues with the seasonal dependence of anthropogenic NO\textsubscript{x} emissions as represented within the NEI inventory. These issues could be linked to assumptions about the summer/winter vehicle fleet composition and their associated NO\textsubscript{x} emissions. Another possibility is that models have seasonal biases in PBL mixing and/or chemistry. For example, Travis et al. (2016) found that during summertime over the SE U.S. GEOS-Chem systematically overestimates surface O\textsubscript{3} concentrations and predicts a flat vertical profile of O\textsubscript{3} within 1 km of the surface, while ozonesonde observations indicate a 7 ppbv increase. They attributed some of the model bias to excessive vertical mixing in the model and net surface O\textsubscript{3} production in the model, while observations would indicate net O\textsubscript{3} loss at the surface. In their evaluation of the CMAQ model, Appel et al. (2017) found that EPA surface observations showed larger NO\textsubscript{2} mixing ratios during winter compared to summer, especially in the early morning, while the CMAQ model predicted the opposite seasonal variation. Henderson et al. (2017) proposed that this discrepancy could be explained by a CMAQ underestimate in vertical mixing during summer morning hours.

In the case of WINTER observations, we reproduce the vertical profile of NO\textsubscript{x} and other surface pollutants, giving us confidence in the representation of vertical mixing. Similarly, the chemistry of NO\textsubscript{x} and its oxidation products appears to be well-represented based on the detailed constraints provided by the WINTER aircraft observations.

In their airborne mass balance study, Salmon et al. (2018) report a factor of 2 overestimate in the NEI 2011 CO emissions over the Washington D.C.-Baltimore region, which combined with the good agreement in NO\textsubscript{x} results in a factor of 2 underestimate in the CO/NO\textsubscript{x} enhancement ratio. For the WINTER observations below 0.8 km altitude we calculate a mean CO/NO\textsubscript{x} enhancement ratio of 5.4±1.2 ppbv/ppbv (based on the correlation between background-subtracted CO and NO\textsubscript{x} for daytime flights over land), similar to the 4.6±0.7 ppbv/ppbv and 5.1±1.5 ppbv/ppbv values reported by Salmon et al. (2018). This is also in agreement with the 4.6-5.2 ppbv/ppbv ratios measured by Wallace et al. (2012) during winter in Boise, Idaho near busy roads. In contrast, the NEI 2011 CO/NO\textsubscript{x} emission ratio is 8.7 ppbv/ppbv for the NE US and the GEOS-Chem CO/NO\textsubscript{x} enhancement ratio sampled along the C-130 flight tracks 10.1±0.6 ppbv/ppbv. Thus, we find that the NEI inventory overestimates CO emissions by factors of 1.6-1.9 over the NE US. This was not initially apparent in the vertical profile in Figure 4 because of the free tropospheric CO underestimate. The CO/NO\textsubscript{x} ratios reported by summertime studies are generally higher, which could potentially reflect a strong seasonal or temperature dependence in the mobile CO/NO\textsubscript{x} emission ratio (Salmon et al., 2018).

### 4.3 Reduction in the HNO\textsubscript{3} and pNO\textsubscript{3}⁻ bias in GEOS-Chem

Previous studies using the GEOS-Chem model have reported a large positive bias in reproducing ground-based observations of pNO\textsubscript{3}⁻ and HNO\textsubscript{3} concentrations as well as nitrate wet deposition fluxes over the Eastern U.S. during winter (Heald et al., 2012; Walker et al., 2012; Zhang et al., 2012), with biases of 50-200%. Implementation of our updated γ(N₂O₅) and νd(HNO₃) leads to lower HNO₃ production and increased dry deposition loss, which together result in a significant improvement of the representation of ground-based winter observations of HNO₃ and pNO₃⁻ (Figure 7). Our results are also sensitive to the assumed NH₃ emissions from livestock, which we have lowered by a factor of 2 due to the cold temperatures (section 3.2), resulting in lower pNO₃⁻. The Reference GEOS-Chem simulation overestimates CASTNET pollution.
observations of HNO₃ by nearly a factor of 3 (NMB=168%) for February 1-March 15 2015, predicting large HNO₃ concentrations (>3 μg/m³) over the Ohio River Valley and the DC-NYC megalopolis, that are not seen by observations (Figure 7, panels a and c). The Reference simulation also overestimates surface observations of pNO₃⁻ from CASTNET, IMPROVE, and CSN for the same period (NMB=64%, Figure 7, panels d and f). In the Improved simulation, these biases are greatly reduced for surface HNO₃ (NMB=20%, Figure 7b and 7c) and pNO₃⁻ (NMB=35%, Figure 7e and 7f).

Improvements are also seen in the comparison to WINTER aircraft observations of HNO₃ and pNO₃⁻ (Figure 4 and Figure 8), where the biases below 1 km altitude are reduced by a factor of 2 (NMB decreasing from 136% to 73% for HNO₃ and from 36% to 17% for pNO₃⁻). The Improved simulation predicts that the highest HNO₃ concentrations occur over the N. Atlantic downwind of the DC-NYC corridor, in agreement with aircraft observations. In contrast, the Reference simulation shows elevated concentrations over the Ohio River Valley, which are not seen in the observations.

Figure 9 displays observations of NO₂ (¹NO₂⁻NOₓ), as well as individual observations of HNO₃, pNO₃⁻ and ∑PNs for RF02, a late afternoon flight taking place on 6 February 2015 during which the C-130 aircraft sampled the region extending over Indiana, Ohio, Kentucky, and West Virginia. We only show the observed timeseries when the aircraft was below 1 km altitude (highlighted in red on the insert of Figure 9a). Over this source region, observed NOₓ accounts for 80-90% of ¹NO₂. On average, 0.19 ppbv HNO₃, 0.46 ppbv pNO₃⁻ and 0.33 ppbv ∑PNs were observed. The Reference simulation displays a +300% bias in HNO₃ + pNO₃⁻ for this flight, while the bias is reduced to +60% in the Improved simulation (Figure 9c).

An example of the impact of the new ν(N₂O₃) on nighttime chemistry is illustrated in Figure 10, which shows observations of NO₂ during RF08 on 1 March 2015, a night-into-day flight in an hour-glass pattern downwind of the DC-NYC region. Sunrise took place at 12 UTC (7 am local time). Observed nighttime NO₂ is dominated by N₂O₅, with little contributions from HNO₃+pNO₃⁻ (<1 ppbv). The Reference simulation predicts rapid heterogeneous conversion of N₂O₅ to HNO₃ (ν(N₂O₅)=0.02) resulting in a factor of 3 overestimate in HNO₃+pNO₃⁻ (Figure 10b). In the Improved simulation, ν(N₂O₅) decreases to 0.005 as a result of the pNO₃⁻ inhibition on SNA and the low ν(N₂O₅) assumed for OA. This leads to a factor of 2.5 decrease in HNO₃, a factor of 3 increase in N₂O₅, and better agreement with the observed partitioning (Figure 10 panels c and f). Figure 10d shows the ν(N₂O₅) calculated by the iterative box modeling analysis of McDuffie et al. (2018), who found ν(N₂O₅)=0.0046±0.0013 (flight average ± standard deviation, 60-s average data) for this flight, consistent with our parameterization in the Improved simulation:  ν(N₂O₅)=0.0049±0.0006. The campaign wide comparison of ν(N₂O₅) between the box model and Improved GEOS-Chem simulation is shown in Figure S24 of the supplement of McDuffie et al. (2018).

The Improved simulation predicts ~100-300 pptv CINO₂, significantly lower than observed values of CINO₂, which varied between 200 and >1000 pptv for this flight (Figure 10d). More generally, we find that GEOS-Chem underestimate CINO₂ by a factor of 2 during the WINTER campaign (Figure 4). This suggests that the GEOS-Chem φ(CINO₂) values are too low, likely related to an underestimate in pCl⁻ concentrations as we neglect anthropogenic
sources of chlorine in this simulation (Section 3.3.3), and potential repartitioning of coarse mode
sea salt chloride to the fine mode population. Indeed, our assumption that 10% of pCl\(^-\) from
submicron sea salt is displaced onto SNA aerosol results in median PM\(_\text{1}\) pCl\(^-\) mixing ratios of 5
pptv (< 1 km) in GEOS-Chem, which is a factor of two lower than the median non-refractory
PM\(_\text{1}\) pCl\(^-\) observed by the HR-ToF-AMS during WINTER (Haskins et al., 2018, under review).
This underestimate in \(\phi\text{(ClNO}_2\text{)}\) means that we underestimate NO\(_x\) recycling via ClNO\(_2\) thus
producing too much HNO\(_3\) and could potentially explain some of the remaining model
overestimate of HNO\(_3\) and underestimate in NO\(_x\).

The remaining model overestimate of HNO\(_3\)/NO\(_x\) could also be the result of an
overestimate in \(\gamma\text{(N}_2\text{O}_3\text{)}\) in GEOS-Chem, as we treat aerosols as liquid and externally mixed. At
low RH, solid NH\(_4\)HSO\(_4\) or (NH\(_4\))\(_2\)SO\(_4\) particles can be present, and organic aerosol can
transition to solid or semi-solid state (Seinfeld & Pandis, 2006; Shiraiwa et al., 2017; Song et al.,
2016). Solid or semi-solid particles at low RH (<30-50%) tend to have much lower \(\gamma\text{(N}_2\text{O}_3\text{)}\),
typically less than 0.001 (e.g., Davis et al., 2008; Abbatt et al., 2012 and references therein).
During nighttime WINTER flights below 1 km altitude, mean observed RH was 48%, with 28%
of observations displaying RH values below 30%. In our \(\gamma\text{(N}_2\text{O}_3\text{)}\) parameterization and aerosol
surface area calculation, we assume that aerosol remain liquid and do not account for the
occurrence of solid or semi-solid particles. In addition, laboratory measurements have shown that
organic coatings on inorganic aerosol can lower \(\gamma\text{(N}_2\text{O}_3\text{)}\) (e.g., Anttila et al., 2006; Gaston et al.,
2014). As we treat aerosol as externally mixed, we do not take this effect into account.

Another possibility is an overly fast daytime production of HNO\(_3\) related either to a
model overestimate in OH concentrations or in the OH+NO\(_2\) kinetic rate constant. GEOS-Chem
uses the rate constant recommended by the NASA Jet Propulsion Laboratory (JPL) panel
evaluation (Sander et al., 2011). Several studies have suggested that this rate constant might be
15-20% lower than the value recommended by JPL (Henderson et al., 2012; Mollner et al.,
2010). As no measurements of OH, HO\(_2\), or H\(_2\)O\(_2\) were made as part of WINTER, we cannot
directly evaluate our modeled OH concentrations. However, our simulation does reproduce
WINTER observations of H\(_x\) precursors (H\(_2\)O, O\(_3\), HCHO, HONO) and controlling species
(NO\(_x\), CO) relatively well, providing indirect evidence that our modeled HO\(_x\) concentrations are
likely reasonable. Furthermore, Schroder et al. (2018) estimated OH concentrations from the
relative decay of pairs of hydrocarbons during WINTER, also finding levels consistent with
those in GEOS-Chem.

4.4 TNO\(_3\) budget over the NE United States during winter

Figure 11 and Table 2 present the budget of TNO\(_3\) in the Improved GEOS-Chem
simulation for the NE US (35-45°N; 88.75-65°W; 0-1.7 km). Half of the TNO\(_3\) burden is in the
form of NO\(_x\) (defined in this section as NO\(_x\) = NO+NO\(_2\)+NO\(_3\)+2N\(_2\)O\(_3\)+HONO+HNO\(_3\)), with
37% being present as HNO\(_3\)+pNO\(_3\)\(^-\), 12% as organic nitrates and 1% as ClNO\(_2\). GEOS-Chem
predicts that 43% of HNO\(_3\)+pNO\(_3\)\(^-\) is in the form of pNO\(_3\)\(^-\), similar to the observed value of 48%
(Guo et al., 2016). This indicates that the pH of aerosol is simulated reasonably well in GEOS-
Chem (as noted in Section 4.1), since partitioning of nitrate between the gas and particle phases
is highly sensitive to pH when nearly equal concentrations are found in the two phases (Guo et
al., 2016; Shah et al., 2018).
We can contrast this $^3$NO$_3$ partitioning to summertime aircraft observations and model simulations reported by Hudman et al. (2007) for the 2004 ICARTT campaign over the NE US. They find that below 2 km altitude, NO$_x$, HNO$_3$, and PAN accounted for 18%, 62%, and 20% of NO$_x$, respectively. The slow photochemistry during winter thus shifts the partitioning strongly in favor of NO$_x$, reducing the relative importance of HNO$_3$ and PAN. Our partitioning for WINTER is generally similar to the seasonal modeling study of Liang et al. (1998) for winter (DJF)-spring (MAM) over the continental US, which calculated 61-40% NO$_x$, 27-32% as HNO$_3$+pNO$_3^-$, and 12-28% as PAN.

In the GEOS-Chem simulation, the lifetime of NO$_x$ against oxidation and deposition is 22 hours. We find that 91% of NO$_x$ is oxidized to produce HNO$_3$, with 7% producing organic nitrates, and 2% ClNO$_2$ (Table 2 and Figure 11). While organic nitrates have the longest lifetimes of all NO$_x$ species (23 days for PN$_3$s and 16 days for AN$_3$s), their production is very slow because of low biogenic VOC emissions. We find that nighttime N$_2$O$_5$ heterogeneous chemistry accounts for 62% of HNO$_3$ production, with 35% due to daytime oxidation by reaction of NO$_2$ with OH, and 3% from reactions of NO$_3$ with VOCs.

Based on WINTER observations of the evolution of NO$_x$ concentrations in the US East Coast boundary layer outflow, Kenagy et al. (2018) calculate an e-folding NO$_x$ lifetime of 29 hours for daytime and 6.3 hours for nighttime. This corresponds to a daily mean lifetime of 10 hours (taking into account the 10h45min length of day), and includes NO$_x$ loss due to chemistry, deposition, and transport to the free troposphere. Taking these three processes into account, we calculate a NO$_x$ lifetime of 19 hours based on Table 1 and Figure 11. If we further examine the NO$_x$ budget in GEOS-Chem restricted to 0-800 m in the oceanic outflow, similar to the domain used by Kenagy et al. (2018), the NO$_x$ lifetime decreases to 11 hours due to enhanced turbulent mixing between 0-800m and the overlaying atmosphere. Kenagy et al. (2018) infer a dry deposition lifetime of HNO$_3$ of 23 hours over the ocean (29 hours during the day and 20 hours at night), similar to the HNO$_3$ dry deposition lifetime calculated in GEOS-Chem (25 hours, Table 1).

With the GEOS-Chem simulation, we find that 42% of the NO$_x$ emitted in the NE US is exported out of the domain (Table 2). Figure 11 shows that export by transport to the free troposphere (63.7 Mmoles d$^{-1}$) is twice as large as export via boundary layer advection (30.6 Mmoles/d$^{-1}$). Export of $^3$NO$_3$ during WINTER is composed of 38% NO$_x$, 40% HNO$_3$+pNO$_3^-$, 17% organic nitrates, and 5% ClNO$_2$. We can compare our WINTER NO$_x$ free tropospheric export efficiency of 28% (defined as the ratio of free troposphere NO$_x$ export/NO$_x$ emissions = 63.7 Mmoles d$^{-1}$/225 Mmoles d$^{-1}$) to values based on analysis of aircraft observations during other seasons. For the July-August ICARTT observations above 2.5 km altitude, Hudman et al. (2007) report an export efficiency of 16% composed of 13% NO$_x$, 47% HNO$_3$, and 42% PAN. Based on aircraft observations obtained during the NARE campaign in September 1997 downwind of the NE US, Li et al. (2004) and Parrish et al. (2004) find an export efficiency of 15-20%, with 6-8% as NO$_x$, 52-57% as HNO$_3$, and 34-36% as PAN. Thus, as expected from a longer NO$_x$ lifetime, the NO$_x$ export efficiency during WINTER is significantly larger than in other seasons. Furthermore, while PAN plays a significant role in NO$_x$ export during summer and fall, it is of minor importance during winter and is replaced by a larger role for direct NO$_x$ export from the boundary layer. The 3-D modeling study of Liang et al. (1998) reports a 34-26% NO$_x$ export efficiency for winter-spring, lower than our 42%. We attribute this difference to the
higher γ(N₂O₅)=0.1 used in Liang et al. (1998), and thus faster HNO₃ production and scavenging prior to export.

4.5 Nitrogen deposition

Table 3 summarizes the main forms of TNO₃ deposition over land for the NE US during the 1 February-15 March 2015 period. The wet deposition values in Table 3 are only over land and include scavenging from the entire troposphere, while values in Table 2, are for both land and ocean but only include scavenging below 1.7 km. Over the NE US in the Improved simulation, we find that TNO₃ deposition is dominated by wet deposition of HNO₃ and dry deposition of HNO₃, which account for 45% and 36% of the TNO₃ deposition flux (51.7 Mg N/month). Other contributions are from wet deposition of pNO₃⁻ (10%), dry deposition of NO₂ (3.9%) and dry deposition of pNO₃⁺ (3.1%) (Table 3). Wet and dry deposition accounts for 55% and 45% of the TNO₃ deposition flux, respectively. TNO₃ deposition over the NE US is responsible for a third of the deposition over the contiguous US, following the distribution of NOx emissions.

Compared to the Reference simulation (Table S2), the Improved simulation leads to a 15% decrease in the TNO₃ wet deposition flux and a 48% increase in the dry deposition flux, thus shifting deposition from wet to dry such that they both contribute to similar amounts of deposition with little change to the total deposition flux (Reference: 49.1 Mg N/month; Improved: 51.7 Mg N/month, Table 3 and Table S3).

Figure 12 shows the spatial distribution of TNO₃ dry and wet deposition for 1 February-15 March 2015 as calculated in the Improved GEOS-Chem simulation. Dry deposition of TNO₃ is dominated by HNO₃ (Table 3, Figure 12a) and follows the spatial distribution of surface HNO₃, which displays relatively uniform concentrations (Figure 7b) and hence uniform dry deposition fluxes throughout the eastern US. Wet deposition of TNO₃ follows the distribution of precipitation, which is enhanced along the Appalachian Mountains (Figure 12b). Figure 12c compares the observed HNO₃+pNO₃⁻ wet deposition flux at NADP/NTN sites to the Improved simulation, showing that on average the GEOS-Chem model overestimate deposition by 19%, in line with our findings of a 20-30% overestimate in HNO₃ concentrations both based on ground based observations and aircraft observations. The Reference simulation displays a larger positive bias of 37% for wet deposition (not shown). The Improved simulation reproduces the maximum in wet deposition observed over upstate New York. Table 3 also lists the ammonia (NH₃) and ammonium aerosol (NH₄⁺) deposition fluxes, which contribute to 27% of the total nitrogen deposition fluxes. The spatial distribution of the total nitrogen deposition flux shows nearly equal contributions of wet and dry deposition fluxes over land, but a dominant role for wet deposition over the ocean (Figure S2).

4 Conclusions

In this work, we have presented a detailed analysis of the chemistry and budget of reactive nitrogen species in the lower troposphere over the NE US, using observations from the WINTER aircraft campaign, concurrent surface observations, and the GEOS-Chem chemical transport model. We found a factor of 2 underestimate of aircraft and ground-based observations of HCHO, which can be eliminated with a five-fold increase in primary emissions of HCHO in the
NEI emission inventory, potentially associated with an underestimate in primary HCHO from cold start mobile emissions and residential wood combustion. Past studies conducted during summer or warm U.S. regions, have reported very large overestimates of NO\textsubscript{x} emissions in the NEI inventory. Unlike these studies, we found that the NEI NO\textsubscript{x} emission inventory is consistent with WINTER \textsuperscript{1}NO\textsubscript{y} to within better than 10%. This suggests potential issues with the NEI seasonal dependence of anthropogenic NO\textsubscript{x} emissions or a bias in the models’ representations of summertime PBL mixing and/or chemistry. Furthermore, based on observed CO/NO\textsubscript{y} enhancement ratios, we found that the NEI inventory overestimates CO emissions by 60-90% over the NE US.

Updates to the dry deposition velocity, to \(\gamma(\text{N}_2\text{O}_3)\), including its dependence on nitrate and organic aerosol, and a good representation of PM\textsubscript{i} pH result in a significant reduction of the long-standing HNO\textsubscript{3} and pNO\textsubscript{3}\textsuperscript{-} overestimate in GEOS-Chem. For ground-based observations, the model HNO\textsubscript{3} bias is reduced from +168% to +20%, while the pNO\textsubscript{3}\textsuperscript{-} bias is reduced from +64% to +30%. For aircraft observations, the HNO\textsubscript{3} and pNO\textsubscript{3}\textsuperscript{-} bias is reduced by a factor of 2 (down to 73% and 17%, respectively). The remaining overestimate HNO\textsubscript{3} and pNO\textsubscript{3}\textsuperscript{-}, combined with a 25-50% underestimate in NO\textsubscript{x}, N\textsubscript{2}O\textsubscript{5}, and ClNO\textsubscript{2} could be due to a combination of three potential factors: i) too low values for \(\phi(\text{ClNO}_2)\); ii) a suppression of \(\gamma(\text{N}_2\text{O}_3)\) on solid or semi-solid aerosol particles or on internally mixed inorganic and organic particles; iii) an overestimate of the daytime production of HNO\textsubscript{3} via OH+NO\textsubscript{2}. In order to resolve these remaining issues, wintertime measurements of HO\textsubscript{x} and H\textsubscript{2}O\textsubscript{2} as well as particle hygroscopicity or morphology would be necessary in addition to the suite of detailed NO\textsubscript{y} and aerosol speciation measurements obtained during WINTER.

The slow rate of NO\textsubscript{x} oxidation chemistry during winter results in a 22-hour lifetime over the NE US, and half of \textsuperscript{1}NO\textsubscript{y} present as NO\textsubscript{3} below 1 km altitude over the NE US with the remaining 37% as HNO\textsubscript{3}+pNO\textsubscript{3}\textsuperscript{-} and 13% mostly as PAN. Nighttime heterogeneous uptake of N\textsubscript{2}O\textsubscript{5} accounts for 58% of NO\textsubscript{x} chemical loss, while daytime reaction of NO\textsubscript{2} with OH leads to 33% of the loss. We find a 42% export efficiency of NO\textsubscript{y} emissions from the NE US, mostly in the form of NO\textsubscript{x} and HNO\textsubscript{3}+pNO\textsubscript{3}\textsuperscript{-}. Over land in the NE US, wet and dry deposition accounts for 55% and 45% of the NO\textsubscript{y} deposition flux, respectively, with 94% of \textsuperscript{1}NO\textsubscript{y} deposition associated with HNO\textsubscript{3} and pNO\textsubscript{3}\textsuperscript{-}.

The extensive WINTER airborne observations targeted emissions and their chemical transformation within the boundary layer, in a specific region and season, with flights encompassing both daytime and nighttime. This provides a model for future aircraft campaigns aimed at different seasons and regions. The chemical and dynamical processes taking place in the boundary layer remain missing links in our understanding of the fate of pollutants within the first few hour-days after they are being emitted.

Acknowledgments

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The authors would like to thank the NSF-NCAR Research Aircraft Facility engineers, scientists, pilots and staff members.

References


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Macintyre, H. L. & Evans, M. J. (2010). Sensitivity of a global model to the uptake of N$_2$O$_5$ by tropospheric aerosol *Atmospheric Chemistry and Physics*, 10, 7409-7414. https://doi.org/10.5194/acp-10-7409-2010


levoglucosan and aerosol mass spectrometer \( \Delta C_2H_4O_2^+ \) and m/z 60. *Journal of Geophysical Research: Atmospheres*, under review.


**Table 1.** Instruments onboard the C-130 aircraft during WINTER used for this study.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Time resolution</th>
<th>Accuracy</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>1 s</td>
<td>3%</td>
<td>CRDS²</td>
<td>Fuchs et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>1 s</td>
<td>10%</td>
<td>TD-LIF³</td>
<td>Wooldridge et al. (2010)</td>
</tr>
<tr>
<td>NO</td>
<td>1 s</td>
<td>4%</td>
<td>CRDS²</td>
<td>Fuchs et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>1 s</td>
<td>10%</td>
<td>Chemiluminescence</td>
<td>Weinheimer et al. (1994)</td>
</tr>
<tr>
<td>N₂O₃</td>
<td>1 s</td>
<td>12%</td>
<td>CRDS²</td>
<td>Dubé et al. (2006)</td>
</tr>
<tr>
<td>ClNO₂</td>
<td>1 s</td>
<td>30%</td>
<td>ToF-CIMS⁴</td>
<td>Lee et al. (2014, 2018)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>1 s</td>
<td>30%</td>
<td>ToF-CIMS⁴</td>
<td>Lee et al. (2014, 2018)</td>
</tr>
<tr>
<td>pNOₓ(&lt;1 μm)</td>
<td>1 s and 1 min</td>
<td>34%</td>
<td>HR-ToF-AMS⁵</td>
<td>DeCarlo et al. (2006); Schroder et al. (2018)</td>
</tr>
<tr>
<td></td>
<td>3 min</td>
<td>20%</td>
<td>PILS-IC⁶</td>
<td>Guo et al. (2016)</td>
</tr>
<tr>
<td>ΣPNs⁷</td>
<td>1 s</td>
<td>10%</td>
<td>TD-LIF²</td>
<td>Wooldridge et al. (2010)</td>
</tr>
<tr>
<td>ΣANs⁷</td>
<td>1 s</td>
<td>25%</td>
<td>TD-LIF²</td>
<td>Wooldridge et al. (2010)</td>
</tr>
<tr>
<td>NOᵧ</td>
<td>1 s</td>
<td>12%</td>
<td>CRDS²</td>
<td>Wild et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>1 s</td>
<td>50%</td>
<td>Chemiluminescence</td>
<td>Weinheimer et al. (1994)</td>
</tr>
<tr>
<td>HONO</td>
<td>1 s</td>
<td>50%</td>
<td>ToF-CIMS²</td>
<td>Lee et al. (2014, 2018)</td>
</tr>
<tr>
<td>O₃</td>
<td>1 s</td>
<td>4%</td>
<td>CRDS²</td>
<td>Washenfelder et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>1 s</td>
<td>5%</td>
<td>Chemiluminescence</td>
<td>Weinheimer et al. (1994)</td>
</tr>
<tr>
<td>CO</td>
<td>1 s</td>
<td>3%</td>
<td>UV fluorescence</td>
<td>Gerbig et al. (1999)</td>
</tr>
<tr>
<td>HCHO</td>
<td>1 s</td>
<td>10%</td>
<td>Laser induced fluorescence</td>
<td>Carzola et al. (2015)</td>
</tr>
</tbody>
</table>

¹Time resolution of reported observations. For this work all observations are averaged over a 1-min timestep.
²Cavity Ring-Down Spectrometer (CRDS).
³Thermal Dissociation-Laser Induced Fluorescence (TD-LIF).
⁴Time-of-Flight Chemical Ionization Mass Spectrometer (ToF-CIMS).
⁵High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS).
⁶Particle-into-Liquid Sampler - Ion Chromatography (PILS-IC).
⁷Total peroxynitrates RO₂NO₂ (ΣPNs) and total alkyl nitrates RONO₂ (ΣANs).
Table 2. NOx budget over the Northeast United States\textsuperscript{1} for 1 February-15 March 2015 in the Improved GEOS-Chem simulation

<table>
<thead>
<tr>
<th>Budget term</th>
<th>Northeast U.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface NOx emissions\textsuperscript{2}, Mmol d\textsuperscript{-1}</strong></td>
<td>225.0</td>
</tr>
<tr>
<td><strong>NOx chemical loss, Mmol d\textsuperscript{-1}</strong></td>
<td>176.1</td>
</tr>
<tr>
<td>(\text{N}_2\text{O}_5\text{aerosols})</td>
<td>103.7 (58%)</td>
</tr>
<tr>
<td>(\text{NO}_2\text{+OH})</td>
<td>56.9 (33%)</td>
</tr>
<tr>
<td>(\text{NO}_2\text{+aerosols/NO}_3\text{+VOCs})</td>
<td>3.9 (2%)</td>
</tr>
<tr>
<td>PNs production</td>
<td>9.6 (6%)</td>
</tr>
<tr>
<td>ANs production</td>
<td>2.0 (1%)</td>
</tr>
</tbody>
</table>

**Dry Deposition, Mmol d\textsuperscript{-1}**

| NOx | 6.0 |
| HNO\textsubscript{3} | 67.0 |
| pNO\textsubscript{3}\textsuperscript{-} | 5.2 |
| PNs | 1.5 |
| ANs | 0.4 |

**Wet Deposition, Mmol d\textsuperscript{-1}**

| HNO\textsubscript{3} | 40.3 |
| pNO\textsubscript{3}\textsuperscript{-} | 12.6 |
| ANs | 0.1 |

**Net Export\textsuperscript{3}, Mmol d\textsuperscript{-1}**

| NOx | 35.9 |
| HNO\textsubscript{3}+ pNO\textsubscript{3}\textsuperscript{-} | 37.7 |
| PNs | 13.8 |
| ANs | 2.3 |
| ClNO\textsubscript{2} | 4.5 |

**Lifetimes\textsuperscript{4}, days**

| NOx | 0.91 |
| HNO\textsubscript{3}+ pNO\textsubscript{3}\textsuperscript{-} | 0.95 |
| PNs | 22.9 |
| ANs | 16.2 |
| ClNO\textsubscript{2} | 0.43 |

**Burden, Mmol**

| NOx | 166.5 |
| HNO\textsubscript{3} | 71.2 |
| pNO\textsubscript{3}\textsuperscript{-} | 53.2 |
| PNs | 34.4 |
| ANs | 8.2 |
| ClNO\textsubscript{2} | 3.5 |

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\textsuperscript{1}In this Table, NOx is defined as \(\text{NO}_x = \text{NO}+\text{NO}_2+\text{NO}_3+2\text{N}_2\text{O}_5+\text{HONO}+\text{HNO}_4\).

\textsuperscript{2}The Northeast U.S. is defined as 35º-45ºN; 88.75º-65ºW; 0-1.6 km, including both land and water.

\textsuperscript{3}NOx emissions include shipping emissions in coastal waters.

\textsuperscript{4}Net export refers to net transport out of the domain (including horizontal and vertical transport). It is defined as positive for a net flux out.

\textsuperscript{5}The NOx lifetime is defined against chemical loss and deposition, the lifetime of ClNO\textsubscript{2} is defined against photolysis, while the lifetimes for other species is defined with respect to deposition.
Table 3. Nitrogen deposition (in Mg N/month) over land over the Northeast United State for February-15 March 2015 in the Improved GEOS-Chem simulation

<table>
<thead>
<tr>
<th>Deposition process</th>
<th>Northeast U.S.¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet HNO₃</td>
<td>23.3</td>
</tr>
<tr>
<td>Dry HNO₃</td>
<td>18.6</td>
</tr>
<tr>
<td>Wet pNO₃⁻</td>
<td>5.3</td>
</tr>
<tr>
<td>Dry NO₂</td>
<td>2.0</td>
</tr>
<tr>
<td>Dry pNO₃⁻</td>
<td>1.6</td>
</tr>
<tr>
<td>Dry PNs</td>
<td>0.48</td>
</tr>
<tr>
<td>Dry N₂O₅</td>
<td>0.30</td>
</tr>
<tr>
<td>Dry ANs</td>
<td>0.12</td>
</tr>
<tr>
<td>Wet ANs</td>
<td>0.04</td>
</tr>
<tr>
<td>Total NO₃ Wet Deposition</td>
<td>28.6</td>
</tr>
<tr>
<td>Total NO₃ Dry Deposition</td>
<td>23.1</td>
</tr>
<tr>
<td><strong>Total NO₃ Deposition</strong></td>
<td><strong>51.7</strong></td>
</tr>
<tr>
<td>Wet NH₄⁺</td>
<td>13.0</td>
</tr>
<tr>
<td>Dry NH₃</td>
<td>2.8</td>
</tr>
<tr>
<td>Dry NH₄⁺</td>
<td>2.8</td>
</tr>
<tr>
<td>Wet NH₃</td>
<td>0.9</td>
</tr>
<tr>
<td>Total NHₓ Wet Deposition</td>
<td>13.9</td>
</tr>
<tr>
<td>Total NHₓ Dry Deposition</td>
<td>5.6</td>
</tr>
<tr>
<td><strong>Total NHₓ Deposition</strong></td>
<td><strong>19.5</strong></td>
</tr>
</tbody>
</table>

¹ The Northeast U.S. is defined as the land area bounded by 35°-45°N; 88.75°-65°W.
Figure 1. Surface NO\textsubscript{x} emissions over the Eastern U.S. for 1 February to 15 March 2015. The WINTER NSF/NCAR C-130 flights tracks are shown in purple. The blue box delineates the Northeast U.S. domain, which we define as the region bounded by 35\textdegree-45\textdegree N and 88.75\textdegree-65\textdegree W.
Figure 2. Comparison between observed and modeled HCHO. Top panels: Mean surface mixing ratio of HCHO for 1 February-31 March 2015 calculated with the (a) Reference and (b) Improved GEOS-Chem simulations. The color-filled symbols show surface observations from the EPA for the same period. (c) Scatter plot between modeled and observed HCHO. The model is sampled at the location of the observations and on the days when observations are collected. Dark gray shows the Reference model and red show the Improved model. The solid lines indicate the reduced-major-axis regression lines. The Normalized Mean Bias (NMB) and slope are given on the insert. (d) Vertical profile of observed and modeled HCHO during the WINTER campaign. The filled circles and error bars are the means and standard deviations of the observations. The NMB corresponds to observations below 1 km altitude.
Figure 3. Spatial distribution of $\gamma$(N$_2$O$_5$) and $\phi$(ClNO$_2$) at 0.6 km altitude (950 hPa) averaged over 1 February to 15 March 2015. (a) $\gamma$(N$_2$O$_5$) in the Reference simulation. (b) $\gamma$(N$_2$O$_5$) in the Improved simulation with the Bertram & Thornton (2009) parameterization on SNA aerosols as a function of LWC, pNO$_3^-$, and pCl$^-$ and the RH dependent $\gamma$(N$_2$O$_5$) on OA from Badger et al. (2006). (c) $\phi$(ClNO$_2$) in the Improved simulation.
Figure 4. Mean vertical profiles of O$_3$, CO, aerosol surface area, $^\text{TNO}_y$ (=NO$_y$+pNO$_3$), NO$_x$, HNO$_3$, pNO$_3^-$, $\sum$PNs, N$_2$O$_5$, ClNO$_2$, and HONO observed (filled circles with error bars indicating the standard deviation) during WINTER and simulated with GEOS-Chem (gray lines for the Reference simulation, red lines for the Improved simulation). We show only nighttime (defined as SZA>90°) profiles for N$_2$O$_5$, ClNO$_2$, and HONO. For the aerosol surface area profiles, we display the median profiles and quartiles instead of the means and standard deviations.
Figure 5. Spatial distribution of $^7$NO$_y$ (NO$_y$+pNO$_3^-$, top panels), NO$_x$ (middle panels) and NO$_x$/^7NO$_y$ (bottom panels) observed during the WINTER campaign and simulated with Improved GEOS-Chem for altitudes within 1 km of the ground. The observations are averaged over the model grid, and the model is sampled at the time and location of the aircraft. The mean and standard deviations of the mixing ratios are shown in the insert.
Figure 6. Comparison between modeled and observed NO$_2$ at EPA AQS surface sites in the NE US for 1 February-15 March 2015 at 14:00-18:00 local time. The Improved GEOS-Chem simulation is sampled at the location of the observations and on the days when observations are collected. There are 93 sites with more than 75% daily coverage of observations for this time period. The NMB and slope are shown in the insert. We also indicate the NMB for the 16 rural sites (green), the 38 suburban sites (orange), and 39 urban sites (purple).
Figure 7. Surface concentrations of HNO$_3$ (top row) and pNO$_3^-$ (bottom row) measured at CASTNET, IMPROVE, and CSN sites and simulated with GEOS-Chem for 1 February to 15 March 2015. The spatial distribution of surface observations (colored symbols) is compared to the Reference (a,d) and to the Improved (b, e) GEOS-Chem simulations. The right panels show scatter plots of simulated versus observed values at individual sites. Correlation coefficients (r), normalized mean biases (NMB), and the slopes of the reduced-major-axis regression lines are listed for the Reference (gray) and Improved (red) simulations. The reduced-major-axis regression line (solid lines) and the 1:1 lines (dashed line) are also shown.
Figure 8. Spatial distribution of HNO₃ (top panels) and pNO₃⁻ (bottom panels) observed during the WINTER campaign and simulated with GEOS-Chem for altitudes within 1 km of the ground. The observations are averaged over the model grid, and the model is sampled at the time and location of the aircraft. The mean and standard deviations of the concentrations are shown in the insert.
Figure 9. Observed and modeled partitioning of NO$_z$ ($=^{TN}_NO_T-NO_x$) during daytime flight RF02 on 6 February 2015. Timeseries of HNO$_3$, pNO$_3^-$, $\sum$PNs, and NO$_z$ are shown for a) observations, b) the Reference simulation, and c) the Improved simulation. For each panel the sum of HNO$_3$, pNO$_3^-$, $\sum$PNs is also indicated. The insert in the left panel shows the flight path, with the part highlighted in red corresponding to the timeseries shown. The altitude of the C-130 is shown with the grey line in panel c).

Figure 10. Observed and modeled partitioning of NO$_z$ ($=^{TN}_NO_T-NO_x$) during sunrise flight RF08 on 1 March 2015 (flight track shown in panel a, with timeseries corresponding to the red part of the track). Timeseries of HNO$_3$, pNO$_3^-$, $\sum$PNs, 2N$_2$O$_5$, and CINO$_2$ and NO$_z$ for a) observations, b) the Reference simulation, and c) the Improved simulation. For each panel the sum of individual NO$_z$ species (sum= HNO$_3$+pNO$_3^-+\sum$PNs+2N$_2$O$_5$+CINO$_2$+HONO) is also indicated. Bottom panels: Same as top panels, but for 2N$_2$O$_5$, CINO$_2$, and HONO. The reactive uptake coefficient for N$_2$O$_5$ ($\gamma_{N2O5}$) is shown in orange (right axis). The values of $\gamma_{N2O5}$ in panel d) are from the box modeling analysis of McDuffie et al. (2018) constrained by WINTER observations, while panels e) and f) correspond to the Reference and Improved GEOS-Chem simulations. The altitude of the C-130 is shown with the grey line in panel c).
Figure 11. NOx budget for the NE US boundary layer (defined as 35-45°N, 89-65°E, 0-1.7 km) simulated by the Improved GEOS-Chem model during 1 February to 15 March 2015. For each species, we indicate its inventory (in Mmoles, with 1 Mmole=10^6 moles) and lifetime in parenthesis (in hours or days). In this figure, NOx is defined as NOx = NO+NO2+NO3+2N2O5+HONO+HNO4. Fluxes are given in Mmoles d⁻¹. The lifetime of NOx is defined with respect to chemical loss and deposition, the lifetime of CINO2 with respect to photolysis, and the lifetime of the other species with respect to deposition. For HNO3+pNO3⁻+CINO2⁺PNs+ANs, we give the overall fluxes due to dry deposition, wet deposition, and transport to the free troposphere as well as the individual fluxes (in grey).
Figure 12. GEOS-Chem mean monthly $\text{NO}_x$ (a) dry deposition and (b) wet deposition fluxes in the Improved Simulation for the period of the WINTER experiment (1 February – 15 March, 2015) in units of kg N ha$^{-1}$ month$^{-1}$. Also shown on panel (b) are the weekly NADP/NTN HNO$_3$+pNO$_3^-$ wet deposition flux observations for that period. (c) Scatter plot of modeled and observed HNO$_3$+pNO$_3^-$ wet deposition.