Surface ozone and its precursors at Summit, Greenland: comparison between observations and model simulations

Yaoxian Huang1,a, Shiliang Wu1,2,3, Louisa J. Kramer1,2,b, Detlev Helmig4, and Richard E. Honrath1,2,†

1Department of Geological and Mining Engineering and Sciences, Michigan Technological University, Houghton, Michigan, USA
2Atmospheric Sciences Program, Michigan Technological University, Houghton, Michigan, USA
3College of Environmental Science and Engineering, Ocean University of China, Qingdao, China
4Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado, USA
a now at: Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, Michigan, USA
b now at: School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, UK
† deceased

Correspondence to: Shiliang Wu (slwu@mtu.edu) and Yaoxian Huang (yaoxianh@mtu.edu)

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Abstract. Recent studies have shown significant challenges for atmospheric models to simulate tropospheric ozone (O₃) and its precursors in the Arctic. In this study, ground-based data were combined with a global 3-D chemical transport model (GEOS-Chem) to examine the abundance and seasonal variations of O₃ and its precursors at Summit, Greenland (72.34° N, 38.29° W; 3212 m a.s.l.). Model simulations for atmospheric nitrogen oxides (NOₓ), peroxyacetyl nitrate (PAN), ethane (C₂H₆), propane (C₃H₈), carbon monoxide (CO), and O₃ for the period July 2008–June 2010 were compared with observations. The model performed well in simulating certain species (such as CO and C₃H₈), but some significant discrepancies were identified for other species and further investigated. The model generally underestimated NOₓ and PAN (by ∼ 50 and 30 %, respectively) for March–June. Likely contributing factors to the low bias include missing NOₓ and PAN emissions from snowpack chemistry in the model. At the same time, the model overestimated NOₓ mixing ratios by more than a factor of 2 in wintertime, with episodic NOₓ mixing ratios up to 15 times higher than the typical NOₓ levels at Summit. Further investigation showed that these simulated episodic NOₓ spikes were always associated with transport events from Europe, but the exact cause remained unclear. The model systematically overestimated C₂H₆ mixing ratios by approximately 20 % relative to observations. This discrepancy can be resolved by decreasing anthropogenic C₂H₆ emissions over Asia and the US by ∼ 20 %, from 5.4 to 4.4 Tg year⁻¹. GEOS-Chem was able to reproduce the seasonal variability of O₃ and its spring maximum. However, compared with observations, it underestimated surface O₃ by approximately 13 % (6.5 ppbv) from April to July. This low bias appeared to be driven by several factors including missing snowpack emissions of NOₓ and nitrous acid in the model, the weak simulated stratosphere-to-troposphere exchange flux of O₃ over the summit, and the coarse model resolution.

1 Introduction

Tropospheric ozone (O₃) and its precursors, including nitrogen oxides (NOₓ = NO + NO₂), carbon monoxide (CO), and volatile organic compounds (VOCs, such as ethane and propane), are important atmospheric species affecting both air quality and climate (e.g., Jacob et al., 1992; Fiore et al., 2002; Unger et al., 2006; Hollaway et al., 2012). Tropospheric O₃ is mainly produced through the photochemical oxidation of CO and VOCs in the presence of NOₓ, with an
additional contribution by transport from the stratosphere. Its major sinks include chemical reactions and dry deposition. As a reservoir species for \( \text{NO}_x \), peroxyacetyl nitrate (PAN) also plays an important role in atmospheric chemistry. PAN, \( \text{O}_3 \), and some of their precursors have relatively long lifetimes in the atmosphere, enabling them to be transported long distances to remote regions such as the Arctic.

Recent studies have shown some significant challenges for atmospheric chemical transport models to simulate \( \text{O}_3 \) and its precursors in the Arctic (e.g., Shindell et al., 2008; Alvarado et al., 2010; Walker et al., 2012; Wespes et al., 2012; Fischer et al., 2014; Monks et al., 2015), but the causes remain unclear. In the multi-model assessment by Shindell et al. (2008), more than a dozen models all showed systematic and persistent underestimation of \( \text{O}_3 \) at the GEOSummit station in Greenland (hereafter referred to as Summit). Alvarado et al. (2010) used \( \text{NO}_x \) and PAN measurements from the ARCTAS (Arctic Research of the Composition of the Troposphere from Aircraft and Satellites) mission in the summer to compare with model simulations. They found that model-simulated \( \text{NO}_x \) mixing ratios were higher than observations, while PAN mixing ratios were lower than the observations in fresh boreal fire plumes. In terms of global PAN simulations, Fischer et al. (2014) directly partitioned 40% of \( \text{NO}_x \) emissions from wildfires to PAN formation, which improved the agreement between the model and observations. However, the model still underestimated PAN surface mixing ratios during springtime in the Arctic. Walker et al. (2012) reported that model-simulated \( \text{O}_3 \) mixing ratios were biased low when compared with balloon data during summertime from two high-latitude sites at Eureka (80°N, 86°W) and Ny-Alesund (79°N, 12°E). Wespes et al. (2012) also revealed that model-simulated \( \text{O}_3 \) mixing ratios within the boundary layer were significantly underestimated during spring–summer compared with ARCTAS measurements. More recently, Monks et al. (2015) further demonstrated that model-simulated \( \text{O}_3 \) mixing ratios in the Arctic at the surface and in the upper troposphere were generally lower than the observations. In addition, a recent study by Christian et al. (2017) compared \( \text{O}_3 \) observations from the ARCTAS campaign to GEOS-Chem model simulations and found consistent low biases with the model-simulated \( \text{O}_3 \) at all altitudes except the surface.

Field measurements at Summit show that the snowpack emits gas-phase \( \text{NO}_x \), PAN, nitrous acid (HONO), and hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) during spring–summer when the solar sun rises (Ford et al., 2002; Honrath et al., 2002). Although several 1-D models (Thomas et al., 2011, 2012; Frey et al., 2013; Murray et al., 2015) have validated the importance of snowpack emissions for surface \( \text{NO}_x \) and \( \text{O}_3 \) formation, current global chemical transport models (CTM) usually do not include these emission sources (Zatko et al., 2016).

In this study, we examine the abundance and seasonal variations of \( \text{O}_3 \) and its precursors at Summit with a global chemical transport model, GEOS-Chem CTM, in conjunction with 2 years of in situ measurement data for 2008–2010. We first evaluate the model performance in simulating surface \( \text{O}_3 \) and its precursors and then implement a series of model updates to resolve the identified model biases. This paper is organized as follows: Sect. 2 describes model methods and observations, followed by detailed comparisons of model simulations against observations for \( \text{O}_3 \) and \( \text{O}_3 \) precursors in Sect. 3; conclusions are summarized in Sect. 4.

2 Observational data and model simulations

In situ measurements of \( \text{NO}_x \), PAN, and non-methane hydrocarbons (NMHCs) were performed at Summit from July 2008 to June 2010 (Helmg et al., 2014b; Kramer et al., 2015). An automated chemiluminescence instrument was used to measure \( \text{NO}_x \) (Ridley and Grahek, 1990), and a commercial PAN gas chromatography analyzer (PAN-GC; Metcon, Inc., Boulder, CO, USA) was employed for the measurement of PAN. Measurements of NMHC relied on an automated gas chromatography–flame ionization detection (GC-FID) system. Readers are referred to Kramer et al. (2015) and Helmg et al. (2014b) for the details of the measurement techniques and equipment setup. In situ surface measurements of \( \text{O}_3 \) at Summit using an ultraviolet light absorption technique (Petropavlovskikh and Oltmans, 2012) and CO data from weekly flask sampling with analysis by using a GC–HgO reduction detection instrument (Novellie et al., 2003) and an analyzer based on CO fluorescence in the ultraviolet vacuum (Gerbig et al., 1999) were conducted by the National Oceanic and Atmospheric Administration (NOAA) and downloaded from the NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) website (http://www.esrl.noaa.gov/gmd/dv/data/) for the periods between July 2008 and June 2010. Vertical ozonesonde data profiles were also downloaded from NOAA ESRL GMD (McClure-Begley et al., 2014).

Simulations of \( \text{O}_3 \) and related species (\( \text{NO}_x \), PAN, NMHCs) were conducted using the GEOS-Chem model (Bey et al., 2001) with a coupled \( \text{O}_3–\text{NO}_x–\text{VOC}–\text{aerosol} \) chemistry mechanism (i.e., these species interact with each other in the model). The GEOS-Chem CTM is driven by assimilated meteorological data from the Goddard Earth Observing System version 5.2.0 (GEOS-5.2.0) of the NASA Global Modeling Assimilation Office. The GEOS-Chem model has been extensively evaluated and applied in a wide range of applications (Martin et al., 2002; Park et al., 2004; Wu et al., 2007; Hudman et al., 2009; Johnson et al., 2010; Huang et al., 2013; Kumar et al., 2013; Zhang et al., 2014; Hickman et al., 2017), including studies in the Arctic (e.g., Alvarado et al., 2010; Monks et al., 2015; Christian et al., 2017). GEOS-Chem v10-1, with a grid resolution of 4° latitude by 5° longitude and 47 vertical layers, was used for the...
Figure 1. Box plot comparison for seasonal variations in (a) NO$_x$, (b) PAN, (c) C$_2$H$_6$, (d) C$_3$H$_8$, (e) CO, and (f) O$_3$ between GEOS-Chem model simulations (red) and measurements (blue) at Summit for the period July 2008–June 2010. Data shown are monthly averages during this period. The thick (thin) bars represent the 67% (95%) confidence intervals. Black and green dots represent median and mean values, respectively. The statistics are based on daily averages.

Table 1. Surface NO$_2$ measurements over Europe during 1 December 2009–31 January 2010.

<table>
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<tr>
<th>Site ID</th>
<th>Site name</th>
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<th>Lon. ($^\circ$ E)</th>
<th>Altitude a.s.l (m)</th>
<th>Technique</th>
<th>Resolution</th>
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<tr>
<td>NO0056R</td>
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<td>404</td>
<td>abs_tube</td>
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</table>
model control simulation. Following McLinden et al. (2000), the Linoz stratospheric O$_3$ chemistry scheme was used. The simulation was run from June 2007 to June 2010, and the results from the last 2 years were used in the final analysis. Time series data were archived with 3 h temporal resolution at the Summit grid box for each model vertical level, including the model bottom layer. For comparison with surface observations at Summit, Greenland, we sampled the data for the model bottom layer. We acknowledge that the topography in GEOS-Chem model is not well resolved at such a coarse model resolution (4° latitude by 5° longitude), and we used the model bottom layer at the Summit grid cell for O$_3$ and its precursor concentrations to compare with surface observations, which worked better than sampling O$_3$ and its precursor concentrations at the model vertical layer at about 3212 m a.s.l. (above the sea level; Summit’s elevation).

Global anthropogenic emissions of NO$_x$, SO$_2$, NH$_3$, and CO in the model were based on the Emission Database for Global Atmospheric Research (EDGAR) v4.2 inventory, which was overwritten by regional emission inventories where applicable, such as the BRAVO inventory for Mexico (Kuhns et al., 2005), the CAC over Canada, the EMEP emissions over Europe, the Model Inter-comparison Study for Asia Phase III (MIX) emissions over Asia (Li et al., 2017), and the US EPA NEI 2011 (NEI11) emission inventory (Simon et al., 2010). The soil NO$_3$ emission scheme followed Hudman et al. (2012). Lightning NO$_x$ emissions were calculated per flash rate based on GEOS-5 computed cloud-top heights (Price and Rind, 1992), which were determined by deep convection and constrained by satellite observations for monthly average flash rates from the Lightning Imaging Sensor and Optical Transient Detector (OTD/LIS; Sauvage et al., 2007; Murray et al., 2012). Biomass burning emissions were from the Global Fire Emissions Database version 4 (GFED4) inventory with monthly resolution (Giglio et al., 2013). The RETRO (Reanalysis of the TROpospheric chemical composition) global anthropogenic NMHC emission inventory (van het Bolscher et al., 2008) was used except for ethane (C$_2$H$_6$) and propane (C$_3$H$_8$), which followed Xiao et al. (2008, hereafter referred to as X08) for the year 2001. In GEOS-Chem, RETRO served as the default global anthropogenic emission inventory for C$_2$H$_6$, the annual budget of which has been shown to show lower compared with observations. The global biofuel emission inventory followed Yevich and Logan (2003), which included emissions for C$_2$H$_6$ and C$_3$H$_8$. For biogenic VOC emissions, the Model of Emissions of Gases and Aerosols from Nature (MEGAN) scheme (Guenther et al., 2006) was used. The dry deposition of species in GEOS-Chem used a standard resistance-in-series scheme (Wesely, 1989), as implemented in Wang et al. (1998). Wet scavenging followed Liu et al. (2001), including scavenging in convective updraft, rainout (in-cloud), and washout (below-cloud) from convective anvils and large-scale precipitation.

We first ran the standard GEOS-Chem model with a priori emissions and compared the simulation results against observations for various species (including NO$_x$, PAN, C$_2$H$_6$, C$_3$H$_8$, CO, and O$_3$, as shown in Fig. 1). Then we focused on the model–observation discrepancies and where applicable made revisions to the model simulations and further evaluated the improvement in model performance, as discussed in detail below.

3 Results and discussion

3.1 NO$_x$

We first combined the 2 years of data for July 2008–June 2010 and analyzed their seasonal variations. As shown in Fig. 1a, the GEOS-Chem model-simulated NO$_x$ agrees well with the observations for July–October. However, compared to observations, the model results significantly overestimate NO$_x$ mixing ratios for November–January by about 150% while underestimating the data in spring and early summer by approximately 60%. Another challenge for the model simulation is that it does not capture the decrease in NO$_x$ for May–November. We find that during the 2009–2010 winter season, model simulations show several high NO$_x$ spikes with peak NO$_x$ mixing ratios reaching ~0.15 ppbv or higher, which is ~15 times greater than typical background levels (Fig. 2). These large peaks in NO$_x$ were not observed in the data. Similar peaks were also seen in the model simulations during the 2008–2009 winter season; however, there are no measurements available for this period to compare with.
Following EDGAR v4.2 (EURO_EDGAR), with other model configurations identical to control simulations. As shown in Fig. 2, the NO\textsubscript{x} mixing ratios over Summit during December 2009–January 2010 agreed much better with observations, especially for January 2010 when the model captured the magnitudes of observational peaks. This is because NO\textsubscript{x} emissions from EDGAR over Europe (1.97 Tg NO) were 12% lower than those from EMEP (2.24 Tg NO) for the months of December 2009 and January 2010. Furthermore, the discrepancy for the differences in surface NO\textsubscript{2} mixing ratios over Europe between EURO_EDGAR and observations was further reduced (by 50%) relative to the control runs, with a model-to-observation slope of 0.92 and a correlation coefficient of 0.83 (Fig. 3b). Similarly, we also tested the sensitivity of surface NO\textsubscript{x} mixing ratios over Summit in response to the changes in the anthropogenic NO\textsubscript{x} emissions from NEI11 over the US and MIX over Asia (including Siberia) during these 2 months and found that surface NO\textsubscript{x} mixing ratios over Summit during these 2 months were quite close to the control simulations (not shown), reflecting the insensitivity to emission perturbations from the US and Asia. Therefore, we conclude that uncertainties in fossil fuel NO\textsubscript{x} emissions of EMEP associated with transport events from Europe in the model are the most likely cause for the wintertime NO\textsubscript{x} spikes over Summit.

For April–July, model-simulated monthly mean NO\textsubscript{x} mixing ratios over Summit were a factor of 2 lower than the observations (Fig. 4a). Experiments at Summit by Honrath et al. (1999, 2000a, b, 2002) showed upward fluxes of NO\textsubscript{x} (2.52 × 10\textsuperscript{8} molecules cm\textsuperscript{-2} s\textsuperscript{-1}) from the photolysis of nitrate in snowpack during the summertime, leading to an enhancement of NO\textsubscript{x} levels in the surface layer by approximately 20 pptv, which was comparable to surface NO\textsubscript{x} mixing ratios in the Arctic from other sources. Similar results were found over the East Antarctic Plateau snow and ice sheet (Frey et al., 2013; Legrand et al., 2014). The standard GEOS-Chem model did not include the photolysis of nitrate from snowpack, implying a missing source for NO\textsubscript{x} in the Arctic–Antarctic boundary layer.

In order to test the sensitivity of model-simulated surface NO\textsubscript{x} mixing ratios to the snowpack emissions, we implemented in the model a constant NO\textsubscript{x} flux of ~2.52 × 10\textsuperscript{8} molecules cm\textsuperscript{-2} s\textsuperscript{-1} during April–July over Greenland (60–85° N, 20–60° W), following the measurements conducted at Summit during summertime by Honrath et al. (2002). As a result, we found that on average the model-simulated surface NO\textsubscript{x} mixing ratios for April to July over Summit more than doubled compared to the control simulation, which improved the agreement between the model and observations for April–June (Fig. 4a). However, the assumed NO\textsubscript{x} flux from snowpack in the model led to an overestimation of NO\textsubscript{x} mixing ratios in July, and the model was still not able to reproduce the decreasing trend of NO\textsubscript{x} for May–October. This decreasing trend of NO\textsubscript{x} may be driven by the decreasing NO\textsubscript{x} production rate in snowpack resulting from a gradual depletion of the snowpack NO\textsubscript{x} reservoir.

Further analyses showed that the model-simulated high NO\textsubscript{x} spikes during wintertime were all associated with transport events from Europe. We carried out a sensitivity study to examine the impacts of European emissions on Arctic NO\textsubscript{x} by manually reducing anthropogenic NO\textsubscript{x} emissions from the EMEP emission inventory over Europe by 50% (EMEP50). The results showed that surface peak NO\textsubscript{x} mixing ratios over Summit during the spike events (e.g., dates around 9 and 15 December 2009, 15 and 22 January 2010) from EMEP50 declined almost proportionally by ~50% during 1 December 2009–31 January 2010 (Fig. 2), which confirmed that the modeled NO\textsubscript{x} spikes at Summit during wintertime were associated with transport from Europe. However, the model-simulated NO\textsubscript{x} was still significantly higher than observations. Comparisons for surface NO\textsubscript{2} mixing ratios between model simulations and 11 in situ observational sites over Europe during this period were conducted with data downloaded from http://ebas.nilu.no. For detailed site information and the NO\textsubscript{2} measurement technique and resolution, refer to Table 1. Measurement data over these 2 months for each site were averaged to compare with the corresponding grid cell in the model. As shown in Fig. 3a, GEOS-Chem overestimated surface NO\textsubscript{2} mixing ratios at these sites by over 66% compared with observations (slope = 1.07; correlation coefficient = 0.88).

In addition to using EMEP, we carried out another sensitivity study to force anthropogenic NO\textsubscript{x} emissions over Europe following EDGAR v4.2 (EURO_EDGAR), with other model configurations identical to control simulations. As shown in Fig. 2, the NO\textsubscript{x} mixing ratios over Summit during December 2009–January 2010 agreed much better with observations, especially for January 2010 when the model captured the magnitudes of observational peaks. This is because NO\textsubscript{x} emissions from EDGAR over Europe (1.97 Tg NO) were 12% lower than those from EMEP (2.24 Tg NO) for the months of December 2009 and January 2010. Furthermore, the discrepancy for the differences in surface NO\textsubscript{2} mixing ratios over Europe between EURO_EDGAR and observations was further reduced (by 50%) relative to the control runs, with a model-to-observation slope of 0.92 and a correlation coefficient of 0.83 (Fig. 3b). Similarly, we also tested the sensitivity of surface NO\textsubscript{x} mixing ratios over Summit in response to the changes in the anthropogenic NO\textsubscript{x} emissions from NEI11 over the US and MIX over Asia (including Siberia) during these 2 months and found that surface NO\textsubscript{x} mixing ratios over Summit during these 2 months were quite close to the control simulations (not shown), reflecting the insensitivity to emission perturbations from the US and Asia. Therefore, we conclude that uncertainties in fossil fuel NO\textsubscript{x} emissions of EMEP associated with transport events from Europe in the model are the most likely cause for the wintertime NO\textsubscript{x} spikes over Summit.

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We then examined the model performance for PAN, which serves as a reservoir for NO$_x$. Figure 1b shows the comparison of model-simulated monthly mean PAN mixing ratios with the measurement data. The model captured the seasonal variation of PAN well, although it significantly (by $\sim$30%) underestimated the PAN mixing ratios for April–June. By running the model simulation with higher horizontal resolution at 2$^\circ$ latitude by 2.5$^\circ$ longitude (hereafter referred to as GEOS-Chem 2 × 2.5), we found that the monthly mean PAN mixing ratios over Summit during April–July increased by up to 23.3 pptv compared to the 4 × 5 simulation (Fig. 4b). This can be explained by two factors. First, the coarse model resolution (e.g., 4 × 5 horizontal resolution) could artificially smear the intense emission sources throughout the entire grid cell (e.g., over urban regions), leading to underestimates of downwind concentrations for species like O$_3$ and O$_3$ precursors (Jang et al., 1995; Yu et al., 2016). Second, ventilation in the lower atmosphere could be better resolved by a finer model resolution, leading to more efficient vertical advection (Wang et al., 2004; Chen et al., 2009; Yu et al., 2016). However, on average, the monthly mean model-simulated PAN mixing ratios were still underestimated by 20% during this period compared with observations. This is consistent with the study by Arnold et al. (2015), which reported that model-simulated PAN mixing ratios in GEOS-Chem were lower than ARCTAS observations in the Arctic. Meanwhile, this study also revealed that GEOS-Chem produced less PAN relative to CO in Arctic air parcels that were influenced by fires compared with other models.

Snowpack can emit not only NO$_x$, but also PAN as indicated based on field studies at Summit during summertime by Ford et al. (2002). GEOS-Chem did not contain snowpack PAN emissions and chemistry. For a sensitivity study similar to snowpack NO$_x$ emissions as discussed in Sect. 3.1, we considered a 24 h constant flux of $2.52 \times 10^8$ molecules cm$^{-2}$ s$^{-1}$ of PAN over Greenland from April to July, following Ford et al. (2002). As a result, model-simulated PAN mixing ratios agreed much better with observations (Fig. 4b). Note that there are also other possible factors that lead to model bias. For instance, a study by Fischer et al. (2014) showed improved agreement between modeled and measured PAN in the high latitudes when assigning a portion of the fire emissions in the model above the boundary layer and also directly partitioning 40% of NO$_x$ emissions from fires into PAN. We carried out a sensitivity test with similar treatments, but no significant improvements in the model-simulated surface PAN were observed at the Summit site. Therefore, we did not include the PAN updates from Fischer et al. (2014) in other model simulations in this study.

3.3 NMHC

Comparisons of observed surface C$_2$H$_6$ and C$_3$H$_8$ mixing ratios with GEOS-Chem simulations at Summit are shown in Fig. 1c and d. The model simulations agreed well with surface measurements of C$_2$H$_6$ but systematically overestimated C$_2$H$_6$ (by approximately 25% annually), with the largest bias...
(0.48 ppbv) occurring during summer. This is consistent with the study from Tzompa-Sosa et al. (2017), which used the same model as our study and pointed out that using X08 as a global anthropogenic C₂H₆ emission inventory systematically overestimated surface C₂H₆ mixing ratios over the Northern Hemisphere compared with ground-based observations. Anthropogenic C₂H₆ emissions over the US from NEI11 were shown to geographically match the distribution of active oil and natural wells (Tzompa-Sosa et al., 2017), and the most recent MIX has been updated to synergize anthropogenic C₂H₆ emissions from various countries in Asia (Li et al., 2017). Therefore, instead of using global anthropogenic fossil fuel emissions of C₂H₆ following X08, we first conducted sensitivity simulations by overwriting global emission inventories by NEI11 over the US and MIX over Asia (hereafter referred to as NEI11_MIX). Both NEI11 and MIX contain emissions for the years from 2008 to 2010, which could realistically represent the annual and seasonal variations in C₂H₆ emissions over the US and Asia and thus be spatially and temporally more representative of anthropogenic C₂H₆ emissions from the midlatitudes transported to the Arctic regions. In general, model control simulations overestimated annual mean surface C₂H₆ mixing ratios primarily in the Northern Hemisphere, with large differences occurring over Asia and the US by up to 5 ppbv compared with NEI11_MIX during the period July 2008–June 2010 (Fig. S1 in the Supplement). All the above changes were driven by the substantial reductions of anthropogenic C₂H₆ emissions between emission inventories, from 3.5 (X08) to 2.5 Tg year⁻¹ (MIX) over Asia and from 1.9 Tg year⁻¹ (X08) to 1.4 Tg year⁻¹ (NEI11) over the US, reflecting the decreasing trend of anthropogenic C₂H₆ emissions during 2001–2009 (Helming et al., 2014a) because the X08 emission inventory is based on the year 2001. Substantial changes in surface C₂H₆ mixing ratios over the US between control simulations and NEI11_MIX reflected tempo-spatial changes in C₂H₆ emissions from oil and gas production during the period 2001–2009. A similar pattern was also found by Tzompa-Sosa et al. (2017). In contrast to the control simulations, NEI11_MIX model simulations showed that monthly mean C₂H₆ mixing ratios over Summit were systematically underestimated by 24 % compared with observations (Fig. 5). Tzompa-Sosa et al. (2017) reported that NEI11 C₂H₆ emissions were likely underestimated by 40 % compared with in situ and aircraft observations over the US. We therefore ran a sensitivity simulation by increasing the NEI11 C₂H₆ emissions by 40 % and keeping other model configurations identical to NEI11_MIX (hereafter referred to as NEI11_40_MIX). We found that this update led to an increase in the model-simulated annual mean surface C₂H₆ mixing ratios over Summit by only 6 % during the period July 2008–June 2010 (figure not shown), which still does not explain the high model bias.

Similar to NEI11_MIX, we further conducted sensitivity studies by only replacing the regional emission inventory for C₂H₆ over the US, with other regions still following X08 (hereafter referred to as NEI11_ONLY). Consequently, model-simulated surface C₂H₆ mixing ratios over Summit agreed better with observations during winter–spring (Fig. 5), decreasing the bias from +15 % (control simulations) to +6 %. However, model-simulated C₂H₆ mixing ratios during summer–fall were higher than the observations by over 30 %.

We then scaled up the MIX emissions for C₂H₆ by 20 % over Asia, with other model configurations identical to NEI11_MIX (hereafter referred to as NEI11_MIX20). By doing this, we increased fossil fuel C₂H₆ emissions from 2.5 to 3 Tg year⁻¹. We found that the simulated annual mean surface C₂H₆ mixing ratios at Summit from NEI11_MIX20 agreed quite well with observations (within 1 %). Similarly, better agreement between the model and observations were found for monthly average values for October–January. However, the new simulation was not able to reproduce the seasonal cycle of C₂H₆; the model significantly underestimated C₂H₆ in February–April but overestimated it in June–September (Fig. 5). This implies that further assessments of anthropogenic C₂H₆ emissions from MIX over Asia are needed and a more accurate global anthropogenic C₂H₆ emission inventory should be developed and validated to replace X08 in the future. It should be noted that our modeling
period reflects a time when there was a reversal of the atmospheric C$_2$H$_6$ trend, most likely reflecting emission changes during that time. Atmospheric C$_2$H$_6$ had a decreasing trend from 1980 to 2009 (Simpson et al., 2012; Helmig et al., 2014a) but then began to increase around 2009 (Franco et al., 2015, 2016; Hausmann et al., 2016; Helmig et al., 2016) in the Northern Hemisphere at a rate of increase that is approximately 4–6 times higher than its earlier rate of decline. It has been argued that the most likely cause for this trend and emission reversal is increasing emissions from oil and gas production, mostly from North America (Franco et al., 2015, 2016; Hausmann et al., 2016; Helmig et al., 2016).

None of the considered inventories considered these emission changes and their timing. Also note that this standard version of GEOS-Chem does not account for the sink of C$_2$H$_6$ from the reaction with chlorine, which could reduce the global annual mean surface C$_2$H$_6$ mixing ratios by 0–30 % and the global burden of C$_2$H$_6$ by about 20 % (Sherwen et al., 2016). This omission likely introduces additional uncertainty into our measurement–model comparison together with uncertainty in the seasonality of C$_2$H$_6$ chemistry.

### 3.4 CO

Figure 1e shows the comparison of model-simulated CO mixing ratios with observations over Summit. Overall, the model generally captures the abundance and seasonal variation of CO. Compared with observations, the annual mean CO mixing ratio was slightly overestimated by about 3 ppbv in the model.

### 3.5 O$_3$

Surface O$_3$ mixing ratios from model simulations and surface observations are compared in Fig. 1f. The GEOS-Chem model captured the seasonal variation of O$_3$ including the spring peak. However, the model shows a systematic low bias for most of the year, in particular for April–July when the surface O$_3$ mixing ratios were underestimated by ∼13 % (∼6.5 ppbv). Here we focus our analysis on the possible causes that led to the model low bias during April–July.

As discussed earlier, snowpack emissions due to the photolysis of nitrate in the snow during late spring and summer could contribute to NO$_3^−$ and HONO levels in the ambient air, which could enhance O$_3$ production (Crawford et al., 2001; Zhou et al., 2001; Dibb et al., 2002; Honrath et al., 2002; Yang et al., 2002; Grannas et al., 2007; Helmig et al., 2008; Legrand et al., 2014). We ran a sensitivity study to test the response of surface O$_3$ mixing ratios to the perturbations of NO$_3^−$ and HONO from snowpack emissions. In addition to snowpack NO$_3^−$ emissions that are described in Sect. 3.1, we implemented in the model a constant flux of HONO (4.64 × 10$^7$ molecules cm$^{-2}$ s$^{-1}$) from April to July (Honrath et al., 2002). As a result, monthly mean model-simulated surface O$_3$ mixing ratios increased by up to 3 ppbv during this period (Fig. 6). The largest effect occurred in July due to relatively strong solar radiation. O$_3$ formation due to the snowpack emissions in our study was slightly higher than that in Zatko et al. (2016) because HONO from snowpack emissions was not considered in their study. However, for the months of April and May, surface O$_3$ mixing ratios only increased by ∼1 ppbv compared with the control runs. That is, even after accounting for the snowpack emissions, the model-simulated O$_3$ mixing ratios were still significantly lower than the observations.

A comparison of the model simulations at different resolutions (4×5 vs. 2×2.5) showed that the finer-resolution simulations substantially increased monthly mean O$_3$ mixing ratios over Summit by up to 6 ppbv for the months of June and July (Fig. 6). As discussed in Sect. 3.2, a fine model resolution can better resolve the emission strengths, which could significantly affect downwind chemical reactions like O$_3$ production efficiency (Liang and Jacobson, 2000). Moreover, terrain elevations from fine model resolution are better represented (thus more representative of Summit’s elevation), and more efficient vertical ventilation of O$_3$ and O$_3$ precursors can be achieved (Wang et al., 2004). Together with the impact of snowpack chemistry, this brought model-simulated surface O$_3$ mixing ratios over Summit into better agreement with observations for June–July. However, there was still a low bias in the model for the months of April and May.

Another possible cause for the low O$_3$ biases in model simulations is the calculated stratosphere–troposphere exchange (STE) O$_3$ flux in the model. Liang et al. (2011) have pointed out that STE could be a significant direct source of O$_3$ in the Arctic during spring–summer. We retrieved vertical profiles of O$_3$ mixing ratios and specific humidity from ozonesondes (0–5 km of elevation above the Summit surface)
launched at Summit for the months of June and July 2008 and compared those data with model control runs. Ozonesondes were launched intensively during these 2 months (a total of 19 times). As shown in Fig. 7, compared with observations the model-simulated O₃ mixing ratios averaged over 0–5 km above ground level were underestimated by 3 and 9 % in June and July 2008 (Fig. 7a). However, specific humidity in GEOS-5 was overestimated by 50 and 81 % (Fig. 7b), respectively. Ozonesonde data showed that Summit frequently encountered high O₃ and low water vapor events (e.g., 9–11 July 2008), which were likely of upper tropospheric or stratospheric origin (Helmig et al., 2007), but these were not captured by the model, which implied that GEOS-Chem possibility underestimated STE for O₃ over Summit. This is consistent with the study by Choi et al. (2017), which found low bias with model-simulated O₃ mixing ratios for the upper troposphere of the high-latitude Northern Hemisphere compared with ozonesonde data and attributed the low bias to an underestimated STE in the model.

Misrepresentation of boundary layer height is another factor that could lead to model–data discrepancy in O₃ mixing ratios. The mean springtime afternoon (12:00–14:00 LT, local time) boundary layer height in the model at Summit for the year 2009 was 160 m, which agreed reasonably well with inferred boundary layer heights from vertical balloon soundings (Helmig et al., 2002). Therefore, it is unlikely that model uncertainties in boundary layer height representation in springtime cause the low bias of O₃ mixing ratios between the model and observations.

4 Conclusions

We combined model simulations with 2-year (July 2008–June 2010) ground-based measurements at Summit, Greenland to investigate the abundance and seasonal variations of surface O₃ and related species in the Arctic. In general, the GEOS-Chem model was capable of reproducing the seasonal cycles of NOₓ, PAN, C₂H₆, C₃H₈, CO, and O₃. However, some major discrepancies between the model and observations, especially for NOₓ, PAN, C₂H₆, and O₃, were identified.

There were significant differences between model-simulated NOₓ mixing ratios and observations for the spring and winter seasons. The model underestimated NOₓ mixing ratios by approximately 50 % during late spring to early summer, which was likely due to the missing NOₓ emissions from nitrate photolysis in the snowpack. At the same time, the model overestimated NOₓ mixing ratios by more than a factor of 2 in wintertime. Model simulations indicated episodic but frequent transport events from Europe in wintertime, leading to NOₓ spikes reaching 15 times typical NOₓ mixing ratios at Summit; these large NOₓ spikes were not seen in the observations. We carried out multiple sensitivity model studies but were still unable to fully reconcile this discrepancy.

The model successfully captured the seasonal cycles and the spring maximum PAN mixing ratios, although it underestimated PAN by over 30 % during late spring and early summer. Model sensitivity studies revealed that this discrepancy could be largely resolved by accounting for PAN emissions from snowpack.

For C₂H₆ and CO, model simulations agreed well overall with the surface measurements. However, the model tended to systematically overestimate surface C₂H₆ mixing ratios by ~20 % on annual average compared with observations. This may be explained by the fact that annual emission budgets of C₂H₆ over the US and Asia from the X08 emission inventory were higher than those from NEI11 and MIX by over 40 %. By replacing X08 over the US with NEI11 for C₂H₆ and scaling up MIX by 20 %, the model–observation bias can be resolved, resulting in an annual mean bias of less than 1 %. However, care must be taken in interpreting this result because we did not take into account other factors that might influence the discrepancy in surface C₂H₆ mixing ratios at Summit between the model and observations, such as the C₂H₆ chemistry with chlorine.

GEOS-Chem was able to reproduce the seasonal variation in surface O₃ at Summit but persistently underestimated O₃ mixing ratios by ~13 % (~6.5 ppbv) from April to July.
This low bias was likely caused by a combination of misrepresentations, including the missing snowpack emissions of NO$_x$ and HONO, an inaccurate representation of Summit’s elevation with a too-coarse model resolution, and the underestimated STE.

All the results presented above reveal the importance of local snowpack emissions in regulating the atmospheric composition and chemistry over the Arctic. Improvements in global CTMs could likely be achieved by coupling snowpack emissions of reactive gases and photochemistry modules in order to better simulate O$_3$ precursors and O$_3$ over snow and ice (Zatko et al., 2016). Moreover, this study also demonstrates that anthropogenic emissions from the midlatitudes play an important role in affecting the Arctic atmosphere.

Data availability. Data used in this study can be provided upon request to the corresponding authors, Yaoxian Huang (yaoxi-anh@mtu.edu) and Shiliang Wu (slwu@mtu.edu).

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