Response to reviewer #1:

We thank Reviewer #1 for his/her valuable and thoughtful comments. Our responses to the comments are provided below, with the reviewer's comments italicized and our responses in plain and bold fonts.

*This paper describes an evaluation of tropospheric ozone and its precursor species simulated by the GEOS-Chem global chemical transport model (CTM) at the Summit observatory station in Greenland. Based on evaluation of the standard GEOS-Chem model, and deficiencies identified through comparison with observations, a number of model changes are implemented (mostly to emissions) which are shown to improve the model performance. The paper serves as a useful documentation of Greenland surface ozone, $NO_y$ and VOC sensitivity to a number of key processes, and highlights processes that warrant further investigation to improve understanding of the surface Arctic ozone budget. These issues are important in light of recent studies demonstrating poor model performance for Arctic tropospheric ozone, as cited by the authors. The paper is generally well written, logically structured and is suitable for the journal. I would recommend publication of this manuscript in ACP, once the following minor issues have been addressed.*

*1) Paragraph beginning Line 69. The discussion of ethane appears a bit out of the blue. The authors should explain more clearly in the manuscript the importance and relevance of ethane to the previous discussion. i.e. give some context for how ethane is relevant to the study - which is motivated by understanding Arctic tropospheric ozone. i.e. as has been done for NOx, PAN.*

**Response: We thank the reviewer for pointing this out. We have reorganized the flow of the text related to ethane in the introduction section - a) we have deleted some discussions on ethane that are not closely related to our study here; b) We have added discussions on the importance of volatile organic compounds (e.g., ethane and propane) for the productions of ozone (lines 43-48) –**

**"Tropospheric ozone ($O_3$) and its precursors, including nitrogen oxides ($NO_x = NO + NO_2$), carbon monoxide (CO), and volatile organic compounds (VOCs, such as ethane, propane, etc.) 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 $O_3$ is**

**mainly produced by photochemical oxidation of CO and VOCs in the presence of $NO_x$, with additional contribution by transport from the stratosphere."**

*2) Lines 109-112: It is unclear here what is meant by fully coupled aerosol? Does this include size-resolved modal aerosol for example? Heterogeneous chemistry, semivolatile nitrate..?*

**Response: We have clarified this part to "Simulations of $O_3$ and related species ($NO_x$, PAN, NMHCs) are conducted using the GEOS-Chem model (Bey et al., 2001) with coupled $O_3$-$NO_x$-VOC-Aerosol chemistry mechanism (i.e. these species interact with each other in the model)." (lines 103-105)**

*3) Lines 112-115: Discussion of previous GEOS-Chem evaluation. It would be helpful here to provide a few sentences for a brief but more critical review of what has been shown in terms of model performance with previous studies specifically using GEOS-Chem in the Arctic. e.g. sensitivity analysis by Christian et al., (2107), the recent POLMIP evaluation (see Monks et al., 2015). These have shown some important limitations and strengths that it would be useful to point out for context.*

**Response: This is an excellent point. We have added the descriptions of previous GEOS-Chem evaluations in the text. In the Introduction part, we have included the discussions of Monks et al. (2015) and Christian et al. (2017) as "More recently, Monks et al. (2015) further demonstrated that model simulated $O_3$ 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 $O_3$ observations from the ARCTAS campaign to GEOS-Chem model simulations and found consistent low biases with the model simulated $O_3$ at all altitudes except the surface." (lines 70-74)**

**In Section 2, we have modified text in lines 112-115 in ACPD as "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 the studies**

**in the Arctic (e.g., Alvarado et al., 2010; Monks et al., 2015; Christian et al., 2017)." (lines 107-111)**

*4) Discussion of model NOx bias (first paragraph of page 5). Perhaps here quote the obs/model slope or model bias. You give figures for the slopes / correlations in the panels of Fig 3 but don't mention the numbers in the text.*

**Response: We agree with the reviewer. Now we have included model $NO_x$ bias in the text as "As shown in Figure 1a, the GEOS-Chem model simulated $NO_x$ agree 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%." (lines 147-150)**

**For Fig. 3, we have included the $NO_x$ model-to-observations slopes and correlation coefficients in the text as "As shown in Figure 3a, GEOS-Chem overestimates surface $NO_2$ mixing ratios at these sites by over 66%, compared with observations (slope=1.07; correlation coefficient=0.88)." (lines 170-171) and "Furthermore, the discrepancy for the differences of surface $NO_2$ mixing ratios over Europe between EURO_EDGAR and observations is 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)." (lines 178-181)**

*5) Lines 206-208: Is the magnitude of the snowpack NOx reservoir depletion of right order to explain this? Is the source linearly dependent on the reservoir? Would it be hard to test this in the model to see if it improves the model bias? i.e. can you scale the monthly emissions according to this finding? Perhaps not necessary, but a brief discussion of the order of magnitude of depletion and how that relates to the model bias would be helpful.*

**Response: Thanks for the excellent questions. Snowpack nitrate photolysis plays an important role in affecting the surface $NO_x$ mixing ratios during late spring and summer over Summit, Greenland. Dibb et al. (2007) demonstrated that nitrate concentrations in the snowpack peaked in June and declined toward fall by ~ 1/3. Moreover, Van Dam et al. (2015)**

**offered the direct evidence that $NO_x$ mixing ratios within the snowpack showed declining trend from June to October, which may partially explain why we would see the declining trend of surface $NO_x$ mixing ratios over Summit from May-October. We have therefore added this discussions in the text "Dibb et al. (2007) reported that nitrate concentrations in the Summit snowpack peaked in June and declined toward fall by ~ 1/3. Van Dam et al. (2015) further showed decreasing trend for $NO_x$ mixing ratios within the snowpack at Summit from June to October. This may partially explain why we would see the declining trend of surface $NO_x$ mixing ratios over Summit from June toward fall. The $NO_x$ emissions from snowpack are affected by a number of factors including nitrate concentrations and solar radiation available and the responses can be very non-linear. Further investigations are needed to account for the seasonal variations of snowpack $NO_x$ emissions from nitrate photolysis in the model, i.e., constrained by seasonal snowpack $NO_x$ emission flux measurements in the future." (lines 209-217)**

*6) Does this model include the PAN budget updates from the Fischer et al. study that is mentioned? This should be stated clearly. Arnold et al., (2105) showed that GEOS-Chem produces less PAN relative to CO than other models in Arctic air masses influenced by fires. It would be useful to refer back to this here to give context to the model performance relative to that found for other models.*

**Response: Points are well taken. We have added clarification and discussion in the text - "For instance, a study by Fischer et al. (2014) showed improved agreement between modeled and measured PAN in the high latitudes when assignining 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." (lines 244-250)**

**We have also added discussion on the reference of Arnold et al. (2015) - "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 over high-latitude**

**atmosphere 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." (lines 233-237)**

*Typographical / editorial corrections:*

*Line 58: ": : :while PAN mixing ratios were lower in fresh boreal fire plumes." This sentence in unclear. Lower than observed? Lower than in other air mass types simulated in the model?*

**Response: Thanks for pointing this out. Model simulated PAN mixing ratios were lower than the observations. Therefore, we have modified the whole sentence as "They found that model simulated $NO_x$ mixing ratios were higher than observations, while PAN mixing ratios were lower than the observations in fresh boreal fire plumes." (lines 60-62)**

*Line 82: ".. that the snowpack emits.."*

**Response: Done.**

*Paragraph beginning Line 141 contains mixed (past / present) tenses. Please adjust the text to make it consistent.*

**Response: Points are well taken. We have corrected the paragraph as "We first run the standard GEOS-Chem model with a-priori emissions and compare the simulation results against observations for various species (including $NO_x$, PAN, $C_2H_6$, $C_3H_8$, CO, and $O_3$, as shown in Fig. 1). Then we focus on the model-observation discrepancies, and where applicable, made revisions to the model simulations and further evaluate the improvement in model performance, as discussed in details below." (lines 139-143)**

*Line 156: " not observed in the data." Better to simply say ".. not observed".*

**Response: Agree. We have deleted "in the data" in the revised text.**

*Line 161: Omit word "mannually" (which should be spelled "manually" in any case).*

**Response: Typo has been corrected.**

Response to Dr. Hongyu Liu's comments:

We thank Dr. Hongyu Liu for his valuable and thoughtful comments. Our responses to the comments are provided below, with Dr. Hongyu Liu's comments italicized and our responses in plain and bold fonts.

*This paper presents a GEOS-Chem model analysis of surface ozone and its precursors (NOx, PAN, C2H6, C3H8, CO) observed at Summit, Greenland during the period of July 2008 - June 2010, with a focus on their concentrations and seasonal variations. Modeling tropospheric ozone in the Arctic has been challenging, and it is very interesting to use a state-of-the art chemical transport model to test and improve our understanding of its sources and variability. The authors identified the discrepancies between the GEOS-Chem simulations and observations, which were then examined using various model perturbation experiments. The results are original, and the paper is concise and very well written. I recommend its publication on ACP with some minor modifications, as itemized below.*

*1). Title - Using "tropospheric ozone" in the title is a bit misleading. Although this study also compared the model vertical profiles of ozone and specific humidity with ozonesonde observations, the main scope of this paper is "surface ozone".*

**Response: We agree with the reviewer's comment. We therefore change the title as "Surface ozone and its precursors at Summit, Greenland: comparison between observations and model simulations".**

*2). Section 2: It is not clear which version of the GEOS-5 meteorological data archive was used. Is it GEOS-5.1.0 or GEOS-5.2.0? See e.g., http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-5_met_field_reprocessing and "http://wiki.seas.harvard.edu/geos-chem/index.php/List_of_GEOS-5_met_fields".*

**Response: Thanks for pointing this out. It is GEOS-5.2.0. We have added this in Section 2 as "The GEOS-Chem model has fully coupled $O_3$-$NO_x$-VOC-Aerosol chemistry mechanism and 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." (lines 105-107)**

*3). Section 2, 2nd paragraph: "Time series data were archived with 3-hr temporal resolution at the Summit grid box" — I think you meant "grid column". Moreover, it is not clear how the model output was sampled in the vertical. The elevation of Summit is 3212m asl. Did you sample the model bottom layer, or the model vertical layer that is about 3212m above the sea level? The latter may very well be different than the former because the topography is not well resolved at coarse resolution. Would the results about model overestimates or underestimates found in this paper be different if the alternative way of model sampling is used (e.g., lines 206-207)?*

**Response: Good points. We archived the time series data with 3-hr temporal resolution at 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. Indeed, the topography is not very well resolved at coarse model resolution, and we believe diagnostics for the model bottom layer would work better than those for the 3212 m level for comparison to the surface measurements.**

*Minor editorial comments:*

*Line 43: change the "and" before "volatile organic compounds" to comma.*

**Response: Changed.**

*Line 56: the ARCTAS mission*

**Response: Corrected.**

*Line 66: What do you mean "O3 mixing ratios below the boundary layer"? Within the boundary layer?*

**Response: Yes, it is within the boundary layer. We have therefore corrected the sentence as "Wespes et al. (2012) also revealed that model simulated $O_3$ mixing ratios within the**

**boundary layer were significantly underestimated during spring-summer, compared with ARCTAS measurements." (lines 68-70)**

*Line 77: "....used to be the global default anthropogenic C2H6 emission inventory" - Do you mean "default" in GEOS-Chem or any other models?*

**Response: Yes, it is the GEOS-Chem default anthropogenic $C_2H_6$ emission inventory.**

*Line 228: add "over Greenland" after "PAN".*

**Response: Added.**

*Line2 268-270: "relative to NEI11_MIX" – isn't this relative to NEI11? Remove it?*

**Response: Well, it is relative to NEI11_MIX. In terms of emissions, you are right because we don't change the MIX emissions in this sensitivity simulation. Therefore, in order to avoid confusion, we give a simulation name for this sensitivity run and change this sentence as "We therefore run a sensitivity simulation by increasing the NEI11 $C_2H_6$ emissions by 40% and keeping other model configuration identical to NEI11_MIX (hereafter referred to as NEI11_40_MIX). We find this update leads to an increase in the model simulated annual mean surface $C_2H_6$ mixing ratios over Summit by only 6% during the period of 07/2008-06/2010 (figure not shown), still not able to explain the high model bias." (lines 283-287)**

*Line2 279-281: The annual mean agrees quite well with observations, but the simulation is worse in summer.*

**Response: Points are well taken. We have changed this sentence to "We find that the simulated annual mean surface $C_2H_6$ mixing ratios at Summit from NEI11_MIX20 agree quite well with observations (within 1%). Similarly, better agreement between model and observations are found for monthly average values for October - January. However, the new simulation is not able to reproduce the seasonal cycle of $C_2H_6$ - the model signficantly underestimates in February – April but overestimates in June – September (Fig. 5)." (lines 296-301)**

*Lines 283-288: Good point, but this long sentence needs a break.*

**Response: Thanks for pointing this out. We have divided the long sentence to "Note that this standard version of GEOS-Chem does not account for the sink of $C_2H_6$ from the reaction with chlorine, which could reduce the global annual mean surface $C_2H_6$ mixing ratio by 0-30%, and the global burden of $C_2H_6$ by about 20% (Sherwen et al., 2016). However, this may introduce additional uncertainty for our measurement-model comparison, together with the uncertainty in the seasonality of $C_2H_6$ chemistry." (lines 304-308)**

*Line 325: "Unfortunately, ..." – "However, ..."*

**Response: Corrected.**

*Lines 339-340: "..., which implies that GEOS-Chem possibly underestimates STE for O3 over Summit" – This is interesting and appears consistent with Choi et al., ACP 2017 (https://www.atmos-chem-phys.net/17/8429/2017/ , see their Fig. 6) , where the GMI CTM driven by MERRA (GEOS-5.2.0) underestimates ozonesonde-observed ozone in the Northern Hemisphere high-latitude upper troposphere.*

**Response: Thank you for providing us a reference source, which also attributed the model low bias to STE. We have included a discussion about this study in the text as "This is consistent with the study by Choi et al. (2017), which found low bias with model simulated $O_3$ mixing ratios over high-latitude upper troposphere of the Northern Hemisphere, compared with ozonesonde data, and attributed the low bias to weak STE in the model." (lines 359-361)**

*Lines 358-359: Summit, Greenland; surface ozone*

**Response: Good suggestion. We have changed the whole sentence to "We combine model simulations with two-year (July 2008 - June 2010) ground based measurements at Summit, Greenland, to investigate the abundance and seasonal variations of surface $O_3$ and related species in the Arctic." (lines 370-372)**

*Figures 2, 3,5, S1: In the caption, state briefly what the perturbation simulations are* *and refer the reader to the text for details.*

**Response: We have added additional descriptions in the captions for Figures 2, 3, 5, and S1. Please refer to our revised manuscripts for details.**

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

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**Abstract.** Recent studies have shown some significant challenges for atmospheric models to simulate tropospheric ozone ($O_3$) and some of its precursors in the Arctic. In this study, ground based data are combined with a global 3-D chemical transport model (GEOS-Chem) to examine the abundance and seasonal variations of $O_3$ and its precursors at Summit, Greenland (72.34° N, 38.29° W, 3212 m.a.s.l). Model simulations for atmospheric nitrogen oxides ($NO_x$), peroxyacetyl nitrate (PAN), ethane ($C_2H_6$), propane ($C_3H_8$), carbon monoxide (CO), and $O_3$ for the period of 07/2008-06/2010 are compared with observations. The model performs well in simulating certain species (such as CO and $C_3H_8$), but some significant discrepancies are identified for other species and further investigated. The model generally underestimates $NO_x$ and PAN (by around 50% and 30%, respectively) for March-June. Likely contributing factors to the low bias include missing $NO_x$ and PAN emissions from snowpack chemistry in the model. At the same time, the model overestimates $NO_x$ mixing ratios by more than a factor of 2 in wintertime, with episodic $NO_x$ mixing ratios up to 15 times higher than the typical $NO_x$ levels at Summit. Further investigation shows that these simulated episodic $NO_x$ spikes are always associated with transport events from Europe, but the exact cause remains unclear. The model systematically overestimates $C_2H_6$ mixing ratios by approximately 20% relative to observations. This discrepancy can be resolved by decreasing anthropogenic $C_2H_6$ emissions over Asia and the US by ~ 20%, from 5.4 to 4.4 Tg/yr. GEOS-Chem is able to reproduce the seasonal variability of $O_3$ and its spring maximum. However, compared with observations, it underestimates surface $O_3$ by approximately 13% (6.5 ppbv) from April to July. This low bias appears to be driven by several factors including missing snowpack emissions for $NO_x$ and nitrous acid in the model, the weak simulated stratosphere-to-troposphere exchange flux of $O_3$ over the Summit, as well as the coarse model resolution.

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## 1. Introduction

Tropospheric ozone ($O_3$) and its precursors, including nitrogen oxides ($NO_x$ = NO + $NO_2$), carbon monoxide (CO), and volatile organic compounds (VOCs, such as ethane, propane, etc.) 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 $O_3$ is mainly produced by photochemical oxidation of CO and VOCs in the presence of $NO_x$, with additional contribution by transport from the stratosphere. Its major sinks include chemical reactions and dry deposition. As a reservoir species for $NO_x$, peroxyacetyl nitrate (PAN) also plays an important role in atmospheric chemistry. PAN and $O_3$, as well as some of their precursors, have relatively long lifetimes in the atmosphere, enabling them to be transported long distance to remote regions such as the Arctic.

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Recent studies have shown some significant challenges for atmospheric chemical transport models to simulate $O_3$ 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 $O_3$ at the GEOSummit station, Greenland (hereafter referred to as Summit). Alvarado et al. (2010) used $NO_x$ and PAN measurements from ARCTAS (Arctic Research of the Composition of the Troposphere from Aircraft and Satellites) in the summer to compare with model simulations. They found that model simulated $NO_x$ 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 $NO_x$ emissions from wildfires to PAN formation, which improved the agreement between 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 $O_3$ 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-Ålesund (79˚, 12˚E). Wespes et al. (2012) also revealed that model simulated $O_3$ 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 $O_3$ 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 $O_3$ observations from the ARCTAS campaign to GEOS-Chem model simulations and found consistent low biases with the model simulated $O_3$ at all altitudes except the surface.

Field measurements at Summit show that the snowpack emits gas-phase $NO_x$, PAN, nitrous acid (HONO), as well as hydrogen peroxide ($H_2O_2$) during spring-summer, when polar 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 $NO_x$ as well as $O_3$ formation, current global chemical transport models (CTMs) usually do not include this emission source (Zatko et al., 2016).

In this study, we examine the abudance and seasonal variations of $O_3$ and its precursors at Summit with a global chemical transport model, GEOS-Chem CTM, in conjunction with two years in-situ measurement data for 2008-2010. We first evaluate the model performance in simulating surface $O_3$ and its precursors, and then implement a series of model updates to resolve the identified model biases. This paper is organized as follows: section 2 describes model methods and observations, followed by detailed comparisons of model simulations against observations for $O_3$ and $O_3$ precursors in section 3; conclusions are summarized in section 4.

## 2. Observational data and model simulations

In situ measurements of $NO_x$, PAN, and non-methane hydrocarbons (NMHCs) were performed at Summit from July 2008 to June 2010 (Helmig et al., 2014b; Kramer et al., 2015). An automated chemiluminescence instrument was used to measure $NO_x$ (Ridley and Grahek, 1990);

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a commercial PAN gas chromatography analyzer (PAN-GC, Metcon, In., Boulder, CO) was employed for the measurement of PAN. Measurements of NMHC relied on an automated Gas Chromatography-Flame Ionization Detection (FID) system. Readers are referred to Kramer et al. (2015) and Helmig et al. (2014b) for the details of the measurement techniques and equipment setup. Surface measurements of $O_3$ using ultraviolet light absorption at 254 nm (Petropavlovskikh and Oltmans, 2012), and CO by GC (Novellie and Masarie, 2015) are from the National Oceanic and Atmospheric Administration (NOAA). Hourly averaged $O_3$ and flask sampled CO between July 2008 and June 2010 were downloaded from the NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) website (http://www.esrl.noaa.gov/gmd/dv/data/). Vertical ozonesonde data profiles were also downloaded from NOAA ESRL GMD (McClure-Begley et al., 2014).

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Simulations of O3 and related species ($NO_x$, PAN, NMHCs) are conducted using the GEOS-Chem model (Bey et al., 2001) with coupled $O_3$-$NO_x$-VOC-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 the studies in the Arctic (e.g., Alvarado et al., 2010; Monks et al., 2015; Christian et al., 2017). GEOS-Chem v10-1 with grid resolution of 4° latitude by 5° longitude, and 47 vertical layers was used for the 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 two years were used in the final analysis. Time series data were archived with 3-hr temporal resolution at the Summit grid box.

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Global anthropogenic emissions of $NO_x$, $SO_2$, $NH_3$, and CO in the model are based on the Emission Database for Global Atmospheric Research (EDGAR) v4.2 inventory, which is 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 $NO_x$ emission scheme follows Hudman et al. (2012). Lightning $NO_x$ emissions are calculated per flash rate based on GEOS-5 computed cloud-top heights (Price and Rind, 1992), which are 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 are from the Global Fire Emission 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 ($C_2H_6$) and propane ($C_3H_8$), which follows Xiao et al. (2008, hereafter referred to as X08) for the year 2001. Global biofuel emission inventory follows Yevich and Logan (2003), which includes emissions for $C_2H_6$ and $C_3H_8$. For biogenic VOC emissions, the Model of Emissions of Gases and Aerosols from Nature (MEGAN) scheme (Guenther et al., 2006) was used. Dry deposition of species in GEOS-Chem uses a standard resistance-in-series scheme (Wesely, 1989), as implemented in Wang et al. (1998). Wet scavenging follows Liu et al. (2001), including scavenging in convective updraft, rainout (in-cloud) and washout (below-cloud) from convective anvils and large-scale precipitation.

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We first run the standard GEOS-Chem model with a-priori emissions and compare the simulation results against observations for various species (including $NO_x$, PAN, $C_2H_6$, $C_3H_8$, CO, and $O_3$, as shown in Fig. 1). Then we focus on the model-observation discrepancies, and where applicable, make revisions to the model simulations and further evaluate the improvement in model performance, as discussed in details below.

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# 3. Results and Discussions

## 3.1 $NO_x$

We first combine the two years of data for July 2008 – June 2010 and anylaze their seasonal variations. As shown in Figure 1a, the GEOS-Chem model simulated $NO_x$ agree 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

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for the model simulation is that it does not capture the decrease of $NO_x$ 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 backgound 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 measurement data available for this period to compare with.

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Further analyses show that the model-simulated high $NO_x$ spikes during wintertime are all associated with transport events from Europe. We carried out a sensitivity study to examine the impacts of European emissions on Arctic $NO_x$ by manually reducing anthropogenic $NO_x$ emissions from the EMEP emission inventory over Europe by 50% (EMEP50). Results show that surface peak $NO_x$ mixing ratios over Summit during the spike events (e.g., dates around 12/09/2009, 12/15/2009, 1/15/2010 and 1/22/2010) from EMEP50 almost decline proportionally by approximately 50% during 2009/12/01-2010/01/31 (Fig. 2), which confirms that the modeled $NO_x$ spikes at Summit during wintertime are associated with transport from Europe. However, the model simulated $NO_x$ is still significantly higher than observations. Comparisons for surface $NO_2$ 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, $NO_2$ measurement technique and resolution, refer to Table 1. Measurment data over these two months for each site were averaged to compare with the corresponding grid cell in the model. As shown in Figure 3a, GEOS-Chem overestimates surface $NO_2$ mixing ratios at these sites by over 66%, compared with observations (slope=1.07; correlation coefficient=0.88).

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Instead of using EMEP, we carried out another sensitivity study to force anthropogenic $NO_x$ emissions over Europe following EDGAR v4.2 (EURO_EDGAR), with other model configurations identical to control simulations. As shown in Figure 2, the $NO_x$ mixing ratios over Summit during 12/2009-01/2010 agree much better with observations, especially for January 2010, where the model captures the magnitudes of observational peaks. This is because $NO_x$ emissions from EDGAR over Europe (1.97 Tg NO) are 12% lower than that from EMEP (2.24 Tg NO) for the months of 12/2009 and 01/2010. Furthermore, the discrepancy for the differences of surface $NO_2$ mixing ratios over Europe between EURO_EDGAR and observations is further reduced (by 50%), relative to the control runs, with a model-to-observation slope of 0.92 and a

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correlation coefficient of 0.83 (Fig. 3b). Similarly, we also tested the sensitivty of surface $NO_x$ mixing ratios over Summit in response to the changes in the anthropogenic $NO_x$ emissions from NEI11 over US and MIX over Asia (including Siberia) during these two months, and found that surface $NO_x$ mixing ratio over Summit during these two months were quite close to the control simulations (not shown), reflecting insenstivity to emission perturbations from US and Asia. Therefore, we conclude that uncertainties in fossil fuel $NO_x$ emissions of EMEP associated with transport events from Europe in the model are the most likely cause for the wintertime $NO_x$ spikes over Summit.

For April-July, model simulated monthly mean $NO_x$ mixing ratios over Summit are a factor of two lower than the observations (Fig. 4a). In-situ measurements at Summit by Honrath et al. (1999, 2000a, 2000b, 2002) showed upward fluxes of $NO_x$ ($2.52 \times 10^8$ molecules $cm^{-2}$ $s^{-1}$) from photolysis of nitrate in snowpack during the summertime, leading to enhancement in $NO_x$ levels in the surface layer by approximately 20 pptv, which is comparable to surface $NO_x$ mixing ratios in the Arctic from other sources. Similar results were found over the East Antarctic Plateau snow/ice sheet (Frey et al., 2013; Legrand et al., 2014). The standard GEOS-Chem model does not include the photolysis of nitrate from snowpack, implying a missing source for $NO_x$ in the Arctic/Antarctic boundary layer.

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In order to test the sensitivity of model simulated surface $NO_x$ mixing ratios to the snowpack emissions, we implement in the model a constant 24-hr $NO_x$ flux ~ $2.52 \times 10^8$ molecules $cm^{-2}$ $s^{-1}$ 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 find that on average, the model simulated surface $NO_x$ mixing ratios for April to July over Summit more than double that from the control simulation, which improves the agreement between model and observations for April-June (Fig. 4a). However, the assumed $NO_x$ flux from snowpack in the model leads to overestimate of $NO_x$ mixing ratios in July and the model is still not able to reproduce the decreasing trends of $NO_x$ for May-October. This decreasing trend of NOx may be driven by the decreasing $NO_x$ production rate in snowpack resulting from a gradual depletion of the snowpack $NO_x$ reservoir (Van Dam et al., 2015), which is not reflected in the model since we implement a simple constant $NO_x$ emission flux. Dibb et al. (2007) reported that nitrate concentrations in the Summit snowpack peaked in June and declined toward fall by ~ 1/3. Van Dam et al. (2015)

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### 3.2 PAN

We then examine 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 captures the seasonal variation of PAN well, although significantly (by ~30%) underestimting the PAN mixing ratios for April-June. By running the model simulation with higher horizontal resolution at 2° latitude by 2.5° longitude (hereafter referred to as GEOS-Chem 2x2.5), we find that the monthly mean PAN mixing ratios over Summit during April-July increased by up to 23.3 pptv compared to the 4x5 simulation (Fig. 4b). This can be explained by two reasons. First, coarse model resolution (e.g., 4x5 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, e.g., $O_3$ and $O_3$ precursors (Jang et al., 1995; Yu et al., 2016). Second, ventilation of 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, monthly mean model simulated PAN mixing ratios are 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 over high-latitude atmosphere 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.

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Snowpack can emit not only $NO_x$, but also PAN, based on field studies at Summit during summertime by Ford et al. (2002). GEOS-Chem does not contain snowpack PAN emissions and chemistry. For a sensitivity study, similar to snowpack $NO_x$ emissions as discussed in section 3.1, we considered a 24-hr constant flux of 2.52 x $10^8$ 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 agree much better with observations (Fig. 4b). Note that there are also other possible reasons 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 can be found when assigning a portion of the fire emissions in the model above the boundary layer and 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.

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### 3.3 NMHC

Comparisons of observed surface $C_2H_6$ and $C_3H_8$ mixing ratios with GEOS-Chem simulations at Summit are shown in Figures 1c and d. The model simulations agree well with surface measurements of $C_3H_8$, but systematically overestimate $C_2H_6$ (by approximately 25% annually), with the largest bias (0.48 ppbv) occuring 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 global anthropogenic $C_2H_6$ emission inventory systematically overestimated surface $C_2H_6$ mixing ratios over the Northern Hemisphere, compared with ground-based observations. Anthropogenic $C_2H_6$ emissions over US from NEI11 are 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 $C_2H_6$ emissions from various countries over Asia (Li et al., 2017). Therefore, instead of using global anthropogenic fossil fuel emissions of $C_2H_6$ following X08, we first conducted sensitivity simulations by overwritting 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 of $C_2H_6$ emissions over the US and Asia, thus spatially and temporally better representative of anthropogenic $C_2H_6$ emissions from mid-latitudes transported to the Arctic regions. In general, model control simulations overestimate annual mean surface $C_2H_6$ 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 of 07/2008-06/2010 (Fig. S1). All the above changes are driven by the substantial reductions of anthropogenic $C_2H_6$ emissions between emission inventories, from 3.5 (X08) to 2.5 Tg/yr (MIX) over Asia, and from 1.9 Tg/yr (X08) to 1.4 Tg/yr (NEI11) over US, reflecting the decreasing trend of anthropogenic $C_2H_6$ emissions during 2001-2009 (Helmig et al., 2014a), because the X08 emission inventory is based on the year 2001. Substantial changes in surface $C_2H_6$ mixing ratios over the US bewteen control simulations and NEI11_MIX reflects that there exist tempospatial changes of $C_2H_6$ emissions from oil and gas productions during the period of 2001-2009. A similar pattern was also found by Tsompa-Sosa et al. (2017). In contrast to the control simulations, NEI11_MIX model simulations show that monthly mean $C_2H_6$ mixing ratios over Summit are systematically underestimated by 24%, compared with observations (Fig. 5). Tsompa-Sosa et al. (2017) reported that NEI11 for $C_2H_6$ emissions were likely underestimated by 40%, compared with in-situ and aircraft observations over the US. We therefore run a sensitivity simulation by increasing the NEI11 $C_2H_6$ emissions by 40% and keeping other model configuration identical to NEI11_MIX (hereafter referred to as NEI11_40_MIX). We find this update leads to an increase in the model simulated annual mean surface $C_2H_6$ mixing ratios over Summit by only 6% during the period of 07/2008-06/2010 (figure not shown), still not able to explain the high model bias.

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**Deleted:** With NEI11 $C_2H_6$ emissions increases by 40%, however, model simulated annual mean $C_2H_6$ mixing ratios over Summit only increase by 6% during the period of 07/2008-06/2010, relative to NEI11_MIX.

Similar to NEI11_MIX, we further conducted sensitivity studies by only replacing the regional emission inventory for $C_2H_6$ over the US, with other regions still following X08 (hereafter referred to as NEI11_ONLY). Consequently, model simulated surface $C_2H_6$ mixing ratios over Summit agree better with observations during winter-spring (Fig. 5), decreasing the bias from +15% (control simulations) to +6%. However, model simulated $C_2H_6$ mixing ratios during summer-fall are higher than the observations by over 30%.

We then scale up the MIX emissions for $C_2H_6$ by 20% over Asia, with other model configurations identical to NEI11_MIX (hereafter referred to as NEI11_MIX20). By doing this, we increase fossil fuel $C_2H_6$ emissions from 2.5 to 3 Tg/yr. We find that the simulated annual mean surface $C_2H_6$ mixing ratios at Summit from NEI11_MIX20 agree quite well with observations (within 1%). Similarly, better agreement between model and observations are found for monthly average values for October - January. However, the new simulation is not able to

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reproduce the seasonal cycle of $C_2H_6$ - the model signficantly underestimates in February – April but overestimates in June – September (Fig. 5). This implies that further assessments of anthropogenic $C_2H_6$ emissions from MIX over Asia are needed and a more accurate global anthropogenic $C_2H_6$ emission inventory should be developed and validated to replace X08 in the future. Note that this standard version of GEOS-Chem does not account for the sink of $C_2H_6$ from the reaction with chlorine, which could reduce the global annual mean surface $C_2H_6$ mixing ratios by 0-30%, and the global burden of $C_2H_6$ by about 20% (Sherwen et al., 2016). This may introduce additional uncertainty for our measurement-model comparison, together with the highly uncertain seasonality of $C_2H_6$ chemistry.

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### 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 seasoanl variation of CO. Compared with observations, the annual mean CO mixing ratios is slightly overestimated by about 3 ppbv in the model.

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### 3.5 $O_3$

Surface $O_3$ mixing ratios from model simulations and surface observations are compared in Figure 1f. The GEOS-Chem model captures the seasonal variation of $O_3$ including the spring peak. However, the model shows a systematic low bias for most time of the year, in particualr for April – July when the surface $O_3$ mixing ratios are underestimated by ~13% (~ 6.5 ppbv). Here we focus our analysis for the possible causes that lead to the model low bias during April-July.

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As discussed earlier, snowpack emissions due to the photolysis of nitrate in the snow during late spring and summer could contribute to $NO_x$ 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 $NO_x$ and HONO from snowpack emissions. In addtion to snowpack $NO_x$ emissions that are described in Section 3.1, we implement in the model a constant flux of HONO ($4.64 \times 10^7$ 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 increase by up to 3 ppbv during this period (Fig. 6). The largest effect occurs in

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July due to relatively strong solar radiation. $O_3$ formation due to snowpack emissions in our study is slightly higher than that in Zatko et al. (2016) because HONO from snowpack emissions is not considered in their study. However, for the months of April and May, surface $O_3$ mixing ratios only increase by ~ 1 ppbv, compared with the control runs. That is, even after accounting for the snowpack emissions, the model simulated $O_3$ mixing ratios are still significantly lower than the observations.

Comparison of the model simulations at different resolutions (4x5 vs. 2x2.5) shows that the finer resolution simulations substantially increase 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 section 3.2, fine model resolution can better resolve the emission strengths, which could significantly affect downwind chemical reactions, e.g., $O_3$ production efficiency (Liang and Jacobson, 2000). Moreover, terrain elevations from fine model resolution are better represented (thus better 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 brings model simulated surface $O_3$ mixing ratios over Summit in much better agreement with observations for June - July. However, there is 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-to-troposphere exchange (STE) $O_3$ flux in the model. Liang et al. (2011) have pointed out that STE could be a significant direct sources 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 elevation above the Summit surface) launched at Summit for the months of June and July in 2008 and compared those data with model control runs. Ozonesondes were launched intensively during these two months (a total of 19 times). As shown in Figure 7, compared with observations, model simulated $O_3$ mixing ratios averaged over 0-5 km above ground level are underestimated by 3% and 9% in June and July 2008 (Fig. 7a). However, specific humidity in GEOS-5 is overestimated by 50% and 81% (Fig. 7b) respectively. Ozonesonde data show that Summit frequently encounters high $O_3$/low water vapors events (e.g., July 9-11, 2008), which are likely of upper tropospheric/stratospheric origin (Helmig et al., 2007b), but these are not captured by the model, which implies that GEOS-Chem possibly underestimates STE for $O_3$ over Summit.

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This is consistent with the study by Choi et al. (2017), which found low bias with model simulated $O_3$ mixing ratios over high-latitude upper troposphere of the Northern Hemisphere, compared with ozonesonde data, and attributed the low bias to weak STE in the model.

Boundary layer height is another factor that could lead to model-data discrepancy in $O_3$ mixing ratios (Grannas et al., 2007; Helmig et al., 2207a, c). The mean springtime afternoon (12:00-14:00, local time) boundary layer height in the model at Summit for the year 2009 is 160 m, which agrees fairly well with observations (156 m) at Summit conducted in spring 2005 (Cohen et al., 2007). Therefore, we exclude that model uncertainties in boundary layer height representation in springtime cause the low bias of $O_3$ mixing ratios between model and observations.

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## 4. Conclusions

**Deleted:** Lastly, we also compared $O_3$ dry deposition velocity ($V_{dry}$) in the model in springtime with observations at Summit. For spring 2009, mean $O_3$ $V_{dry}$ in the model at Summit is 0.009 cm $s^{-1}$, which is within the range of -0.01-0.01 cm $s^{-1}$ observed at Summit (Helmig et al., 2009). Helmig et al. (2009) revealed that afternoon (12:00-18:00, local time) $O_3$ $V_{dry}$ during springtime was close to 0.01 cm $s^{-1}$. For other times during the day, $O_3$ $V_{dry}$ was either close to zero or negative (i.e., $O_3$ production over the snow outweighs its dry deposition). As a result, the net mean $O_3$ $V_{dry}$ from observations during springtime is about 4-6 times lower than model simulations. Therefore, model overestimation of $O_3$ loss via surface uptake is another factor that contributes to the low bias of surface $O_3$ mixing ratios at Summit in the model during springtime.

We combine model simulations with two-year (July 2008 - June 2010) ground based measurements at Summit to better understand the abundance and seasonal variations of tropospheric $O_3$ and related species in the Arctic. In general, the GEOS-Chem model is capable of reproducing the seasonal cycles of $NO_x$, PAN, $C_2H_6$, $C_3H_8$, CO, and $O_3$. However, some major discrepancies between model and observations, especially for $NO_x$, PAN, $C_2H_6$, and $O_3$ are also identified.

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

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

For $C_3H_8$ and CO, model simulations overall agree well with the surface measurements. However, the model tends to systematically overestimate surface $C_2H_6$ mixing ratios by ~ 20% on an annual average, compared with observations. This may be explained by that annual emission budgets of $C_2H_6$ over US and Asia from X08 emission inventory are higher than those from NEI11 and MIX by over 40%. By replacing X08 over the US with NEI11 for $C_2H_6$, and scaling up MIX by 20%, the model-observation bias can be resolved, resulting in annual mean bias less than 1%. However, care must be taken to interpret this result because we do not take into account other factors that may influence the discrepancy of surface $C_2H_6$ mixing ratios at Summit between model and observations, such as the $C_2H_6$ chemistry with chlorine.

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GEOS-Chem is able to reproduce the seasonal variation of surface $O_3$ at Summit but persistently underestimates $O_3$ mixing ratios by ~ 13% (~ 6.5 ppbv) from April to July. This low bias is likely caused by a combination of misrepresentations, including the missing snowpack emissions of $NO_x$ and HONO, inaccurate representation of Summit's elevation with a too coarse model resolutions, as well as the underestimated STE.

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All the results presented above reveal the importance of local snowpack emissions in regulating the air quality over the Arctic. Improvements in global CTM could likely be achieved by coupling snowpack emissions of reactive gases and photochemistry modules in order to better simulate $O_3$ and $O_3$ precursors over snow and ice in the Arctic (Zatko et al., 2016). Moreover, this study also demonstrates that anthropogenic emissions from midlatitudes play an important role in affecting the Arctic air quality.

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**Acknowledgements** This research was funded by U.S. EPA grant 83518901). Its contents are solely the responsibility of the grantee and do not necessarily represent the official views of the U.S. EPA. Further, U.S. EPA does not endorse the purchase of any commercial products or services mentioned in the publication. Superior, a high performance computing cluster at Michigan Technological University, was used in obtaining results presented in this publication. L. J. Kramer, D. Helmig and R. E. Honrath thank NASA (grant NNX07AR26G) for supporting the measurements at Summit. S. Wu acknowledges the sabbatical fellowship from the Ocean

University of China. We acknowledge the observational dataset of $O_3$ and CO provided by NOAA ESRL. Technical supports from M. Sulprizio and C. Keller are also acknowledged.

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**Table 1.** Surface $NO_2$ measurements over Europe during 2009/12/01-2010/01/31.

| Site ID | Site name | Lat. (°N) | Lon.(°E) | Altitude a.s.l (m) | Technique | Resolution |
|---|---|---|---|---|---|---|
| BE0001R | Offagne | 49.88 | 5.20 | 430 | chemiluminescence | hourly |
| BE0032R | Eupen | 50.63 | 6 | 295 | chemiluminescence | hourly |
| DE0001R | Westerland | 54.93 | 8.31 | 12 | NaJ_solution | daily |
| DK0008R | Anholt | 56.72 | 11.52 | 40 | UV_fluorescence | hourly |
| FI0096G | Pallas | 67.97 | 24.12 | 340 | chemiluminescence | hourly |
| GB0014R | High Muffles | 54.33 | -0.8 | 267 | chemiluminescence | daily |
| NL0009R | Kollumerwaard | 53.33 | 6.28 | 1 | chemiluminescence | hourly |
| NO0001R | Birkenes | 58.38 | 8.25 | 190 | glass sinter | daily |
| NO0039R | Kårvatn | 62.78 | 8.88 | 210 | glass sinter | daily |
| NO0056R | Hurdal | 60.37 | 11.08 | 300 | glass sinter | daily |
| SE0005R | Bredkälen | 63.85 | 15.3 | 404 | abs_tube | daily |

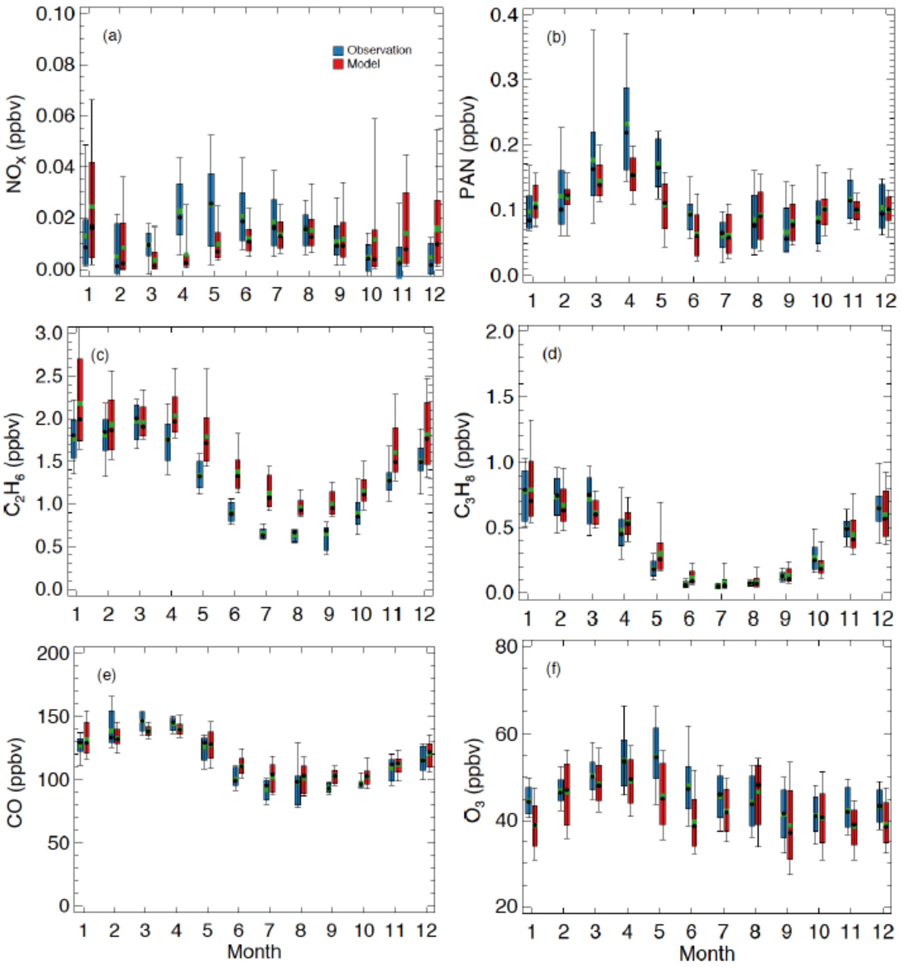

**Fig. 1.** Box plot comparison for seasonal variations of (a) NO$_x$, (b) PAN, (c) C$_2$H$_6$, (d) C$_3$H$_8$, (e) CO, and (f) O$_3$ between GEOS-Chem model simulations (red) and in-situ measurements (blue) over Summit for the period of 2008/07-2010/06. Data shown are monthly averages during this period. 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.

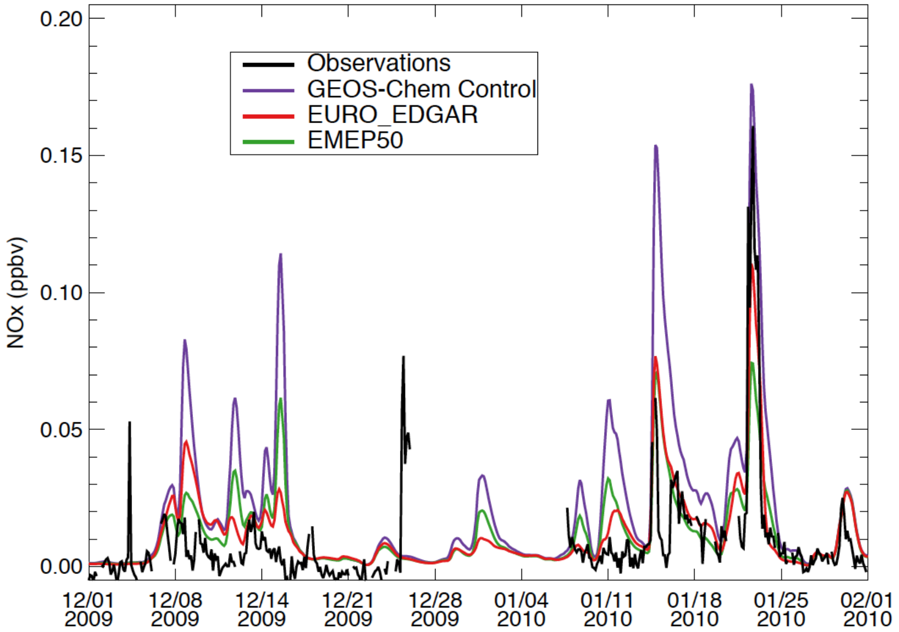

**Figure 2.** Timeseries of surface $NO_x$ mixing ratios over Summit from observations, GEOS-Chem model control simulations, EURO_EDGAR, and EMEP50 during 2009/12/01-2010/01/31. EURO_EDGAR represents simulations with anthropogenic $NO_x$ emissions over Europe following EDGAR v4.2, while EMEP50 denotes simulations with anthropogenic $NO_x$ emissions from the EMEP emission inventory over Europe reduced by 50%, with other model configurations identical to the control simulations. Readers are referred to the text for details.

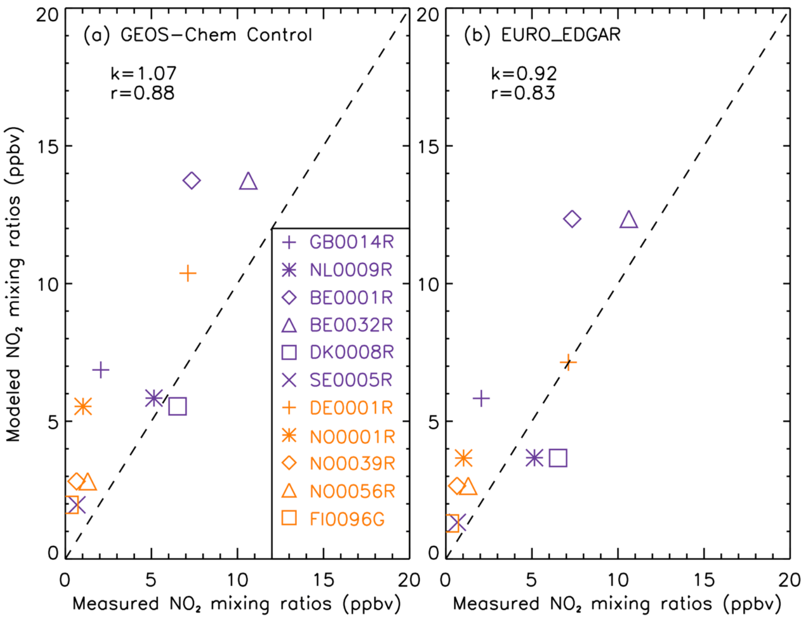

**Figure 3.** Scatter plots between measured monthly mean $NO_2$ mixing ratios at 11 observational sites over Europe and model simulations from (a) GEOS-Chem control simulations and (b) EURO_EDGAR during 2009/12/01-2010/01/31; also shown is the corresponding model-to-observation slopes (k) and correlation coefficients (r) for each panel. The dashed line is the 1:1 ratio. Explanations of site abbreviations are listed in Table 1. EURO_EDGAR represents simulations with anthropogenic $NO_x$ emissions over Europe following EDGAR v4.2, with other model configurations identical to the control simulations.

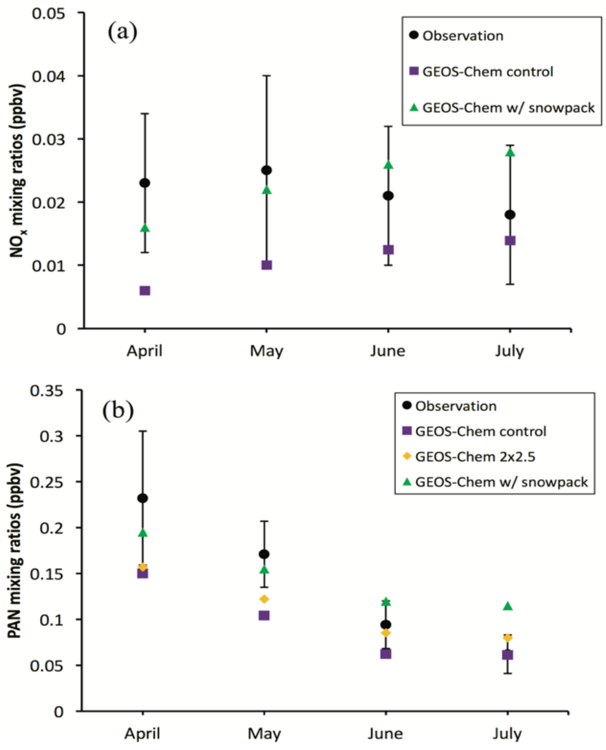

**Figure 4.** Monthly mean surface (a) NO$_x$ and (b) PAN mixing ratios from observations (black circles), simulations with (green triangles) /without (purple squares) snowpack emissions, and GEOS-Chem simulations with horizontal grid resolution 2° x 2.5° (orange diamonds) over the period of April- July during 07/2008-06/2010. Vertical bars denote standard deviations over the course of observations for each month.

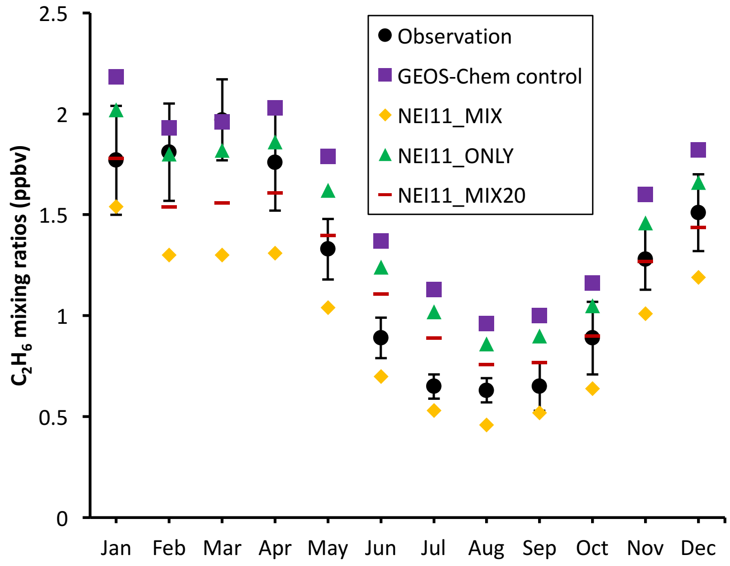

**Figure 5**. Monthly mean surface $C_2H_6$ mixing ratios at Summit from observations (black circles), GEOS-Chem model control simulations (purple squares), NEI11_MIX (orange diamond), and NEI11_ONLY (green triangles) simulations during 2008-2010; vertical bars denote the standard deviation over the course of observations for each month. NEI11_MIX represents model perturbations with global $C_2H_6$ emission inventories overwritten by NEI11 over US and by MIX over Asia, with other model configurations identical to the control simulations. NEI11_ONLY denotes the simulation that is the same with the control simulation except that the $C_2H_6$ emission inventory over US is overwritten by NEI11. NEI11_MIX20 is the simulation that is identical to NEI11_MIX except the 20% increased MIX $C_2H_6$ emission inventory over Asia. Readers are referred to the text for details.

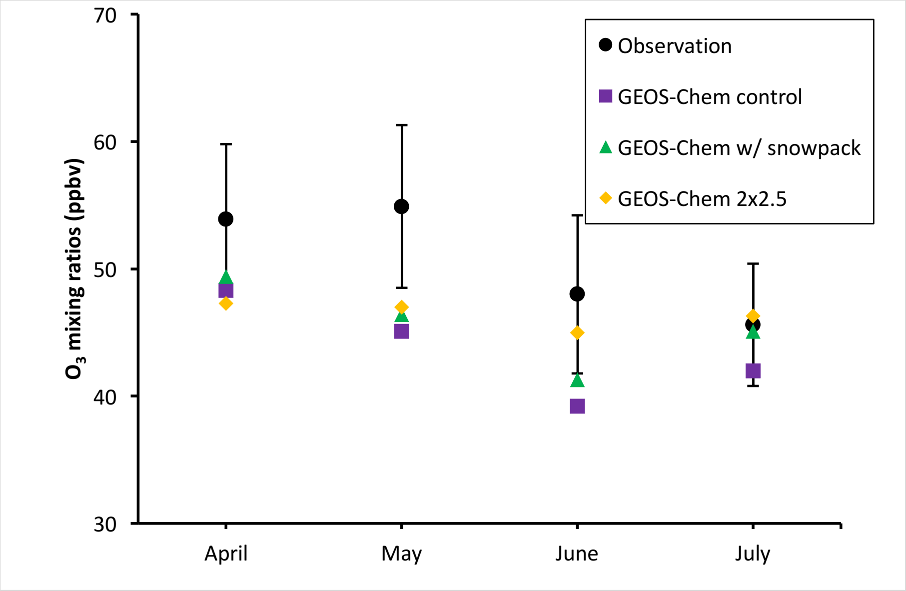

**Figure 6**. Monthly mean surface $O_3$ mixing ratios from observations (black circles), GEOS-Chem control runs (purple squares), with snowpack chemistry (green triangles), and horizonal grid resolution 2° x 2.5° (orange diamonds) for April-July. Vertical bars denote the variability over the course of observations for each month.

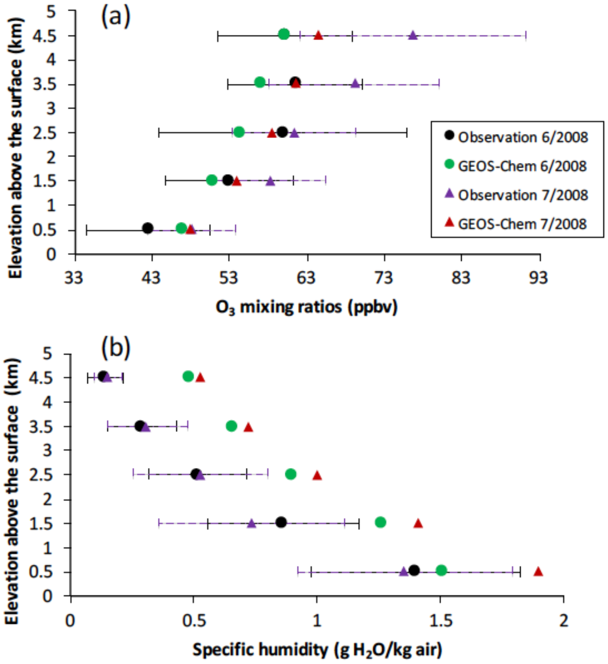

**Figure 7.** Comparisons of vertical profiles of (a) $O_3$ and (b) specific humidity between GEOS-Chem simulations and ozonesondes in June and July 2008 respectively, averaged over 1-km altitude bins. Black and green solid circles represent observations and simulations in June 2008 while purple and red triangles denote observations and simulations for July 2008 respectively. Solid and dash horizontal error bars represent observational standard deviations for June and July respectively.