

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 NO_x , 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 ($\text{NO}_x = \text{NO} + \text{NO}_2$), 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 O₃ 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 O₃ and related species (NO_x, PAN, NMHCs) are conducted using the GEOS-Chem model (Bey et al., 2001) with coupled O₃-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 O₃ 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 O₃ observations from the ARCTAS campaign to GEOS-Chem model simulations and found consistent low biases with the model simulated O₃ 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 NO_x 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 NO₂ 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 NO₂ 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 NO_x 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 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.” (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 is 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, C₂H₆, C₃H₈, CO, and O₃, 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 “manually” (which should be spelled “manually” in any case).

Response: Typo has been corrected.