

The impact of snow nitrate photolysis on boundary layer chemistry and the recycling and redistribution of reactive nitrogen across Antarctica in a global chemical transport model

Zatko et al. [2015]

Responses to Reviewer 2:

Thank you for taking the time to provide thoughtful comments about this manuscript. We agree that it would be best to take the approach where we stress that this manuscript examines nitrogen recycling and redistribution using an *idealized* snowpack that accounts for spatial variability in parameters important to snow nitrate photolysis (snow accumulation rates, snow black carbon concentration, fraction of photolabile nitrate). The goal of this research is to investigate the potential spatial variability in the flux of snow-sourced NO_x associated with snow nitrate photolysis along with the recycling, loss, and spatial redistribution of nitrogen across Antarctica, an environment in which observations of these parameters over large spatial scales are difficult to obtain. This modeling study is used to perform sensitivity studies aimed to guide future lab and field campaigns. We have clearly stated this goal in the abstract and also in the last paragraph of the introduction.

My impression is that a global model with a 2 x 2.5 degree grid, no realistic treatment of the atmospheric boundary layer, and no snow actually in the model is not the right tool to advance understanding of these issues.

Although there are disadvantages associated with using a global chemical transport model with relatively coarse (2°x2.5°) resolution, this type of modeling framework is the only way to examine the large scale transport and redistribution of nitrogen associated with snow nitrate photolysis. For example, Erbland et al., ACPD, 2015 took a very different approach to this problem by using a snow column model with the atmosphere as a boundary condition. In order to calculate snow $\delta^{15}\text{N}(\text{NO}_3^-)$ in their model, they had to assume a fraction of snow-sourced NO_x that is transported away from a given ice-coring site, something for which there is no observational constraint. Our modeling approach can at least provide an estimate of the potential range of this fraction. Indeed, we have included a figure showing this calculation across the Antarctic continent for use in future snow modeling studies.

Additionally, the parameterization that has been incorporated into GEOS-Chem can easily be updated as more is learned about these reactions. The model can also be run at finer resolution in the future to assist in the interpretation of observations from a specific field campaign.

This mismatch is exacerbated by the small number of observations across Antarctica (and tendency for the few that exist to cluster in space) of the critical parameters the team attempts to model, making it nearly impossible to assess whether the model has any skill.

Although observations of chemicals associated with or important for snow nitrate photolysis are sparse across Antarctica, we feel that it is important to compare modeled parameters with observations despite the idealized nature of the snowpack. For example, it is useful to compare modeled F_{NO_x} with observations when using two very different values of the quantum yield, as one clearly deviates from the observations by several orders of magnitude. Despite the idealized treatment of the snowpack, comparing model output to observations can at least allow the authors and readers to get an order of magnitude sense of model-measurement agreement. Including observations in these plots allows for a quick visualization of this agreement. Additionally, readers are able to see where observations exist for various parameters. However, we now have removed all statements about how well the modeling results agree with observations.

On the other hand, the simulations, and especially the sensitivity studies may be useful if the authors admit that they are creating an idealized Antarctic ice sheet...

Thank you for suggesting that we acknowledge that this simulation uses an idealized snowpack. This has been our thought all along, and we thank the reviewer for helping us to better articulate our approach. We now use terminology such as “idealized snowpack” throughout the manuscript, especially in the abstract, introduction, and the conclusions to make this point clear.

In section 2.1.2. the team outlines key parameters that control the depth dependence of actinic flux into the off-line snowpack.

The model snowpack is embedded within GEOS-Chem and some of the chemical and optical properties in the snow are updated at every time step.

Troublesome assumptions include that insoluble LAI are always strictly externally mixed with the snow grains and homogenously distributed in the full depth of the photic zone

We have made simplifying assumptions about the location of light-absorbing impurities (LAI) in snow because observations of this parameter across Antarctica are limited. A detailed snow module (e.g. SNICAR) would likely be able to simulate the location of LAI with respect to a snow grain and also the heterogeneity of LAI throughout the snowpack. However, the incorporation of a detailed snow chemical and physical model would greatly increase computation time in GEOS-Chem and is beyond the scope of this project. We have performed numerous sensitivity studies that evaluate the impact of changing LAI concentration in snow and also alteration of snow grain shape (see section 2.2 and 3.2). While these sensitivity studies do not directly address the location of LAI in snow, they provide a sense of the influence that changes in LAI have on the flux of snow-sourced NO_x .

The depth profile of effective radius of snow grains measured at one location is applied to the entire ice sheet

Thank you for bringing up this point. While there have been a number of satellite-based snow grain radius (r_e) in Antarctica (e.g., Jin et al., 2008), ground observations are limited [Gallet et al., 2011, Grenfell et al., 1994, Klein, 2014].

We use an r_e scheme that allows for vertical r_e variation (r_e increases with increasing snow depth) and temporal r_e variation (snow surface r_e increases throughout summer) based upon measurements at Dome C, Antarctica [Gallet et al., 2011] and in Dronning Maud Land, Antarctica [Klein, 2014]. We have varied r_e in sensitivity studies to assess the influence of r_e on snow-sourced NO_x fluxes. Section 2.1.2. provides a description of the r_e profiles used in this study and sections 2.2. and 3.2. describe the r_e sensitivity studies.

Measurements of BC at a single location are applied to the entire continent by assuming constant deposition flux modeled by variations in snow accumulation (as predicted by the model)

The authors tested a variety of techniques to calculate annual mean snow black carbon (C_{BC}) in GEOS-Chem. In addition to scaling C_{BC} by accumulation rate, anchored to C_{BC} observations at Vostok, a regression equation between annual mean snow black carbon concentration observations and modeled snow accumulation rates was developed, however this method would be more appropriate if many C_{BC} observations were available. Additionally, snow C_{BC} was calculated by dividing the total annual wet and dry deposition of hydrophilic and hydrophobic black carbon (ng yr⁻¹) by the total annual accumulation rate (g yr⁻¹) in each grid box. The spatial pattern and magnitude of snow C_{BC} calculated using black carbon deposition and accumulation rates are similar to the observed spatial pattern and magnitude of C_{BC} presented in Figure 3b (see Figure 1 below).

Since the dilution of insoluble black carbon in snow with increasing snow accumulation rates is well-documented (e.g., Doherty et al., 2010), we feel that scaling black carbon concentration in snow is appropriate. Additionally, the modeled C_{BC} and observed C_{BC} are in general agreement (see Table 1 below), although specific comments on how well the model agrees with the observations have been removed from the text due to the idealized nature of the snowpack. Also shown below is a table comparing modeled accumulation rates to observed accumulation rates (Table 2). In section 3.2., sensitivity studies are described where concentrations of C_{BC} are halved and doubled and the implications for snow-sourced NO_x are assessed.

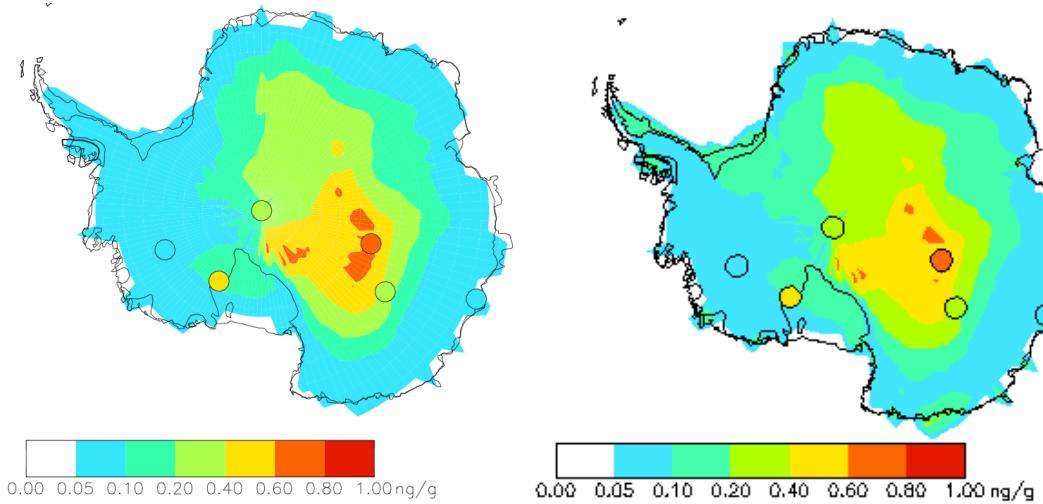


Figure 1. Annual mean snow black carbon concentrations (C_{BC} , ng g^{-1}) calculated by (a) scaling C_{BC} by snow accumulation rate tied to C_{BC} observations at Vostok (Figure 3b) and (b) by dividing the total annual wet and dry deposition of hydrophilic and hydrophobic black carbon (ng yr^{-1}) by the total annual accumulation rate (g yr^{-1}) in each grid box.

Table 1. Annual mean snow black carbon concentrations (ng g^{-1})

Location	Observed	Modeled	Reference
WAIS-Divide	0.08	0.08	Bisiaux et al. [2012]
Law Dome	0.08	0.08	Bisiaux et al. [2012]
Siple Dome	0.5	0.08	Chylek et al. [1992]
South Pole	0.1	0.2	Warren et al. [1990]
Dome C	0.3	0.4	Warren et al. [2006]
Vostok	0.6	0.6	Grenfell et al. [1994]

Table 2. Total annual snow accumulation rate ($\text{kg m}^{-2} \text{a}^{-1}$)

Longitude	Latitude	Observed ^a	Modeled
139.8	-66.7	558	366
138.6	-67.4	515	149
136.7	-67.9	334	167
135.2	-68.5	246	186
134.3	-69.3	216	77
134.1	-70.3	160	32
133.0	-71.6	121	33
132.8	-71.5	96	33
130.5	-72.3	68	36
128.7	-74.0	53	17
126.9	-73.8	43	17
124.5	-74.7	34	19
123.3	-75.1	25	19
123.3	-75.1	25	19
123.3	-75.1	25	19
123.3	-75.1	25	19
123.3	-75.1	25	19
120.2	-75.7	28	12
113.0	-76.7	22	13
110.6	-77.7	29	14
106.8	-78.5	21	13
106.8	-78.5	21	13
106.8	-78.5	21	13
0	-90	80	47
-112.1	-79.3	220	114

^aObserved or inferred total annual snow accumulation rates from Erbland et al. [2013], Fegyveresi et al. [2011], Grenfell et al., [1994].

In section 2.1.3. the depiction of how nitrate is distributed across the ice sheet, and partitioned between photolabile and more stable forms is presented. Extreme simplifications include the decision to assume uniform concentration (60 ng g^{-1}) below 2 cm and 360 ng g^{-1} 0-2 cm everywhere. The first number is based on wide ranging surface traverses where 60 was the median of a distribution that ranges from 4 to 800 ng g^{-1} , and the surface amplification is a mid range value of observations that range from near zero in some places to 100 or more at others.

Although there is a wide range of multi-year, sub-surface snow NO_3^- concentrations measured across Antarctica during the ITASE campaign [Bertler et al., 2005], there is no clear spatial pattern associated with these observations. NO_3^- concentrations in snow are influenced both by snow accumulation rates and by post-depositional processing and associated redistribution of snow-sourced NO_x and NO_3^- . We have

chosen to apply the median value of observed sub-surface snow NO_3^- concentration (60 ng g^{-1}) in our idealized snowpack. However, we have performed a number of sensitivity studies to investigate the impact of snow NO_3^- concentration on snow-sourced NO_x . In sensitivity studies, snow NO_3^- concentrations are halved and doubled, the NO_3^- enhancement factor is varied from 1 to 10, and, in an additional sensitivity study, it is assumed that all NO_3^- is photolabile (see section 3.2.).

There is a wide range of NO_3^- enhancement factors in the top 2 cm of snow. This range can be even larger if the NO_3^- concentrations in the snow skin layer (very top surface, $\sim 1 \text{ mm}$) are compared to NO_3^- concentrations in sub-surface layers. An enhancement factor of 6 has been chosen because it is a mid-range value of many observed enhancement factors (see references in 2.1.3.), and this enhancement factor is applied across Antarctica. Similar to snow NO_3^- and LAI concentrations, the NO_3^- enhancement factor in the top 2 cm of snow is varied from 1 to 10 in sensitivity studies to investigate the impacts of this parameter on snow-sourced NO_x (see section 3.2.).

Regarding whether the nitrate is photolabile or relatively stable, it is assumed that the dry deposited fraction is on surface of snow grain, hence readily photolyzed, but the partitioning between wet and dry deposited nitrate is model defined with no validation that the model is anywhere close to correct on this critical factor.

Unfortunately, no observational constraints on the relative importance of wet- and dry-deposited NO_3^- across Antarctica exist for model assessment. However, both the wet deposition scheme [Amos *et al.*, 2012] and dry deposition schemes over snow [Fisher *et al.*, 2011] have been recently updated in GEOS-Chem. The spatial pattern of wet deposition in the model is at least qualitatively what we would expect; the amount of wet deposited nitrate is highest at the coasts (closest to ocean) and lowest on the East Antarctic plateau (furthest from ocean).

These decisions guarantee that the model is dealing with snow that has some resemblance to that which is found in Antarctica, but the spatial and vertical distributions in the model snowpack intentionally smooth variations that are known to exist across the actual Antarctic snowpack.

Thank you for mentioning this fact. We agree and have made sure to mention that this study uses an idealized snowpack. Additionally, we have included an appendix that illustrates the spatial variability in F_{NO_x} associated with a variety of sensitivity studies.

It is particularly puzzling why the authors assume a constant flux of BC but impose constant concentrations on nitrate. They could have made the same choice for both, or they could have combined the model estimates of spatially distributed deposition (combined wet and dry) of both BC and nitrate with modeled snow accumulation that would at least have internally consistent spatial variations in these parameters.

Snow NO_3^- concentrations are altered by both post-depositional processing associated with snow NO_3^- photolysis and snow accumulation rates, while snow black carbon concentrations are only influenced by snow accumulation rates (i.e., black carbon does not undergo photolytic recycling, and is thought to be well-preserved in ice as long as there is no surface melting). Therefore, it is necessary to make different assumptions about modeled snow NO_3^- and black carbon.

However, given that the team starts with a snowpack that is not like Antarctica (by choice), I see no point in comparing model predictions smoothed in an undefined way to relatively few spot observations in the series of maps shown in Fig. 2, 3, 4, and 9. It is also a problem that these comparisons are all described as “good” with no objective criteria, but if the figures go away this issue will too.

We have removed all model-measurement comparison statements in this manuscript although we feel that it is still instructive to compare model output to observations where available. This allows readers to obtain a rough ‘order-of-magnitude’ idea of model-measurement agreement. Additionally, these observations are laid out spatially, which allows readers to see where observations exist for various parameters.

I think this paper needs a major rewrite that admits the simulations are based on highly idealized snowpack that may be more like Antarctica than Greenland or smaller icecaps in other parts of the world and focuses on an expanded discussion of the sensitivity studies and what they may reveal about fundamental processes and where more focused studies would be most fruitful.

Thank you for all of these suggestions. We now refer to the snowpack as ‘idealized’ throughout the manuscript. Additionally, throughout the text we describe the main results of our sensitivity studies and how these results can be used to shape future field and laboratory experiments (see section 3.2 and conclusions). The flux of snow-sourced NO_x is most sensitive to the quantum yield and the concentration of photolabile nitrate, and these parameters are likely related to each other. We have also included an appendix (Appendix A) that shows the spatial pattern of F_{NO_x} for many of our sensitivity studies.

Specific technical edits and comments:

18964/25 to 18965/3: Not sure that this last statement in the abstract is supported by the rest of the manuscript. There is no clear advice on how ice-core N-15 is going to answer these questions.

We have updated section 3.6. to describe the significant correlations between NRF , f , and $\delta^{15}\text{N}(\text{NO}_3^-)$ in more detail. Additionally, in the conclusions section we have included a sentence about one possible application of this work for ice-core NO_3^- interpretation.

18966/13-14: Not sure what is meant by “partially transferred to the gas phase during transport from the LLR to interstitial air”. Seems only NO₂ that leaves aqueous phase could get into the interstitial air. Related point is that here you cite work that suggests some stays in the LLR, but the model pushes all of it directly into the bottom layer of the atmosphere. In addition to retention in LLR, is there not also a fraction that could recycle to nitrate in the interstitial air and redeposit before getting out of the snow.

We have reworded this statement to “The aqueous phase NO₂ produced in E1 can be transferred to the gas phase and subsequently transferred to the interstitial air”. For simplicity, we have assumed that all NO₂ produced through the photolysis of snow NO₃⁻ can escape from the LLR into the boundary layer and have specifically stated this assumption in section 2.1.1.

The efficiency of transport of NO₂ from the interstitial air to the overlying boundary layer was evaluated in Zatko et al. [2013] by comparing the lifetime of NO_x against escape out of the snow (diffusion and windpumping) to the lifetime of NO_x against chemical decay (combination of NO_x with BrO, IO, OH) at a variety of polar locations. The lifetime of NO_x against escape was always shorter than the lifetime of NO_x against chemical conversion, so we assume that all NO_x in the interstitial air can escape to the atmosphere. Although there have been numerous laboratory studies aimed to learn more about the LLR (or QLL), there are still many uncertainties associated with nitrate photolysis in the LLR [Domine et al., 2013].

18966/21: 0.003-0.44 does not span the full range (0.003-0.6) mentioned in the 2 preceding sentences

Thank you for catching this. We have reworded this sentence to ‘In a recent study by Meusinger et al. [2014], $\phi=0.003-0.44$ molec photon⁻¹ for E1, which nearly spans the full range of previously reported quantum yields.’

18966/23: “as well as and” should be “and” or “as well as”

Thank you for catching this as well. We have removed ‘and’ from the sentence.

18971/10: Seems you need to say something about how the model was tweaked to deal with the compression of longitude at very high latitude. Are there really 144 grid cells between 88 and 90 S, and how are they all forced to agree at the pole?

There are 144 grid cells between 88 and 90 S. In the advection scheme that GEOS-Chem uses, there is special treatment at the poles because the scheme is based on calculation of the slopes between neighboring grid boxes. The grid boxes at the poles are treated as one circular grid cell.

18971/12: I think this should be May 2009

Yes, thank you for catching this typo.

18971/23-25: Is this statement correct? Looking at a bunch of short lived stuff with surface source and it does not matter if you dilute this into a 100 versus

300 m deep BL? If it is accurate, it really reinforces my very early statement that a CTM run at 2x2.5 degree resolution is the wrong tool for the problem

Thank you for questioning this statement because we found a minor error in this part of the code. The mixing ratios of these species are dependent on which vertical grid boxes are considered. We have now removed this sentence from the manuscript.

18972/14-15: see earlier comment about citation of Boxe et al. [2005]

We have changed this sentence to "We assume that all NO_x formed in E7 is immediately desorbed into the gas-phase and transported from the LLR to the interstitial air and then into the overlying boundary layer [Zatko *et al.*, 2013]." Additionally, at the end of section 2.1.3., we discuss the implications of assuming that all NO_x from the LLR is transferred to the gas-phase for the flux of snow-sourced NO_x.

18973/3: It is unusual to have the figure callouts out of order. You have not referred to Fig 2 yet, so perhaps what is now Fig 3 needs to be Fig 2.

We have removed the figure callouts (Figure 2a and Figure 3c) that are out of order in section 2.1.2 and 2.1.3.

18975/11: here (and consistently afterward through the rest of the manuscript) you say 0.0013 for the yield found by Chu and Anastasio, but in the intro you say 0.003. These authors actually document both pH and temperature dependencies and quote 0.0017-0.0054 from 239 to 268K as the yield from nitrate doped ice. It seems something closer to 0.003 might be more appropriate for a lot of the Antarctica in the summer. However, later it says that based on the sensitivities studies you decide to use 0.0013 for all following analyses. Please check what value was used, and explain why you used something lower than Chu and Anastasio, if that is correct.

Thank you very much for pointing out this error. We use $\phi=0.002$ (corresponding to T=244K, pH=5) for the following analyses, not $\phi=0.0013$. Table 3 has been updated to reflect this change.

18976/10 Section 2.2.: really ought to be more than this short paragraph and Table 2. It is the most useful part of this study and needs to be the focus of the discussion.

Section 2.2. and Table 3 have been expanded in the latest version of this manuscript. We have also included an appendix in the manuscript that shows mean austral summer F_{NOx} for a variety of sensitivity studies.

18979/23-24: While this statement may be true in the model as it is set up, I doubt that the photolabile fraction of nitrate in real snow will remain constant as a layer slowly sinks lower in the photic zone. Easily photolyzed nitrate will be, and if it is recycled and dry deposited, it will be in the current surface layer. So, I would expect the stable fraction to grow in the original due to loss of photolabile molecules (some have discussed this photobleaching).

We agree that the fraction of photolabile nitrate will likely decrease as a layer sinks lower in the photic zone. The fraction (F_R/F_{NOx}) in the equation for f represents the fraction of nitrate lost in 1 year in the photic zone, not the fraction of photolabile nitrate in the snow. We have slightly updated this sentence in an attempt to provide more clarity:

"Provided that there are no major changes in parameters that influence snow photochemistry (e.g., LAI, overhead ozone abundance) from year to year, the fraction of photolabile NO_3^- lost from the snow **over 1 year** will be stable from year to year."

18981/8-10: Who says this is “good” agreement. On what basis? More importantly, what do you really mean by “total snow accumulation rates” in the model. Is this just snowfall, or does it consider sublimation, diamond dust, fog, drifting and blowing snow? I can not imagine that these BL processes are well captured in the model, so I am guessing that you are comparing accumulation to model precip, which is not really appropriate. However, as noted earlier, there are way too few observations to make this comparison very rigorous and I suggest you not even try. I will not make similar comments related to subsequent statements about model/observation comparisons, but you should be assured that I noted them in the marginalia.

We have removed all judgments about model-measurement agreement from this manuscript due to the idealized nature of the model snowpack.

The model does not simulate sublimation, diamond dust, fog, drifting and blowing snow in the boundary layer. Observed or inferred snow accumulation rates are compared to modeled total annual precipitation (mm liquid water equivalent year⁻¹) that has been converted to total snow accumulation (kg m⁻² yr⁻¹) using a typical Antarctic snow density (360 kg m⁻³).

A related comment that applies throughout section 3, and probably also in section 2. If you are going to keep all of the maps (against my advice) I think you need to describe how the gridded data were contoured. There is a lot of fine structure in some of these that probably is not really captured at 2 x 2.5 degrees.

GEOS-Chem calculates one value for each grid box (2° x 2.5°) and this data is then smoothed using bilinear interpolation algorithms in the GAMAP plotting routines. The TVMAP GAMAP routine uses the TVIMAGE function, which in turn uses the (http://acmg.seas.harvard.edu/gamap/doc/by_alphabet/gamap_t.html#TVIMAGE) TV routine (http://www.exelisvis.com/docs/TV_Procedure.html), a core routine in IDL.

We have included a sentence about the smoothing algorithm in section 2.1.1. Figure 2 shows both gridded and smoothed data. The fine structure in the data is not lost when gridded data is smoothed, as can be seen in the two plots below.

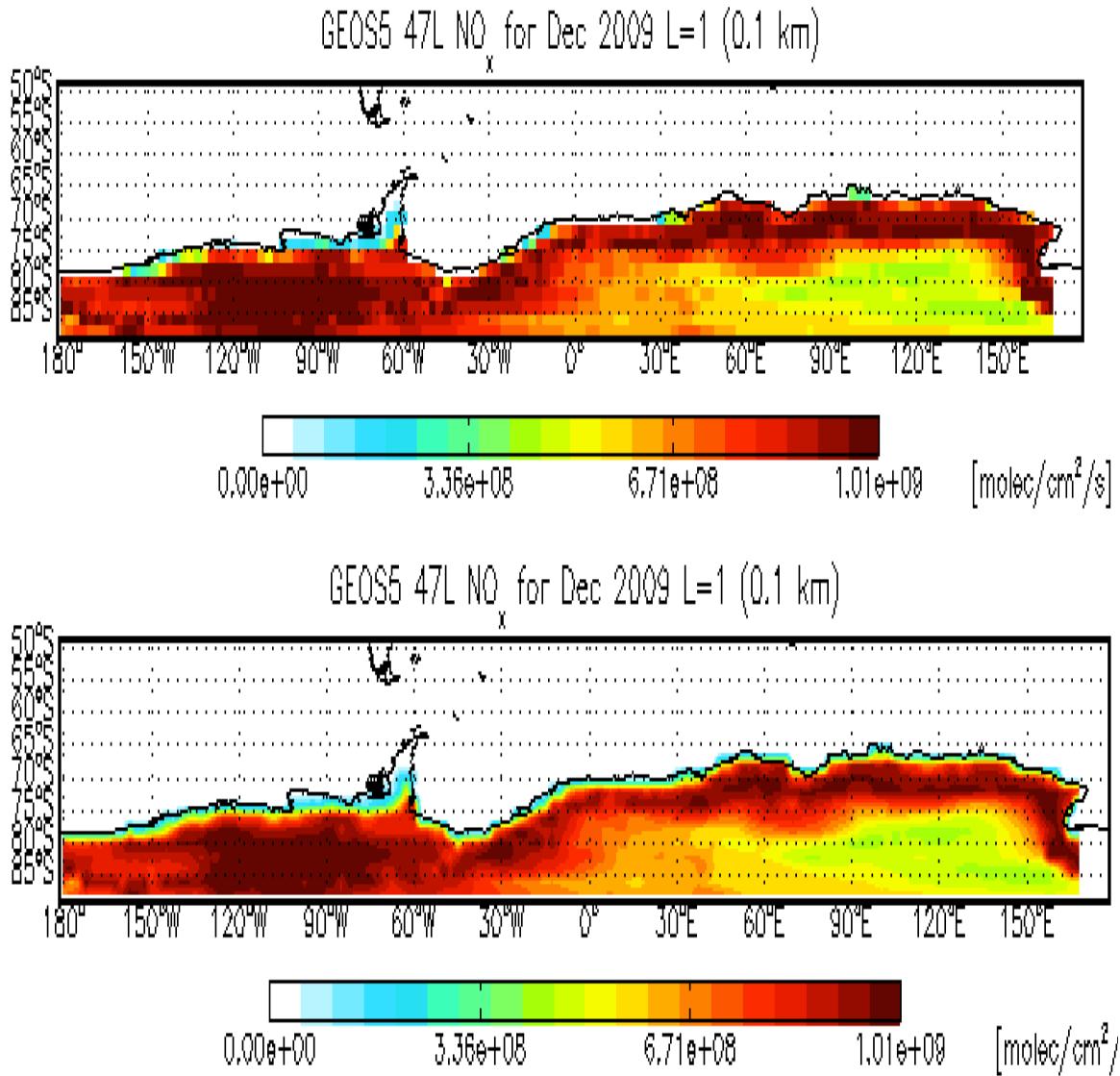


Figure 2. (top) gridded data. (bottom) smoothed data.

18984/1: Does it really make sense to average fluxes purporting to be peak noon values and 24 hour averages and weeks or months long campaign averages together?? I do not think so.

In order to overplot observations onto the model results, we need to have one single value for each station. Due to the idealized nature of the snowpack in the model, an order-of-magnitude level comparison is relevant here. Station-averaged NO_x flux values in Figures 4c and 4d allow for such a comparison. However, we have removed all model-measurement NO_x flux comparisons in section 3.2. and have provided the full range of observed NO_x fluxes at each station in section 3.2.

18984/7: Not being able to take advantage of all the work at Halley and Neumayer because the model grid is too coarse goes back to a familiar point,

is a global CTM the right tool? More generally, given the huge gradients in just about everything within 2 degrees of the coast of Antarctica having a lot of contaminated grid cells in this very interesting region seems a pretty big problem

The incorporation of snow nitrate photolysis into a global chemical transport model is perhaps the only way to assess the large scale nitrogen recycling and redistribution associated with snow nitrate photolysis across Antarctica. Global chemical transport models, including GEOS-Chem, may be run with much finer resolution than $2^\circ \times 2.5^\circ$, which would allow one to better resolve the coast as well as small scale features throughout the entire continent, although with much greater computational cost.

Although the e-folding depths, and thus F_{NO_x} are not properly resolved directly at the coast in this modeling project, much of Antarctica is not on the coast and is therefore unaffected by mixed surface grid boxes. Additionally, we have removed a sentence from the conclusion that mentioned a possible result in coastal Antarctica.

18989/8: I assume that section 3.6. is supposed to justify the final sentence in the abstract but it does not succeed for me.

There is a strong relationship between the degree of photolysis-driven loss of snow NO_3^- and the degree of nitrogen recycling between the air and snow in regions of Antarctica with a snow accumulation rate greater than $85 \text{ kg m}^{-2} \text{ a}^{-1}$ in the present day. We have expanded on this analysis in section 3.6 and have added a sentence in the conclusions section about how this relationship could be used to aide in the interpretation of nitrate in ice core records. Please also see our response to your other comment above.

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