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Atmospheric Chemistry and Physics Discussions

Interactive comment on "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" *by* M. C. Zatko et al.

Anonymous Referee #2

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This paper presents simulations with the global chemical transport model GEOS-Chem, extended to include parameterization of photolysis of nitrate in snow, to examine conversion of snow nitrate to NOx, fractions of this NOx that is either exported from the site or recycled back to nitrate and redeposited, and how these processes impact the N isotopic composition of nitrate that is eventually buried below the photic zone. These are all very interesting questions that have attracted a lot of recent and current attention, including field and laboratory studies and process modeling studies at much smaller spatial scales.

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Interactive Discussion
Discussion Paper

My impression is that a global model with a 2 x 2.5 degree grid, no realistic treatment of the atmospheric boundary layer (bottom 3 levels in the model atmosphere are each 100 m deep), and no snow actually in the model is not the right tool to advance understanding of these issues. 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.

In the next paragraph I will detail parameterizations or lower boundary conditions imposed to represent the snow photolytic source of NOx that push the model version of Antarctica even further from the real version and making model/observation comparisons of snow characteristics even less diagnostic. 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 that has similar topography and geography as the real one, and experiences similar weather, but that is covered by a hypothetical snowpack that clearly differs in many respects from the real one.

In section 2.1.2 the team outlines key parameters that control the depth dependence of actinic flux into the off-line snow pack (that provides "snow-sourced NOx" to GEOS-Chem). 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; the depth profile of effective radius of snow grains measured at one location is applied to the entire ice sheet; and measurements of BC at a different single location are applied to the entire continent by assuming a constant deposition flux modulated by variations in snow accumulation (as predicted by the model). 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) below 2 cm and 360 ng/g 0-2 cm, everywhere. The first number is based on wide ranging surface traverses where 60 was the median of a distribution that ranges 4-800 ng/g, and the surface amplification

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is a mid range value of observations that range from near zero in some place to 100 or more at others. Regarding whether the nitrate is photolabile or relatively stable, it is assumed that dry deposited fraction is on suface 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. 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. 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.

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.

I think this paper needs a major rewrite that admits the simulations are based on a 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 sensitity studies and what they may reveal about fundamental processes and where more focused studies would be most fruitful.

If other reviewers and the authors (and editor) disagree and this paper gets published in ACP insomething like its present form I offer the following list of specific technical edits and comments the authors should consider. These are referenced to page and line numbers in the “printer friendly” manuscript on ACPD.

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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 anwer these question.

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 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.

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

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

18971/10 Seems you need to say something about how the model grid 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?

18971/12 I think this should be May 2009 (would not make sense to spin up Nov 07 through Apr 08 and then leap a year to start the production run)

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 2 x 2.5 degree resolution is the wrong tool for the problem.

18972/14-15 see earlier comment about citation of Boxe et al 2005 (page 18966)

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.

18975/11 here (and consistently afterward through the rest of manuscript) you say

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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 268 K as the yield from nitrate doped ice. It seems something closer to 0.003 might be more appropriate for a lot of 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.

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 discussion.

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 the photolabile molecules (some have discussed this photobleaching).

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 am guessing 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 marginalia.

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

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that probably is not really captured at 2 x 2.5 degrees.

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.

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 18963, 2015.