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Atmospheric
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Discussions

Interactive
Comment

Interactive comment on "Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NO_x release from the Arctic and coastal Antarctic snowpack" *by* C. S. Boxe and A. Saiz-Lopez

Anonymous Referee #2

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General comments

This manuscript utilizes a novel model that includes multiple phases of nitrate (CON-AIR) to realistically simulate the flux of NOx from snow based on the photolysis of nitrate in and on snow surfaces. The model includes a quasi-liquid layer on the surface of snow grains and the authors discuss the impact that this presence has on the chemical reactions of nitrate and photochemically derived products. The authors compare their results with observed NOx fluxes from the snowpack based on others' field measurements in both the Arctic and coastal Antarctica. Additionally, the authors compute vertical profiles of NO and NO2 above the snowpack. This subject is definitely relevant for ACP, is an excellent addition to the growing body of literature on heterogenous chemistry, and represents a contribution that nicely ties together field and laboratory measurements in a way that is and will be useful to several disciplines.

Overall, the manuscript is well written, the scientific methods are valid, the abstract and title of the paper are representative of the work, and other work in the subject area is given proper credit. Still, there are several points in the manuscript that are in need of clarification (specified below). More significantly, the paper lacks a well-structured set of conclusions, and the manuscript would benefit from an additional section at the end clearly summarizing the authors' findings. The authors cite observations from a variety of field measurements made in very different environments within the Arctic and Antarctic, while making it seem that their results are broadly applicable across these different environments. It would behoove the authors to more adeptly outline the parameters that are most important (i.e. most sensitive) in their formulations and summarize this in a table or a conclusions section. This would make their work more easily comparable and useful to other researchers. A few additional references are mentioned in the comments below with respect to specific points in the manuscript. Finally, it would be interesting to know how much the nitrate and nitrite concentrations of the snowpack change with the calculated flux of NOx.

Specific comments

Introduction

p. 6011, lines 11-15: The Blunier et al. study suggests that "physical and photochemical processing of nitrate" can alter its nitrogen ISOTOPIC signature. In the first half of this sentence it would be more appropriate to cite studies that discuss changes in the concentration of nitrate in surface snow, e.g., Rothlisberger et al., Annals of Glaciology, v35, 2002), then make mention of those that discuss the isotopes of nitrate (e.g., Blunier et al., McCabe et al., and you might consider adding Hastings et al., JGR, D20306, 2004).

p. 6011, line 17: Remove reference to "Reaction (R8)" or specify "see below" since you have not introduced these reactions yet.

p. 6012, lines 15-18: Is this statement meant to refer to the "thickness" of the QLL or instead to the existence of the QLL itself?

p. 6013, starting at line 10: The Jones et al., (2007) study is based on a field campaign at Halley station in coastal Antarctica. While the Honrath, Dibb, and Simpson studies mentioned take place in different Arctic environments that exhibit significant differences in temperature, pressure, accumulation rate, snow density, etc; and the Jones et al., 2000 study takes place at yet another site in Antarctica (Neumeyer). The authors should specify where the ranges of NOx volume fluxes apply (i.e., coastal Antarctica in the first sentence, and then confine the second range to Arctic sites only). This point about differences among environments in the Arctic will be raised several times in the rest of the manuscript; I do not think it is necessary for the authors to restrict their results to one particular environment but currently the manuscript makes it seem as if it is broadly applicable to all of these environments, which may not be the case.

Model Description

p.6014, line 10: Does this temperature range apply to all of the sites in the Arctic for which other observations are mentioned in the manuscript (e.g., Summit, Greenland; Alert, Canada; and ?). There should be a reference for where this temperature range comes from. Additionally, does this temperature range encompass temperatures above the snowpack as well as interstitial temperatures within the snowpack?

Along similar lines, atmospheric pressure (1 atm) is not applicable across the Arctic sites. Most of Greenland is not at standard temperature and pressure. In fact, Summit, Greenland, where most of the Honrath and Dibb studies that are cited take place, is ˜3000 meters above sea level, yet STP is used in all model calculations in this study.

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How much does this affect the results? (As mentioned above, it would be useful to have a table that outlines the most important inputs to the model so that others can make the best/most realistic use of the results reported here).

p. 6014, starting at line 15: This sentence does not make sense and should be rephrased. To what snowpack depth do these bulk concentrations apply?

p. 6016, line 11-12: Where does 0.00139 cm3 come from? (0.05 cm3 was just calculated)

p. 6016, line 13: What does "both old and new" refer to?

p. 6016, lines 14-15: Why is a snow depth of 54 cm chosen? How sensitive are the model results to density since density varies considerably among the Arctic environments for which you have cited other observations and varies with depth? Take a look at the density values reported by Dibb and Fahnestock (JGR, D24113, 2004)

With 54 cm of snowpack to consider do the authors take into account the possibility of nitrate diffusion and/or HNO3 evaporation?

p. 6016, line 19: Terminology on this page and in the rest of the text can become somewhat confusing - here you are referring to a snowpack "surface" that is actually 54 cm of snow depth; there is the "surface" of the snowpack above which the atmosphere/boundary layer is considered; there is the QLL at the "surface" of snow grains. Please rephrase here and be careful throughout the text to be very clear about what you mean by "surface."

Results and Discussion

p. 6020, lines 10-16: The several sentences here need to be rephrased for clarity. Is this "ice layer" or QLL? Are you calculating the depth BELOW which NO2- photolysis will NOT occur? How can NO2 "photolytic processing" occur at "deeper depths" when above you have stated that photolysis will not occur? Also, the numbers used in Figure 1 disagree (by an order of magnitude) with what is calculated here.

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p. 6020, lines 20-22: You mention here the gamma (ratio) of 0.8 to 2.0, which you previously referred to as the ratio of NO/NO2. So my interpretation here is that the formation of HONO subsequently results in release to the gas phase such that it drives the ratio of NO/NO2 to unreasonably high values (˜1500). Is this the case or is the 0.8 to 2.0 also applicable to NO/HONO ratios?

p. 6022: To what depth is photolysis considered to occur in the snowpack? Most studies suggest that photolysis should not occur beyond ˜20 cm - Qiu et al., 2002 is cited here and reports an e-folding depth of 12-30 cm and Anastasio et al., Atmos. Environ., 2007 suggests an even shallower depth for OH production from snow grains collected at Summit, Greenland (where a significant amount of the "Arctic" fieldwork cited throughout this manuscript takes place). Yet, all of the calculations consider a QLL volume that is calculated over all 54 cm of snowpack.

It also seems worth considering Lee-Taylor and Madronich, JGR, D24, 2002 in your discussion on this and the next page.

p. 6023, lines 1-3: There is a need to rephrase the sentences starting with "Furthermore..." as your conclusion here does not follow from your previous statements. My interpretation is that the precursor of NO absorbs at longer wavelengths than NO3- (nitrate), and as shown in figure 2 NO2- (nitrite) absorbs at longer wavelengths and therefore is likely the precursor source of NO. How does the second statement, that nitrite is more photolabile, follow from this? Is this not clear directly from figure 2? And when you say that NO2- is the precursor of NO, is this not clear from your R6-R12 above? And the source of NO2- is photolysis of NO3-, correct? Has it previously been suggested in the literature that NO3- was a direct source of NO? If so, then please reference this to give context for the conclusions you are making here (i.e. make it clear in your discussion that your model results suggest the following...despite previous suggestions that...).

p.6023: The last paragraph here seems more appropriate as part of the previous dis-

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cussion of the results of this study. The previous (long) paragraph beginning on page 6022 seems more appropriate as part of a conclusions section and could further include interpretation of this study's results in a broader context. This paper would benefit from a conclusions/summary section. Additionally, the implications of this work are not clearly outlined although the discussion of implications is promised in the Introduction of the manuscript.

Finally, it would be interesting to know how much the bulk concentrations of NO3- and NO2- change with the calculated volume fluxes of NO and NO2 out of the snowpack. Many measurements of NO3- concentrations have been made in snow from a variety of environments, though a significant focus has been made in polar regions because understanding the preservation of NO3- at the surface can be used to interpret ice core records. The lack of a significant change in NO3- concentration, for example, at Summit, Greenland (Hastings et al., JGR, D20306, 2004; and Burkhart et al., JGR, D19302, 2004) has seemed surprising given the significant fluxes of NOx out of the snow and it has thus been argued in these papers that significant post-depositional processing of nitrate must therefore not occur. Does a significant change in concentration only in the QLL explain the lack of change in bulk concentration of the snow?

Technical corrections:

Figure 1: The caption mentions a 500 micron thick QLL, which is different than what is discussed in the text and shown in the figure. The caption also states that NO2 photolysis occurs AND does NOT occur at $<$150 microns (there needs to be a less than AND a greater than symbol in this sentence) and the text calculates a thickness of 15 microns not 150?

Figure 3: It is nearly impossible to distinguish the different lines in this figure; please modify this with symbols or better line types/colors.

Figure 4: Add "above the snowpack" at the end of the caption.

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