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Atmospheric Chemistry and Physics Discussions

Interactive comment on "1-D air-snowpack modeling of atmospheric nitrous acid at South Pole during ANTCI 2003" *by* Wei Liao and D. Tan

Anonymous Referee #2

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[General Comments]

This ACPD paper by Liao and Tan describes an attempt to simulating the source, sink and transport of HONO in summertime snowpack at South Pole by using their new 1-D model of snowpack photochemistry and physics constrained by in-situ chemical and meteorological measurements during the ANTCI 2003 field campaign. The scope of the work definitely fits to ACP readership and is timely. To my knowledge, this work is the first attempt ever to simulating the vertical profile of HONO in the snowpack interstitial air.

The authors, however, should make the following points listed below clear before I can recommend the publication of the paper to ACP. The general approach of the

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model appears quite promising and elaborated fairly well so that, once appropriately organized and applied, the model can probably make a significant contribution to the issues of snowpack HONO chemistry and more.

[Specific Comments]

1) Unfortunately the description of model setup is rather unclear and confusing at some places and does not start from the major governing equation(s) so that I had to go back and forth in the manuscript to understand what is generally done by the model. I have no doubt to believe that Sections 2.1-2.4 all describe important components of snowpack processes for the fate of HONO. But, after all, it appears that the model calculates a single set of continuity equation for gas-phase HONO mixing ratio in the snowpack interstitial air, represented by Eq. (3) with a number of assumptions. If this is correct, the authors should have started from Eq. (3) in the model description/setup section.

2) And it is not clearly stated in the present paper, but it also appears that the main source of gas-phase HONO in the interstitial air is multiphase transfer of HONO from "QLL" to the gas phase, i.e. the last term in RHS of Eq. (3), at least for the baseline case. And this HONO(aq) in the "QLL" appears to be derived from Eq.(6) - although with significant typos in it (see Technical Suggestions below) - by specifying the vertically uniform bulk NO2- concentration in the snowpack. If this is correct, I think a major question in the present study should have been the required rate of NO2- supply in each layer of the snowpack in order to balance the loss of HONO to the air. This quantity is actually the last term of in RHS of Eq. (3) itself and can be easily compared with the "Qg" term representing a source from NO3- photolysis. Also, Eqs.(5)-(6) should go to the model setup section.

3) It is not clear to me what the top boundary condition for Eq. (3) is like. There is no quantitative statement about the simulated flux of HONO from the snowpack to the overlying atmosphere. Nevertheless, this issue is mentioned qualitatively by the

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authors as a motivation as well as an outcome for the present study. So I think the authors should make a clearer description of what they did in the present model runs. For example, high HONO mixing ratios in the interstitial air are simulated at low wind speeds. The authors seem to indicate that the gas-phase HONO thus accumulated in the snowpack interstitial air may be pumped out later when it gets a bit windy, but can it be substantial enough even if air contained in the 30 cm deep snowpack is diluted in the near-surface ambient air of 10 m deep or so?

4) The authors stress the role of windpumping in the behavior of HONO in the snowpack. It should be very interesting if the authors switch off their windpumping term and then see what happens and compare with Fig. 4. Again, can the snowpack-to-atmosphere flux of HONO change significantly by switching on and off the windpumping term? Also, the windpumping term was implemented by a pseudo-diffusion term in the work of Toyota and McConnell (2005), but it appears from the Eq. (3) as if the present authors have introduced an explicit advection term, i.e. the second term in RHS of Eq. (3). I wonder how the authors dealt with recurring upward and downward air flow associated with the wind pumping in the 1-D continuity equation. This point is unclear to me even after I read the McConnell et al. (1998) paper. A more explicit description should be added with regard to technical details of the advection term implemented to the model.

[More Minor Comments]

- P9737, L22

Is the NO2 column is large enough at South Pole to influence the ground-level J values?

- P9739, L22

It is stated here that the HONO photolysis is assumed to be the most important sink for HONO in the interstitial air. From the context I presume this photolysis occurs in the gas phase, but no reference is cited for the sigma and phi data of gas-phase HONO in

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Sect. 2.3. Were they taken from the TUV model? In any case, the reference(s) should be added.

- P9739, L14-19

What is the range of Dm in the present case? Is it greater than Dg? Also, are pore velocities (1E-2 to 1E-4 m/s) used for the Dm calculation linked to the wind-pumping velocity "U" in RHS of Eq.(3)?

- P9739, L23

It is stated here that NO3- photolysis provides a source of HONO in the model. But it is not clearly stated how the authors took into account both of the two main channels of the NO3- photolysis:

NO3- + hv -> NO2 + O- (a)

-> NO2- + O (b)

The channel (a) may be followed by a disproportionation reaction:

NO2 + NO2 + H2O -> NO2- + NO3- + 2H+

NO2- concentration is fixed in the present model, so I presume 50% of the NO2 production via channel (a) was assumed to go to the HONO production in the model. I also presume that the NO2- production via channel (b) is then added to obtain the overall HONO production rate. Correct or not, the authors should detail a bit more about the Qg term.

- P9739, L26

Why is the J value of nitrite mentioned here? Was it calculated and used in the model runs? If not, please remove this statement because it may confuse the readers.

- P9740, L3-4:

How large is the UNH bulk nitrite concentration used for the model run? Does it change

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with time?

- P9740, L16

How large is "alpha" for HONO? And reference?

- P9740, L17

Is "a", the snow grain radius, taken as half of "d", the pore diameter (= 2 mm)?

- P9740, L18

Reference for Henry's law of HONO?

- P9740, L21-22

Why is it reasonable to assume that delta-C/delta-t = 0?

- P9741, L17-19

Do the boundary layer height and its static stability play a direct role in Eq.(3)? I suspect not, so please rephrase.

- P9742, Eq.(6)

"pKa1" and "pKa2" should be all corrected to "Ka1" and "Ka2", respectively. If these are not typos but indeed formulated in the model, it would call for the re-calculation of all the results shown in the paper. I also wonder if the authors set the total N(III) concentration (= [H2ONO+(aq) + HONO(aq) + NO2-(aq)]) to the UNH bulk nitrite concentration measurement(s).

- P9758, Fig.6

This figure is virtually identical to Fig. 7 of Riordan et al. (2005). Well, I am not convinced enough that it should be presented like this in the present paper as long as pKa1 and pKa2 values are mentioned in the text.

[Technical Suggestions]

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First of all, the quality of English usage can be improved substantially. So I strongly suggest that the authors should once let a native English speaker go over the manuscript.

- P9734, L11

"(Jones et al., 2007), etc.)" -> "(Jones et al., 2007, and references therein)"

- P9735, L6

"life time" -> "lifetime"

- P9735, L18

"comprises of" -> "is comprised of"

- P9736, L23

"Pole. during ANTCI 2003" -> "Pole during ANTCI 2003."

- P9737, L27

This one sentence paragraph should be moved/merged to the end of the previous paragraph.

- P9738, L15

"Master equation and model results" -> "Master equation"

- P9739, L4

"where" -> "whereas"

- P9739, L5

"with" -> "by"

- P9742, L13

"quasiliquid" -> "quasi-liquid"

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- P9742, L1 and P9748

The Riordan et al. (2005) paper is missing in the References list.

Riordan, E., Minogue, N., Healy, D., O'Driscoll, P., and Sodeau, J.R., Spectroscopic and Optimization Modeling Study of Nitrous Acid in Aqueous Solution J. Phys. Chem. A, 109, 5, 779 - 786, 2005, 10.1021/jp040269v

- P9759, Fig.7

The legend "Model Setting" should be changed to "Baseline" or similar.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9731, 2008.

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