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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

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1) 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.

Please see the response to the reviewer immediately preceding this. Please keep in mind that we do not support the idea that the NO2- supply comes solely from NO3- photolysis (see line 13-14 on page 9735).

2) 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?

There is no constraint for the upper and lower boundary and they are solved numerically (forward integration in Matlab). The vertical depth is 30 cm below snow surface and we use 20 uniformly distributed layers (1.5 cm per layer). The sensitivity analysis of model parameters is tabulated in Table 3. This has been clarified in the manuscript.

We have a subsequent paper to address the effect of snowpack on atmospheric HONO measurements which will address snowpack-atmosphere coupling. Attempting to include the atmospheric modeling makes for a very large and cumbersome paper, and it was felt that splitting the snowpack modeling from the atmosphere made a complex system somewhat more tractable.

3) 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-toatmosphere 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.

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The windpumping drives the distribution of HONO in the snowpack. Turning this off leads to a mostly uniform distribution with respect to time, as the remaining dispersion/diffusion term is larger than the net chemical term, which ultimately derive from J(NO3-) and J(HONO). The depth profile would resemble the shallow boundary layer period. Toyota and McConnell did extensive model testing and their 1D windpumping model is almost equivalent to 2D advection averaged over the whole wavelength of microtopography when they work with discrete equations for numerical integrations.

[More Minor Comments] - P9737, L22 Is the NO2 column is large enough at South Pole to influence the ground-level J values?

J (NO2) is derived from radiometer data using, in part, the NO2 column over South Pole.

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

We will add "from TUV model (Madronich and Flocke, 1998)"; after "at wavelength lambda"; on line 5 page 9738.

- 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)?

The range of Dm is 1.5e-8 to 7.5e-6 m2s-1, it is less than Dg. 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

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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.

We use the quantum yield for HONO formation of 3.8e-4 by nitrate photolysis (Bartels-Rausch, T. and Donaldson, D. J.: HONO and NO2 evolution from irradiated nitrate doped ice and frozen nitrate solutions, Atmos. Chem. Phys. Discuss., 6, 10713-10731, 2006.). Please see the reference for details.

- 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.

We will change "The J values of nitrate and nitrite have similar behavior with depth through out snowpack" to "The J values of nitrate have similar behavior with depth through out snowpack"

- P9740, L3-4: How large is the UNH bulk nitrite concentration used for the model run? Does it change with time?

We will change "here we use the UNH bulk nitrite and assume a constant concentration of nitrite with snow depth" to "here we use the UNH bulk nitrite and assume a constant concentration of nitrite (2x10-8 M) with snow depth and time"

- P9740, L16 How large is "alpha" for HONO? And reference?

Alpha=0.1 Sportisse, B. and Djouad, R.: Some aspects of multi-time scale issues for the numerical modeling of atmospheric chemistry. Atmospheric Modeling. Series: The

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IMA Volumes in Mathematics and its Applications, 130., 39-59. Springer, New York, 2000.

- P9740, L17 Is "a", the snow grain radius, taken as half of "d", the pore diameter (= 2 mm)?

Yes

- P9740, L18 Reference for Henry's law of HONO?

Park, J.-Y., and Lee, Y.-N.: Solubility and decomposition kinetics of nitrous acid in aqueous solution. J. Phys. Chem., 92, 6294-6302, 1988. This is now included in the text.

- P9740, L21-22 Why is it reasonable to assume that delta-C/delta-t = 0?

Essentially the assumption is that HONO neither builds up nor depletes in the time period of the model. This is of course insupportable at polar dawn and dusk, and may not apply for transient events during the modeling period (just as it would not apply for high solar zenith angle and transient events in any steady state photochemical model). While it is a simplifying assumption, it is harder to justify a buildup or depletion of HONO when conditions are not changing rapidly, as was the case for most of ANTCI 03.

- 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.

The boundary layer height and its static stability do not play a direct role on the wind pumping velocity (U in equation 3). They are correlated through the wind speed, but there is no implication that BL height and stability control wind pumping.

- 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

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nitrite concentration measurement(s).

"pKa1" and "pKa2" are typos. We set the total N(III) concentration(= [H2ONO+(aq) + HONO(aq) + NO2-(aq)]) to the UNH bulk nitrite concentration measurement(s).

[Technical Suggestions] We would like to thank the reviewer for the technical suggestions.

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

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