Modelling the Reversible Uptake of Chemical Species by Ice Particles, by V. Marécal et al., Atmospheric Chemistry and Physics Discussions, 2010

Reviewer - Jeff Snider, University of Wyoming, Laramie

Overview

Marécal et al. use parameterizations describing Langmuir equilibrium absorption to evaluate trace gas uptake by ice particle surfaces. The particles are followed along trajectories passing through a modeled cloud. In addition, the semi-empirical theory of Kärcher is used to describe volume uptake of nitric acid by ice particles. The authors compare and contrast model results for eleven trace gases (equilibrium surface uptake) and apply the Kärcher theory (trapping into the bulk) within the context of the cloud model.

The motivation for the study is the recognition that cloud motions are important for the distribution of gaseous pollutants; both passive substances (for example, carbon monoxide) and those which have and affinity for condensed water. There is a long history to this, going back to the seminal work of Chatfield and Crutzen (1984) and the observational studies that the Chatfield/Crutzen model inspired (e.g., Dickerson et al., 1987). In Marécal et al., the emphasis is on ice/pollutant interactions at temperatures colder than 235 K (-38 C). That is, in regions of cloud likely to be completely glaciated.

Substantial Criticisms

Marécal et al. state “For the trapping approach, only HNO3 is studied since the necessary parameters are only available for this process” (p.24366). This statement is true in the sense that HNO3 was the only compound examined by Kärcher et al. (2009). I feel that it is also important to recognize that data does exist for the trapping of other trace gases in ice during vapor growth. For example, temperature-dependent volume uptake coefficients are available for four of the eleven compounds selected by Marécal et al. (Huffman and Snider, JGR, 109, D01302, doi:10.1029/2003JD003778, 2004). Given that alternate evaluations of the trapping are available, and also parameterized for use in models (see the final two columns of Table 1 of Huffman and Snider (2004) and their Equation 4), it is my opinion that an opportunity has been missed. I encourage the authors to apply these additional descriptions of trapping in their model analysis. At a minimum, I am insisting that the authors recognize that the vapor growth / trapping mechanism has been studied for four of the eleven selected compounds. I also encourage the authors cite, and evaluate, the Diehl et al. (2005) trapping results for HCl - one of the eleven compounds examined using the surface adsorption (equilibrium) mechanism.

Although there is brief discussion of the issue, on p.24377, sedimentation complicates interpretation of the ratio of mixing ratios (gas phase divided by the total). This would seem to be particularly vexing for species which partition efficiently to the condensed phase. As a consequence I am uneasy about several aspects of the analysis: 1) The figures 8 and 9 showing the gas mixing ratio, 2) the surface percentages provided on p.24387, and 3) the rates reported in figure 11. I encourage the authors to explain, quantitatively, how sedimentation influences these values (concerns 1, 2 and 3).

Other Criticisms

p.24365, and elsewhere
"…air parcel trajectories encountering….." I recommend different phrasing, for example, "…air parcel trajectories within….", or if the motions outside the cloud are also important (see #4 on p.24365), you could say "...air parcel trajectories derived from a simulation of a convective cloud by the BRAMS."

p.24365
Are bullets #2 and #4 relevant to this study? For example, you restrict your investigation to temperatures colder than -38 C, so why should there be relevance in this study to freezing and the resulting degassing?

p. 24364
"The simulations showed large concentrations of ozone….in the ice phase."
On the IUPAC site, experimental data for the ozone/ice interaction is summarized. In contrast to the molecules modeled by Marécal et al., there is negligible affinity ice/ozone affinity. Given that result, how is it possible that the ice-phase ozone concentrations were large?
(http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/O3+ice_V.A1.2.pdf)

p.24364, l24
This sentence is written as a statement of fact: "HNO3 in the ice phase is only located at the edge of the convective turrets."
My recommendation is that this be stated less emphatically.

Figures 1 and 2 – These are organized differently (columns and rows) than they are explained in the figure caption.

p.24367
There is no mention, at this point, that "D" is a volume equivalent diameter; unless I missed it, this explanation comes several pages later (p.24375).

p.24367 and p. 24368
Although it is used several times in the context of the discussion about Equations 1 and 2, the "gamma" is not defined. That definition comes several pages later (24376).

p.24366, l.17
Should "steady state" be replaced with "equilibrium"?

p.24370, and else where
To my ears, "dry ice" is referring to solid carbon dioxide. Rather, you are referring to the families of pristine, snow and aggregate ice. Is there a way to do this differently? Also, the model may carry liquid water on the surface of graupel and hail, but in reality, do you expect liquid to be present on those particles in the cold conditions you are analyzing?

p.24371
“that experienced” -> experienced by

p.24372
The gas concentration (ng) is introduced before it is used in an equation.

p.24372
There is a type in the parenthetical definition of ns.

p.24373
“In case” - > In the case
“needed e-g-” -> E.g.,

Figure 6
Since these are functions, I suggest that no points be shown. Also, I suggest that the functions be plotted different over the range that measurements were made (solid line, for example) versus the range over which extrapolations are made (dashed line, for example).

Equation 9
Would this be simpler if the “gammas” were incorporated into a constant? Should the “A”, the “Nt” and the “Dn” be subscripted with a “j”, to be consisted with Equation 8?

p.24377, first paragraph
The concept you introduce is simple, but the presentation (Figure 7) is complicated. There is the (mass) mixing ratio (commonly, the “mixing ratio”), the surface area mixing ratio and the number mixing ratio. From the preceding discussions, it is relatively clear what these are. Now you introduce the “volume mixing ratio.” The latter concept (volume mixing ratio) does not seem necessary, either for the discussion on p.24377 or for the presentation. Figure 7 should be revised.

p.24379
“asessment”->assessment

p.24380
“relatively”->relative, and elsewhere

p.24385
“water vapour saturation coefficient above ice”->ice saturation ratio
“due to relatively”->due to the relatively

p.24386
“According to relation (Eq. 18)”->According to Eq. 18,

Throughout
Calling a gas mixing ratio a “concentration” can cause confusion and should be avoided. For an example, see the Y-axis labels for Figure 9.