

## ***Interactive comment on “A novel model to predict the physical state of atmospheric H<sub>2</sub>SO<sub>4</sub>/NH<sub>3</sub>/H<sub>2</sub>O aerosol particles” by C. A. Colberg et al.***

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Comment offered by Scot T. Martin, Harvard University, December 29, 2002

This manuscript provides a state-of-the-art treatment of the assessment of the phase (including aqueous state and crystalline ammonium sulfate, letovicite, and ammonium bisulfate) of atmospheric particles with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O chemistry. A major emphasis of the work is to employ trajectories (numbering in excess of 10000) to provide time histories of temperature and relative humidity, which is the first effort ever to assess hysteresis effects of tropospheric particles on a global basis. I offer comments and questions below that I hope will aid the authors to further improve their excellent manuscript.

I believe the authors have done an excellent job in offering creative ground-breaking

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work, but I also believe the authors would do well to point out some of the limitations, i.e., in several places I think the authors are claiming too much. The authors state in the abstract, for example, that they take "full account of the deliquescence/efflorescence hysteresis." Perhaps, better would be "offer an initial treatment of...". Why do I say this?

Example #1: From my understanding (which may not be accurate—see below the section on "clarity of presentation"),  $ASR(x,y,z)$  is a fixed climatology for July. At each grid point, the RH and T are determined from trajectory input at 6 hr intervals. I think mixing climatology for ASR and time-resolved RH and T is an uneven match: at 6 hr intervals, ASR will certainly have variance and likely even have correlation with RH and T (e.g., more  $NH_3$  emissions at high temperature).

Example #2: How is subgrid variability of RH incorporated into the trajectory treatment?

Example #3: In conclusions on page 18, "The direct aerosol forcing effect is very sensitive to the water uptake properties of particles (Adams et al., 2001). Therefore the physical state of atmospheric aerosol particles is of high importance." As the authors point out in their introduction, Boucher and Anderson (1995) have determined the effect of phase to be under 20% on global radiative forcing, and many other studies seem to concur (including Adams et al., 2001). Compared to other uncertainties (e.g., emissions, RH field, and more), it is my understanding of published literature incorporated into IPCC assessments that particle phase is of second order importance in accuracy of radiative forcing. The effect of optical constants (e.g., letovicite versus crystalline ammonium sulfate) also appears to be of second-order importance. The published literature hence downplays the importance of phase in radiative forcing. Some of these calculations should undoubtedly be revisited by scientists who have a primary focus on the effects of particle phase. My main point here is simply that I do not think the cited literature supports the authors' strong statements. I think moderated statements would be more appropriate.

Example #4: Why is the aerosol treatment most closely analyzed for 400-600 mbar?

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Most of the aerosol mass is at surface level. [What are the uncertainties that preclude surface level investigations?]

### Detailed Questions and Clarity of Presentation

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1. How is the 4 deg by 5 deg ASR climatology reconciled with the 5 deg by 5 deg trajectories?
2. Because ASR is a climatology fixed for either July or January, it is probably misleading to label  $ASR(x,y,z,t)$  as done on page 6. The "t" functionality suggests equivalency to  $RH(x,y,z,t)$  and  $T(x,y,z,t)$ , which I believe are on 6 hour time steps. It would probably be better to label  $ASR(x,y,z,July)$ .
3. The caption to Figure 2 has some problems, e.g., only left panel is explicitly mentioned.
4. Section 2.1.2 mentions "ASR climatology" while section 2.1.3 mentions "temporal development of ASR". Isn't there a contradiction here?
5. BIG POINT ON CLARITY: "fraction". What is fraction? By number? By dry mass? By wet mass? By mole fraction? My inference from studying the manuscript is that there is no number resolution. Hence, I am guessing fraction "by dry mass". However, page 15, "a higher percentage of solid-containing particles" suggests fraction by number, as does other phrasing throughout the manuscript. Perhaps, "dry mass fraction" should be used throughout manuscript.
6. I think there is no evidence in literature for soot as good heterogeneous nuclei. Section 3.6 should be backed up by literature (if any!). DeMott and ten Brink have published evidence showing soot to be a poor heterogeneous nucleus.
7. Caption to Figure 5 and elsewhere throughout manuscript. "Fraction of particles in July." Given the trajectories are at 6 hour intervals, "in July" requires averaging. How is

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the averaging done?

8. Section 3.5.1. I don't understand why the authors feel they need to address possible heterogeneous nucleation of a second phase. Haven't their lab experiments addressed this topic? Do the lab experiments show any heterogeneous nucleation? If so, the processes should be included. If not, the processes need not be included.

9. I have studied section 3.5.1 and Figure 11 for some time, and I do not understand the authors' presentation. Can it be clarified? What does the curvature in the black-dashed and solid-dashed lines mean? Shouldn't the connection from point 1 to 2 be vertical for a supersaturated solution (as discussed in text)? What is the meaning of discontinuity in the lines at low RH? Of course, I understand in general what the authors want to say regarding chemical compositions and possible heterogeneous nucleation; however, I feel my understanding comes more from my background in this field than the paragraphs in section 3.5.1 and Figure 11. Hence, I encourage the authors to clean up this section.

10. Section 3.5.2 is also confusing. I understand the general problem the authors need to deal with (i.e., forced ice saturation in ECMWF does not allow deliquescence), and I understand they have invoked something in the algorithm to test this point and found the effect to be minimal, i.e., deliquescence below the eutectic is not a phenomenon occurring often in the atmosphere (at least that is my inference from what I understand in this paragraph). I think the key sentence where I am lost is: "To obtain a lower bound... we put RH to the value..." This sentence seems critical, but I do not understand it.

Continued into part 2 (4 page limit)

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