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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Global modeling of cloudwater acidity, rainwater acidity, and acid inputs to ecosystems" *by* Viral Shah et al.

Anonymous Referee #1

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Shah et al. report global predictions of cloud and precipitation acidity from an updated version of GEOS-CHEM. The addition of formic and acetic acids and of dust enable the model to better capture regionally important influences on hydrometeor pH and to better match spatial variations in acidity relative to other recent model predictions. The work is thorough, carefully conducted and, for the most part, clearly explained. I have a few comments and suggestions:

1. abstract, lines 21-22: please clarify that the model successfully reproduces annual mean rainwater pH observations.

2. The authors refer to rainwater acidity and go to the trouble of somewhat strangely defining rainwater to include snow. Why not just use the more general term "precipitation" throughout?

3. The addition of formic and acetic acids captures important influences on cloud and precipitation acidity. a. it would be useful to mention that future work might also warrant consideration of other key dicarboxylic acids (e.g., oxalic, succinic) that can be abundant in clouds. b. I was disappointed to see the authors recognize their new scheme continues to significantly underpredict acetic acid concentrations, as evidenced by comparison to source strengths considered by others as well as observed wet deposition fluxes (a factor of 4) but did not take action to correct for this discrepancy. They point out that a biogenic emissions scaling could correct this discrepancy similar to how they corrected for HCOOH underpredictions. Why not make that correction as part of this paper?

4. Eq'n. 1: The authors exclude both CO32- and OH- from this charge balance equation, arguing that both are small for pH<8. I am OK with this omission of CO32- but worry about artifacts in their higher pH simulations due to omission of OH-. At pH 7, for example [OH-] equals [H+], meaning that omission of OH- introduces a relatively significant error in the H+ concentration obtained from eq'n 1 in this pH range. Why not just include OH- and eliminate this high pH artifact? How does this artifact of OH- omission at high pH influence the comparison with other cloud models at high pH (e.g., p.9, lines 59+)

5. The authors discuss the importance of NH4+ and carboxylic acid buffering on cloud pH when strong acid inputs decrease. It would be good to mention here that other buffers may also play an important role, including HCO3- (see, e.g., Collett et al. (1999) Internal acid buffering in San Joaquin Valley fog drops and its influence on aerosol processing. Atmos. Environ., 33, 4833-4847).

6. p. 13, lines 89-92: Again talking about the pH buffering effect, the authors point out that a factor of 2 decrease in sulfate and nitrate inputs yields a pH increase of 1 unit, with buffering, vs. 2.1 units predicted w/o buffering. Have they examined historical time series of cloud pH to see if this effect is apparent in ambient observations? One simple comparison to ballpark this might be to look at the pH trends over time in various

regions of the world as summarized by Pye et al. (2020) vs. known changes in NOx and SOx emissions in those regions.

7. The manuscript would benefit from a more detailed discussion of how cloud pH data were selected for comparison to model predictions. The authors include several observational studies in a number of regions, but certainly not all. I understand that some points are omitted due to source proximity and some, I think, were omitted due to being from an era far from the 2013 simulation and its emissions levels (although some fairly old measurements are included). Others (e.g., several studies from Japan mountain sites and the recent Kim et al. observations from the northern Pacific (https://doi.org/10.1007/s10874-020-09403-8)) are not included. A more robust discussion of why various datasets were included/excluded would give the reader greater confidence in the very promising matches shown with modeled pH values by region.

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