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Atmospheric Chemistry and Physics Discussions

Interactive comment on "How alkaline compounds control atmospheric aerosol acidity" *by* Vlassis A. Karydis et al.

Anonymous Referee #2

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This paper uses a model to predict fine particle (PM2.5) pH globally. They find more acidic particles in the more anthropogenically-influenced regions and basic particles in regions of high non-volatile cations, a finding that is not highly surprising but which does provide a general verification of the method. Their major finding is on how alkaline compounds control PM2.5 particle acidity and these trends over the past 50 years.

The devil is in the details and this is especially true when assessing aerosol particle pH and particle pH impacts. As noted by the 1st reviewer, the pH predicted by the model is off by a wide margin in some locations relative to predictions supported by data. I would note that the model is often significantly off in locations where the pH predictions have been assessed through comparisons between observed gas/particle partitioning of HNO3 and NH3 to predicted values and where partitioning of at least of these species is sensitive to pH, meaning there is high confidence in the pH reported for these cases. The first reviewer provided significant details on this issue. I will not repeat those suggestions and instead look a a broader view.

I calculate that the mean (median) pH difference (simulated – field derived) from the data provided in Table S1 is 1.61 (1.4), suggesting the model is systematically predicting a high pH globally (the authors may wish to check my calculations).

I suggest the authors spend more time on first making sure, and discussing in more detail, the quality of the pH predictions. What causes this high pH bias compared to other reported studies and what are the implications. A greater focus on this apparent discrepancy is important since this manuscript is based only on a model prediction and incorrectly predicted pH has significant ramifications. First, a major finding reported is on the role of alkaline species that raises the particle pH; a high bias pH would indicate that the role of alkaline species is overstated in this analyses. Second, the paper also focuses on the partitioning of HNO3, which is highly non-linear with pH, where HNO3 can change from all in the gas phase to all in the particle phase over a change in pH of about 1 to 2 units, near the level of the mean difference found in the comparison, as noted above. Thus the bias could have a large impact on this finding as well. Overall, it is not clear what new contribution this paper makes on understanding aerosol pH. Substantial modification based on a better assessment of the model should be required prior to consideration for publication.

Aside, I do not see the seasonality in mid N American latitudes (noted in lines 67-68, Fig 2), which also seems to disagree with two independent observational studies (Wong et al, 2020; Tao et al, 2019) and which has significant implications.

Tao, Y., and J. G. Murphy. 2019. 'The sensitivity of PM2.5 acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites', Atm. Chem. Phys., 19: 9309-20.

Wong, J. P. S., Y. Yang, T. Fang, J. A. Mulholland, A. Russell, S. Ebelt, A. Nenes, and R. J. Weber. 2020. 'Fine particle iron in soils and road dust is modulated by coal-fired power plant sulfur', Envir. Sci Technol., 54: 7088-96.

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