Anonymous Referee #2

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.

We thank the reviewer for his/her review of our manuscript and the helpful comments. Below is a point by point response to his/her comments.

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 analysis. 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.

As discussed in response to the second comment by the first reviewer, the calculation of aerosol acidity on a global scale requires the advanced treatment of atmospheric aerosol chemical complexity, analogous to the real atmosphere and beyond the conventional methods used by the current chemistry-climate models (CCM). The atmospheric chemistry model system EMAC is the ideal tool for this purpose since it is one of the most comprehensive CCM containing advanced descriptions of the aerosol thermodynamics (including the dust-pollution interactions) and organic aerosol formation and atmospheric aging (affecting the aerosol water). Therefore, the comprehensive global atmospheric multiphase chemistry simulations of the past 50 years presented in this study enabled us for the first time to provide advanced aerosol acidity calculations

and the associated sensitivities. Our model calculations for aerosol acidity are based on several important processes/factors that are not included explicitly, or usually neglected, by most of the model-calculations used to constrain the aerosol acidity from observations, and this leads to higher pH values in our analysis. In brief, these factors are the following and are further analyzed in our response to the first reviewer: 1/ the stable/metastable assumption, 2/ The lack of crustal species in the observations, 3/ the omission of the organic aerosols contribution to the aerosol water, 4/ The use of the reverse mode of ISORROPIA, or the lack of gas phase species (e.g., NH_3, HNO_3) in the pH calculations, 5/ Uncertainties on the methods used to derive the campaign-average (or for 3D models the simulated average) pH, 6/ Coding errors in the stable state assumption of ISORROPIA II model in past studies, 7/ The type of thermodynamic model used (e.g., E-AIM vs. ISORROPIA), 8/ Measurement artifacts associated with the volatilization of ammonium nitrate from filters, 9/ The mixing state of aerosol due to the location and height of observational samples compared to the well-mixed aerosols from our model with grid size $1.9^{o} \times 1.9^{o}$ and ~67m height.

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.

This is correct. A clear seasonal pattern is mostly evident over highly polluted regions like East Asia and not over Europe and Eastern USA. The Northern extratropical Oceans also exhibit seasonality. We have corrected the text accordingly.

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.