

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

Anonymous Referee #1

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This paper from Karydis et al. predicts fine particle acidity, which is an important aerosol property linked to many particulate physicochemical processes, on the global scale and over a long historic period of 50 years. It discovers some interesting long-term trends in particle acidity with discussions on seasonal variabilities. Most importantly, it highlights the important roles of alkaline salts, such as ammonium and crustal cations, to buffer and elevate the global pH. The results are of interest to the geoscience community and supported by high-quality modeling, thus suitable for the scope of ACP Letter. However, several issues should be clarified before acceptance for publication, especially the large discrepancies in pH prediction (in some cases more than 2 units) when compared to observationally-constrained pH in previously reported studies, since the overestimation of pH results in exaggerating the importance of alkaline salts and

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the accuracy of pH prediction determines its implications to atmospheric chemistry.

Major comments:

- Line 50&Line 218: the assumption of aerosol mode (solid+liquid vs. liquid) matters for pH prediction. For instance, it changes the estimated pH by more than 3 units in Pasadena. The current text in the method section lacks the explanation why the stable mode was chosen over metastable mode. More discussions would be useful to validate the model results. The Pasadena pH estimation in Guo et al. (2017) assumes metastable aerosols due to the high RH observed in that study ($79 \pm 17\%$). Considering the even higher RH after sunset, particles are highly likely to get deliquesced and stay so even in the daytime when RH drops below DRH (deliquescence relative humidity) but above ERH (efflorescence relative humidity). Such an effect would be observed in a place with a similar RH diurnal cycle. I wonder if a better way to present the model results is to choose the metastable mode for high RH cases/regions (such as the average RH of 60% and with nighttime/max RH over mutual DRH) and the stable mode for low RH cases/regions, especially when the two results deviate from each other by more than one pH unit. But the key judgment is which particle-phase assumption works the best to predict gas-particle partitioning of semi-volatile species comparing to observations (while the particle phase measurement/modeling is not available on the global scale). - Table S1 summarizes the comparison of simulated fine particle pH in this study to observationally-constrained pH in previous studies. In most cases, the simulated pH is higher, and the differences range from sub-one units up to six units. It is acknowledged that some previous estimations are biased low for lack of gas-phase input (e.g., Line 76). However, large differences are seen when compared to some observationally-constrained pH with gas-phase input, such as Pye et al. (2018) (7.0 vs. 1.1) and Murphy et al. (2017) (4.2 vs. 1.6). Also, the prediction of remote air in the Atlantic and Pacific Oceans (roughly 5-6 in Figure 1 other than lower values of 3 predicted for the northern parts that are heavily affected by anthropogenic emissions) is much higher than pH estimations based on ATom aircraft studies (roughly 0-1) (Nault et

al., 2020). Although the ATom estimations are based on submicron particles (and this study focuses on PM_{2.5}), it is hard to believe that sea salts or mineral dust between 1 and 2.5 μm can elevate particle pH by 4-7 units on average. In summary, the results are very different, such as nearly neutral vs. highly acidic fine particles (i.e., very different implications for chemistry), requiring more discussions on the causes (e.g., crustal elements, mixing state, or particle phase). Possibilities include 1) that the simulated crustal elements may be externally mixed with sulfate/nitrate/ammonium aerosols or 2) the overestimation of crustal elements or the sum of ammonia and ammonium. In either case, the effects of alkaline compounds on the global fine particle acidity would be less than proposed. One way to tell the key factor(s) is by comparing the thermodynamic model inputs between the simulated ones and the field observations and do some sensitivity tests. - Caution should be paid towards Ca (especially for the cases of high Ca mass concentrations) due to the precipitation of CaSO₄ as ISORROPIA-II assumes it to be completely insoluble. Some sensitivity tests may be carried out such as done in Kakavas et al. (2021). - Line 26: Please elaborate on how the cited papers show the effects of aerosol acidity on particle hygroscopic growth and its lifetime. The three papers talk about the importance of mineral dust in thermodynamic modeling. For example, Karydis et al. (2016) highlight that the tropospheric nitrate burden increases by 44% when considering dust aerosol chemistry but the connection between aerosol acidity to hygroscopicity or lifetime seems to be buried. - Line 66: "The aerosol pH over the anthropogenically-influenced northern hemispheric mid-latitudes exhibits a clear seasonal pattern with lower values during boreal summer and higher ones during winter, driven by the availability of ammonium and by the aerosol water content (Fig. 2)." First, please specify the locations after "northern hemispheric mid-latitudes". Second, it is not clear these regions exhibit clear seasonal variations as stated. For instance, the curves of the eastern US and Europe are nearly flat throughout the year, while the western US shows lower pH in the winter months (e.g., Dec, Jan, and Feb), opposite to the trends stated in the text. - Line 101: Suggest rephrasing the sentence as "Over North America, aerosol acidity also decreased with reduced SO₂ and NO_x

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emissions.” However, it seems to be more complicated for NO_x than SO₂, since more total nitrate may increase pH given the same amount of sulfate, transferring aerosols from a more acidic ammonium sulfate (or ammonium bisulfate) system to a less acidic ammonium nitrate system. - Line 118: The dominant H₂O₂ pathway at pH < 5 is for cloud droplets, not fine particles. Cheng et al. (2016) state that the NO₂ pathway dominates at pH > 5 and the TMI pathway (transition metal ions) dominates at pH < 4.5 for the Beijing haze conditions. So even if the authors chose to only calculate the H₂O₂ pathway (which is probably the most important one for the less polluted cases at pH < 5) for the past 50 years, it is worth mentioning the other possible dominant pathway. - Line 131: Stating that NH₃ is a major buffer is reasonable since it is often found in both gas and particle phases. Thus, it can redistribute between the two phases to buffer the pH. It remains to be explained though if the crustal elements simply increase particle pH or buffer the pH since they are non-volatile. For instance, although carbonate or bicarbonate is not considered in the ISORROPIA-II calculation, it could be the anion paired with crustal elements to buffer high pH for the H₂CO₃ pK_a of 6.4 (The pK_a of HCO₃⁻ is 10.3, which is too high to buffer the predicted pH predicted in this study). - Line 211: It would be useful to specify if the kinetic limitations affect simulations in this study and by what extent. The thermodynamic simulations based on observations often don't find the signs of kinetic limitations for fine particles (i.e., the predicted gas-particle partitioning agrees with observations, e.g. (Guo et al., 2017; Liu et al., 2017)), unless very fresh aerosols are sampled near the sources. - Line 267: It is not clear why Equation A2 is used to investigate the impact of pH on nitrate partitioning but not the results directly from ISORROPIA. The two should be equivalent. Please explain.

Minor comments:

- Line 31: Consider deleting “In the past” and changing the past form to present form since the ion balance and molar ratio methods still have these limitations and also don't consider the partial disassociation of acids, which could be added here. - Line 56: Change “high pH's are found...” to “high pH are found”. - Line 78: Add “(Fig.

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1)” after the sentence “Over the Arctic and the northern Atlantic and Pacific Oceans, aerosol acidity is significantly enhanced by strong sulfur emissions from international shipping and pollution transport from industrialized areas.” Since the former and latter sentences are talking about Fig. 2. - Line 90: Does it make sense to have the most points in Fig. S1 with larger than one cation/anion ratios? Not for liquid only particles but reasonable for solid+liquid aerosols. So it would be great to explain this better either in the main text or in Fig. S1 caption. - Line 96: Provide kappa for ammonium sulfate and ammonium nitrate. - Fig. 1 caption: Add “during the period 1970-2020” after “Surrounding panels show the temporal pH evolution at locations defined in Table 1” to specify the time range (although it can be easily told from the panels). - Line 126: do you mean “overestimate”? Since the SO₂ emission reduces drastically in Asia, the inventories are not updated in time to catch the reductions. Therefore, I would think overestimation makes more sense here logically. - Line 128: consider change “the large SO₂ trends” to “the significant SO₂ reduction trends” or “the long-term SO₂ trends”. - Line 154: add “is” after “NH₃” to be “NH₃ is also proved to be. . .” - Line 237: consider adding a reference for $\kappa_{\text{org}} = 0.14$. Also, while the Greek alphabet of κ is used here, “kappa” is used in Fig. 4. Better to be consistent.

References:

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