Anonymous Referee #1

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

We would like to thank the reviewer for his/her positive response and for the very thoughtful review. By raising important issues, the reviewer helped us further to better present our results and improve the manuscript. Below is a point by point response on the comments and suggestions.

Major comments

1. *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 ± 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).*

We agree with the reviewer that the aerosol state assumption is important for the pH calculations with ISORROPIA and needs further attention in our manuscript. Here we used a revised ISORROPIA-II model which includes modifications proposed by Song et al. (2018), who resolved coding errors related to pH calculations when the stable state assumption is used. Applying the revised model during winter haze events in Beijing, they have found that the assumed particle phase state, either stable or metastable, does not significantly impact the pH predictions. However, a sensitivity simulation in our study (e.g., applying both stable and metastable assumptions on a global scale) revealed that even if the assumed

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particle phase state does not significantly impact the pH calculations over oceans and polluted regions (i.e., characterized by high RH values), the metastable assumption produces more acidic particles (up to 2 units of pH) in regions affected by high concentrations of crustal cations (i.e., downwind of desert areas) and consistently low RH values. Fountoukis et al. (2007) have shown that the metastable solution predicts significant amounts of water below the mutual DRH (MDRH, where all salts are simultaneously saturated with respect to all components). In addition, the presence of high calcium concentrations downwind of the deserts results in increasing pH values due to the missing precipitation of insoluble salts such as the $CaSO_4$. This is something that the metastable state assumption fails to reproduce since it treats only the ions in the aqueous phase. In general, high amounts of crustal species can significantly increase the aerosol pH which is consistent with the presence of excess carbonate in the aerosol phase (Meng et al., 1995). Since our model is applied on a global scale, we believe that the stable state assumption can reproduce the sensitivities of pH more accurately given that the focus of our manuscript is on insights regarding the impacts of alkaline species on aerosol acidity. The stable state assumption gives almost identical results with the metastable in areas with high NH_3 concentrations (e.g., over central Europe) and at the same time is more appropriate for regions affected by crustal elements (i.e., close to deserts). Overall, the stable state assumption used here as a basecase simulation produces about 0.5 units higher global average pH than the metastable assumption.

Polluted areas that are downwind of crustal sources (like Pasadena) are of special interest and will be discussed more elaborately in the manuscript. When calculating species concentrations, the stable state solution algorithm of ISORROPIA II starts with assuming a completely dry aerosol and based on the ambient RH dissolves each of the salts depending on their DRH. However, in the ambient atmosphere, when the RH over a wet particle is decreasing, the wet aerosol may not crystallize below the MDRH but instead remain in a metastable state affecting the uptake of water by the aerosol and thus the pH. We agree with the reviewer that this can happen in some locations with high diurnal variations of RH. However, over Pasadena, the observed RH is always high (87±9%) for the period used for our model comparison (second half of the campaign where $PM_{2.5}$ were measured). Our sensitivity analysis revealed that the aerosol state was not affected by the state assumption since over Pasadena, both stable and metastable assumptions predict the same amount of water in the aerosol. We believe that the differences on pH are due to the high concentrations of calcium from the Great Basin Desert which results in the precipitation of high amounts of $CaSO_4$, lowering the particle acidity (but without affecting the water activity since $CaSO_4$ is insoluble and does not contribute to the MDRH depression). It is worth mentioning that calcium was not included in the Guo et al. (2017) study which can explain the differences in the observed and simulated aerosol acidity. Our sensitivity analysis shows that the simulated particle-phase fraction of nitrate over Pasadena is 40% using the stable state assumption and 32% using the metastable assumption, compared to the observed 51%. This is in accordance with the findings of Ansari and Pandis (2000) who suggested that the stable state results in higher concentrations of aerosol nitrate when the RH is low (<35 %) and/or sulfate to nitrate molar ratios are low (<0.25). Karydis et al. (2016) have shown that while the aerosol state assumption has a marginal effect on the calculated nitrate aerosol tropospheric burden (2% change), it can be important over deserts at very low RHs where nitrate is reduced by up to 60% by using the metastable assumption.

2. *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 PM2.5), 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.*

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 accurate 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 model calculations used to constrain the aerosol acidity from observations. These are the following:

1/ As discussed above, the stable/metastable assumption does not affect the simulated pH most of the time, however, in some case with low RHs and the presence of crustal cations, the metastable assumption results in lower pHs.

2/ Crustal species from surrounding deserts and Na^+ from sea salt can elevate the pH significantly in some locations, however, these are often neglected from observations.

3/ The organic aerosols (which are treated comprehensively by our model using the module ORACLE and the volatility basis set framework) can contribute significantly to the aerosol water, and thus increase the aerosol pH. This contribution is not considered by many observational studies.

4/ The inclusion of gas phase species (e.g., NH_3, HNO_3) in the pH calculations is important, since using only the aerosol-phase as input (i.e., reverse mode) the inferred pH exhibits a bimodal behavior with very acidic or alkaline values depending on whether anions or cations are in excess (Hennigan et

al., 2015). Even if the forward mode is used (without gas phase input), the calculated aerosol pH is biased low (approximately 1 unit of pH) due to the repartition of semivolatile anions (i.e., NH_3) to the gas phase to establish equilibrium (Guo et al., 2015).

5/ Another important aspect, usually not mentioned in many studies, relates to the methods used to derive the campaign-average (or for 3D models the simulated average) pH. In our model the aerosol pH is calculated online (2-minute time resolution), while output is stored every five hours based on instantaneous concentrations of fine aerosol H_2O and H^+. According to Jensen's inequality (Jensen, 1906), the average of the instantaneous pH values is less than or equal to the pH calculated based on the average of the H_2O and H^+ instantaneous values. We estimate that the average pH calculated based on 5-hourly instantaneous values is approximately 1-3 (~2 globally averaged) units higher than the pH calculated based on the average H_2O and H^+ concentrations. If other models are using average values (and not instantaneous) as output, or if field-derived pH calculations are using average observed H_2O and H^+ values, this can result in important underestimations of aerosol pH.

6/ Some unrealistically high pH values in a few past studies resulted from coding errors in the stable state assumption of ISORROPIA II model, which have been fixed in our study following the recommendation of Song et al. (2018).

7/ The type of thermodynamic model used is also important. Song et al. (2018) has found that ISORROPIA-II produces somewhat higher pH (by 0.1-0.7 units, negatively correlated with RH) compared to the thermodynamic model E-AIM, which is used to observationally-constrain pH in some studies.

8/ Measurements of PM2.5 nitrate are not always reliable because of artifacts associated with the volatility of ammonium nitrate (Schaap et al., 2004). Ammonium and nitrate can partially evaporate from Teflon filters at temperatures between 15 to 20 ^oC and can evaporate completely at temperatures above. The evaporation from quartz filters is also significant at temperatures higher than 20 ^oC. This systematic underestimation of ammonium nitrate can affect the observed chemical composition of the aerosol and thus the pH calculations.

9/ A final important issue refers to the comparison between global model output and observations at specific locations. This also concerns the aerosol concentrations but is especially important for a tentative property like the aerosol acidity. Apart from the size of our grid cells (which is 1.9^ox1.9^o), the altitude is also important. Our model has a first layer which is approximately 67m in height. On the other hand, ground observations are typically collected in a height up to 3 m. While the aerosols within size modes simulated in our model are well-mixed, perhaps this is not the case for the aerosols observed so close to the surface and potentially to sources, and thus the aerosol acidity may be higher (e.g., due to the higher contribution from local primary sources like SO_4^{-2}, lower water in the aerosol, or lower semivolatile cations like NH_4^+)

All the above points are now extensively discussed in the manuscript. Concerning the comparison with observationally derived pH from aircraft campaigns, we need to emphasize that all pH values reported in our study are near the surface and cannot be directly compared to aircraft campaigns. Every aerosol size mode in our model is well mixed while the size modes are externally mixed. Therefore, we agree with the reviewer that our crustal elements are in many cases externally mixed with sulfates and ammonium but nitrates do exist in our large particles as well since they condense to the coarse (and

accumulation) mode particles in order to maintain the charge balance in the aerosol phase. However, the aerosol pH of $PM_{2.5}$ is calculated based on the total H_2O and H^+ in the aerosol until the cut-off point of 2.5 μm in our aerosol lognormal distributions. Our model predicts important amounts of crustals and Na^+ in the $PM_{1\text{-}2.5}$ size range, therefore the pH of $PM_{2.5}$ is meaningfully higher than that of PM_1. Finally, it is worth mentioning that Nault et al. (2020) did not include Na^+ in their suit of components.

3. *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).*

This indeed is a critical point as discussed earlier in our response for the case of Pasadena. Calcium is the major crustal component of dust in most deserts (Karydis et al., 2016) and unlike Mg, K, and Na it can react with sulfate ions and form insoluble $CaSO_4$, which precipitates out of the aerosol aqueous phase. This interaction reduces the aqueous sulfate and thus the aerosol acidity. In our sensitivity simulation without crustal component emissions, this effect is evident in the western United States and East Asia where high concentrations of sulphate interact with strong emissions of calcium emitted from the Great Basin and the Gobi deserts, respectively, resulting in the increase of pH by up to two units (Figure 1 of the manuscript). The role of $CaSO_4$ in this sensitivity response is now emphasized in the revised text.

4. *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.*

We agree with the reviewer that the Karydis et al. (2016) study focuses more on the thermodynamic interactions between mineral dust anions and inorganic cations and their impact on nitrate aerosol formation. In the revised text we have replaced this study with the Karydis et al. (2017) work where the impacts of these thermodynamic interactions on aerosol hygroscopicity and cloud droplet formation are revealed.

5. *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*

This is correct. Not every region of the Northern Hemisphere exhibits this behavior. This is mostly evident over highly polluted regions like East Asia and not over Europe and Eastern USA. The Northern extratropical Oceans also show the same clear seasonal pattern. We have corrected the text accordingly.

6. *Line 101: Suggest rephrasing the sentence as "Over North America, aerosol acidity also decreased with reduced SO2 and NOx emissions." However, it seems to be more complicated for NOx 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.*

The SO_2 emissions over North America have decreased more steeply compared to the NO_x emissions. However, even if this was not the case, the reduction of NO_x alone cannot affect the sulfate concentrations (by replacing it with nitrates in the aerosol). The available sulfuric acid condenses instantaneously onto the aerosol phase and form ammonium sulfate (or ammonium bisulfate) and only then the nitric acid can form ammonium nitrate with the free NH_3 left.

7. *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.*

What we have calculated in our work is the O_3 pathway which is important for both cloud droplets and aerosols for pH above 5 units. However, we agree with the reviewer that the reference to the H_2O_2 pathway in the text is misleading, and now we refer to the other important SO_2 oxidation pathways in the aqueous aerosol phase (e.g., NO_2 above pH=5 and TMI below pH=5).

8. *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 pKa of 6.4 (The pKa of HCO3- is 10.3, which is too high to buffer the predicted pH predicted in this study).*

Overall, in the text we refer to the buffering capacity of crustal elements as a term to describe their activity to decrease the pH of the aerosol with respect to an increase in the acid concentrations (i.e., owing to the anthropogenic activities). We recognize that the term is not completely accurate since crustal cations are non-volatile and can only increase the pH (and not buffer it). Following the reviewer's comment, we have revised the text accordingly.

9. *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.

The assumption of thermodynamic equilibrium is a good approximation for fine-mode aerosols that can reach equilibrium very fast. However, the equilibrium timescale for large particles is typically larger than the time step of the model (Meng and Seinfeld, 1996) leading to errors in the size distribution of semi-volatile ions like nitrate. Since the current study include reactions of nitric acid with coarse sea-salt and dust aerosol cations, the competition of fine and coarse particles for the available nitric acid can only be accurately represented by taking into account the kinetic limitations during condensation of HNO_3 in the coarse mode aerosols. This information has been added to the text.

10. *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.*

Indeed, equation A2 is in theory equivalent with the instant calculations of ISOROPIA II within our global model EMAC. However, the output of our model is not every timestep (is every 5 hours), and only after every other process in the model is calculated. Therefore, if we use the model output (e.g., gas-phase HNO_3 and NO_3^- in 4 size modes) the result would be subject to uncertainties from other processes (e.g., deposition, coagulation, transport, etc.). The use of Eq. 2 can provide us a clearer picture of the impact of pH on HNO_3 gas/particle partitioning. We have added this information in the text.

Minor comments

1. *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.*

Thank you for pointing this out. We have revised the sentence accordingly.

2. *Line 56: Change "high pH's are found. . ." to "high pH are found".*

Done.

3. *Line 78: Add "(Fig. 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.*

Thank you for the suggestion.

4. *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.*

Yes, the cation/anion ratio include all ions from both solid salts and the liquid phase. This is now explained in the text.

5. *Line 96: Provide kappa for ammonium sulfate and ammonium nitrate.*

The kappa hygroscopicity parameters for ammonium sulfate and ammonium nitrate are 0.53 and 0.67, respectively. The information has been added to the text.

6. *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).*

The sentence has been revised as "Surrounding panels show the temporal pH evolution during the period 1970-2020 at locations defined in Table 1."

7. *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.*

We meant that inventories tend to underestimate the real trends (reductions) in emissions. Admittedly, this was quite confusing and now we have rewritten the sentence as "SO_2 emission trends since 2007 have been so drastic that inventories and scenarios tend to overestimate the emitted SO_2."

8. *Line 128: consider change "the large SO2 trends" to "the significant SO2 reduction trends" or "the long-term SO2 trends".*

Done.

9. *Line 154: add "is" after "NH3" to be "NH3 is also proved to be. . ."*

Done.

10. *Line 237: consider adding a reference for κorg = 0.14. Also, while the Greek alphabet of κ is used here, "kappa" is used in Fig. 4. Better to be consistent.*

Done.

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Anonymous Referee #2

This paper uses a model to predict fine particle ($PM_{2.5}$) 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^ox1.9^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.

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How alkaline compounds control atmospheric aerosol acidity

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Abstract. The acidity of atmospheric aerosols regulates the particulate mass, composition and toxicity, and has important consequences for public health, ecosystems and climate. Despite these broad impacts, the global distribution and evolution of aerosol acidity are unknown. We used the ~~particular,~~ comprehensive atmospheric multiphase chemistry – climate model EMAC to investigate the main factors that control aerosol acidity~~,~~ and uncovered remarkable variability and unexpected trends during the past 50 years in different parts of the world. We find that alkaline compounds, notably ammonium, and to a lesser extent crustal cations, ~~buffer~~regulate the aerosol pH on a global scale. Given the importance of aerosols for the atmospheric energy budget, cloud formation, pollutant deposition and public health, alkaline species hold the key to control strategies for air quality and climate change.

1. Introduction

Aerosol acidity is a central property of atmospheric particulates that influence clouds, climate and air quality, including impacts on human health (Raizenne et al., 1996;Lelieveld et al., 2015). It affects the partitioning of semi-volatile acids between the gas and aerosol phases (Guo et al., 2016;Guo et al., 2017;Guo et al., 2018;Nenes et al., 2020), secondary organic aerosol (SOA) formation (Xu et al., 2015;Marais et al., 2016), the solubility of trace metals in aerosols ~~(Oakes et al., 2012)~~(Oakes et al., 2012), associated with their toxicity ~~(Fang et al., 2017)~~(Fang et al., 2017) and nutrient capacity (Jickells et al., 2005), the activation of halogens that act as oxidants (Saiz-Lopez and von Glasow, 2012), the conversion of sulfur dioxide (Seinfeld and Pandis, 2006;Cheng et al., 2016), the particle hygroscopic growth and lifetime (Metzger et al., 2006;Abdelkader et al., 2015;Karydis et al., ~~2016~~2017), and atmospheric corrosivity (Leygraf et al., 2016). Direct measurement of aerosol acidity is difficult and associated with much uncertainty, being dependent on filter sampling and the H^+ molality in the aqueous extract, which is sensitive to artifacts ~~(Pathak et al., 2004)~~(Pathak et al., 2004). Therefore, particle pH, a commonly used acidity metric of aqueous aerosols, is typically inferred by proxy techniques (Hennigan et al., 2015;Pye et al., 2020). Two of the most common are the ion balance and the molar ratio methods. ~~In the past, these~~These methods ~~did~~do not consider the effects of aerosol water and multiphase interactions with gas phase species as well as the partial dissociation of acids (Hennigan et al., 2015). The simultaneous measurement of gas phase species can improve aerosol pH estimates by accounting for the phase partitioning of semi-volatile species (e.g., NH_3, HNO_3). However, the accuracy of this approach relies on the availability of information on these species in both the gas and aerosol phase, being scant in most cases.

The ~~best~~most reliable estimates of pH are obtained with thermodynamic equilibrium models, although the accuracy can be limited by not accounting for all ionic species. For example, most atmospheric chemistry models do not consider crustal elements (e.g., Ca^{2+}, Mg^{2+}, K^+~~).~~) and Na^+ in sea salt. These species affect the ion balance by influencing the phase partitioning of nitrate and ammonium, especially in areas where aeolian dust is abundant (Karydis et al., 2016). Here we present 50-year global acidity trends of fine aerosols (i.e. with a diameter < 2.5 μm) by employing the EMAC chemistry – climate model (Jöckel et al., 2010). The pH calculations are performed online with the ISORROPIA II thermodynamic equilibrium model (Fountoukis and Nenes, 2007).

2. Results and Discussion

2.1 Global variability of aerosol acidity

Figure 1 shows the modeled near-surface distribution of fine aerosol acidity for the 2010-2015 period. We find predominantly acidic particles over the anthropogenically influenced regions in the northern hemisphere and the tropical biomass burning zones, and mostly alkaline particles over deserts and oceans, especially over the southern oceans. The pH typically ranges from 4.0 to 6.7 (5.3 on average) over the western USA since it is affected by crustal cations from the surrounding deserts. ~~Therefore,~~Polluted areas located downwind of crustal sources are of special interest since the pH calculations ~~in this region are~~ can be sensitive to the aerosol state assumption~~.~~ (see section 4.3). Over Pasadena, the base case

model using the stable state mode estimates a mean pH of 5.9 units, while the sensitivity simulation with only liquid aerosols results in 2.7 pH units (equal to Guo et al. (2017) estimations by using the metastable assumption; Table S1). Our sensitivity analysis revealed that the aerosol state itself is not affected by the state assumption since both stable and metastable predict the same amount of water in the aerosol. Differences in the calculated pH can be due to the high concentrations of calcium from the Great Basin Desert which results in the precipitation of high amounts of $CaSO_4$, lowering the particle acidity (but without affecting the water activity since $CaSO_4$ is insoluble and does not contribute to the MDRH depression). It is worth mentioning that calcium was not included in the Guo et al. (2017) study which helps explain the differences in the observed and simulated aerosol acidity. The simulated particle-phase fraction of nitrate over Pasadena is 40% using the stable state assumption and 32% using the metastable assumption, compared to the observationally derived 51%. Over Europe, the pH ranges from 2.6 to 6.7 (3.9 on average). Observational estimates of aerosol pH from the Po Valley (Squizzato et al., 2013;Masiol et al., 2020) and Cabauw (Guo et al., 2018) support the relatively low acidity of fine aerosols over Europe (Table S1). Model calculations compare well with observational estimates from Cabauw, however, result in higher pH (~1 unit) compared to values from Po Valley (estimated by using the E-AIM model). Over East Asia the average pH is 4.7, ranging from 2.6 to 7.4. Relatively high ~~pH's~~pH are found over regions where anthropogenic aerosols are mixed with aeolian dust, e.g., from the Gobi Desert, which ~~buffer~~decrease the acidity (e.g., ~6 pH units over Hohhot, which agrees well with the estimations of Wang et al. (2019a)). The relatively low pH in large parts of Asia is explained by strong SO_2 emissions and associated sulfate, which have increased strongly in the past decades (e.g., over Guangzhou, supported by estimations of Jia et al. (2018)). Estimates of unrealistically high aerosol acidity can result from omitting the gas phase concentrations of semi-volatile ions from the pH calculations (e.g., estimates over Hong Kong (Yao et al., 2007;Xue et al., 2011), Singapore (Behera et al., 2013) and Shanghai (Pathak et al., 2009); Table S1). At the same time, SO_2 emissions have decreased over Europe and USA, and recently in China. However, aerosols over the eastern USA have remained acidic, with an average pH of 3.0 until recently, corroborating the findings of Weber et al. (2016) and Lawal et al. (2018) that aerosol acidity over this region is less sensitive to SO_2 than to NH_3 emissions.

The aerosol pH over ~~the anthropogenically influenced~~polluted northern hemispheric mid-latitudes (e.g., over East Asia) and the northern extratropical oceans 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). This is evident from both our model calculations and from observational estimates mostly in heavily populated areas such as the Po Valley (Squizzato et al., 2013), Beijing (Tan et al., 2018), and Tianjin (Shi et al., 2017), and to a lesser extent over areas strongly affected by aeolian dust (e.g., Hohhot; Wang et al., 2019b) (Table S1). Over tropical regions, fine particulates have a pH between 3.2 and 7.4, being strongly influenced by pyrogenic potassium, i.e., from widespread biomass burning (Metzger et al., 2006), and a high aerosol water content. Observational estimates from Sao Paulo support these high pH values (Vieira-Filho et al., 2016), albeit with 1 unit bias mainly related to the use of the E-AIM model. Over deserts, aerosols are relatively alkaline, with a pH up to 7.4. Aerosols in the marine environment tend to be alkaline also, with a pH up to 7.4 over the southern oceans. Observational estimates report highly acidic aerosols over the southern oceans due to the lack of gas phase input for the pH calculations (Dall'Osto et al., 2019). 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. (Fig. 1). The pH over the northern extratropical oceans and the Arctic ranges from 2.0 to 7.0 with an average of about 5.2. The annual cycle of aerosol acidity over these regions is strongly influenced by anthropogenic

pollution, being relatively high during boreal summer. Over the Antarctic, aerosol pH ranges from 4.5 to 7.0 and follows a clear seasonal pattern (Fig. 2).

2.2 Temporal evolution of aerosol acidity

Figure 1 and Table 1 present the aerosol pH over the period 1970-2020. We investigated the impacts of alkaline species by omitting the emissions of ammonia and mineral cations in two sensitivity simulations.

2.2.1 Europe

Over Europe, the pH has increased strongly from about 2.8 during the 1970s to 3.9 recently. Especially during the 1990s NH_3 emissions over Europe increased significantly by 14%, while at the same time NOx and SO_2 emissions decreased by 13% and 49%, respectively. While this trend has continued in the past decade, pH changes slowed because the sulfate and nitrate decreases have been compensated through volatilization of ammonia from the particles. In addition, the recently increasing cation/anion ratio is accompanied by a reduction of aerosol water, preventing a significant decrease of the aerosol acidity (Fig. S1). Overall, the increase of aerosol pH by more than 1 unit during the last 50 years had a significant impact on the gas-particle partitioning of semi-volatile acids, e.g., nitric acid, since their dissociation into ions enhances their solubility (Nah et al., 2018). Here, the fraction of nitrate in the particle phase relative to total nitrate (gas plus particle) has increased from ~70% to 85% (Fig. 3). The increase in aerosol pH has been accompanied by an increase in aerosol kappa hygroscopicity (Fig. 4). After the substantial reduction of SO_2 emissions, sulfate salts (e.g., ammonium ~~sulphate~~sulfate with kappa=0.53) are replaced by more hygroscopic nitrate salts (e.g., ammonium nitrate with kappa=0.67) in the aerosol composition. In addition, the decrease of organic compound emissions during the last 50 years contributed to the increase of the aerosol hygroscopicity. Our sensitivity simulations reveal that aerosol acidity over Europe is highly sensitive to NH_3 emissions. Despite the decline of both SO_2 and NOx during the past decades, the aerosol would have remained highly acidic (pH ~1) in the absence of NH_3.

2.2.2 North America

Over North America, aerosol acidity also decreased with SO_2 and NOx emissions. Nevertheless, these emissions are still relatively strong in the eastern USA (5 times higher than in the western USA) resulting in very acidic aerosols, with a pH ranging from 2.2 in 1971 to 3.3 recently (Figs. 1 and S1). Such acidic conditions promote the dissolution of metals (e.g., Fe, Mn, Cu) in ambient particles ~~(Fang et al., 2017)~~(Fang et al., 2017). Soluble transition metals in atmospheric aerosols have been linked to adverse health impacts since they generate reactive oxygen species, leading to oxidative stress and increased toxicity of fine particulate matter (Fang et al., 2017;Park et al., 2018). Since the solubility of transition metals increases exponentially below a pH of 3, the decrease of aerosol acidity over the eastern USA reported here suggests that the particles have become substantially less toxic in the past few decades. Similar to Europe, the increasing pH has resulted in a growing aerosol nitrate fraction from ~50% during the 1970s to 65% recently (Fig. 3), and to a strong increase of aerosol

hygroscopicity by ~0.15 units at the cloud base (Fig. 4). The role of NH_3 is critically important; without it the aerosol pH over the eastern USA would be close to zero. Over the western USA, the aerosol pH is higher (~5), being affected by aeolian dust from the Great Basin Desert, although NH_3 is still the most important alkaline buffer.

2.2.3 East and South Asia

In Asia, SO_2 and NOx emissions have increased drastically since 1970. However, the simultaneous increase of NH_3 emissions along with the presence of mineral dust from the surrounding deserts (i.e., Gobi, Taklimakan, Thar) decelerated the increase of aerosol acidity. Over East Asia, the aerosol pH decreased from about 5.3 during the 1970s to 4.5 in 2010. This change in aerosol acidity has affected the predominant pathway of sulfate formation through ~~aqueous phase chemistry. Under acidic conditions, SO_2 is mainly oxidized by dissolved H_2O_2, while at pH > 5 the oxidation by O_3 predominates (Seinfeld and Pandis, 2006).~~aerosol aqueous phase chemistry. Under acidic conditions, SO_2 is mainly oxidized by transition metal ions, while at pH > 5 the oxidation by O_3 and NO_2 predominates (Cheng et al., 2016). Therefore, the decrease of pH during the last 50 years, even though being relatively modest, was sufficient to turn-off sulfate production from O_3 oxidation (Fig. 5). At the same time, the increased aerosol acidity hinders the partitioning of nitric acid to the aerosol phase, reducing the aerosol nitrate fraction from 90% to 80% (Fig. 3). Remarkably, the aerosol hygroscopicity has increased from ~0.3 in the 1970s to 0.45 recently (Fig. 4), revealing a reverse development compared to Europe and the USA. Here, the fraction of mineral dust in the aerosol is higher; therefore, the particles gained hygroscopicity by the acquired pollution solutes. Recently, the SO_2 emissions have dropped and the NOx emission increase has slowed in East Asia, while SO_2 emissions are soaring in South Asia. SO_2 emission trends since 2007 have been so drastic that inventories and scenarios tend to ~~underestimate them.~~overestimate the emitted SO_2. Satellite observations indicate that India has recently overtaken China as the world largest emitter of SO_2 (Li et al., 2017). Following the satellite observations, we implemented the ~~large~~significant SO_2 reduction trends into our model (Fig. S2). Surprisingly, the effect only becomes noticable over East Asia after 2016, when the aerosol pH started increasing by about 0.3 units, while we do not find any change over South Asia. This corroborates the strong buffering that we found over other regions such as Europe. Fig. 1 shows that NH_3 has been the major buffer, supporting the recent findings of Zheng et al. (2020) that the acid-base pair of NH_4^+/NH_3 provides the largest buffering capacity over East and South Asia. However, we also found that in East Asia and to a lesser extent in South Asia crustal elements, not considered in the study of Zheng et al. (2020), have contributed significantly on maintaining a mean pH of 4.5 – 5 in the past decade (Fig. 1). Calcium is the major crustal component of dust from the Gobi and Taklimakan deserts (Karydis et al., 2016) and unlike other crustal compounds it can react with sulfate ions and form insoluble $CaSO_4$, which precipitates out of the aerosol aqueous phase. This interaction reduces the aqueous sulfate and thus the aerosol acidity.

2.2.4 Tropical forests, Middle East

Over tropical forests, aerosols are typically not very acidic with pH values >4. Note that organic acids were not included in the aerosol pH calculations, however, their contribution to the total ionic load is small (Andreae et al., 1988;Falkovich et al.,

2005), and aerosol acidity can be attributed to inorganic acids. Over the Amazon and Congo basins, the aerosol pH remained around 5 since 1970. The Southeast Asian forest atmosphere is affected by pollution from mainland Asia, and the aerosol pH decreased to around 4 recently. This pH drop has enhanced SOA formation from isoprene, since under low-NOx conditions (typical over rainforests) the presence of acidifying sulfate increases the reactive uptake of epoxydiols (Xu et al., 2015;Surratt et al., 2010). Nevertheless, NH_3 emissions provide a remarkably strong buffer over all three tropical regions while mineral dust cations are also important over the Amazon and Congo forests. Further, the Middle East is affected by strong anthropogenic (fossil fuel related) and natural (aeolian dust) aerosol sources. Due to the high abundance of mineral dust, the pH has remained close to 7. Without crustal cations, the pH would drop to about 4. Despite the omnipresence of alkaline species from the surrounding deserts, NH_3 still plays a central role in controlling the acidification of mineral dust aerosols, which can affect their hygroscopic growth and hence their climate forcing (Klingmuller et al., 2019;Klingmüller et al., 2020).

2.2.5 Oceans

Over the Arctic and northern extra-tropical oceans, aerosol acidity is strongly affected by pollution transport from the urban-industrial mid-latitudes. The Arctic aerosol pH is highly variable, remaining relatively low up to 1990 (~4.2), after which it increased to about 5.2. Crustal cations are found to play a significant ~~buffering~~ role lowering the aerosol acidity. Over the northern extra-tropical oceans, aerosol pH has remained relatively constant (~4.8). NH_3 provides an important alkaline buffer, and without it the aerosol pH would have been below 3. NH_3 is also proved to be important over the tropical and southern extra-tropical oceans, where a noticeable increase in aerosol acidity occurred after June 1991, when the eruption of Mount Pinatubo in the Philippines released ~20 million tons of SO_2 into the stratosphere (McCormick et al., 1995). The impact of Pinatubo sulfate, after returning to the troposphere, on aerosol acidity is mostly evident over Antarctica, where the pH dropped by 2 units, as the stratospheric circulation is strongest in the winter hemisphere. Over Antarctica concentrations of dust and especially of NH_3 are very low, and Fig. 1 illustrates that only in this pristine environment the large Pinatubo anomaly could overwhelm the buffering by alkaline species. Except after Pinatubo, the pH has remained nearly constant at 5.8 over Antarctica and about 5.5 in the tropics and 6.8 in the southern extra-tropics.

3. Conclusions

We find that aerosol pH is generally well-buffered by alkaline compounds, notably NH_3 and in some areas crustal elements. NH_3 is found to supply remarkable buffering capacity on a global scale, from the polluted continents to the remote oceans. In the absence of NH_3, aerosols would be highly (to extremely) acidic in most of the world. Therefore, potential future changes in NH_3 are critically important in this respect. Agriculture is the main NH_3 source and a controlling factor in fine particle concentrations and health impacts in some areas (e.g., Europe) (Pozzer et al., 2017). The control of agricultural ammonia emissions must therefore be accompanied by very strong reductions of SO_2 and NOx to avoid that aerosols become highly acidic with implications for human health (aerosol toxicity), ecosystems (acid deposition and nutrient availability), clouds and climate (aerosol hygroscopicity).

4. Appendix A: Materials and Methods

4.1 Aerosol-chemistry-climate model

We used the ECHAM5/MESSy Atmospheric Chemistry (EMAC) model, which is a numerical chemistry and climate simulation system that describes lower and middle atmosphere processes (Jöckel et al., 2006). EMAC uses the Modular Earth Submodel System (MESSy2) (Jöckel et al., 2010) to link the different sub-models with an atmospheric dynamical core, being an updated version of the 5th generation European Centre - Hamburg general circulation model (ECHAM5) (Roeckner et al., 2006). EMAC has been extensively described and evaluated against in situ observations and satellite retrievals to compute particulate matter concentrations and composition, aerosol optical depth, acid deposition, gas phase mixing ratios, cloud properties, and meteorological parameters (Karydis et al., 2016;Pozzer et al., 2012;Tsimpidi et al., 2016;Karydis et al., 2017;Bacer et al., 2018). The spectral resolution of EMAC used in this study is T63L31, corresponding to a horizontal grid resolution of approximately 1.9°x1.9° and 31 vertical layers extending up to 10 hPa (i.e., 25 km) from the surface. The presented model simulations encompass the 50-year period 1970-2020.

EMAC calculates fields of gas phase species online through the Module Efficiently Calculating the Chemistry of the Atmosphere (MECCA) Submodel (Sander et al., 2019). MECCA calculates the concentration of a range of gases, including aerosol precursor species (e.g. SO_2, NH_3, NO_x, DMS, H_2SO_4 and DMSO) and the major oxidant species (e.g. OH, H_2O_2, NO_3, and O_3). Aerosol microphysics are calculated by the Global Modal-aerosol eXtension (GMXe) module (Pringle et al., 2010). The organic aerosol formation and atmospheric evolution are calculated by the ORACLE Submodel (Tsimpidi et al., 2014, 2018). The aerosol size distribution is described by seven lognormal modes: four hydrophilic modes that cover the aerosol size spectrum of nucleation, Aitken, accumulation and coarse modes, and three hydrophobic modes that cover the same size range except nucleation. The aerosol composition within each size mode is uniform (internally mixed), however, it varies between modes (externally mixed). Each mode is defined in terms of total number concentration, number mean radius, and geometric standard deviation (Pringle et al., 2010). The removal of gas and aerosol species through wet and dry deposition is calculated within the SCAV (Tost et al., 2006) and DRYDEP (Kerkweg et al., 2006) submodels, respectively. The sedimentation of aerosols is calculated within the SEDI submodel (Kerkweg et al., 2006). The cloud cover, microphysics and precipitation of large scale clouds is calculated by the CLOUD Submodel (Roeckner et al., 2006) which uses a two-moment stratiform microphysical scheme (Lohmann and Ferrachat, 2010), and describes liquid droplet (Karydis et al., 2017) and ice crystal (Bacer et al., 2018) formation by accounting for the aerosol physicochemical properties. The effective hygroscopicity parameter κ is used to describe the influence of chemical composition on the cloud condensation nuclei (CCN) activity of atmospheric aerosols. κ is calculated using the mixing rule of Petters and Kreidenweis (Petters and Kreidenweis, 2007) and the individual κ parameter values for each inorganic salt (Petters and Kreidenweis, 2007;Sullivan et al., 2009). Organic aerosol species are assumed to have a constant hygroscopicity kappa parameter ~~κ~~ of 0.14 while bulk mineral dust and black carbon are assumed to have zero hygroscopicity.

4.2 Emissions

The vertically distributed (Pozzer et al., 2009) CMIP5 RCP8.5 emission inventory (van Vuuren et al., 2011) is used for the anthropogenic and biomass burning emissions during the years 1970-2020. Direct emissions of aerosol components from biofuel and open biomass burning are considered by using scaling factors applied on the emitted black carbon based on the findings of Akagi et al. (Akagi et al., 2011) (Table S2). Dust emission fluxes and emissions of crustal species (Ca^{2+}, Mg^{2+}, K^+, Na^+) are calculated online as described by Klingmuller, et al. (Klingmuller et al., 2018) and based on the chemical composition of the emitted soil particles in every grid cell (Karydis et al., 2016); Table S3.

NO_x produced by lightning is calculated online and distributed vertically based on the parameterization of Grewe, et al. (Grewe et al., 2001). The emissions of NO from soils are calculated online based on the algorithm of Yienger and Levy (Yienger and Levy, 1995). The oceanic DMS emissions are calculated online by the AIRSEA Submodel (Pozzer et al., 2006). The natural emissions of NH_3 are based on the GEIA database (Bouwman et al., 1997). Emissions of sea spray aerosols (assuming a composition suggested by Seinfeld and Pandis (Seinfeld and Pandis, 2006); Table S2) and volcanic degassing emissions of SO_2 are based on the offline emission data set of AEROCOM (Dentener et al., 2006).

4.3 Thermodynamic model

The inorganic aerosol composition, which is of prime importance for the accurate pH calculation, is computed with the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007). ISORROPIA-II calculates the gas/liquid/solid equilibrium partitioning of the K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosol system and considers the presence of 15 aqueous phase components and 19 salts in the solid phase. ISORROPIA-II solves for the equilibrium state by considering the chemical potential of the species and minimizes the number of equations and iterations required by considering specific compositional "regimes". ~~Furthermore, to~~The assumption of thermodynamic equilibrium is a good approximation for fine-mode aerosols that rapidly reach equilibrium. However, the equilibrium timescale for large particles is typically larger than the time step of the model (Meng and Seinfeld, 1996) leading to errors in the size distribution of semi-volatile ions like nitrate. Since the current study include reactions of nitric acid with coarse sea-salt and dust aerosol cations, the competition of fine and coarse particles for the available nitric acid can only be accurately represented by taking into account the kinetic limitations during condensation of HNO_3 in the coarse mode aerosols. To account for kinetic limitations by mass transfer and transport between the gas and particle phases, the process of gas/aerosol partitioning is calculated in two stages (Pringle et al., 2010). First, the gaseous species that kinetically condense onto the aerosol phase within the model timestep are calculated assuming diffusion limited condensation (Vignati et al., 2004). Then, ISORROPIA-II re-distributes the mass between the gas and the aerosol phase assuming instant equilibrium between the two phases.

ISORROPIA-II is used in the forward mode, in which the total (i.e., gas and aerosol) concentrations are given as input. Reverse mode calculations (i.e. when only the aerosol phase composition is known) should be avoided since they are sensitive to errors and infer bimodal ~~behavior~~behaviour with highly acidic or highly alkaline particles, depending on whether anions or cations are in excess (Song et al., 2018). While it is often assumed that aerosols are in a metastable state (i.e., composed only of a supersaturated aqueous phase), here we use ISORROPIA-II in the thermodynamically stable state mode where salts are allowed to precipitate once the aqueous phase becomes saturated. For this purpose, we have used the revised ISORROPIA-II model which includes modifications proposed by Song et al. (2018), who resolved coding errors related to pH calculations when the stable state assumption is used. ~~A sensitivity simulation with only liquid aerosols (i.e., metastable) revealed that the assumed particle phase state does not significantly impact the pH calculations over oceans and polluted regions (e.g., Europe), however, the metastable assumption produces more acidic particles (up to 2 units of pH) in regions affected by high concentrations of crustal cations (Fig. S3). Overall, the stable state assumption used here produces about 0.5 units higher global average pH than the metastable assumption.~~ By comparing with the benchmark thermodynamic model E-AIM, Song et al. (2018) found that ISORROPIA-II produces somewhat higher pH (by 0.1-0.7 units, negatively correlated with RH). However, E-AIM model versions either lack crustal cations from the ambient mixture of components (e.g. version II) (Clegg et al., 1998), or only include Na^+ with the restriction that it should be used when RH> 60% (e.g. version IV) (Friese and Ebel, 2010). Song et al. (2018) applied the revised ISORROPIA-II during winter haze events in eastern China and found that the assumed particle phase state, either stable or metastable, does not significantly impact the pH predictions.

We performed a sensitivity simulation with only liquid aerosols (i.e., metastable), which revealed that the assumed particle phase state does not significantly impact the pH calculations over oceans and polluted regions (e.g., Europe), however, the metastable assumption produces more acidic particles (up to 2 units of pH) in regions affected by high concentrations of crustal cations and consistently low RH values (Fig. S3). ~~4.3~~Fountoukis et al. (2007) have shown that the metastable solution predicts significant amounts of water below the mutual deliquescence relative humidity (MDRH, where all salts are simultaneously saturated with respect to all components). Further, the generally high calcium concentrations downwind of deserts results in increasing pH values due to the precipitation of insoluble salts such as the $CaSO_4$. The metastable state assumption fails to reproduce this since it treats only the ions in the aqueous phase. In general, high amounts of crustal species can significantly increase the aerosol pH which is consistent with the presence of excess carbonate in the aerosol phase (Meng et al., 1995). It is worth mentioning that the stable state solution algorithm of ISORROPIA II starts with assuming a dry aerosol, and based on the ambient RH dissolves each of the salts depending on their DRH. However, in the ambient atmosphere, when the RH over a wet particle is decreasing, the wet aerosol may not crystallize below the MDRH but instead remain in a metastable state affecting the uptake of water by the aerosol and thus the pH. This could be the case in some locations with high diurnal variations of RH. Our sensitivity calculations show that, overall, the stable state assumption produces an about 0.5 units higher global average pH than the metastable assumption. Karydis et al. (2016) have shown that while the aerosol state assumption has a marginal effect on the calculated nitrate aerosol tropospheric burden (2% change), it can be important over and downwind of deserts at very low RHs where nitrate is reduced by up to 60% by using the metastable assumption. This is in accord with the findings of Ansari and Pandis (2000) who suggested that the stable state results in higher concentrations of aerosol nitrate when the RH is low (<35 %) and/or sulfate to nitrate molar ratios are low (<0.25).

4.4 pH calculations

The pH is defined as the negative decimal logarithm of the hydrogen ion activity ($a_{H^+} = \gamma x_{H^+}$) in a solution~~:~~

~~$pH = -\log_{10}\left(\gamma x_{H^+}\right)$~~~~;~~

$$pH = -\log_{10}\left(\gamma x_{H^+}\right) \quad (A1)$$

where x_{H^+} is the molality of hydrogen ions in the solution and γ is the ion activity coefficient of hydrogen. Assuming that γ is unity, the aerosol pH can be calculated by using the hydrogen ion concentration in the aqueous aerosol phase calculated by ISORROPIA-II (in mole m^{-3}) and the aerosol water content calculated by GMXe (in mole Kg^{-1}). GMXe assumes that particle modes are internally mixed~~,~~ and takes into account the contribution of both inorganic and organic (based on the organic hygroscopicity parameter, ~~$\kappa_{org} = 0.14$~~)kappa=0.14 (Tsimpidi et al., 2014)) species to aerosol water.

The aerosol pH is calculated online at each timestep, and output stored every five hours based on instantaneous concentrations of fine aerosol water and hydrogen ions. The average pH values shown in the manuscript are based on the calculated instantaneous mean pH values. According to the Jensen's inequality (Jensen, 1906), the average of the instantaneous pH values is less than or equal to the pH calculated based on the average of the water and hydrogen ion instantaneous values. We estimate that the average pH calculated based on 5-hourly instantaneous values is approximately 1-3 (~2 globally averaged) units higher than the pH calculated based on the average water and hydrogen ion concentrations. By including online gas-particle partitioning calculations of the NH_3/HNO_3 system in polluted air, as applied here, we find that the aerosol pH is higher by approximately one unit (Guo et al., 2015). Hence by neglecting these aspects the aerosol pH would be low-biased by about 3 ~~points~~units.

4.5 Comparison against pH estimations from field derived $PM_{2.5}$ compositional data

The pH calculated here is compared against pH estimations from field derived $PM_{2.5}$ compositional data around the world compiled by Pye et al. (2020) (Table S1). pH data derived from other aerosol sizes (e.g., PM_1) has been omitted since aerosol acidity can vary significantly with size (Zakoura et al., 2020). It should be emphasized that the comparison presented in Table S1 aims to corroborate the spatial variability of pH found in this study and not to ~~strictly evaluate the model calculations. Observationally estimated aerosol pH is derived from a variety of methods that can affect the result significantly as discussed above (i.e., the use of E-AIM or ISORROPIA, stable/metastable assumption, forward/reverse mode, and the availability of gas phase NH_3/HNO_3, crustal species, and organic aerosol water observations).~~ evaluate the model calculations. Since direct measurements of aerosol acidity are not available, the observation-based aerosol pH is estimated by employing thermodynamic equilibrium models (e.g., ISORROPIA) and making assumptions that can significantly affect the results, especially when the data are averaged over extended periods, while RH conditions during data collection are not always accounted for, e.g. in studies based on filter sampling. The calculation of aerosol acidity on a global scale requires the advanced treatment of atmospheric aerosol chemical complexity, representing the real atmosphere, and beyond the conventional methods used by chemistry-climate models (CCM). The atmospheric chemistry model system EMAC is an ideal tool for this purpose since it is one of the most comprehensive CCM containing advanced descriptions of the aerosol thermodynamics (including e.g. dust-pollution interactions) and organic aerosol formation and atmospheric aging (affecting the aerosol water). Our model calculations for aerosol acidity are based on some processes/factors that are not included explicitly, usually neglected by model calculations used to constrain the aerosol acidity from observations. Sources of discrepancy between the pH calculations can be the following:

- ~~4.4~~The stable/metastable assumption does not affect the pH most of the time, however, in some cases with low RHs and the presence of crustal cations, the metastable assumption results in lower pHs (see section 4.3).
- Crustal species from deserts and Na^+ from sea salt can elevate the pH significantly in some locations, however, these are often neglected in observations.
- The organic aerosols (which are treated comprehensively by our model using the module ORACLE and the volatility basis set framework (Tsimpidi et al., 2014)) can contribute significantly to the aerosol water, and thus increase the aerosol pH. This contribution is not considered by many observational studies.
- Including gas phase species (e.g., NH_3, HNO_3) in the pH calculations is important. Using only the aerosol-phase as input (i.e., reverse mode) the inferred pH exhibits bimodal behaviour with very acidic or alkaline values depending on whether anions or cations are in excess (Hennigan et al., 2015). Even if the forward mode is used (without gas phase input), the calculated aerosol pH is biased low (approximately 1 pH unit) due to the repartition of semi-volatile anions (i.e., NH_3) to the gas phase to establish equilibrium (Guo et al., 2015).
- Another important aspect, not explicitly mentioned in many studies, relates to the methods used to derive the campaign-average (or for 3D models the simulated average) pH. In our model the aerosol pH is calculated online (2-minute time resolution), while output is stored every five hours based on instantaneous concentrations of fine aerosol H_2O and H^+. This mimics 5-hourly aerosol sampling. Then, the average pH values are calculated from the instantaneous mean pH values (see section 4.4). Often models use average values (and not instantaneous) as

output, or field-derived pH calculations use average observed H_2O and H^+ values, which can result in important underestimation (by ~ 1-3 units) of the aerosol pH (Jensen, 1906).

- Some unrealistically high pH values in a few past studies resulted from coding errors in the stable state assumption of the ISORROPIA II model, which have been corrected in our study following the recommendation of Song et al. (2018).
- The type of thermodynamic model used is also important. Song et al. (2018) found that ISORROPIA-II produces somewhat higher pH (by 0.1-0.7 units, negatively correlated with RH) compared to the thermodynamic model E-AIM, which is used to observationally-constrain pH in some studies.
- Measurements of $PM_{2.5}$ nitrate are not always reliable because of artifacts associated with the volatility of ammonium nitrate (Schaap et al., 2004). Ammonium and nitrate can partially evaporate from Teflon filters at temperatures between 15 to 20 °C and can evaporate completely at temperatures above. The evaporation from quartz filters is also significant at temperatures higher than 20 °C. This systematic underestimation of ammonium nitrate can affect the observed chemical composition of the aerosol and thus the pH calculations.
- The comparison between global model output and observations at specific locations. This also concerns the aerosol concentrations but is especially important for the aerosol acidity. Apart from the size of the model grid cells (i.e., ~ 1.9°x1.9°), the altitude is also important. The first vertical layer of EMAC is approximately 67m in height. On the other hand, ground observations are typically collected in a height up to 3 m. While the aerosols within size modes simulated in our model are well-mixed, perhaps this is not the case for the aerosols observed at the surface and potentially close to sources, and thus the aerosol acidity may be higher (e.g., due to the higher contribution from local primary sources like SO_4^{-2}, lower water amounts in the aerosol, or lower concentrations of semi-volatile cations like NH_4^+)

4.6 ~~Emissions~~

~~The vertically distributed (Pozzer et al., 2009) CMIP5-RCP8.5 emission inventory (van Vuuren et al., 2011) is used for the anthropogenic and biomass burning emissions during the years 1970-2020. Direct emissions of aerosol components from biofuel and open biomass burning are considered by using scaling factors applied on the emitted black carbon based on the findings of Akagi, et al. (Akagi et al., 2011) (Table S2). Dust emission fluxes and emissions of crustal species (Ca^{2+}, Mg^{2+}, K^+, Na^+) are calculated online as described by Klingmuller, et al. (Klingmuller et al., 2018) and based on the chemical composition of the emitted soil particles in every grid cell (Karydis et al., 2016); Table S3. NO_x produced by lightning is calculated online and distributed vertically based on the parameterization of Grewe, et al. (Grewe et al., 2001). The emissions of NO from soils are calculated online based on the algorithm of Yienger and Levy (Yienger and Levy, 1995). The oceanic DMS emissions are calculated online by the AIRSEA~~

~~Submodel (Pozzer et al., 2006). The natural emissions of NH_3 are based on the GEIA database (Bouwman et al., 1997). Emissions of sea spray aerosols (assuming a composition suggested by Seinfeld and Pandis (Seinfeld and Pandis, 2006); Table S2) and volcanic degassing emissions of SO_2 are based on the offline emission data set of AEROCOM (Dentener et al., 2006).~~

~~4.5~~ Partitioning of nitric acid between the gas and aerosol phases

The impact of pH on the fraction of nitrate in the particle phase relative to total nitrate (gas plus particle), i.e., $\varepsilon(NO_3^-)$, during the 50 years of simulation in specific regions is calculated as follows (Nah et al., 2018):

$$\varepsilon(NO_3^-) = \frac{H^*_{HNO_3} WRT(0.987 \times 10^{-14})}{\gamma_{NO_3^-}\gamma_{H^+}10^{-pH} + H^*_{HNO_3} WRT(0.987 \times 10^{-14})} \quad (A2)$$

Where $H^*_{HNO_3}$ is the combined molality-based equilibrium constant of HNO_3 dissolution and deprotonation, γ's represent the activity coefficients, W is the aerosol water, R is the gas constant, and T is the ambient temperature. Eq. A2 is equivalent with the instantaneous calculations of ISOROPIA II within EMAC. However, the model output is produced after considering all processes in the model and is not calculated at every timestep. Therefore, the use of Eq. 2 can provide a clearer picture of the impact of pH on HNO_3 gas/particle partitioning since the model output (e.g., gas-phase HNO_3 and nitrate in 4 size modes) is subject to uncertainties related to other processes (e.g., deposition, coagulation, transport, etc.).

4.~~6~~7 Sulfate formation in aqueous aerosols

The sulfate production rate on aqueous aerosols from the heterogeneous oxidation of S(IV) with the dissolved O_3 is given by

$$R_0 = k\,[O_3]\,[\,] \quad (A3)$$

. The first-order uptake rate, k, from monodisperse aerosols with radius r_a and total aerosol surface A, is calculated following Jacob (Jacob, 2000):

$$k = \left(\frac{r_\alpha}{D_g} + \frac{4}{\upsilon\gamma}\right)^{-1} A \quad (A4)$$

where υ is the mean molecular speed of O_3 and D_g is its gas-phase molecular diffusion coefficient calculated as follows:

$$D_g = \frac{9.45 \times 10^{17} \times \sqrt{T\left(3.47 \times 10^{-2} + \frac{1}{M}\right)}}{\rho_{air}} \quad (A5)$$

where T is the ambient air temperature, ρ_{air} is the air density, and M the molar mass of O_3. γ is the reaction probability calculated following Jacob (Jacob, 2000) and Shao et al. (Shao et al., 2019).

$$\gamma = \left(\frac{1}{\alpha} + \frac{\upsilon}{4HRT\sqrt{D_a K}}\frac{1}{f_r}\right) \quad (A6)$$

where α is the mass accommodation coefficient, Da is the aqueous-phase molecular diffusion coefficient of O3, H is the effective Henry's law constant of O_3 (Sander, 2015), R is the ideal gas constant, f_r is the reacto-diffusive correction term (Shao et al., 2019), and K is the pseudo-first order reaction rate constant between S(IV) and O_3 in the aqueous phase (Seinfeld and Pandis, 2006).

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Author contributions: V.A.K. and J.L. planned the research, V.A.K., A.P.T. and A.P. performed the model calculations, V.A.K., A.P., and J.L. analyzed the results, V.A.K. and J.L. wrote the paper. All authors contributed to the manuscript.; **Competing interests:** Authors declare no competing interests. **Code/Data availability:** Data and related material can be obtained from V.A.K. (v.karydis@fz-juelich.de) upon request.

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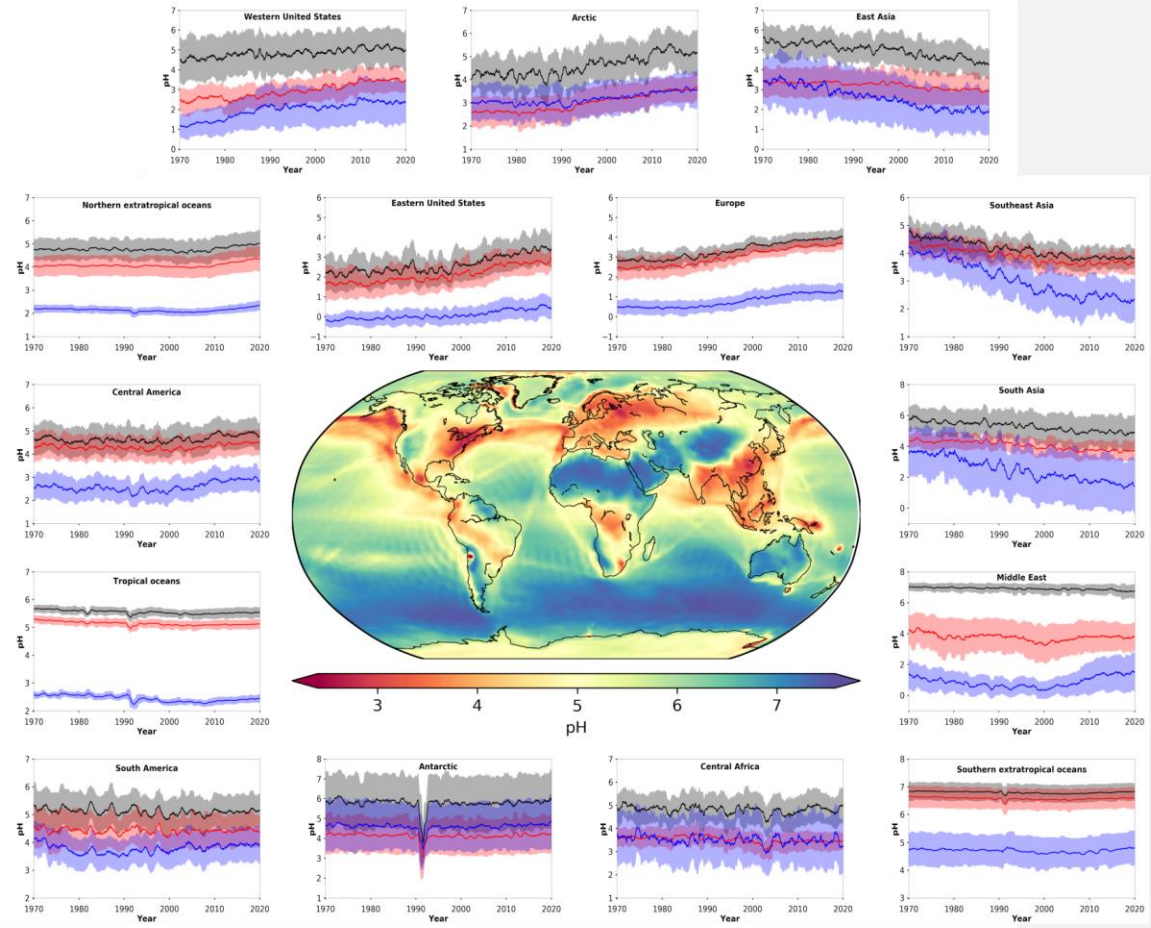
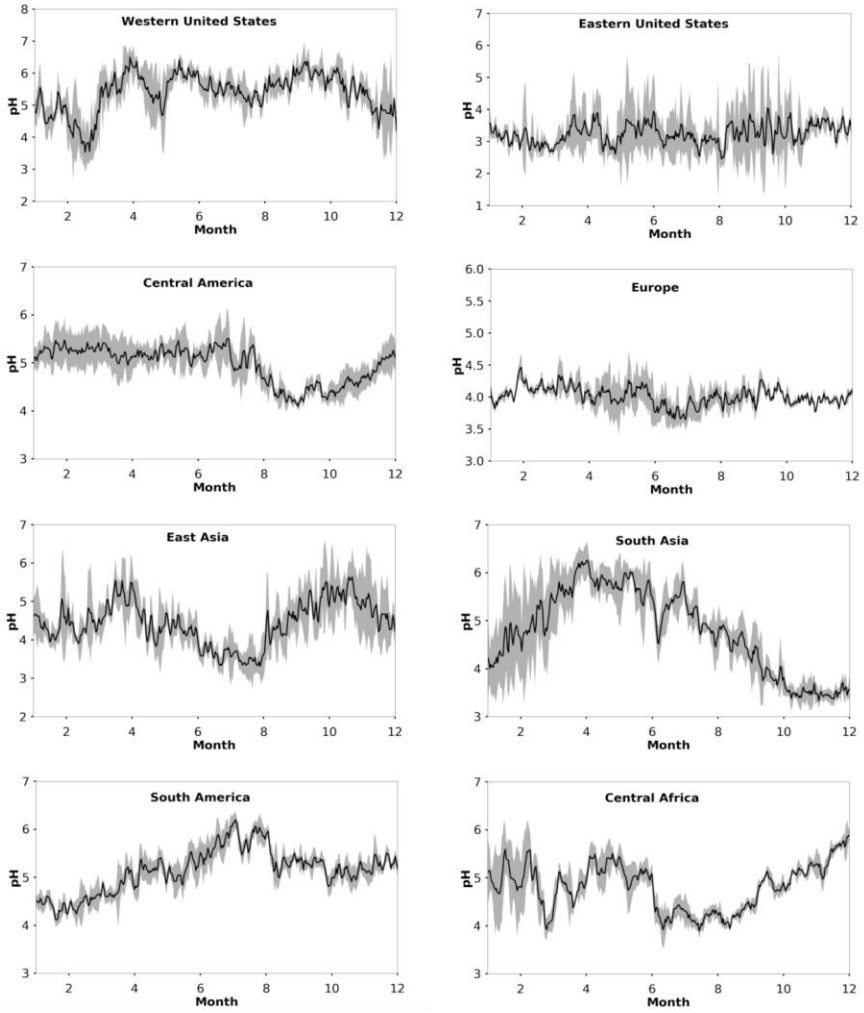


Figure 1: Mean, near-surface fine aerosol pH during the period 2010-2015 (central panel). Surrounding panels show the temporal pH evolution during the period 1970-2020 at locations defined in Table 1. Black lines represent the reference simulation. Red and blue lines show the sensitivity simulations in which crustal particle and NH_3 emissions are removed, respectively. Ranges represent the 1σ standard deviation. The anomaly in 1991/2 is related to the Mt Pinatubo eruption.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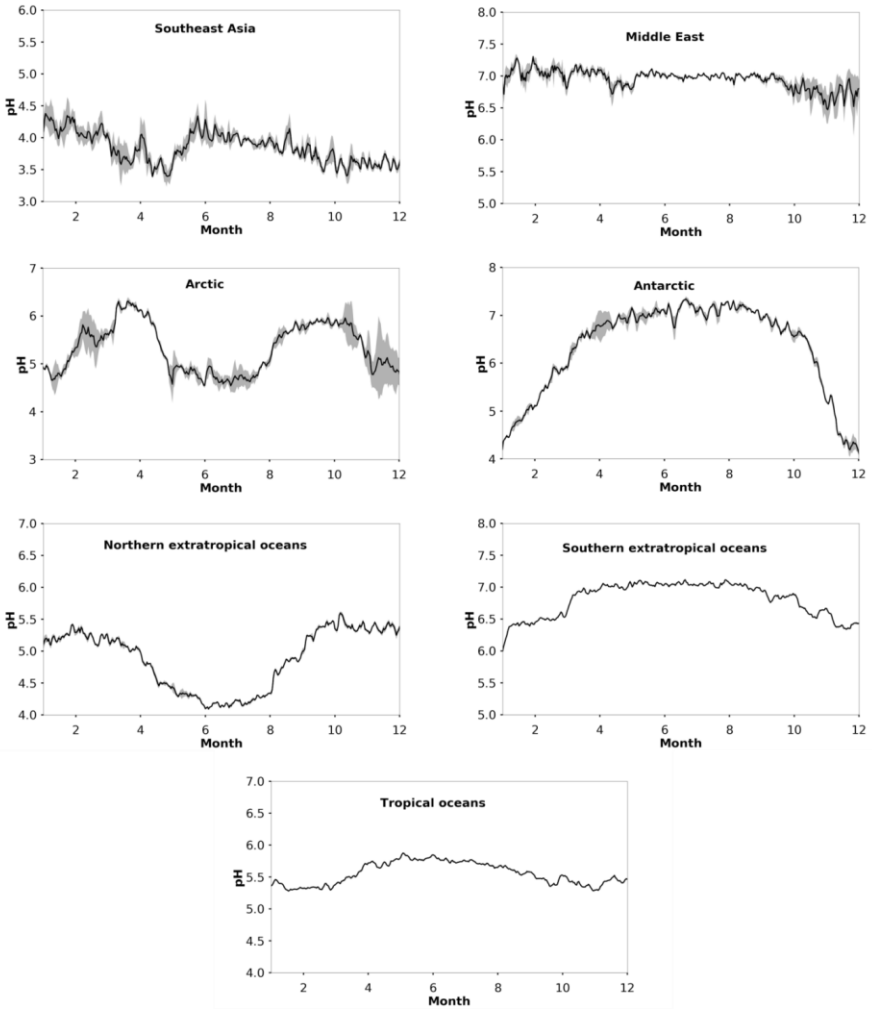


Figure 2: Average seasonal cycle of modelled pH during the period 2010-2015 at locations defined in Table 1. Ranges represent the 1σ standard deviation.

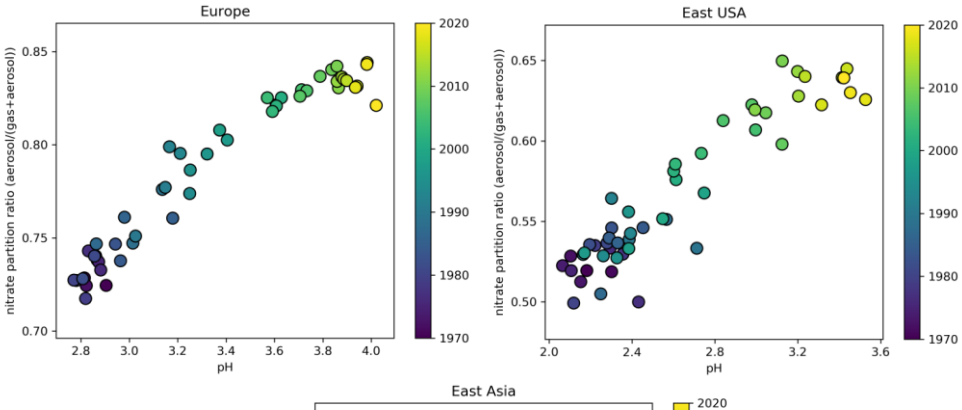


Figure 3: Time evolution of particle phase fraction of total nitrate as a function of pH over Europe (left), the Eastern USA (right) and East Asia (bottom) during the period 1970-2020.

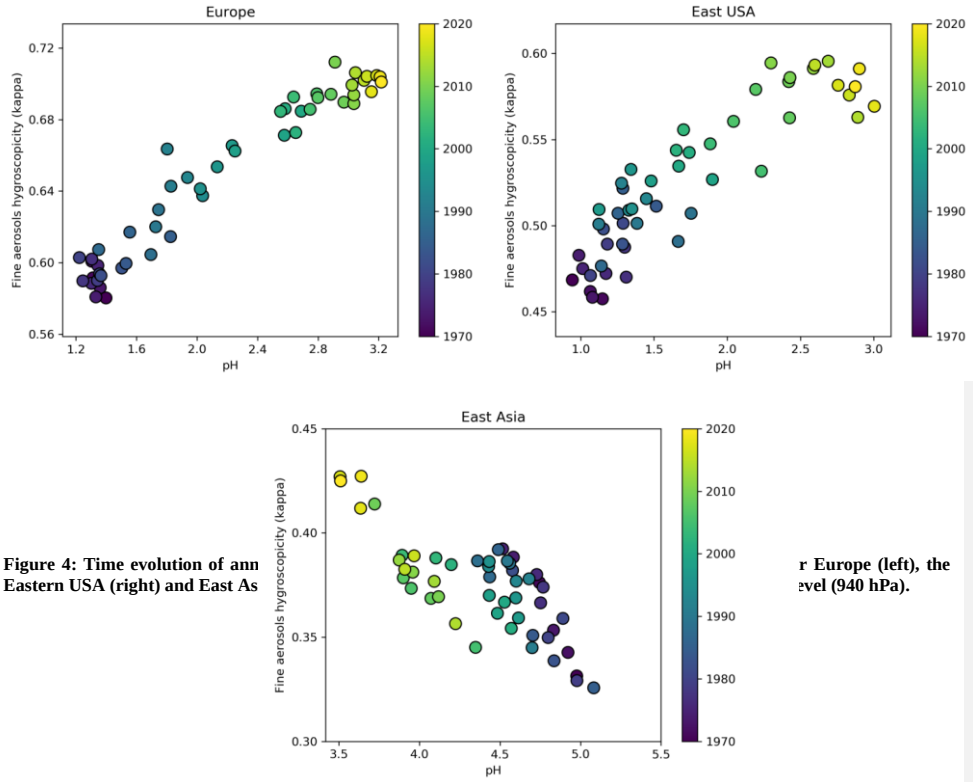


Figure 4: Time evolution of ann **r Europe (left), the Eastern USA (right) and East As** **evel (940 hPa).**

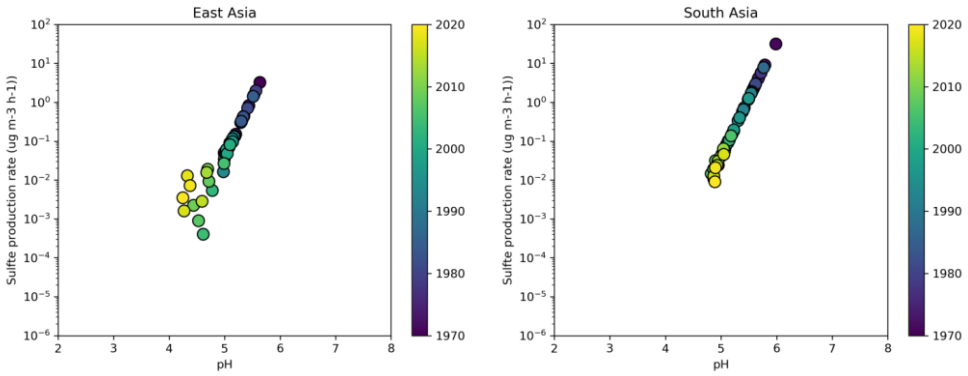


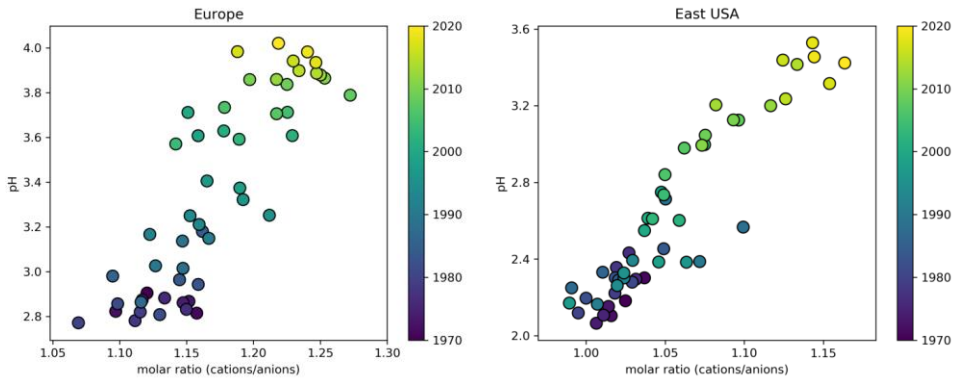
Figure 5: Time evolution of the sulfate production rate on aqueous aerosols from the SO_2+O_3 multiphase chemistry reaction as a function of aerosol pH over East Asia (left) and South Asia (right) during the period 1970-2020.

Table 1: Decadal averages of aerosol pH.

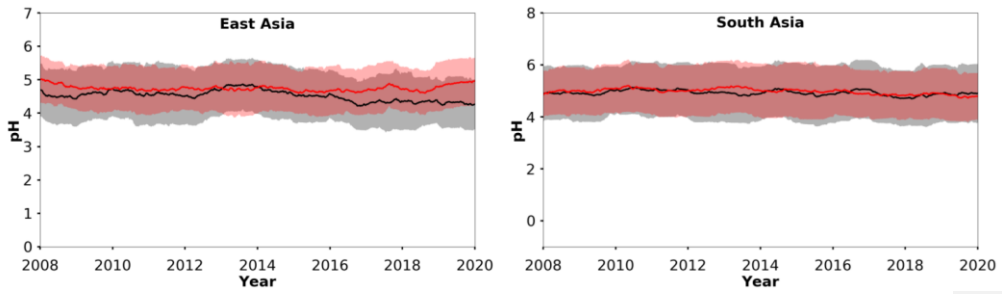
Region	Longitude	Latitude	1971-1980	1981-1990	1991-2000	2001-2010	2011-2020
Western USA[1]	90°-70°W	30°-46°N	4.6	4.8	4.8	5.0	5.1
Eastern USA[1]	124°-114°W	30°-52°N	2.2	2.4	2.4	2.9	3.3
Central America[1]	106°-52°W	4°-28°N	4.6	4.6	4.6	4.7	4.9
Europe[1]	12°W-36°E	34°-62°N	2.8	3.0	3.3	3.7	3.9
East Asia[1]	100°-114°E	20°-44°N	5.3	5.2	5.1	4.7	4.5
South Asia[1]	68°-94°E	8°-32°N	5.6	5.5	5.3	5.0	4.9
South America[1]	75°-35°W	30°-0°S	5.2	5.1	5.1	5.1	5.1
Central Africa[1]	10°-40°E	10°S-10°N	4.9	4.8	4.8	4.7	4.9
Southeast Asia[1]	94°-130°E	12°S-20°N	4.5	4.3	4.1	3.9	3.8
Middle East[1]	36°-60°E	12°-34°N	7.0	7.0	6.9	6.9	6.8
Arctic	0°-360°	60°-90°N	4.2	4.2	4.6	4.8	5.2
North extratropics[2]	0°-360°	20°-60°N	4.8	4.8	4.7	4.7	4.9
Tropical oceans[2]	0°-360°	20°S-20°N	5.6	5.6	5.5	5.5	5.5
South extratropics[2]	0°-360°	60°-20°S	6.8	6.8	6.8	6.8	6.8
Antarctic	0°-360°	90°-60°S	5.9	5.9	5.6	5.8	5.8

[1]Only values over land are considered for the calculation of pH
[2]Only values over oceans are considered for the calculation of pH

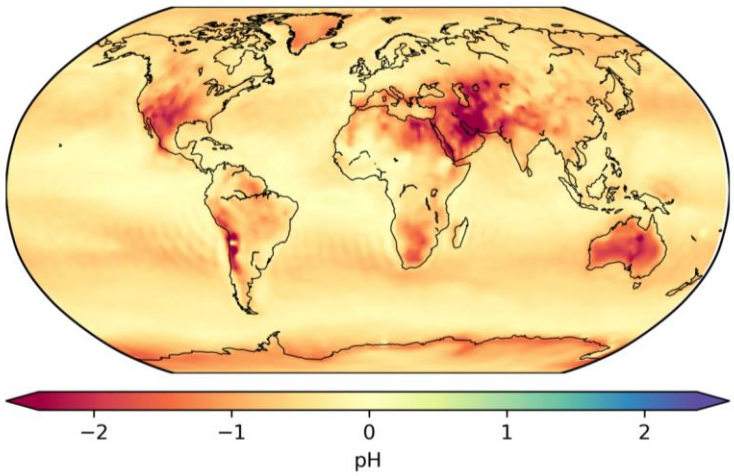
~~Supplementary Materials~~



~~Figure S1: Time evolution of annual average pH as a function of cation/anion molar ratio over Europe (left) and the Eastern USA (right) during the period 1970-2020.~~



~~Figure S2: Temporal pH evolution in East and South Asia during the period 2008-2020. Black lines represent the reference simulation. Red lines show the sensitivity simulation in which SO_2 emissions are reduced by 75% in East Asia and increased by 50% in South Asia. Ranges represent the 1σ standard deviation.~~



~~**Figure S3: Absolute change in the calculated mean near-surface fine aerosol pH during the period 2010-2015 (cf. central panel in Fig. 1) by assuming that aerosols are always aqueous solution droplets (metastable state). A negative change corresponds to more acidic particles compared to the stable state assumption.**~~

Table S1: Fractional emission factors of aerosol components for biofuel combustion, and savannah and tropical forest biomass burning (Akagi et al., 2011), and for sea salt (Seinfeld and Pandis, 2006).

Location	Latitude	Longitude	Time period	Simulated mean pH	Field derived mean pH	Method used	Reference
Pellston, MI, USA	45.55°N	84.78°W	Jul 2016	3.8	3.5	pH indicator paper/ colorimetric image	Craig et al., 2018
Ann Arbor, MI, USA	42.28°N	83.74°W	Aug 2016	4.3	3.5	pH indicator paper/ colorimetric image	Craig et al., 2018
Centreville, AL, USA	32.9°N	87.25°W	Jun 1998 – Aug 2013	6.4	1.2	ISORROPIA (no NH_3)	Weber et al., 2016
Centreville, AL, USA	32.9°N	87.25°W	Jun – Jul 2013	7.0	1.1	ISORROPIA	Pye et al., 2018
Egbert, ON, Canada	44.23°N	79.78°W	Jul – Sep 2012	3.9	2.1	E-AIM Model II	Murphy et al., 2017
Harrow, ON, Canada	42.03°N	82.89°W	Jun – Jul 2007	4.2	1.6	E-AIM Model II	Murphy et al., 2017
Pasadena, CA, USA	34.14°N	118.12°W	Jun 2010	5.9	2.7	ISORROPIA (metastable)	Guo et al., 2017
Toronto, Canada	43.66°N	79.40°W	2007-2013	4.0	2.6	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Toronto, Canada	43.66°N	79.40°W	2014-2016	4.1	2.7	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Ottawa, Canada	45.43°N	75.68°W	2007-2016	4.0	2.5	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Simcoe, Canada	42.86°N	80.27°W	2007-2016	4.4	2.41	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Montreal, Canada	45.65°N	73.57°W	2007-2016	4.0	2.4	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Windsor, Canada	42.29°N	83.07°W	2007-2010	4.4	2.1	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Windsor, Canada	42.29°N	83.07°W	2012-2016	4.5	2.4	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
St. Anicet, Canada	45.12°N	74.29°W	2007-2016	4.0	2.5	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy, 2019
Sao Paulo, Brazil	23.55°S	46.63°W	Aug – Sep 2012	6.2	4.8	E-AIM	Vieira-Filho et al., 2016
Po Valley, Italy	45.40°N	12.20°E	Mar 2009 – Jan 2010	4.5	3.1	E-AIM Model IV	Squizzato et al., 2013

Po Valley, Italy	45.40°N	12.20°E	Spring 2009	4.3	3.6	E-AIM Model IV	Squizzato et al., 2013
Po Valley, Italy	45.40°N	12.20°E	Summer 2009	4.8	2.3	E-AIM Model IV	Squizzato et al., 2013
Po Valley, Italy	45.40°N	12.20°E	Fall 2009	4.5	3	E-AIM Model IV	Squizzato et al., 2013
Po Valley, Italy	45.40°N	12.20°E	Winter 2009-2010	4.4	3.4	E-AIM Model IV	Squizzato et al., 2013
Po Valley, Italy	45.40°N	12.20°E	Winter 2012-2013	4.2	3.9	ISORROPIA (metastable, no NH_3)	Masiol et al., 2020
Po Valley, Italy	45.40°N	12.20°E	Spring 2012	4.1	2.3	ISORROPIA (metastable, no NH_3)	Masiol et al., 2020
Cabauw, Netherlands	51.97°N	4.93°E	Jul 2012 – Jun 2013	4.0	3.7	ISORROPIA	Guo et al., 2018
Cabauw, Netherlands	51.97°N	4.93°E	Jun – Aug 2013	3.6	3.3	ISORROPIA	Guo et al., 2018
Cabauw, Netherlands	51.97°N	4.93°E	Dec – Feb 2012	4.1	3.9	ISORROPIA	Guo et al., 2018
Beijing, China	39.99°N	116.30°E	Nov 2015 – Dec 2016	4.9	4.2	ISORROPIA	Liu et al., 2017
Guangzhou, China	23.13°N	113.26°E	Jul 2013	2.6	2.5	E-AIM Model IV	Jia et al., 2018
Beijing, China	39.97°N	116.37°E	Nov 2014 –Dec 2014	4.5	4.6	ISORROPIA	Song et al., 2018
Beijing, China	40.41°N	116.68°E	Oct 2014 – Jan 2015	5.6	4.7	ISORROPIA (metastable)	He et al., 2018
Beijing, China	39.99°N	116.31°E	Jan – Dec 2014	4.9	3.0	ISORROPIA (metastable)	Tan et al., 2018
Beijing, China	39.99°N	116.31°E	Winter 2014	5.5	4.1	ISORROPIA (metastable)	Tan et al., 2018
Beijing, China	39.99°N	116.31°E	Fall 2014	6.0	3.1	ISORROPIA (metastable)	Tan et al., 2018
Beijing, China	39.99°N	116.31°E	Spring 2014	5.4	2.1	ISORROPIA (metastable)	Tan et al., 2018
Beijing, China	39.99°N	116.31°E	Summer 2014	3.1	1.8	ISORROPIA (metastable)	Tan et al., 2018
Tianjin, China	39.11°N	117.16°E	Dec 2014 – Jun 2015	4.4	4.9	ISORROPIA (metastable)	Shi et al., 2017

Tianjin, China	39.11°N	117.16°E	Aug 2015	1.4	3.4	ISORROPIA (metastable)	Shi et al., 2017
Beijing, China	39.98°N	116.28°E	Feb 2017	4.7	4.5	ISORROPIA	Ding et al., 2019
Beijing, China	39.98°N	116.28°E	Apr – May 2016	5.2	4.4	ISORROPIA	Ding et al., 2019
Beijing, China	39.98°N	116.28°E	Jul – Aug 2017	2.2	3.8	ISORROPIA	Ding et al., 2019
Beijing, China	39.98°N	116.28°E	Sep – Oct 2017	4.5	4.3	ISORROPIA	Ding et al., 2019
Guangzhou, China	23.13°N	113.26°E	Jul – Sep 2013	2.7	2.4	E-AIM Model III	Jia et al., 2018
Hohhot, China	40.48°N	111.41°E	Summer 2014	5.5	5	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Hohhot, China	40.48°N	111.41°E	Autumn 2014	6.8	5.3	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Hohhot, China	40.48°N	111.41°E	Winter 2014	5.8	5.7	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Hohhot, China	40.48°N	111.41°E	Spring 2015	6.1	6.1	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Hohhot, China	40.48°N	111.41°E	2014 - 2015	6.2	5.6	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Beijing, China	40.41°N	116.68°E	Oct 2014 – Jan 2015	5.6	7.6	ISORROPIA (stable state)	He et al., 2018
Xi'an, China	34.23°N	108.89°E	Nov – Dec 2012	5.7	6.7	ISORROPIA	Wang et al., 2016
Beijing, China	39.99°N	116.30°E	Jan – Feb 2015	5.0	7.6	ISORROPIA	Wang et al., 2016
Beijing, China	40.35°N	116.30°E	Jun – Aug 2005	4.2	0.6	E-AIM Model II (only aerosols)	Pathak et al., 2009
Shanghai, China	31.45°N	121.10°E	May – Jun 2005	3.5	0.7	E-AIM Model II (only aerosols)	Pathak et al., 2009
Lanzhou, China	36.13°N	103.68°E	Jun – Jul 2006	6.8	0.6	E-AIM Model II (only aerosols)	Pathak et al., 2009
Beijing, China	40.32°N	116.32°E	Jan 2005 – Apr 2006	5.1	0.7	E-AIM Model II (only aerosols)	He et al., 2012
Chongqing, China	29.57°N	106.53°E	Jan 2005 – Apr 2006	3.6	1.5	E-AIM Model II (only aerosols)	He et al., 2012

Beijing, China	40°N	116.33°E	Jan 2013	4.6	5.8	ISORROPIA (forward & reverse, estimated NH_3)	Wang et al., 2016
Singapore	1.3°N	103.78°E	Sep – Nov 2011	3.2	0.6	E-AIM Model IV	Behera et al., 2013
Hong Kong	22.34°N	114.26°E	Jul 1997 – May 1998	3.3	0.3	E-AIM Model II (for RH >= 70%)	Yao et al., 2007
Hong Kong	22.34°N	114.26°E	Nov 1996 – Nov 1997	3.4	-1	E-AIM Model II (for RH < 70%)	Yao et al., 2007
Hong Kong	22.34°N	114.26°E	Oct 2008	5.0	0.6	E-AIM Model III (only aerosols)	Xue et al., 2011
Hong Kong	22.34°N	114.26°E	Nov 2008	3.7	0.5	E-AIM Model III (only aerosols)	Xue et al., 2011
Hong Kong	22.34°N	114.26°E	Jun – Jul 2009	1.6	0.1	E-AIM Model III (only aerosols)	Xue et al., 2011
Pacific Ocean	47.5°S	147.5°E	Nov - Dec 1995	7.0	1.0	EQUISOLV	Fridlind and Jacobson, 2000
South Ocean	61°S	45°W	Jan 2015	6.9	1.4	ISORROPIA (no NH_3)	Dall' Osto et al., 2019
South Ocean	64°S	65°W	Jan – Feb 2015	6.9	3.8	ISORROPIA (no NH_3)	Dall' Osto et al., 2019

Table S2: Fractional emission factors of aerosol components for biofuel combustion, and savannah and tropical forest biomass burning (Akagi et al., 2011), and for sea salt (Seinfeld and Pandis, 2006).

Source	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
Biofuel combustion	-	0.014	-	-	0.093	0.022	0.073	-
Grassfire burning	0.05	0.04	0.62	0.01	0.62	0.04	0.06	0.01
Forest fire burning	0.25	0.21	0.29	0.01	0.56	0.08	0.16	0.01
Sea salt	0.077	-	0.55	0.306	0.011	0.037	0.012	-

Table S3: Fractional chemical composition of mineral dust emissions (Karydis et al., 2016).

Desert	Na^+	K^+	Ca^{2+}	Mg^{2+}	Other
Great Basin	0.064	0.023	0.053	0.018	0.842
Mojave	0.015	0.027	0.059	0.019	0.880
Sonoran	0.025	0.012	0.037	0.006	0.920
Patagonia	0.012	0.015	0.021	0.013	0.939
Monte	0.023	0.018	0.025	0.009	0.925
Atacama	0.069	0.007	0.018	0.005	0.901
Kalahari/ Namibia	0.030	0.050	0.120	0.090	0.710
Sahara	0.011	0.035	0.075	0.030	0.849
Saudi Arabia	0.010	0.004	0.034	0.006	0.946
Thar/Lut	0.022	0.033	0.082	0.022	0.841
Taklimakan	0.012	0.030	0.120	0.028	0.810
Gobi	0.012	0.021	0.077	0.017	0.873
Great Sandy/ Simpson	0.028	0.001	0.005	0.003	0.963
Other	0.012	0.015	0.024	0.009	0.940

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Supplementary Materials

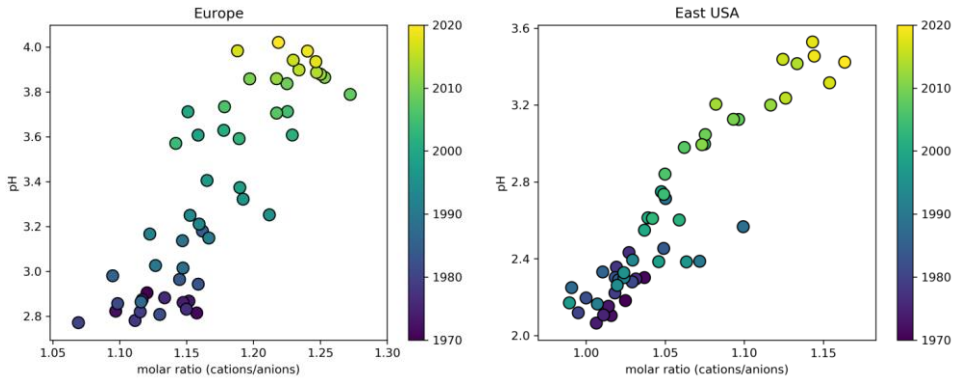

Figure S1: Time evolution of annual average pH as a function of cation/anion molar ratio over Europe (left) and the Eastern USA (right) during the period 1970-2020. The calculated ratio includes all ions from both solid salts and the liquid phase.

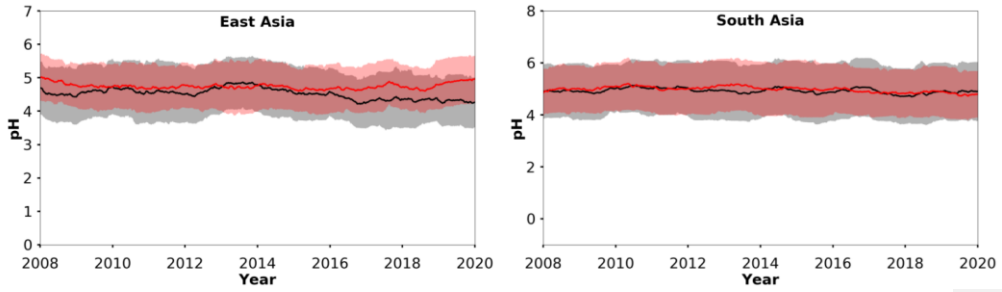

Figure S2: Temporal pH evolution in East and South Asia during the period 2008-2020. Black lines represent the reference simulation. Red lines show the sensitivity simulation in which SO_2 emissions are reduced by 75% in East Asia and increased by 50% in South Asia. Ranges represent the 1σ standard deviation.

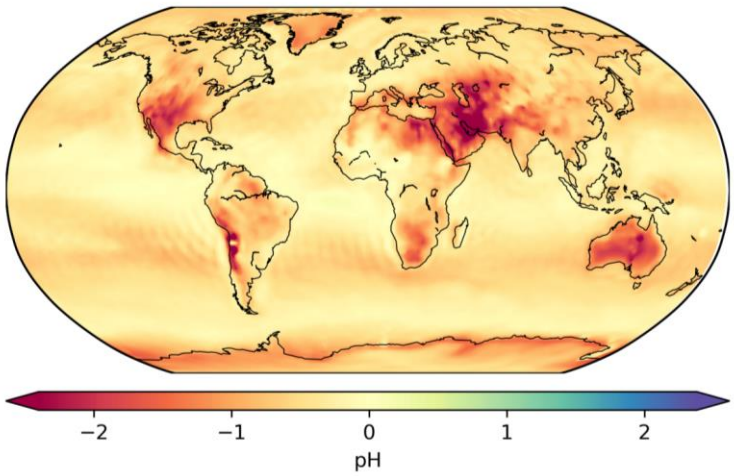

Figure S3: Absolute change in the calculated mean near-surface fine aerosol pH during the period 2010-2015 (cf. central panel in Fig. 1) by assuming that aerosols are always aqueous solution droplets (metastable state). A negative change corresponds to more acidic particles compared to the stable state assumption.

Table S1: Simulated fine aerosol pH compared to observationally-constrained estimates of fine aerosol acidity compiled by Pye et al. (2020).

Location	Latitude	Longitude	Time period	Simulated mean pH (Stable)	Simulated mean pH (Metastable)	Field derived mean pH	Method used	Reference
Pellston, MI, USA	45.55°N	84.78°W	Jul 2016	3.8	3.1	3.5	pH indicator paper/ colorimetric image	Craig et al. (2018)
Ann Arbor, MI, USA	42.28°N	83.74°W	Aug 2016	4.3	3.0	3.5	pH indicator paper/ colorimetric image	Craig et al. (2018)
Centreville, AL, USA	32.9°N	87.25°W	Jun 1998 – Aug 2013	6.4	5.7	1.2	ISORROPIA (no NH_3)	Weber et al. (2016)
Centreville, AL, USA	32.9°N	87.25°W	Jun — Jul 2013	7.0	6.5	1.1	ISORROPIA	Pye et al. (2018)
Egbert, ON, Canada	44.23°N	79.78°W	Jul – Sep 2012	3.9	3.5	2.1	E-AIM Model II	Murphy et al. (2017)
Harrow, ON, Canada	42.03°N	82.89°W	Jun – Jul 2007	4.2	3.0	1.6	E-AIM Model II	Murphy et al. (2017)
Pasadena, CA, USA	34.14°N	118.12°W	Jun 2010	5.9	2.7	2.7	ISORROPIA (metastable)	Guo et al. (2017)
Toronto, Canada	43.66°N	79.40°W	2007-2013	4.0	3.6	2.6	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Toronto, Canada	43.66°N	79.40°W	2014-2016	4.1	3.7	2.7	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Ottawa, Canada	45.43°N	75.68°W	2007-2016	4.0	3.9	2.5	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Simcoe, Canada	42.86°N	80.27°W	2007-2016	4.4	3.7	2.41	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Montreal, Canada	45.65°N	73.57°W	2007-2016	4.0	3.9	2.4	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Windsor, Canada	42.29°N	83.07°W	2007-2010	4.4	3.6	2.1	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Windsor, Canada	42.29°N	83.07°W	2012-2016	4.5	3.7	2.4	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
St. Anicet, Canada	45.12°N	74.29°W	2007-2016	4.0	3.9	2.5	E-AIM I (with gas NH_3, HNO_3)	Tao and Murphy (2019)
Sao Paulo, Brazil	23.55°S	46.63°W	Aug – Sep 2012	6.2	6.1	4.8	E-AIM	Vieira-Filho et al. (2016)
Po Valley, Italy	45.40°N	12.20°E	Mar 2009 – Jan 2010	4.5	3.6	3.1	E-AIM Model IV	Squizzato et al. (2013)
Po Valley, Italy	45.40°N	12.20°E	Spring 2009	4.3	3.7	3.6	E-AIM Model IV	Squizzato et al. (2013)
Po Valley, Italy	45.40°N	12.20°E	Summer 2009	4.8	3.0	2.3	E-AIM Model IV	Squizzato et al. (2013)
Po Valley,	45.40°N	12.20°E	Fall 2009	4.5	3.6	3	E-AIM Model IV	Squizzato et al.

Italy								(2013)
Po Valley, Italy	45.40°N	12.20°E	Winter 2009-2010	4.4	4.0	3.4	E-AIM Model IV	Squizzato et al. (2013)
Po Valley, Italy	45.40°N	12.20°E	Winter 2012-2013	4.2	4.0	3.9	ISORROPIA (metastable, no NH_3)	Masiol et al. (2020)
Po Valley, Italy	45.40°N	12.20°E	Spring 2012	4.1	3.1	2.3	ISORROPIA (metastable, no NH_3)	Masiol et al. (2020)
Cabauw, Netherlands	51.97°N	4.93°E	Jul 2012 – Jun 2013	4.0	3.8	3.7	ISORROPIA	Guo et al. (2018)
Cabauw, Netherlands	51.97°N	4.93°E	Jun – Aug 2013	3.6	3.4	3.3	ISORROPIA	Guo et al. (2018)
Cabauw, Netherlands	51.97°N	4.93°E	Dec – Feb 2012	4.1	4.1	3.9	ISORROPIA	Guo et al. (2018)
Beijing, China	39.99°N	116.30°E	Nov 2015 – Dec 2016	4.9	4.2	4.2	ISORROPIA	Liu et al. (2017)
Guangzhou, China	23.13°N	113.26°E	Jul 2013	2.6	1.9	2.5	E-AIM Model IV	Jia et al. (2018)
Beijing, China	39.97°N	116.37°E	Nov 2014 –Dec 2014	4.5	5.3	4.6	ISORROPIA	Song et al. (2018)
Beijing, China	40.41°N	116.68°E	Oct 2014 – Jan 2015	5.6	4.9	4.7	ISORROPIA (metastable)	He et al. (2018)
Beijing, China	39.99°N	116.31°E	Jan – Dec 2014	4.9	4.0	3.0	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Winter 2014	5.5	4.4	4.1	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Fall 2014	6.0	4.6	3.1	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Spring 2014	5.4	4.5	2.1	ISORROPIA (metastable)	Tan et al. (2018)
Beijing, China	39.99°N	116.31°E	Summer 2014	3.1	2.4	1.8	ISORROPIA (metastable)	Tan et al. (2018)
Tianjin, China	39.11°N	117.16°E	Dec 2014 – Jun 2015	4.4	3.7	4.9	ISORROPIA (metastable)	Shi et al. (2017)
Tianjin, China	39.11°N	117.16°E	Aug 2015	1.4	1.2	3.4	ISORROPIA (metastable)	Shi et al. (2017)
Beijing, China	39.98°N	116.28°E	Feb 2017	4.7	4.8	4.5	ISORROPIA	Ding et al. (2019)
Beijing, China	39.98°N	116.28°E	Apr - May 2016	5.2	4.7	4.4	ISORROPIA	Ding et al. (2019)
Beijing, China	39.98°N	116.28°E	Jul - Aug 2017	2.2	1.9	3.8	ISORROPIA	Ding et al. (2019)
Beijing, China	39.98°N	116.28°E	Sep - Oct 2017	4.5	3.7	4.3	ISORROPIA	Ding et al. (2019)

Guangzhou, China	23.13°N	113.26°E	Jul – Sep 2013	2.7	2.2	2.4	E-AIM Model III	Jia et al. (2018)
Hohhot, China	40.48°N	111.41°E	Summer 2014	5.5	4.0	5	ISORROPIA (metastable, no NH_3)	Wang et al., 2019
Hohhot, China	40.48°N	111.41°E	Autumn 2014	6.8	5.3	5.3	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Hohhot, China	40.48°N	111.41°E	Winter 2014	5.8	5.0	5.7	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Hohhot, China	40.48°N	111.41°E	Spring 2015	6.1	5.1	6.1	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Hohhot, China	40.48°N	111.41°E	2014 - 2015	6.2	5.0	5.6	ISORROPIA (metastable, no NH_3)	Wang et al. (2019)
Beijing, China	40.41°N	116.68°E	Oct 2014 – Jan 2015	5.6	4.9	7.6	ISORROPIA (stable state)	He et al. (2018)
Xi'an, China	34.23°N	108.89°E	Nov – Dec 2012	5.7	4.5	6.7	ISORROPIA	Wang et al. (2016)
Beijing, China	39.99°N	116.30°E	Jan – Feb 2015	5.0	3.8	7.6	ISORROPIA	Wang et al. (2016)
Beijing, China	40.35°N	116.30°E	Jun – Aug 2005	4.2	3.3	0.6	E-AIM Model II (only aerosols)	Pathak et al. (2009)
Shanghai, China	31.45°N	121.10°E	May – Jun 2005	3.5	3.1	0.7	E-AIM Model II (only aerosols)	Pathak et al. (2009)
Lanzhou, China	36.13°N	103.68°E	Jun – Jul 2006	6.8	5.1	0.6	E-AIM Model II (only aerosols)	Pathak et al. (2009)
Beijing, China	40.32°N	116.32°E	Jan 2005 – Apr 2006	5.1	4.1	0.7	E-AIM Model II (only aerosols)	He et al. (2012)
Chongqing, China	29.57°N	106.53°E	Jan 2005 – Apr 2006	3.6	2.7	1.5	E-AIM Model II (only aerosols)	He et al. (2012)
Beijing, China	40°N	116.33°E	Jan 2013	4.6	4.5	5.8	ISORROPIA (forward & reverse, estimated NH_3)	Wang et al. (2016)
Singapore	1.3°N	103.78°E	Sep – Nov 2011	3.2	3.0	0.6	E-AIM Model IV	Behera et al. (2013)
Hong Kong	22.34°N	114.26°E	Jul 1997 – May 1998	3.3	3.0	0.3	E-AIM Model II (for RH >= 70%)	Yao et al. (2007)
Hong Kong	22.34°N	114.26°E	Nov 1996 – Nov 1997	3.4	2.9	-1	E-AIM Model II (for RH < 70%)	Yao et al. (2007)
Hong Kong	22.34°N	114.26°E	Oct 2008	5.0	3.2	0.6	E-AIM Model III (only aerosols)	Xue et al. (2011)
Hong Kong	22.34°N	114.26°E	Nov 2008	3.7	2.7	-0.5	E-AIM Model III (only aerosols)	Xue et al. (2011)
Hong Kong	22.34°N	114.26°E	Jun - Jul 2009	1.6	2.0	-0.1	E-AIM Model III (only aerosols)	Xue et al. (2011)
Pacific Ocean	47.5°S	147.5°E	Nov - Dec 1995	7.0	6.5	1.0	EQUISOLV	Fridlind and Jacobson (2000)

South Ocean	61°S	45°W	Jan 2015	6.9	6.7	1.4	ISORROPIA (no NH_3)	Dall'Osto et al. (2019)
South Ocean	64°S	65°W	Jan – Feb 2015	6.9	6.8	3.8	ISORROPIA (no NH_3)	Dall'Osto et al. (2019)

Table S2: Fractional emission factors of aerosol components for biofuel combustion, and savannah and tropical forest biomass burning (Akagi et al., 2011), and for sea salt (Seinfeld and Pandis, 2006).

Source	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
Biofuel combustion	-	0.01 4	-	-	0.09 3	0.02 2	0.07 3	-
Grassfire burning	0.05	0.04	0.62	0.01	0.62	0.04	0.06	0.01
Forest fire burning	0.25	0.21	0.29	0.01	0.56	0.08	0.16	0.01
Sea salt	0.07 7	-	0.55	0.30 6	0.01 1	0.03 7	0.01 2	-

Table S3: Fractional chemical composition of mineral dust emissions (Karydis et al., 2016).

Desert	Na^+	K^+	Ca^{2+}	Mg^{2+}	Other
Great Basin	0.064	0.023	0.053	0.018	0.842
Mojave	0.015	0.027	0.059	0.019	0.880
Sonoran	0.025	0.012	0.037	0.006	0.920
Patagonia	0.012	0.015	0.021	0.013	0.939
Monte	0.023	0.018	0.025	0.009	0.925
Atacama	0.069	0.007	0.018	0.005	0.901
Kalahari/ Namibia	0.030	0.050	0.120	0.090	0.710
Sahara	0.011	0.035	0.075	0.030	0.849
Saudi Arabia	0.010	0.004	0.034	0.006	0.946
Thar/Lut	0.022	0.033	0.082	0.022	0.841
Taklimakan	0.012	0.030	0.120	0.028	0.810
Gobi	0.012	0.021	0.077	0.017	0.873
Great Sandy/ Simpson	0.028	0.001	0.005	0.003	0.963
Other	0.012	0.015	0.024	0.009	0.940

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