Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality.

14th Dec 20

Dear Dr Nault,

Please allow me to apologise for the delay in sending a decision on your manuscript titled "Models underestimate the increase of acidity with remoteness biasing radiative impact calculations". It has now been seen by 3 reviewers, and I include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in Communications Earth & Environment, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

In addition, please ensure that the revised manuscript addresses the following editorial thresholds:

Provide a compelling and robust argument that existing chemical transport models are likely underestimating the acidity of aerosols in remote regions

Ensure that all terms and ideas are clearly defined and their background introduced at their first appearance in the text

Fully discuss all limitations and uncertainties associated with the study and caveat your interpretations and conclusions accordingly

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the referees' comments (which should be in a separate document to any cover letter) and the completed checklist:
[link redacted]
** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first **

We hope to receive your revised paper within six weeks; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we may close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Joe Aslin

Associate Editor,
Communications Earth & Environment
https://www.nature.com/commsenv/
Twitter: @CommsEarth

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REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Review of Nault et al., “Models underestimate the increase of acidity with remoteness biasing radiative impact calculations”

In this manuscript, Nault et al., analyze the results from the application of a range of global chemical transport models to assess their ability to capture various aerosol characteristics, including pH, and then assess how the results impact radiative forcing. They find that the models tend to have a bias high in the calculated pH due to the simulated aerosol characteristics, and this would tend to lead to a low bias in radiative forcing by about 0.2 W m-2 in the direct radiative effect (DRE). The paper shows a significant effort towards getting at the question of how the biases might influence DRE, and they conducted additional work to identify and quantify the impact of potential issues.
Like many papers I have reviewed lately, this paper really needed a bit more care in its editing. As an example, I will look at the 6th paragraph as that is the one where it went from o.k., to a bit annoying:
1. Line 107. “Including” is used incorrectly as NH4_bal and pH are no inorganic aerosols, but characteristics of such. Thus it should be “…aerosols, and associated characteristics such as NH4_bal and pH”

2. Line 113 “most”… maybe it is more robust, maybe not, depending on your viewpoint. Most is a bit extreme. For one, is NH4_bal the best chemical coordinate? IO thought Hennigan et al (2015) came up with a different conclusion.
3. “Sensitivity” is used incorrectly here, at least in the scientific context (the sensitivity is usually taken as the derivative). It should be how the DRE is changed when using the adjusted results. Individually, these are small, but they add up.

The article is also written for a very specialized audience. This is highlighted by their use of “post-AeroCom-II” in line 124 without ever defining what AeroCom-II is. In line 507 they do not say what is different about AM4.1 (that sentence is awkward as well). If they are looking to have it published in a more general Earth/Environment/Science journal such as Earth and Environment, they need to bring in more of the readership and provide more background on such specifics.

They never discuss the difference between pHF (line 453) and pH and why it might matter.

All of the CTMs used here are global. Other work on acidity has been done using regional CTMs. How do the results compare?

It struck me as odd that they note models tend to overestimate NHx lifetime, but then only look at a longer NHx lifetime case. If the argument is that the lifetimes are too long, Fig. 7 is misleading in that the other cases shown are in the direction of what they view as correct (I think), but the longer NHx case is not, and it has the biggest impact. Why not do a shorter lifetime case in one or two of the other models?

The Abstract is vague and needs to be more quantitative as well as informative.
In the end, the paper represents high quality science, though the presentation is lacking a bit. It is also rather specialized. While I would not recommend publication at this point, with work on the presentation, it would become a nice contribution.

Reviewer #2 (Remarks to the Author):

Review summary:
This study estimates the ammonium ion balance and pH based on extensive airborne observations and simulation results from 9 different chemistry transport models for remote regions and continental regions. The results show that the model predicts a relative more ammonium enrich and higher pH than the observations. They conclude the discrepancy is due to the bias in ammonia emission and the presence of sea-salt. This study also estimates the impact of simulated aerosol hygroscopicity on the radiative cooling effect. Overall, the results are very interesting for the understanding of the observations data, the recent and future tend of aerosol acidity, and the impact of aerosol composition on climate change. This manuscript is suitable for publication after a minor revision by considering the comments listed as below.
Major Comments:
1. Page 10, Line 214-216. The phase separation relative humidity of several pure organic compounds is plotted in Figure 1e. Can these pure organic compounds represent the organic products in the organic aerosols in the scope of the data used in this study? In addition, not only PH but the inorganic compositions also significantly impact on aerosol phase transition, for example the phase

separation relative humidity is little low in the presence of nitrate compare to sulfate (You et al., 2013;). It would be better to include both PH and inorganic composition together when discuss the physical properties such as phase states.
2. Fig 3. For the model averaged results in the Atlantic Ocean regions, the ammonium balance at the equator is near 1 (~800hPa), however, the simulated pH is still very acidic ranging from -0.5 to 0.5. What is the reason that the predicted aerosols were significantly dominated by neutral salts, such as ammonium sulfate, but the aerosol were still super acidic? For comparison, the calculated pH from the observed data in the continental regional (near equator) is high (~2) when ammonium balance is around 1, which is more reasonable to me.
3. Page 9, line 202-204. What is the reason the model significantly overestimates the ammonium balance over the continental regions? The ion balance is very biased, especially for the region where latitude larger than 60. Is it because the overestimation of ammonia emission or the missing sources of anions?
4. Page 9, line 205-207. Similar to the results in the equator of Atlantic Ocean regions, the predicted inorganic compositions are dominant by neutral salts, but why the model pH is still super acidic, mostly below pH 1?
5. Page 9, line 208-209. Which geological location does author referred when authors discuss about the results in the boreal forest BL? It would be helpful to add some more location information for the boreal forest BL regions. And is these results visualized in Figure 3?
6. Page 11, line 236. The secondary organic acid formed in the aerosols are generally weak acid. Are these organic ammonium salts stable in the strong acidic aerosols which pH is below 2?
7. Page 11, line 243-247. It is not clear which data in the Figures (e.g., Figure S8) are the regions without deep convection and which are the regions has deep convection.
8. Page 12, line 268-271. If the ammonium on the filter samples are biased by the ammonia from aircraft cabin, the observation may overestimate the ammonium concentration. However, the current ammonium balance is overestimated by the model which means there is even more discrepancy between modeled results and actual concentration if considering the ammonia bias from aircraft cabin. Therefore, this reference may not explain the current difference between the observation and modeled results but is still valuable to be discussed as one of the potential uncertainties.
9. Figure 5 and 6. The predicted results is mostly consistent, but some is very different. For example, the predicted slope is even negative for CCSM4 model in the BL surface. What might be the reason to have these very different results from different models?
10. What is the major source of SO2 in the remote oceans? Can these SO2 practically contributed by the long-range transport SO2 originated from the continental polluted regions? In addition, the oxidation of SO2 to sulfuric acid is much fast during the daytime when gas phase oxidants are abundant. In addition, the RH and temperature are also significantly different between day and night. Is there any evident difference for the ammonium balance and pH between daytime and nighttime?
11. Page 13, line 282-284. Besides the temperature dependency on the NHx emission, is there temperature dependency on the NHx uptake onto aerosols?
12. Page 14, line 302-318. Even though the sea-salt aerosol is not considered in this study, can the ammonia uptake be impacted by sea-salt aerosols? If yes, then the back calculation of ammonia concentration from the inorganic composition of NSS aerosol will be biased in both measurements and model simulation results.
13. Page 17, line 377. This conclusion is conflicted with the discussion in page 7 line 157 where authors declared that the NHx emissions are generally low in both the Atlantic and Pacific regions.
14. As mentioned in the section of thermodynamic calculation, the E-AIM thermodynamic model

was used for observation and model which do not calculate online. While the online calculation of pH is by ISSOROPIA v2 (GEOS-Chem, AM4.1). Can the prediction of pH partially cause by the difference of thermodynamic model used? For example in the Figure 6d-f, the results of solid lines (use ISORROPIA) are obviously different from the dash line (using EAIM).
Minor Comments:
1. Figure 1. Is the value of “uptake” in 1a refers uptake coefficient?
2. In the text when discussing about the results from Figure 1, it would be better to point out which sub figure is discussed instead of point to wholly Fig 1.
3. Figure S6. It is not clear how the hygroscopic growth factor was estimated for the model simulation. Is the factor directly output from the model simulations or recalculated externally based on the modeled inorganic compositions from CTM models? It would be better to add some more explanation in the Section S2.
4. Figure 4. It is not clear what is the data of the points with the notes of altitude location. Are these data averaged from each campaign in that regions or calculated from model simulations?
5. What is the black area in the Figure 5 and Figure 6? It would be better to also clarified this area type data in the legend separately from line type legends.
6. Page 17, line 386. “.” is missing after “more acidic aerosol”.

References
You, Y., L. Renbaum-Wolff, and A. K. Bertram. "Liquid-liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride." Atmospheric Chemistry & Physics Discussions 13.7 (2013).

Reviewer #3 (Remarks to the Author):

Strong paper, see attached review.

Review of “Models underestimate the increase of acidity with remoteness biasing radiative impact calculations”

Overview

This paper describes how observations show that models are likely underestimating how acidic the aerosol in remote regions actually is, based on extensive and unique measurements during the ATom flights. The paper is a tour-de-force and should be strongly considered for publication. The authors go through an extensive set of measurements and show a surprising result for folks that are used to the assumption that more remote regions are less acidic than polluted or continental regions. Frankly the idea that the oceans are an acidifying force on remote atmospheric aerosol is not something that has been discussed much in the aerosol pH literature and a very novel finding (frankly only possible due to the unique flights the paper is based on). The strong desire to exclude sea salt aerosol, which is not measured well by the primary instrument used, is a bit strong. Simply acknowledging that there is another population of aerosol present with different pH does not undercut the main findings of the paper and that section/discussion should be softened. There are some other suggestions of items to consider and revisions that would improve the paper, but overall this is an important paper and should be published after revision.

Main Points

- Water content? Do the authors have any way of determining (or estimating) water content within these aerosol? Particularly at the higher elevations? It would seem that at < 200 hPa there is likely not much water left. Going back to the work of Martin and co-workers (which the authors cite) is there expected to be enough water there for the aerosol to be considered deliquesced [*Martin et al.*, 2003]?
- Role of organics? Beyond the discussion of Figure 4, organic acid impacts are minimally discussed. What mass fraction does organic aerosol contribute in these remote regions? Since the governing ammonium balance equation does not account for organics, do they play a negligible role? Was this explored and ruled out or just assumed?
- Line 98: The authors claim that non-refractory chloride is a minor portion of PM_1 based on referencing Jimenez et al. 2009 *Science*. For urban areas that is likely true, but in remote and coastal areas over oceans (without transport from polluted areas) I highly suspect that the contribution of sea spray aerosol to submicron PM can be significant, or at least non-negligible [*Ault et al.*, 2009; *Spencer et al.*, 2008]. How would this impact the authors decision to focus on ammonium? This is expanded upon when the author argue on page 14 that sea salt aerosol should be ignored with respect to pH. While the authors argue that sea salt aerosol is minimal or not important ‘sea salt should not be included for pH estimations”, this feels a bit too easy. The argument feels like, the instrument does not measure it well, so we’re ignoring it. However, in Figure 1 the authors make the point that certain processes are really important at higher pH values. This section instead of working to dismiss sea salt, could instead focus on the caveat that the aerosol measured and discussed in this paper focuses on what it can measure well, which is really interesting and important in and of itself. The portion on page 15 where it states GEOS-Chem does better is sea salt is removed, is not convincing. Simply removing a factor because it is challenging to represent is not evidence that it should be removed. The presence of another population of aerosol with higher pH is noteworthy and could lead to second order effects that are not being considered.
- Line 165-167: Perhaps I’m not up on the oceanic literature, but the idea that the oceans are essentially an “acidifying agent” for aerosol over remote regions is really interesting and not something I’ve seen discussed much. As there are no references provided, could the authors expand a bit more on this point. It is kind of an undersold, but important point.

Minor Points

- Line 75: Though inorganic nitrate is listed as “minor” outside of biomass burning plumes, urban areas, etc. While spatially this is certainly true it seems dismissive since the first motivation on line 61 is “human health” and more people live in urban areas globally and certainly those most likely to have negative health consequences from inhaling atmospheric PM. Would suggest rephrasing slightly.
- The recent paper by the Poeschl group is probably worth citing as it discusses [*Zheng et al.*, 2020] many of the phenomena you are covering in this manuscript.
- Line 106: Is this total PM_1 or non-refractory PM_1? Should be made clear either way.
- This is a minor aesthetic suggestion, but it would be useful to plot altitude as well as (or in place of) pressure, as that will be more clear for many non-atmospheric scientists or atmospheric chemistry readers.
- Figure 3: It is remarkable to see such a well-defined air mass with pH substantially higher than the air to all sides of it for the pH of the Atlantic Ocean. One question this raises is how frequent or representative are these flights of the overall values considered by the model?
- Figure 5: This figure is incredibly data-rich, but really dense and not easily accessible. I would recommend attempting to simplify this somehow for the main text and retaining the incredible depth of the figure in the supporting information.

References

Ault, A. P., M. J. Moore, H. Furutani, and K. A. Prather (2009), Impact of emissions from the Los Angeles port region on San Diego air quality, *Environmental Science & Technology*, *43*(10), 3500-3506.

Martin, S. T., J. C. Schlenker, A. Malinowski, H. M. Hung, and Y. Rudich (2003), Crystallization of atmospheric sulfate-nitrate-ammonium particles, *Geophysical Research Letters*, *30*(21), 4.

Spencer, M. T., J. C. Holecek, C. E. Corrigan, V. Ramanathan, and K. A. Prather (2008), Size-resolved chemical composition of aerosol particles during a monsoonal transition period over the Indian Ocean, *113*(D16).

Zheng, G., H. Su, S. Wang, M. O. Andreae, U. Pöschl, and Y. Cheng (2020), Multiphase buffer theory explains contrasts in atmospheric aerosol acidity, *Science*, *369*(6509), 1374-1377.

Response to reviewers' comments on the paper "Models often underestimate the increase of acidity with remoteness biasing radiative impact calculations"

We would like to thank the reviewers for their time and for their useful comments that have helped to improve and clarify our paper. For ease, comments from reviewers are in black, responses in blue, and new text added to paper in **bold blue**.

Reviewer #1

1.0. In this manuscript, Nault et al., analyze the results from application of a range of global chemical transport models to assess their ability to capture various aerosol characteristics, including pH, and then assess how the results impact radiative forcing. They find that the models tend to have a bias high in the calculated pH due to the simulated aerosol characteristics, and this would tend to lead to a low bias in radiative forcing by about 0.2 W m-2 in the direct radiative effect (DRE). The paper shows a significant effort towards getting at the question of how biases might influence DRE, and they conducted additional work to identify and quantify the impact of potential issues.

Like many papers I have reviewed lately, this paper really needed a bit more care in its editing. As an example, I will look at the 6th paragraph as that is the one where it went from o.k., to a bit more annoying:

1. Line 107. "Including" is used incorrectly as NH4_bal and pH are no inorganic aerosols, but characteristics of such. Thus it should be "...aerosols, and associated characteristics such as NH4_bal and pH"

   Corrected.

2. Line 113 "most"....maybe it is more robust, maybe not, depending on your viewpoint. Most is a bit extreme. For one, is NH4_bal the best chemical coordinate? I thought Hennigan et al. (2015) came up with a different conclusion.

   We respectfully disagree on this point. We are only using NH_{4_Bal} as a chemical coordinate (which is one variable used for the y-axis along with pH as another variable for y-axis, and inorganic non-refractory PM_1 for the x-axis in both). We only highlighted two studies that recommend using chemical coordinates as a way to evaluate the emissions and chemistry and to remove potentially confounding issues of meteorology and transport. Thus, the general statement we are making here is correct and is separate from other usages of $NH_{4\_Bal.}$

   Further, throughout this manuscript, we never stated anywhere that NH_{4_Bal} is predictive of the pH, which is the point of Hennigan et al. (2015) and also discussed in Pye et al.

(2020). However, there is potential evidence that the conclusion of Hennigan et al. (2015) may be influenced by the limited range of conditions in their study. Schueneman et al. (2020) has shown that outside the boundary layer and in more remote locations, NH_{4_Bal} may allow estimation of pH. This point though did not seem necessary or appropriate for the present paper.

3. "Sensitivity" is used incorrectly here, at least in the scientific context (the sensitivity is usually taken as the derivative). It should be how the DRE is changed when using the adjusted results.

   We have changed this text to say in line 135:

   "Finally, we used sensitivity simulations to explore ways to improve modeled pH and NH_{4_Bal} relative to observations. Through these sensitivity simulations, we estimated the impact on direct radiative effect from the model assumptions, which are changed to best represent observations."

Individually, these are small, but they add up.

We have carefully re-read the paper and attempted to correct any wording that could be potentially confusing.

1.1 The article is also written for a very specialized audience. This is highlighted by their use of "post-AeroCom-II" in line 124 without ever defining AeroCom-II is. In line 507 they do not say what is different about AM4.1 (that sentence is awkward as well). If they are looking to have it published in a more general Earth/Environment/Science journal such as Earth and Environment, they need to bring in more of the readership and provide more background on such specifics.

We have added the following text, line 147, to explain this point:

"The 9 CTMs include 4 models that were part of a large collaborative model intercomparison study, used to investigate differences in model results with similar emissions, herein called AeroCom-II models (Tsigaridis et al., 2014), and 5 CTMs that were run several years after the AeroCom-II study, herein called post-AeroCom-II models (see SI Table S4 for more information)."

1.2 They never discuss the difference between pHF (line 453) and pH and why it might matter.

In line 450 - 452, we define the difference between pH_F and pH (molality of H^+, excluding activity (m_{H^+})).

We have added the following text to further explain this difference at line 561:

"As shown in Pye et al. (2020), pH_F may underestimate pH, depending on the atmospheric conditions (RH, temperature, and aerosol composition); however, this effect is generally smaller than 0.5 pH units. The ability to compare against prior studies and against CTMs, as both use the definition of pH_F, is more important than a potential 0.5 pH unit difference to better evaluate the differences in observations versus models."

1.3 All of the CTMs used here are global. Other work on acidity has been done using regional CTMs. How do the results compare?

The results have varied, depending on the regional CTM used and whether aerosols were size-resolved or lumped into fine ($PM_{2.5}$) categories (e.g., Pye et al., 2020; Zakoura et al., 2020). The regional models that grouped all sizes together (and thus nonvolatile cations along with ammonium, nitrate, and sulfate) generally show more constant pH and potentially minimal correlation for pH and inorganic mass concentration (Pye et al., 2020; Tao et al., 2020). Other models have generally had issues with the predicted versus observed ammonium balance (e.g., Pye et al., 2018). One model that has separated the PM sizes to better account for nonvolatile cations generally showed higher pH in areas of higher pollution (and thus higher PM_1) and decreasing pH with increasing altitude; however, there were no comparisons with observationally constrained pH to determine how well the model captured observations (Zakoura et al., 2020). Thus, similar to the results discussed here, the results vary by CTM. However, due to their limited spatial scale compared to the global CTMs used here, they were not included for comparisons; though they generally show similar differences.

We have added the following to briefly address this point at line 151:

"Regional CTMs have also been used to investigate NH_{4_Bal} and pH (Pye et al., 2020; Tao et al., 2020; Zakoura et al., 2020) and have in general found large spread in the predicted NH_{4_Bal} and pH. As this study focuses on global observations and trends, only global models are used here."

1.4 It struck me as odd that they note models tend to overestimate NHx lifetime, but then only look at a longer NHx lifetime case. If the argument is that the lifetimes are too long, Fig. 7 is misleading in that the other cases shown are in the direction of what they view as correct (I think), but the longer NHx case is not, and it has the biggest impact. Why not do a shorter lifetime case in one or two of the other models?

The concern was that the main thing that would control NH_x lifetime is the wet deposition of ammonia. Wet deposition is strongly influenced by the Henry's law constant (H) of $NH_3(g)$ used in the model. However, the default H for most models, including GEOS-Chem, is already high (of the order of 1×10^6 M atm^{-1}, Bian et al. (2017)).

As part of the revision process, we conducted an additional sensitivity test with GEOS-Chem, where we increased the value of H for ammonia to 3.3×10^8 M atm^{-1} (two orders of magnitude higher than the default value), in an attempt to increase wet deposition. There was no difference in the modeled results as with the default versus higher wet deposition, indicating the wet deposition is already saturated for removal of ammonia. We have added another bar to Figure 7 to illustrate this point.

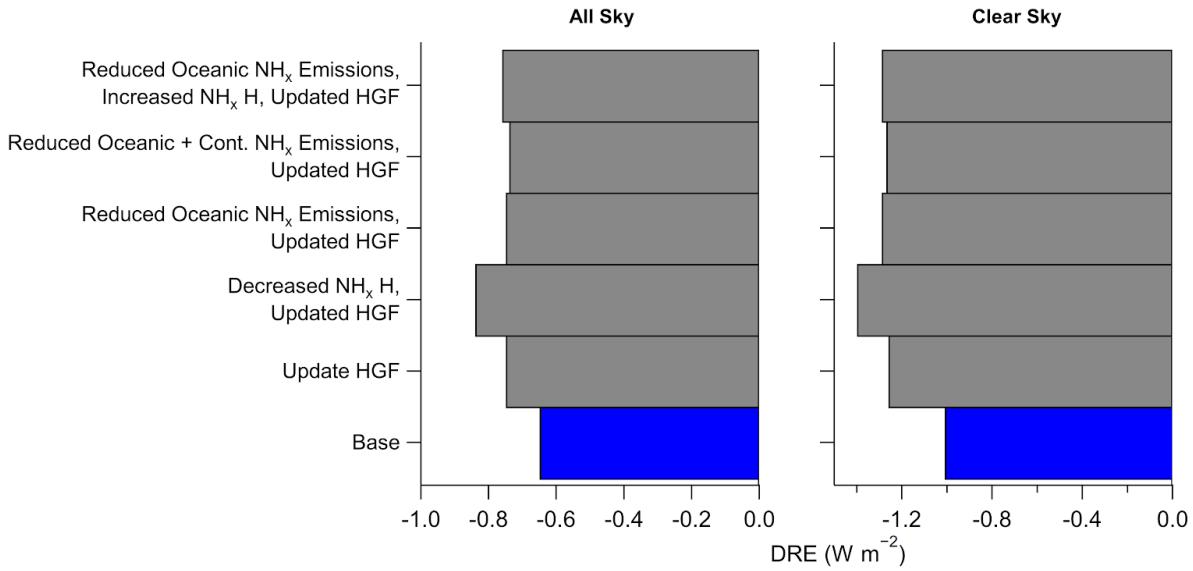
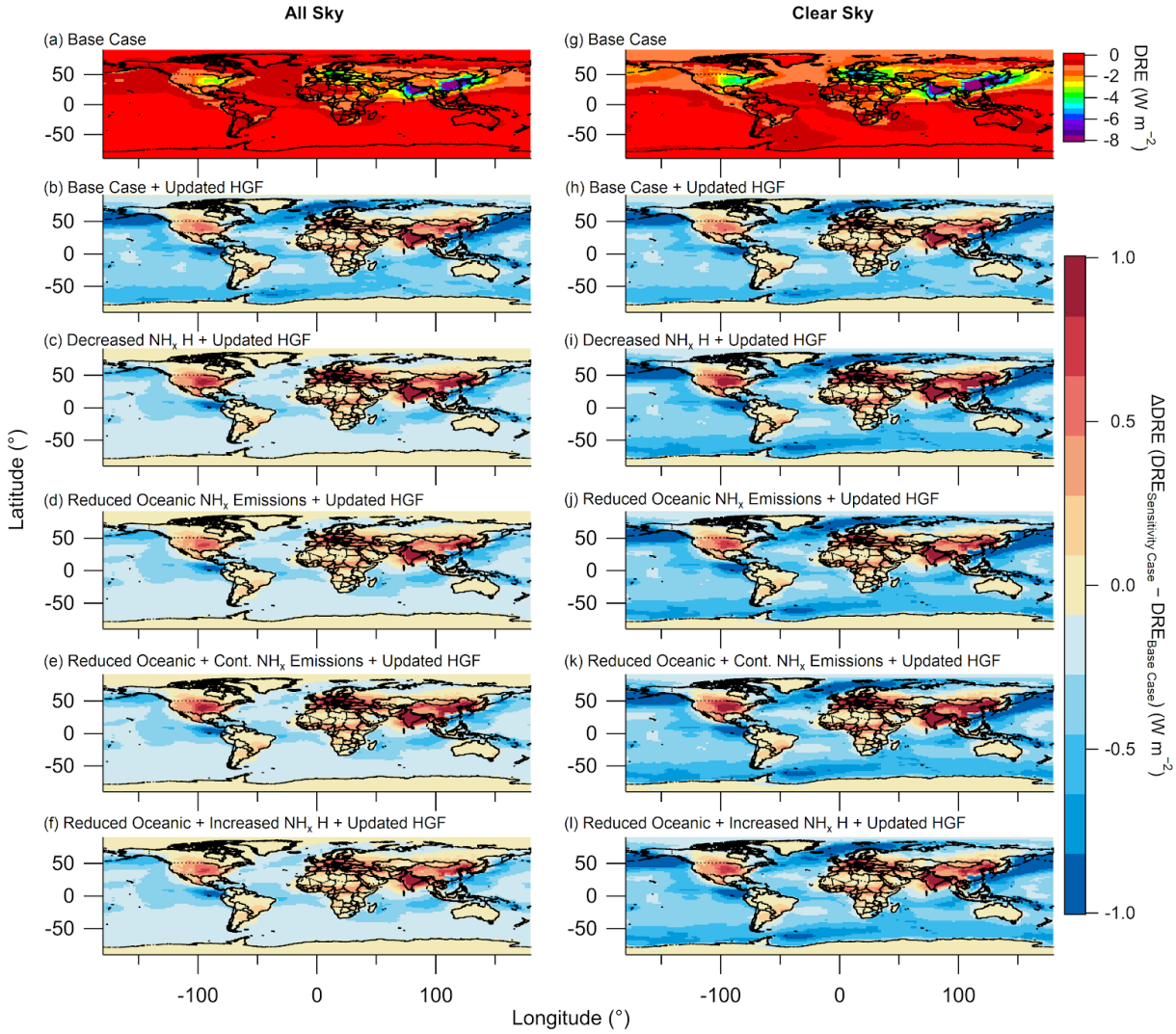


Fig. 7. Annual, global average direct radiative effect (DRE) for SO_4 + NO_3 + NH_4 (and associated aerosol water) for all sky (left) and clear sky (right) for Base Case and the various updated cases (see Table S7 for description of each updated case). See Fig. S17 for annually average DRE Base Case and absolute differences with each updated case. Here, increased/decreased NH_x H refers to Henry's law constant, which controls NH_x wet deposition (and thus lifetime).



139

140 **Figure S17. Calculated, annually averaged, short wave direct radiative forcing (DRE) from**
141 **sulfate, nitrate, and ammonium (and associated water), from GEOS-Chem, for all sky (left**
142 **column) and clear sky (right column) (a,g) Base Case, (b,h) Base Case with updated HGF,**
143 **(c,i) decreased Henry's law constant (H) for increased wet deposition lifetime with updated**
144 **HGF, (d,j) reduced NH_x oceanic emissions with updated HGF, and (e,k) reduced NH_x**
145 **oceanic and continental emissions with updated HGF, and (f,l) reduced NH_x oceanic**
146 **emissions, increased Henry's law constant (H) for decreased wet deposition lifetime, and**
147 **updated HGF. See Table S7 for description of the different cases and Fig. 7 for annual**
148 **average DRE.**

149

150 To clarify this point, we have rephrased line 354 to say:

151

152 **"The UT shows less sensitivity to NH_x emissions and more sensitivity to increased NH_x**
153 **lifetime compared to the BL (Fig. S11). This would imply that a shorter lifetime for NH_x**
154 **would be necessary to improve agreement. However, the Henry's law constant of ammonia,**

which strongly influences its wet deposition, already uses a high default value (3.3×10^6 M atm^{-1}), limiting further removal of ammonia (Bian et al., 2017). Thus, at this time, it is unclear what is needed to reconcile the differences in UT NH_{4_Bal} between observations and CTMs, although errors in the spatiotemporal pattern of precipitation might play a role."

1.5 The Abstract is vague and needs to be more quantitative as well as informative.

We have updated the abstract, in an attempt to make it more quantitative and informative, to say:

"Inorganic fraction of fine atmospheric aerosol affects numerous physical and chemical processes. However, there is large uncertainty in its burden, composition, and lifetime due to limited global measurements. Here, we use airborne observations from 11 different campaigns to investigate how two measures of aerosol acidity, which controls composition, change from polluted to remote regions. Both parameters, aerosol pH and ammonium balance, show increasing acidity with remoteness, at all altitudes, with pH decreasing from ~3 to ~-1 and ammonium balance decreasing from ~1 to ~0. This indicates that the oceans acidify fine aerosol through the imbalance between emissions of NH_x and those of sulfate precursors. The two acidity metrics show high correlation with inorganic particulate mass concentration ($R^2 > 0.57$). The observations are compared against 9 widely used chemical transport models, and the simulations tend to show more scatter (generally $R^2 < 0.50$) for both aerosol acidity metrics and typically predict less acidic aerosol in the most remote regions. The impacts of the differences in acidity include model underestimation of the predicted direct radiative cooling effect for sulfate, nitrate, and ammonium aerosol by 15-39%. These results indicate the need for better constraints on the emissions and lifetime of inorganic aerosol precursors."

1.6 In the end, the paper represents high quality science, though the presentation is lacking a bit. It is also rather specialized. While I would not recommend publication at this point, with work on the presentation, it would become a nice contribution.

We thank the reviewer for their input. We hope we have addressed their concerns with these revisions, as well as those in response to the other reviewers.

Reviewer #2

2.0 This study estimates the ammonium ion balance and pH on extensive airborne observations and simulation results from 9 different chemistry transport models for remote regions and continental regions. The results show that the model predicts a relative more ammonium enrich and higher pH than the observations. They conclude the discrepancy is due to the bias in

ammonia emissions and the presence of sea-salt. This study also estimates the impact of simulated hygroscopicity on the radiative cooling effect. Overall, the results are very interesting for the understanding of the observations data, the recent and future tend of aerosol acidity, and the impact of aerosol composition on climate change. This manuscript is suitable for publication after a minor revision by considering the comments as below.

2.1 Page 10, Line 214-216. The phase separation relative humidity of several pure organic compounds is plotted in Figure 1e. Can these pure organic compounds represent the organic products in the organic aerosols in the scope of the data used in this study? In addition, not only pH but the inorganic composition also significantly impact on aerosol phase transition, for example the phase separation relative humidity is little low in the presence of nitrate compare to sulfate (You et al., 2013). It would be better to include both pH and inorganic composition together when discuss the physical properties such as phase states.

We agree this is of interest but it is too complex to include in the already very complex figure. Instead, we have added the following lines to point out that more than pH impacts this process in line 263:

"Note that not only pH, but also aerosol composition, including organic mixtures, can impact phase separation (You et al., 2013)."

2.2 Fig. 3. For the model averaged results in the Atlantic Ocean regions, the ammonium balance at the equator is near 1 (~800 hPa), however, the simulated pH is still very acidic ranging from -0.5 to 0.5. What is the reason that the predicted aerosols were significantly dominated by neutral salts, such as ammonium sulfate, but the aerosol were still super acidic? For comparison, the calculated pH from the observed data in the continental regional (near equator) is high (~2) when ammonium balance is around 1, which is more reasonable to me.

This can stem from the non-linear response of acidity that results from a variation in aerosol composition, relative humidity, and temperature (Pye et al., 2020). We have conducted additional box model simulations to more clearly illustrate this point. The inputs of these simulations were: total ammonium ($NH_{3,g}$ + $NH_4^+{}_{,p}$) remained constant at 200 nmol m^{-3}; sulfate varied from 5 to 5000 nmol m^{-3}; relative humidity varied from 30 to 95%; and, for two different temperatures (298 and 243 K). These are similar to the box model simulations reported by Murphy et al. (2017). The following figure has been added to the paper to document this sensitivity study, along with the text below.

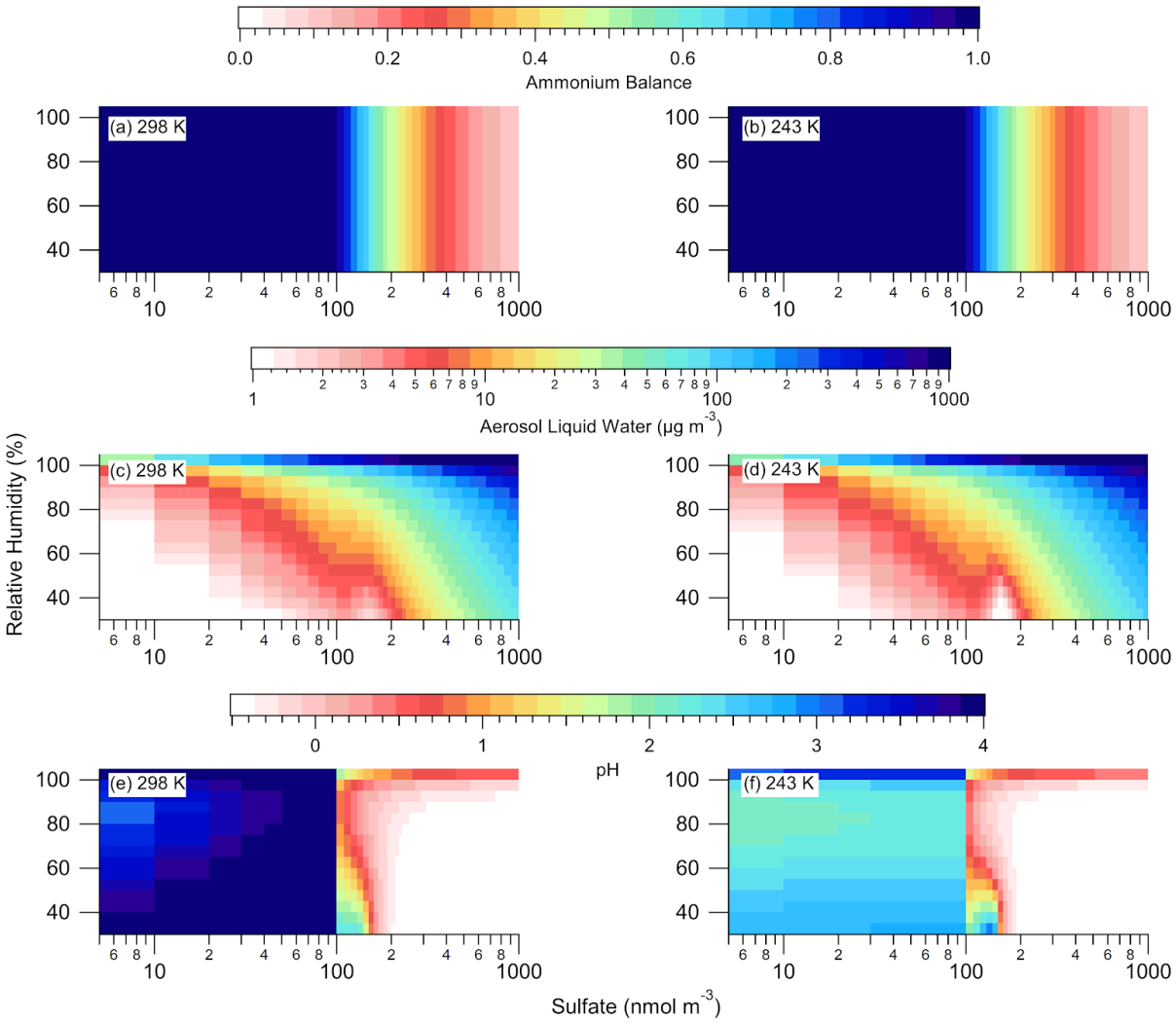


Figure S8. Results from a box model calculation for aerosol pH using E-AIM, where total ammonium ($NH_{3,g}$ + $NH_4^+{}_{,p}$) remained constant at 200 nmol m^{-3}, sulfate varied between 5 to 1000 nmol m^{-3}, relative humidity varied between 30 to 95%, and temperature varied between 298 K ((a), (c), and (e)) and 243 K ((b), (d), and (f)).

As shown in Fig. S8, where NH_{4_Bal} starts decreasing from 1, there can be large variability in aerosol pH for both temperatures, depending on the local RH. Thus, RH can have a large impact on the aerosol pH and make areas with higher NH_{4_Bal} have low pH.

Fig. S8 has been added to the SI, and the following text has been added to line 217 of the main paper:

"Finally, there is relatively high NH_{4_Bal} in the tropics of the Atlantic Ocean; however, there is large variability in aerosol pH (~-1.0 to 2.0). This can arise from the combination of RH and temperature, which impacts both the aerosol liquid water and the equilibrium

distribution of semivolatile compounds (nitrate and ammonium), impacting the aerosol pH (Guo et al., 2016). Using a simple sensitivity study (see SI for details), the predicted pH shows very high variability for the conditions when NH_{4_Bal} starts decreasing from ~1 to ~0.5 (Fig. S8) due to changes in RH. Thus, both aerosol composition and RH control aerosol pH, making direct comparison of NH_{4_Bal} and pH in Fig. 3 challenging."

And at line 252:

"As described above and shown in Fig. S8, the variability in pH with nearly constant NH_{4_Bal} is due to the non-linear response of pH to variations in aerosol composition, RH, and temperature."

In the SI, we have added the following section to describe the new figure:

"S3 Theoretical E-AIM Calculation to Investigate Impact of RH and Aerosol Composition on Ammonium Balance and pH

Here, we describe a simple sensitivity study in the role of RH and aerosol composition on aerosol pH. These sensitivity calculations were designed to study the large variation in relative responses between NH_{4_Bal} and pH shown in Fig. 3. We adapted the theoretical model described by Murphy et al. (2017). Similar to Murphy et al. (2017), total ammonium ($NH_{3,g} + NH_4^+{}_{,p}$) was kept constant at 200 nmol m^{-3}, sulfate was varied between 5 to 1000 nmol m^{-3}, total nitrate ($HNO_{3,g} + NO_3^-{}_{,p}$) was kept constant at 0.01 nmol m^{-3}, and RH varied between 30 to 95%. We performed the simulations for two temperatures, 298 and 243 K. The same E-AIM (Model IV) and definition of pH was used as throughout the paper. This is a significant difference compared to Murphy et al. (2017), in that they used the pH definition based on the mole fraction of H^+ instead of molality of H^+. The results of the model are described in the main text."

2.3 Page 9, line 202-204. What is the reason the model significantly overestimates the ammonium balance over the continental regions? The ion balance is very biased, especially for the region where latitude larger than 60. Is it because the overestimation of ammonia emission or the missing sources of anions?

As highlighted in Fig. S8 of the original text (Fig. S9 of the updated text), the modeled NH_3 is 2 to 4 orders of magnitude higher than the observationally constrained NH_3.

We have added the following text at line 247 to clarify this point:

"The consistently higher NH_{4_Bal} for model output >60°N most likely arises from the models having too much ammonia throughout the troposphere, where it is 2 to 4 orders of magnitude higher than observationally constrained ammonia (Fig. S9)."

2.4 Page 9, line 205-207. Similar to the results in the equator of the Atlantic Ocean regions, the predicted inorganic compositions are dominant by neutral salts, but why the model pH is still super acidic, mostly below pH 1?

See response to comment 2.2.

2.5 Page 9, line 208-209. Which geological location does author referred when authors discuss about the results in the boreal forest BL? It would be helpful to add some more location information for the boreal forest BL regions. And is these results visualized in Figure 3?

These results are visible in Fig. 3. The following text has been added to line 254 to clarify this point:

"Also, the models partially capture the differences in aerosol pH over polluted (< ~50°N) versus boreal (> ~50°N) continental regions; however, the models predict higher aerosol pH in the boreal forest BL, compared to observationally constrained pH."

2.6 Page 11, line 236. The secondary organic acid formed in the aerosols are generally weak acid. Are these organic ammonium salts stable in the strong acidic aerosols which pH is below 2?

For an ideal solution (e.g., dilute, laboratory setting solutions), the pH reported here may be too low for the organic acids to be dissociated, depending on the compound's pKa value. However, as has been recently discussed in studies (Guo et al., 2018; Liu et al., 2020; Zheng et al., 2020), atmospheric aerosols are often a very concentrated, non-ideal solution, meaning that the compounds in the aerosol have non-unity activity coefficients, which changes the equilibrium and partitioning within the aerosol phase. As there is so far very limited research on this topic, the impacts of non-ideal solutions on the partitioning of organic acids are not well known.

We have added the following text at line 296 to clarify this point:

"Though the pH may be lower than the pKa values of various organic acids, the aerosol system is a non-ideal solution (Guo et al., 2018; Liu et al., 2020; Zheng et al., 2020). As there has been little research in regards to the partitioning and thermodynamics of these organic acids at low pH in non-ideal solutions, it is not certain whether these organics are present as ammonium salts or not."

2.7 Page 11, line 243-247. It is not clear which data in the Figures (e.g., Figure S8) are the regions without deep convection and which are the regions has deep convection.

The following text has been added to line 313 to clarify this point:

"The deep convection (continental observations between 15° and 50°N) observed during DC3, compared to SEAC^{4}RS (similar location but less deep convection sample), led to aerosol with large differences in NH_{4_Bal} (0 versus 0.77 for SEAC^{4}RS and DC3, respectively) and pH (-0.93 versus 1.35 for SEAC^{4}RS and DC3, respectively) in the UT."

2.8 Page 12, line 268-271. If the ammonium on the filter samples are biased by the ammonia from aircraft cabins, the observation may overestimate the ammonium concentration. However, the current ammonium balance is overestimated by the model which means there is even more discrepancy between modeled results and actual concentration if considering the ammonia from aircraft cabin. Therefore, this reference may not explain the current difference between the observation and modeled results but is still valuable to be discussed as one of the potential uncertainties.

The purpose of this line/reference is that models were previously evaluated against and optimized to match observations that were biased due to sample handling. We have modified this point (line 332) to make this point clearer:

"Numerous factors may lead to the differences in NH_{4_Bal} between observations and models. Observations of NH_{4_Bal} above the BL previously used in the evaluation of CTMs have typically been based on aerosols collected onto Teflon filters and analyzed off-line (Wang et al., 2008). However, as discussed in Nault et al. (and references therein (Nault et al., 2020)), acidic aerosol collected onto filters will react with ammonia in the aircraft cabin, biasing the ammonium mass concentration and NH_{4_Bal}."

2.9 Figure 5 and 6. The predicted results is mostly consistent, but some is very different. For example, the predicted slope is even negative for CCSM4 model in the BL surface. What might be the reason to have these very different results from different models?

This is already discussed extensively on p11-13 of the submitted paper. For example, as stated in line 271 of the previously submitted paper:

"Another potential factor is overestimated oceanic (Paulot et al., 2015, 2020) and/or continental (Dammers et al., 2019) NH_x emissions in models."

CCSM4 is one of the models that uses the EDGAR base value of 8 Tg yr^{-1} NH_x emissions from ocean surfaces (Paulot et al., 2015). This study also shows relatively high bias in ammonium

nitrate compared to observations, indicating overall high bias in the volatile components in the modeled aerosol phase compared to observations.

Further, as stated in line 277 of the previously submitted paper:

"An additional potential factor, as discussed in Bian et al. (2017), is that models may underestimate the pH-dependent wet deposition of NH_x."

This is the problem with the GISS models, which would lead to a too long NH_3 lifetime and higher NH_{4_Bal}.

2.10 What is the major source of SO2 in the remote oceans? Can these SO2 practically contributed by the long-range transport SO2 originated from the continental polluted regions? In addition, the oxidation of SO2 to sulfuric acid is much fast during the daytime when gas phase oxidants are abundant. In addition, the RH and temperature are also significantly different between day and night. Is there any evident difference for the ammonium balance and pH between daytime and night?

Oxidation of DMS and other sulfur compounds are thought to be the largest source of SO_2 in the marine environment (Faloona, 2009). Transport of SO_2 from anthropogenic regions can also play a role (e.g., outflow from Asia over northern Pacific and from North America over northern Atlantic) as can volcanic emissions at some locations. This is well known so we have not expanded the paper to address this point.

The large majority of these flights occurred during daytime due to various flying restrictions; thus, no direct statements can be provided about day- versus night-time ammonium balance and pH due to changes in RH and temperature. However, other studies have shown that these changes are important, especially in the boundary layer where changes in T & RH are stronger (e.g., Guo et al., 2015, 2017; Battaglia et al., 2017). These effects should be less important in the free and upper troposphere.

2.11 Page 13, line 282-284. Besides the temperature dependence on the NHx emissions, is there temperature dependency on the NHx uptake onto aerosols?

Yes, as discussed in various papers (e.g., Guo et al., 2015, 2016, 2017), there is a dependence of NH_x uptake onto aerosol due to the temperature dependence of the Henry's law constant (Seinfeld and Pandis, 2006). This is also partially addressed above in response to comment 2.2.

We have added the following text to line 350 to further clarify this point:

"Finally, there may be a temperature dependence on the continental NH_x emissions (Shah et al., 2018) and there is a temperature dependence on the NH_x partitioning to aerosol (Guo et al., 2016); however, as most of the campaigns focused on spring- and summer-time, exploration of this dependence was not possible."

2.12 Page 14, line 302-318. Even though sea-salt is not considered in this study, can ammonia uptake be impacted by sea-salt aerosols? If yes, then the back calculation of ammonia concentration from inorganic composition of NSS aerosol will be biased in both measurements and model simulation results.

Though ammonium may be present in sea-salt (Bondy et al., 2018), the pH of sea-salt aerosol is generally not favorable for ammonia uptake. This stems from sea-salt pH generally being greater than 2 (Keene and Savoie, 1998; Keene et al., 2002, 2004; Smith et al., 2007), where >90% of total NH_x (gas + particle) will be in the gas-phase versus the particle phase (e.g., Figure 1 in the main paper, and shown in our response to comment R2.15). This agrees with observations that show the aerosol with high pH from sea-salt has minimal particle-phase ammonium content (Keene et al., 2002, 2004; Smith et al., 2007), indicating minimal ammonia uptake. We have added the following to emphasize that point:

"S4.7 Minimal Partitioning of Ammonia to Sea-Salt (and Other Less Acidic Aerosol)

Another important aspect of sea-salt and other aerosols impacted by NVCs is that the pH is increased, which leads to lower partitioning of ammonia to the particle-phase (Guo et al., 2017). Prior studies have observed that the pH for aerosol strongly impacted by sea-salt is > 2 (Keene and Savoie, 1998; Keene et al., 2002, 2004; Smith et al., 2007), which generally leads to >90% of total NH_x (gas + particle) partitioning to the gas-phase (Guo et al., 2017). Note, this aerosol is also mainly coarse aerosol. This has been further verified in that the aerosol with high sea-salt and high pH has minimal ammonium content (Keene et al., 2002, 2004; Smith et al., 2007). Thus, it is expected that neglecting ammonium uptake for sea-salt aerosols will not bias the results described here."

2.13 Page 17, line 377. This conclusion is conflicted with the discussion in page 7 line 157 where authors declared that the NHx emissions are generally low in both the Atlantic and Pacific regions.

We have changed the text to clarify what we were meaning to say in line 478:

"(1) too high ammonia emissions in the CTMs, especially over oceanic environments,..."

2.14 As mentioned in the section of thermodynamic calculation, the E-AIM thermodynamic model was used for observation and model which do not calculate online. While the online calculation of pH by ISSOROPIA v2 (GEOS-Chem, AM4.1). Can prediction of pH partially be cause by the difference of thermodynamic model used? For example, in the Figure 6d-f, the results of solid lines (use ISORROPIA) are obviously different from the dash line (using E-AIM).

For Fig. 6, the solid lines are mainly for pH calculated off-line with E-AIM while the dashed lines are mainly for pH calculated online with ISORROPIA (GEOS-Chem v10, v12, and AM4.1). The dashed-lines using ISORROPIA agree fairly well with the observed trends that used E-AIM to calculate pH for comparisons < 800 hPa, indicating the two thermodynamic models agree fairly well, which is similar to prior studies (Song et al., 2018; Pye et al., 2020).

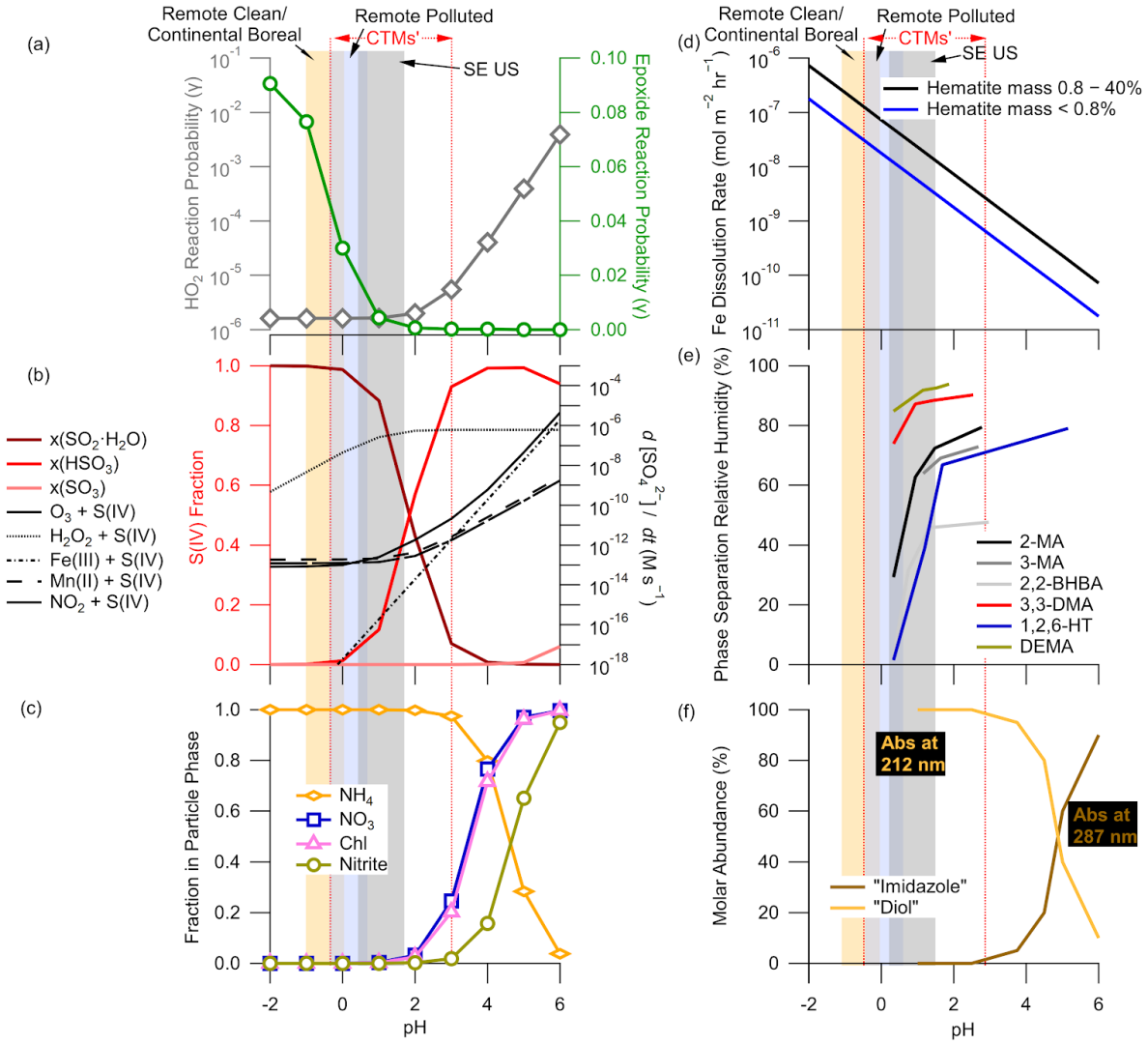
The following has been added at line 374 to clarify this point:

"Note, the models that calculate the aerosol pH online use ISORROPIA (GEOS-Chem v10, GEOS-Chem v12, and AM4.1). ISORROPIA is not as explicit a model as E-AIM (Fountoukis and Nenes, 2007; Pye et al., 2020), and they generally produce similar results (Pye et al., 2020)."

Minor comments:

2.15 Figure 1. Is the value of "uptake" in 1a refers to uptake coefficient?

We have updated the figure title and subsequent usage of uptake to be reaction probability. Also, we found a typo in the caption as we had removed the line from the figure but not the corresponding text referencing N_2O_5. The updated figure and figure caption are shown below:



476

477 **Fig. 1. Effects of pH on important atmospheric chemistry and aerosol processes. See SI for**
478 **references (Table S1), analytical equations. (a) Reaction probability uptake of gas-phase**
479 **epoxides and HO_2 vs pH. (b) Fractional S(IV) species vs pH in equilibrium (left) and rates**
480 **of oxidizing S(IV) to S(VI) through several mechanisms vs pH (right). (c) Fraction of total**
481 **nitrate ($HNO_{3(g)} + NO_3^-{}_{(p)}$), ammonia ($NH_{3(g)} + NH_4^+{}_{(p)}$), chloride ($HCl_{(g)} + Cl^-_{(p)}$), and nitrite**
482 **($HONO_{(g)} + NO_2^-{}_{(p)}$) in the particle phase vs pH. (d) Rate of dissolution of iron (Fe^{3+}) to Fe^{2+}**
483 **vs pH. (e) Measured phase separation relative humidity for different organic compounds**
484 **(2MA = 2-methylglutaric acid, 3MA = 3-methylglutaric acid, 2,2-BHBA =**
485 **2,2-bis(hydroxymethyl)butyric acid, 3,3-DMA = 3,3-dimethylglutaric acid, 1,2,6-HT =**
486 **1,2,6-hexanetriol, and DEMA = diethylmalonic acid) vs pH. (f) Molar abundance of**
487 **imidazole-2-carboxaldehyde ("imidazole"), and its geminal diol form ("diol") vs pH. Range**
488 **of observation-based pH values for remote clean/continental boreal, remote polluted, SE**
489 **US (southeastern United States), and CTMs' (SI Files) for the BL is shown for reference.**
490

491 2.16 In the text when discussing about the results from Figure 1, it would be better to point out
492 which sub figure is discussed instead of point to wholly Fig 1.

Thanks for this suggestion. For the couple of instances where we were referencing a specific panel instead of Fig. 1 in general, we have included the reference to the specific panel. The updates can be found on (main document) page 11, line 257, page 11, line 260, (SI) page 2, line 19, page 16, line 296.

2.17 Figure S6. It is not clear how the hygroscopic growth factor was estimated from the model simulation. Is the factor directly output from the model simulation or recalculated externally based on the modeled inorganic composition from CTM models? It would be better to add some more explanation in the Section S2.

We have added the following text for clarification of this point:

"The HGF shown in Fig. S6 for the CTMs was calculated by using the average RH and NH_{4_Bal} to estimate the HGF from the look-up table (Fig. S5)."

2.18 Figure 4. It is not clear what is the data of the points with the notes of altitude locations. Are these data averaged from each campaign in that regions or calculated from model simulations?

We have added the following text to the figure caption to clarify this point:

"Each point represents the average observed value for each campaign at the specified pressure level and latitude zone (see SI Files)."

2.19 What is the black area in the Figure 5 and Figure 6. It would be better to also clarified this area type data in the legend separately from line type legends.

The black area is the observed values so that it more easily stuck out. However, as discussed in response to comment 3.10, we have updated and simplified the figure to make it more accessible for the main paper and easier to understand in the SI.

2.20 Page 17, line 386. "." is missing after "more acidic aerosol".

Added

Reviewer #3

3.0 This paper describes how observations show that the models are likely underestimating how acidic the aerosol in remote regions actually is, based on extensive and unique measurements during the ATom flights. The paper is a tour-de-force and should be strongly considered for

publication. The authors go through an extensive set of measurements and show a surprising result for folks that are used to the assumption that more remote regions are less acidic than polluted or continental regions. Frankly the idea that the oceans are an acidifying force on remote atmospheric aerosol is not something that has been discussed much in the aerosol pH literature and a very novel finding (frankly only possible due to the unique flights the paper is based on). The strong desire to exclude sea salt aerosol, which is not measured well by the primary instruments used, is a bit strong. Simply acknowledging that there is another population of aerosol present with different pH does not undercut the main findings of the paper and that section/discussion should be softened. There are some other suggestions of items to consider and revisions that would improve the paper, but overall this is an important paper and should be published after revision.

3.1 Water content? Do the authors have any way of determining (or estimating) water content within these aerosol? Particularly at the higher elevations? It would seem that at < 200 hPa there is likely not much water left. Going back to the work of Martin and co-workers (which the authors cite) is there expected to be enough water there for the aerosol to be considered deliquesced (Martin et al., 2003)?

We agree there is concern about the amount of aerosol liquid water left for air pressure < 200 hPa. That is why we only used data for > 250 hPa (pg 22, line 467 - 469) to ensure there was enough water to calculate aerosol pH. Further, we removed any observations where the water supersaturation relative to ice would lead to homogenous ice nucleation (pg 22, line 465 - 467). Finally, we filter for ionic strengths greater than 40 mol kg^{-1} as those are the highest values from laboratory studies that E-AIM was based on (Clegg and Brimblecombe, 1990; Friese and Ebel, 2010), which can be found on pg 23, line 464 - 466.

Further, Murray and Bertram (2008) showed that acidic aerosol is likely to be aqueous (retain water). Thus, since we are showing that the aerosol has lower ammonium balance than Martin et al. (2003) and thus the aerosol is more acidic, we expect it to be aqueous for the subset of the data that we selected (with the criteria just mentioned) in order to predict pH.

We have added the following at line 580 to clarify this point:

"Finally, only values calculated for pressure levels of 250 hPa or greater are reported here, to further limit calculated pH to T and RH, where the E-AIM model has been verified in laboratory studies (Clegg and Brimblecombe, 1990; Clegg et al., 1998; Friese and Ebel, 2010). These acidic aerosols are expected to be aqueous (retain water) even at the lower temperatures in the UT (Murray and Bertram, 2008)."

3.2 Role of organics? Beyond the discussion of Figure 4, organic acid impacts are minimally discussed. What mass fraction does organic aerosol contribute in these remote regions? Since the governing ammonium balance equation does not account for organics, do they play a negligible role? Was this explored and ruled out or just assumed?

Organic aerosol was between 10 to 60% of the mass fraction in the remote oceanic locations (Hodzic et al., 2020). However, AMS does not have the ability to identify the functional groups and molecules of the organic aerosol, meaning it is hard to determine the amount of acidic functional groups as well as the molecular weight of the organic aerosol. It was assumed that organic acids played a minimal role in both aerosol pH and ammonium balance. This topic has also been addressed in response to comment 2.6.

A prior study attempted to estimate organic acids with AMS signal for continental regions (Yatavelli et al., 2015), but the estimation had large uncertainty. Further, due to the lack of similar studies for oceanic regions or the remote atmosphere, applying the estimated organic acids from AMS signal for observations to the ATom observations would have led to very large uncertainty.

3.3 Line 98: The authors claim that non-refactory chloride is a minor portion of PM_1 based on referencing Jimenez et al. 2009 *Science*. For urban areas that is likely true, but in remote and coastal areas over oceans (without transport from polluted areas) I highly suspect that the contribution of sea spray aerosol to submicron PM can be significant, or at least non-negligible (Ault et al., 2009; Spencer et al, 2008). How would this impact the authors decision to focus on ammonium? This is expanded upon when the author argue on page 14 that sea salt aerosol should be ignored with respect to pH. While the authors argue that sea salt aerosol is minimal or not important 'sea salt should not be included for pH estimations", this feels a bit too easy. The argument feels like, the instrument does not measure it well, so we're ignoring it. However, in Figure 1 the authors make the point that certain processes are really important at higher pH values. This section instead of working to dismiss sea salt, could instead focus on the caveat that the aerosol measured and discussed in this paper focuses on what it can measure well, which is really interesting and important in and of itself. The portion on page 15 where it states GEOS-Chem does better is sea salt is removed, is not convincing. Simply removing a factor because it is challenging to represent is not evidence that is should be removed. The presence of another population of aerosol with higher pH is noteworthy and could lead to second order effects that are not being considered.

Due to word limitations, some aspects were removed in this argument before the initial submission. To respect the word limitation and to address this concern, the majority of the discussion about non-volatile cations has been moved to the SI.

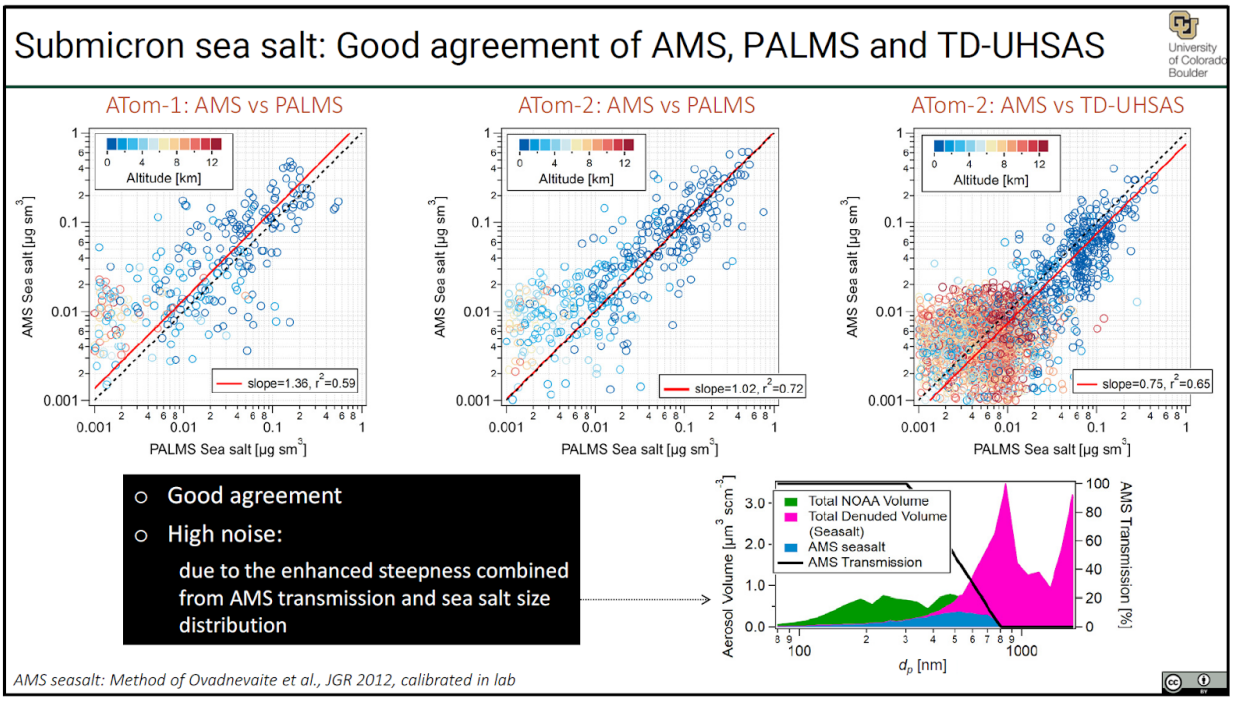
We have changed the section in the main paper (line 380) to say:

"The potential impact of non-volatile cations (NVC), specifically sodium from sea-salt and potassium from dust, on PM_1 pH has been investigated and discussed in detail in SI (Section S4 and Fig. S13, Fig. S14, and Fig. S15). In summary, other aerosol measurements showed that there were two main aerosol populations: (1) fine aerosol, within the AMS size range, dominated by sulfate and organics, and with very little NVC, and (2) coarse aerosol, or larger particles, dominated by NVC (mostly sea-salt and dust), of which only a very small fraction is within the AMS size range (Fig. S13). These two populations will have different pH and thus different chemical and physical properties; however, the focus of this paper and comparisons with models is for population (1), the fine aerosol. The models generally calculate aerosol pH for fine aerosol internally mixed with submicron sea-salt as a single value, leading to higher pH. By not treating the particle populations separately, the models are missing different important chemical reactions due to missing these different aerosol populations. Further, as discussed in Hodzic et al. (2020) and Murphy et al. (2019), ATom-2 had significantly higher sea-salt than ATom-1 (~20% versus 2% of data in ATom-2 versus -1 had sea-salt composing greater than 20% of fine aerosol composition). Removing the ATom-2 observations from the results in Fig. 4 did not statistically change the slopes at a 95% confidence interval. Finally, as shown in Hodzic et al. (2020) and Murphy et al. (2019), sea-salt is negligible outside the marine boundary layer. Thus, NVCs are negligible for the sulfate-organic fine mode (Fig. S13) and do not impact fine mode aerosol pH."

And the following at line 426:

"A sensitivity run in GEOS-Chem, where sea-salt (accumulation mode, as coarse mode is by default not included in the thermodynamic calculations (Pye et al., 2009)) was removed from the calculation of aerosol pH to be reflective of the externally mixed sulfate-organic-dominated aerosol population described above. This leads to the model better representing the trend in pH versus inorganic PM_1 (Fig. S16a)."

We also note that the AMS does measure sea-salt well within its size range, as demonstrated by e.g., this presentation at the 2020 EGU meeting: https://meetingorganizer.copernicus.org/EGU2020/EGU2020-11863.html, with the key slide reproduced below. We have not one but three measurements of sea-salt within the AMS submicron size range, and they are consistent with each other. This work is now being written up for publication. So the reviewer's statement that "the argument feels like, the instrument does not measure it well, so we're ignoring it" is simply incorrect. Indeed sea-salt represents a separate mode of the aerosol population with a different pH, but its impact on the pH of the global accumulation mode is minor.



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653

654 We have added the following text in the SI, line 86, to clarify this point:

655

656 **"Here, we investigate the importance of non-volatile cations (NVCs) in fine mode aerosol,**
657 **and any potential impact NVCs may have on NH_{4_Bal} and pH. During ATom-1 and -2, the**
658 **AMS measured sea-salt in the marine boundary layer (Guo et al., May 4 - 8, 2020), using**
659 **the techniques described in Ovadnevaite et al. (2012). However, this measurement does not**
660 **provide information on whether the sea-salt was internally or externally mixed with**
661 **sulfate-organic dominated fine mode aerosol. The following section investigates whether**
662 **the sea-salt is internally or externally mixed into the fine aerosol and any potential error in**
663 **assuming sea-salt is externally mixed into the sulfate-organic dominated fine mode aerosol.**
664 **The summary of this section is that there are two main modes: (1) fine mode, dominated**
665 **by sulfate and organics, with minimal NVCs. Any NVCs are externally mixed, and even if**
666 **they were internally mixed, they would have minimal impact on NH_{4_Bal} and pH. (2) The**
667 **coarse mode, dominated by NVC, would subsequently have a different pH. The focus of the**
668 **paper is the fine mode aerosol."**

669

670 We further clarify this point of fine versus coarse aerosol in line 525:

671

672 **"In this work, we are studying the acidity of fine mode aerosol, in which sulfate and**
673 **organics are typically internally mixed, versus the coarse mode, which includes sea-salt and**
674 **dust and is typically externally mixed from the fine aerosol."**

675

3.4 Line 165-167: Perhaps I'm not up on the oceanic literature, but the idea that oceans are essentially an "acidifying agent" for aerosol over remote regions is really interesting and not something I've seen discussed much. As there are no references provided, could authors expand a bit more on this point. It is kind of an undersold, but important point.

We appreciate this comment and have incorporated it into the abstract and throughout the text.

This includes in the abstract:

"Both parameters, aerosol pH and ammonium balance, show increasing acidity with remoteness (distance from source), at all altitudes, with pH decreasing from ~3 to ~-1 and ammonium balance decreasing from ~1 to ~0. This indicates that the oceans acidify fine aerosol through the imbalance between emissions of NH_x and those of sulfate precursors."

Line 200:

"This overall indicates that oceanic emissions act to acidify submicron aerosols. CTMs often do not capture this effect. This is especially the case for those models that have too high oceanic NH_x emissions."

Line 275:

"For the observations, there is robust correlation (R^2 = 0.54–0.76) between NH_{4_Bal} (or pH) and inorganic dry PM_1 mass concentration. This result holds for all three tropospheric altitude regions (Fig. 4) and has not been previously reported, to our knowledge. This further supports that oceans promote acidifying submicron aerosol due to the imbalance between the emissions of NH_x and those of sulfate precursors."

Line 338:

"Decreasing the oceanic NH_x emissions, from 8 Tg N yr^{-1} (GEIA (Bouwman et al., 1997)) to the observationally-constrained emissions of 2.4-3.2 Tg N yr^{-1} (Paulot et al. (2015, 2020)), together with a reduction in the continental NH_x emissions of 25%, better captures the observations in the BL and the acidification of submicron aerosol with remoteness (Fig. S9)."

3.5 Line 75: though inorganic nitrate is listed as "minor" outside biomass burning plumes, urban areas, etc. While spatially this is certainly true it seems dismissive since the first motivation on line 61 is "human health" and more people live in urban areas globally and certainly those most

likely to have negative health consequences from inhaling atmospheric PM. Would suggest rephrasing slightly.

We have rephased this text (line 95) to clarify this point as:

"The inorganic nitrate contribution to global PM_1 aerosol is minor (Jimenez et al., 2009; Hodzic et al., 2020). Exceptions include near combustion sources, such as biomass burning (BB) plumes (Akagi et al., 2012; Paulot et al., 2017), urban areas (DeCarlo et al., 2008), and in deep convection over polluted regions (Höpfner et al., 2019). This is due to the volatility of nitrate and the decrease of aerosol pH with distance from sources, which leads to partitioning of particle-phase nitrate into the gas-phase (Fig. 1c) (DeCarlo et al., 2008; Guo et al., 2016)."

3.6 The recent paper by the Poeschl group is probably worth citing as it discusses (Zheng et al., 2020) many of the phenomena you are covering in this manuscript.

We have included this reference in one segment of updated text concerning pKa (see response to comment 2.6).

Further, we have added a figure (see response to comment 2.2) the following text into the main paper (line 281):

"A recent study suggested that the two largest factors controlling aerosol pH were aerosol liquid water (potentially caused by different species concentrations) and temperature (Zheng et al., 2020). These factors create a buffer that maintains a relatively constant pH for a given region; however, this was for areas near emission sources. Much of our study is for regions removed from emissions sources. As shown in Fig. S8, pH has a non-linear response to ammonium, RH, temperature, and aerosol liquid water. This indicates more factors control the pH away from emission sources. The simple parameterization suggested in Zheng et al. (2020) may not apply for the observations investigated here, in agreement with those authors' conclusion that only ~40% of the continental surface was in the regime that buffered aerosol pH with aerosol liquid water."

3.7 Line 106: Is this total PM_1 or non-refractory PM_1? Should be made clear either way.

We have updated the text (line 126) to clarify this point as:

"Here, observations of inorganic non-refractory PM_1 from 11 different aircraft campaigns. .."

3.8 This is a minor aesthetic suggestion, but it would be useful to plot altitude as well as (or in place of) pressure, as that will be more clear for many non-atmospheric scientists or atmospheric chemistry readers.

We have revised Fig. 3 to address this point, showing pressure altitude as the left Y axis and pressure as the right Y axis, as shown below:

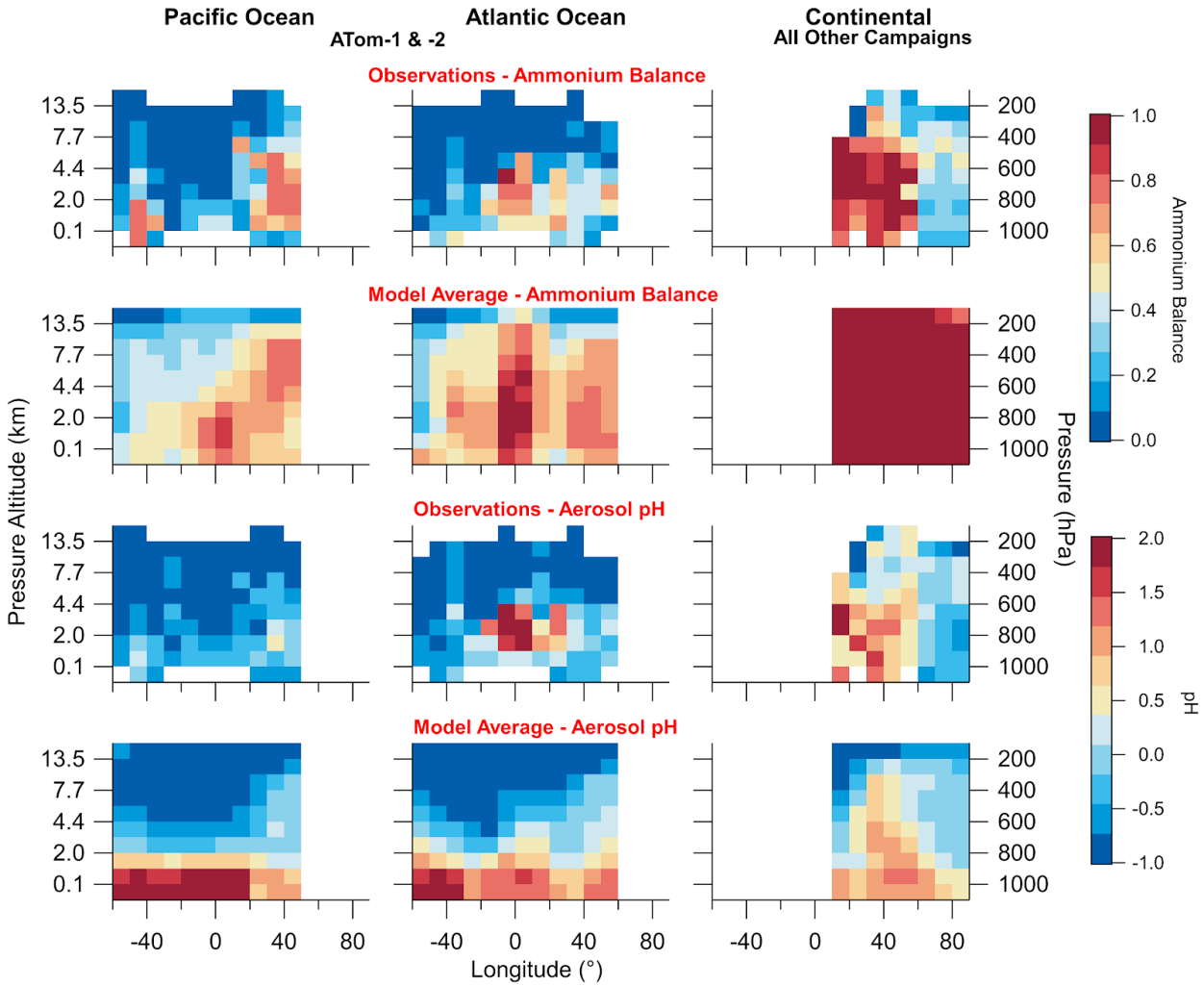


Fig. 3. Curtain plots of NH_{4_Bal} (first and second row) and pH (third and fourth row) for observations (first and third row) and model (second and fourth row) for Pacific Ocean (ATom-1 and -2), Atlantic Ocean (ATom-1 and -2), and above continents (other campaigns). Campaigns and their coordinates are listed in Table S2. For NH_{4_Bal}, the model results are the averages of 9 CTMs (Table S4); whereas, for the pH, the model results are the averages of 3 CTMs that calculate pH on-line (Table S4).

3.9 Figure 3: It is remarkable to see such a well-defined air mass with pH substantially higher than air to all sides of it for the pH of the Atlantic Ocean. One question this raises is how frequent or representative are these flights of the overall values considered by the model?

We added the following to line 629 to clarify one point that was missing:

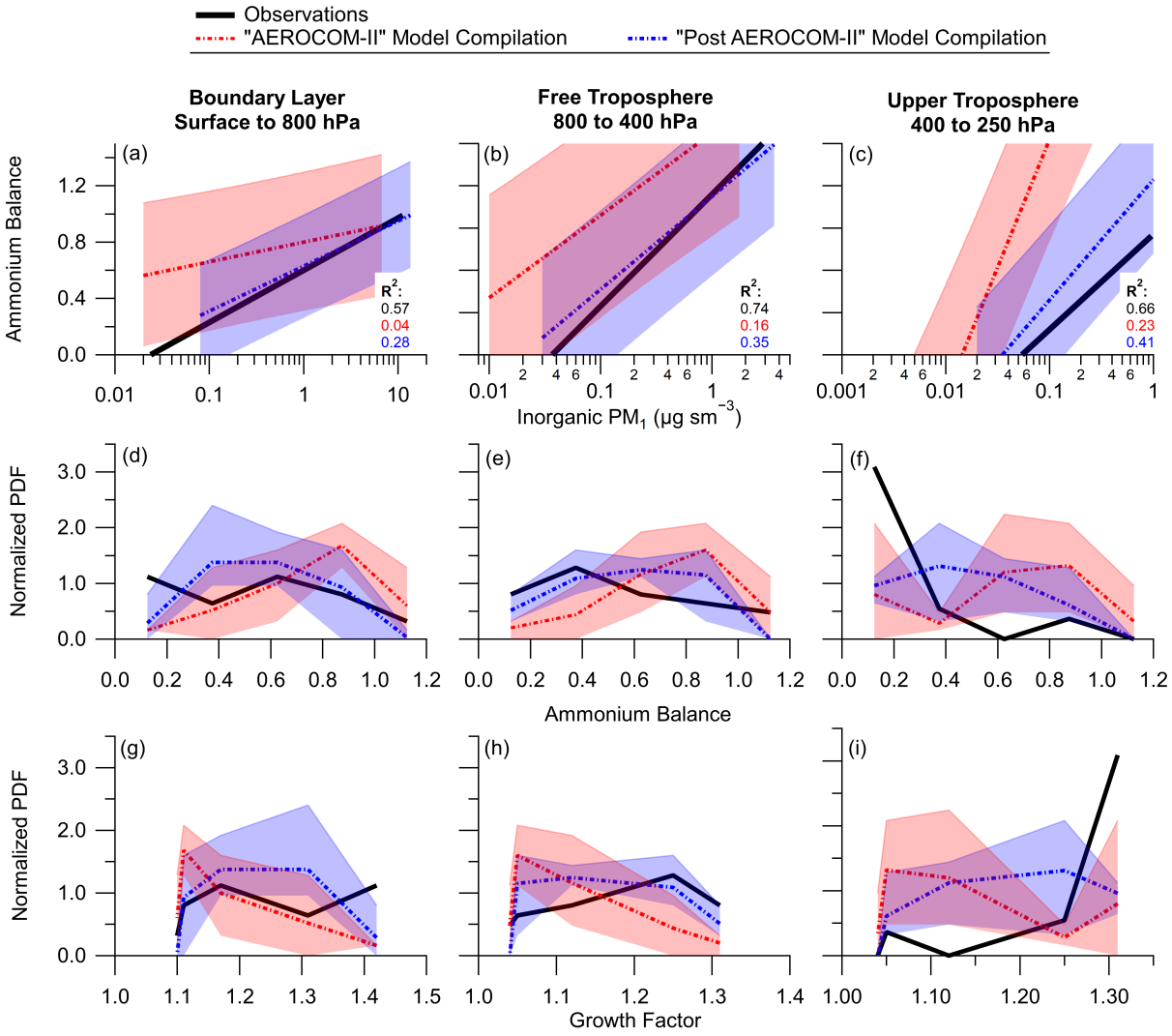
"Further, we used model results for similar months as the observations."

Further, we have added the following text (line 177) to address this point:

"This region in the Atlantic basinc is also associated with consistently high ammonia, as observed in some prior studies (Khan et al., 2020; Someya et al., 2020). Thus, these features appear to be representative for the Atlantic basin."

3.10 Figure 5: This figure is incredibly data-rich, but really dense and not easily accessible. I would recommend attempting to simplify this somehow for the main text and retaining the incredible depth of the figure in the supporting information.

We struggled with this issue before submission. We have kept the previous version of Figure 5 in the Supp. Info. as new Fig. S10, so that interested readers and look at the detailed results of individual models. We have then revised Fig. 5 in the main paper to simplify it, by averaging the models into two curves, one for the AEROCOM-II models and another one for the post-AEROCOM-II models, as shown below:



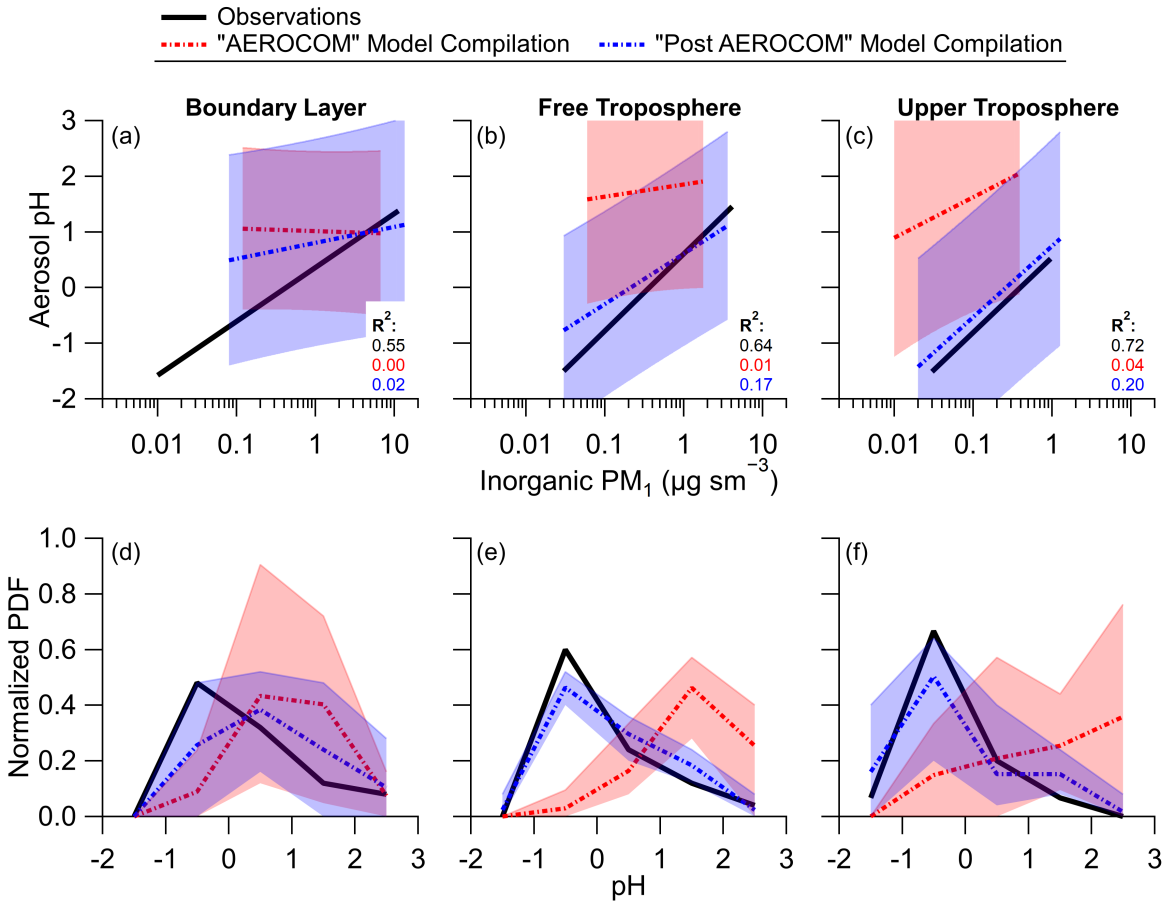
793

794 **Figure 5. Comparison of observations and averages of AEROCOM-II and**
795 **post-AEROCOM-II model results for (a–c) NH_{4_Bal} versus log_{10}(inorganic PM_1) slopes, (d–f)**
796 **normalized probability distribution function (PDF) of NH_{4_Bal}, and (g–i) normalized PDF of**
797 **estimated HGF for observations. For (g-i), the HGF values are from Fig. S5, and for**
798 **average values of RH from observations (~50%, ~35%, and ~35% for BL, FT,and UT,**
799 **respectively). For all data from models in comparison with observations, see Fig. S10. The**
800 **model bands shown represent the range in the model results. The respective composite R^2**
801 **are shown in (a) - (c).**

802

803 We similarly reduced the complexity of Fig. 6 for consistency, and moved the figure with all the
804 individual models to SI as Fig. S12.

805



806

807 **Figure 6. Comparison of observations and averages of AEROCOM-II and**
808 **post-AEROCOM-II model results for (a–c) pH versus $\log_{10}$(inorganic PM_1) slopes and (d–f)**
809 **normalized probability distribution function (PDF) of pH. For all data from models in**
810 **comparison with observations, see Fig. S12. The model bands shown represent the range in**
811 **the model results. The respective composite R^2 are shown in (a) - (c).**

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12th Mar 21

Dear Dr Nault,

Your manuscript titled "Models often underestimate the increase of acidity with remoteness biasing radiative impact calculations" has now been seen by our reviewers, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work. In particular, please look back over your text to ensure that all specialist terms and concepts are clearly explained on first usage and to limit the use of acronyms as much as possible.

EDITORIAL REQUESTS:

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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The paper still needs editing. This now starts with the first sentence of the Abstract, which requires an article. The other responses could also have been more responsive to the comments.

As an example, in their rebuttal, they state " We are only using NH 4_Bal as a chemical coordinate", but in the revised Abstract they state "...how two measures of aerosol acidity, which controls composition, change from polluted to remote regions. Both parameters, aerosol pH and ammonium balance,..." then later state "The two acidity metrics show high correlation". Those statements appear to be contradictory. Maybe they can state that NH4_Bal is not predictive of pH.

Given that model resolution has been found to impact ozone levels, and the models tested have a rather coarse resolution, would that also carry over to pH-related metrics? Have you explored this?

Reviewer #2 (Remarks to the Author):

All of the points raised in the previous review have been satisfactorily addressed.

Reviewer #3 (Remarks to the Author):

The authors have satisfactorily addressed my prior comments and I support publication at this point.

Response to reviewers' comments on the paper "Models often underestimate the increase of acidity with remoteness biasing radiative impact calculations"

We would like to thank the reviewers for their time and for their useful comments that have helped to improve and clarify our paper. For ease, comments from reviewers are in black, responses in blue, and new text added to paper in **bold blue**.

Reviewer #1

1.0 The paper still needs editing. This now starts with the first sentence of the Abstract, which requires an article.

We have gone through the paper and edit many sections, including shortening sentences.

1.1 The other responses could also have been more responsive to the comments.

As an example, in their rebuttal, they state " We are only using NH 4_Bal as a chemical coordinate", but in the revised Abstract they state "...how two measures of aerosol acidity, which controls composition, change from polluted to remote regions. Both parameters, aerosol pH and ammonium balance,..." then later state "The two acidity metrics show high correlation". Those statements appear to be contradictory. Maybe they can state that NH4_Bal is not predictive of pH.

We apologize for the confusion. NH_{4_Bal} is a measure of acidity, although not as direct as pH, and it is also used as a chemical coordinate. We have added the following to address this point:

"Note, however, NH_{4_Bal} is only predictive of pH under some conditions (Schueneman et al., 2020), but generally not in other conditions (e.g., polluted boundary layer), as NH_{4_Bal} does not include the impacts of, e.g., aerosol liquid water and temperature (Hennigan et al., 2015; Pye et al., 2020), and these may be conditions where aerosol pH is highly buffered (Zheng et al., 2020)."

1.2 Given that model resolution has been found to impact ozone levels, and the models tested have a rather coarse resolution, would that also carry over to pH-related metrics? Have you explored this?

Model resolution has been found to potentially impact the modeled HNO_3 (Zakoura and Pandis, 2018); however, as we state in lines 93-97 and line 158-161, nitrate plays a minimal role in the aerosol composition and thus its role on pH. As noted by Pye et al. (2020), differences in the pH may stem from many aspects, including resolution, emissions, and meteorology. These

differences may be important if looking at specific impacts of small source regions (e.g., agriculture as discussed in Pye et al. (2020)). However, this is less likely in this study as we are looking at averages of large spatial regions, and focus on remote regions where strong spatial gradients are less common. We state this in line 283, as well, where we indicate we are removed from emission sources.

However, we have not been able to explore this question specifically, and believe it is beyond the scope of this paper.

We have added the following to clarify this point in the conclusions:

"Note, another potential reason the CTMs may not capture these trends is due to model resolution (Pye et al., 2020); however, as average values for a campaign are compared against the comparable averaged value from CTMs, we do not believe any potential impacts from resolution affect the results here."

Reviewer #2

2.0 All of the points raised in the previous review have been satisfactorily addressed.

Thank you.

Reviewer #3

3.0 The authors have satisfactorily addressed my prior comments and I support publication at this point.

Thank you.

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