Response to Anonymous Referee #1

Manuscript: *Significant contrasts in aerosol acidity between China and the United States*

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Comment 1

The title is actually "Unites" States, NOT "United" as I am sure the authors intended to write.

Response

Thank you for pointing out this typo. “Unites” was changed to “United” in the title of the revised version.

Comment 2

The authors identify an important issue in atmospheric chemistry, namely the distribution in pH values across the globe and focus on 2 regions where SOx and NOx, two main contributors to aerosol acidity, are prevalent, the U.S. and China. the authors find that pH is generally higher in China than in the U.S. as a consequence of ammonia/ammonium and nitrate/nitric acid.

Response

We thank the reviewer for their review and the constructive comments. In the revised manuscript, we added the discussion about the impacts of the long duration of the CASTNET sampling approach on estimated pH and the potential reasons for the bias in modeled temporal variation. We clarified that the results based on observations in China are more representative of North China Plain to avoid misunderstanding and added more results and discussion on the nationwide model simulations. We hope that this new version of the manuscript addressed all the reviewer’s concerns.

Comment 3

Species focused on in this study, e.g., ammonium nitrate are volatile and are often not well described quantitatively in weekly (or longer) aggregated samples, as is characteristic of the U.S. samples used in this analysis. The authors point out that CASTNET’s accuracy for most species, with the exception of NH4+, is ’good’. I find this troubling because of the high time resolution measurements in China, to which the U.S. measurements are compared, and ammonium losses to the gas phase are a function of temperature, which changes over a week+ (U.S. measurements) and less so over and hour (China measurements). I find the lack of attention to the measurements hinders holistic interpretation of the results.

Response

We thank the reviewer for pointing out this issue regarding the long duration of the CASTNET sampling system. Through a literature search, we found that a previous study (Sickles et al., 1999) conducted a comprehensive comparison of the CASTNET weekly-duration sampling approach with a 24-h-duration sampling approach. Both approaches used filter packs. They found that compared to the 24-h duration, the weekly duration led to low biases of -5%, -5%, and -0.7%, on average, in measured HNO_3, NO_3^-, and NH_4^+, respectively, and high biases of 4% and 16%, on average, in SO_4^{2-} and SO_2, respectively. In the revision, we conducted a sensitivity test that incorporated these reported biases associated with the long-duration of CASTNET sampling approach to adjust the calculated pH values in the United States. The sensitivity test suggested that the adjusted pH values showed little difference from the original ones (2.69±0.85 and 2.74±0.83 on average for the original pH and the adjusted pH,

respectively). We added the description of this sensitivity test in Sect. 2.1 (observational data, lines 108-115) and the results of this test in Sect. 3.1.1 (the pH difference based on observations, lines 196-200) to point out the potential biases associated with the long duration of CASTNET samples.

The text added in Sect. 2.1 is as follows,

"*It should be noted that the weekly (or longer) duration of the CASTNET samples in the US may lead to biases in the measured concentrations especially for volatile species such as ammonium nitrate. Sickles et al. (1999) conducted a comprehensive comparison of measurements using the CASTNET weekly-duration sampling approach with those using a 24-h-duration sampling approach. Both approaches used filter packs. They found that compared to 24-h sampling, weekly sampling led to low biases of -5%, -5%, and -0.7%, on average, in measured* HNO_3, NO_3^-, *and* NH_4^+, *respectively, and high biases of 4% and 16%, on average, in* SO_4^{2-} *and* SO_2, *respectively. To evaluate the potential biases in the calculated aerosol pH due to the weekly-duration sampling, we conduct a sensitivity test to adjust the CASTNET-measured concentrations based on the reported average differences between weekly-duration and 24-h-duration samples (Sickles et al., 1999) (Results and Discussion).*"

The text added in Sect. 3.1.1 is as follows,

"*The sensitivity test to adjust the CASTNET-measured concentrations based on the reported average differences between weekly-duration and 24-h-duration samples shows little difference between the unadjusted and adjusted pH values in the US (2.69±0.85 and 2.74±0.83 on average for the unadjusted and adjusted pH, respectively), suggesting that the weekly duration of the CASTNET sampling has little impact on the calculated aerosol pH. Therefore, we proceed with our subsequent analyses using the unadjusted pH.*"

Comment 4

For example, the authors point out that their model evaluation of partitioning ratios compares more favorably in the U.S. than in China and attribute this to "even more partitioning". They also state later in the manuscript: "On the other hand, the simulation in the United States captures the trends of almost all the components though is biased low for SO42- and NH4+in summer (Fig. S6b, h). These results indicate the need for better quantification of the monthly emission trends in China which are currently subject to high uncertainty." It is not immediately clear to me that this, in fact, means monthly emission trends in China are the driver. What about reasons for biases in the U.S.?

Response

We are sorry for the confusion. In this study, we conducted two comparisons. The first comparison was based solely on measurement data, whereby we compared the measured gas/particle partitioning ratios with the ratios re-partitioned by ISORROPIA-II using measured total (gas+particle) concentrations as inputs. This is a common approach to checking measurement data quality (Guo et al., 2016; Guo et al., 2017). The second comparison was to compare the measured concentrations with CMAQ-predicted concentrations. This comparison was used to evaluate the CMAQ model performance. The results of the first comparison were shown in Fig. S3, and the results of the second comparison in Fig. S4–6. The two statements mentioned by the reviewer, i.e., "more even partitioning" and "On the other hand, the simulation in the United States…", interpreted results of different comparisons, which could lead to confusion if they were thought to come out of the same comparison.

To avoid this confusion, the sentence in line 165 (line 161 in the original version), "We evaluate the

model performance by comparing the gas-particle partitioning of semi-volatile compounds between measured and simulated values such as $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$", was revised as "*We compare the directly measured gas-particle partitioning ratios of semi-volatile compounds with the ratios re-partitioned by ISORROPIA-II using measured total (gas+particle) concentrations as inputs. The purpose of this comparison, as conducted in previous studies (Guo et al., 2016; Guo et al., 2017), is to examine the measurement data quality.*"

The sentences in lines 169-172 (lines 163-166 in the original version) were revised as follows to further clarify that the statement, "more even partitioning", refers to the results from the first comparison (i.e., the comparison between measured and ISORROPIA-II-re-calculated partitioning ratios),

"*The correlation coefficients and the slopes of linear regression are all close to 1, suggesting good agreement between the measured and ISORROPIA-re-calculated partitioning ratios. In terms of these partitioning ratios, the model (ISORROPIA-II) performs better in the US than in China, which may be attributable, in part, to the more even partitioning of the species between gas and particle phase in the US.*"

In response to the second statement mentioned in this comment, the sentences in lines 247-252 (lines 232-235 in the original version) as revised as follows to provide possible reasons for the biases in the US,

"*For example, the simulation in the US captures the trends of almost all components, though it is biased high for SO_4^{2-} and NH_4^+ in summer (Fig. S6 b and h); the simulation in China misses the peaks of SO_4^{2-} in winter and NH_3 in summer, and has high biases for HNO_3 in summer (Fig. S6 a, i, and e). Measurement-related biases may contribute to the disparity in the temporal trends between observed and modeled concentrations. The uncertainty in monthly profiles of emission estimates may also play an important role. For example, CASTNET's long sampling period could lead to a larger measurement bias in summer than in winter (Sickles and Shadwick, 2008); the large uncertainty in the current estimates of NH_3 emissions in China, especially the reported underestimation of summertime emissions as indicated by an inversion analysis (Kong et al., 2019), may cause the absence of the summertime NH_3 peak in the simulated trend (Fig. S6i). Further investigation is needed to better understand the factors underpinning the disparity between observations and model simulations.*"

Comment 5

In the abstract the authors state: "Considering the historical emissions trends, the difference in aerosol acidity between these two countries is expected to continue as SO2 and NOx emissions are further controlled." If both countries are reducing emissions, it is not clear why this is the case when they do not provide context for this statement.

Response

Thank you for pointing this out. This sentence in the abstract as well as the discussion of the emission trend in Discussions and Implications (Section 4 in original version) has been removed in the updated manuscript.

Comment 6

Throughout the manuscript in the text and figures, the authors say "United States" and China, but more precisely mean the contiguous U.S. and Northern China Plains.

Response

We thank the reviewer for pointing this out. In this study, we compared the aerosol pH difference between these two countries based on multiple sources, including monitoring networks and model simulations. The monitoring network in China only covers Northern China Plains (NCP), as pointed out by the reviewer and clarified in multiple places in the manuscript. The model simulations, on the other hand, covers entire areas in China and the contiguous United States. In Sect. 3.1.2, we reported significant differences in aerosol acidity between these two countries even considering areas other than NCP in China. In Fig. 2(b), we derived the cumulative distribution function (CDF) based on model simulations that cover the entire China and the contiguous United States domains. We found that the cumulative frequency at the same pH level is always higher in China than in the contiguous United States, both with and without population as weight. In lines 260 and 266, we calculated the domain-wide average pH levels in these two countries, and the values are 2.7±0.6 in China and 0.8±0.8 in the contiguous United States without population as weight, and 3.3±0.4 in China and 2.2±0.5 in the contiguous United States with population as weighted.

In Sect. 3.2.2, we used Multivariable Taylor Series Method (MTSM) based on both observations and simulations to characterize the contribution of each component. The simulation data in this analysis again covered the entire areas in China and the contiguous United States. Analyses based on both observations and simulations (Fig. 6) consistently showed that TNH_3 and SO_4^{2-} have the largest contribution to aerosol acidity difference while others have relatively small contribution.

In response to this comment, we further clarified in line 275 that observations in China were clustered in NCP as follows,

"*It should be noted that the monitoring sites in China were clustered in NCP and, thus, may not be representative of the whole of China.*"

We changed the term "China" to "*NCP*" or "*China (NCP)*" when interpreting the results based on observations in China. We also changed the term "the United States" or US to "*the contiguous United States*" or the contiguous US in proper places in the text. For example, the title of section 3.2.1 was revised as "*Gaseous and aerosol compound profiles between China (NCP) and the contiguous US*"; lines 277 was revised as "*…measured in China (NCP) and the contiguous US…*"; lines 279 was revised as "…concentrations in China (NCP)…"; lines 284 was revised as "In China (NCP)…" as well as multiple places elsewhere.

In the revised section 3.2.2 and the newly added section 3.2.3, we focused our interpretation on three groups. Two groups were derived from model simulations to ensure a nationwide coverage of our analyses. Please see these two sections for details.

In Supplementary Information, we added more analyses and discussion of the effect of TNH_3 based on nationwide simulation results (Text S1, Sect. 3.2.3 in the original version)

Fig. S10 (Fig. 7 in the original version) was revised to add the results based on simulations as follows,

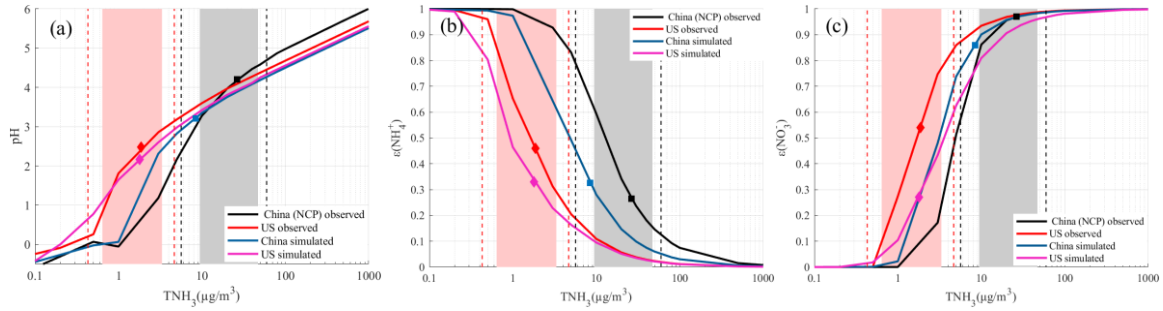


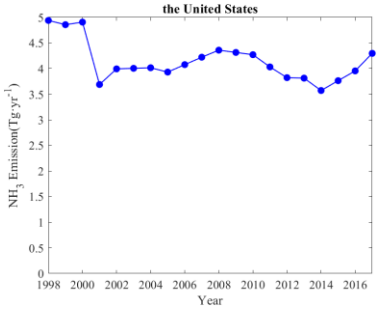
Fig.S10 Responses of pH, ε(NH_4^+) and ε(NO_3^-) to the change of TNH_3 from 0.1 to 1000 μg·m^{-3} while keep all other components constant at their annual average levels. The shaded areas show the TNH_3 concentration ranges that covers 75% of the observed cases in the countries, the dashed lines show the 5th and 95th percentiles of the observed cases, the black square and the red diamond mark the average TNH_3 levels in China and the United States, respectively.

Comment 7

Page 15, Line 442: The authors state that emissions of NH3 in the U.S. have remained constant. Can they provide a reference? I do not think this is an accurate statement.

Response

We derived this conclusion based on Figure 12 in original version, and the data is from the National Emission Inventory (NEI) released by United States Environmental Protection Agency (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data). In a 14-year period from 1998 to 2011, the NH_3 emission changed from 4.94 Tg·yr^{-1} to 4.03 Tg·yr^{-1}. The variation is much less than that of SO_2 and NO_x. The NEI document provided the emission data from a longer period (1990-2019), which shown in the following figure.



Yearly trend of the emission of NH_3 in the United States, the data in the United States are from Air Emissions Inventories by United States Environmental Protection Agency (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data)

This figure and related discussion have been removed from the revised manuscript.

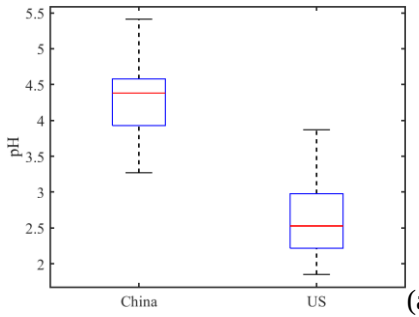
Comment 8

Does the midline in Figure 1 actually depict the average and not the median? Statistical software often defaults to the median.

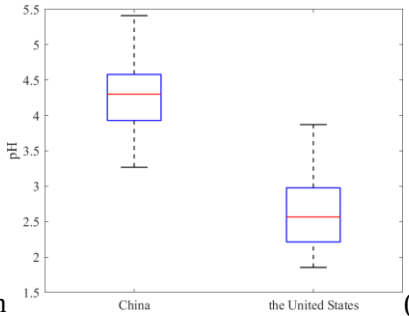
Response

Thanks for pointing this out. Yes, the midlines in the original figure depict the median. We have removed the previous midlines and added the lines representing the averages.

For comparison, the figure changed from (a) to (b).



(a) median



(b) average

The following sentence was added to the end of the figure caption to clarify this,
"*The arithmetic mean (midline), the interquartile range (box), and the minimum-maximum range (whiskers) are shown in the box plot.*"

Comment 9

Figure 4: What do the error bars represent?

Response

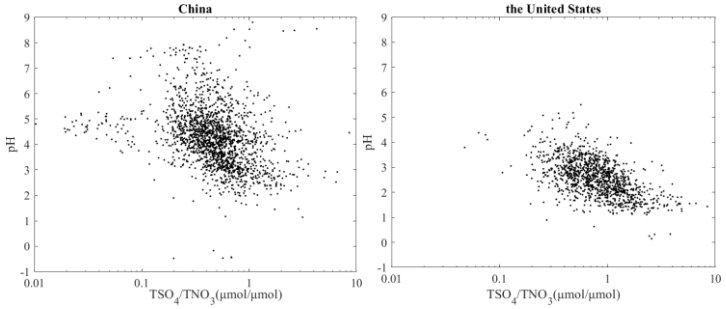
The error bars represent the standard deviation of all the cases in each month, which indicate the variation among different sites in two countries. In response to this comment, we added the description "*The error bars represent the standard deviation of all the cases in each month*" in the caption of Fig. 4 and Fig. S6.

Comments 10

It would be best to make the y-axis the same in each panel

Response:

Thanks for the suggestion, we have made the y-axis the same in each panel as follows. This figure has been moved to SI as Fig. S12 in the revised manuscript.



Comments 11

There are several awkward English statements. I only list two: line 21:"adequate enough", page 8, line 226:"reasonable justified".

Response

In response to this comment, the language of the revised manuscript was checked by two native English speakers. Nash Skipper was added to the author list due to his contribution to the editing of the revised manuscript.

We thank the reviewer for their constructive comments and detailed suggestions. The quality of the manuscript has been substantially improved thanks to their review.

Reference

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