Manuscript ID: acp-2021-455

TITLE: Long-term trends and drivers of aerosol pH in eastern China

We thank the editor and the reviewers for the comments and suggestions concerning our manuscript. They are valuable in helping us improve our manuscript. Below please find our point-by-pint responses to reviewers' comments.

Comments of Reviewer #1:

1. Line 166: Authors should include the standard deviation in Figure 1a. Based on the daily pH values, the pH changes from 2011 to 2019 are neglected.

Response: We thank the reviewer for the comments. We've added the standard deviation of 30-day moving average pH in Figure 1a (shaded area).

Modifications in manuscript:

Line 223-233: "

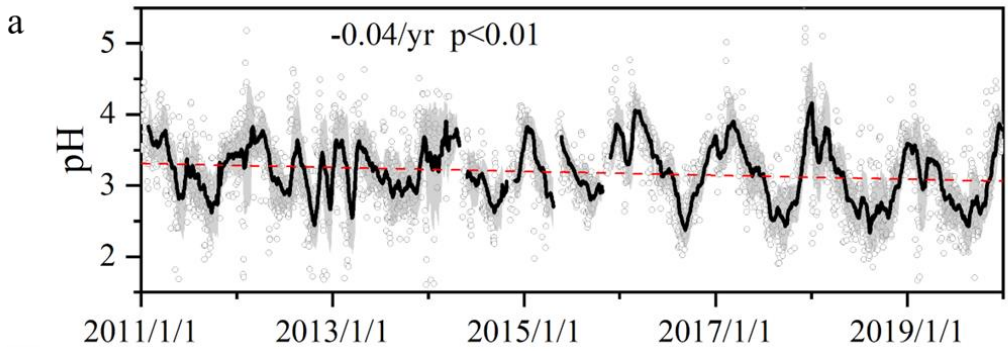

Figure R1 *(revised Figure 1(a) in the manuscript)*. Long-term trends in aerosol pH during 2011–2019 in Shanghai. Gray dots and black lines represent the daily pH values and 30-day moving average pH values, respectively. Shaded areas mark the standard deviation of 30-day moving average pH values."

2. Line 179: The average pH changed 0.24 in 9 years, I don't think it is convincing to be called "moderate change".

Response: We thank the reviewer for the comments. We revised this sentence into: "Despite the substantial change of aerosol abundance and composition, the aerosol pH only shows a minor change."

3. Line 181: This sentence does not make sense, please refine it. What do you mean by "moderately acidic"? pH 1.15 is quite acidic.

Response: We thank the reviewer for the comments. Here the "moderately acidic" refer to the average pH levels, and not the lowest pH level of 1.15. We've changed this into: "The $PM_{2.5}$ in Shanghai was moderately acidic with a daily pH averaging 3.18 and ranging from 1.15 to 5.62". We consider such an average pH level as "moderately acidic" compared with the "quite acidic" regions like SE-US ranging 0~2 (Guo et al., 2015; Pye et al., 2018; Nah et al., 2018).

4. Line 184: Can author be more specific with pH values? It would be helpful to list what pH value you are comparing to in different places?

Response: We've specified the pH values in the revised manuscript as follows (see Line 191-194): "Compared with other countries globally (Table S1), aerosol pH values in Chinese cities of 1.82 to 5.70 were higher than those in US cities of 0.55 to 2.20 (Guo et al., 2015; Pye et al., 2018; Nah et al., 2018), yet similar to those in European cities of 2.30 to 3.90 (Guo et al., 2018; Masiol et al., 2020)."

5. Figure 1b: this plot is very confusing to read, what's the unit of each colored bar? They all look like not have the same length, how to compare them together?

Response: We thank the reviewer for the comments. To better show the factor contributions of the ΔpH between two adjacent scenarios, we've modified Figure 1b, 3 and 5 into waterfall plots. The waterfall plots show how an initial value (for example, the initial pH) is affected by a series of positive and negative values (https://support.microsoft.com/en-us/office/create-a-waterfall-chart-8de1ece4-ff21-4d37-acd7-546f5527f185; https://r-charts.com/flow/waterfall-chart/).

Modifications in manuscript:

（1）Line 223-233: "

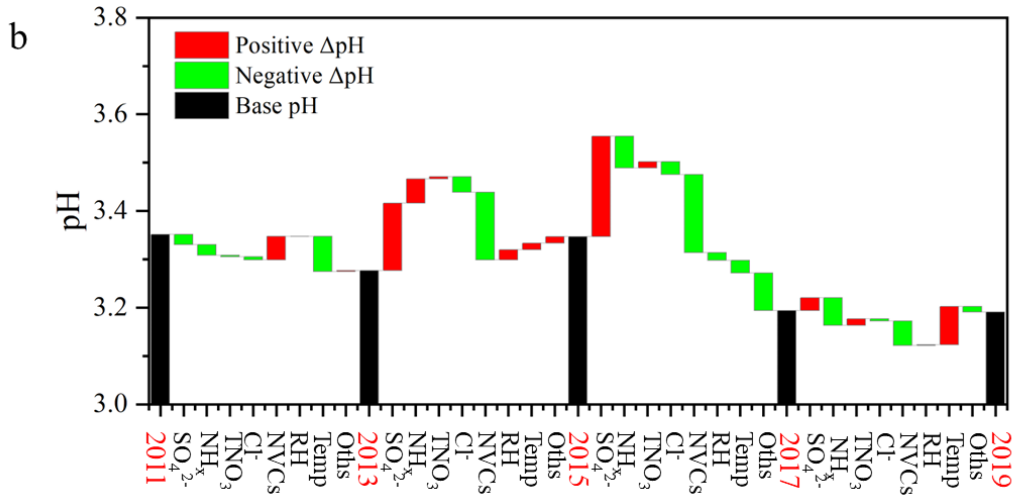

Figure R2 *(revised Figure 1(b) in the manuscript)*. Contributions of individual factors to the ΔpH from 2011 to 2019. Here the black bars indicate the mean pH of different years, and the red and green bars represent the positive and negative effects of individual factors on ΔpH between two adjacent scenarios, e.g., 2011 to 2013, respectively. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH_x, total ammonia; TNO_3, total nitrate; Oths, others."

（2）Line 264-273: "

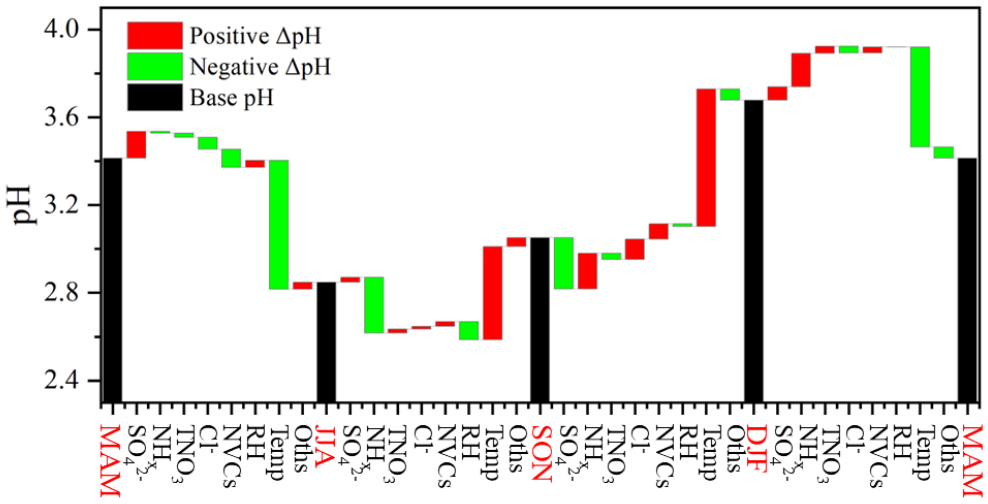

Figure R3（*revised Figure 3 in the manuscript*）. Contributions of individual factors to the ΔpH across the four seasons. Here the black bars indicate the mean pH of different seasons, and the red and green bars represent the positive and negative effects of individual factors on ΔpH between two adjacent scenarios, e.g., spring (MAM) to summer (JJA), respectively. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH_x, total ammonia; TNO_3, total nitrate; Oths, others."

（3）Line 302-309: “

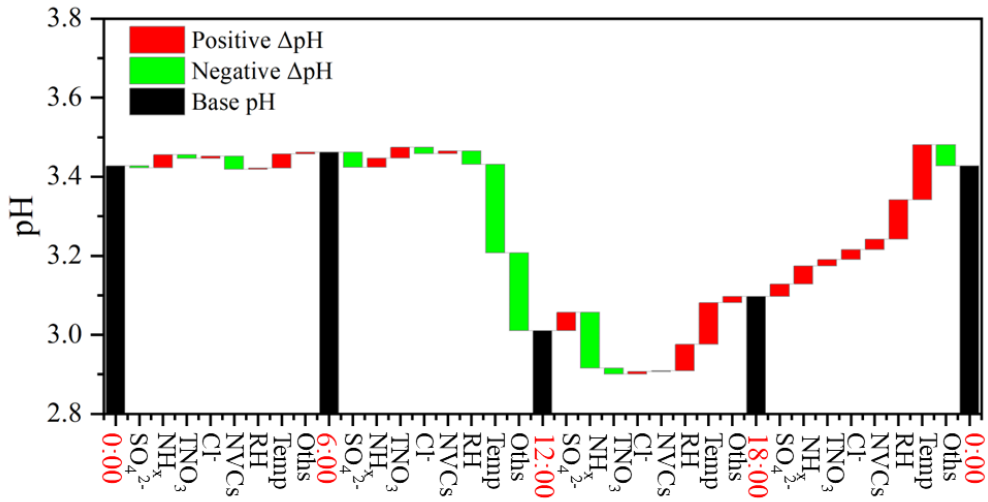

Figure R4（*Revised Figure 5 in the manuscript*）. Contributions of individual factors to the ΔpH between day and night. Here the black bars indicate the mean pH of different hours, and the red and green bars represent the positive and negative effects of individual factors on ΔpH between two adjacent scenarios, e.g., 0:00 to 6:00, respectively. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH_x, total ammonia; TNO_3, total nitrate; Oths, others.”

6. Line 235: Based on Figure 3, the temperature has a positive impact on summer and fall (JJA-SON), but a negative impact on spring and winter. Can author explain more about how the temperature changes the pKa and how much changes in temperature in those seasons?

Response: As explained in the caption of Fig. 3, the color bars represent the ΔpH between two adjacent seasons, e.g., spring to summer. The change of temperature, ΔT, is 11.8, -8.4, -13.3 and 10.0 ℃ during 4 scenarios, respectively, including spring to summer, summer to fall, fall to winter, and winter to spring. This will cause the pK_a^* to change by -0.59, 0.41, 0.72 and -0.54, respectively (see detailed calculation method in Zheng et al. 2020), which are roughly in line with ΔpH levels.

7. Figure 5, same as an earlier comment, the colored bars is very confusing with different length and not easy to compare.

Response: Please see our response to comments #5.

8. Line 274: In Figure 4, it seems like RH has a similar trend with pH, especially at midnight and noon time. Do you think that the RH will be a factor that drives the change of pH, as lower RH (less water) leads to higher pH? Can author provide some discussion?

Response: To clarify that, Figure 4 shows that lower RH (less water) corresponds to lower pH, and not higher pH. Yes, RH is a factor driving the change of aerosol pH. According to the multiphase buffer theory (Zheng et al. 2020), lower ALWC leads to lower pH under an NH_4^+/NH_3 buffer system. Because the diurnal variation of $PM_{2.5}$ is rather weak (varying between 46~50 μg m^{-3}), the change of ALWC is mainly driven by the change of RH and lower ALWC corresponds to lower RH. We modified the ALWC axis in Fig. 4 to make the trend more clearly displayed. Please see the following changes.

Modifications in manuscript:

Line 296-299: "

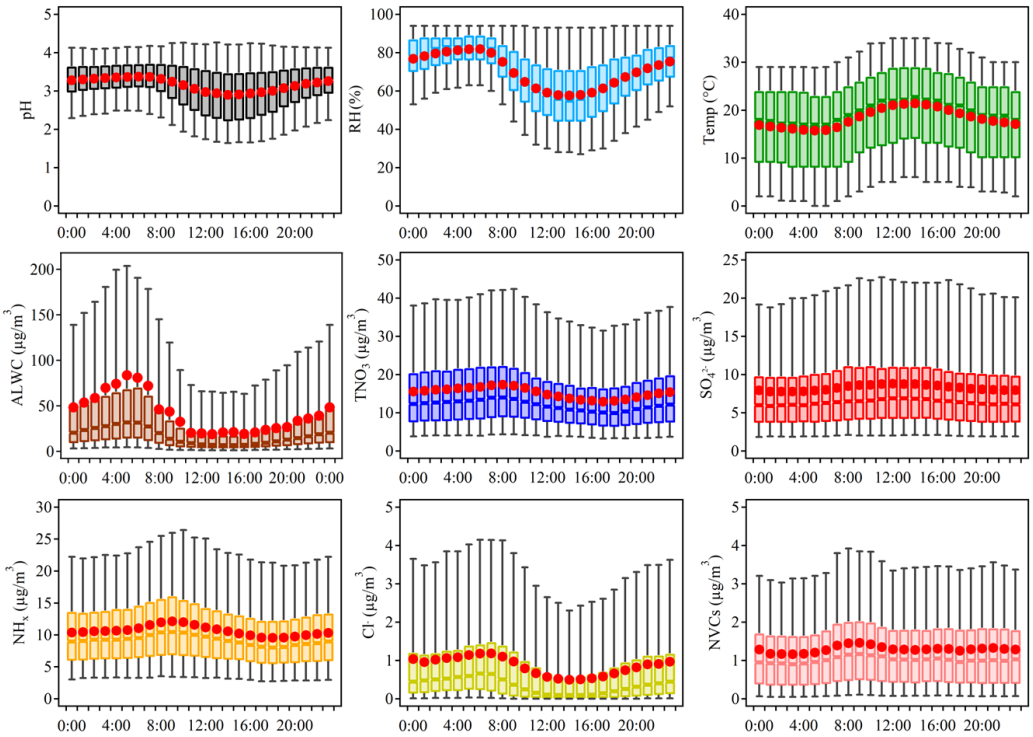

Figure R5 *(revised Figure 4 in the manuscript)* Diurnal variations of the mass concentrations of major ions in $PM_{2.5}$, relative humidity (RH), temperature (Temp), predicted aerosol liquid water content (ALWC) and aerosol pH during 2011–2019 in Shanghai."

Comments of Reviewer #2:

1. One of the main concerns for the paper is the approach to assign the delta(pH) into

the contribution from sulfate, ammonium, ect… I do not quite follow the physical meaning of this calculation. It feels rather like a statistical approach to me. If we want pH1-pH2=pH(sulfate1)-pH(sulfate2) + pH(ammonium1)-pH(ammonium2) … then it needs to have linear relationship to all these factors? In reality, the pH response to these factors can be quite non-linear and have very different sensitivity in different regions. The authors try to address this issue with an additional "others" term, but the physical meaning of this term is doubtful, it can be the non-linear response not considered by the previous calculation treatment. In the Figure S3 of a separate study (Revisiting the Key Driving Processes of the Decadal Trend of Aerosol Acidity in the U.S, 10.1021/acsenvironau.1c00055), it looks ISORROPIA also has some non-smooth response to the parameters. Will such behavior affect the accuracy of this calculation approach?

Response: Indeed, the response can be nonlinear. Nevertheless, this one-at-a-time method (OAT) is a common sensitivity analysis method for evaluating the impact of changing one factor at a time in turn (Saltelli A, et al. 2000; Saltelli A, et al., 2007). Many early studies have adopted the OAT analysis to characterize the sensitivity of pH to different factors (Ding et al., 2019; Wang et al., 2020; Tao and Murphy, 2019). We've clarified this in the revised manuscript as (see Line 167-168): "Note that because of the nonlinear dependence of pH to different factors, the sum of contributions of individual factors can be slightly different from the overall contributions of all factors."

The reviewer was referring to cases of SE-US in summer 2008 (Fig. S3 of Zheng et al., 2022) as shown below. We've examined our case in Shanghai, and find no abrupt changes.

2. The dataset did not include gaseous HCl but treat the particulate Cl as overall Cl, while ammonium chloride formation can be a significant contributor to haze formation, at least in winter. Can the authors perform a sensitivity test for this assumption?

Response: We thank the reviewer for the comments. As shown in Fig. R6, we have performed a sensitivity test and compared the differences in pH calculated from simulations with and without gaseous HCl. Because of the relatively low abundance of gaseous HCl, the overall Cl (HCl + Cl^-) shows a minor change resulting in little difference in pH between two simulations.

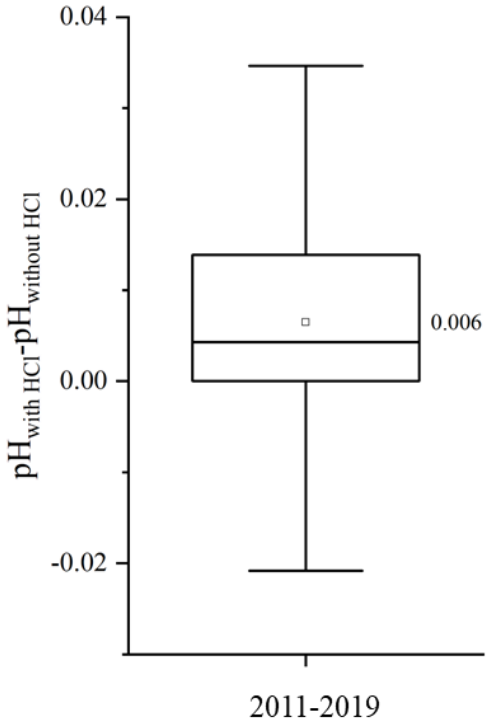

Figure R6 The differences in pH calculated from simulations with and without gaseous HCl from 2011 to 2019.

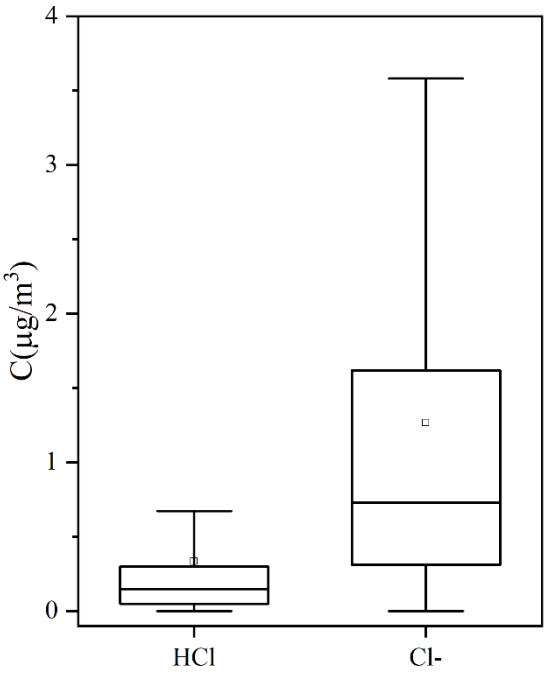

Figure R7 The box plots of HCl and Cl^- concentrations from 2011 to 2019.

3. Section 3.1.1 & 3.1.2, it's better for the authors to present the annual trends of meteorological parameters prior to chemical composition changes since temperature and RH are also influencing pH values.

Response: We thank the reviewer for this constructive suggestion. We've added the related analysis on trends of temperature and RH in the revised manuscript and supplement. Details are provided as follows:

Modifications in manuscript:

Line 114-117: "Temperature and RH, which are important factors affecting aerosol pH, were also measured at a time resolution of 1 min. Annually averaged temperature and RH from 2011 to 2019 are shown in Figure S6. The t-test results revealed that temperature rose significantly at a rate of 1.2 %/yr ($p < 0.01$), while RH changed little."

Modifications in* supplement*:

We've added the Figures S6 in the revised supplement as: "

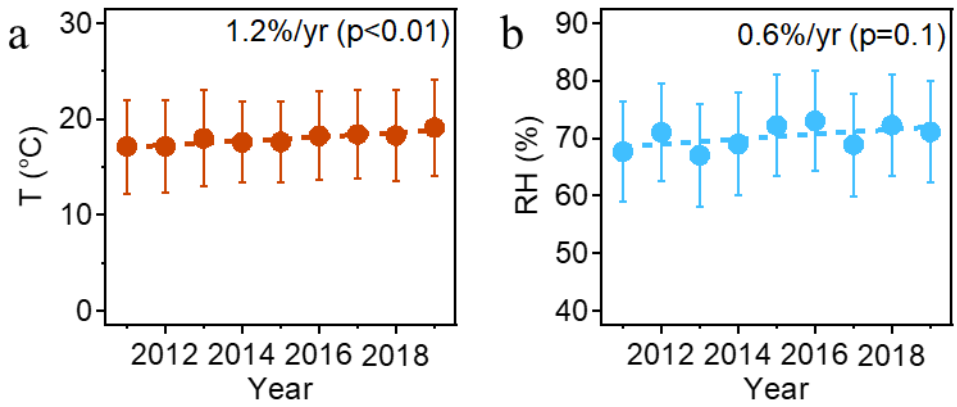

Figure R8 *(added Figure 6 in the manuscript)* Annual values of temperature (T) and relative humidity (RH) from 2011 to 2019"

Some other comments:

4. Line 29-30: It's better to address which approach is used to get these numbers in the abstract.

Response: Thanks for the suggestion. We added the description of the approach in the abstract as follows:

Modifications in manuscript:

Line 23-24: "Here, we reported the first trend analysis of aerosol pH from 2011 to 2019 in eastern China, calculated with ISORROPIA model based on observed gas and aerosol compositions."

5. Line 226-227: I don't understand how concentrations of aerosol chemical composition impact pH. Is there a relationship such as lower PM days having higher

pH values?

Response: We thank the reviewer for the comments. This is well explained in Zheng et al. 2020, that at given RH and temperatures, the lower aerosol concentrations will lead to lower ALWC at similar chemical composition characteristics, which will lead to lower pH.

6. Line 35: formation in the gas phase?

Response: Thanks for the comments. We revised this sentence into: "The corresponding aerosol pH in eastern China is estimated to increase by ~0.19, resulting in 4% more NO_3^- and 12% more NH_4^+ partitioning in the gas phase,"

7. Line 102: equivalent concentrations of cation and anion? Should be more specific.

Response: Thanks for the comments. Here the equivalent concentrations mean charge equivalent concentrations. We've further clarified this point as (see Line 102-104): "To ensure the data quality, the ion balance between the measured charge equivalent concentrations of cation (NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) and anion (SO_4^{2-}, NO_3^- and Cl^-) species was examined as shown in Figure S2."

Comments of Editor:

I note the substantial improvements based on the reviewer comments.

Still, further improvements are required; besides the ones of the reviewers I note the following ones (all line numbers refer to the file 455-ATC2):

8. L333: the statement 'the sulfate concentrations generally correlated linearly with that of the SO2 emissions' is not correct: Fig. S10 shows that the SO2 emission decreases by a factor of 4, while the sulfate concentration decreased by less than a factor of 2. This is not linear, so the authors should rephrase this and give an explanation why these two variable do not behave linearly.

Response: Thanks for the comments. As shown in Fig. S10, the sulfate concentrations are generally linear (following the relationship of $y = kx + b$) rather than proportional (following the relationship of $y = kx$) to SO_2 emissions. The sulfate concentrations and SO_2 emissions are reduced by different proportions due to the presence of the intercept. The intercept indicates that, even if the anthropogenic SO_2 emissions are reduced to zero, there will still be background SO_4^{2-} aerosol from natural sources and regional transport.

9. I also note that there are drastic differences in Fig. 6, e.g, for pH in the BHE scenario (6d) between the previous and the current version. What are the reasons for these differences? And are the authors convinced that these numbers are now the correct ones?

Response: The difference is due to the change of scenario projections of sulfate concentrations. Instead of assuming sulfate concentration is proportional to SO_2 emissions (previous version, we now adopt a linear dependence, i.e., aerosol concentrations = k * (precursor emissions) + b. We consider the current projection more robust as they're supported by the historical trends.

10. I also appreciate the substantial improvements in the text. Still, this manuscript will profit from a further thorough English editing; the following points are just examples:

L25: Yangtze: add 'the'

L28: units: not needed. If you want to use it, it should read units (make it consistent throughout the manuscript)

L36: formation in the gas phase: not clear, as neither NO3- nor NH4+ is formed in the gas phase.

L45: solubility(Cheng: please make sure to add required space before references here and in all future instances (many).

L86: providing scientific: add 'a'

L93: this sampling site represent: add 's'

L104: thus is: replace by 'are'

L107: Lithium Bromide: no capitals

L108: the multi-points calibrations: replace by multi-point calibrations

L110: ion balance: add 'the'

L113: R2: all symbols should be italic; between the cation and anion: add 's' to both

L161: are not well corrected: do you mean correlated?

L163: be attribute: add 'd'

L165: are high uncertainty: wrong English; correct

L171: differs with: replace by differs from

L186: 0.04 unit pH per year: replace by 0.04 pH units per year

L190: before the implement of the Action Plan: implementation

L194:were kept being: replace by remained

L203: aerosol pH: add ‘values’

L226: from 2013 to 2019, respectively: replace by , respectively from 2013 to 2019

L236: implementation of Action Plan: add ‘the’

L252: similar seasons: replace by the

L287: were depicted: replace by are depicted

L288: effects individual: add ‘of’

L289: Bar plot: add ‘the’

L295: max: replace by ‘maximum’

L297: with ALWC reached: replace by.. ‘reaching’

L330: reference scenario that without: delete ‘that’

L346: and 2.6 μg/m3: add ‘, respectively

L351: NH4+ partitioning ratio: add ‘the’

L362: indicating that more ammonium will exist in the gas phase as NH3: replace by ..relatively more ammonium.. (as NH3 emission and concentration will be reduced)

L378: are: replace by is

L381: are: replace by is

L413: in YRD region: add ‘the’

Response: We thank the reviewer for the comments and have corrected accordingly in the revised manuscript. In addition, we’ve read through the manuscript and did the grammar checks carefully.

Reference

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmospheric Chemistry and Physics, 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmospheric Chemistry and Physics, 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

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ammonia reduction on control of fine particle nitrate, Atmospheric Chemistry and Physics, 18, 12241-12256, 10.5194/acp-18-12241-2018, 2018.

Masiol, M., Squizzato, S., Formenton, G., Khan, M. B., Hopke, P. K., Nenes, A., Pandis, S. N., Tositti, L., Benetello, F., Visin, F., and Pavoni, B.: Hybrid multiple-site mass closure and source apportionment of PM2.5 and aerosol acidity at major cities in the Po Valley, Sci Total Environ, 704, 135287, 10.1016/j.scitotenv.2019.135287, 2020.

Nah, T., Guo, H., Sullivan, A. P., Chen, Y., Tanner, D. J., Nenes, A., Russell, A., Ng, N. L., Huey, L. G., and Weber, R. J.: Characterization of aerosol composition, aerosol acidity, and organic acid partitioning at an agriculturally intensive rural southeastern US site, Atmospheric Chemistry and Physics, 18, 11471-11491, 10.5194/acp-18-11471-2018, 2018.

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Saltelli, A. Ratto, M., Andres, T., Campolongo, F., Cariboni, J. Gatelli, D., Saisana, M., Tarantola, S. Global Sensitivity Analysis. The Primer, John Wiley & Sons, New York. 2007.

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Wang, S., Wang, L., Li, Y., Wang, C., Wang, W., Yin, S., and Zhang, R.: Effect of ammonia on fine-particle pH in agricultural regions of China: comparison between urban and rural sites, Atmospheric Chemistry and Physics, 20, 2719-2734, 10.5194/acp-20-2719-2020, 2020.

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

Zheng, G., Su, H., and Cheng, Y.: Revisiting the Key Driving Processes of the Decadal Trend of Aerosol Acidity in the U.S, ACS Environmental Au, 10.1021/acsenvironau.1c00055, 2022.