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:

Major concerns:

This manuscript revision has addressed many of the concerns raised by the Referees in the first review. However, there are still some major issues with the manuscript that must be addressed before it can be published. Many of the issues are problems with the revised portions of the text. My specific concerns are:

1. The results and discussion in Section 3.4 (Future Projections) need significant revision. Firstly, many prior studies have examined the sensitivity of PM2.5 to the precursors SO2, NOx, and NH3. None of those prior studies are cited or discussed. This work, as it relates to PM2.5 (and the individual aerosol species), is not novel. It is a much more simplified treatment of the topic than prior studies that use either a chemical transport model or a more rigorous thermodynamic analysis of the system, the typical approaches to this topic. The effect of the emissions scenarios on aerosol pH is quite novel and should be the focus of this section. Therefore, I recommend a substantial revision of this section (this comment also pertains to the Abstract and Conclusions where these results are discussed). As part of this revision, the limitations and uncertainties associated with their analysis should also be discussed. If the authors choose to keep the core analysis, i.e., presenting the partitioning ratios in addition to pH, then major revisions should include a more detailed analysis of the thermodynamic system under each emission scenario. See as an example Nenes et al. (2021) and Vasilakos et al. (2018). It should also include a thorough discussion of prior studies that have examined the SNA system and sensitivity of aerosol abundances to precursor emissions.

Response: We thank the reviewer for the comments. Following the reviewer's suggestion, we've modified section 3.4 focusing mainly on the influence of emission scenarios on aerosol pH. We first tested the sensitivity of aerosol abundances to precursor emissions with the historical data (Fig. R1 and R2), and then estimated the future scenario predictions based on the relationship between aerosol abundances and precursor emissions (Fig. R3). The limitations and uncertainties associated with this analysis are also discussed. The detailed modifications are listed below.

We've modified Section 3.4 into (Line 330-407):

"*We first tested the sensitivity of aerosol abundances to precursor emissions with the historical data (Fig. S10), the emissions of Shanghai were obtained by the Multi-resolution Emission Inventory for China (MEIC, http://meicmodel.org/, last access: 15 January 2020). We found that the non-volatile sulfate concentrations generally correlated linearly with that of the SO_2 emissions. For the volatile TNO_3 and NH_X, the correlations are less linear, likely due to the different deposition velocities of gases and particles (Nenes et al., 2021; Pye et al., 2020; Weber et al., 2016). The historical emission reductions have resulted in a moderate pH decrease (Figure 1), a moderate increase (0.2% per year) in the NO_3^- partitioning, and a decrease (-0.6% per year) in the NH_4^+ partitioning (Figure S11).*

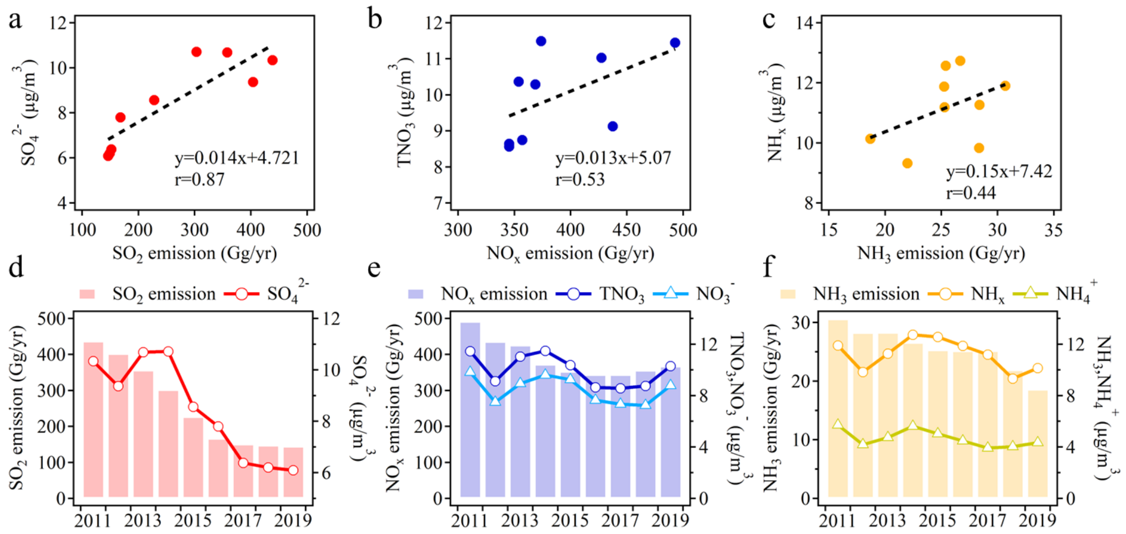

Figure R1 *(added as Fig. S10 in the revised supplement)*. (a)-(c) Correlations of aerosol abundances to precursor emissions from 2011 to 2019, including (a)SO_4^{2-} vs. SO_2, (b) TNO_3 vs. NO_x and (c)NHx vs. NH_3. (d)-(f) Annual values of aerosol abundances and precursor emissions from 2011 to 2019, including (d)SO_4^{2-} and SO_2 emission, (e)TNO_3, NO_3^-, and NO_x emission, and (f) NHx, NH_4^+, and NH_3 emission.

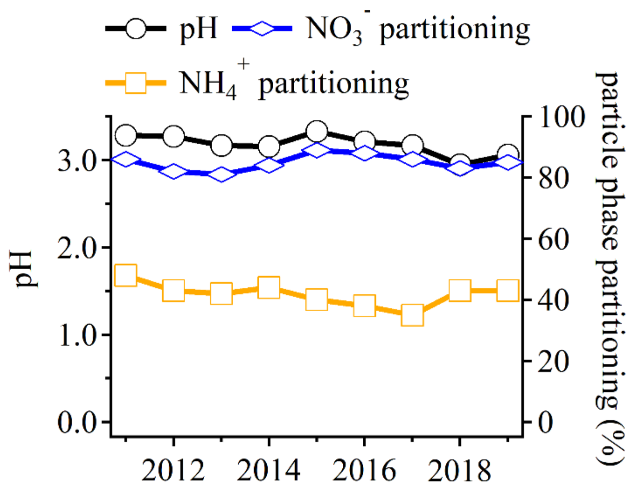

Figure R2*(added as Fig. S11 in the revised supplement)*. Annual values of pH, NO_3^- partitioning (NO_3^- / (NO_3^- + HNO_3)), and NH_4^+ partitioning (NH_4^+ / (NH_4^+ + NH_3)) from 2011 to 2019.

For a first-order estimation, we applied the average Δaerosol /Δprecursor emissions in (μg/m^3)/(Gg/yr) as derived from the historical data (Figure S10a-c) to the future scenario predictions. Figure 6 shows the emissions of SO_2, NO_x, NH_3 and predicted pH levels and the effects of major chemical components (NH_x, SO_4^{2-}, and TNO_3) to the ΔpH in Shanghai from 2015 to 2050 under the three scenarios. Base on this assumption, the concentrations of SO_4^{2-}, NO_3^- and NH_4^+ are expected to drop to ~6.3, 5.7 and 2.6 μg/m^3 in 2050 with the SSP1-26-BHE scenario, generally in agreement with the predicted $PM_{2.5}$ levels of ~15 μg/m^3 under such scenario (Shi et al., 2021).

Under the reference scenario of SSP3-70-BAU with weak control policy (blue dashed lines in Figure 6 a-f), SO_2 and NO_x are predicted to increase, while the NH_x is relatively stable. NH_x, SO_4^{2-}, and TNO_3 have minor effects on ΔpH (Figure 6g). Correspondingly, there are little changes in aerosol pH and the predicted NO_3^- partitioning ratio (NO_3^- / (NO_3^- + HNO_3)). However, NH_4^+ partitioning ratio (NH_4^+ / (NH_4^+ + NH_3)) will increase substantially, suggesting an enhanced formation of ammonium aerosols. Under the moderate control policy (SSP2-45-ECP), the emissions of SO_2, NO_x, and NH_3 in 2050 will be reduced by 62.7%, 49.0% and 25.0%, respectively with corresponding decreases in SO_4^{2-}, TNO_3 and NH_x. The predicted pH will increase by ~0.13, and the NH_4^+ partitioning ratio will decrease by 0.09, indicating that more ammonium will exist in the gas phase as NH_3. The NO_3^- partitioning ratios are relatively stable, suggesting its general insensitivity in the predicted pH ranges(Nenes et al., 2020). Changes in the SO_4^{2-}, TNO_3 and NH_x will result in ΔpH of +0.18, -0.05 and -0.02 units from 2015 to 2050, respectively (Figure 6h).

With the strict control policy (SSP1-26-BHE), the emissions of SO_2, NO_x and NH_3 in 2050 will decrease by 86.9%, 74.9% and 41.7%, respectively, and the concentrations *of SO_4^{2-}, TNO_3 and NH_x decrease substantially. The pH value will increase continuously by ~0.19 (from 3.36 in 2015 to 3.55 in 2050). Changes in SO_4^{2-} are more important determinants of ΔpH, resulting in ΔpH of +0.28 units from 2015 to 2050. Changes in the TNO_3 and NH_x are associated with 0.04 and 0.09 decreases in ΔpH, respectively. Moreover, the NO_3^- and NH_4^+ partitioning ratios will decrease by 0.04 and 0.12, respectively, indicating a benefit of NH_3 and NO_x emission controls in mitigating haze pollution in eastern China.*"

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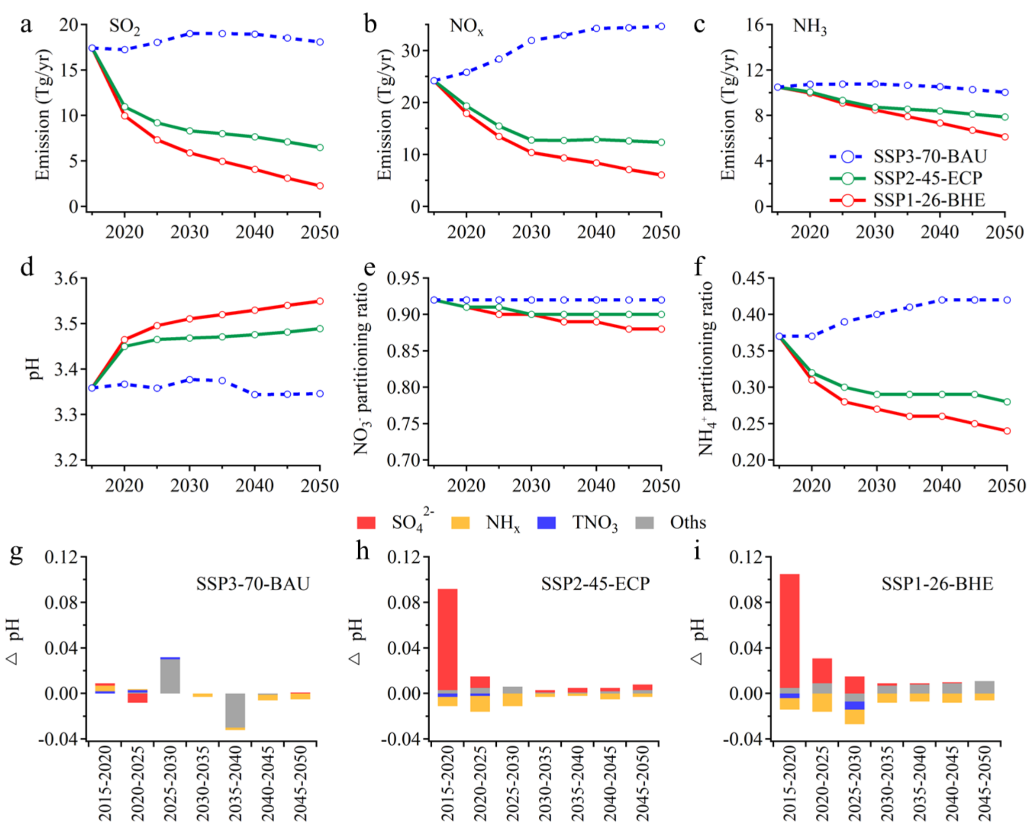

Figure R3 *(revised Fig. 6 in the manuscript)*. Emissions of SO_2 (a), NO_x (b), NH_3 (c), predicted pH (d), NO_3^- partitioning (NO_3^- / (NO_3^- + HNO_3)) (e) and NH_4^+ partitioning (NH_4^+ / (NH_4^+ + NH_3)) (f) in China from 2015 to 2050 under the three scenarios published in Tong et al.(2020). Predicted contributions of individual factors to the ΔpH under the three scenarios, including SSP3-70-BAU (g), SSP2-45-ECP (h) and SSP1-26-BHE (i). The stacked color bars below the dashed line represent the factors that had negative impacts on ΔpH and the stacked color bars above the dashed line represent the increase in ΔpH. The meanings of the abbreviations: NH_x, total ammonia; TNO_3, total nitrate; Oths, others."

We added discussions on the limitations and uncertainties of this analysis as (see Line 378-381):

"*We also note that above analysis based on the historical average Δaerosol /Δ(precursor emissions) are subject to uncertainties associated with changes in the* *atmospheric oxidation capacity, meteorological conditions, etc.. It is only a first-order estimation, and a full examination with 3-D chemical transport models are recommended in the future.*"

We've modified Abstract and Conclusions accordingly as:

(1) Line 34-38: "*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/formation in the gas phase, which suggests that* NH_3 *and* NO_x *emission controls are effective in mitigating haze pollution in eastern China.*"

(2) Line 430-445: "*We found that under the weak control policy (SSP3-70-BAU), the future aerosol pH and* NO_3^- *partitioning ratio will only have subtle changes. While our results also demonstrate that future aerosol pH will increase under both strict control policy (SSP1-26-BHE) and moderate control policy (SSP2-45-ECP), the former will result in a more dramatic increase. The significant increase in aerosol pH is mainly associated with the decrease in* SO_4^{2-}*. In addition, the increase in aerosol pH with strict control policy and moderate control policy will lead to more nitrate and ammonium partitioning in the gas phase, which is beneficial for future* $PM_{2.5}$ *pollution control. These results highlight the potential effects of precursors reductions on aerosol pH employing future pollution control policy.*"

In addition, we've added Fig. R1 and R2 as Fig. S10 and S11 in the revised supplement.

Furthermore, we'd like to emphasize that this part is not the key point of this study. The main focus and novelty of our study are for the first time to explain the "Long-term trends and drivers of aerosol pH in eastern China". These main conclusions stand independent of future implications (Sect. 3.4). Thus, we are also open to remove Sect 3.4 and focus on the main content if the reviewers prefer with this option.

Technical/Minor Comments

There are some minor, mostly technical corrections that should also be made:

- Line 73: change "particulate" to particles
- Line 113: delete "using meteorological parameters monitor"
- Line 169-170: suggest changing "the one-at-a-time method" to a more technical description
- Line 187: delete "obvious"

- Line 189: change “the implement” to “implementation”
- Line 194: change “Despite of the” to “Despite the”
- Line 198: change “with daily pH ranged” to “with a daily pH range”
- Line 199-200: I do not think Table S1 is necessary, especially because it is not discussed to compare and contrast the present results
- Line 201: it is not correct to call it a “pH level”
- Line 221: delete “the”
- Line 237-238: the sentence beginning “This is with similar seasonal…” needs to be revised for grammar
- Line 280-282: the sentence beginning “After sunrise, increase of temperature…” needs to be revised for grammar
- Line 288: change “roles” to “role”
- Section 3.4: “partition ratio” should be “partitioning ratio”
- Line 377: change “on” to “to”
- Line 380: suggest changing “revealed”
- Line 381: suggest adding a period after “respectively”
- Line 389: delete “existed”
- In addition to the above technical corrections, the entire manuscript should be carefully reviewed and edited for grammar, especially any changes made to the manuscript

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.

Comments of the Editor:

The comments of reviewer 1 should be carefully followed. In the following, some comments from the editor, partly on similar points as Reviewer 1.

2. The question of how organic carbon was measured is not answered satisfactorily. The time resolution is not given for example: was this also with 1 hour resolution as for the MARGA measurements? I doubt that this was the case. So it is important to mention in the manuscript that ALWCo is only a minor fraction of total ALWC. (Otherwise it would not be possible to determine reasonable diurnal variations). Also, make sure that all other relevant information given in the answers to the reviewers is also mentioned

in the manuscript.

Response: We thank the editor for the comments. The Thermal/Optical Carbon Aerosol Analyzer has a time resolution 1 hour, but the ALWCo was calculated using the annual average data. We've recalculated the ALWCo with the hourly data, and added the relevant information in the revised manuscript as follows:

Modifications in manuscript:

(1) Line 120-122: "*A Thermal/Optical Carbon Aerosol Analyzer (model RT-4, Sunset laboratory Inc.) equipped with a $PM_{2.5}$ cyclone was used for the organic carbon measurement at a time resolution of 1 hour.*"

(2) Line 143-147: "*The concentration of organic aerosol was estimated by multiplying the measured concentration of organic carbon by a factor of 1.6 (Turpin and Lim, 2001). The average concentrations of $ALWC_o$ and $ALWC_i$ in Shanghai from 2011 to 2019 were 4.1 (±10.2) and 32.6 (±52.5) μg/m^3, respectively. $ALWC_o$ only accounted for 11.1% of the total aerosol liquid water content.*"

3. I still find the figure captions in Fig. 1, 3 and 5 not clear enough. You might wish to list this as follows, or similar: a colored bar below the dashed line (decrease in pH) means an increase in the concentrations of sulfate, xx, and a decrease in yyy, and vice versa.

Response: We thank the editor for the comments. We've added more captions in Fig. 1, 3 and 5 in the revised manuscript as follows:

Modifications in manuscript:

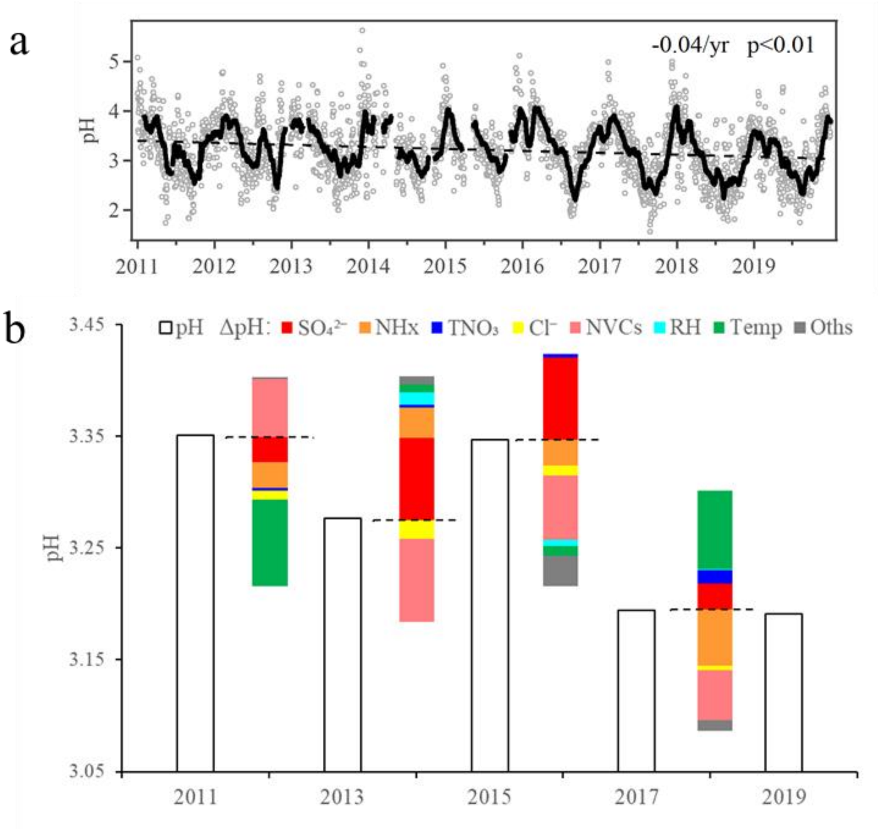

Figure R4 *(revised Fig. 1 in the manuscript)*. (a) Long-term trends in aerosol pH during 2011–2019 in Shanghai. Gray dots and black lines represent the daily pH values and 30-day moving average pH values, respectively. (b) Contributions of individual factors to the ΔpH from 2011 to 2019. Here the coloured bar plots indicate the factors contributing to the ΔpH between two adjacent scenarios, e.g., 2011 to 2013. The stacked color bars below the dashed line represent the factors that had negative impacts on ΔpH, and the stacked color bars above the dashed line represent the factors that had positive impacts on ΔpH. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH_x, total ammonia; TNO_3, total nitrate; Oths, others.

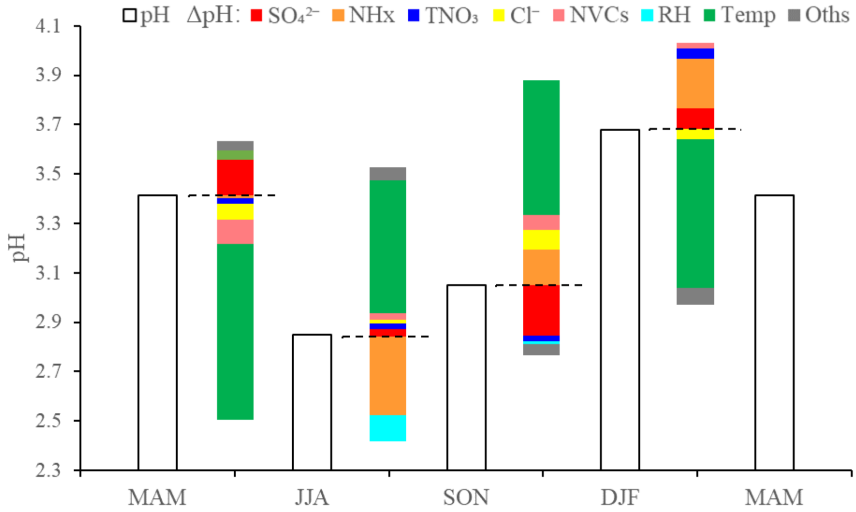

Figure R5 *(revised Fig. 3 in the manuscript)*. Contributions of individual factors to the ΔpH across the four seasons. Here the bar plots indicate the factors contributing to the ΔpH between two adjacent seasons, e.g., spring (MAM) to summer (JJA). The stacked color bars below the dashed line represent the factors that had negative impacts on ΔpH and the stacked color bars above the dashed line represent the increase in ΔpH. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH_x, total ammonia; TNO_3, total nitrate; Oths, others.

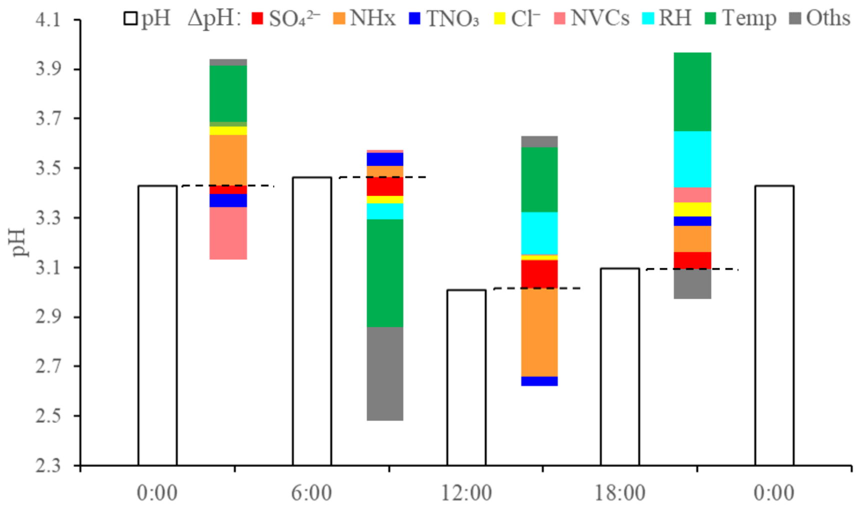

Figure R6 *(revised Fig. 5 in the manuscript)*. Contributions of individual factors to the ΔpH between day and night. Here the bar plots indicate the factors contributing to the ΔpH between two adjacent hour periods, e.g., 0:00 to 6:00. The stacked color bars below the dashed line represent the factors that had negative impacts on ΔpH and the stacked color bars above the dashed line represent the increase in ΔpH. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH_x, total ammonia; TNO_3, total nitrate; Oths, others.

4. I also agree with Reviewer 1 that the description in Section 3.4 is still not sufficient.

The revision should include a more detailed analysis of the thermodynamic system under each emission scenario. Explanations for changes in the partitioning ratios should be given in all cases. For example, an explanation needs to be given why for the moderate scenario the partitioning ratio decreases, while it increases for the BHE scenario. The explanation for the trend change in the nitrate partitioning after 2040 is not convincing (there is no sharp decrease in SO42- between 2040 and 2050). Also, the NVCs and ALWC have been shown to have a strong impact on the pH for the measurement period. Therefore, the assumed changes in NVCs and calculated ALWC for the scenarios need to be shown as well.

Response: Thanks for the comment. We've rewrote this section. Please see our response to comment #1.

5. Finally, there are still a lot of English corrections needed. A (non-exhaustive) list of examples is given by Reviewer 1, sometimes the text is even not clear because of the wording. All "partition ratios" should be changed to "partitioning ratios", not only in the text, but also in Figure 6. As there are many more examples of required English corrections, the manuscript will definitely profit from a thorough English editing.

Response: We thank the editor for the comments. We've corrected the relevant wording and made a thorough English editing.

Reference

Nenes, A., et al., 2021. Aerosol acidity and liquid water content regulate the dry deposition of inorganic reactive nitrogen. Atmospheric Chemistry and Physics. 21**,** 6023-6033.

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Weber, R. J., et al., 2016. High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. Nature Geoscience. 9**,** 282-285.