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 concerning our manuscript. They are valuable in helping us improve our manuscript. Below please find our point-by-pint responses to reviewers' comments.

Comments to the Author

1. Overall, my main concern with the manuscript is that the methods section is much too brief. The authors need to provide a lot more explanation of how they generated the data that are presented in Figures 1, 3, 5, and 6. Since each of there figures represents perturbations or trends to some previous averaging period, the way in which the data are averaged (and perturbed) needs to be explained more clearly. For the long-term trend in Figure 1, the approach seems fairly obvious, but the way in which the seasonal and diel cycles are formulated in Figure 3 and 5 is quite confusing.

Response: Thanks for the comment. We've added the more description of methods in the revised manuscript. Please see the following changes.

Changes in manuscript:

(1) Line 150-178: We rewrote the section 2.3 as:

> "**2.3 Drivers of aerosol pH variations**
>
> To investigate the factors that drive changes in aerosol pH, sensitivity tests of pH variations to different factors, including temperature, RH, SO_4^{2-}, TNO_3, NH_x, Cl^- and NVCs, were performed with the one-at-a-time method. For illustration, assume the aerosol pH estimated under scenario I (pH_I) differs with that under scenario II (pH_{II}), and the pH difference, $\Delta pH = pH_{II} - pH_I$, are caused by the variations in the factors listed above. To quantify the contributions of individual factors, we varied the factor i from the level in scenario I to that in scenario II while keeping the other factors fixed. The corresponding pH changes, ΔpH_i, are assumed to represent the contribution of this individual factor change to the overall aerosol pH variations. The unresolved contributors to pH differences, i.e., $\Delta pH - \sum_i \Delta pH_i$, are attributed to "others", which may represent the contribution of covariations between the factors. This method is applied in Fig. 1b, Fig. 3 and Fig. 5, where the corresponding scenarios represent the average conditions in different years (Fig. 1b), seasons (Fig. 3) or diurnal periods (Fig. 5)."

(2) Line 204-206: We added some descriptions as: "Figure 1b shows the contributions of individual factors to the ΔpH from 2011 to 2019. Here the bar plots indicate the factors contributing to the ΔpH between two adjacent scenarios, e.g., 2011 to 2013. See Fig. S9a for the factor contribution to the variation from average conditions."

(3) Line 241-245: We added some descriptions into: "Figure 3 shows the 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). See Fig. S9b for the factor contribution to the variation from average conditions. The aerosol pH was calculated from the mean averages of input parameters in four seasons, and the ΔpH was estimated by varying one factor while holding the other factors fixed in different seasons."

(4) Line 273-278: We added some descriptions into "Figure 5 shows the effects 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. See Fig. S9c for the factor contribution to the variation from average conditions. The aerosol pH was calculated from the mean averages of input parameters in 0:00, 6:00, 12:00 and 18:00, and ΔpH was estimated by varying one factor while holding the other factors fixed in different hours."

2. P1 L33-36 It is hard to understand the meaning of this sentence. Are the authors suggesting that NH_3 and NO_x emission controls are not going to be effective in the time period leading up to 2050, or that they won't be effective after that point? Further – is it appropriate to examine the values just on their own – what would happen if only SO_2 reductions were implemented? Presumably NH_4^+ and NO_3^- would increase much more.

Response: Thanks for the comment. Here we are discussing about the efficiency of PM reduction concentrations against the precursor reduction concentrations. To further clarify our points, we've revised the corresponding manuscript, and added the prediction of the changes in major chemical components (NH_4^+, SO_4^{2-}, NO_3^- and Cl^-) as Fig. 6g-i. See detailed modifications below.

Changes in manuscript:

(1) Line 34-38: We've revised the statement into: "The corresponding aerosol pH in eastern China is estimated to increase by ~0.9, and the reduction in particle phase NO_3^- and NH_4^+ is less than the reduced amount of total HNO_3 and total NH_3. This suggests a reduced benefit of NH_3 and NO_x emission control in mitigating haze pollution in eastern China."

(2) Discussions in section 3.4: We've revised Fig. 6 and the corresponding discussions into (Line 320-366 in the revised section 3.4):

> "Under the reference scenario of SSP3-70-BAU with weak control policy (blue lines in Fig. 6 a-f), SO_2 and NOx are predicted to increase, while the NHx is relatively stable. Correspondingly, both SO_4^{2-} and NO_3^- will increase, and NH_4^+ will also increase in response (Fig. 6g). Considering the stable NHx, NH_4^+ partition ratio (NH_4^+ / (NH_4^+ + NH_3)) will increase. In comparison, there is little change in aerosol pH and the predicted NO_3^- partition ratio (NO_3^- / (NO_3^- + HNO_3)).
>
> 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. Correspondingly, SO_4^{2-}, NO_3^- and NH_4^+ will all decrease (Fig. 6h), with a total PM reduction of ~14.4 $\mu g\ m^{-3}$. Moreover, the predicted pH will increase by ~0.5, and the NO_3^- and NH_4^+ partition ratios will decrease by 0.14 and 0.23, respectively (green lines in Fig. 6d-f). That is, more nitrate and ammonium will exist in the gas phase as HNO_3 and NH_3, thus the reduced NH_4^+ and NO_3^- is higher than the reduced NHx and TNO_3, which is a control bonus in terms of reduced PM per reduced emissions for this scenario.
>
> 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. Its effect on PM reductions resembles that of the moderate one (SSP2-45-ECP) before 2040. Afterwards, however, the NO_3^- partition ratio increased despite the increasing pH, and reached near 1 in 2050 (Fig. 6 d, e). On second check, we found this pattern is due to the sharp decrease in SO_4^{2-} and constant NVCs. After 2040, there will be a major anion deficit considering the non-volatile species only (sulfate and Ca^{2+}, K^+, Mg^{2+}), and therefore more NO_3^- will be captured by the NVCs to the particle phase. As a result, NO_3^- partition ratio even increased from 0.92 in 2015 to 1.00 in 2050. Although NH_4^+ partition ratio showed a

continuous decrease, in 2050 both the reduced NH_4^+ and NO_3^- is smaller than the reduced NHx and TNO_3 (Fig. 6i). That is in contrast with the effect of the moderate one (SSP2-45-ECP). Correspondingly, the total reduced PM is only slightly larger for the strict SSP1-26-BHE policy (~18.6 μg m^{-3}) than the moderate SSP2-45-ECP policy (~14.4 μg m^{-3}) indicating a reduced efficiency in terms of PM controls in responses to the emission controls. This would suggest a reduced benefit of NH_3 and NO_x emission control in mitigating haze pollution in eastern China, especially after 2040."

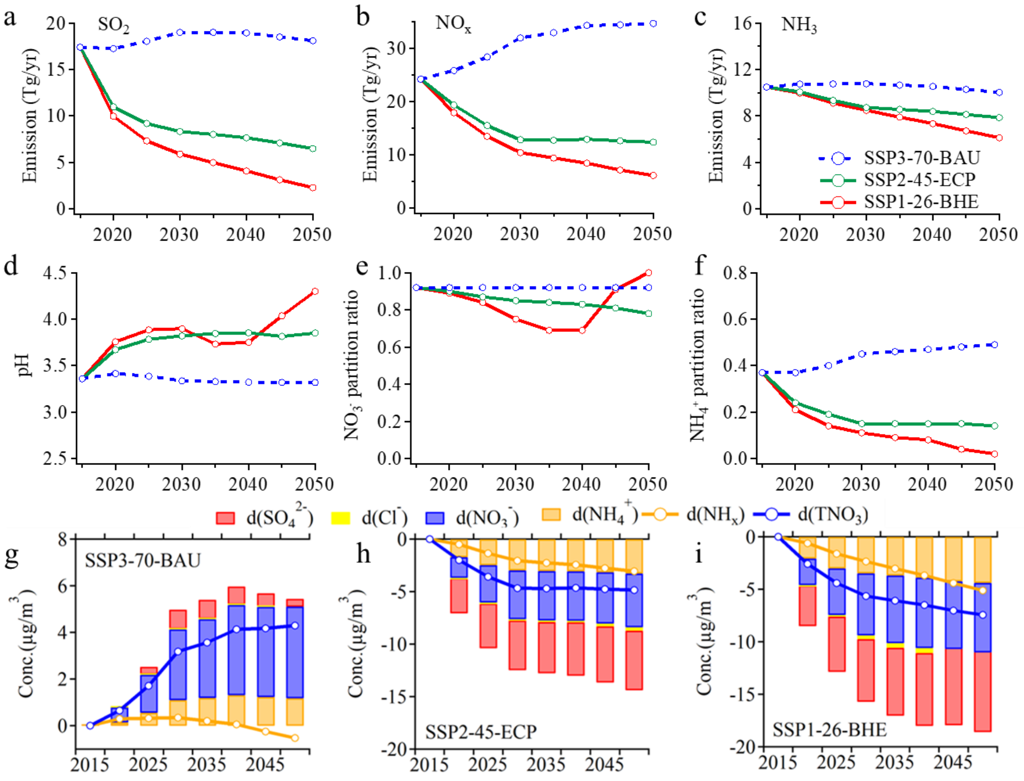

Figure R1 ***(revised Fig. 6 in the manuscript)*****. Emissions of SO_2 (a), NO_x (b), NH_3 (c), predicted pH (d), NO_3^- partition (NO_3^- / (NO_3^- + HNO_3)) (e) and NH_4^+ partition (NH_4^+ / (NH_4^+ + NH_3)) (f) in China from 2015 to 2050 under the three scenarios published in Tong et al.(2020). Predicted the changes in major chemical components (NH_4^+, SO_4^{2-}, NO_3^- and Cl^-) and reductions in TNO_3 and NHx under the three scenarios, including SSP3-70-BAU (g), SSP2-45-ECP (h) and SSP1-26-BHE (i).**

In addition, following the reviewer's suggestion, we also examined the changes of SO_4^{2-}, NH_4^+ and NO_3^- aerosol concentrations if only one gaseous precursor reduction is implemented (Figure R2). As shown in Figure R2, if only SO_2 reduction is implemented, NH_4^+ and SO_4^{2-} concentrations will show a significant decrease from 2015 to 2050, while NO_3^- concentration will generally keep constant between 2015-2040 and then increase slightly during 2040-2050. If only NH_x reduction is implemented, NH_4^+ and NO_3^- concentrations will be slightly reduced while SO_4^{2-} concentration will remain unchanged from 2015 to 2050. However, if only NO_x reduction is implemented, both NH_4^+ and NO_3^- concentrations will be significantly reduced.

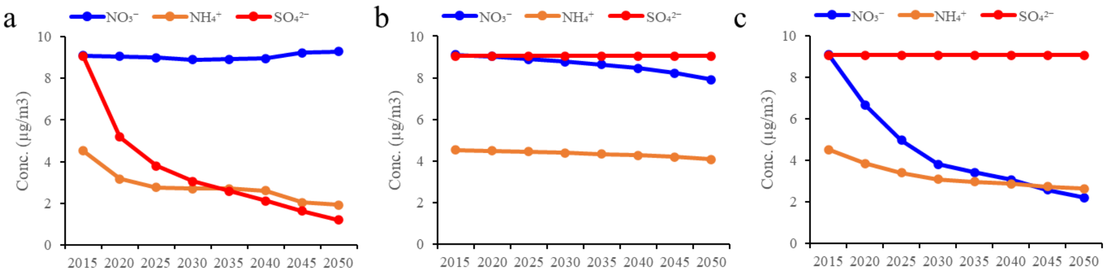

Figure R2 The mass concentrations of SO_4^{2-}, NH_4^+ and NO_3^- aerosol from 2015 to 2050 if only SO_2(a), NH_x(b) and NO_x(c) reductions were implemented under the SSP1-26-BHE scenario published in Tong et al.(Tong et al., 2020)

3. The data in Figure S2 look much more tightly correlated in the later years. Can the authors comment on whether this reflects improvements in the accuracy/precision of the measurements or whether the relative importance on the measured ions to the overall ion balance may have changed?

Response: Thanks for the comment. Indeed, the occurrence possibility of of high C/A ratios (larger than 1.1) is significantly lower during 2017-2019 than that during 2011-2013 and 2014-2016 (Fig. R3), which is the major reason of the more scattered data in 2011-2016 than that in 2017-2019. To investigate into the potential reasons, we further compared the chemical profiles at different C/A ratio levels (Fig. R4). We found that the high C/A ratio samples are mainly driven by the increased NVCs, while the other chemical compositions (anions and NH_4^+) show little dependence with C/A ratios. Accordingly, the decreased fraction of sample with high C/A ratios in recent years is due to the significant decreases in Ca^{2+}, K^+ and Mg^{2+} from 2011 to 2019, with the annual decrease rates of 14.4%, 30.0% and 15.2%, respectively (Fig. R5). This decrease in NVCs can be attributed to the nationwide control of fugitive dust and biomass burning (An et al., 2021; Cheng et al., 2019; Ding et al., 2019). That is, the less scattered data in 2017-2019 is due to the decreased occurrence of dusty periods in recent years. We've added this information into Supplement as Figure S3-S5 and more descriptions in the section 2.1. Please see the following changes.

Changes in manuscript:

Line 102-105: We added some descriptions into: "Figure S2 compares the sum of SO_4^{2-}, NO_3^- and Cl^- with the sum of NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} in neq/m^3 to check the charge balance. Data in 2011-2016 were more scattered than that in 2017-2019, mainly due to the significant decreases in Ca^{2+}, K^+ and Mg^{2+} from 2011 to 2019 (Fig S3-S5)."

Changes in* supplement of *manuscript:

Line 71-79: We've added the Figures S3-S5 in the revised supplement as:

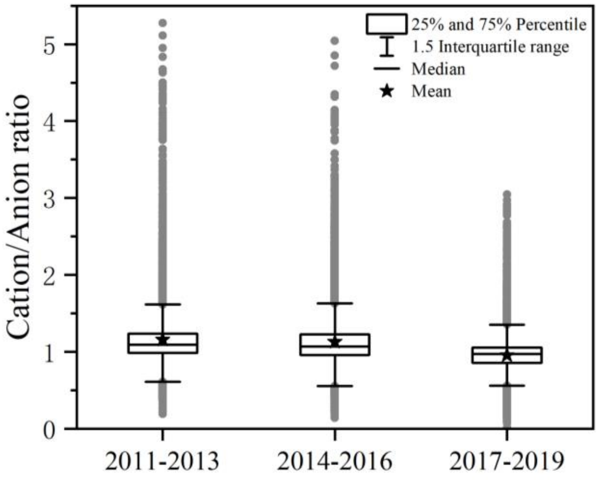

Figure R3 (*added as Fig. S3 in the revised supplement*) The box plots of Cation/Anion ratios during 2011-2013, 2014-2016, and 2017-2019

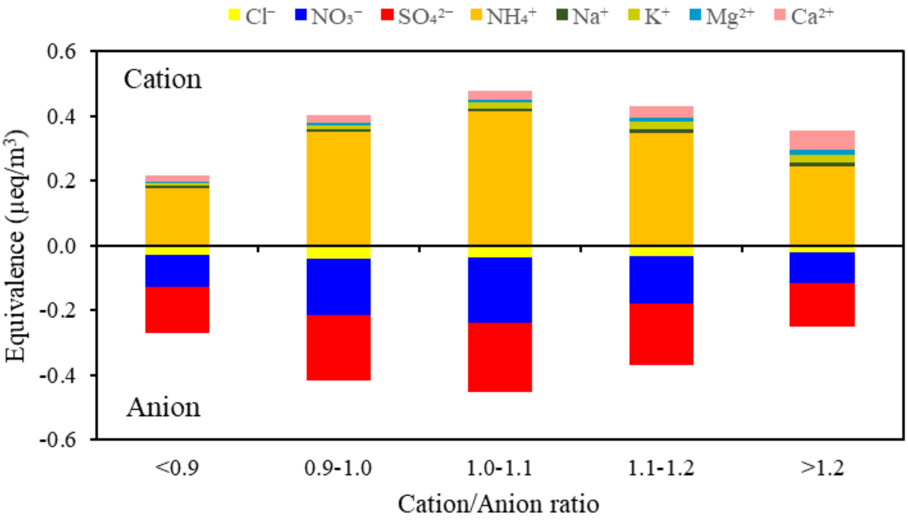

Figure R4 (*added as Fig. S4 in the revised supplement)* Average equivalence concentrations of cation and anion at different level of Cation/Anion ratio

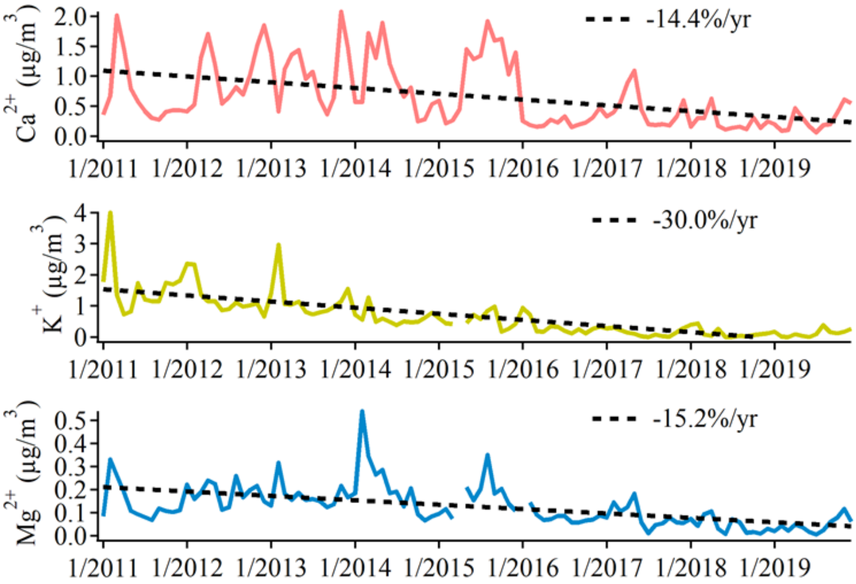

Figure R5 (*added as Fig. S5 in the revised supplement)* Monthly mean concentrations of Ca^{2+}, K^+ and Mg^{2+} from 2011 to 2019

4. The sensitivity tests mentioned in Section 2.3 (lines 143-152) and in Figure S4 are not sufficiently well-described. What did the authors alter and what did they hold constant in each test? The results appear to span a different range of ALWC for each variable. In general, I did not find this section added much to the manuscript, and only made me confused about the method. I suggest removing this section unless it can be much more clearly explained.

Response: Thanks for the comment. We've deleted this paragraph following the reviewer's suggestion. We tried to give a general view in how a factor is related to aerosol pH (i.e., positively or negatively) when other factors are kept constant, but we agree with the reviewer in that this part is not closely related to the main points in this study.

5. The language in Section 3.4 is a little confusing because the authors describe the changes in absolute amounts of particle and gas phase ammonium and nitrate somewhat interchangeably with their partitioning ratios and it becomes hard to keep track of what metric is being described. It might be more clear to focus first on the absolute particle phase amounts and then explain the changes in the context of the partitioning. The sharp increase in the particle phase partitioning of nitrate between 2040 and 2050 is quite difficult to understand in the BHE scenario – what explains it?

Response: Thanks for the comment. We've added more panels in Fig. 6 and rewrote this section. Please see our response to your comment #2.

6. Figure S6 – The caption should explain why are the rates of change only calculated starting in 2013 when the data record starts in 2011. And why a separate slope is calculated for the latter part of the record.

Response: Thanks for the comment. We analyzed the trend before and after 2013 separately as the Air Pollution Prevention and Control Action Plan is implemented in 2013. We've added more explanation in the caption of Figure S8.

Changes in supplement of manuscript:

Line 100-106: We revised the caption of this figure in the supplement of manuscript, the specific modifications are as follows:

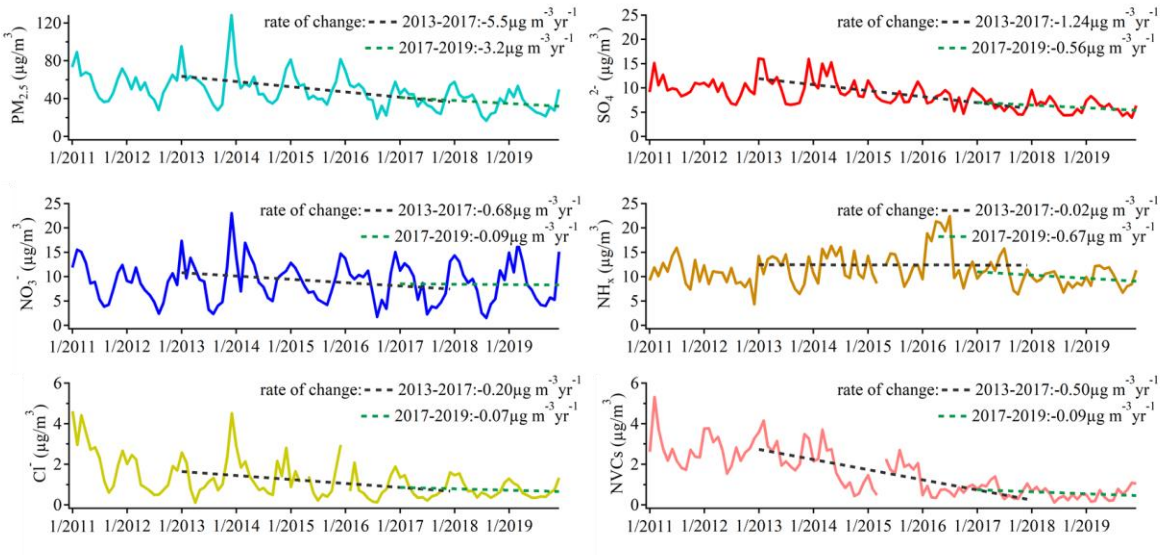

Figure R6 (*revised as Fig. S8 in the revised supplement)* Monthly mean of PM$_{2.5}$, SO$_4^{2-}$, NO$_3^-$, NH$_x$, Cl$^-$ and NVCs from 2011 to 2019. The years of 2011-2013, 2013-2017 and 2017-2019 represent the Pre-Action Plan, Action Plan and Post-Action Plan period, respectively. Here we focused on the changes in trends between the Action Plan (2013-2017; black dashed lines) and Post-Action Plan (2017-2019; green dashed lines) periods.

Reference

An, J., et al., 2021. Emission inventory of air pollutants and chemical speciation for specific anthropogenic sources based on local measurements in the Yangtze River Delta region, China. Atmospheric Chemistry and Physics. 21**,** 2003-2025.

Cheng, J., et al., 2019. Dominant role of emission reduction in PM2.5 air quality improvement in Beijing during 2013–2017: a model-based decomposition analysis. Atmospheric Chemistry and Physics. 19**,** 6125-6146.

Ding, A., et al., 2019. Significant reduction of PM2.5 in eastern China due to regional-scale emission control: evidence from SORPES in 2011–2018. Atmospheric Chemistry and Physics. 19**,** 11791-11801.

Tong, D., et al., 2020. Dynamic projection of anthropogenic emissions in China: methodology and 2015–2050 emission pathways under a range of socio-economic, climate policy, and pollution control scenarios. Atmospheric Chemistry and Physics. 20**,** 5729-5757.