

**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-point responses to reviewers' comments.

## Referee 1

### Comments to the Author

#### Major Comments

1. The estimates  $ALWC_o$  seem unreasonably small (lines 120 - 127)? How was organic aerosol measured? Was it  $PM_{2.5}$  as well, or was it  $PM_1$ ?

**Response:** 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). 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. The annual concentrations of organic carbon in Shanghai were 5.6–10.6  $\mu\text{g}/\text{m}^3$  from 2011 to 2019, and the relative humidity were 69–75%.  $ALWC_o$  was calculated by the following equation (Guo et al., 2015).

$$ALWC_o = \frac{m_{org}\rho_w}{\rho_{org}} \frac{k_{org}}{\left(\frac{1}{RH}-1\right)} \quad (1)$$

where  $m_{org}$  is the mass concentration of organic aerosol,  $\rho_w$  is the density of water ( $\rho_w=1.0\text{g}/\text{cm}^3$ ),  $\rho_{org}$  is the mean density of organics assumed to be  $1.4\text{g}/\text{cm}^3$ (Guo et al., 2015), and  $k_{org}$  is the hygroscopicity parameter of organic aerosol ( $k_{org} = 0.087$ )(Li et al., 2016). Adopting these values, we estimate that the annual  $ALWC_o$  and  $ALWC_i$  from 2011 to 2019 are approximately  $1.4\text{--}2.5\mu\text{g}/\text{m}^3$  and  $25.8\text{--}35.8\mu\text{g}/\text{m}^3$ , respectively. That is  $ALWC_o$  accounted for 4.3%–7.5% of the total aerosol liquid water content from 2011 to 2019.

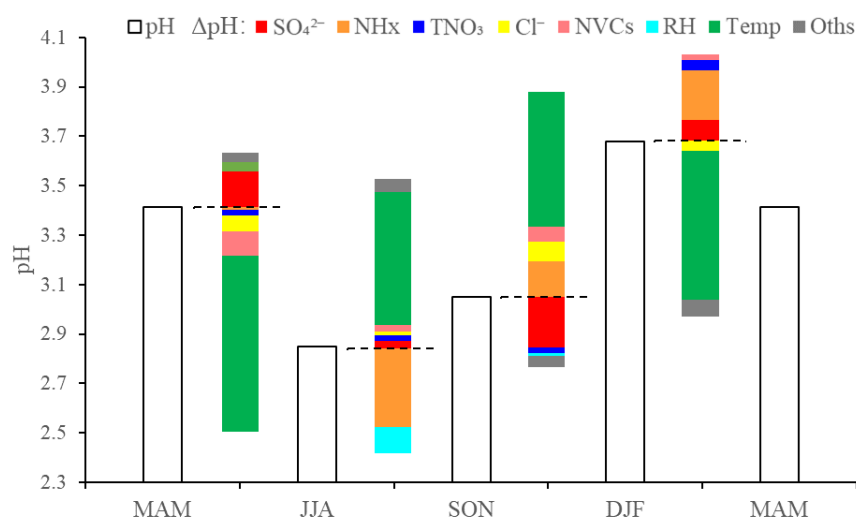
2. I found the convention used in Figures 1b, 3, and 5 very confusing. The pie charts below each figure are useful and seem straightforward to interpret, but the bar charts need substantial editing. For example, in Figure 1b, the effect of NVCs on the pH trends changes signs with time. Ultimately, using Fig. S6, I was able to deduce that the positive value associated with NVCs for 2011–2013 meant that NVCs had gone up, and the negative value associated with NVCs for 2013 – 2015 meant that NVCs had gone down. However, it took far too much time to interpret and is still not easily understandable even after spending much time on it. The convention used by Tao and Murphy (2021) is much clearer – I suggest edits to follow their approach.

**Response:** Thanks for the comment. To study the driving factors of aerosol pH, different sensitivity analysis methods have been used in previous studies (Ding et al., 2019; Tao and Murphy, 2021; Zheng et al., 2020). The convention used in Tao and Murphy (2021) defined the base scenario as the average condition, aiming at illustrating the contribution of different factors to the deviation from the base scenario. However, the base scenario can change with the analysis time periods. In comparison, our bar plot here aimed at showing the factor contribution of the  $\Delta\text{pH}$  between two adjacent scenarios (i.e., two continuous years or two continuous hour periods), and is not subject to change in the average conditions. That is, our plots emphasized differently with that used in Tao and Murphy (2021). We've clarified this in the revised figure captions. In addition, to provide more viewpoints, we've added the figures with Tao

and Murphy's approach in the supplement following the reviewer's suggestion.

**Changes in manuscript:**

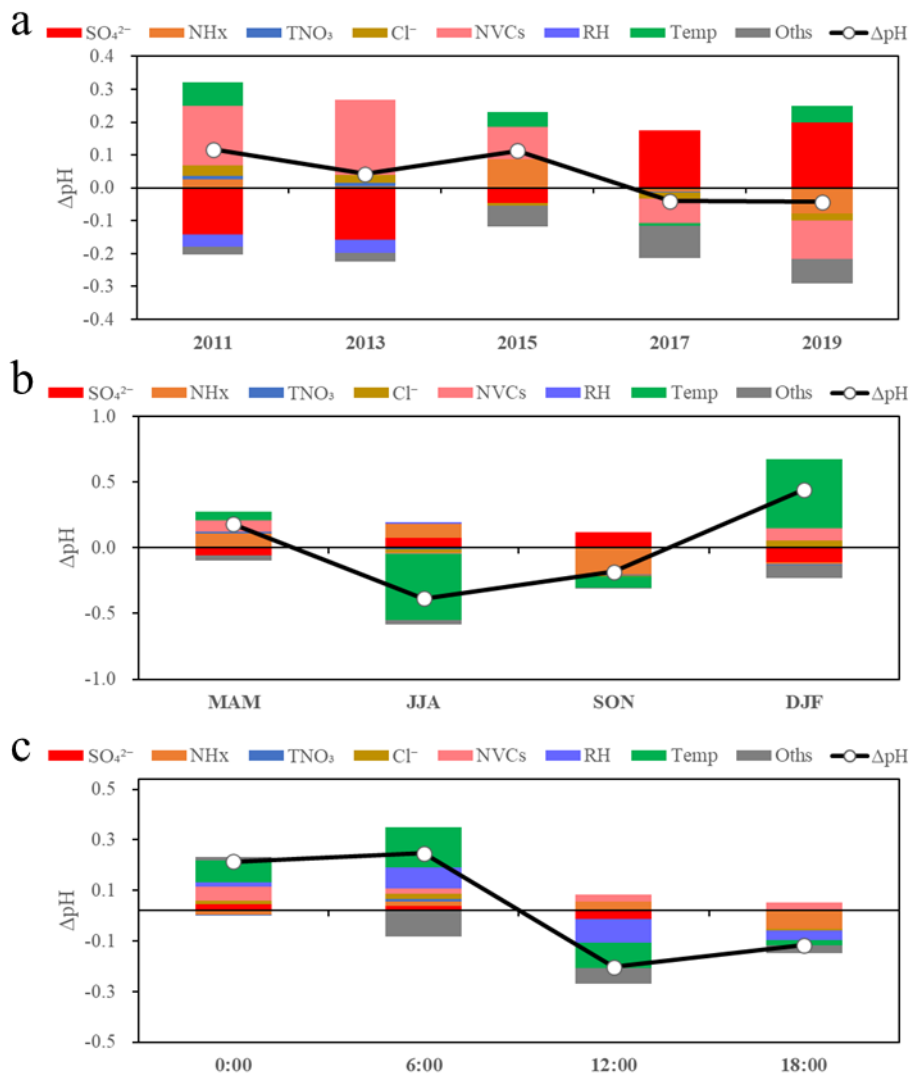
- (1) Line 204-206: "Figure 1b shows the contributions of individual factors to the  $\Delta\text{pH}$  from 2011 to 2019. Here the bar plots indicate the factors contributing to the  $\Delta\text{pH}$  between two adjacent scenarios, e.g., 2011 to 2013. See Fig. S9a for the factor contribution to the variation from average conditions."
  - (2) Line 241-243: "Figure 3 shows the contributions of individual factors to the  $\Delta\text{pH}$  across the four seasons. Here the bar plots indicate the factors contributing to the  $\Delta\text{pH}$  between two adjacent seasons, e.g., spring (MAM) to summer (JJA). See Fig. S9b for the factor contribution to the variation from average conditions."
  - (3) Line 273-275: "Figure 5 shows the effects of individual factors to the  $\Delta\text{pH}$  between day and night. Here the bar plots indicate the factors contributing to the  $\Delta\text{pH}$  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."
- We've revised Fig. 1b, 3 and 5 in the manuscript and added more description in the captions. For example, we've revised Fig. 3 into:



**Figure R1 (revised Fig. 3 in the manuscript). Contributions of individual factors to the  $\Delta\text{pH}$  across the four seasons.** Here the bar plots indicate the factors contributing to the  $\Delta\text{pH}$  between two adjacent seasons, e.g., spring (MAM) to summer (JJA). The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations; NH<sub>x</sub>, total ammonia; TNO<sub>3</sub>, total nitrate.

**Changes in supplement of manuscript:**

Line 111-117: We've added the Figures S9 in the revised supplement as:



**Figure R2 (added as Fig. S9 in the revised supplement). Fractional contribution of individual factors to the variations in aerosol pH from average conditions (i.e., averages of all observational data) during 2011–2019. (a) Annual variation; (b) Seasonal variation, and (c) diurnal variation. The meanings of the abbreviations: RH, relative humidity; Temp, temperature; NVCs, non-volatile cations;  $\text{NH}_x$ , total ammonia;  $\text{TNO}_3$ , total nitrate.**

3. Discussion about the limited effects of future emissions control measures on haze pollution (e.g., line 35-36, 298-299) is just wrong. Although the partitioning of  $\text{NH}_3$  and  $\text{HNO}_3$  may shift towards the particulate phase in the future, it does not mean their total PM concentration has increased. If the total concentration (i.e.,  $\text{NH}_3 + \text{NH}_4^+$ ) decreased enough, then a shift in partitioning towards the particle phase could still occur with a decrease in the aerosol  $\text{NH}_4^+$ . This discussion would be much better with associated predictions of the  $\text{PM}_{2.5}$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  aerosol concentrations.

**Response:** Thanks for the comment. We agree that the precursor decrease will finally lead to a PM decrease. 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 figures with more detailed explanations. In addition, we've added the prediction of the changes in major chemical components ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ) as Fig. 6g-i following the reviewer's suggestion. See detailed modifications below.

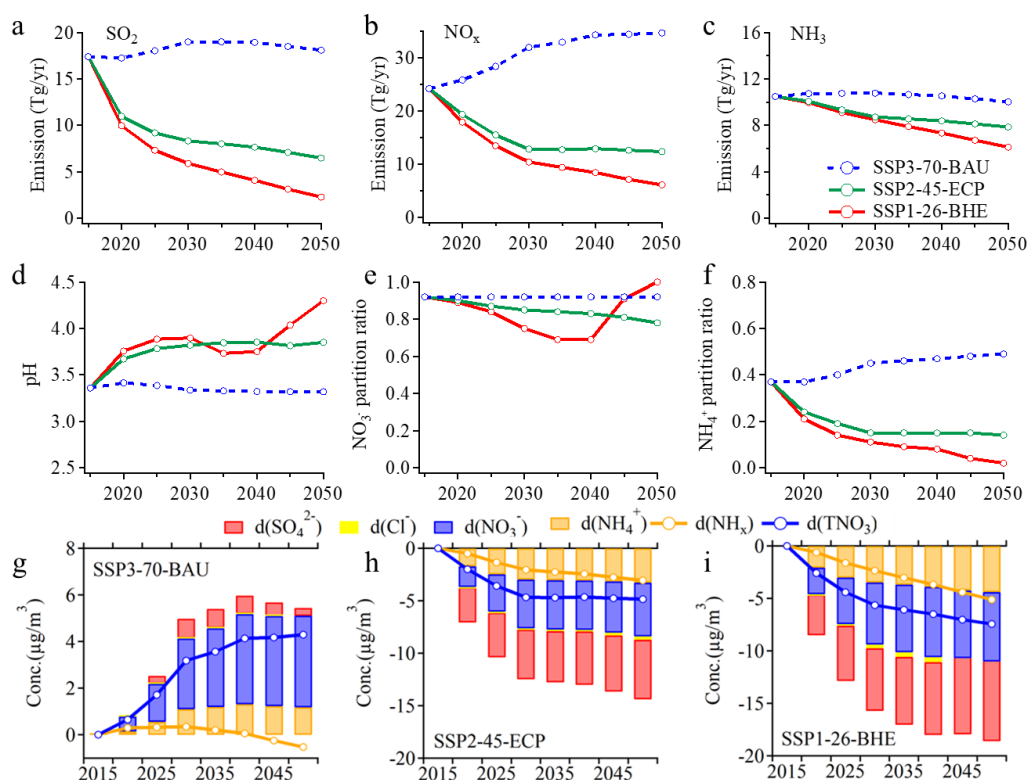
*Changes in manuscript:*

- (1) Line 34-38: We've revised the statement into: "The corresponding aerosol pH in eastern China is estimated to increase by  $\sim 0.9$ , and the reduction in particle phase  $\text{NO}_3^-$  and  $\text{NH}_4^+$  is less than the reduced amount of total  $\text{HNO}_3$  and total  $\text{NH}_3$ . This suggests a reduced benefit of  $\text{NH}_3$  and  $\text{NO}_x$  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),  $\text{SO}_2$  and  $\text{NO}_x$  are predicted to increase, while the  $\text{NH}_x$  is relatively stable. Correspondingly, both  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  will increase, and  $\text{NH}_4^+$  will also increase in response (Fig. 6g). Considering the stable  $\text{NH}_x$ ,  $\text{NH}_4^+$  partition ratio ( $\text{NH}_4^+ / (\text{NH}_4^+ + \text{NH}_3)$ ) will increase. In comparison, there is little change in aerosol pH and the predicted  $\text{NO}_3^-$  partition ratio ( $\text{NO}_3^- / (\text{NO}_3^- + \text{HNO}_3)$ ).

Under the moderate control policy (SSP2-45-ECP), the emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  in 2050 will be reduced by 62.7%, 49.0% and 25.0%, respectively. Correspondingly,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  will all decrease (Fig. 6h), with a total PM reduction of  $\sim 14.4 \mu\text{g m}^{-3}$ . Moreover, the predicted pH will increase by  $\sim 0.5$ , and the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  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  $\text{HNO}_3$  and  $\text{NH}_3$ , thus the reduced  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is higher than the reduced  $\text{NH}_x$  and  $\text{TNO}_3$ , 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  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{NH}_3$  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  $\text{NO}_3^-$  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  $\text{SO}_4^{2-}$  and constant NVCs. After 2040, there will be a major anion deficit considering the non-volatile species only (sulfate and  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ), and therefore more  $\text{NO}_3^-$  will be captured by the NVCs to the particle phase. As a result,  $\text{NO}_3^-$  partition ratio even increased from 0.92 in 2015 to 1.00 in 2050. Although  $\text{NH}_4^+$  partition ratio showed a continuous decrease, in 2050 both the reduced  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is smaller than the reduced  $\text{NH}_x$  and  $\text{TNO}_3$  (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 ( $\sim 18.6 \mu\text{g m}^{-3}$ ) than the moderate SSP2-45-ECP policy ( $\sim 14.4 \mu\text{g m}^{-3}$ ) indicating a reduced efficiency in terms of PM controls in responses to the emission controls. This would suggest a reduced benefit of  $\text{NH}_3$  and  $\text{NO}_x$  emission control in mitigating haze pollution in eastern China, especially after 2040."



**Figure R3 (revised Fig. 6 in the manuscript).** Emissions of SO<sub>2</sub> (a), NO<sub>x</sub> (b), NH<sub>3</sub> (c), predicted pH (d), NO<sub>3</sub><sup>-</sup> partition ( $\text{NO}_3^- / (\text{NO}_3^- + \text{HNO}_3)$ ) (e) and NH<sub>4</sub><sup>+</sup> partition ( $\text{NH}_4^+ / (\text{NH}_4^+ + \text{NH}_3)$ ) (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<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>) and reductions in TNO<sub>3</sub> and NH<sub>x</sub> under the three scenarios, including SSP3-70-BAU (g), SSP2-45-ECP (h) and SSP1-26-BHE (i).

4. The Conclusions section needs substantial revision. A brief recap is ok, but Section 4 is mostly redundant with the prior section. Rather than just reiterating what has already been said, more discussion of the significance of the work is warranted.

**Response:** Thanks for the comment. We rewrote the conclusions section. Please see the following changes.

**Changes in manuscript:**

Line 369-415: The specific modifications are as follows:

“The aerosol pH values at an urban site in Shanghai during 2011–2019 were calculated using ISORROPIA II. The trend analysis of aerosol pH in Shanghai during 2011–2019 was reported firstly based on observed gas and aerosol composition. Although significant variations of aerosol compositions were observed from 2011 to 2019 in YRD region, the aerosol pH estimated by model only slightly declined by 0.24 unit. We quantified the contributions from individual factors on the variation of aerosol pH from 2011 to 2019. We revealed that besides the multiphase buffer effect, the opposite effects of SO<sub>4</sub><sup>2-</sup> and non-volatile cations changes with a contribution of +0.38 and –0.35 unit on aerosol pH, respectively play a key role in determining the moderate pH trend from 2011 to 2019.

Distinct seasonal variations in the aerosol pH were observed, with maximum and minimum aerosol pH of  $3.59 \pm 0.57$  in winter and  $2.89 \pm 0.49$  in summer, respectively. Seasonal variations in aerosol pH

were mainly driven by the temperature, with the max  $\Delta\text{pH}$  of 0.63 existed between fall and winter. The diurnal cycle of particle pH was driven by the combined effects of temperature and relative humidity which could result in  $\Delta\text{pH}$  of -0.22 and +0.10 units, respectively. These results emphasized the importance of meteorological conditions in controlling the seasonal and diurnal variations of aerosol pH.

Finally, to explore the effects of China's future anthropogenic emission control pathways on aerosol pH and compositions, we chose three different emission reduction scenarios proposed by Tong et al. (2020) for future haze mitigation, naming SSP3-70-BAU, SSP2-45-ECP and SSP1-26-BHE as case studies. We estimated that the future trend of aerosol pH and  $\text{NO}_3^-$  partition ratio will change little under the weak control policy (SSP3-70-BAU), while  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  will increase substantially. The results also demonstrate that future aerosol pH will increase under both strict control policy (SSP1-26-BHE) and moderate control policy (SSP2-45-ECP), but more drastically under former scenario. The significant increase in aerosol pH with the strict control policy will lead to the reduced aerosol  $\text{NH}_4^+$  and  $\text{NO}_3^-$  is smaller than the reduced amount of total  $\text{NH}_3$  and total  $\text{HNO}_3$ , which is in contrast with effect of the moderate control policy. This suggests that a reduced efficiency in terms of PM controls in responses to the emission controls with the strict control policy. These results highlight the importance of proportional reductions in precursors and follow-up variations in aerosol pH in future pollution control policy."

5. Finally, the entire manuscript needs to be edited for language consistency – specifically, verb tenses change within and between paragraphs. There are too many instances to list here.

**Response:** Thanks for the comment. The language consistency in the manuscript has been polished, please see the modifications in the revised manuscript.

#### Technical/Minor Comments

1. Line 25: define all acronyms on their first use (e.g., NVCs, YRD)
2. Line 28-29: sentence needs grammatical editing.
3. Line 39: suggest deleting "studies"
4. Line 44-45: cite also Tilgner et al. (2021) in this group.
5. Line 73: cite also Vasilakos et al. (2018) and Nenes et al. (2020)
6. Line 77: "composition" should be singular
7. Line 78: suggest changing "characterizing" to "characterize"
8. Line 96: change "to be" to "were"
9. Line 96: "calibration" is not the right term here – LiBr is used as an internal standard
10. Line 102: due to unmeasured species (organic acid ions, carbonate) – it is quite possible to measure the aerosol inorganic composition accurately and not achieve an ion balance. Given what we know about organic acid concentrations, it is actually surprising that such a balance is observed.
11. Line 104: cite also Stieger et al. (2018)
12. Line 106: suggest deleting "techniques"
13. Line 107: give the instrument(s) used to measure T and RH
14. Line 128: cite also Battaglia Jr., et al. (2019)
15. Line 237-238: the diurnal behavior of aerosol pH is not just consistent with Beijing, but is far more consistent (qualitatively) with many other locations like the SE USA (Guo et al., 2015), eastern US (Battaglia et al., 2017), Chicago (Battaglia et al., 2017), which shows the important influences of T and RH on aerosol pH.
16. Line 274: "active actions" should be changed

17. Line 284: comma needed before “respectively”

**Response:** Thanks for the comments. We’ve revised the manuscript based on the above comments. Please see the following changes.

**Changes in manuscript:**

- (1) Lines 24-26: We added the definition of NVCs and YRD. Please see the details as follows: “The implementation of the Air Pollution Prevention and Control Action Plan led to -35.8%, -37.6%, -9.6%, -81.0% and 1.2% changes of PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, NH<sub>x</sub>, non-volatile cations (NVCs) and NO<sub>3</sub><sup>-</sup> in Yangtze River Delta (YRD) region during this period.”
- (2) Lines 26-30: We rewrote this sentence, please see the details as follows: “Different from the fast changes of aerosol compositions due to the implementation of the Air Pollution Prevention and Control Action Plan, aerosol pH showed a moderate change of -0.24 unit over the 9 years. Besides the multiphase buffer effect, the opposite effects from the changes of SO<sub>4</sub><sup>2-</sup> and non-volatile cations played key roles in determining the moderate pH trend, contributing to a change of +0.38 and -0.35 unit, respectively”
- (3) Line 41: We deleted the word “studies”, please see the details as follows: “Aerosol acidity is an important parameter in atmospheric chemistry.”
- (4) Line 44-47: We added the cite of Tilgner et al. (2021) as: “Aerosol acidity has attracted an increasing concern in recent years because of its impacts on the thermodynamics of gas-particle partitioning, pH-dependent condensed-phase reactions and trace metal solubility(Cheng et al., 2016; Fang et al., 2017; Guo et al., 2017; Guo et al., 2016; He et al., 2018; Song et al., 2018; Su et al., 2020; Tilgner et al., 2021; Weber et al., 2016).”
- (5) Line 73-76: We added the cites of Vasilakos et al. (2018) and Nenes et al. (2020), please see the details as follows: “Aerosol pH may change due to the significant changes of the chemical composition in PM<sub>2.5</sub>, which may feedback to the multiphase formation pathways of aerosols such as sulfate, nitrate and ammonium (Cheng et al., 2016; Nenes et al., 2020; Vasilakos et al., 2018)”
- (6) Line 78-80: We edited this sentence as: “A thermodynamic model, ISORROPIA II (version 2.1) (Fountoukis and Nenes, 2007) was applied to estimate the pH based on 9-year continuous online measurements of PM<sub>2.5</sub> composition at an urban site in Shanghai.”
- (7) Line 80-81: We edited this sentence, please see the details as follows: “The main purposes of this study are to: (1) characterize the long-term trend of aerosol pH;”
- (8) Line 98-99: We edited this sentence into: “To better track the retention time changes of different ion species and ensure their concentrations were measured successfully,”
- (9) Line 98-100: We rewrote this sentence into: “To better track the retention time changes of different ion species and ensure their concentrations were measured successfully, an internal standard check was conducted every hour with Lithium Bromide (LiBr) standard solution (Qiao et al., 2014; Zhou et al., 2016).”
- (10) Line 105-108: Indeed, the measurements of organic acid ions were lacked in our study. However, we find that in previous studies, the concentrations of organic acid in Shanghai area were low. Ding et al., (2021) found that total dicarboxylic acids in Chongming Island in Shanghai during the day and night was 375±282 ng/m<sup>3</sup> and 341±270 ng/m<sup>3</sup>, respectively, and the ketocarboxylic acids ranged from 3.3 ng/m<sup>3</sup> to 125 ng/m<sup>3</sup>. Yao et al., (2002) also found that the sum of oxalate, malonate and succinate only account for 0.3-2% of the total mass of the water-soluble ions in Shanghai. The concentrations of organic ions were significantly lower than that of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, which were the main anions in aerosol of Shanghai. Due to the low concentrations of organic acids in PM<sub>2.5</sub>, they

may have minor effects on ion balance. Meanwhile, we also find that the average equivalent ratios of cation/anion(C/A) were close to unity in many cities of China (Huang et al., 2014; Shen et al., 2010; Sun et al., 2006; Zhang et al., 2018). In our study, the modelled and measured  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations were in good agreement based on observed aerosol composition, further indicating that the measurement of the ions was accurate. We rewrote this sentence as: “The correlation between cation and anion was strong ( $R^2=0.94$ ), with a slope of 1.00, indicating that these ion species were charge balanced and well represented major components in  $\text{PM}_{2.5}$ .”

- (11) Line 108-110: We added the cites of Stieger et al. (2018) as: “In previous studies, intercomparison experiments between MARGA and filter-based method have been carried out, and the data measured by MARGA showed acceptable accuracy and precision (Rumsey et al., 2014; Huang et al., 2014; Stieger et al., 2018)”
- (12) Line 110-113: We edited this sentence as: “The mass concentrations of  $\text{PM}_{2.5}$  were simultaneously measured using an on-line beta attenuation PM monitor (FH 62 C14 series, Thermo Fisher Scientific) at a time resolution of 5 min.”
- (13) Line 112-114: We added the instrument information used to measure T and RH, please see the details as follows: “The temperature and RH were also measured using meteorological parameters monitor (Metone 597, Met One Instruments) at a time resolution of 1 min.”
- (14) Line 135-137: We added the cite of Battaglia Jr., et al. (2019) in this sentence as: “The use of  $ALWC_i$  to predict pH is therefore fairly accurate and common(Battaglia Jr et al., 2019; Battaglia et al., 2017; Ding et al., 2019)”
- (15) Line 270-272: We rewrote this sentence into: “Figure 4 shows the diurnal variations in the aerosol pH and its potential drivers. Aerosol pH in Shanghai exhibits notable diurnal variations, being higher during nighttime.”
- (16) Line 314-315: We rewrote this sentence into: “SSP3-70-BAU is a reference scenario that without additional efforts to constrain emissions.”
- (17) Line 330-333: We edited this sentence into: “Moreover, the predicted pH will increase by  $\sim 0.5$ , and the  $\text{NO}_3^-$  and  $\text{NH}_4^+$  partition ratios will decrease by 0.14 and 0.23, respectively (green lines in Fig. 6d-f).”

## Referee 2

### 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 these 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,  $\text{SO}_4^{2-}$ ,  $\text{TNO}_3$ ,  $\text{NH}_x$ ,  $\text{Cl}^-$  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,  $\Delta pH_i$ , 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  $\Delta pH$  from 2011 to 2019. Here the bar plots indicate the factors contributing to the  $\Delta pH$  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  $\Delta pH$  across the four seasons. Here the bar plots indicate the factors contributing to the  $\Delta pH$  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  $\Delta pH$  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  $\Delta pH$  between day and night. Here the bar plots indicate the factors contributing to the  $\Delta pH$  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  $\Delta pH$  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  $\sim 0.9$ , 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.”

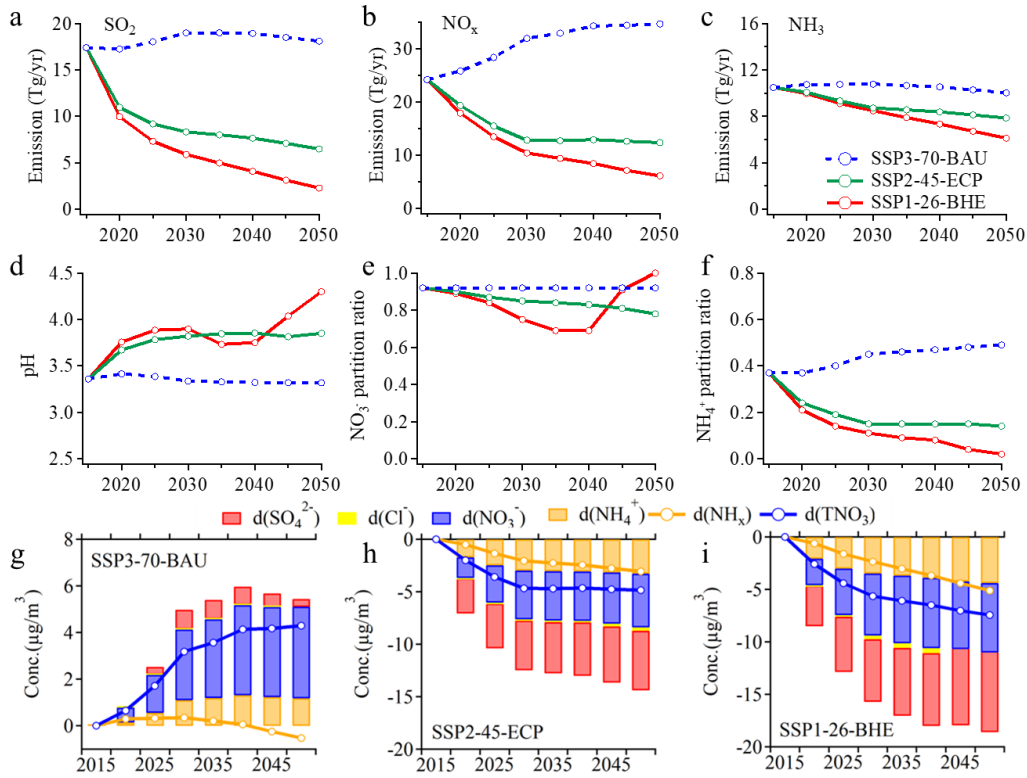
(2) Discussions in section 3.4: We've revised Fig. 6 and the corresponding discussions into (Line 320-

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<sub>2</sub> and NO<sub>x</sub> are predicted to increase, while the NH<sub>x</sub> is relatively stable. Correspondingly, both SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> will increase, and NH<sub>4</sub><sup>+</sup> will also increase in response (Fig. 6g). Considering the stable NH<sub>x</sub>, NH<sub>4</sub><sup>+</sup> partition ratio (NH<sub>4</sub><sup>+</sup> / (NH<sub>4</sub><sup>+</sup> + NH<sub>3</sub>)) will increase. In comparison, there is little change in aerosol pH and the predicted NO<sub>3</sub><sup>-</sup> partition ratio (NO<sub>3</sub><sup>-</sup> / (NO<sub>3</sub><sup>-</sup> + HNO<sub>3</sub>)).

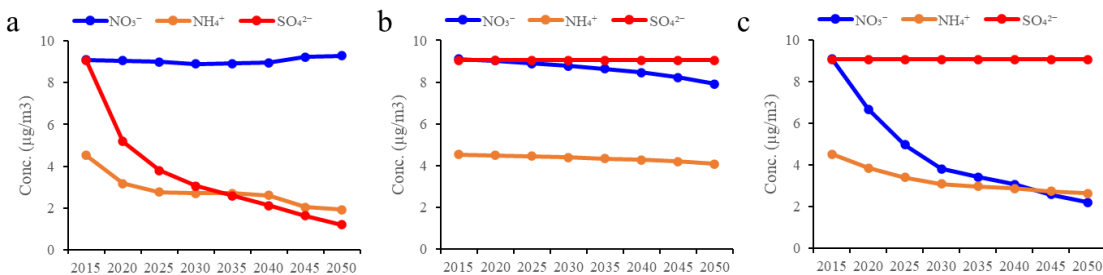
Under the moderate control policy (SSP2-45-ECP), the emissions of SO<sub>2</sub>, NO<sub>x</sub>, and NH<sub>3</sub> in 2050 will be reduced by 62.7%, 49.0% and 25.0%, respectively. Correspondingly, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> will all decrease (Fig. 6h), with a total PM reduction of ~14.4 μg m<sup>-3</sup>. Moreover, the predicted pH will increase by ~0.5, and the NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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<sub>3</sub> and NH<sub>3</sub>, thus the reduced NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> is higher than the reduced NH<sub>x</sub> and TNO<sub>3</sub>, 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<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> 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<sub>3</sub><sup>-</sup> 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<sub>4</sub><sup>2-</sup> and constant NVCs. After 2040, there will be a major anion deficit considering the non-volatile species only (sulfate and Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>), and therefore more NO<sub>3</sub><sup>-</sup> will be captured by the NVCs to the particle phase. As a result, NO<sub>3</sub><sup>-</sup> partition ratio even increased from 0.92 in 2015 to 1.00 in 2050. Although NH<sub>4</sub><sup>+</sup> partition ratio showed a continuous decrease, in 2050 both the reduced NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> is smaller than the reduced NH<sub>x</sub> and TNO<sub>3</sub> (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<sup>-3</sup>) than the moderate SSP2-45-ECP policy (~14.4 μg m<sup>-3</sup>) indicating a reduced efficiency in terms of PM controls in responses to the emission controls. This would suggest a reduced benefit of NH<sub>3</sub> and NO<sub>x</sub> emission control in mitigating haze pollution in eastern China, especially after 2040.”



**Figure R4 (revised Fig. 6 in the manuscript).** Emissions of  $\text{SO}_2$  (a),  $\text{NO}_x$  (b),  $\text{NH}_3$  (c), predicted pH (d),  $\text{NO}_3^-$  partition ( $\text{NO}_3^- / (\text{NO}_3^- + \text{HNO}_3)$ ) (e) and  $\text{NH}_4^+$  partition ( $\text{NH}_4^+ / (\text{NH}_4^+ + \text{NH}_3)$ ) (f) in China from 2015 to 2050 under the three scenarios published in Tong et al.(2020). Predicted the changes in major chemical components ( $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ) and reductions in  $\text{TNO}_3$  and  $\text{NH}_x$  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  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  aerosol concentrations if only one gaseous precursor reduction is implemented (Figure R4). As shown in Figure R4, if only  $\text{SO}_2$  reduction is implemented,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  concentrations will show a significant decrease from 2015 to 2050, while  $\text{NO}_3^-$  concentration will generally keep constant between 2015-2040 and then increase slightly during 2040-2050. If only  $\text{NH}_x$  reduction is implemented,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations will be slightly reduced while  $\text{SO}_4^{2-}$  concentration will remain unchanged from 2015 to 2050. However, if only  $\text{NO}_x$  reduction is implemented, both  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations will be significantly reduced.



**Figure R5** The mass concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  aerosol from 2015 to 2050 if only

SO<sub>2</sub>(a), NH<sub>x</sub>(b) and NO<sub>x</sub>(c) reductions were implemented under the SSP1-26-BHE scenario published in 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. R6), 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. R7). We found that the high C/A ratio samples are mainly driven by the increased NVCs, while the other chemical compositions (anions and NH<sub>4</sub><sup>+</sup>) 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<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> from 2011 to 2019, with the annual decrease rates of 14.4%, 30.0% and 15.2%, respectively (Fig. R8). 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., 2019a). 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<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> with the sum of NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> in neq/m<sup>3</sup> 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<sup>2+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> 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:

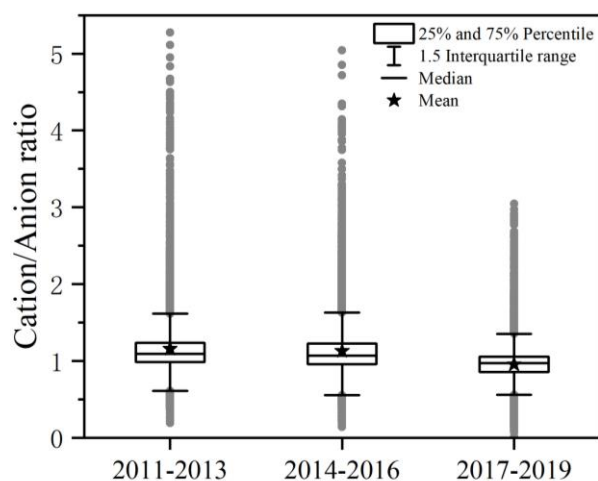


Figure R6 (added as Fig. S3 in the revised supplement) The box plots of Cation/Anion ratios during 2011-2013, 2014-2016, and 2017-2019

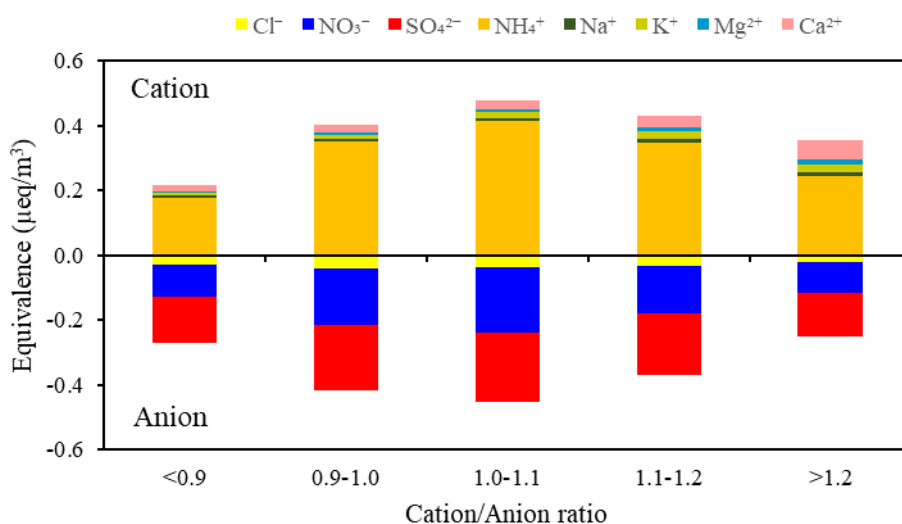


Figure R7 (added as Fig. S4 in the revised supplement) Average equivalence concentrations of cation and anion at different level of Cation/Anion ratio

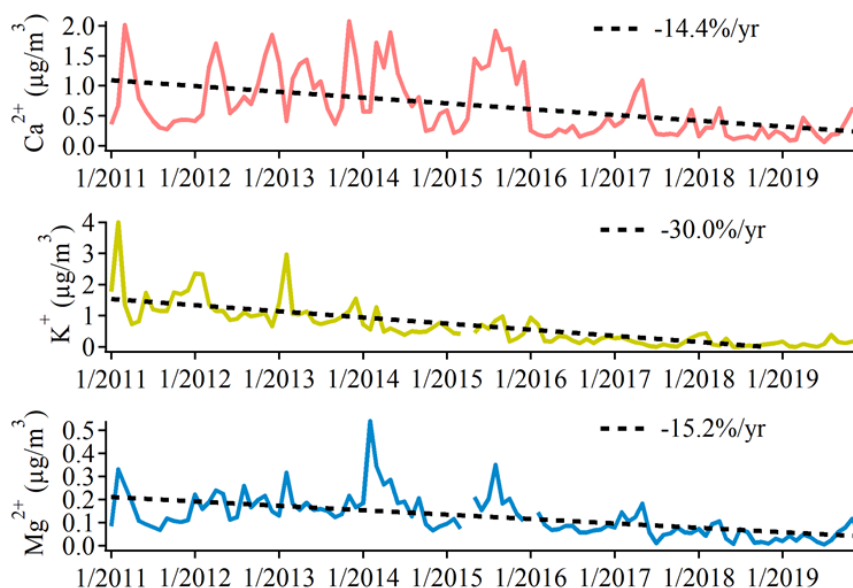


Figure R8 (added as Fig. S5 in the revised supplement) Monthly mean concentrations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  from 2011 to 2019

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.

- 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?

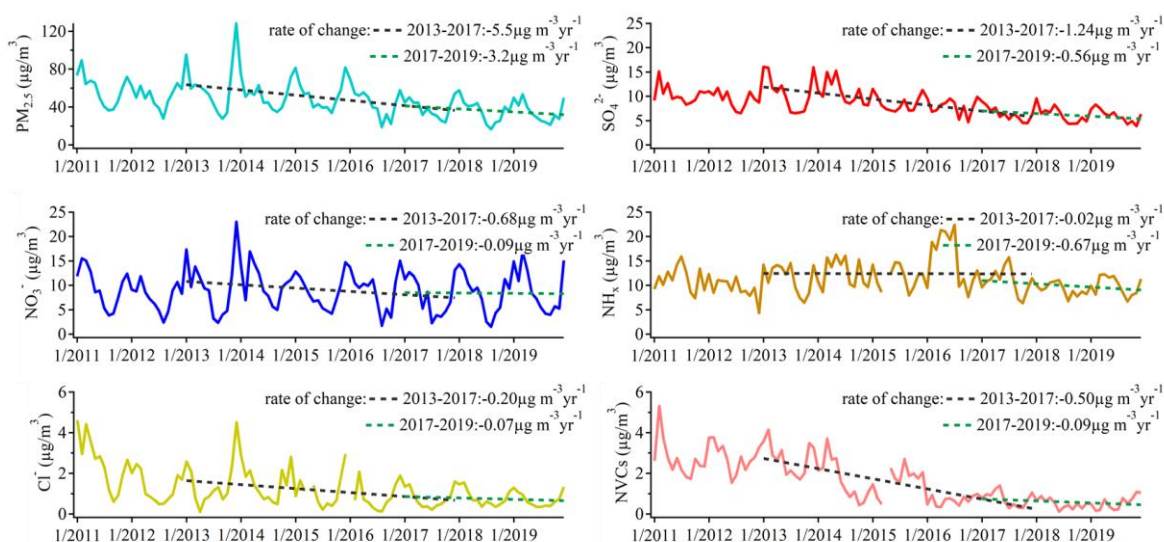
**Response:** Thanks for the comment. We've added more panels in Fig. 6 and rewrote this section. Please see our response to your comment #2.

- 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 R9 (revised as Fig. S8 in the revised supplement) Monthly mean of PM<sub>2.5</sub>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>x</sub>, Cl<sup>-</sup> 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.

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