Atmospheric Chemistry and Physics
Ref: egusphere-2025-2204

Long–term Trends in $PM_{2.5}$ Chemical Composition and Its Impact on Aerosol Properties: Field Observations from 2007 to 2020 in Pearl River Delta, South China

Response Letter to Reviewer's Comments

Dear reviewer:

We sincerely thank you for your time and valuable comments. We have carefully revised the manuscript to improve its clarity and enhance the readers' understanding. Our point-by-point responses are marked in blue and the corresponding changes to the original text are shown below each response. We hope that these revisions adequately address the comments and concerns.

Comment 1. Properly define $PM_{2.5}$.

Response: We change it as "particulate matter with aerodynamic diameter less than 2.5 µm" in the introduction.

Particulate matter with aerodynamic diameter less than 2.5 µm ($PM_{2.5}$) is a major air pollutant with significant implications for global climate, air quality, and human health.

Comment 2. Define ALWC.

Response: We have added definition of ALWC as "aerosols liquid water content" in the introduction.

This change has an important impact on aerosol acidity, aerosol liquid water content (ALWC), and light extinction.

Comment 3. The IMPROVE equation was developed by the US National Park Service with some support from the EPA. There are two IMPROVE equations. The first, IMPROVE equation 1 (EPA, 2003), was based on the work in Malm et al., (1994). This was replaced in 2007 with the IMPROVE equation 2 (Pitchford et al., 2007) based on the work of Malm et al., (2007) and Hand et al., (2007). The IMPROVE equation 1 uses constant scattering efficiencies base on fixed size distributions for the different aerosol components. In IMPROVE equation 2 the scattering efficiencies are dependent on the aerosol concentrations. Specifically, the scattering efficiencies are a weighted average of the scattering efficiency derived from a small and large size distribution and the weights are proportional to the aerosol concentration (Pitchford et al., 2007). Which IMPROVE equation is used in this work is not discussed and needs to be clarified.

Response: We give a brief introduction about the first and revised IMPROVE equations, and clarify that we used the revised IMPROVE equation in this study.

To estimate the light extinction coefficient (b_{ext}), the first Interagency Monitoring of Protected Visual Environments (IMPROVE) equation was developed by the U.S. National Park Service with support from the U.S. Environmental Protection Agency (EPA) (Malm et al., 1994; EPA, 2003), but this equation tended to underestimate/overestimate the highest/lowest b_{ext} values. Consequently, the revised IMPROVE equation was then proposed (Malm and Hand, 2007; Pitchford et al., 2007).

We also calculated b_{ext} by the revised IMPROVE equation and compared to the local parameter scheme.

Comment 4. "The hygroscopic growth factor (f(RH)), which has been suggested to depend on secondary inorganic fractions (e.g., sulfate, nitrate, and ammonium), sea salt components, and water-soluble organic carbon, is solely a function of relative humidity (RH) in the algorithm" If IMPROVE equation 2 is being used then this is an incorrect statement.

Response: We added the information that f(RH) in the revised IMPROVE equation is not only dependent on RH but also particle size distribution (based on aerosol mass concentration).

In addition, the calculation of hygroscopic growth factor (f(RH)) in the revised equation depends on relative humidity (RH) and particle size distribution (or aerosols mass), but does not account for the chemical composition in aerosols, which has been shown to significantly affect f(RH) (Li et al., 2021). These simplifications could lead to large discrepancies in polluted regions.

Comment 5. "IMPROVE program in the United States, initiated in 1985, tracks visibility trends and their driving factors (Epa, 2011)". The EPA reference is not in the reference list. There are many journals article reporting on the purpose of the IMPROVE program and use of the data and should be used as the reference instead of an EPA report. For example, see Hand et al., (2024) and references there in.

Response: We apologize for the error in citation. We have changed it to journal article.

Many long-term monitoring programs have been implemented to formulate pollution control strategies and explore underlying factors of aerosol properties variation. For example, the IMPROVE program in the United States, initiated in 1985, tracks visibility trends and their driving factors (Hand et al., 2024).

Comment 6. "anions (.e. Cl-, NO3- and SO42-) were analyzed with an ion-chromatography system…" The authors should note that some ammonium nitrate volatilizes from the quartz fiber filters during sampling and handling causing underestimations in NH4+ and NO3- concentrations (Yu et al., 2006). In addition, if possible, provide an estimate of the underestimation, which should be carried over into the discussion of particulate nitrate concentrations.

Response: We acknowledge that the volatilization of ammonium nitrate can lead to negative bias in measurements of NO_3^- and NH_4^+ and have included relevant discussion into Set. 2.2 and 3.2.2. According to previous studies, this volatilization may result in underestimations of 8%–16% for NO_3^- and 10%–28% for NH_4^+. Because our measurements were conducted in winter, the relatively lower temperature and relative humidity did not favor the volatilization, thereby reducing the extent of underestimation. In addition, the measurements were conducted in the same season and such losses are expected to be systematic over time. Consequently, it would not significantly influence the long-term trends in NO_3^- and NH_4^+.

Due to the negative mass artifacts associated with the volatilization of ammonium nitrate, the measured concentrations of $NO_3^−$ and NH_4^+ may be underestimated (Chow et al., 2005; Yu et al., 2006).

Previous studies reported that the volatilization of ammonium nitrate during sampling can cause negative mass artifacts, leading to the underestimation of both $NO_3^−$ (8%–16%) (Chow et al., 2005) and NH_4^+ (10%–28%) (Yu et al., 2006). The volatilization is highly dependent on the changes in relative humidity (RH) and temperature. However, such losses are expected to be systematic over time and therefore are unlikely to significantly affect their general trends in this study, because our measurements were conducted in the same season.

Comment 7. Measuring long-term trends is very challenging, and seemingly, small changes in sampling and analysis protocols can introduce discontinuities in the PM trends. This is particularly true for thermal optical carbon analyses, since the measured OC and EC are operationally defined and sensitive to changes in the method. The authors should note any changes in the monitoring protocols over the 14-year time span and discuss any evidence for or against these changes introducing discontinuities in the trends.

Response: In this long-term observation, we consistently employed the same measurement instruments and analytical protocols. Field and laboratory blank samples were analyzed in the same way as field samples. All the OC/EC and cation/anion data were corrected using the field blanks. As shown in Fig. S1, all measured compounds exhibited minimal variability in the blank filter samples. This indicated that the influence of analytical or sampling bias related to blank subtraction and experimental procedures was limited, further supporting the reliability of the long-term trends observed in this study. We add this statement in QA/QC section.

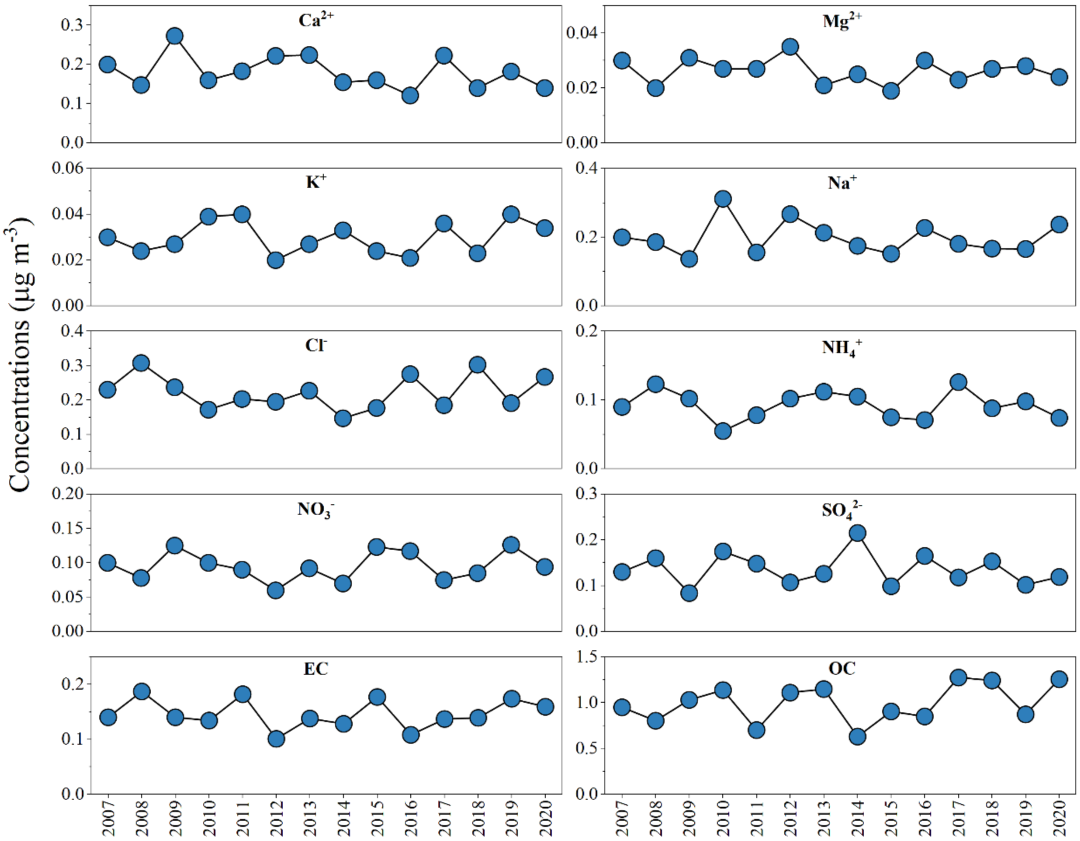


Figure S1. Annual variations in measured compounds of blank filter samples.

Comment 8. "Bayesian Inference Approach and suggested it had significant advantages in accurately estimating POC and SOC". All of methods to estimate POC and SOC from OC and EC data are highly uncertain. This should be conveyed in the paper. For example, instead of saying "suggested it had significant advantages in accurately estimated..." could use "suggested it more accurately estimated…"

Response: Thanks for correcting that. We should deliver that all methods to estimate POC and SOC will introduce uncertainty.

Recently, Liao et al. (2023) proposed Bayesian Inference Approach and suggested it more accurately estimated POC and SOC compared to the conventional method, such as EC–tracer method, minimum ratio value, minimum R squared, and multiple linear regression.

Comment 9. The annual bar chart in Figure 2 provides the change in the absolute concentrations overtime. It is difficult to see the trends in the changing PM2.5 composition. I suggest the authors include a graph similar to Figure 2a of the annual relative contributions of aerosol components to PM2.5 in the main document or supplemental information.

Response: Thanks for suggestion. This graph will make changes in chemical composition more visible. We have added the similar graph into supplement.

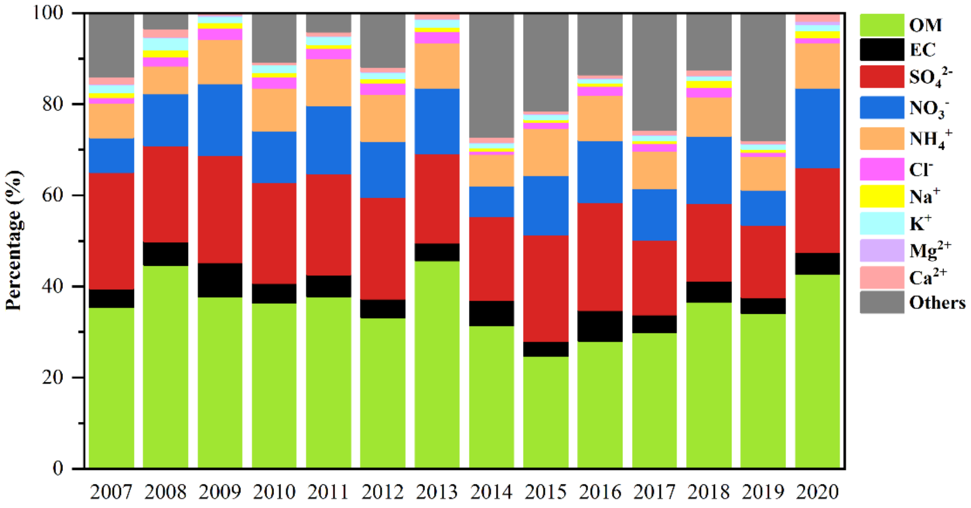
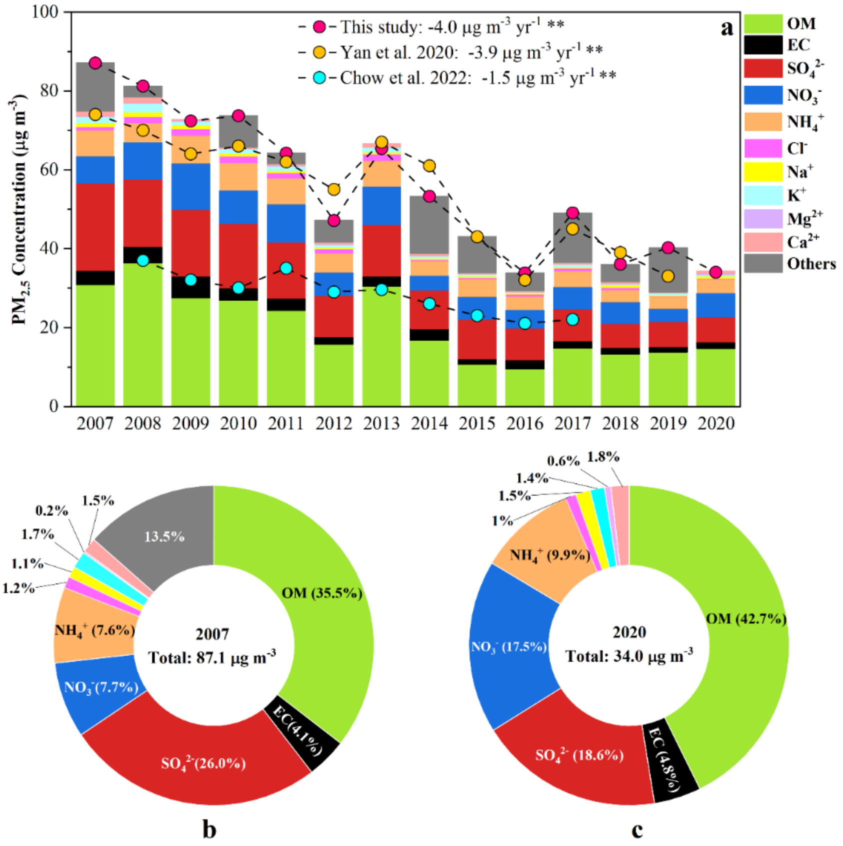


Figure S4. The changes in percentage of $PM_{2.5}$ chemical composition.

Comment 10. In Figure 2, could some indication of the SOC and POC concentrations be included?



Response: We considered that OM = conversion factor 1 × POC + conversion factor 2 × SOC. It is unreasonable to replace OM with POC and SOC, and we want to highlight the changes in OM here. In addition, we have presented the variations in POA and SOA in supplement, which could indicate the change in POC and SOC. In addition, we add the detailed information about POC and SOC into Table S1 in supplement.

Table S1. The variations in PM2.5 main components, meteorological parameters, and other species from 2007 to 2020

	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
I. Gaseous pollutants (μg m^{-3})														
SO$_2$	71.3 ± 21.4	73.5 ± 20.1	59.8 ± 20.3	49.5 ± 20.3	35.6 ± 9.9			32.4 ± 11.0	23.8 ± 8.8	20.8 ± 7.1	26.4 ± 6.3	18.3 ± 3.9	14.0 ± 3.2	12.2 ± 3.5
NO$_2$	58.3 ± 10.3	72.1 ± 28.0	71.0 ± 16.5	49.6 ± 16.3	59.0 ± 14.8			54.2 ± 17.8	49.1 ± 17.3	40.6 ± 19.9	54.8 ± 19.8	53.4 ± 16.3	47.6 ± 19.7	44.7 ± 13.5
O$_3$	75.3 ± 31.4	63.2 ± 17.3	51.6 ± 25.0	69.1 ± 27.0	54.3 ± 22.8			53.0 ± 18.1	78.9 ± 37.0	59.9 ± 31.2	72.0 ± 38.7	60.1 ± 27.7	105.1 ± 21.9	74.5 ± 37.5
II. PM$_{2.5}$ main components (μg m^{-3})														
PM$_{2.5}$	87.1 ± 15.5	81.2 ± 18.0	72.4 ± 21.3	73.7 ± 37.5	64.2 ± 13.6	47.1 ± 14.0	65.4 ± 24.2	53.2 ± 14.6	43.0 ± 17.9	33.8 ± 12.8	49.1 ± 18.2	36.0 ± 9.6	40.2 ± 11.2	34.0 ± 11.3
OM	30.9 ± 7.6	36.3 ± 12.6	27.5 ± 11.2	26.9 ± 12.7	24.3 ± 8.7	15.6 ± 6.9	30.4 ± 14.1	16.7 ± 6.1	10.6 ± 5.1	9.5 ± 4.1	14.7 ± 4.9	13.2 ± 4.8	13.7 ± 3.6	14.6 ± 4.3
POC	10.4 ± 3.1	13.5 ± 3.4	10.9 ± 4.5	11.0 ± 4.9	9.4 ± 3.1	4.5 ± 1.4	11.0 ± 3.6	8.2 ± 4.6	4.4 ±1.9	4.4 ± 1.7	4.3 ± 2.1	5.0 ± 2.1	4.3 ± 1.8	4.4 ± 1.1
SOC	7.7 ± 2.2	7.2 ± 2.4	5.4 ± 1.9	4.4 ± 2.0	4.7 ± 1.5	3.9 ± 1.6	6.0 ± 4.3	1.6 ± 0.5	1.6 ± 0.7	1.1 ± 0.4	4.7 ± 2.0	2.5 ± 0.9	4.0 ± 1.2	3.9 ± 1.7
SO$_4^{2-}$	22.2 ± 6.0	17.1 ± 5.5	17.0 ± 5.9	16.3 ± 6.5	14.2 ± 4.7	10.5 ± 4.4	13.1 ± 9.1	9.7 ± 3.2	10.1 ± 4.6	8.0 ± 2.7	8.1 ± 3.4	6.1 ± 2.0	6.4 ±1.9	6.6 ±2.9
NO$_3^-$	6.7 ± 3.1	9.2 ± 4.2	11.5 ± 4.6	8.4 ± 4.8	9.6 ± 4.0	5.8 ± 5.4	9.6 ± 8.4	3.6 ± 2.3	5.6 ± 5.2	4.6 ± 3.8	5.5 ± 3.8	5.3 ± 2.9	3.1 ± 2.2	6.3 ± 3.4
NH$_4^+$	6.6 ± 1.7	4.9 ± 2.4	7.1 ± 2.3	6.9 ± 3.8	6.6 ± 2.3	4.8 ± 2.1	6.6 ± 4.4	3.7 ± 1.4	4.5 ± 2.4	3.4 ± 1.7	4.0 ± 1.7	3.1 ± 1.3	3.0 ± 0.9	3.4 ± 1.4
Cl$^-$	1.01 ± 0.54	1.61 ± 1.27	1.80 ± 1.03	1.49 ± 1.16	1.46 ± 0.93	1.21 ± 0.74	1.44 ± 1.12	0.38 ± 0.33	0.55 ± 0.37	0.52 ± 0.34	0.75 ± 0.66	0.75 ± 0.72	0.36 ± 0.36	0.39 ± 0.15
Na$^+$	0.97 ± 0.66	0.93 ± 0.61	0.89 ± 0.18	0.60 ± 0.29	0.56 ± 0.16	0.40 ± 0.14	0.56 ± 0.26	0.36 ± 0.10	0.27 ± 0.08	0.25 ± 0.14	0.34 ± 0.14	0.52 ± 0.34	0.27 ± 0.14	0.48 ± 0.20
K$^+$	1.49 ± 0.57	2.23 ± 0.01	0.97 ± 0.41	1.20 ± 0.61	1.14 ± 0.46	0.69 ± 0.32	1.13 ± 0.81	0.60 ± 0.21	0.49 ± 0.25	0.30 ± 0.13	0.59 ± 0.24	0.35 ± 0.15	0.46 ± 0.15	0.48 ± 0.22
Mg^{2+}	0.15 ± 0.05	0.11 ± 0.05	0.23 ± 0.09	0.04 ± 0.04	0.08 ± 0.02	0.07 ± 0.03	0.10 ± 0.05	0.07 ± 0.02	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.02	0.05 ± 0.02	0.05 ± 0.02	0.21 ± 0.12
Ca^{2+}	1.30 ± 0.57	1.46 ± 0.72	0.27 ± 0.17	0.33 ± 0.14	0.53 ± 0.12	0.47 ± 0.35	0.85 ± 0.49	0.64 ± 0.16	0.27 ± 0.21	0.26 ± 0.13	0.52 ± 0.22	0.45 ± 0.15	0.27 ± 0.14	0.10 ± 0.03
III. Meteorological parameters														
Temperature (℃)	22.2 ± 2.1	17.2 ± 2.9	17.0 ± 3.1	19.7 ± 3.2	19.9 ± 3.8	22.1 ± 1.4	20.9 ± 1.1	20.2 ± 4.4	25.1 ± 2.4	23.8 ± 3.8	21.3 ± 3.2	22.4 ± 2.9	21.7 ± 2.7	20.2 ± 5.1
RH (%)	57 ± 11	47 ± 12	67 ± 13	64 ± 11	57 ± 11	61 ± 7	50 ± 13	57 ± 14	63 ± 8	67 ± 7	56 ± 13	63 ± 12	48 ± 11	55 ± 13
SSR (W m^{-2})	161.3 ± 41.3	156.5± 28.3	135.2 ± 36.3	141.8 ± 51.4	134.7 ± 36.9	101.2 ± 40.4	125.2 ± 46.2	95.3 ± 49.1	149.0 ± 36.2	122.4 ± 44.0	128.9 ± 53.1	122.2 ± 39.9	165.0 ± 29.4	145.5 ± 31.9
Wind speed (m s^{-1})	1.3 ± 0.2	1.3 ± 0.4	1.7 ± 0.5	1.7 ± 0.7	1.8 ± 0.9	1.2 ± 0.6	1.3 ± 0.3	1.9 ± 0.6	1.5 ± 0.3	1.6 ± 0.4	1.7 ± 0.4	1.6 ± 0.5	1.6 ± 0.3	1.7 ± 0.4
IV. Other species														
ALWC (μg m^{-3})	20.6 ± 10.0	11.3 ± 7.9	28.8 ± 11.4	22.0 ± 10.8	19.3 ± 9.9	13.5 ± 5.6	12.0 ± 7.5	10.8 ± 5.4	12.5 ± 6.2	12.0 ± 7.3	9.9 ± 6.5	11.0 ± 6.7	5.1 ± 2.5	9.5 ± 3.9
pH	1.51 ± 1.07	2.60 ± 0.71	1.94 ± 0.29	1.97 ± 1.00	2.54 ± 0.37	2.55 ± 0.43	2.69 ± 0.42	2.29 ± 0.33	2.13 ± 0.33	2.05 ± 0.46	2.60 ± 0.45	2.66 ± 0.37	2.31 ± 0.63	2.86 ± 0.49

Comment 11. Despite the slight decline in their concentrations, our result showed that the relative reductions of EC (-9% yr-1)…" This is confusing. What is meant by "slight decline"? A 9% decrease per year is not slight.

Response: We apologize for this misunderstanding. What we want to deliver is that the reduction in absolute concentration ($–0.97$ µg m^{-3} yr^{-1}) was slight. It will lead to misunderstand and is irrelevant with the main point so we delete it.

Our result showed that the relative reductions of EC (–9% yr^{-1}), K^+ (–12%) and Ca^{2+} (–11% yr^{-1}) were greater than that of $PM_{2.5}$ (–7% yr^{-1}), confirming that control measures for these sources had been effective.

Comment 12. "When NO2 levels are low, the accumulation of nitrate is hindered due to volatilization losses." This is a confusing sentence. What are the volatilization losses? Those from the filter? Also, ammonium nitrate volatilization from the filter is not really dependent on NO2 levels, but is dependent on temperature and relative humidity.

Response: Thanks for pointing this confusing statement. The "volatilization losses" should be put as "partitioning of nitrate from particle phase to gas phase". When NO_2 level is low, the formation of HNO_3, gaseous precursor of NO_3^- is suppressed. Therefore, the reaction in eq. 2 tends to proceed to the left. This indicates that more NO_3^- will partition into gas phase, leading to less NO_3^- accumulates in particle phase.

$$OH\ (g) + NO_2\ (g) + M \rightarrow HNO_3\ (g) + M \qquad \text{(eq. 1)}$$

$$HNO_3(g) + NH_3\ (g) \leftrightarrow NO_3^-(aq) + NH_4^+(aq) \qquad \text{(eq. 2)}$$

The generally lower intercepts observed in the NO_3^-/NO_2 regression compared to those in the SO_4^{2-}/SO_2 regression can be explained by the semi-volatile nature of nitrate (Yu et al., 2006). The formation of HNO_3, gaseous precursor of NO_3^-, is suppressed under low NO_2 level. Therefore, the reaction in R2 tends to proceed to the left. This facilitates partitioning of NO_3^- into gas phase, leading to less accumulation of NO_3^- in particle phase. In contrast, sulfate is the least volatile among all the inorganic aerosol components (Kang et al., 2022), allowing it to be stably retained in the particle phase once formed.

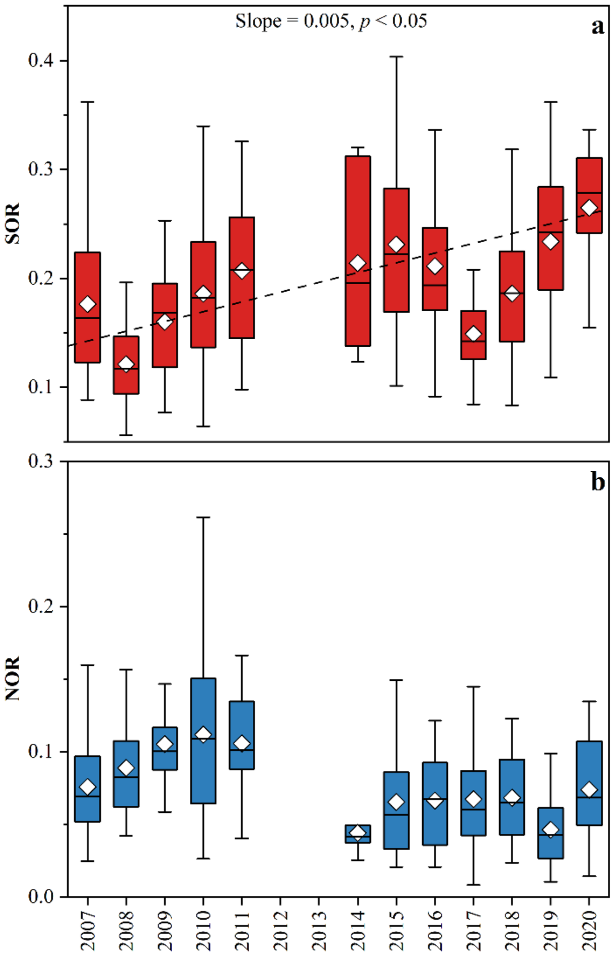
Comment 13. "As shown in Fig 5a, a dramatic increase in SOR was observed during 2007–2020 ($p < 0.05$). The SOR value in 2020 (0.24 ± 0.09) was twice as high as that in 2008 (0.12 ± 0.07)". Comparing 2008 to 2020 is a bit of cherry picking. There is a lot of variability in the data and 2007 SOR are only 30-40% smaller than 2020. I suggest a robust trend line, e.g. use Theil regression, is calculated from the data, and then use the slope of the trend line to estimate the change over time.

Response: Thanks for pointing out our mistake. We double checked the result and found that an extreme point in 2020 was not excluded when we conducted average calculation, which was not included in the plot. We have corrected it. Comparing 2008 to 2020 is not reasonable. Instead, we compared the beginning point (2007) with the end point (2020). We used the slopes derived from

Theil-Sen regression in to represent the change rates of different species in this study, and we added this clarification in QA/QC section. A robust line was also added into the SOR plot.

The change rates were calculated using the slopes derived from Theil–Sen regression and evaluated for statistical significance via the non-parametric Mann–Kendall test, providing a robust and reliable assessment of temporal variations.

As shown in Fig. 5a, the SOR value in 2020 (0.26 ± 0.09) was 44% higher than that in 2007 (0.18 ± 0.07). In general, SOR exhibited a significant upward trend during 2007–2020, increasing at a rate of 0.005 yr^{-1} (3% yr^{-1}, $p < 0.05$).



Comment 14. This meant that the conversion of NO2 to NO3- became weaker, resulting in a greater reduction in NO3- compared to NO2." This is not obvious to me. How do you know that the difference in the trends is not driven by changes in the partitioning of NO3 between the gas and particle phase?

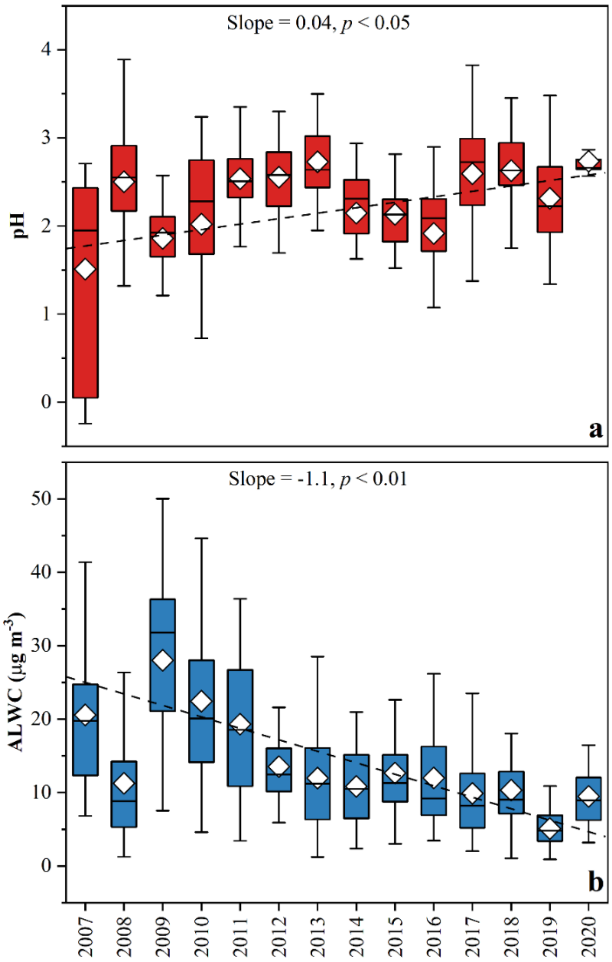
Response: Our statement here was not precise. To make it more structure and logical, we combined the results of correlation analysis to illustrate that the lower NOR was caused by both weaker heterogeneous formation pathway of nitrate and enhanced partitioning of nitrate from particle phase into gas phase.

The largest regression coefficient and the strongest correlation between ALWC and NOR suggested that the change in NOR was primarily driven by ALWC. The lower ALWC levels after

2013 (Fig. 6b) suppressed heterogeneous formation pathway of nitrate and enhanced the partitioning of nitrate from particle phase into gas phase, leading to the overall lower NOR after 2013.

Comment 15. “Aerosol pH increased from 1.51 ± 1.07 to 3.29 ± 1.43, at a rate of 0.06 yr–1 ($p < 0.05$*).” In figure 6a, the largest pH is about 2.7 not 3.29. Also, I do not see a trend in these data. Similar to the suggestion for figure 5, it would be best to fit a robust trend line through the data and use its slope to define the change over time.*

Response: Thanks for pointing out our mistake. Same as mentioned in response 13, there was an extreme point which was not excluded in calculation and we have corrected that. The pH value in 2020 should be 2.86 ± 0.49. In addition, we also derived a robust line into the graph, with the slope derived from Theil-Sen regression.



Comment 16. Which IMPROVE equation is being used to estimate the light extinction?

Response: We add clarification before comparing the result.

We also calculated b_{ext} by the revised IMPROVE equation and compared to the local parameter scheme (Fig. S21). Generally, b_{ext} estimated by the revised IMPROVE equation (335.72 ± 219.64 Mm^{-1}) was significantly higher than that estimated by local parameter scheme (262.67 ± 143.82 Mm^{-1}).

Comment 17. "Our results indicated that the IMPROVE equation tend to overestimate bext in elevated pollution periods." The authors did not provide any evidence that one bext equation was better than the other was, so they should only say that the IMPROVE equation had higher bext than that estimated from equations 5-8 for high PM2.5 concentrations. This is important, because many studies have shown that scattering efficiencies of secondary aerosols are correlated with concentrations. It was this observation that drove the development of the IMPROVE equation 2. Therefore, it is quite possible that the fixed scattering efficiencies in equation 5 would cause an underestimation of the bext.

Response: Due to lack of real measurements of bext, it unreasonable to say the revised IMPROVE equation tend to overestimate bext in elevated pollution periods. We have changed the statement.

Our results indicated that the revised IMPROVE equation tended to generate higher b_{ext} in elevated pollution periods. Thus, more site–specific parameters and local parameter scheme are needed in those areas to predict b_{ext} more accurately.