General.

We would like to appreciate the editor and reviewers for providing the valuable comments and a better perspective on our work to improve the manuscript. In particular, we are very grateful to the editor and reviewers for giving us the opportunity to make revision. We have revised our manuscript by fully taking the reviewers' comments into account. Responses to specific comments raised by the reviewers are described below. All the changes made and appeared in the revised text are shown in red. All detailed answers to comments are displayed in blue.

Comments of Referee #1 and our responses to them

The manuscript entitled "Measurement report: Characteristics of aminiums in PM2.5 during winter clean and polluted episodes in China: aminium outbreak and its constraint" presents the pollution characteristics of amine organic compounds in PM2.5 in 11 regions of China. It focuses on the comparative analysis of clean and polluted days. While the study has certain scientific significance, the analysis and discussion part of the study is not in-depth enough, and there are still some problems that the author needs to further answer or improve.

Response: We appreciate your professional review for our article. We have revised the manuscript to address the comments. Our responses to the specific comments and changes made in the manuscript are given below.

Specific comments:

1) *Q1: The English writing of the article required modification prior to publication. The text contained numerous descriptions that were overly complex, rendering them opaque and indirect. For example, Lines 175-179.*

Response: We are very sorry for the confusion caused by our expression. We have shortened and updated the long sentences.

Lines 185–188: …$MMAH^+$ and $DMAH^+$ (as the second most abundant species) constituted over 63% of the total aminium concentrations in those northern cities. The relatively minor species, including $DEAH^+$, EAH^+, PAH^+, BAH^+, and $PYRH^+$, contributed between 1% and 18% of the total aminium concentrations…

Lines 250–253: …Additionally, this region is surrounded by barren mountains and sandy land (Ma et al., 2024) (Figure 2). Apparently, the weak amine emission intensity appears to be responsible for the low levels of aminiums in the WLMQ…

Lines 389–393: …Accordingly, it can be concluded that the observed increase in aminium concentrations in XA and BJ during the polluted days is not adequately explained by the effects of atmospheric oxidation and temperature. Furthermore, the insignificant correlation between aminiums and acidic components in XA and BJ suggests that other factors affecting aminium formation must be considered…

2) *Q2: The whole study only analyzes and explores the correlation and ratio relationship between regions and components. The reasons for the clarification need to be further demonstrated. There is no analysis of the mechanism relationship between amines and*

particulate matter, and much experimental literature has been studied.

Response: We greatly appreciate your comments and fully understand your considerations. Please allow me to provide a brief summary of the highlights or writing logic of this manuscript.

(1) We discussed the pollution characteristics of aminiums in winter aerosols in China.

(2) We found that the acid-base chemistry was significantly associated with the formation of aminiums in $PM_{2.5}$ in all cities excepting Xi'an and Beijing.

(3) Based on the correlation analysis and sensitivity analysis, we proposed the possibility of the competitive uptake of ammonia versus amines on acidic aerosols or the displacement of aminiums by ammonia in Xi'an and Beijing (constraining aminium outbreaks).

For the highlight (3), there are only a few mechanism studies available for reference. We have discussed this in the manuscript (Lines 494–498).

Thus, this paper presents the observation results in the form of measurement reports.

In particular, we not only emphasized the limitations of the observation results but also clarified the need for further research to confirm our observations.

Lines 44–47: …Overall, this study deepens the understanding of the spatiotemporal differences in aminium characteristic and formation in China. However, the uptake of amines on particles to form aminiums and the relevant influencing factors require further mechanistic research…

Lines 494–498: …Although a recent study has also demonstrated that the possibility of

individual aminium was displaced by ammonia in an environment of high ammonia level (Chen et al., 2022a), the uptake of amines on particles to form aminiums and the relevant influencing factors are still not fully understood in terms of mechanism…

Lines 506–509: …Further laboratory validation experiments are required to substantiate this inference. In particular, it is essential to conduct prolonged observational research in settings with elevated ammonia levels and depleted amine concentrations in the near future…

3) *Q3: The article only stays at the level of analyzing phenomena. The organic amines on the filter membrane are still aged particulate organic matter. The results are not accurate enough for source estimation using correlation and ratio.*

Response: We did not consider the impact of continuous aging of aminiums collected on the filter on the measurement results. This is mainly due to the following reasons. The $PM_{2.5}$ samples investigated in this study are all acidic (Tables S1-S3), promoting the protonation of amino groups. The protonated amino group is difficult to undergo oxidation by oxidants (e.g., hydroxyl radicals and ozone) (Nielsen et al., 2012).

Lines 157–162: …It should be noted that we did not consider the impact of continuous aging of aminiums collected on the filter on the measurement results. This is mainly due to the following reasons. The $PM_{2.5}$ samples investigated in this study are all acidic (Tables S1-S3), promoting the protonation of amino groups. The protonated amino group is difficult to undergo oxidation by oxidants (e.g., hydroxyl radicals and ozone)

(Nielsen et al., 2012).

4) *Q4: The article mentions that the XA and BJ sampling sites differ more than others. The reason should be compared and analyzed to recent 2-3 years of literature on the source of air pollution. And while Figure 5 of the article only shows the correlation of NH4+ with NO3-, SO42-, and total organic acids in XA and BJ, how does a clean day compare to a polluted day?*

Response: We thank you for these important comments. We are very sorry for any confusion caused by our discussions. We did not mention the differences between the sampling points of XA and BJ and others.

The concentrations of the total aminiums in LZ, TY, HEB, WLMQ, CD, WH, HZ, GZ, and GY were significantly correlated with those of the NH_4^+ and acidic components (Figure 4 and Figure S3), indicating that NH_4^+ was also significantly correlated with the acidic components. However, this case did not appear in XA and BJ. Thus, Figure 5 is only to determine the correlation of NH_4^+ with NO_3^-, SO_4^{2-}, and total organic acids in XA and BJ. Furthermore, since most of the days studied in XA were polluted days, we did not compare the difference in this correlation between clean and polluted days.

In particular, for Figure 5, our intention is as follows. The concentrations of total aminiums in LZ, TY, HEB, WLMQ, CD, WH, HZ, GZ, and GY showed significant positive correlations ($P < 0.01$) with those of the acidic components (e.g., NO_3^-, SO_4^{2-}, organic acids, and acidity (expressed as $(NO_3^- + 2SO_4^{2-}) - NH_4^+$)), whereas an insignificant correlation ($P > 0.05$) was found between them in BJ and XA. However, we found that the concentrations of NH_4^+ were strongly ($P < 0.01$) correlated with those

of acidic components in XA and BJ (**Figures 5c–h**). The concentration of ammonia in the atmosphere is 1 to 3 orders of magnitude higher than that of low-molecular-weight alkylamines. The particles are acidic at all study sites, with an average pH value ranging from 2.4 to 5.7. These results indicate that the acidity of the particles was sufficient for the uptake of ammonia and amines to form ammonium and aminiums in XA and BJ.

5) *Q5: Line 20-122, please accurately describe the sampling times for particulate filters.*

Response: The revisions have been made in the revised manuscript.

Lines 121–126: …. Specifically, the sampling periods in LZ, TY, HEB, BJ, XA, WLMQ, CD, WH, HZ, GZ, and GY were Dec. 2–30, 2017, Dec. 2–30, 2017, Dec. 18, 2017 – Jan. 15, 2018, Dec. 22, 2017 – Jan. 21, 2018, Dec. 22, 2017 – Jan. 20, 2018, Mar. 3–28, 2018, Dec. 1 – 31, 2017, Dec. 6–29, 2017, Dec. 4–31, 2017, Dec. 1–30, 2017, and Dec. 10, 2017 – Jan. 11, 2018, respectively (**Tables S1-S3**)…

6) *Q6: Line 250-251: Figure 4 does not reflect the different seasons, please correct this.*

Response: Here we are referring to Table S4 (Line 264).

7) *Q7: Line 251-257: The conclusions of the presentation in this paragraph are comparable to those of the previous study. It would be beneficial to include the data from the previous research results in a comparison in the figure.*

Response: We greatly appreciate your suggestions. Due to the large number of references and data cited, it is difficult to present all the data aesthetically on one figure. And hence, we summarized all the data in **Table S4**. Furthermore, we have specified the range of concentration in the revised manuscript, which can directly reflect the results of data comparison.

Lines 268–271: …Moreover, the average TA concentrations investigated here (4.16 ng m^{-3} – 56.90 ng m^{-3}) were also within the observation ranges reported in previous studies (1.49 ng m^{-3} – 329.80 ng m^{-3}) (Table S4)…

8) *Q8: Line 311-312: This passage has illustrated the inadequacy of traditional correlation analysis to account for research discrepancies. Moreover, the subsequent conclusions have not been further explored in terms of new methods.*

Response: We are very sorry for any confusion caused by our descriptions. Here, we want to emphasize that the prerequisite for amine source apportionment using the correlation between aminiums and indicators is that the gas-phase amines can be largely converted into aminiums in $PM_{2.5}$ through secondary processes without the influence of constrained factors. Namely, our focus is on the main factors affecting the formation of aminiums in particles. Thereby, we can answer why the concentrations of aminiums in XA and BJ showed insignificant positive correlations with those of the acidic components.

We have rewritten the relevant content.

Lines 315–317: …Clearly, the formation of particle-phase aminiums was closely associated with the origins of the corresponding gas-phase amines (as precursors of aminiums)…

Lines 321–327: …Thus, although lacking sufficient indicators (e.g., biogenic source traces) to trace the source of amines, our results can at least indicate that fossil fuel combustion or biomass burning may be important contributors to atmospheric amines in most of the investigated cities during the winter. This consideration was also supported by previous studies about the potential source analysis of aerosol aminiums in Guangzhou, Xuzhou, and Wulumuqi during the winter (Yang et al., 2023b; Shu et al., 2023; Ma et al., 2024)…

Lines 343–347: …Presumably, the prerequisite for amine source apportionment using the correlation between aminiums and indicators is that the gas-phase amines can be largely converted into aminiums in $PM_{2.5}$ through secondary processes without the influence of constrained factors. To further explore this issue, the following discussion focuses on the main factors affecting the formation of aminiums in particles…

9) *Q9: Line 319-322: The text is ambiguous. What is the author's intention here?*

Response: We have rewritten these contents.

Lines 343–347: …Presumably, the prerequisite for amine source apportionment using the correlation between aminiums and indicators is that the gas-phase amines can be largely converted into aminiums in $PM_{2.5}$ through secondary processes without the

influence of constrained factors. To further explore this issue, the following discussion focuses on the main factors affecting the formation of aminiums in particles…

10) *Q10: Line 359-360: Is it accurate to discuss atmospheric oxidation here and compare it with the average values? It is suggested that the changing trend of amine pollution level and atmospheric oxidation level should be further analyzed.*

Response: Indeed, we did not discuss in detail the specific mechanism by which atmospheric oxidation affects amine abundance here. In addition, the protonated amino group has been suggested to be difficult to undergo oxidation by hydroxyl radicals and ozone (Nielsen et al., 2012). In general, we just want to clarify that the observed increase in aminium concentrations in XA and BJ during the polluted days is not adequately explained by the effects of atmospheric oxidation.

Some revisions have been made in the revised manuscript.

Lines 384–386: …In particular, the protonated amino group has been suggested to be difficult to undergo oxidation by hydroxyl radicals and ozone (Nielsen et al., 2012)…

Lines 389–393: …Accordingly, it can be concluded that the observed increase in aminium concentrations in XA and BJ during the polluted days is not adequately explained by the effects of atmospheric oxidation and temperature. Furthermore, the insignificant correlation between aminiums and acidic components in XA and BJ suggests that other factors affecting aminium formation must be considered….

11) *Q11: Line 394-402: This paragraph is analyzed using the ratio relationship between total amines and ammonium salts. Is there a literature reference for this conclusion? Please add literature for further clarification.*

Response: There are no other observational studies that carry out our similar discussion. Thus, our study may provide valuable data references for future studies.

Generally, due to a lack of sufficient laboratory simulation experiments, this paper presents our observation results in the form of measurement reports. However, we not only emphasized the limitations of the observation results but also clarified the need for further research to confirm our observations.

Lines 44–47: …However, the uptake of amines on particles to form aminiums and the relevant influencing factors require further mechanistic research…

Lines 494–498: …Although a recent study has also demonstrated that the possibility of individual aminium was displaced by ammonia in an environment of high ammonia level (Chen et al., 2022a), the uptake of amines on particles to form aminiums and the relevant influencing factors are still not fully understood in terms of mechanism…

Lines 506–509: …Further laboratory validation experiments are required to substantiate this inference. In particular, it is essential to conduct prolonged observational research in settings with elevated ammonia levels and depleted amine concentrations in the near future…

12) *Q12: This paper discusses that although the component characteristics of TY and GZ*

areas are similar, there are great differences according to the scatter diagram. What are the reasons for the differences?

Response: $DEAH^+$ was the most abundant aminium species in TY. The composition characteristic of aminiums in the city of GZ was similar to that observed in TY. Anthropogenic emissions, including vehicle exhaust and industrial production are considered to be the main contributors to aerosol $DEAH^+$ in urban areas (Chen et al., 2022; Chen et al., 2019; Yang et al., 2023; Chang et al., 2022). A recent study has suggested that ethanol gasoline vehicles can emit a large amount of ethyl-amines, leading to the outbreak of $DEAH^+$ during the haze episodes in Hebei Province (North China) (Feng et al., 2022). Thus, the relative emission strength of anthropogenic DEA in the investigated amines was probably higher in TY (an inland city with application of ethanol gasoline vehicles) than in other cities. In addition, previous studies have suggested that aerosol $DEAH^+$ can also be largely derived from marine emissions (Facchini et al., 2008; Dall'osto et al., 2019). Since GZ is a developed coastal city, local aerosol aminiums may be influenced by large gaseous DEA inputs from both local industrial production and marine sources.

The added descriptions in the revised manuscript are shown below.

Lines 218–227: …. A recent study has suggested that ethanol gasoline vehicles can emit a large amount of ethyl-amines, leading to the outbreak of $DEAH^+$ during the haze episodes in Hebei Province (North China) (Feng et al., 2022). Thus, the relative emission strength of anthropogenic DEA in the investigated amines was probably higher in TY (an inland city with application of ethanol gasoline vehicles) than in other

cities. In addition, previous studies have suggested that aerosol $DEAH^+$ can also be largely derived from marine emissions (Facchini et al., 2008; Dall'osto et al., 2019). Since GZ is a developed coastal city, local aerosol aminiums may be influenced by large gaseous DEA inputs from both local industrial production and marine sources…

At last, we deeply appreciate the time and effort you've spent in reviewing our manuscript.

Reference:

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