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 Reviewer #2 and our responses to them

Comments:

This work presents the measurements of aminiums in PM2.5 collected from 11 cities in China during winter, and compares their characteristics and chemistry between the clean and polluted periods to investigate the key factors influencing the aminium outbreak during the polluted periods. The authors suggested that the competitive uptake of ammonia versus amines on acidic aerosols and/or the displacement of aminiums by ammonia in ambient aerosols are the key to limiting aminium outbreaks. I find this to be a useful contribution to the literature to advance knowledge about amines. Indeed, amines (/aminiums) are important in many aspects of atmospheric chemistry. These datasets are valuable for amine-related chemistry in the atmosphere. In general, the paper is well written, and this reviewer recommends its publication after addressing the following minor comments.

Response: We appreciate the reviewer's valuable comments on our work. Our responses

to the specific comments and changes made in the manuscript are given below.

Specific Comments:

1) *The aliphatic amines are typically in the gas-phase, thus their presence in aerosol particles should be attributable to acid-base chemistry and/or other processes. This implies that all aminiums reported here were predominantly formed through secondary processes. In discussing sources, you refer to the sources of gas-phase amines. It is important to highlight that these gas-phase amines from diverse sources are mainly partitioned into the particle phase through secondary processes. This should be clear.*

Response: We greatly thank you for your professional review of our article. These are very critical issues. We have emphasized this in the revised manuscript.

Lines 312–317: …. It is well documented that aminiums in $PM_{2.5}$ can be formed mainly via the uptake of their gaseous form (i.e., amines) by aqueous particles, followed by acid-base neutralization reactions (Ge et al., 2011; Xie et al., 2018; Sauerwein and Chan, 2017; Qiu and Zhang, 2013; Liu et al., 2023). Clearly, the formation of particle-phase aminiums was closely associated with the origins of the corresponding gas-phase amines (as precursors of aminiums)…

2) *Line 232: Significant figures should be unified.*

Response: The revision has been made in the revised manuscript (Line 245).

3) RH is another important factor affecting the formation of aliphatic aminiums in addition to acidity. This should be considered.

Response: We thank the reviewer for this insightful comment. The updated discussions about this are shown below.

Lines 372–376: …Significantly increased RH values (i.e., high ALW) (**Figure 5a**) and acidic components (**Figure 5b**) on polluted days were also observed in XA and BJ. Nevertheless, the insignificant correlation between aminiums and acidic components and ALW concentrations in XA and BJ, together with a relatively small proportional increase in aminiums (**Figure 2**) from clean to polluted days at these two sites suggest that besides acidity and RH, there were other key factors affecting aminium formation in XA and BJ…

4) Line 301: Please consider using a more suitable word instead of "roughly".

Response: We have rewritten this sentence in the revised manuscript.

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)…

5) *Lines 363–366: Please rephrase the sentence.*

Response: The sentence has been rewritten.

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…

6) *Regarding the sensitivity analysis of the aminiums/ammonium ratio to ammonium changes, the results presented here are very intuitive and interesting. Have similar comparisons been made in previous studies? Alternatively, can the datasets be compared with previous observations?*

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…

7) *Lines 433–435: Please rephrase this part. For example, "The concentrations, compositions, and temporal and spatial variations of aminiums in PM2.5 in 11 different Chinese cities during the winter were systematically investigated to reveal the key factors affecting the aminium outbreak during the polluted days".*

Response: We have simplified and rewritten this section.

Lines 460–463: …The concentrations, compositions, and temporal and spatial variations of aminiums in $PM_{2.5}$ in 11 different Chinese cities during the winter were systematically investigated to reveal the key factors affecting the aminium outbreak during the polluted days…

8) *The author has proposed some meaningful conclusions based on field observation data, such as "the competitive uptake of ammonia against amines on acidic aerosols in the ambient atmosphere in XA and BJ". I know that the atmospheric environment in the real*

world is very complex, so the author should point out in the article that further laboratory validation experiments for this conclusion or long-term observation studies in high ammonia and low amine environments are necessary in future research.

Response: More discussions have been added to the manuscript.

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., 2022), 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…

9) *Lines 473–477: The author should point out that the occurrence of this situation may lead to an insignificant correlation between aminiums and indicators in the particle phase.*

Response: The revision has been made in the manuscript.

Lines 501–506: …Furthermore, if the uptake of amines is significantly constrained by

the aforementioned factors, the traditional source apportionment methods using correlation analysis between particle aminiums and tracers will have significant uncertainty due to the weakened partitioning of the amines into the particle phase (i.e., causing insignificant correlations between aminiums and indicators)…

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

Reference:

Chen, D., Yao, X., Chan, C. K., Tian, X., Chu, Y., Clegg, S. L., Shen, Y., Gao, Y., and Gao, H.: Competitive Uptake of Dimethylamine and Trimethylamine against Ammonia on Acidic Particles in Marine Atmospheres, Environmental Science & Technology, 56, 5430-5439, 10.1021/acs.est.1c08713, 2022.

Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part II. Thermodynamic properties and gas/particle partitioning, Atmospheric Environment, 45, 561-577, https://doi.org/10.1016/j.atmosenv.2010.10.013, 2011.

Liu, T., Xu, Y., Sun, Q.-B., Xiao, H.-W., Zhu, R.-G., Li, C.-X., Li, Z.-Y., Zhang, K.-Q., Sun, C.-X., and Xiao, H.-Y.: Characteristics, Origins, and Atmospheric Processes of Amines in Fine Aerosol Particles in Winter in China, J. Geophys. Res.: Atmos., 128, e2023JD038974, https://doi.org/10.1029/2023JD038974, 2023.

Qiu, C. and Zhang, R.: Multiphase chemistry of atmospheric amines, Physical Chemistry Chemical Physics, 15, 5738-5752, 10.1039/C3CP43446J, 2013.

Sauerwein, M. and Chan, C. K.: Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles, Atmos. Chem. Phys., 17, 6323-6339, 10.5194/acp-17-6323-2017, 2017.

Xie, H., Feng, L., Hu, Q., Zhu, Y., Gao, H., Gao, Y., and Yao, X.: Concentration and size distribution of water-extracted dimethylaminium and trimethylaminium in atmospheric particles during nine campaigns - Implications for sources, phase states and formation pathways, Science of The Total Environment, 631-632, 130-141, https://doi.org/10.1016/j.scitotenv.2018.02.303, 2018.