

Dear ACP editor:

After reading the comments from you and the reviewers, we have carefully revised our manuscript. Our responses to the comments are itemized below.

Anything for our paper, please feel free to contact Prof. Gehui Wang via ghwang@geo.ecnu.edu.cn.

All the best

Can Wu

On behalf of Prof. Gehui Wang

August 16, 2026

Reviewer(s)' Comments to Author:

Reviewer 1

General comments

The manuscript presents a valuable and timely multi-site winter dataset on water-soluble BrC across the North China Plain, combining multiple analytical approaches. This integrative framework is a clear strength and provides important insights into the role of nitrogen-containing organic compounds in BrC formation. That said, some of the central conclusions, particularly regarding the causal role of $\text{NH}_3/\text{NH}_4^+$, remain somewhat stronger than what the current evidence can fully support. These issues are largely addressable through clarification, improved framing, and more cautious interpretation.

Reply: We greatly appreciate the reviewer's valuable and constructive comments. In response, we have carefully revised the manuscript, and further softened corresponding statements to ensure a more accurate interpretation of our results. See details below.

Major comments:

1. The manuscript states that secondary NOCs were mainly formed through aerosol aqueous reactions with ammonia playing an important role, and further argues for NH_3 emission control as indispensable for BrC mitigation. However, the evidence is still largely correlational. NH_4^+ , ALWC, pH, $\text{PM}_{2.5}$, nitrate, RH, and haze accumulation are strongly coupled in winter NCP haze. Even with RF/SHAP and GAM analysis, the results show association, not chemical causality. The authors should further soften wording such as “mainly formed” and “indispensable” or provide stronger mechanistic

evidence.

Reply: We thank the reviewer for this important comment. We agree that the RF/SHAP and GAM results demonstrate statistical associations rather than chemical causality. To provide additional chemical evidence, we analyzed nine imidazole compounds (IMs) in the available subset of samples from Beijing and Jinan during the humid haze period. As shown in Figure R1, both the total concentration of IMs (Σ IMs) and their mass fraction in organic matter (OM) strongly correlated with NH_4^+ , which was consistent with our previous results. These results provide additional support for the involvement of ammonia/ammonium-associated aqueous-phase chemistry in WSON formation, even though their quantitative contribution cannot yet be precisely determined based on the currently available data and analytical approaches.

Unfortunately, the limited amounts of samples remaining from the other sites are insufficient for the additional analyses described above. Therefore, we are unable to provide stronger mechanistic evidence at this stage. In accordance with the reviewer's suggestion, we have further softened the relevant interpretations throughout the revised manuscript. See page 2, line 58; page 22, line 502-504.

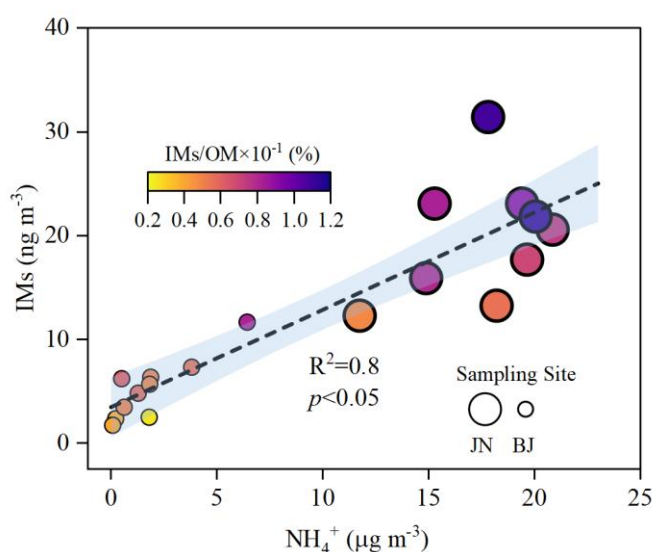


Figure R1 correlation between IMs-related fragments and NH_4^+ with different IMs/OM ratios.

Comment:

2. The authors added GAM analysis and VIF values to address covariance among predictors. However, low VIF in a nonlinear model does not prove that NH_4^+ independently drives WSON formation. The sensitivity test in which NH_4^+ is artificially reduced while other variables are held constant is model-based and may simply reflect the fitted dependence structure rather than a real atmospheric perturbation. This

limitation should be explicitly acknowledged.

Reply: Suggestion taken. This limitation has now been explicitly acknowledged in the revised manuscript. See page 17, line 387-389; page 4, line 107-109 in supporting information.

“These results reflect the statistical relationships and may not fully capture the responses of the actual atmosphere.

“Notably, these model-based results may not fully capture actual atmospheric responses and should therefore be further corroborated by chemical evidences.”

Comment:

3. The manuscript extends an EC-tracer method from SOC to WSON and NACs, assuming primary WSON and EC share combustion sources. This is a major assumption because WSON can have non-combustion primary sources and different emission ratios from EC. The added 10/15/20 percentile sensitivity test is useful, but it does not fully cc the method. The secondary fractions should be presented as semi-quantitative estimates rather than definitive values.

Reply: Suggestion taken. As noted by the reviewer, the EC-tracer method to estimate secondary WSON indeed involves substantial uncertainty. To date, no widely accepted method has been established for accurately distinguishing primary from secondary WSON in ambient aerosols, thus this method was also adopted in related studies (Cai et al., 2022; Ren et al., 2024). In response to the reviewer’s concern, we have rewritten the relevant sections, and acknowledged explicitly that derived secondary fractions should be interpreted as semi-quantitative estimates. See page 16, line 359-367; page 20, line 449,

To provide a more direct and intuitive comparison of the relative spatial differences in secondary WSON formation among the sampling sites, we retained some numerical estimates in the Discussion section. These values are intended solely to illustrate spatial patterns rather than provide precise source apportionment, and have therefore been omitted from the Abstract and Conclusions to avoid overinterpretation.

“This approach assumes that combustion-related primary WSON ($WSON_{pri}$) share the common sources with EC and can be approximated using a representative primary WSON/EC ratio. Based on the sensitivity tests, the primary WSON/EC ratios used here can capture temporal variations of the $WSON_{pri}$, which positively correlated with CO at all sampling sites. Even so, the secondary

WSO_N (WSO_Nsec) may still be overestimated because a fraction of WSO_Npri may arise from non-combustion sources. Therefore, the derived secondary fractions should be interpreted as semi-quantitative estimates rather than precise source apportionments.”

Comment:

4. The study focuses on water-soluble BrC, but total BrC includes both water-soluble and water-insoluble chromophores. The response adds a methanol-extract comparison and reports that water-soluble absorption accounts for ~72% of methanol-soluble absorption during wet haze. This helps, but the manuscript should still avoid general statements about “BrC” without specifying “water-soluble BrC,” especially in the title, abstract, and conclusions.

Reply: Suggestion taken. we have carefully revised the manuscript, and replaced general references to “BrC” with “water-soluble BrC” throughout the Title, Abstract, Results and Discussion, and Conclusions. While the broader term “BrC” has been retained only where it refers to the general concept or where the cited literatures.

Comment:

5. The manuscript acknowledges that $C_3H_3N_2^+$ and $C_3H_4N_2^+$ fragments may originate from other nitrogen-containing precursors and cannot represent actual molecular abundances. This is appropriate, but the discussion later still uses these fragments to support NH_3 -induced imidazole/NOC formation rather strongly. These data should be described as supportive indicators only, not direct molecular evidence.

Reply: During the campaign, aerosol samples were also collected concurrently at Xianghe, a suburban site located near Beijing and Tianjin (Figure R1). Nine imidazole compounds in these samples were independently analyzed using Orbitrap mass spectrometry. We compared the IMs measured by Orbitrap mass spectrometry with the imidazole-related $C_3H_3N_2^+$ and $C_3H_4N_2^+$ fragment obtained from the offline AMS analysis. A significant positive correlation was observed between the two independent measurements. Therefore, we think that these fragment signals can characterize the variation of IMs during the campaign, and similar fragment-based approaches were also applied in previous studies (De Haan et al., 2009; Chen et al., 2026). In addition, these fragment signals are indeed used only as supportive indicators, rather than to precisely quantify the concentrations of individual compounds, and we have further emphasized the limitations of this approach in the revised manuscript. See page 18, line 409-414.

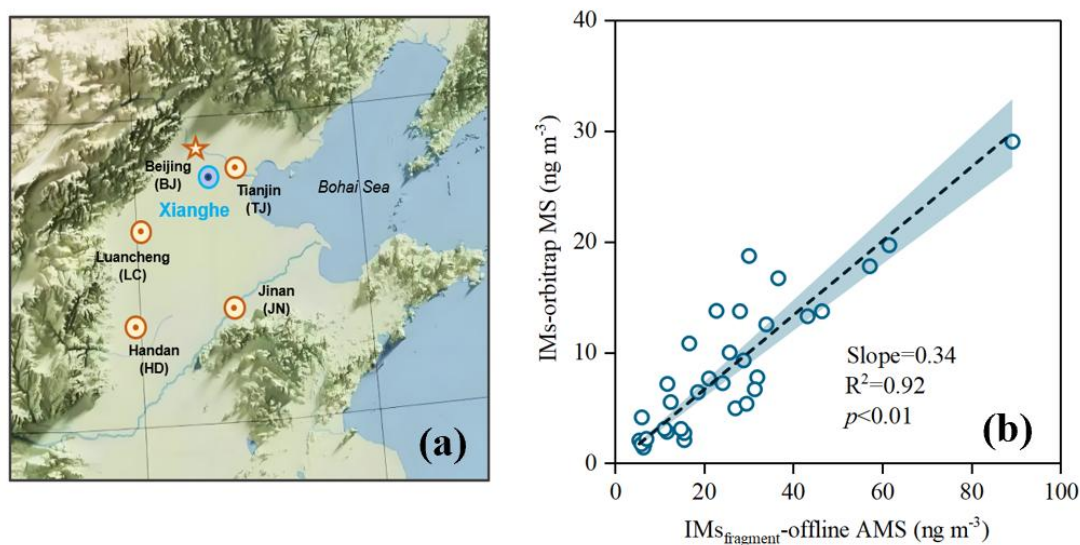


Figure R2 Comparison of the IMs-related fragments derived from offline AMS and IMs concentration determined by orbitrap mass spectrometry at Xianghe site during the campaign.

Comment:

6. The manuscript argues that secondary NACs are mainly formed through gas-phase oxidation because they correlate with NO_2 but weakly with NO_2^- , ALWC, and HMSA/MSA fragments. However, weak ALWC correlation alone does not exclude aqueous nitration, especially because pH, oxidants, nitrite availability, and precursor concentrations can vary simultaneously. The authors should frame this as “consistent with an important gas-phase contribution” rather than “highlighting” gas-phase oxidation as the major pathway.

Reply: Suggestion taken. we have revised the relevant discussion to avoid overinterpreting these statistical associations. And the original statement that gas-phase oxidation represented the major formation pathway has been replaced with the more appropriate conclusion. See page 20, line 457-462.

“secondary NACs ($\text{NACs}_{[\text{sec}]}$) at all sites except TJ correlated strongly with NO_2 ($p < 0.05$) but displayed no significant relationships with levoglucosan and BkF, suggesting a potentially important role of gas-phase oxidation in NACs formation.”

“However, secondary NACs ($\text{NACs}_{[\text{sec}]}$) exhibited weak correlations with NO_2^- and ALWC (Figure 6c) and no significant correlation with the ionic fragments of MSA (Figure S10), a species formed predominantly through aqueous-phase processing. These patterns were consistent with an important contribution of gas-phase oxidation to $\text{NACs}_{[\text{sec}]}$ formation during the campaign.”

Comment:

7. The study covers only winter 2023 and five NCP sites. The role of NH_3 may differ in summer, cleaner periods, lower-ALWC regions, or aerosol regimes with different acidity. The conclusion that targeted NH_3 control is “indispensable” for alleviating haze and BrC pollution across China should be narrowed to “may be important under moist winter haze conditions in ammonia-rich regions.”

Reply: Sorry for our inaccurate expression. Following the reviewer’s suggestion, we have revised the relevant statements in both the Abstract and Conclusions sections. See page 2, line 57-61; page 22, line 509-512.

These results elucidate the substantial contribution of NOCs to atmospheric BrC in the NCP, and further suggest a potentially important role of NH_3 emission control in alleviating wintertime haze and BrC pollution under moist conditions in this region.”

“ This effect is likely to be particularly pronounced during moist winter haze episodes, when enhanced aerosol liquid water facilitates aqueous-phase reactions. Accordingly, targeted NH_3 emission control may be important for further mitigating haze and BrC pollution under such conditions in ammonia-rich regions.”

Reviewer 2

General comments:

Line 283: "the filed observations," please correct.

Line 361 : "our found that" please rephrase.

Line 392: "aqueous-phase reaction via " use plural "reactions"

Reply: Sorry for our carelessness. We have carefully revised the manuscript accordingly.

References

- Cai, D. M., Wang, X. K., George, C., Cheng, T. T., Herrmann, H., Li, X., and Chen, J. M.: Formation of Secondary Nitroaromatic Compounds in Polluted Urban Environments, *Journal of Geophysical Research-Atmospheres*, 127, 10.1029/2021jd036167, 2022.
- Chen, L. Y., Li, R. J., Xiao, B. Y., Li, Z., Li, R., Chen, K. T., Zhang, J. K., Cao, C., Yu, J. Z., Guo, H., and Wang, G. H.: Atmospheric Nitrogen-Containing Organic Aerosols in Wintertime Sichuan Basin of China: A Key Role of Aqueous-Phase Process in Secondary Production and Optical Absorption, *Environmental Science & Technology*, 10.1021/acs.est.6c05422, 2026.
- De Haan, D. O., Corrigan, A. L., Smith, K. W., Stroik, D. R., Turley, J. J., Lee, F. E., Tolbert, M. A., Jimenez, J. L., Cordova, K. E., and Ferrell, G. R.: Secondary Organic Aerosol-Forming Reactions of Glyoxal with Amino Acids, *Environmental Science & Technology*, 43, 2818-2824, 10.1021/es803534f, 2009.
- Ren, Y. Q., Wu, Z. H., Ji, Y. Y., Bi, F., Li, J. L., Zhang, H. J., Zhang, H., Li, H., and Wang, G. H.: Non-negligible secondary contribution to brown carbon in autumn and winter: inspiration from particulate nitrated and oxygenated aromatic compounds in urban Beijing, *Atmospheric Chemistry and Physics*, 24, 6525-6538, 10.5194/acp-24-6525-2024, 2024.