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
April 26, 2026

Reviewer(s)' Comments to Author:

Reviewer 1

General comments

This manuscript presents a comprehensive multi-site wintertime dataset of water-soluble brown carbon (BrC) across the North China Plain (NCP). By combining optical measurements, molecular markers, PMF source apportionment, and statistical (random forest) analysis, the authors argue that nitrogen-containing organic compounds (NOCs), largely formed via ammonia-driven aqueous chemistry, play a dominant role in BrC light absorption during haze events. The dataset is extensive, spatially representative, and timely. The topic is of high relevance to atmospheric chemistry, particularly given increasing attention to ammonia-rich environments and nitrogen-dominated BrC absorption. The manuscript is generally well written and technically competent, and many results are consistent with recent literature. However, several key conclusions are currently overstated, and important methodological assumptions require stronger justification or sensitivity analysis. I therefore recommend major revision before the manuscript can be considered for publication.

Reply: We thank the reviewer's valuable comments. We have carefully revised our manuscript according to the comments. See details below.

Major comments:

A central conclusion of the manuscript is that "ammonia-driven aqueous reactions were identified as the predominant pathway governing the secondary formation of NOCs." While the presented evidence is suggestive, it remains primarily correlational. The RF/SHAP analysis identifies NH_4^+ and ALWC as the most influential predictors of WSONsec; however, variable-importance metrics alone do not establish causality. During winter haze in the NCP, NH_4^+ is tightly covariant with $PM_{2.5}$ mass, nitrate, RH/ALWC, and stagnation-driven accumulation, making it difficult to disentangle whether NH_4^+ acts as a true chemical driver, a co-product of the same processes, or simply an indicator of the broader haze/aerosol-water regime.

Reply: Suggestion taken. During haze episodes, secondary inorganic ions, ALWC and other factors indeed interact and mutually reinforce one another, ultimately leading to the accumulation of WSON. To address multicollinearity among driving factors, a generalized additive model (GAM) was applied here. As a nonparametric modeling framework, GAM model is inherently data-driven rather than bound by statistical distribution constraints, and excels at capturing complex nonlinear relationships between explanatory variables and the target response. As exhibited in Figure R1(a), the GAM model can robustly reproduced WSONsec, as confirmed by their adjusted R^2 (0.87) and deviance (88%). To quantify multicollinearity among explanatory variables, the variance inflation factor (VIF) was applied here, where a higher VIF value denotes stronger collinearity of one variable with the others. According to the empirical criterion (Lin et al., 2018), VIF exceeding 4.0 implies severe collinearity and unstable regression fitting. From Figure R1(c), VIF values of all explanatory variables were <4, implying a weak multicollinearity among these factors when reconstructing WSONsec loadings. Given the lack of sufficient evidence to support that ammonia directly participates in or drives WSONsec formation, we do not overemphasize the conclusion regarding the importance of ammonia-driven aqueous-phase reactions to secondary WSON formation in the revised version. Above discussions have been added in the revised manuscript and supporting information. See page 17, line 379-388 in manuscript; and page 3-4, line 78-105 in supporting materials.

Comment:

Figure 5 combines EC-tracer estimates, RF/SHAP analysis, and correlation analyses to support ammonia-driven aqueous formation of WSONsec. However, NH_4^+, ALWC, $PM_{2.5}$, and pH are strongly covariant under winter haze conditions. The authors should clarify to what extent the relationships shown in Fig. 5b-d demonstrate a causal role of NH_4^+, rather than reflecting co-variation with aerosol water content and stagnationenhanced secondary processing. In particular, it would be important to demonstrate whether NH_4^+ retains explanatory power for WSONsec when controlling for $PM_{2.5}$ and/or ALWC.

Reply: Suggestion taken. Additional sensitivity tests were carried out, in which all other explanatory variables were held constant while only NH_4^+ and NACs were proportionally reduced, to further evaluate their individual impacts on WSONsec. As demonstrated in Figure R1(d), the variation of the predicted WSONsec is far more sensitive to change. This result was consistent with our findings, further highlighting the important role of NH_4^+ on WSONsec. Above discussion was also supported in the supporting material (Text S4)

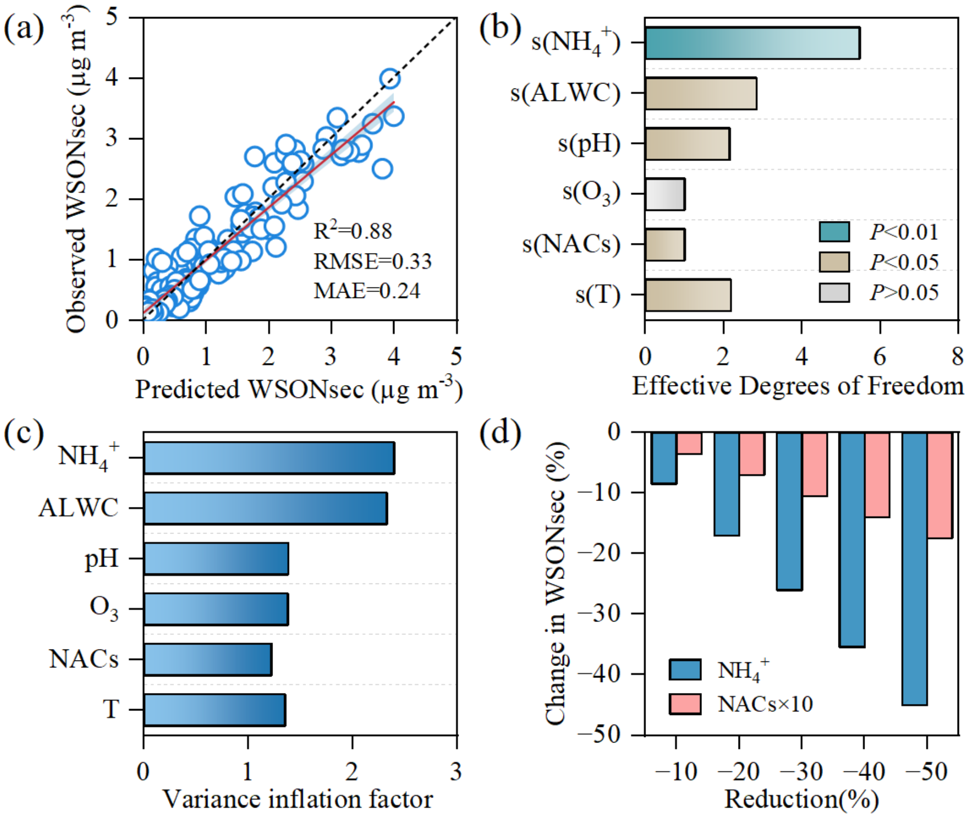

Figure R1 GAM model analysis for recognizing the key factors controlling WSONsec in the NCP. (a-c) Evaluation parameters of model simulation; (d) Sensitivity tests on the response of WSONsec to the reductions of NH_4^+ and NACs.

Comment:

The EC-based tracer approach is extended from SOC to WSON and further to NACs. This is a non-trivial assumption. EC is an imperfect tracer in regions with mixed combustion sources (coal, biomass burning, traffic), and secondary nitrogen-containing species may not scale with EC in the same manner as SOC. Moreover, the choice of the "lowest 15%" percentile to define primary ratios is somewhat arbitrary, and its sensitivity is not explored. A sensitivity analysis using alternative cutoffs (e.g., 10% and 20%) would help assess the robustness of the inferred secondary fractions.

Reply: Suggestion taken. We quantified the relative differences (RD, Eq R1) among WSON/EC ratios between the 15th percentile and other alternative percentiles. As shown in Table R1, almost all RD values were less than 20%, indicating that the estimation of secondary WSON was robust using the 15th percentile as the threshold for defining primary ratios. Moreover, similar to EC, CO mainly originates from biomass burning and fossil fuel combustion. The robust and positive correlation between primary WSON and CO can indirectly indicate that the EC-based method is credible for capturing temporal variations in secondary WSON. Above discussions have been added in the supporting materials (see page 3, line 66-75) and revised manuscript (see page 16, line 357-365)

$$\mathrm{RD}=\frac{|C_{x\%}-C_{15\%}|}{(C_{x\%}+C_{15\%})/2}\times 100\% \qquad \mathrm{R1}$$

Where, $C_{x\%}$ and $C_{15\%}$ denote the lowest X% and 15% of $[\frac{\mathrm{WSON}}{\mathrm{EC}}]$ or $[\frac{\mathrm{NACs}}{\mathrm{EC}}]$, respectively.

Table R1 Statistical metrics for evaluating the EC-based method of secondary WSON and NACs

Sites	WSON			NACs		
	$RD_{15\%\ vs.\ 10\%}$	$RD_{15\%\ vs.\ 20\%}$	$R^2\ _{WSONpri\&CO}$	$RD_{15\%\ vs.\ 10\%}$	$RD_{15\%\ vs.\ 20\%}$	$R^2\ NACs_{pri\&CO}$
BJ	8±13	19±13	0.52^{**}	20±15	9±9	0.68^{**}
TJ	12±16	18±13	0.78^{**}	16±17	17±20	0.73^{**}
LC	12±23	18±24	0.74^{**}	14±17	12±8	0.70^{**}
HD	17±11	19±14	0.30^{*}	12±4	18±20	0.56^{**}
JN	15±30	8±7	0.37^{**}	27±12	19±13	0.58^{**}

Note: $RD_{15\%\ vs.\ 10\%}$ indicates the relative difference between WSON/EC results from the 15% and 10% lowest percentiles; $RD_{15\%\ vs.\ 20\%}$ indicates the relative difference between WSON/EC results from the 15% and 20% lowest percentiles; $R^2\ _{WSONpri\&CO}$ denotes the correlation coefficient between primary WSON and CO; $R^2\ NACs_{pri\&CO}$ denotes the correlation coefficient between primary NACs and CO (**: p<0.01; *: p<0.05).

Comment:

The use of offline AMS analysis on filter extracts to infer imidazole-related species is innovative but raises concerns. Nebulization and drying of extracts may alter chemical speciation, and fragment ions such as $C_3H_3N_2^+$ are not unique to imidazoles. These measurements should therefore be framed more cautiously as supporting rather than definitive evidence for specific N-heterocyclic compounds, with clearer discussion of potential artifacts and uncertainties.

Reply: Suggestion taken. The $C_3H_3N_2^+$ and $C_3H_4N_2^+$ fragments indeed can be derived from other nitrogen-containing precursors, which inevitably introduces uncertainties into the quantification. Thus, the abundances of above fragments do not strictly correspond to the concentration of the real molecules. However, we think that the fragment ion levels can still indicate the variation trends of imidazole N-heterocycles. This can be supported by our previous field observations, in which the concentrations of imidazole species quantified by orbitrap mass spectrometry were significantly and positively correlated with the signal intensities of $C_3H_3N_2^+$ and $C_3H_4N_2^+$ determined via offline-AMS. Above explanations have been incorporated into the 2.2 section of the revised version. See page 7, line 171-180.

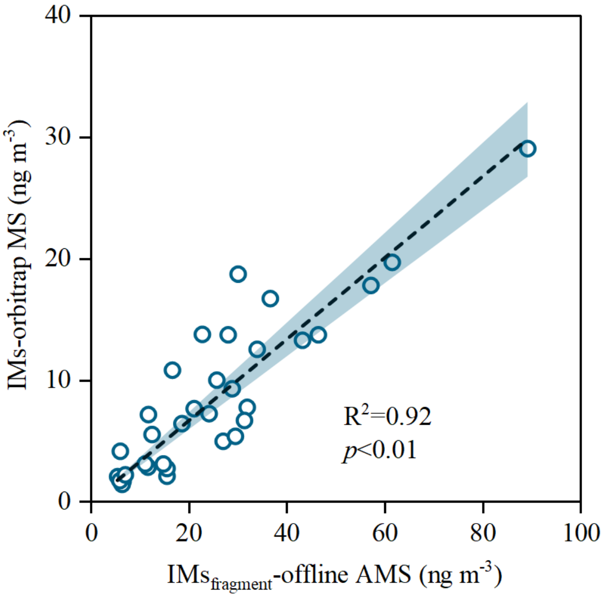

Figure R2 Scattering plot of IMs-related fragments derived from offline AMS (unpublish data) and IMs concentration determined by orbitrap mass spectrometry (Xiao et al. (2025)).

Comment:

The manuscript concludes that gas-phase photochemical oxidation dominates NAC formation, while aqueous pathways are limited. However, the weak correlation with ALWC alone does not rule out aqueous-phase nitration, particularly given the known importance of aerosol pH. In addition, the interpretation of temperature dependence focuses primarily on gas-particle partitioning, while potential impacts on reaction kinetics are not discussed.

Reply: Suggestion taken. In our study, ALWC is not the only evidence supporting the weak contribution of aqueous reactions to NACs formation. As revealed by previous studies (Vione et al., 2004; Barsotti et al., 2017), aqueous-phase NO_2 radical derived from nitrous acid could react with aromatic compounds (e.g., phenol or catechol) to yield corresponding NACs, which is one of the key pathways for the aqueous formation of NACs. Nevertheless, no significant correlation was observed between nitrite and secondary NACs in our dataset. This finding was consistent with our conclusion. Moreover, we further analyzed the ionic fragments of hydroxy methanesulfonic acid (MSA) during humid haze episode, a species conventionally regarded as predominantly formed via aqueous-phase reactions. Similarly, no significant correlation was observed between the ionic fragments of HMSA and secondary NACs (Figure R3), further consolidating the rationality of our conclusions. Above discussion has been supported in page 20, line 451-453.

Finally, temperature indeed regulates the abundance of NACs by modulating the rates of various chemical reactions. However, limited observational data restrict in-depth discussion, and only a brief analysis is provided below.

"In addition, temperature can also affect the abundance of NACs regulating the rates of numerous photochemical reactions. For instance, Lignell et al. (2014) found that low temperature substantially restrained the photolysis of 2, 4-Dinitrophenol in secondary organic aerosols, with its decay rate at 0 °C dropping by nearly one order of magnitude relative to 25 °C. Correspondingly, the low-temperature atmospheric environment likely inhibited the photolysis of NACs during the campaign, thereby facilitating their accumulation in the particle phase. This may be one of the reasons for the significant negative correlation between NACs and temperature."

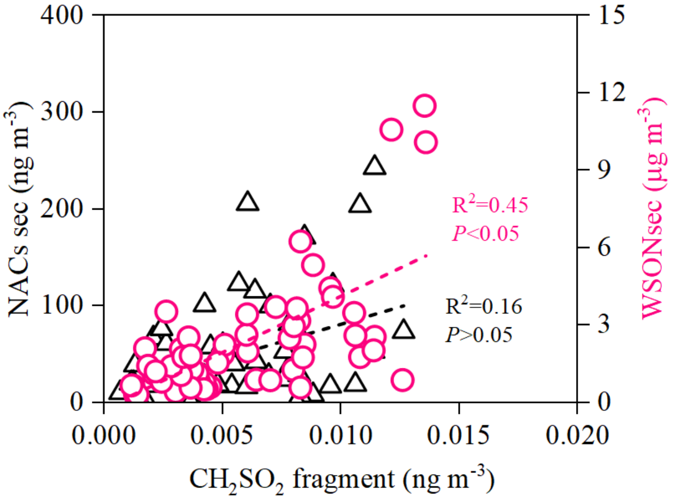

Figure R3 The relationship between CH_2SO_2 fragment, secondary NACs and WSON during humid haze episode.

Comment:

The conclusion that NH_3 emission control is required to mitigate BrC pollution is directionally reasonable but currently overgeneralized. The study is limited to winter conditions in the NCP, where ALWC and secondary processing are enhanced. The relative importance of NH_3 may differ under summer conditions, lower ALWC, or in cleaner environments. This limitation should be more explicitly acknowledged when discussing broader implications.

Reply: Sorry for our inaccurate expression. We have revised it as shown below.

"NH_3 is probably one of the important factors contributing to the high loading of strongly light-absorbing BrC within the boundary layer across China. This phenomenon would be pronounced under moist winter haze episodes, as such environments can accelerate aerosol liquid phase formation and promote aqueous chemical processes. Thereby, targeted NH_3 emission control is indispensable for further alleviating haze and BrC pollution in the country."

Reviewer 2

General comments:

This study investigates the composition and formation pathways of secondary brown carbon (BrC) and their contribution to aerosol light absorption during winter in the North China Plain (NCP). The authors show that particulate nitrogen-containing organic compounds (NOCs) are important contributors to BrC in this region. They report that combustion emissions, particularly biomass burning, represent important BrC sources at the rural site. At the four urban sites, BrC particles exhibit lower absorption at 365 nm, which the authors attribute to the stronger influence of traffic emissions and/or the atmospheric aging of light-absorbing aerosols. In addition, the light absorption at 365 nm is enhanced during haze conditions and coincides with elevated NOC concentrations.

The authors quantify the contribution of secondary water-soluble organic nitrogen (WSONsec) using a tracer-based approach, suggesting that secondary formation dominates across all sites. Using Random Forest analysis, they further show that WSONsec formation is associated with elevated levels of NH_4^+ and aerosol liquid water content (ALWC), suggesting that NOCs may form through ammonia-related aqueous-phase processing. In addition, the authors identify an alternative formation pathway during a haze episode in which secondary nitro-aromatic compounds (NACs) are produced through gas-phase oxidation of aromatic precursors followed by partitioning into the particle phase.

Based on these results, the authors emphasize the importance of controlling ammonia emissions in order to mitigate wintertime haze and elevated BrC concentrations in the NCP.

Overall, the manuscript presents a comprehensive dataset and combines several analytical approaches to investigate the formation pathways of NOCs and their relationship with water-soluble aerosol light absorption. The methodology is generally sound and the figures are clear and informative. The study provides valuable insights into the potential role of aqueous-phase chemistry in BrC formation in the NCP. However, some interpretations appear somewhat stronger than what can be directly supported by the presented analyses, and some aspects would benefit from further clarification or discussion.

Reply: We greatly appreciate the reviewer's valuable and constructive comments, and have carefully revised the manuscript accordingly, with detailed revisions listed below.

Major comments:

The manuscript attributes an important role to ammonia-driven aqueous chemistry in the formation of secondary WSON and BrC based on the observed relationships between WSONsec , NH_4^+, and aerosol liquid water content (ALWC). While these correlations indeed suggest that aqueous-phase processing plays a significant role, they do not necessarily demonstrate that ammonia-induced reactions dominate the formation of BrC. ALWC represents a key parameter controlling multiphase chemistry in atmospheric particles, and elevated ALWC can promote various aqueous reactions. Therefore, the observed correlations may more generally indicate enhanced aqueous processing rather than specifically ammonia-driven chemistry. Additional discussion acknowledging this limitation would help avoid overinterpretation of the results. Furthermore, the manuscript itself identifies alternative pathways for WSONsec formation, such as the formation of secondary NACs through gas-phase oxidation of aromatic precursors followed by gas-to-particle partitioning. This pathway highlights that gas-phase photochemistry may also contribute significantly to secondary BrC formation during haze episodes. The relative importance of these competing mechanisms would benefit from further discussion.

Reply: Suggestion taken. During haze episodes, secondary inorganic ions, ALWC and other factors indeed interact and mutually reinforce one another, ultimately leading to the accumulation of WSON. To address multicollinearity among driving factors, the generalized additive model (GAM) was applied here. As a nonparametric modeling framework, GAM model is inherently data-driven rather than bound by statistical distribution constraints, and excels at capturing complex nonlinear relationships between explanatory variables and the target response. As exhibited in Figure S1(a), the GAM model can robustly reproduced WSONsec, as confirmed by their adjusted R^2 (0.87) and deviance (88%). To quantify multicollinearity among explanatory variables, the variance inflation factor (VIF) was applied here, where a higher VIF value denotes stronger collinearity of one variable with the others. According to the empirical criterion (Lin et al., 2018), VIF exceeding 4.0 implies severe collinearity and unstable regression fitting. From Figure R1(c), VIF values of all explanatory variables were <4, implying a weak multicollinearity among these factors when reconstructing WSONsec loadings.

In addition, a sensitivity test was carried out, in which all other explanatory variables were held constant while only NH_4^+ and NACs were proportionally reduced, to further evaluate their individual impacts on WSONsec. As demonstrated in Figure S1(d), the variation of the predicted WSONsec is far more sensitive to change, further highlighting the key importance of NH_4^+ on WSONsec. Given the lack of sufficient evidence to support that ammonia directly participates in or drives WSONsec formation, the revised manuscript does not overly highlight the significance of ammonia-driven aqueous-phase reactions for WSONsec formation. Above discussions have been added in the revised manuscript and supporting information. See page 17, line 379-388 in manuscript; and page 3-4, line 78-105 in supporting materials.

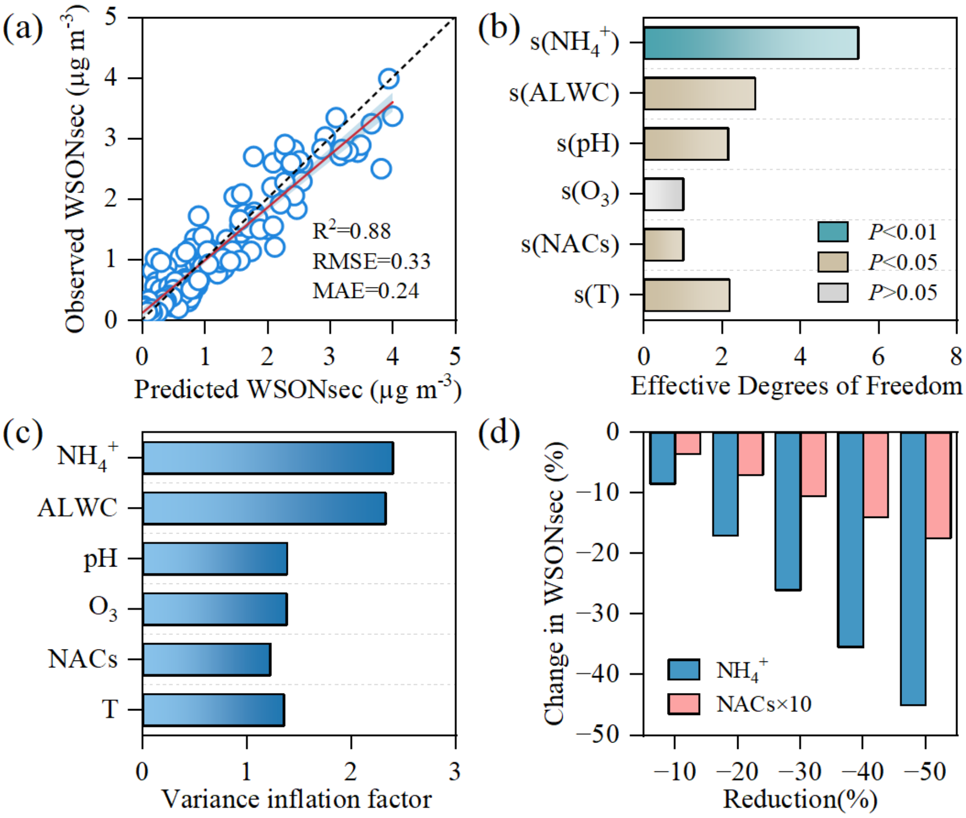

Figure R1 GAM model analysis for recognizing the key factors controlling WSONsec in the NCP. (a-c) Evaluation parameters of model simulation; (d) Sensitivity tests on the response of WSONsec to the reductions of NH_4^+ and NACs.

Major comments:

The study focuses primarily on the water-soluble fraction of organic nitrogen and its relationship with BrC absorption. However, brown carbon is composed of a broad range of compounds, including both water-soluble and water-insoluble components. For example, Huang et al. (2020) reported that insoluble organics dominate BrC absorption in Wintertime in Beijing. If the water-soluble fraction represents only part of the total BrC absorption, this may influence the interpretation of the dominant formation mechanisms discussed in the manuscript. To less extent, other light-absorbing aerosol components could also contribute to the observed absorption, including sulfur-containing organic aerosols and mineral dust, acknowledging their potential influence would provide a more complete picture.

Reply: Thank you for your constructive comment. Previous study have demonstrated that over 85% of total organic carbon can be extracted by methanol (Cheng et al., 2016). Accordingly, we re-analyzed all samples collected during wet haze periods using methanol extraction, and found that the light absorption coefficient of the water-soluble fraction (abs-W) averagely accounts for 72% of the methanol-soluble fraction (abs-M) (Figure R4). However, the sampling campaign in Huang's study was conducted in 2014, when primary emissions from biomass burning and coal combustion in the North China Plain were not yet effectively regulated. Therefore, water-insoluble chromophores (e.g., PAHs) likely contributed a considerably larger fraction of their samples. In addition, our earlier work has verified that, with the continuous control of primary pollutant emissions in recent years, the proportion of water-soluble organic compounds in total organic matter (f_{WSOCp}) has gradually increased across China (Figure R5). Collectively, these evidences suggest that the light absorption derived from water extraction in this study can be representative of the optical properties of atmospheric BrC in the North China Plain.

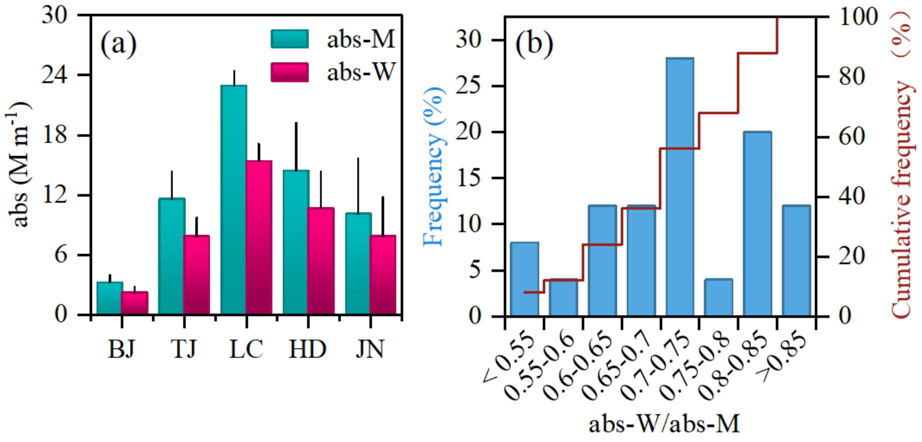

Figure R4 The abs for water and methanol extracts at sampling sites during the humid haze event.

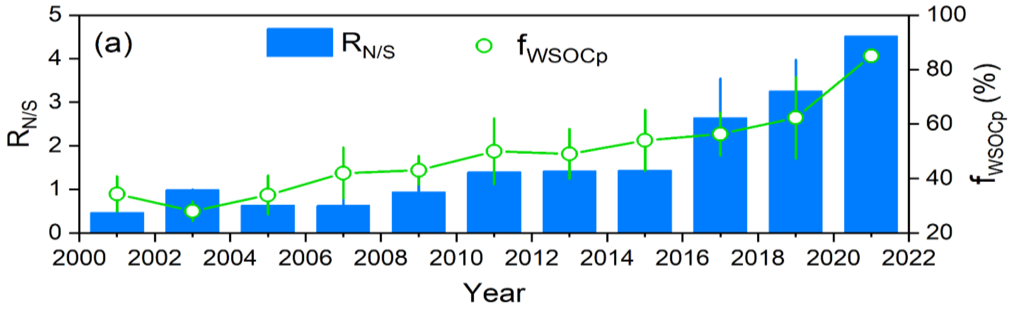

Figure R5 Temporal variations of the molar ratio of nitrate to sulfate ($R_{N/S}$) and WSOCp mass fraction in OC (f_{WSOCp}) over the past 20 years in China. (From Lv et al. (2023))

Minor comments and technical corrections:

Comments

The authors occasionally alternate between the terms NOCs, WSON, and NACs. A clearer distinction between these terms would improve readability.

Reply: We appreciate the reviewer's valuable comment. We have carefully considered this issue, but we have not identified more appropriate alternative abbreviations to replace them. In addition, these abbreviations have been adopted in previous relevant studies to represent the corresponding chemical components, and thus we retain them in the current manuscript.

Comment:

Methodology: In section 2.2 it is mentioned that WSOC and WSTN are estimated using a total organic carbon analyser. Then, in section 2.4 the term WSON is introduced without mentioning how it is estimated. A brief sentence would help and having the contribution of WSON to WSOC in a pie chart or histogram in the SI would be beneficial.

Reply: Suggestion taken. A brief description of the WSON estimation is included in the revised manuscript (page 7, line 155-157), and a histogram showing WSON/WSOC ratios at all sampling sites has also been provided accordingly.

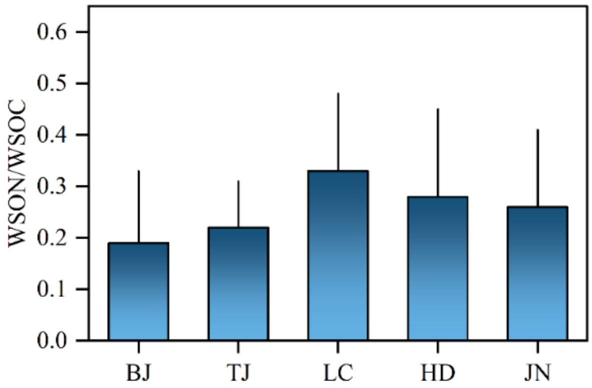

Figure R6 The WSON/WSOC ratio in different sampling sites.

Comment:

In some figures it could be useful to indicate in the captions what the markers and the bars represent (average/median, sites, standard deviation at all sites). Also, are similar trends also observed when considering individual sites or urban/rural sites?

Reply: Detailed information regarding the markers in Figure 4-6 was provided in the corresponding figure captions, see page 32, line 900-922. We further confirmed that these statistical relationships depicted in above figures remain valid at individual sites, despite scattered data at some sites.

Comment:

Line 50: “while”

Reply: Suggestion taken.

Comment:

Line 55: Replace “were the important” with “were important”

Reply: Suggestion taken.

Comment:

Lines 70, 76, 99, 112 … recurrent throughout the manuscript: Replace “;” with “.”

Reply: We have followed your suggestion and carefully revised the entire manuscript accordingly.

Comment:

Line 109: Replace “the stringent […]” with “stringent […]”, I would also suggest to name the specific emissions control measures that were expected to reduce BrC primary emissions.

Reply: Suggestion taken. In recent years, China has implemented a series of measures to reduce primary emissions and alleviate air pollution, including ultralow” emission standard for power plants, strengthening of industrial/vehicle emission standards, phasing out small high-emitting factories, replacing residential coal use with electricity/natural gas, and soon on. These mitigation measures also affected the BrC emission, and have been provided as reviewer’s advice. See page 5, line 108-113.

Comment:

Line 117: It would be beneficial to the reader to know the sources that lead to the increase in oxidation capacity and NH_3 levels, not just quoting the papers referring to it.

Reply: Suggestion taken. Atmospheric oxidation capacity, as reflected by the levels of major oxidants (OH and NO_3 radical, etc), has increased notably in recent year due to remarkable decrease of NO_2 as revealed by Zhu et al. (2023). Meanwhile, elevated O_3 level further strengthen enhanced atmospheric oxidation capacity by local nonlinear photochemistry. Furthermore, the NH_3 levels in the North China Plain have remained persistently high as the insufficient controls on agricultural emissions. Above discussion has been incorporated into the revised manuscript. See page 5, line 116-120.

Comment:

Line 148: remove « the » after 40 mL.

Reply: Suggestion taken.

Comment:

Line 195: Maybe the authors could provide some explanation regarding the principle of SHAP analysis.

Reply: Following your advice, we have added a brief introduction to the basic principle of SHAP analysis in the revised manuscript to improve its interpretability. See page 9, line 208-212.

Comment:

Line 222: repeat of “f denotes the fraction of organic matter in particle”

Reply: Sorry for our carelessness. We have removed the repetitive explanation regarding "*f*".

Comment:

Line 234-235: the reference should be to Figure S2 and "3-flod" needs to be corrected.

Reply: Sorry for the oversight. The error has been corrected in the revised manuscript.

Comment:

Line 251: Could the authors introduce what BkF stands for before using the abbreviation (same comment for other PAHs)?

Reply: Suggestion taken. The full names corresponding to all abbreviations have been supplemented. See page 12, line 267.

Comment:

Line 267: "filed observations"

Reply: Suggestion taken.

Comment:

Line 292: Correct the word "countries".

Reply: Sorry for our carelessness.

Comment:

Line 306: Introduce CWT term before using the abbreviation.

Reply: Suggestion taken.

Comment:

Line 317: Spell out all PAHs before using abbreviations and maybe explain why the ratios of BeP/(BaP+BeP) supports the idea that the lower MAE measured in BJ is due to BrC aging?

Reply: BaP is readily degraded by atmospheric oxidation, while BeP is comparatively stable. Thus, a higher BeP/(BaP+BeP) ratio implies a more aged aerosol. As BrC light-absorbing properties would be decayed during aging, the higher BeP/(BaP+BeP) ratio in Beijing and its negative relationship with MAE_{365} together support that the lower MAE values were due to BrC aging. Following your advice, above discussion has been added in the manuscript. See page 15, line 329-336.

Comment:

Lines 328-331: The correlation between abs_{365} and N:C shows that chromophores and N-containing organic compounds might be co-emitted or co-transported.“(NOCs) were the pivotal chromophores governing BrC optical properties in the NCP,” seems a strong statement.

Reply: Suggestion taken. We have revised the above inappropriate and overstated descriptions. See page 16, line 348-350.

Comment:

Line 331: to which extent are abs and N:C correlated? Also, it is true of the average of all data but the points at some sites are quite scattered.

Reply: Abs_{365} and N:C were significantly correlated at the 0.01 level, and this result has been included in Figure 4b. Despite the scattered data points at some sites, a significant correlation between Abs_{365} and N:C was found at each site at the $p<0.05$ significance level (Figure R7). Thus, the Abs_{365} significantly correlate with N:C in the North China Plain.

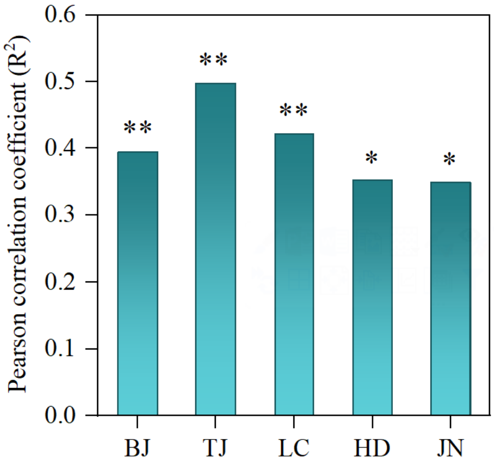

Figure R7 The correlate analysis between Abs_{365} and N:C at each sampling site. (** indicates statistical significance at $p < 0.01$, * denotes significance at $p < 0.05$)

Comment:

Line 375: “corrected” change to “correlated”

Reply: Suggestion taken.

Comment:

Lines 392-393: “through carbonyl-to-NH_3 reactions”

Reply: Suggestion taken.

Comment:

Lines 408-410, “correlation between secondary NACs and NO_2 was indicative of gas-phase oxidation being a significant formation pathway for NACs”, need to be careful here as both species could be co-emitted by combustion sources.

Reply: Thank you for the valuable suggestion. We have further analyzed the relationships between secondary NACs, levoglucosan, and BkF, and found no significant positive correlations among these species at all sampling sites except Tianjin (Figure R8). This finding further indicated that the gas-phase oxidation was a key formation pathway of atmospheric NACs in the North China Plain. Above discussion has been revised accordingly in the manuscript, see page 22, line 443-446.

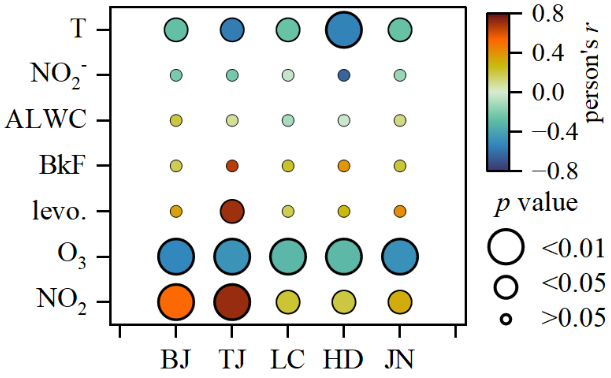

Figure R8 Pearson coefficients between $\mathrm{NACs}_{[sec]}$ and various influencing factors across sampling sites.

Comment:

Supplements:

Test S2: Maybe add a reference to the original approach. The tracer-based approach here assume that EC is a stable tracer of primary emissions in order to estimate secondary WSON and NAC. Nonetheless, organic to EC ratios can vary depending on the sources (e.g. traffic, biomass burning or coal combustion) and perhaps to less extent during atmospheric processing. Would a fix ratio of WSON/EC be representative of all sources for both urban and rural sites? Also, EC is generally associated with water-insoluble primary organic aerosols, whereas WSOC is largely composed of secondary / processed organic compounds. Using EC as a tracer to estimate primary contributions therefore imply that primary emissions contribute proportionally to both the water-soluble and water-insoluble fractions, which may not always be the case. Could this potentially lead to an overestimation of the secondary WSON/NAC fraction. A brief discussion of the uncertainties regarding this approach would help contextualize the conclusion that secondary WSON dominates across all sites.

Reply: Suggestion taken. The tracer-based approach indeed leads to an overestimation of secondary WSON or NACs, when a fraction of primary WSON is not derived from combustion sources. To evaluate the robustness of these results upon secondary WSON and NACs, we quantified the relative differences (RD, Eq. R1) in WSON/EC ratios between the 15th percentile and other alternative percentiles. As summarized in Table R1, nearly all RD values were less than 20%, demonstrating that our secondary WSON estimates are reliable and stable. Furthermore, it is well-known that CO shares similar emission characteristics with EC, with both primarily sourced from biomass burning and fossil fuel combustion. The robust and positive correlations between primary WSON (or, NACs) and CO can indirectly indicate that the EC-based method is feasible to reflect the temporal evolution of secondary WSON. Above discussions have been added in the supporting materials (see page 3, line 66-75) and revised manuscript (see page 16, line 357-365)

$$\mathrm{RD}=\frac{|C_{x\%}-C_{15\%}|}{(C_{x\%}+C_{15\%})/2}\times 100\% \qquad \mathrm{R1}$$

Where, $C_{x\%}$ and $C_{15\%}$ denote the lowest X% and 15% of $[\frac{\mathrm{WSON}}{\mathrm{EC}}]$ or $[\frac{\mathrm{NACs}}{\mathrm{EC}}]$, respectively.

Table R1 Statistical metrics for evaluating the EC-based method of secondary WSON and NACs

Sites	WSON			NACs		
	$RD_{15\%\ vs.\ 10\%}$	$RD_{15\%\ vs.\ 20\%}$	$R^2_{\ WSONpri\&CO}$	$RD_{15\%\ vs.\ 10\%}$	$RD_{15\%\ vs.\ 20\%}$	$R^2\ NACs_{pri\&CO}$
BJ	8±13	19±13	0.52^{**}	20±15	9±9	0.68^{**}
TJ	12±16	18±13	0.78^{**}	16±17	17±20	0.73^{**}
LC	12±23	18±24	0.74^{**}	14±17	12±8	0.70^{**}
HD	17±11	19±14	0.30^{*}	12±4	18±20	0.56^{**}
JN	15±30	8±7	0.37^{**}	27±12	19±13	0.58^{**}

Note: $RD_{15\%\ vs.\ 10\%}$ indicates the relative difference between WSON/EC results from the 15% and 10% lowest percentiles; $RD_{15\%\ vs.\ 20\%}$ indicates the relative difference between WSON/EC results from the 15% and 20% lowest percentiles; $R^2_{\ WSONpri\&CO}$ denotes the correlation coefficient between primary WSON and CO; $R^2\ NACs_{pri\&CO}$ denotes the correlation coefficient between primary NACs and CO (**: p<0.01; *: p<0.05).

Comment:

Text S3: Are the references to equation 5 and 6 correct or is it equation S2 and S3?

Reply: Sorry for our carelessness. It has been fixed, see page 4, line 115 in supporting materials.

Comment:

Text S4 line 92-93: “HNH3*is equilibrium constant calculated by Eq S4”, isn’t it S6?

Reply: The H_{NH3}* was indeed calculated via Eq S6, and we have corrected it in the revised version.

Comment:

Fig S3: Typo in caption “BbF”. Also, the levoglucosan+BfK levels exceed 200ug/m3 at LC and TJ, when your hourly concentrations of $PM_{2.5}$ rarely exceed 200 ug/m3 and OM only representing up to 25% of $PM_{2.5}$. Could levoglucosan concentrations be overestimated?

Reply: Sorry for our oversight. The unit for levoglucosan+BkF in Figure S3 is ng/m3 rather than µg/m3, so the levoglucosan concentrations are not overestimated. And all typographical errors have been revised accordingly.

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