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 all comments into account. 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

This study investigated the pollution characteristics and composition of NACs during the wintertime in 11 Chinese cities. Furthermore, the formation mechanism of NACs was explored based on variations in RH, ALW, and oxidants during clean and polluted days. In fact, the composition, abundance, and sources of NACs have been frequently reported in recent years. It is recommended that the authors conduct a thorough analysis of the NAC formation mechanism to support the innovative perspective presented in this paper.

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

General comments:

1. Section 2: The methodology section lacks detailed descriptions, probably resulting in unreliable data.

Detailed descriptions of each sampling site should be added to the main text or supplementary materials, such as the sampling site type (urban, rural, or remote site?) Are

there point sources in the vicinity of the sampling sites? What is the impact of vehicle emissions? Moreover, the locations of monitoring stations used to obtain meteorological parameters and air pollutant concentrations should be described in detail, or their locations were added to Fig. S1.

Response: All sampling sites in the investigated cities were located on the rooftops of 4- to 6-story buildings, either within or adjacent to university or research institute campuses. In addition, all sites were situated in urban areas with free of nearby point pollution sources such as factories, power plants, waste incineration plant, or farmland, ensuring the representativeness of regional urban atmosphere. In particular, none of the selected buildings were close to major urban arterial roads. Thus, although the urban sampling sites may be subject to the regional transport of traffic-related pollutants, the aerosol samples collected herein are not representative of ambient environments under direct, high-intensity influence from local traffic emission sources. Detailed information on all sampling sites (**Figure S1**) was shown as follows. The sampling site in Taiyuan was located at the Wucheng Campus of Shanxi University, approximately 6.5 km from the Dongshan Wulong Suburban Forest Park. The sampling site in Harbin was situated in Nangang District, adjacent to the Harbin Institute of Technology. The sampling site in Xi'an was set at the Xingqing Campus of Xi'an Jiaotong University. The sampling site in Lanzhou was located in Anning District, near Lanzhou Jiaotong University. The sampling site in Beijing was situated in a typical urban area near the Chinese Research Academy of Environmental Sciences, approximately 1–2 km from the Olympic Forest Park. The sampling site in Chengdu was located at Chengdu University of Technology in Chenghua District. The sampling site in Kunming was set at the Lianhua Campus of Kunming University of Science and Technology. The sampling site in Wuhan was located at the Wuhan Branch of the Chinese Academy of Sciences in Wuchang District. The sampling site in Hangzhou was situated at the Zhaohui

Campus of Zhejiang University of Technology, approximately 3.5 km from the West Lake Scenic Area. The sampling site in Guangzhou was located near the South China Botanical Garden, Chinese Academy of Sciences, midway between the Baiyun Mountain Scenic Area and Huolu Mountain Forest Park. The sampling site in Guiyang was situated at the Institute of Geochemistry, Chinese Academy of Sciences in Guanshanhu District, with the Yueshan Lake Wetland Park within a 2 km radius of the site.

Meteorological parameters and ambient air pollutant data were obtained from the nearest environment monitoring stations to each sampling site. If the geographic locations of these monitoring stations were also illustrated in **Figure S1**, it will show near-complete overlap with our sampling sites due to their close proximity. As detailed previously, all sampling sites in this study were located in urban areas free of local point pollution sources. Thus, although data from these monitoring stations cannot fully capture the exact spatial average of meteorological parameters and pollutant concentrations at the sampling locations, the temporal dynamics (i.e., time-series variation trends) of the obtained data were representative of those at the sampling sites. This supports the reliability of the results derived from the correlation analysis conducted in this study.

Supporting information

S1. Site Description

All sampling sites in the investigated cities were located on the rooftops of 4- to 6-story buildings, either within or adjacent to university or research institute campuses. In addition, all sites were situated in urban areas with free of nearby point pollution sources such as factories, power plants, waste incineration plant, or farmland, ensuring the representativeness of regional urban atmosphere. In particular, none of the selected buildings were close to major urban arterial roads. Thus, although the urban sampling sites

may be subject to the regional transport of traffic-related pollutants, the aerosol samples collected herein are not representative of ambient environments under direct, high-intensity influence from local traffic emission sources. Detailed information on all sampling sites (**Figure S1**) was shown as follows. The sampling site in Taiyuan was located at the Wucheng Campus of Shanxi University, approximately 6.5 km from the Dongshan Wulong Suburban Forest Park. The sampling site in Harbin was situated in Nangang District, adjacent to the Harbin Institute of Technology. The sampling site in Xi'an was set at the Xingqing Campus of Xi'an Jiaotong University. The sampling site in Lanzhou was located in Anning District, near Lanzhou Jiaotong University. The sampling site in Beijing was situated in a typical urban area near the Chinese Research Academy of Environmental Sciences, approximately 1–2 km from the Olympic Forest Park. The sampling site in Chengdu was located at Chengdu University of Technology in Chenghua District. The sampling site in Kunming was set at the Lianhua Campus of Kunming University of Science and Technology. The sampling site in Wuhan was located at the Wuhan Branch of the Chinese Academy of Sciences in Wuchang District. The sampling site in Hangzhou was situated at the Zhaohui Campus of Zhejiang University of Technology, approximately 3.5 km from the West Lake Scenic Area. The sampling site in Guangzhou was located near the South China Botanical Garden, Chinese Academy of Sciences, midway between the Baiyun Mountain Scenic Area and Huolu Mountain Forest Park. The sampling site in Guiyang was situated at the Institute of Geochemistry, Chinese Academy of Sciences in Guanshanhu District, with the Yueshan Lake Wetland Park within a 2 km radius of the site.

Meteorological parameters and ambient air pollutant data were obtained from the nearest environment monitoring stations to each sampling site. As detailed previously, all sampling sites in this study were located in urban areas free of local point pollution sources. Thus, although data from these monitoring stations cannot fully capture the exact spatial

average of meteorological parameters and pollutant concentrations at the sampling locations, the temporal dynamics (i.e., time-series variation trends) of the obtained data were representative of those at the sampling sites. This supports the reliability of the results derived from the correlation analysis conducted in this study.

2. Were $PM_{2.5}$ samples collected using the same sampler at all sites? e.g., the high-volume air sampler (KC-1000, Laoying, China)? Do the 154 filter samples include field blank samples? How many filed blank samples were collected at each sampling site? Please provide clarification in the main text.

Response: We greatly appreciate your comments. The same air samplers and similar sampling period were applied to all study sites. A total of 154 filter samples were collected, including 2 field blanks per sampling site.

Lines 138–139: …$PM_{2.5}$ samples were acquired using a high-volume air sampler (KC-1000, Laoying, China) operated at a constant flow rate of ~1.05 ± 0.03 m^3 min^{-1} at all study sites…

Lines 143–144: …Two field blank samples were prepared at each site by mounting filters in an identical but non-operating air sampler…

3. The pretreatment processes of filters were not described in detail. For example, what is the area of filter used for NACs analysis? What is the volume of methanol used? How long should the ultrasonication last?

Response: Thank you very much for your comment. We have added more descriptions in

the revised manuscript.

Lines 159–170: …Briefly, a 10 cm^2 section of the filter was cut. The extraction was performed by sonicating the filter piece in 3 mL of methanol in an ice bath for 30 min, and this procedure was repeated twice. The extracts were then filtered through a 0.22 μm polytetrafluoroethylene syringe filter (CNW Technologies GmbH). The filtrate was concentrated under a gentle stream of nitrogen and adjusted with methanol containing 2,4,6-trinitrophenol to a final volume of 300 μL. After homogenization and centrifugation, the supernatant was analyzed using an Acquity ultrahigh-performance liquid chromatography (UPLC; Waters, USA) system coupled to a Xevo G2-XS Quadrupole time-of-flight mass spectrometer (ToF-MS; Waters, USA). The mass spectrometer was equipped with an electrospray ionization (ESI) source operated in negative ion mode. An ACQUITY UPLC HSS T3 column (2.1 mm × 100 mm, 1.8 μm; Waters, USA) was used for reversed-phase liquid chromatographic separation.

4. Please add the model of UPLC-MS/MS and ion chromatography, the chromatography and mass spectrometry parameters of UPLC-MS/MS, and the method performance for analyzing NACs, including precision, accuracy, matrix effects, and limit of quantification, which are essential for ensuring data reliability.

Response: We have updated the relevant content in the revised manuscript.

Lines 166–172: …the supernatant was analyzed using an Acquity ultrahigh-performance liquid chromatography (UPLC; Waters, USA) system coupled to a Xevo G2-XS Quadrupole time-of-flight mass spectrometer (ToF-MS; Waters, USA). The mass spectrometer was

equipped with an electrospray ionization (ESI) source operated in negative ion mode. An ACQUITY UPLC HSS T3 column (2.1 mm × 100 mm, 1.8 μm; Waters, USA) was used for reversed-phase liquid chromatographic separation...

Lines 175–187: …The recoveries of the standard reference materials varied between 94% and 105%, which is within the ranges reported in previous studies with UPLC-MS/MS-based NAC analysis (Frka et al., 2022; Huang et al., 2023; Kitanovski et al., 2012). The limits of detection and quantification ranged from 0.05 μg L^{-1} (for 5-nitrosalicylic acid) to 0.5 μg L^{-1} (for 4-nitroguaiacol) and from 0.15 μg L^{-1} (for 5-nitrosalicylic acid) to 1.5 μg L^{-1} (for 4-nitroguaiacol) for the target analytes, respectively. These values fell within the ranges established in previous UPLC-MS/MS methodology for NAC analysis (Frka et al., 2022; Huang et al., 2023; Li et al., 2020). The repeatability for each standard, expressed as the relative standard deviation (n = 6), was less than 4.5%. None of these NACs were detectable in blank samples when analyzed using the identical measurement protocol. Furthermore, the UPLC-MS/MS analysis of these target NACs in atmospheric particles was found to be free of significant matrix effects (Kitanovski et al., 2012; Frka et al., 2022)…

Lines 197–198: …Analysis was conducted via ion chromatography (Dionex ICS-5000+, Thermo Scientific, USA) to…

5. Both gas (e.g., NH_3, HNO_3) and particulate phase data for major inorganic components were required to conduct ISORROPIA-II thermodynamic model, how can gases data be obtained? Neglecting the gas phase may lead to significant deviations in aerosol pH and ALW, especially in southern China.

Response: We greatly appreciate the reviewer's critical and constructive comments regarding the predictions of pH and ALW in our manuscript. In this study, gaseous precursor species were not incorporated as input parameters for pH and ALW calculation using the ISORROPIA-II thermodynamic model. We fully agree with the reviewer that the exclusion of gaseous species may introduce deviations in the accuracy of the calculated pH, with an average uncertainty of approximately 1 pH unit as documented in previous relevant studies (Guo et al., 2015; Wang et al., 2021). In contrast, the impact of excluding gaseous species on ALW is expected to be negligible, as ALW is predominantly governed by ambient relative humidity, aerosol ionic strength, and the organic fraction (Xu et al., 2020; Nguyen et al., 2016; Xu et al., 2023; Fountoukis and Nenes, 2007).

We acknowledge that the accuracy of the ISORROPIA-II-derived pH and ALW may be compromised when gas-phase species are not included in the model inputs. However, it should be noted that omitting gaseous species from model inputs is a widely adopted approach in the field observation studies focusing on aerosol NACs (Cai et al., 2022; Shi et al., 2023; Liu et al., 2023; Huang et al., 2024). This is because the objective of most field-based studies, including ours, is to elucidate the potential interactions between pH(/ALW) and target parameters by comparing their synchronous temporal variation trends. Importantly, even without gaseous species as model inputs, the temporal dynamics and variation trends of the calculated pH and ALW remain representative of the actual conditions in the study areas.

In the revised manuscript, we have added relevant discussion to clarify the constraints and uncertainties of the calculated pH and ALW results.

Supporting information

S2. Predictions of aerosol liquid water (ALW) and pH

ALW concentration and aerosol pH were predicted using the ISORROPIA-II thermodynamic model, which has been extensively validated for the calculation of such parameters (Nguyen et al., 2016; He et al., 2018; You et al., 2026; Xu et al., 2023). This model is applicable across a broad range of ambient conditions, including relative humidity (RH) > 20% and typical tropospheric temperatures (Guo et al., 2015; Ding et al., 2019; Yang et al., 2024; Fountoukis and Nenes, 2007; Nguyen et al., 2014). The model simulations were run in forward mode under the assumption of a thermodynamically metastable state, with input datasets including particle-phase inorganic ion concentrations, ambient air temperature, and RH. The methodological details are available in our previous studies (Xu et al., 2020; Yang et al., 2024). It should be noted that the contribution of aerosol organic components to ALW was not considered in this study, as it is likely relatively minor compared to ALW derived from inorganic aerosol components (Xu et al., 2020; Nguyen et al., 2016; Xu et al., 2023).

Aerosol pH was also derived from ISORROPIA-II outputs. Specifically, the pH was predicted by considering both the equilibrium particle hydronium ion concentration per volume air (H^+_{air}) and the predicted inorganics-derived water (W_i), which was detailed below (Guo et al., 2015).

$$pH = -\log_{10}H_{aq}^{+} = -\log_{10}\frac{1000H^+_{air}}{w_i} \quad (S1)$$

where both H^+_{air} and W_i were direct outputs from the ISORROPIA-II simulations. H^+_{aq} (mol L^{-1}) represents the hydronium ion concentration in the aqueous aerosol phase. H_{aq}^{+} value is estimated by dividing H^+_{air} by the ALW concentration.

A critical methodological constraint was addressed during pH calculation, which was detailed below. When ISORROPIA-II is run in forward mode with exclusive particle-phase composition inputs, it simulates the equilibrium gas-particle partitioning of NH_4^+. This

process results in a portion of particle-phase NH_4^+ partitioning to the gas phase as NH_3, lowering the effective particulate NH_4^+ concentration (Ding et al., 2019; Song et al., 2018). This may introduce a systematic underestimation of aerosol pH, with prior study documenting a bias of ~1 pH unit when gas-phase NH_3 measurements are unavailable as model inputs (Guo et al., 2015; Wang et al., 2021). However, it is important to note that our correlation analysis was designed to explore the synchronous temporal co-variation trends between parameters, rather than their absolute value fluctuations. Thus, the adopted ALW and pH prediction framework does not undermine the robustness or reliability of our correlation analysis results.

6. How to quantify LGA? The unit of LGA in Figure 2 was not shown.

Response: In this study, levoglucosan (LGA) was determined by UPLC-MS/MS. During the batch analysis of our field samples, we did not use LGA calibration standards with a sufficiently broad and appropriate concentration range, which resulted in a large proportion of the measured data points falling outside the linear dynamic range of the established calibration curve. Accordingly, we did not report the absolute quantitative concentration data of LGA in the manuscript. Instead, we only used the peak area of LGA (a semi-quantitative indicator that directly reflects the relative abundance of LGA in the samples) to conduct correlation analysis with other key environmental parameters. Since our correlation analysis focuses on the synchronous temporal variation trends between parameters rather than their absolute concentration levels, this semi-quantitative approach does not affect the reliability of our analytical results.

Lines 193–194: …In this study, the abundance of LGA is characterized by signal intensity…

7. Section 3.1: Table S1-S4: Please double check the concentrations of 4M5NC, as they are significantly lower than the levels observed in previous winter studies. I recommend that the authors compare these findings with published data and explain the reasons for the discrepancy. In addition, how many days are classified as pollution days and clean periods, respectively? The number of days (e.g., n=5) should be added below Average, Clean period, Poll. Period in Table S1-S4.

Response: In this study, the mean concentrations of 4M5NC in $PM_{2.5}$ across all investigated cities ranged from 0.16 ± 0.03 ng m^{-3} (HZ) to 0.49 ± 0.32 ng m^{-3} (TY).

Wang et al. (2019) measured a mean 4M5NC concentration of 0.56 ± 0.40 ng m^{-3} in winter $PM_{2.5}$ from urban Beijing, while Li et al. (2020) reported a substantially higher mean 4M5NC value of 6.50 ± 6.38 ng m^{-3} for wintertime urban Beijing. In addition, for wintertime $PM_{2.5}$ in urban China, Huang et al. (2024) reported that mean 4M5NC concentrations varied from 0.52 ± 0.53 ng m^{-3} (Beijing) to 14.97 ± 9.23 ng m^{-3} (Harbin). For Shanghai, Liu et al. (2023) observed a wintertime 4M5NC concentration of 0.11 ± 0.15 ng m^{-3} in $PM_{2.5}$ in suburban areas, whereas Cai et al. (2022) reported a much higher concentration of 1.32 ± 1.14 ng m^{-3} in urban Shanghai, where the sampling site was surrounded by multiple major traffic arterial roads.

These results show that 4M5NC concentrations in winter $PM_{2.5}$ vary widely even within the same city. This variation is largely dependent on sampling location and meteorological conditions. The relatively low 4M5NC levels in our study may be partly attributed to the absence of prominent local pollution sources (especially traffic emissions) near all sampling sites.

More discussions have been added to the revised manuscript.

Lines 273–288: …Furthermore, we observed that the 4M5NC concentrations measured in

this study were lower than those reported in several previous studies conducted in winter across urban China. For example, Wang et al. (2019) measured a mean 4M5NC concentration of 0.56 ± 0.40 ng m^{-3} in winter $PM_{2.5}$ from urban BJ, while Li et al. (2020) reported a substantially higher mean 4M5NC value of 6.50 ± 6.38 ng m^{-3} for wintertime urban BJ. Huang et al. (2024) further reported that mean 4M5NC concentrations in winter $PM_{2.5}$ across urban China varied from 0.52 ± 0.53 ng m^{-3} (BJ) to 14.97 ± 9.23 ng m^{-3} (HEB). For Shanghai, Liu et al. (2023) observed a wintertime 4M5NC concentration of 0.11 ± 0.15 ng m^{-3} in $PM_{2.5}$ in suburban areas, whereas Cai et al. (2022) reported a much higher concentration of 1.32 ± 1.14 ng m^{-3} in winter $PM_{2.5}$ at an urban site surrounded by multiple major traffic arterial roads. These results suggest that 4M5NC concentrations in winter $PM_{2.5}$ vary widely even within the same city. This variation is expected to be largely dependent on sampling location and meteorological conditions. Presumably, the relatively low 4M5NC levels in this study may be partly attributed to the absence of prominent local pollution sources (especially traffic emissions) near all sampling sites...

Furthermore, we have added the specific sampling period and sample number in the headers of Tables S1–S4.

8. Table S1-S4: The value of ALW varied significantly across different cities. For example, XA and CD reached as high as 113 and 138 μg m^{-3}, while KM and GZ were only around 15 μg m^{-3}. What causes such substantial differences? It seems that the differences of $PM_{2.5}$ concentrations among different cities are not so significant.

Response: Sulfate and nitrate concentrations in aerosol samples from XA and CD (average range: 10–22 μg m^{-3} for sulfate, 21–41 μg m^{-3} for nitrate) were markedly higher than those

in samples from KM and GZ (8–9 μg m^{-3} for sulfate, 5–6 μg m^{-3} for nitrate). The mass loading of sulfate and nitrate is a key driver of aerosol hygroscopicity. When coupled with the distinct spatial differences in ambient RH across our study regions, this results in substantial variability in ALW content calculated via the ISORROPIA-II thermodynamic model. Consistently, $PM_{2.5}$ mass concentrations in XA and CD were also significantly elevated compared to those in KM and GZ.

Furthermore, it should be clarified that the $PM_{2.5}$ mass concentrations reported in this study reflect the regional average levels, rather than the actual measured values from individual filter samples (Lines 152–154).

9. Line 265-266: what components are important contributors to haze? NACs are minor constituents in $PM_{2.5}$, which were not the primary cause of the heavy pollution.

Response: We greatly appreciate your valuable comment. Although the absolute mass concentrations of NACs are far lower than that of bulk $PM_{2.5}$, they are well recognized for their strong light-absorbing properties (Huang et al., 2025; Harrison et al., 2005; Wang et al., 2022). It has been reported that NAC species can contribute up to 50% or more to brown carbon light absorption (Mohr et al., 2013; Huang et al., 2024; Gu et al., 2022) (Lines 50–51). During haze episodes, the elevated $PM_{2.5}$ mass concentration is accompanied by a synchronous increase in NACs concentrations, which further enhances the overall light absorption capacity of ambient aerosols. This light absorption enhancement may partly drive the significant reduction in atmospheric visibility during haze events, which creates the intuitive perception of heavy pollution for the public.

10. Section 3.2: Figure 2 shows that the sampling frequency is irregular. It is recommended to list the sampling periods for all samples in Figure 2, or to add a table in the supplementary materials detailing the sampling periods for all sampling sites?

Response: We greatly appreciate your insightful and constructive suggestions. We have supplemented the relevant information in the headers of Tables S1–S4 in the revised SI.

It should be noted that to expand the valid sample size and further enhance the robustness and reliability of our correlation analysis results, we separately pooled all valid datasets from the southern and northern study regions respectively, and performed the Mantel test correlation analysis and principal component analysis on the two independent grouped datasets (**Figure 6**).

11. Section 3.3: Equation (1) is not applicable for calculating secondary NACs in this study, because only around 13 samples were collected at each site, which may result in large uncertainties. In addition, the secondary NACs cannot be calculated based on data from all sites due to differences in formation mechanisms and primary sources.

Response: We greatly appreciate your valuable comment. The core calculation principle of the adopted method has no inherent dependence on the number of samples, and this approach has been well validated in previous peer-reviewed work. For example, a previous study conducted in Shanghai employed the identical calculation framework with only over ten samples (Liu et al., 2023). For the common NACs investigated in this work and previous studies, the chemical reaction pathways governing their oxidative formation are widely accepted to be fundamentally similar across different urban environments and independent field studies (Lines 67–83 and Lines 456–466).

Instead, the observed spatial variability in aerosol NACs concentrations across regions

is mainly attributed to the net effect of multiple ambient environmental factors that either promote or inhibit NACs formation or degradation. This spatial heterogeneity shaped by field environmental conditions is also the core focus we aim to highlight in this study.

12. As the authors noted that primary emission sources such as coal combustion and biomass burning exhibited relatively high emission factors for 4NC and 4NP (lines 245–250). Yet it is difficult to believe that secondary NACs contribute over 80% of emissions, as shown in Figure 4, especially in winter. I recommend that the author rewrite this section and conduct a comparative analysis with relevant reports in the literature. In addition, I suggest providing precursor data, which may make the discussion on secondary formation of NACs more persuasive.

Response: Primary combustion sources both directly emit particle NACs and release gaseous precursors that drive the secondary atmospheric formation of NACs. This leads to a critical inherent limitation of receptor models for apportioning combustion-related NAC sources. Specifically, the receptor models are unable to disentangle primary and secondary contributions to NACs when apportioning combustion-related sources, which is also the methodological constraint we highlight in this study (Lines 386–395). Thus, we adopted the calculation method described in Equation 1 in the revised manuscript to assess the secondary source contribution to ambient aerosol NACs, an approach that has been widely validated and applied in previous studies (Chen et al., 2022; Liu et al., 2023). For example, a previous study in suburban Shanghai found that secondary sources contributed over 84% of total aerosol NACs in wintertime $PM_{2.5}$ (Liu et al., 2023), while another study in urban Shanghai reported that secondary formation accounted for up to 75% of total aerosol NACs in winter $PM_{2.5}$ (Cai et al., 2022).

Furthermore, gaseous NACs were not quantified in the present study. It is also important to note that the oxidative reaction pathways for the formation of these common NACs are widely accepted to be fundamentally similar across different urban environments and independent field studies (Lines 67–83 and Lines 457–467).

13. Section 3.4: In this section, I find this discussion rather confusing. Correlation analysis indicates that NAC concentrations in northern cities show negative correlations with RH, ALW, and oxidants. The authors also mentioned that secondary contributions are significant. What are the possible mechanisms for the secondary formation of NACs in northern cities? I mean that through analyzing the influencing factors, can the author propose secondary formation mechanisms for NACs in each city and provide sufficient data to support it?

Response: NACs can be secondarily formed through gas-phase and liquid-phase oxidation of various precursors, such as toluene, benzene, xylene, phenol, catechol, m-cresol, guaiacol, and methyl catechol, in the presence of nitrogen oxides (NO_x), with their eventual distribution between gas and particle phases being significantly affected by gas-particle partitioning (Harrison et al., 2005; Wang and Li, 2021; Mayorga et al., 2021; Salvador et al., 2021; Vidović et al., 2019). The oxidative reaction pathways for the formation of these common NACs are widely accepted to be fundamentally similar across different urban environments and independent field studies (Lines 67–83 and Lines 457–467).

Importantly, the NAC concentrations quantified in this study represent time-integrated bulk averages over the sampling periods. Accordingly, the reported NAC concentrations inherently reflect the net balance between the simultaneous secondary formation and photolytic degradation of NACs in the ambient atmosphere. Thus, the negative correlations observed between aerosol NAC concentrations and key parameters including RH, ALW, and

atmospheric oxidants only demonstrate that these factors did not drive a statistically significant increase in the net yield of NACs under real-world ambient conditions. It cannot be interpreted as evidence of insignificant secondary formation of NACs.

Actually, the novelty or highlights of this study are as follows.

Previous observational and chamber studies have highlighted the significant promoting effects of RH or ALW on the secondary formation of aerosol NACs. However, our multi-city field observations across a large spatial scale reveal that the widely recognized RH- and ALW-driven promotion of NAC formation may not be universally interpretable in complex real atmospheric environments, where multi-factor interactions play a critical role.

Specific comments:

1. Line 49: NACs are not abundant compounds in PM2.5 compared to water-soluble ions and carbonaceous components, which typically accounted for less than 5% of PM2.5 mass.

Response: We greatly appreciate your constructive comment and fully concur with your consideration. The relevant sentence has been rephrased in the revised manuscript. In addition, we would like to clarify that the original intended meaning of the sentence is that NACs are an important component of $PM_{2.5}$, which, despite their low mass abundance, exert a significant impact on the light absorption properties of aerosols.

Lines 47–49: …NACs are important constituents of atmospheric fine particulate matter ($PM_{2.5}$) and are well recognized for their strong light-absorbing properties (Huang et al., 2025; Harrison et al., 2005; Wang et al., 2022)…

2. Line 146: the unit of PM2.5 concentration is incorrect.

Response: We greatly appreciate your careful and thorough review of our manuscript, and the corresponding revision has been made accordingly in the revised manuscript (Line 150).

3. Figure 2: Area charts are not suitable for representing SO_2 and PM2.5 concentrations; line charts are suggested.

Response: We greatly appreciate your suggestion. The revision has been made in the revised manuscript.

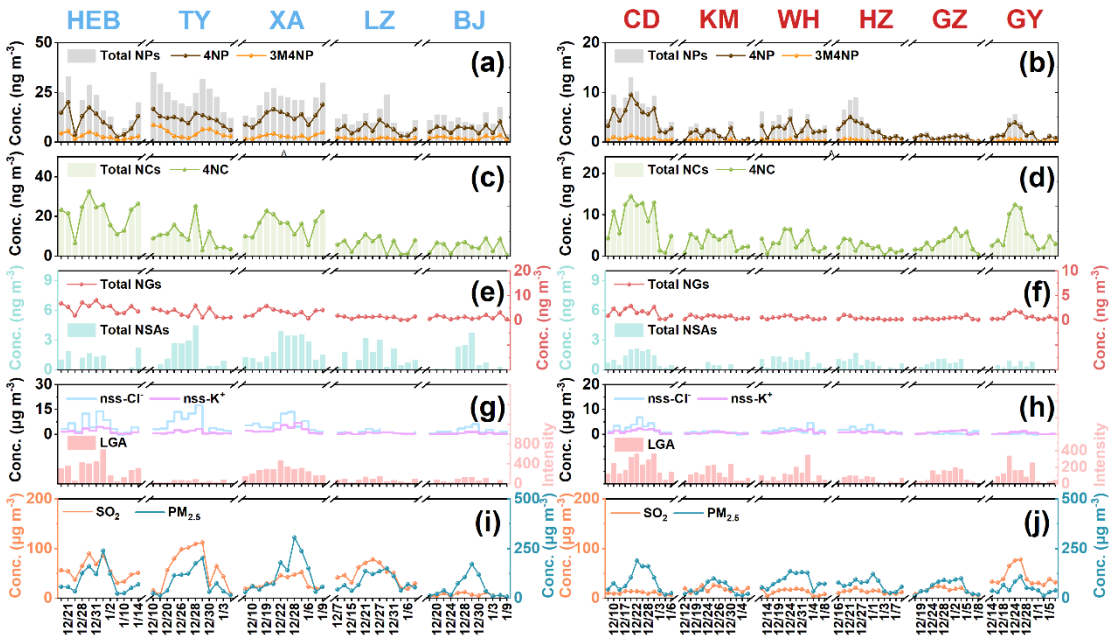

Figure 2. Temporal variations in (a–f) various NAC species and (g–l) key parameters in 11 Chinese cities.

*4. Line 337-338: 'Symbols * and ** indicate P < 0.05 and P < 0.01, respectively', what is meaning of '***' in Figure 3? How to calculate the frequency of significant positive correlations? 5. Line 485: 'Chins' is a typo.*

Response: Symbols '***', '**', and '*' denote $P < 0.001$, $P < 0.01$, and $P < 0.05$, respectively. The frequency of statistically significant correlations was calculated by counting each individual correlation event one by one and then summing up the counts. The typo 'Chins' has been corrected to 'China'.

Lines 379–380: …Symbols '***', '**', and '*' denote $P < 0.001$, $P < 0.01$, and $P < 0.05$, respectively…

Line 527: …in northern China…

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

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Comments of Referee #2 and our responses to them

This manuscript presents a valuable large-scale synchronous field observation on nitroaromatic compounds in PM2.5 across northern and southern Chinese cities during winter, with a focused investigation on the effects of relative humidity and aerosol liquid water on nitroaromatic compound formation. The key finding of this study is that the widely reported promoting effects of relative humidity and/or aerosol liquid water on nitroaromatic compound formation are not universally observed in this large-scale field study and may be modulated or offset by other factors. Based on my understanding, some previous observational studies have also presented similar results, though they were not the primary focus of discussion. The clear north-south comparative analysis of this study underscores the complexity of real atmospheric chemical systems. Thus, the overall results may provide important insights into the necessity of considering complex field conditions in future mechanistic research on nitroaromatic compound formation. In summary, the manuscript is generally well-written, the methodology is sound, and the conclusions are supported by the

data. I recommend acceptance after the authors address the following minor points to further strengthen the manuscript's clarity and impact.

Response: We are very grateful for your professional and thoughtful review of our manuscript. 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 suggestions:

1. ALW is a core variable for the conclusions. However, the method for calculating ALW is not described in either the Materials and Methods section or the SI. It is recommended that the authors provide a detailed methodology for obtaining ALW data, including thermodynamic models, key parameters, and input variables used.

Response: Thank you for your valuable comment. More discussions have been added to the revised manuscript.

Supporting information

S2. Predictions of aerosol liquid water (ALW) and pH

ALW concentration and aerosol pH were predicted using the ISORROPIA-II thermodynamic model, which has been extensively validated for the calculation of such parameters (Nguyen et al., 2016; He et al., 2018; You et al., 2026; Xu et al., 2023). This model is applicable across a broad range of ambient conditions, including relative humidity (RH) > 20% and typical tropospheric temperatures (Guo et al., 2015; Ding et al., 2019; Yang et al., 2024; Fountoukis and Nenes, 2007; Nguyen et al., 2014). The model simulations were run in forward mode under the assumption of a thermodynamically metastable state, with input datasets including particle-phase inorganic ion concentrations, ambient air

temperature, and RH. The methodological details are available in our previous studies (Xu et al., 2020; Yang et al., 2024). It should be noted that the contribution of aerosol organic components to ALW was not considered in this study, as it is likely relatively minor compared to ALW derived from inorganic aerosol components (Xu et al., 2020; Nguyen et al., 2016; Xu et al., 2023).

Aerosol pH was also derived from ISORROPIA-II outputs. Specifically, the pH was predicted by considering both the equilibrium particle hydronium ion concentration per volume air (H^+_{air}) and the predicted inorganics-derived water (W_i), which was detailed below (Guo et al., 2015).

$$pH = -\log_{10}H_{aq}^{+} = -\log_{10}\frac{1000H^+_{air}}{W_i} \quad (S1)$$

where both H^+_{air} and W_i were direct outputs from the ISORROPIA-II simulations. H^+_{aq} (mol L^{-1}) represents the hydronium ion concentration in the aqueous aerosol phase. H_{aq}^{+} value is estimated by dividing H^+_{air} by the ALW concentration.

A critical methodological constraint was addressed during pH calculation, which was detailed below. When ISORROPIA-II is run in forward mode with exclusive particle-phase composition inputs, it simulates the equilibrium gas-particle partitioning of NH_4^+. This process results in a portion of particle-phase NH_4^+ partitioning to the gas phase as NH_3, lowering the effective particulate NH_4^+ concentration (Ding et al., 2019; Song et al., 2018). This may introduce a systematic underestimation of aerosol pH, with prior study documenting a bias of ~1 pH unit when gas-phase NH_3 measurements are unavailable as model inputs (Guo et al., 2015; Wang et al., 2021). However, it is important to note that our correlation analysis was designed to explore the synchronous temporal co-variation trends between parameters, rather than their absolute value fluctuations. Thus, the adopted ALW and pH prediction framework does not undermine the robustness or reliability of our

correlation analysis results.

2. For the 154 total filter samples across 11 cities, please supplement the number of samples per city in either the Materials and Methods section or the SI.

Response: We greatly appreciate your suggestions. More descriptions have been added to the Supporting information (Tables S1–S4).

3. Line 127: Please confirm the abbreviation for Harbin. It is suggested that the authors change 'Haerbin (i.e., Harbin; HEB)' to 'Harbin (i.e., Haerbin; HEB)'.

Response: The revision has been made.

Line 126: …Harbin (i.e., Haerbin; HEB)…

4. Lines 129-133: Please refine the expression: "with average air temperatures sustained above 4°C in the southern cities generally below 2°C in the northern cities". It is suggested that the authors revise it to "with average air temperatures sustained above 4°C in the southern cities, and generally below 2°C in the northern cities". In addition, please refine the description of biomass/coal burning in northern and southern cities to be more precise (e.g., Biomass and coal combustion activities are prevalent in both southern and northern Chinese cities. However, as winters are typically colder in northern China, the demand for fossil fuels for heating is significantly higher there than in the south. For instance, the centralized winter heating policy in China is generally implemented only in northern

regions during the cold season.), which is consistent with the study's conclusions.

Response: We are very grateful for your professional and thoughtful review of our manuscript. The relevant content has been rephrased in the revised manuscript.

Lines 129–137: …A striking north-south temperature discrepancy was observed during this period. Specifically, the average ambient air temperature remained above 4°C in all southern cities, whereas it was generally below 2°C across the northern cities (**Tables S1–S4**). It is noteworthy that biomass and coal combustion activities are prevalent during winter in both southern and northern Chinese cities (Yang et al., 2025; Huang et al., 2024). However, as winters are typically colder in northern China, the demand for fossil fuels for heating is significantly higher there than in the south. For instance, the centralized winter heating policy in China is generally implemented only in northern regions during the cold season.....

5. It is stated that "the constraining effects from O3, ·OH, and solar radiation on NAC formation were stronger in northern China due to higher levels of light-absorbing air pollution", but the measurement/calculation method of ·OH concentration is not mentioned in the manuscript. Please supplement the method for obtaining ·OH data (e.g., detailed empirical model calculation or estimation from precursor concentrations).

Response: We are very grateful for your professional and thoughtful review of our manuscript. The relevant content has been added in the revised manuscript.

Supporting information

S3. Prediction of hydroxyl radical (·OH) concentrations

The concentrations of ·OH were estimated in this study using a widely validated empirical parameterization developed by Ehhalt and Rohrer (2000), as defined below.

$$[\cdot OH] = 4.1 \times 10^9 \times (J_{NO2})^{0.19} \times (J_{O^1D})^{0.83} \times \frac{140[NO_2]+1}{0.41[NO_2]^2+1.7[NO_2]+1} \quad (S2)$$

where J_{NO2} and J_{O^1D} denote the photolysis rate coefficients of nitrogen dioxide (NO_2) and ozone (O_3), respectively. These photolysis rate coefficients were simulated using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model, accessed via the official interactive web (https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/). Other required input parameters for the model simulations, including aerosol optical depth (AOD), cloud optical depth (COD), aerosol single scattering albedo (SSA), Ångström exponent (AE), cloud top height, and O_3 column concentration, were derived from the Moderate Resolution Imaging Spectroradiometer (MODIS) Level-3 daily gridded (1° × 1°) dataset (MOD08_D3/MYD08_D3). To better represent diurnal variations across sampling days, the data from Terra (morning) and Aqua (afternoon) satellites were combined and averaged. A constant surface albedo of 0.2 was prescribed for simulations. Hourly NO_2 concentration data were obtained from the official national air quality monitoring network operated by the China National Environmental Monitoring Center (http://www.cnemc.cn/).

We acknowledge that inherent uncertainties exist in our ·OH predictions, primarily driven by the complexity of tropospheric ·OH chemistry, which involves numerous interconnected production and loss pathways beyond those captured by the empirical parameterization (Vaughan et al., 2012). Nevertheless, the predicted ·OH levels remain broadly within the same order of magnitude as the measured ambient ·OH levels (Yan et al., 2019; Li et al., 2018; Hofzumahaus et al., 2009; Wang et al., 2020; Yin et al., 2026). Accordingly, these validations confirm that our predicted ·OH concentrations are broadly representative of ambient levels in the study regions. Critically, even if uncertainties remain in the absolute concentration values of ·OH, the temporal dynamics and variation trends of

the predicted ·OH dataset are robust and reliably reflect those of ambient ·OH levels, which is the focus of our correlation analysis.

6. Line 215: City abbreviation error. "HW" is a typo and it should be WH (Wuhan). Please unify all city abbreviations throughout the text.

Response: Thank you for your careful review. The revision has been made (Line 236).

7. Line 287: "Figure 2d,d,f" is duplicated. Please correct to the correct labels (e.g., Figure 2b,d,f).

Response: Thank you for your careful review. The revision has been made (Line 323).

8. Lines 280-281: Please revise "the highest total NC event occurred in HEB" to "the highest total NC concentration occurred in HEB" for accuracy. When summarizing the city-level concentration order, please double-check and confirm the ranking sequence to avoid inconsistency.

Response: Thank you for your suggestion. The revision has been made (Line 317).

9. Lines 311-316: Please strengthen the logic slightly. When interpreting weak correlations between NACs and vehicle emission tracers, please add one short sentence to clarify that this does not exclude traffic-related precursor contributions to secondary NACs.

Alternatively, this does not imply that the contribution of traffic-related precursors to secondary NACs is negligible, since only particulate-phase traffic tracers were employed in the analysis.

Response: Thank you for your suggestion. The relevant content has been added in the revised manuscript.

Lines 352–354: …However, this does not imply that the contribution of traffic-related precursors to secondary NACs is negligible, since only particulate-phase traffic tracers were employed in the analysis…

Lines 368–371: …Given that NACs in the actual atmospheric environment are affected not only by primary emissions but also by secondary formation and removal processes, insignificant or weak correlations between various NACs and source-specific tracers do not necessarily indicate a lack of substantial influence from corresponding sources…

10. Lines 321-325: When referring to Figure S5 (the fire spot map), please add further explanation to support the observation of higher biomass burning intensity in southern cities. In fact, although open fire spots are less frequent in the north, the colder climate there leads to widespread indoor use of biomass materials for heating and cooking in rural households, such as through traditional heated beds (kang).

Response: Thank you for your suggestion. The relevant content has been added in the revised manuscript.

Lines 362–366: …Importantly, although open fire spots are less frequent in the north, the colder climate there leads to widespread indoor use of biomass materials for heating and

cooking in rural households, such as through traditional heated beds (kang). Thus, the above findings do not necessarily indicate that biomass burning released more NACs in southern China…

11. Line 485: It is a typo. Please correct "in northern Chins" to "in northern China".

Response: Thank you for your comment. The revision has been made (Line 527).

12. Lines 486-487: Please change the sentence "SR was distributed in a nearly opposite direction to NCs, NPs, and NGs in the PCA plot" to "SR showed an opposite vector direction to NCs, NPs, and NGs in the PCA plot, indicating a notable inhibitory effect…".

Response: Thank you for your comment. The revision has been made (Lines 528–529).

13. When addressing the discrepancy between chamber results (RH/ALW significantly promote NACs) and field observations (no significant promotion), please briefly emphasize both the nonlinear or multi-factor interactions present in the real atmosphere and the current limitations in understanding the underlying laboratory mechanisms.

Response: Thank you for your suggestion. More discussions have been added to the revised manuscript.

Lines 581–588: …However, this large-scale observational study suggests that the generalizability of such RH- and ALW-regulated promotional effects on NAC formation in real atmospheric environments requires further validation. We acknowledge that individual factors (e.g., RH or ALW) play a crucial role in governing aerosol NAC formation.

Nevertheless, field environments are often more complex than laboratory-simulated scenarios. Thus, the overall results highlight that future investigations into NAC formation mechanisms should consider the impacts of multi-factor interactions…

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

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