General.

We would like to appreciate the editor and reviewer 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 reviewer 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 #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.

References

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.

Ehhalt, D. H. and Rohrer, F.: Dependence of the OH concentration on solar UV, J. Geophys. Res.: Atmos., 105, 3565-3571, 10.1029/1999jd901070, 2000.

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+–Ca 2+–Mg 2+–NH 4+–Na+–SO 4 2−–NO 3−–Cl−–H 2 O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 2007.

Guo, H. Y., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J., Carlton, A., Lee, S. H., Bergin, M., and Ng, N.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228. https://doi.org/5210.5194/acp-5215-5211-2015, 2015.

He, Q. F., Ding, X., Fu, X. X., Zhang, Y. Q., Wang, J. Q., Liu, Y. X., Tang, M. J., Wang, X. M., and Rudich, Y.: Secondary Organic Aerosol Formation from Isoprene Epoxides in the Pearl River Delta, South China: IEPOX- and HMML-Derived Tracers, J. Geophys. Res.: Atmos., 123, 6999-7012, 2018.

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702-

1704, doi:10.1126/science.1164566, 2009.

Huang, S., Shen, Z., Yang, X., Bai, G., Zhang, L., Zeng, Y., Sun, J., Xu, H., Ho, S. S. H., Zhang, Y., and Cao, J.: Nitroaromatic compounds in six major Chinese cities: Influence of different formation mechanisms on light absorption properties, Sci. Total Environ., 930, 172672, https://doi.org/10.1016/j.scitotenv.2024.172672, 2024.

Li, Z., Xue, L., Yang, X., Zha, Q., Tham, Y. J., Yan, C., Louie, P. K. K., Luk, C. W. Y., Wang, T., and Wang, W.: Oxidizing capacity of the rural atmosphere in Hong Kong, Southern China, Sci. Total Environ., 612, 1114-1122, 10.1016/j.scitotenv.2017.08.310, 2018.

Nguyen, T. K. V., Zhang, Q., Jimenez, J. L., Pike, M., and Carlton, A. G.: Liquid water: ubiquitous contributor to aerosol mass, Environ. Sci. Tech. Let., 3, 257-263. https://doi.org/210.1021/acs.estlett.1026b00167, 2016.

Nguyen, T. K. V., Petters, M., Suda, S., Guo, H., Weber, R., and Carlton, A.: Trends in particle-phase liquid water during the Southern Oxidant and Aerosol Study, Atmos. Chem. Phys., 14, 10911-10930. https://doi.org/10910.15194/acp-10914-10911-12014, 2014.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

Vaughan, S., Ingham, T., Whalley, L. K., Stone, D., Evans, M. J., Read, K. A., Lee, J. D., Moller, S. J., Carpenter, L. J., Lewis, A. C., Fleming, Z. L., and Heard, D. E.: Seasonal observations of OH and HO2 in the remote tropical marine boundary layer, Atmos. Chem. Phys., 12, 2149-2172, 10.5194/acp-12-2149-2012, 2012.

Wang, G., Jia, S., Li, R., Ma, S., Chen, X., Wu, Z., Shi, G., and Niu, X.: Seasonal variation characteristics of hydroxyl radical pollution and its potential formation mechanism during the daytime in Lanzhou, J. Environ. Sci., 95, 58-64, https://doi.org/10.1016/j.jes.2020.03.045, 2020.

Wang, Y., Hu, M., Hu, W., Zheng, J., Niu, H., Fang, X., Xu, N., Wu, Z., Guo, S., Wu, Y., Chen, W., Lu, S., Shao, M., Xie, S., Luo, B., and Zhang, Y.: Secondary Formation of Aerosols Under Typical High-Humidity Conditions in Wintertime Sichuan Basin, China: A Contrast to the North China Plain, J. Geophys. Res.: Atmos., 126, e2021JD034560, https://doi.org/10.1029/2021JD034560, 2021.

Xu, Y., Dong, X. N., He, C., Wu, D. S., Xiao, H. W., and Xiao, H. Y.: Mist cannon trucks can exacerbate the formation of water-soluble organic aerosol and PM2.5 pollution in the road environment, Atmos. Chem. Phys., 23, 6775-6788, 10.5194/acp-23-6775-2023, 2023.

Xu, Y., Miyazaki, Y., Tachibana, E., Sato, K., Ramasamy, S., Mochizuki, T., Sadanaga, Y., Nakashima, Y., Sakamoto, Y., Matsuda, K., and Kajii, Y.: Aerosol Liquid Water Promotes the Formation of Water-Soluble Organic Nitrogen in Submicrometer Aerosols in a Suburban Forest, Environ. Sci. Technol., 54, 1406-1414. https://doi.org/1410.1021/acs.est.1409b05849, 2020.

Yan, C., Tham, Y. J., Zha, Q., Wang, X., Xue, L., Dai, J., Wang, Z., and Wang, T.: Fast heterogeneous loss of N2O5 leads to significant nighttime NOx removal and nitrate aerosol formation at a coastal background environment of southern China, Sci. Total Environ., 677, 637-647, https://doi.org/10.1016/j.scitotenv.2019.04.389, 2019.

Yang, T., Xu, Y., Wang, Y. C., Ma, Y. J., Xiao, H. W., Xiao, H., and Xiao, H. Y.: Non-biogenic sources are an important but overlooked contributor to aerosol isoprene-derived organosulfates during winter in northern China, Atmos. Chem. Phys., 25, 2967-2978, 10.5194/acp-25-2967-2025, 2025.

Yang, T., Xu, Y., Ma, Y.-J., Wang, Y.-C., Yu, J. Z., Sun, Q.-B., Xiao, H.-W., Xiao, H.-Y., and Liu, C.-Q.: Field Evidence for Constraints of Nearly Dry and Weakly Acidic Aerosol Conditions on the Formation of Organosulfates, Environ. Sci. Technol. Lett., 11, 981-987, 10.1021/acs.estlett.4c00522, 2024.

Yin, M.-J., Xu, Y., Zhu, R.-G., Wang, Y., Sun, Q.-B., Gui, L., You, Y.-C., Tao, J.-L., Xiao, H.-W., Xiao, H., and Xiao, H.-Y.: Field New Insights into Bioaerosol Amino Acid Origin and Atmospheric Degradation: Significant Dust Contribution and Drying Effect, Environ. Sci. Technol., 60, 688-699, 10.1021/acs.est.5c12980, 2026.

You, Y.-C., Yang, T., Xu, Y., Gui, L., Wang, Y.-C., Yin, M.-J., Xiao, H., Xiao, H.-W., and Xiao, H.-Y.: Novel Discoveries about the Potential Nonsecondary Origins of C2–C3 Organosulfates in Ambient Aerosol Particles, Environ. Sci. Technol., 60, 6298-6309, 10.1021/acs.est.5c18511, 2026.