

General.

We would like to appreciate the editor for providing the valuable comments on our work. We have revised our manuscript by fully taking the editor's comments into account. Responses to specific comments raised by the editor are described below. **All the changes made and appeared in the revised text are shown in red.** **All detailed answers to comments are displayed in blue.**

Comments of the editor and our responses to them

Comments:

I would like to thank the authors for taking the Reviewers' comments seriously and having revised the manuscript accordingly.

Response: We appreciate your professional review for our article. 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 comments:

1) *For the comment about the potential influence of using 0.1% formic acid. The authors argued that the particles are inherently acidic (generally $\text{pH} < 3$), which needs more support. In Northern China, particles are generally less acidic nowadays. CHON compounds which can go hydrolysis could be potentially affected by the low pH.*

Response: We appreciate the editor's comments regarding pH conditions and the potential hydrolysis of CHON compounds. Below, we address the concerns in detail:

1. Acidity of aerosols in Northern China

According to recent studies (Wang et al., 2021b; Zhang et al., 2023a; Li et al., 2024; Wang et al., 2023; Zhang et al., 2023b), aerosols during haze episodes in Northern China typically were acidic, with pH values ranging from 4 to 5. These findings were similar to our observations in Harbin and Beijing during haze periods. In contrast, in Hangzhou, aerosol acidity was higher (an average pH value of 3) (Li et al., 2025; Nah et al., 2023). These results indicate that aerosols remain acidic or weakly acidic during winter haze periods in our study regions.

2. Potential impact of pH on CHON compound hydrolysis

We recognize that CHON compounds susceptible to hydrolysis might be influenced by low pH conditions. However, the likelihood of such reactions significantly altering our results is minimized for the following reasons:

The LC gradient elution time in this study was only 18 minutes, which was substantially shorter than the sampling duration and aging time of the particles. This short elution time reduced the probability of significant chemical changes to the compounds.

Additionally, numerous laboratory and field studies (Zhao et al., 2018; Zhang et al., 2016; Zhang et al., 2024; Abudumutailifu et al., 2024; Wang et al., 2021a) using formic acid in LC mobile phases have not reported substantial artifacts or adverse effects on analytes under similar conditions.

In response to these concerns, we have provided additional clarification in **Sect. S1. UPLC-ESI-QToFMS Analysis** in the Supporting Information (SI). The added content is as follows (Pages S3-S4):

The addition of formic acid to the mobile phase played a crucial role in optimizing chromatographic separation and enhancing ionization efficiency during ESI– MS analysis (Núñez and Paolo, 2014; Kuehnbaum and Britz-Mckibbin, 2013). This

approach is commonly employed in the analysis of atmospheric organic compounds (Zhang et al., 2024; Abudumutailifu et al., 2024; Wang et al., 2021a). Although the acidic conditions introduced by formic acid may affect certain CHON compounds through hydrolysis or acid-catalyzed reactions, the aerosols analyzed in this study were generally acidic or mildly acidic (average pH values of 3–5). Additionally, the short elution time (18 minutes) minimized the likelihood of significant chemical changes to the compounds.

2) *Line 192, change to "CHN+ compounds"*

Response: The revision has been made in the revised manuscript (Line 192).

3) *Line 264, change "contributed" to "contribute"*

Response: The revision has been made in the revised manuscript (Line 264).

4) *Line 278, use "mean values"*

Response: The revision has been made in the revised manuscript (Line 278).

5) *Line 583-585, change this sentence to "In contrast, due to the absence of heating for generally mild winters and the implementation of stricter pollution control measures"*

Response: We greatly appreciate your suggestions. The revision has been made in the revised manuscript (Lines 583-584).

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

Reference:

Abudumutailifu, M., Shang, X., Wang, L., Zhang, M., Kang, H., Chen, Y., Li, L., Ju, R., Li, B., Ouyang, H., Tang, X., Li, C., Wang, L., Wang, X., George, C., Rudich, Y., Zhang, R., and Chen, J.: Unveiling the Molecular Characteristics, Origins, and Formation Mechanism of Reduced Nitrogen Organic Compounds in the Urban Atmosphere of Shanghai Using a Versatile Aerosol Concentration Enrichment System, *Environ. Sci. Technol.*, 10.1021/acs.est.3c04071, 2024.

Kuehnbaum, N. L. and Britz-McKibbin, P.: New Advances in Separation Science for Metabolomics: Resolving Chemical Diversity in a Post-Genomic Era, *Chem. Rev.*, 113, 2437-2468, 10.1021/cr300484s, 2013.

Li, G., Su, H., Zheng, G., Zhou, M., Han, W., Zhang, Y., Ma, N., Wang, H., Klimach, T., and Cheng, Y.: Novel Device for in Situ and Real-Time Detection of the Acidity of Ambient Aerosols: Laboratory Characterization and Ambient Measurements, *Environ. Sci. Technol.*, 59, 659-667, 10.1021/acs.est.4c09221, 2025.

Li, W., Qi, Y., Liu, Y., Wu, G., Zhang, Y., Shi, J., Qu, W., Sheng, L., Wang, W., Zhang, D., and Zhou, Y.: Daytime and nighttime aerosol soluble iron formation in clean and slightly polluted moist air in a coastal city in eastern China, *Atmos. Chem. Phys.*, 24, 6495-6508, 10.5194/acp-24-6495-2024, 2024.

Nah, T., Lam, Y. H., Yang, J., and Yang, L.: Long-term trends and sensitivities of PM_{2.5}

- pH and aerosol liquid water to chemical composition changes and meteorological parameters in Hong Kong, South China: Insights from 10-year records from three urban sites, *Atmos. Environ.*, 302, 119725, <https://doi.org/10.1016/j.atmosenv.2023.119725>, 2023.
- Núñez, O. and Paolo, L.: Applications and uses of formic acid in liquid chromatography-mass spectrometry analysis, in: *Advances in Chemistry Research*, edited by: Taylor, J. C., Nova Science Publishers, 71-86, 2014.
- Wang, K., Huang, R.-J., Brüeggemann, M., Zhang, Y., Yang, L., Ni, H., Guo, J., Wang, M., Han, J., Bilde, M., Glasius, M., and Hoffmann, T.: Urban organic aerosol composition in eastern China differs from north to south: molecular insight from a liquid chromatography-mass spectrometry (Orbitrap) study, *Atmos. Chem. Phys.*, 21, 9089-9104, <https://doi.org/10.5194/acp-21-9089-2021>, 2021a.
- Wang, T., Liu, Y., Zhou, S., Wang, G., Liu, X., Wang, L., Fu, H., Chen, J., and Zhang, L.: Key Factors Determining the Formation of Sulfate Aerosols Through Multiphase Chemistry—A Kinetic Modeling Study Based on Beijing Conditions, *J. Geophys. Res.-Atmos.*, 128, e2022JD038382, <https://doi.org/10.1029/2022JD038382>, 2023.
- Wang, W., Liu, M., Wang, T., Song, Y., Zhou, L., Cao, J., Hu, J., Tang, G., Chen, Z., Li, Z., Xu, Z., Peng, C., Lian, C., Chen, Y., Pan, Y., Zhang, Y., Sun, Y., Li, W., Zhu, T., Tian, H., and Ge, M.: Sulfate formation is dominated by manganese-catalyzed oxidation of SO₂ on aerosol surfaces during haze events, *Nature Communications*, 12, 1993, [10.1038/s41467-021-22091-6](https://doi.org/10.1038/s41467-021-22091-6), 2021b.

- Zhang, M., Cai, D., Lin, J., Liu, Z., Li, M., Wang, Y., and Chen, J.: Molecular characterization of atmospheric organic aerosols in typical megacities in China, *npj Climate and Atmospheric Science*, 7, 230, 10.1038/s41612-024-00784-1, 2024.
- Zhang, X., Dalleska, N. F., Huang, D. D., Bates, K. H., Sorooshian, A., Flagan, R. C., and Seinfeld, J. H.: Time-resolved molecular characterization of organic aerosols by PILS + UPLC/ESI-Q-TOFMS, *Atmos. Environ.*, 130, 180-189, <https://doi.org/10.1016/j.atmosenv.2015.08.049>, 2016.
- Zhang, X., Tong, S., Jia, C., Zhang, W., Wang, Z., Tang, G., Hu, B., Liu, Z., Wang, L., Zhao, P., Pan, Y., and Ge, M.: Elucidating HONO formation mechanism and its essential contribution to OH during haze events, *npj Climate and Atmospheric Science*, 6, 55, 10.1038/s41612-023-00371-w, 2023a.
- Zhang, Y., Chen, Y., Jiang, N., Wang, S., Zhang, R., Lv, Z., Hao, X., and Wei, Y.: Chemical-composition characteristics of PM₁ and PM_{2.5} and effects on pH and light-extinction coefficients under different pollution levels in Zhengzhou, China, *Journal of Cleaner Production*, 409, 137274, <https://doi.org/10.1016/j.jclepro.2023.137274>, 2023b.
- Zhao, R., Kenseth, C. M., Huang, Y., Dalleska, N. F., and Seinfeld, J. H.: Iodometry-Assisted Liquid Chromatography Electrospray Ionization Mass Spectrometry for Analysis of Organic Peroxides: An Application to Atmospheric Secondary Organic Aerosol, *Environ. Sci. Technol.*, 52, 2108-2117, 10.1021/acs.est.7b04863, 2018.