Response to the Reviewer Comments

Dear Editor and Reviewers,

Thank you for your valuable comments and suggestions, which have led to significant improvements in our paper. Below, we provide a point-to-point response to each comment.

Response to Reviewer #1:

This manuscript presents a comprehensive characterization of aqueous-phase secondary organic aerosol (aqSOA) formation in suburban Nanjing during the wintertime of 2020, based on high-resolution AMS measurements, PMF source apportionment, and the estimated ALW and aerosol acidity. The study identifies two distinct diurnal patterns of aqSOA driven respectively by aqueous-phase chemistry and daytime photochemical oxidation. The findings provide meaningful insights into the evolving roles of nitrate, ALW, and acidity in SOA formation mechanisms in Eastern China. Overall, the manuscript is clearly written, scientifically sound, and suitable for publication after dealing with the below comments.

Response: We thank the reviewer for their thoughtful comments, which have helped us to substantially improve the manuscript.

1. Line 21. The statement that "its formation mechanisms remain unclear due to limited observational evidence" is somewhat overstated. A more precise phrasing would be: "…its formation pathways under real ambient conditions in Chinese urban regions remain insufficiently constrained…" This better reflects the current state of knowledge without implying a lack of global understanding. Same for Line 46-47.

Response: Thanks for the thoughtful comment. We agree that the original phrasing could be refined to more accurately reflect the current state of research. As suggested, we have revised the statement on Line 21 to: "…its formation pathways under real ambient conditions in Chinese urban regions remain insufficiently constrained…" A similar adjustment has been made on Lines 48.

2. Line 92. Replace "more" with "abundant"

Response: Thank you for pointing this out. We have changed "more" to "abundant" on Line 94 as suggested.

3. In Section 2.3 (Line 123), the authors calculate aerosol liquid water (ALW) solely based on inorganic aerosol thermodynamics using E-AIM. However, recent field and laboratory studies have demonstrated that organic aerosol (OA) also contributes substantially to ALW, especially under high-RH conditions that are relevant in this

study. For typical urban environments, OA hygroscopicity ($\kappa \approx 0.08–0.20$) can lead to organic-associated ALW that is comparable in magnitude to inorganic-associated ALW, particularly when OA mass concentrations are high (Kuang et al., 2021; Nguyen et al., 2016; Zhang et al., 2024).

Given that one of the central conclusions of the manuscript is that ALW strongly modulates aqSOA formation, it is important to either: (1) Include OA-derived ALW in the analysis (e.g., using κ-Köhler parameterizations with measured OA composition), or (2) Provide a justification for omitting it—for example, demonstrating that inorganic ALW dominates under the specific composition and RH conditions at this site, or showing that including OA-ALW would not change the interpretation of Figures 2–3. At minimum, a short discussion acknowledging the potential magnitude of OA-ALW and its implications for the aqSOA–ALW relationship should be added.

Response: Thanks for the valuable comments. We have calculated the concentration of organic-associated ALW following the method of Nguyen et al. (2016). The average concentration of OA-derived ALW was 1.95 μg/m³, accounting for approximately 10.7% of the ALW of inorganic aerosols. Given that this proportion is relatively low, OA-ALW is negligible in our study. Therefore, we only consider aerosol liquid water associated with inorganic aerosols.

Revised text:

In this study, the ALW associated with the hygroscopicity of organics was estimated following the method of Nguyen et al. (2016) using the κ-Kohler theory and the Zdanovskii−Stokes−Robinson mixing rule. The estimated organic-associated ALW was only 10.7% of that associated with the inorganic aerosols. Therefore, the organic-associated ALW was neglected in the subsequent analysis. (Lines 134-138)

4. Lines 147–153 should be moved to a position before Line 138. As currently written, the discussion at Line 138 is confusing because the manuscript begins interpreting aqSOA characteristics before explaining how aqSOA is identified.

Response: Thanks for raising this important point regarding the flow of the manuscript. We have revised the manuscript as suggested.

5: Line 197-203, the authors reported a strong correlation between aqSOA and total nitrate and interpreted this as evidence that nitrate enhances aqSOA formation. However, it is possible that organic nitrate ($NO_{3,org}$) contributes significantly to the total nitrate signal in the AMS, particularly under humid conditions, and that the apparent correlation may partly reflect joint formation pathways involving biogenic VOCs (e.g., isoprene, monoterpenes, etc.). Numerous studies (Boyd et al., 2015, 2017; Takeuchi & Ng, 2019; Zhang et al., 2020) have shown that aqueous and multiphase processing of

organic nitrates can produce highly oxygenated organics with a tight relationship between aqSOA and $NO_{3,org}$.

I would suggest the author separates NO3 to inorganic and organic compounds following the method described by Farmer et al. (2010), and analyze how each component ($NO_{3,inorg}$ vs. $NO_{3,org}$) relates to aqSOA. This would largely benefit Section 3.2 discussion.

Response: Thanks for raising the insightful comments. As suggested, we have separated the nitrate into inorganic and organic components using the method described by Farmer et al. (2010). We adopted a NO^+ to NO_2^+ ratio of 10 for organic nitrates. The results show that the organic nitrate ($NO_{3,org}$) contributed an average of only 9.5% to the total nitrate signal. This relatively low fraction of organic nitrates indicates that the strong correlation between aqSOA and the total nitrate was dominated by the inorganic nitrates.

We have added the following text to the revised manuscript:

"We estimated that the average contribution of organic nitrates to the total nitrate was approximately 9.5% by assuming a NO^+ to NO_2^+ ratio of 10 for organic nitrates (Farmer et al., 2010). Thus, organic nitrates can be considered negligible in this study."

(Lines215-218)

Response to Reviewer #2:

I. General Evaluation

This manuscript presents an autumn field campaign in suburban Nanjing and combines HR-ToF-AMS measurements with PMF and E-AIM modeling to discuss aqSOA and its coupling with nitrate/ALW/acidity and photochemical processes, and further proposes Type I/II diurnal patterns. Overall, the research question is clear, and the dataset and analytical framework are relatively complete with regional relevance. However, several key criteria and parameter assumptions (e.g., Type classification, E-AIM inputs/uncertainties, CE) still need to be made more transparent and reproducible. In addition, parts of the mechanistic discussion should adopt more cautious causal language and clarify relevant boundary conditions. Therefore, I recommend minor revision.

Response: We thank the reviewer for their valuable comments, which have led to substantial improvements in our paper.

II. Major Comments

To minimize potential confusion with MO-OOA and other highly oxidized factors, please consider adding the following in the Supplementary Information (SI): (i) a side-by-side comparison of the mass spectral profiles of aqSOA and MO-OOA; and (ii) a comparison of their correlations with nitrate and ALW (optionally, if offline dicarboxylic acid/oxalate data are available, these may be included as additional constraints). Please also briefly summarize the key interpretation points for Figs. S1–S3 and the major sources of uncertainty.

Response: Thank you for the constructive suggestion to clarify the distinction between aqSOA and MO-OOA. We have added a dedicated section to the Supplementary Information featuring a side-by-side comparison of their mass spectral profiles and their respective correlations with nitrate and ALW.

The analysis shows that (i) although both are highly oxidized factors, aqSOA exhibits stronger signals at m/z 28 and 43. Its elemental ratios, including H/C, O/C, and N/C, are also significantly higher (Fig.R1). (ii) More importantly, aqSOA shows strong correlations with both nitrate and ALW, whereas MO-OOA shows no significant correlation with either (Fig.R2).

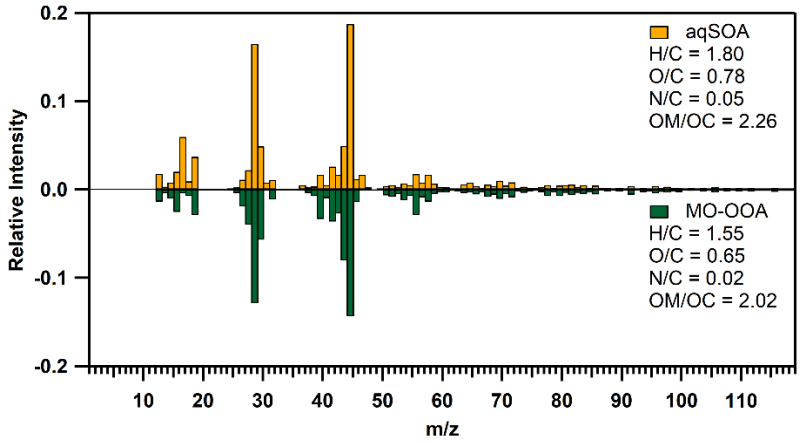

Fig. R1. Comparison of mass spectra of aqSOA and MO-OOA.

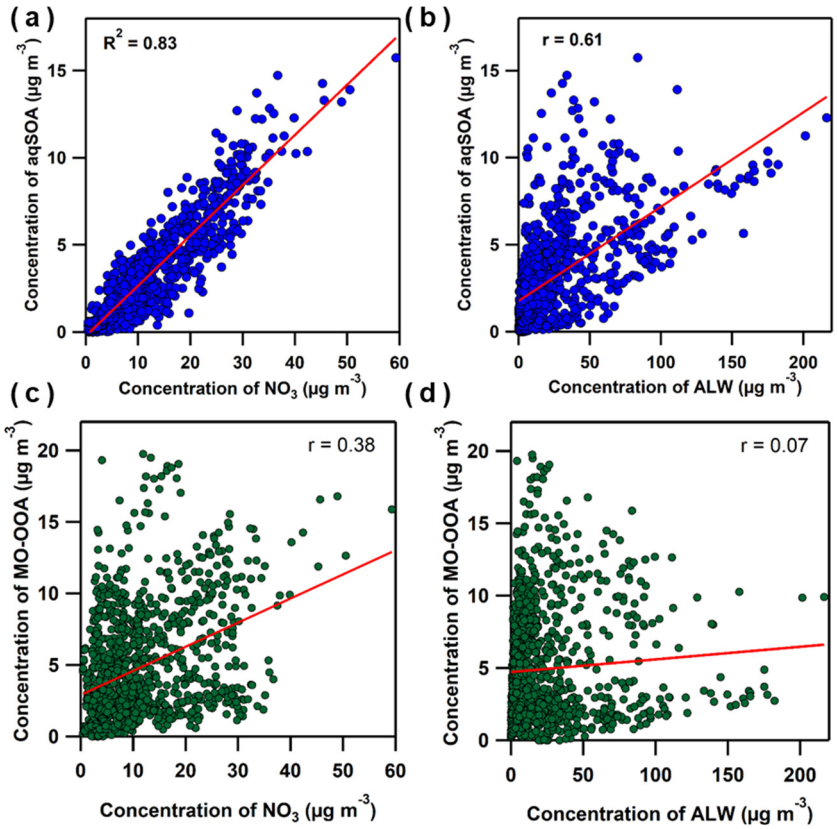

Fig. R2. Scatter plots of aqSOA and MO-OOA versus nitrate and ALW.

Please also briefly summarize the key interpretation points for Figs. S1–S3 and the major sources of uncertainty.

Response: The PMF diagnostic plots are illustrated in Fig. S1. We observed a substantial decrease in Q/Q_{exp} as the number of factors increased gradually from 2 to 5. However, this decreasing trend became less pronounced when the number of factors exceeded 5. When we explored solutions with more than 6 factors, the Variation displayed notable variability across different fpeak values. Then based on the interpretability of the factors, we ultimately identified a solution comprising 5 factors,

including one primary factor, one nitrogenous OA (NOA) factor, and three SOA factors, namely, less-oxidized oxygenated OA (LO-OOA), more-oxidized OOA (MO-OOA), and aqSOA.

The mass spectra, time series and diurnal variations of these five factors are given in Fig. S2. Notably, when we examine the elemental ratios, including H:C, O:C, N:C, and OM:OC, for each factor (Fig. S2), a distinct pattern emerges. POA and NOA exhibit significantly higher H:C compared to LO-OOA and MO-OOA, while displaying markedly lower O:C than these secondary factors. AqSOA exhibits higher N:C than LO-OOA and MO-OOA.

POA exhibits a notable predominance of $C_xH_y^+$ fragments over $C_xH_yO_1^+$ and $C_xH_yO_{>1}^+$ fragments. The strong alignment in the time series between POA and BC (Fig. S2a) further corroborates the correlation between this factor and motor vehicle emissions. The diurnal variation in POA emissions exhibits a pronounced morning peak, coinciding with the timing of motor vehicle emissions during the morning rush hour.

The mass spectra of LO-OOA and MO-OOA show a prominent feature is the predominant contribution from $C_xH_yO_1^+$ and $C_xH_yO_{>1}^+$ fragments, particularly in MO-OOA. In the mass spectra of both LO-OOA and MO-OOA, the contribution of $C_2H_3O^+$ (m/z 43) exceeds that of CO_2^+ (m/z 44). The contribution of $C_xH_y^+$ fragments in the mass spectra of LO-OOA is relatively higher than that of MO-OOA. Regarding diurnal variations, LO-OOA exhibits no significant daily changes, whereas MO-OOA shows a slow upward trend during daylight hours, which may be attributed to photochemical reactions.

AqSOA exhibited strong correlations with unique fragment ions that are widely recognized as markers of aqueous-phase secondary products, such as $C_2O_2^+$ (m/z 56, r = 0.77) and CH_3SO^+ (m/z 63, r = 0.90) (Fig. S3). The aqSOA exhibits strong correlations with sulfate (r = 0.74), nitrate (r = 0.91), and ammonium (r = 0.93), indicating its strong correlation with aqueous-phase processes.

NOA is characterized with more evident contributions from $C_xH_yN_z^+$ fragments compared to other factors. Additionally, its N:C is significantly higher than that of the other factors (Fig. S2e).

We have added above discussion to the revised SI.

Please clearly specify the classification criteria (e.g., peak timing window, whether double peaks are allowed, whether smoothing is applied), the definition of "rainy days," and provide a "date–type" list (can be placed in the SI) to facilitate independent verification.

Response: The peak timing window for classification is 7:00–10:00 local time; double peaks are allowed (though only 4 days exhibited a secondary peak, occurring at 15:00, 22:00, 23:00, and 23:00, respectively); and no smoothing was applied to the data.

"Rainy days" are defined as those with recorded rainfall >0 mm, based on measurements from the automatic weather station at the SORPES site. Additionally, as recommended, a "date–type" list has been provided in the Supplementary Information to facilitate verification.

Table R1. Date–type list

UTC+8	Diurnal pattern	UTC+8	Diurnal pattern
2025/10/13	Incomplete data	2025/11/7	I
2025/10/14	Incomplete data	2025/11/8	I
2025/10/15	Rainy	2025/11/9	II
2025/10/16	Rainy	2025/11/10	II
2025/10/17	I	2025/11/11	II
2025/10/18	I	2025/11/12	I
2025/10/19	I	2025/11/13	I
2025/10/20	I	2025/11/14	I
2025/10/21	Rainy	2025/11/15	I
2025/10/22	I	2025/11/16	I
2025/10/23	I	2025/11/17	Rainy
2025/10/24	II	2025/11/18	Rainy
2025/10/25	II	2025/11/19	Rainy
2025/10/26	II	2025/11/20	Rainy
2025/10/27	I	2025/11/21	Rainy
2025/10/28	Rainy	2025/11/22	Rainy
2025/10/29	Rainy	2025/11/23	Rainy
2025/10/30	I	2025/11/24	Rainy
2025/10/31	I	2025/11/25	Rainy
2025/11/1	II	2025/11/26	Rainy
2025/11/2	I	2025/11/27	Rainy
2025/11/3	II	2025/11/28	I
2025/11/4	II	2025/11/29	I
2025/11/5	I	2025/11/30	Incomplete data

Without introducing additional complex quantitative analyses, please add a short discussion acknowledging that boundary-layer evolution and physical mixing/dilution in the morning may modulate the observed peak shape around 09:00–10:00. Please clarify that the main conclusions are primarily inferred under chemically constrained conditions.

Response: Thanks for your comments. We have added a brief discussion acknowledging that morning boundary-layer evolution and physical mixing/dilution could modulate the observed peak shape around 09:00–10:00. We have also clarified that the main conclusions of this study are drawn primarily under chemically constrained conditions.

Revised text:

It should be noted that the observed morning peak around 09:00–10:00 may be modulated not only by chemical production but also by concurrent physical processes, such as morning boundary-layer evolution and mixing/dilution effects. Nevertheless, the diurnal patterns and classification discussed herein are interpreted primarily under chemically constrained conditions, and the main conclusions about aqSOA formation pathways rely chiefly on chemical relationships and correlations. (Lines 269-275)

Please provide the key E-AIM inputs (e.g., whether gas-phase NH_3 is included) and the main uncertainty sources. Please also explain the basis for adopting the pH = 3 threshold and include a simple sensitivity test (SI is sufficient). In terms of wording, please prioritize "supports/indicates/is consistent with" over overly strong causal statements.

Response: Thanks for your comments. The key inputs to the E-AIM model include temperature, relative humidity, and the concentrations of inorganic ions (sulfate, nitrate, ammonium, chloride) as well as gas-phase ammonia (NH_3). The main sources of uncertainty stem from thermodynamic parameters and the uncertainties of measured inorganic ions.

The pH threshold of 3 was selected primarily to ensure a balanced distribution of data points across the two subgroups for meaningful statistical comparison. With this threshold, the subsets pH < 3 and pH ⩾ 3 contained 772 and 320 points, respectively, providing sufficiently large and comparable sample sizes. Other tested thresholds (e.g., pH = 2 or 3.5) resulted in highly uneven distributions (e.g., 43 vs. 1049 points at pH = 2; 1058 vs. 34 points at pH = 3.5, Fig. R3), which would compromise the robustness of the comparison. A simple sensitivity test illustrating the impact of different pH thresholds has been included in the Supplementary Information.

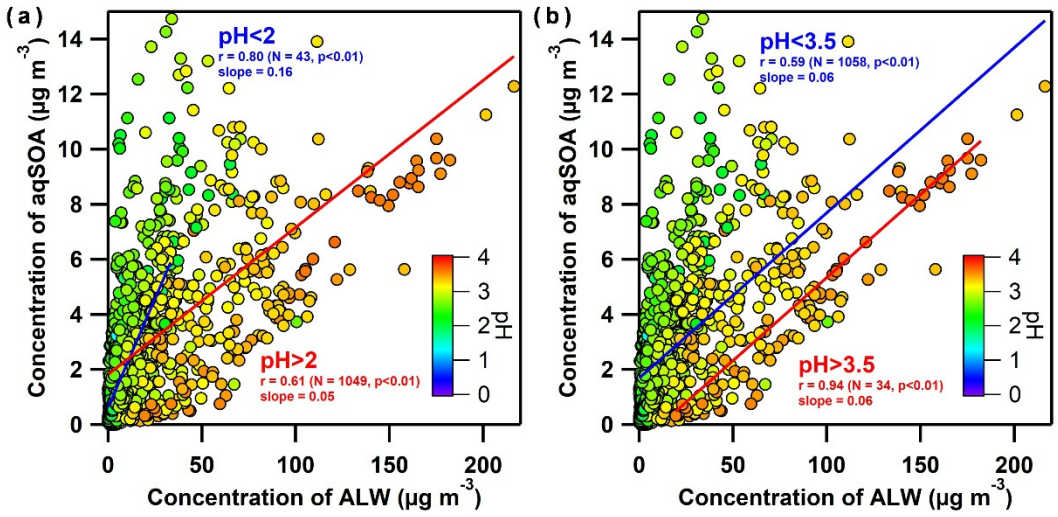

Fig. R3. Scatter plots of aqSOA versus ALW, (a) data divided at pH=2, (b) data divided at pH=3.5.

We have added the following text to the revised manuscript:

The key inputs to the E-AIM model include temperature, relative humidity, and the concentrations of inorganic ions (sulfate, nitrate, ammonium, chloride) as well as gas-phase ammonia. The main sources of uncertainty stem from thermodynamic parameters and the uncertainties of measured inorganic ions. (Lines 130-134).

We have reworded the strong causal statements as suggested.

Revised text:

*This suggests that nitrate aerosols **may contribute** importantly to aqSOA formation in Nanjing, **potentially mediated by** their influence on ALW and/or aqueous reactions. **(Lines 213-215)***

*The presence of ALW promotes the partitioning of water-soluble organic precursors and **allows for** subsequent aqueous-phase reactions **contributing to** aqSOA formation. **(Lines 230-232)***

III. Specific / Line-by-Line Comments

L49–52: Please add 1–2 recent regional studies and/or review papers to support the statement that "OA decreases while the SOA fraction increases."

Response: We have added recent regional studies/review papers to better support the statement regarding OA and SOA trends (Huang et al., 2025).

Revised text:

*In recent years, concentrations of OA have gradually declined across many regions in China due to the implementation of air pollution control measures, but the relative contribution of SOA has increased markedly **(Chen et al., 2024; Huang et al., 2025)**, with aqSOA constituting a substantial fraction. **(Lines 50-53)***

L120–122: Please add one sentence noting the potential bias/uncertainty of assuming CE = 0.5 during nitrate-rich periods.

Response: Thanks for the suggestion. We have added a sentence to state the potential uncertainty of CE = 0.5 during nitrate-rich periods.

Revised text:

As well, the collection efficiency (CE) was assigned a typical value of 0.5 for common environments, ***although it is recognized that this constant value may introduce additional uncertainty during periods with high nitrate content. (Lines 123-124)***

L249–253: Please provide the criteria for defining rainy days (threshold, data source, and whether post-rain hours are excluded) and list the excluded dates in the SI.

Response: "Rainy days" are defined as those with recorded rainfall > 0 mm, based on measurements from the automatic weather station at the SORPES site. Post-rain hours were not excluded from the analysis.

We have included the above discussion in the SI. The "date–type" list has been provided in Table S1.

L258–260: Please clarify how the ~1 h lag was estimated (e.g., peak-time difference, cross-correlation) and add one sentence on its possible implications for kinetics and/or phase-state transitions.

Response: The ~1 h lag was estimated based on the average peak-time difference in the diurnal cycles between aqSOA and nitrate. This may be attributed to the kinetic limitations of nitrate-mediated aqSOA formation processes.

Revised text:

Notably, the aqSOA peak lagged behind the nitrate peak by about one hour ***(based on the average peak-time difference)****, and nocturnal increases in nitrate, ALW, and aqSOA were highly synchronized.* ***This ~1 h lag may be attributed to the kinetic limitations of the nitrate-mediated aqSOA formation processes. (Lines 278-282).***

L279–281: Please correct the grammar ("This suggest" → "This suggests") and soften the causal chain phrasing (e.g., "photochemistry → nitrate → mediates aqSOA").

Response: Done.

Figure 4: Please report the sample size N, and provide either the p-value or the 95% confidence interval (either one is sufficient).

Response: The statistical details for each condition (sample size N and p-value) are reported as follows. For diurnal pattern type I, the correlation coefficient was -0.22 ($N = 151$, $p < 0.01$) during daytime with RH < 60%, and $r = -0.14$ ($N = 59$, $p = 0.3$) when RH > 60%. For diurnal pattern type II, the correlation coefficient was 0.49 ($N = 67$, $p < 0.01$) under RH < 60%, and $r = 0.78$ ($N = 23$, $p < 0.01$) under RH > 60%.

Revised text:

Figure 4. Scatter plots of aqSOA and O_x for Diurnal pattern types I (a) and II (b). Data points are colored by RH, with red and blue lines representing fits for RH > 60% and RH < 60% respectively. **For diurnal pattern type I, the correlation coefficient was -0.22 ($N = 151$, $p < 0.01$) during daytime with RH < 60%, and $r = -0.14$ ($N = 59$, $p = 0.3$) when RH > 60%. For diurnal pattern type II, the correlation coefficient was 0.49 ($N = 67$, $p < 0.01$) under RH < 60%, and $r = 0.78$ ($N = 23$, $p < 0.01$) under RH > 60%. (Lines 313-318).**

Added references:

Chen, Q., Miao, R., Geng, G., Shrivastava, M., Dao, X., Xu, B., Sun, J., Zhang, X., Liu, M., Tang, G., Tang, Q., Hu, H., Huang, R.-J., Wang, H., Zheng, Y., Qin, Y., Guo, S., Hu, M., and Zhu, T.: Widespread 2013-2020 decreases and reduction challenges of organic aerosol in China, Nat Commun, 15, 4465, https://doi.org/10.1038/s41467-024-48902-0, 2024.

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, Proc. Natl. Acad. Sci. U.S.A., 107, 6670–6675, https://doi.org/10.1073/pnas.0912340107, 2010.

Huang, R.-J., Li, Y. J., Chen, Q., Zhang, Y., Lin, C., Chan, C. K., Yu, J. Z., de Gouw, J., Tong, S., Jiang, J., Wang, W., Ding, X., Wang, X., Ge, M., Zhou, W., Worsnop, D., Boy, M., Bilde, M., Dusek, U., Carlton, A. G., Hoffmann, T., McNeill, V. F., and Glasius, M.: Secondary organic aerosol in urban China: A distinct chemical regime for air pollution studies, Science, 389, eadq2840, https://doi.org/10.1126/science.adq2840, 2025.

Nguyen, T. K. V., Zhang, Q., Jimenez, J. L., Pike, M., and Carlton, A. G.: Liquid water: Ubiquitous contributor to aerosol mass, Environ. Sci. Technol. Lett., 3, 257–263, https://doi.org/10.1021/acs.estlett.6b00167, 2016.