Response to Reviewer #1

We are grateful to the reviewer for the thoughtful comments, which are very helpful for improving our manuscript. Our point-to-point responses to each comment are as follows (the reviewer's comments are in black text, our responses are in blue text, and revised texts that appear in the manuscript are in red text).

General Comments:

This study presents measurements of isoprene and its SOA products in Shanghai across summer and wintertime in 2015, 2019, 2021. The study examines isoprene SOA response to emissions reductions, particularly the hydroperoxy pathway (IEPOX-SOA) and NOx-dominated pathway (HMML, MAE). CMAQ modeling captures some trends in experimental data, including a decreasing IEPOX-SOA over the study period. The study concludes that emissions reductions can decrease biogenic SOA in urban areas, and that a deeper understanding of isoprene-derived SOA is needed.

I have major technical concerns about the manuscript that should be addressed prior to reconsideration for publication. Additionally, there are numerous opportunities for more thorough comparisons of the modeled and experimental data. Similarly, there is opportunity for thorough and meaningful comparisons of the current study to literature more specific to urban areas.

Response: Thanks for the reviewer's comments. To address the reviewer's technical concerns, we have conducted additional experiments to evaluate the matrix effect of iSOA OSs. The evaluation shows that the matrix effect of OSs exhibited a strong dependence on the $PM_{2.5}$ mass concentration. Accounting for the significantly larger matrix effects for $PM_{2.5}$ samples collected in 2015 than in 2021, the abundance of 2-MT-OS would exhibit a sharper decreasing tend and 2-MG-OS would also show a declining trend. Overall, these observations are consistent with CMAQ model simulations, which predicted a decreasing inter-annual trend for both 2-MT-OS and 2-MG-OS during the observation period.

In the revised manuscript, we have added additional analyses and discussions about the matrix effect on the abundance, inter-annual trend, and relative ratios between different pathway products. Additionally, we have provided more thorough comparisons between modeled and measured data, as well as between the current study and literature (see our responses to specific comments below).

Specific Comments:

1. I have major technical concerns about the potential for matrix effects and interferences in the selected analytical measurements, and how these may influence the results of the current study.

a. Recent work demonstrates that use of reversed phase liquid chromatography (RPLC) with mass spectrometry (MS) can caused significant underestimation of some isoprene-derived organosulfates (OS) with little retention on reversed phase LC columns (Liang et al. 2025, pubs.acs.org/doi/10.1021/acs.est.5c01846). OS co-elute from the RPLC column with sulfate and other inorganic ions, which can suppress OS signal. Changes to the aerosol matrix can thus be misinterpreted as changes in OS concentrations. Because the author's OS measurement method is likely subject to matrix suppression, there is concern about the validity of the OS concentrations and relative ratios presented in this study.

Response: Thanks for the reviewer's comment. Previous studies have illustrated that the use of PRLC-MS in the quantification of low-molecular-weight OS compounds could cause significant matrix effect (Liang et al., 2025; Liu et al., 2024; Bryant et al., 2020). In the present work, because of lack of authentic standards of isoprene-derived OSs, we are not able to quantify the absolute value of underestimation in the concentration of 2-MT-OS and 2-MG-OS due to the matrix effect. However, using ambient $PM_{2.5}$ samples with different concentrations, we can quantify the relative extent of underestimation in OS concentrations due to matrix effect in different samples, which allows for an evaluation of uncertainties in the abundance, trend, and relative ratios of different isoprene SOA (iSOA) tracers and the validity of the major conclusions in this study.

To this end, we have conducted a set of experiments where the extracts of ambient $PM_{2.5}$ samples with different concentrations were mixed and the measured signals of 2-MT-OS and 2-MG-OS in mixed extracts were compared to the sum of OS signals detected separately in individual extracts. The concentrations of $PM_{2.5}$, sulfate, as well as 2-MT-OS and 2-MG-OS in ambient samples used for this evaluation are listed in Table S3. The relative matrix effect factor (F_{matrix}), defined as the ratio of the measured OS signals in mixed extracts to the sum of OS signals measured in each extract before mixing, are used to evaluate the matrix effects of OSs. A F_{matrix} value of less than 1 indicates the presence of matrix effect.

As shown in Figure S2, the F_{matrix} values were significantly smaller than 1 in both summer and winter, indicating that the signal responses of 2-MT-OS and 2-MG-OS in mixed extracts were largely suppressed due to the matrix effect. Notably, F_{matrix} exhibited a significant negative dependence on the reduced mass (μ, μg m^{-3}), a proxy used to represent effective mass loadings of the mixed $PM_{2.5}$ extracts, defined as:

$$\mu = \sqrt{m_1 * m_2/(m_1 + m_2)}$$

where m_1 and m_2 are the $PM_{2.5}$ mass loading of individual samples. This observation suggests that the concentrations of iSOA OSs in $PM_{2.5}$ samples collected in 2015 were underestimated more than those in 2021, given that ambient $PM_{2.5}$ concentrations declined by 39.8% and 47.0% from 2015 to 2021 in summer and winter, respectively.

As $PM_{2.5}$ concentrations in ambient samples used for the matrix effect evaluation generally represent lower (e.g., Low 1 and Low 3 in Table S3) or upper (e.g., High 1 and High 3) ends of $PM_{2.5}$ concentrations during the observation period, the relative differences in measured F_{matrix} values at varying reduced mass (Figure S3) may roughly reflect the differences in the extent of underestimation in OS concentrations for samples collected across 2015-2021. During summer, the F_{matrix} value decreased from 0.71 to 0.63 for 2-MT-OS and from 0.85 to 0.58 for 2-MG-OS with increasing reduced mass, indicating that the concentrations of these two iSOA OSs were a factor of 1.2 and 1.5 more underestimated in 2015 than in 2021 due to matrix effect. Similarly, during winter the F_{matrix} values of iSOA OSs decreased from 0.9 to 0.6 with rising reduced mass, implying a factor of 1.5 greater underestimation in OS concentrations in 2015 than in 2021. In this study, the measured concentration of 2-MT-OS exhibited a decreasing inter-annual trend, while 2-MG-OS showed insignificant variation between 2015-2021. Accounting for the significantly larger matrix effects in 2015 samples compared to 2021 samples, the true concentrations of 2-MT-OS would show a sharper decrease and 2-MG-OS would exhibit a declining trend.

Table S3. Major components in eight $PM_{2.5}$ filter samples used for evaluating matrix effect of 2-MT-OS and 2-MG-OS during LC-MS analysis.

Season	Sample	Sampling date	$PM_{2.5}$ (μg m^{-3})	SO_4^{2-} (μg m^{-3})	2-MG-OS (ng m^{-3})	2-MT-OS (ng m^{-3})
Summer	High 1	2015/7/28	35.66	7.74	13.04	157.89
	High 2	2019/7/24	31.76	4.58	12.36	100.61
	Low 1	2019/8/5	10.04	2.29	0.58	0.83
	Low 2	2021/8/5	12.21	1.48	0.18	0.18
Winter	High 3	2022/1/2	77.76	6.28	1.80	0.47
	High 4	2022/1/3	65.38	5.41	1.54	0.41
	Low 3	2021/12/25	18.04	3.42	0.49	0.07
	Low 4	2021/12/26	23.71	3.01	0.70	0.08

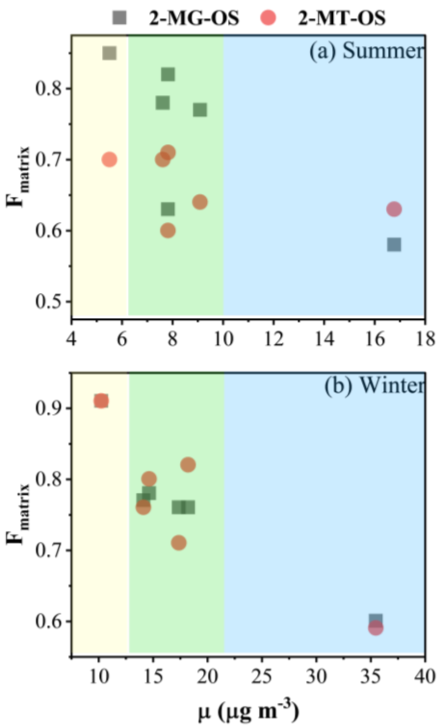

Figure S2. Relative matrix effect factors (F_{matrix}, defined as the ratio of signal response in mixed extracts to the sum of signal response in individual extracts) of 2-MT-OS and 2-MG-OS under different mixture type in summer (a) and winter (b) (yellow background represents low-plus-low mixture, green background represents high-plus-low mixture, and blue background represents high-plus-high mixture).

The significant matrix effect of iSOA OSs was also considered when discussing their relative ratios of different tracers. Considering the stronger matrix effects for 2015 samples than for 2019 and 2021 samples, the downward trend of 2-MT-OS/2-MTs would be sharper, while the slight upward trend of 2-MG-OS/2-MG might be reversed since the true trend of 2-MG-OS was downward and 2-MG had no significant variation.

We have revised the associated content in the manuscript as follows:

Lines 221-255: "Previous studies have demonstrated that the concentrations of 2-MT-OS and 2-MG-OS were significantly underestimated due to matrix effect by using reversed phase liquid chromatography-mass spectrometry (RPLC-MS) (Hettiyadura et al., 2015; Bryant et al., 2020; Bryant et al., 2021). In the present work, because of lack of authentic standards of isoprene-derived OSs, we are not able to quantify the absolute value of underestimation in the concentration of 2-MT-OS and 2-MG-OS due to the matrix effect. However, using ambient $PM_{2.5}$ samples with different concentrations, we can quantify the relative extent of underestimation in OS concentrations due to matrix effect in different samples, which allows for an evaluation of uncertainties in the abundance, trend, and relative ratios of different iSOA tracers in this study. In the matrix effect experiments, the extracts of ambient $PM_{2.5}$ samples with different concentrations were mixed and the measured signals of 2-MT-OS and 2-MG-OS in mixed extracts were compared to the sum of OS signals detected separately in individual extracts. The concentrations of $PM_{2.5}$, sulfate, as well as 2-MT-OS and 2-MG-OS in ambient samples used for this evaluation are listed in Table S3. The relative matrix effect factor (F_{matrix}), defined as the ratio of the measured OS signals in mixed extracts to the sum of OS signals measured in each extract before mixing, are used to evaluate the matrix effect of OSs. A F_{matrix} value of less than 1 indicates the presence of matrix effect.

As shown in Figure S2, the F_{matrix} values were significantly smaller than 1 in both summer and winter, indicating that the signal responses of 2-MT-OS and 2-MG-OS in mixed extracts were largely suppressed due to the matrix effect. Notably, F_{matrix} exhibits a significant negative dependence on the reduced mass (μ, μg m^{-3}), a proxy used to represent effective mass loadings of the mixed $PM_{2.5}$ extracts, defined as:

$$\mu = \sqrt{m_1 * m_2/(m_1 + m_2)} \qquad (1)$$

where m_1 and m_2 are the $PM_{2.5}$ mass loading of individual samples. This observation suggests that the concentrations of iSOA OSs in $PM_{2.5}$ samples collected in 2015 were underestimated more than those in

2021, given that ambient $PM_{2.5}$ concentrations declined by 39.8% and 47.0% from 2015 to 2021 in summer and winter, respectively.

As $PM_{2.5}$ concentrations in ambient samples used for the matrix effect evaluation generally represent lower or upper ends of $PM_{2.5}$ concentrations during the observation period (see Table S3), the relative differences in measured F_{matrix} values at varying reduced mass (Figure S3) may roughly reflect the differences in the extent of underestimation in OS concentrations for samples collected across 2015-2021. During summer, the F_{matrix} value decreased from 0.71 to 0.63 for 2-MT-OS and from 0.85 to 0.58 for 2-MG-OS with increasing reduced mass, indicating that the concentrations of these two iSOA OSs were a factor of 1.2 and 1.5 more underestimated in 2015 than in 2021 due to matrix effect. Similarly, during winter the F_{matrix} values of iSOA OSs decreased from 0.9 to 0.6 with rising reduced mass, implying a factor of 1.5 greater underestimation in OS concentrations in 2015 than in 2021."

Lines 371-379: "However, the inter-annual trend of iSOA OSs could be altered due to the matrix effect. The measured concentration of 2-MT-OS exhibited a decreasing inter-annual trend, while 2-MG-OS showed insignificant variation between 2015-2021. Accounting for the significantly larger matrix effects in 2015 samples compared to 2021 samples (see Section 2.3), the true concentrations of 2-MT-OS would decrease more sharply and 2-MG-OS might also exhibit a declining trend."

b. There are additional concerns about C_5 alkene-triols being artifacts of gas chromatography (GC) MS analysis (Frauenheim, et al. doi/10.1021/acs.estlett.2c00548). The extent to which these may be artifacts in the current study should be considered, especially following the result that they are the dominant product observed by GCMS.

Response: Thanks for the reviewer's comment. Frauenheim et al. (2022) have found that the thermal decomposition of 3-methyltetrahydrofuran-2,4-diols (less than 15%) could transfer to two isomers of C_5-alkene trols (cis-/trans-3-methyl-but-3-ene-1,2,4-triols) during GC/MS analysis. In our work, we quantified the concentrations of 3-methyltetrahydrofuran-2,4-diols using 2-methylerythritol as a surrogate standard. The concentrations of 3-methyltetrahydrofuran-2,4-diols were less than 5% of C_5-alkene triols in summer but had comparable levels in winter. This result indicates that 3-methyltetrahydrofuran-2,4-diols was a minor contributor to C_5-alkene triols in summer but an important source for C_5-alkene triols in winter.

In addition, the thermal degradation of 2-MT-OS and its oligomers during GC-MS analysis could be a potential contributor to C_5-alkene triols. Cui et al. (2018) found that thermal degradation of 2-MT-OS could generate all three isomers of C_5-alkene triols and such processes accounted for 14.7 and 42.7% of C_5-alkene triols observed in urban Manaus, Brazil and southeastern U.S., respectively. In contrast, Yee et al. (2020) found that the thermal decomposition of 2-MT-OS could only produce one isomer, 3-methyl-2,3,4-trihydroxy-1-butene. In this study, we are not able to conduct a quantitative assessment of the transformation of 2-MT-OS to C_5-alkene triols during GC-MS analysis due to the lack of authentic standards. Assuming that all the isomers of C_5-alkene triols could come from the thermal degradation of 2-MT-OS, a considerable fraction of C_5-alkene triols could be artifacts since the concentrations of 2-MT-OS (with matrix effect considered) were significantly higher than C_5-alkene triols. However, if only 3-methyl-2,3,4-trihydroxy-1-butene was the product of 2-MT-OS degradation, the concentrations of C_5-alkene triols would be overestimated by no more than 23.8% since the 3-methyl-2,3,4-trihydroxy-1-butene on average accounted for 23.8% of the concentrations of C_5-alkene triols. Thus, C_5-alkene triols were likely overestimated mainly due to the thermal decomposition of 2-MT-OS, with the 3-methyltetrahydrofuran-2,4-diols likely being an important source in winter.

Because of the lack of authentic standards of C_5-alkene triols, it is challenging to quantify artifacts resulting from the thermal degradation of 2-MT-OS during GC/MS analysis in the present work. In addition, inconsistent results regarding the quantification uncertainties of C_5-alkene triols have been reported in the literature (Cui et al., 2018; Frauenheim et al., 2022). Therefore, we do not discuss the abundance or inter-annual trends of C_5-alkene triols in detail in this study, but instead focus on 2-MTs, 2-MG, and OSs. In addition, they were excluded from the correlation analysis. When discussing the relative ratios (including IEPOX-SOA/HMMML&MAE-SOA and iSOA OSs/polyol tracers), the measurement uncertainties of C_5-alkene triols were considered.

The manuscript has been revised as follows:

Lines 354-371: "However, the concentrations of C_5-alkene triols might be overestimated since previous studies have reported that concentrations of C_5-alkene triols could be artifacts of thermal degradation products of 3-methyltetrahydrofuran-2,4-diols and 2-MT-OS during GC/MS analysis (Cui et al., 2018;

Frauenheim et al., 2022). Frauenheim et al. (2022) found that less than 15% of 3-methyltetrahydrofuran-2,4-diols could transfer to two isomers of C_5-alkene triols (cis-/trans-3-methyl-but-3-ene-1,2,4-triols). In the present study, using 2-methylerythritol as a surrogate standard, the concentrations of 3-methyltetrahydrofuran-2,4-diols were determined to be less than 5% of C_5-alkene triols in summer but had comparable concentrations to C_5-alkene triols in winter. This result indicates that 3-methyltetrahydrofuran-2,4-diols was a minor contributor to C_5-alkene triols in summer but an important source for C_5-alkene triols in winter. In contrast, the contribution from the thermal degradation of 2-MT-OS might be more significant, though the specific contribution remains to be quantified; Cui et al. (2018) found that thermal degradation of 2-MT-OS could generate all three isomers of C_5-alkene triols, while Yee et al. (2020) found that the thermal decomposition of 2-MT-OS could only produce one isomer, 3-methyl-2,3,4- trihydroxy-1-butene. Given these uncertainties, it is difficult to quantitatively evaluate the artifact formation of C_5-alkene triols during GC/MS analysis. Therefore, the abundance and inter-annual trend of C_5-alkene triols were not discussed in detail in the present work."

Lines 398-404: "Although C_5-alkene triols might be largely artifacts of GC/MS analysis (Cui et al., 2018; Frauenheim et al., 2022), the concentrations of IEPOX-SOA excluding C_5-alkene triols were still dominant over HMML&MAE-SOA in summer. In addition, previous studies have demonstrated that the concentrations of 2-MT-OS were underestimated more than 2-MG-OS by a factor of 5.7-9.1 in Beijing (Bryant et al., 2020) and 2.9 in Guangzhou (Bryant et al., 2021). If 2-MT-OS was also more significantly underestimated than 2-MG-OS in the present study, the predominance of IEPOX-SOA over HMML&MAE-SOA would be more pronounced."

Lines 411-413: "However, given the significant underestimation of iSOA OSs due to matrix effect and overestimation of C_5-alkene triols due to their potential artifact formation, the true concentration of iSOA OSs would predominate over that of polyol tracers."

c. Taken together, the suppression of OS and potential artifact formation of C_5 alkene triols raises questions to the validity of the paragraph that discusses "the dominance of iSOA polyol tracers over OS tracers…" With one signal being enhanced and the other suppressed, such comparisons have very large uncertainties.

Response: Thanks for the reviewer's suggestion. We have added a discussion about the uncertainties from the suppression of OS and potential artifact formation of C_5-alkene triols in manuscript. Considering both the underestimation of iSOA OSs due to matrix effect and overestimation of C_5-alkene triols (as discussed in response to comment #1b), iSOA OSs were found to predominate over polyol tracers. The text in manuscript was revised as follows:

Lines 411-418: "However, given the significant underestimation of iSOA OSs due to matrix effect and overestimation of C_5-alkene triols due to their potential artifact formation, the true concentration of iSOA OSs would predominate over that of polyol tracers. The iSOA OSs prevailing over polyol tracers is consistent with urban observations using HILIC-MS, such as in Manaus, Brazil (Cui et al., 2018) and Guangzhou, China (Liu et al., 2025) (see Table S6). Using RPLC-MS, Bryant et al. (2020) also observed higher concentrations of iSOA OSs than polyol tracers in Beijing, China. Considering the potential underestimation of iSOA OSs due to matrix effect, the concentration of iSOA OSs would be even higher than that of polyol tracers in their study."

d. The potential for bias in measurements mentioned should be thoroughly considered and discussed in downstream calculations and comparisons, including SOA estimates, relative ratios of isoprene SOA products, correlation analysis, model comparisons, etc.

Response: Thanks for the reviewer's comment. We have added detailed analyses and discussions regarding the uncertainties in the measurements of OSs and C_5-alkene triols, as well as the subsequent SOA estimates and relative ratios of isoprene SOA products (see our responses above). We have also modified the discussions about comparisons between measurements and model simulations of iSOA tracers (see below).

Lines 439-446: "For iSOA tracers, the Case 1 showed a better prediction than the Base Case. Overall, the simulated IEPOX-SOA tracers were biased low in summer, but biased high in winter (Figure 3b and 3c). In contrast, the 2-MG and 2-MG-OS were biased low in both seasons (Figure 3d and 3e). The underestimation of 2-MG is consistent with previous simulations at 14 sites across China in the summer of 2012 (Qin et al., 2018). Accounting for the underestimation of OSs due to the matrix effect, simulated concentrations of 2-MT-OS would be more biased low in summer but might be close to observations in winter. Similarly, the under-prediction of 2-MG-OS would be more significant in both seasons."

In addition, we have conducted a sensitivity test to evaluate the influence of measurement uncertainties on the correlation analysis between iSOA tracers and different influencing factors. Recently, Liang et al. (2025) has illustrated that the concentrations of low-molecular-weight (C_2 and C_3) OSs quantified with RPLC-MS were 1-2 orders of magnitudes lower than those measured with HILIC-MS duo to the matrix effect. Additionally, both the results in Liang et al. (2025) and the matrix effect experiments in our work have found a greater signal suppression of OSs at higher $PM_{2.5}$ mass loadings. Since the retention time of 2-MT-OS and 2-MG-OS was very close to $C_{2\text{-}3}$ OSs (see Figure S1a), we roughly assumed that the concentrations of 2-MT-OS and 2-MG-OS were also underestimated by up to 100 times and that the underestimation extent is linearly dependent on the $PM_{2.5}$ concentration. We then performed a correlation analysis using the corrected concentrations of 2-MT-OS and 2-MG-OS. As shown in Tables S4, iSOA OSs still exhibited the strongest correlation with the concentrations of O_3 and Ox in summer and sulfate, nitrate, and LWC in winter, although the correlation coefficients (r^2) with O_3 and O_x were slightly decreased (less than 0.1) while those with sulfate increased by 0.1-0.4 compared to the correlation analysis with the observed data. This result indicated that the measurement uncertainties did not significantly influence the correlation analysis and the evaluation of the dominant influencing factors for the formation of iSOA OSs in this study.

We have added a statement regarding the sensitivity test result to the main text and the details about this test to Section S5 in the supplement:

Lines 499-500: “A sensitivity test considering the measurement uncertainties of iSOA tracers did not significantly influence the correlation analysis results (see details in Section S5).”

Lines 103-121 in the supplement:

“S5. Evaluation of the influence of matrix effect on correlation analysis of iSOA OSs

We have conducted a sensitivity test to evaluate the influence of measurement uncertainties on the correlation analysis between iSOA OSs and different influencing factors. Recently, Liang et al. (2025) has illustrated that the concentrations of low-molecular-weight (C_2 and C_3) OSs quantified with RPLC-MS were 1-2 orders of magnitudes lower than those measured with HILIC-MS duo to the matrix effect. Additionally, both the results in Liang et al. (2025) and the matrix effect experiments in our work have found a greater signal suppression of OSs at higher $PM_{2.5}$ mass loadings. Since the retention time of 2-MT-OS and 2-MG-OS was very close to $C_{2\text{-}3}$ OSs (see Figure S1a), we roughly assumed that the concentrations of 2-MT-OS and 2-MG-OS were also underestimated by up to 100 times and that the underestimation extent was linearly dependent on the $PM_{2.5}$ concentration. We then performed a correlation analysis using the modified concentrations of 2-MT-OS and 2-MG-OS. As shown in Tables S7, iSOA OSs still exhibited the strongest correlation with the concentrations of O_3 and Ox in summer and sulfate, nitrate, and LWC in winter, although the correlation coefficients (r^2) with O_3 and O_x were slightly decreased (by less than 0.1) while those with sulfate increased by 0.1-0.4 compared to the correlation analysis with the observed concentrations of OSs. This result indicates that the measurement uncertainties did not significantly influence the correlation analysis results and the evaluation of the dominant influencing factors for the formation of iSOA OSs in this study.”

Table S7. Coefficients of correlation (r^2) between 2-MG-OS and 2-MT-OS and various influencing factors in summer and winter of 2015, 2019, and 2021.

		nitrate	sulfate	LWC	pH	NO_2	O_3	O_x	isoprene	T
2-MG-OS	Summer-2015	0.01	0.24	0	0.19	0.19	0.61	0.61	0.55	0.56
	Summer-2019	0.19	0.32	0.02	0.01	0.53	0.42	0.51	0	0.27
	Summer-2021	0.57	0.54	0.21	0.02	0.37	0.72	0.68	0.04	0.21
	Winter-2015	0.75	0.64	0.47	0.04	0.32	0.23	0.1	/	0.02
	Winter-2019	0.69	0.63	0.19	0.03	0.29	0.02	0.24	0.02	0.12
	Winter-2021	0.6	0.71	0.68	0.04	0.21	0.04	0	0.15	0.03
2-MT-OS	Summer-2015	0.05	0.11	0.04	0.2	0.18	0.61	0.61	0.3	0.66
	Summer-2019	0.11	0.24	0	0	0.52	0.33	0.42	0	0.27
	Summer-2021	0.3	0.26	0.1	0.01	0.14	0.51	0.35	0.1	0.26
	Winter-2015	0.8	0.6	0.48	0.04	0.41	0.26	0.14	/	0.05
	Winter-2019	0.58	0.67	0.28	0.28	0	0.17	0.01	0.13	0.1
	Winter-2021	0.65	0.79	0.64	0.06	0.13	0.03	0	0.07	0.02

e. The current treatment of matrix effects is insufficient at lines 221-225. While the expected extent of matrix effects may be informative, correction factors are not valid across studies. The authors must discuss the relevance of the sample matrix in the study by Bryant et al. (2021) and their work. Similarly, it is not a valid approach to extrapolate relative ionization efficiencies observed by others (i.e. Bryant et al. (2021, line 169)) across studies, because ionization changes day-to-day within an instrument, and depends upon specific instrumental conditions and mobile phase composition. Ratios of relative responses are reported to 2-3 significant figures at lines 169-173, while in reality these estimates are known with much less certainty.

Response: We agree with the reviewer that the matrix effect factors and relative ionization efficiencies reported by Bryant et al. (2021) may not be valid for the present study, given that these factors could vary significantly across studies due to the differences in ambient samples analyzed and in analytical instruments and specific instrumental conditions. We have conducted additional experiments to evaluate the matrix effect of OS measurements using ambient samples in Shanghai and modified the relevant discussions (see our response to comment #1a).

In addition, we have removed the discussion about ratios of relative responses of OSs in lines 169-173 and added the following sentence to the manuscript.

Lines 162-163: "Use of surrogate standards would lead to uncertainties in measured concentrations of 2-MT-OS and 2-MG-OS (Bryant et al., 2021; Bryant et al., 2020), but not alter the inter-annual trend of iSOA OSs."

2. There are also opportunities for more thorough comparisons of the modeled and experimental data. These are mentioned in the text, but should be integrated into figures. These additions would strengthen the conclusions of the paper and improve clarity.

a. Extend Figure 2 be expanded to also show $PM_{2.5}$ mass, OC (or OM), sulfate, nitrate, and other relevant PM component or atmospheric parameters (NOx, O_3). This would be a useful way to provide context for understanding changes in isoprene SOA that are discussed subsequently.

Response: Thanks. The relevant PM components and atmospheric parameters have been added in Figure 2.

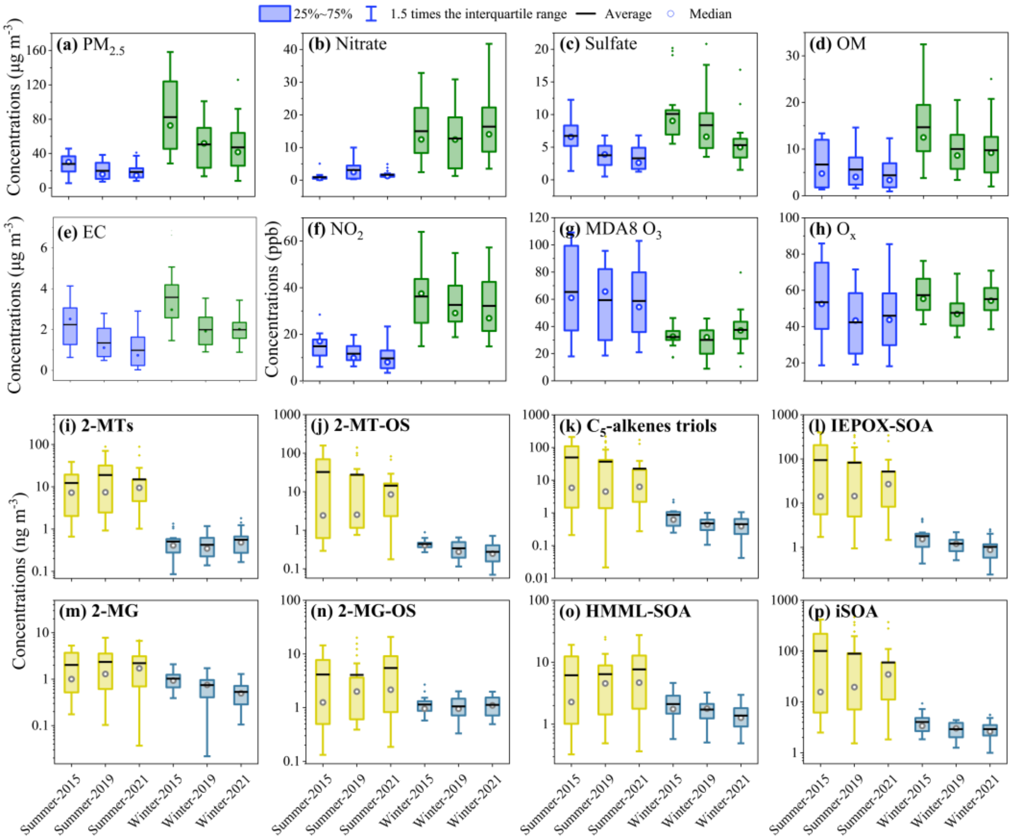

Figure 2. Seasonal and inter-annual variations concentration of $PM_{2.5}$ and its major components (a-e), gas-phase anthropogenic pollutants (f-h), as well as particulate iSOA tracers, including (i)2-MTs, (j) 2-MT-OS, (k) C_5-alkene triols, (l) IEPOX-SOA (the sum of 2-MTs, 2-MT-OS, and C_5-alkene triols), (m) 2-MG, (n) 2-MG-OS, (o) HMML&MAE-SOA (2-MG plus 2-MG-OS), and (p) iSOA (the sum of all tracers).

b. In figures 6 and 7, include experimental data be for comparison to modeled values.

Response: Thanks. The observed data have been added in Figure 6 and 7 as follows:

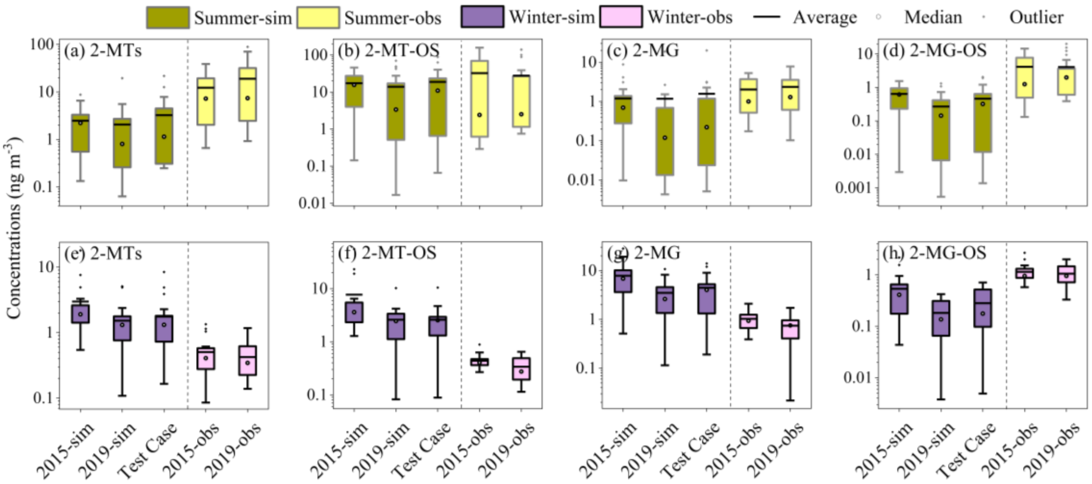

Figure 6. Simulated concentrations of 2-MTs, 2-MT-OS, 2-MG and 2-MG-OS in summer (a-d) and winter (e-h) in Case 1 (2015-sim and 2019-sim) and Test Case (simulations with 2015 emissions and 2019 meteorological conditions). The observed concentrations of 2-MTs, 2-MT-OS, 2-MG, and 2-MG-OS in 2015 and 2019 are also displayed (Detailed model-measurement comparisons are provided in Section 3.2; after accounting for matrix effect, 2-MT-OS would decrease more sharply and 2-MG-OS would show a descending inter-annual trend, consistent with model simulations).

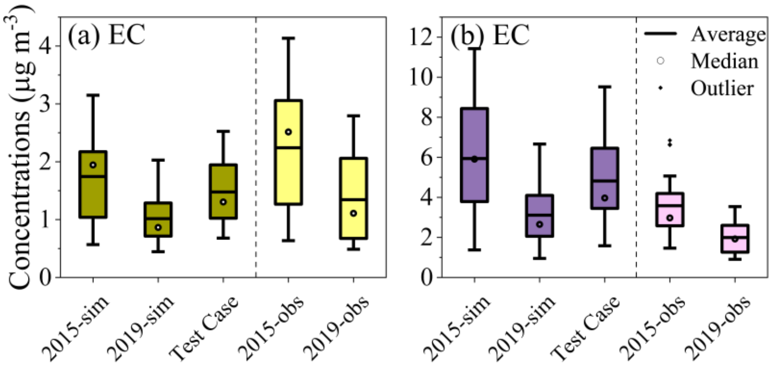

Figure 7. Simulated EC concentrations in Case 1 (2015-sim and 2019-sim) and Test Case (simulations with 2015 emissions and 2019 meteorological conditions) in (a) summer and (b) winter.

c. Also in figures 6 and 7 – the x-axis labels are confusing. Can they be simplified?

Response: Thanks. We have revised the x-axis labels in Figures 6 and 7 (see above).

3. In many places, the authors compare the current study to select literature references. Many of these comparisons are to background or rural locations (i.e. central Amazonia and rural sites in the Southeastern United States), raising question as to their relevance to Shanghai. To better understand the urban influence (and the emissions reductions) on isoprene SOA chemistry, the authors should more thoroughly compare and discuss their work in relation to prior studies in urban locations in Asia and elsewhere.

Response: Thanks for the reviewer's suggestion. We have thoroughly compared our measurements to prior studies in urban regions (see Table S6) and revised the discussion in the manuscript accordingly. The revised text of the relative abundance of iSOA OS tracers to polyol tracers in our work compared to other measurements is provided in our response to comment #1c, and other results in our work, including dominance of IEPOX-SOA over HMML&MAE-SOA and correlation relationship between 2-MG and ozone, has been compared to previous measurements (see below).

Lines 404-407: "The dominance of IEPOX-SOA over HMML&MAE-SOA in summer is in agreement with RPLC-MS measurements in Beijing, Hefei and Kunming in China (Zhang et al., 2022b) and Birmingham, US (Rattanavaraha et al., 2016), as well as hydrophilic interaction liquid chromatography-mass spectrometry (HILIC-MS) measurements conducted in urban Guangzhou, China (Liu et al., 2025)."

Lines 485-486: "Such correlations between 2-MG and ozone were also observed in previous measurements in urban areas in southeastern US (Rattanavaraha et al., 2016)…"

Table S6. Concentrations (ng m^{-3}) of 2-MT-OS, 2-MTs, 2-MG-OS and 2-MG measured in different urban environments

Sampling sites	Sampling time	OS detection method	2-MT-OS	2-MTs	2-MG-OS	2-MG	Refs.
Urban Beijing, China	Summer, 2014	RPLC/ESI-MS	0.5 [a]	7.52 [b]	0.99 [a]	2.76 [b]	Zhang et al. (2022a)
Urban Hefei, China	Summer, 2014	RPLC/ESI-MS	0.71 [a]	17.7 [b]	1.68 [a]	4.37 [b]	Zhang et al. (2022a)
Urban Kunming, China	Summer, 2014	RPLC/ESI-MS	1.43 [a]	25.1 [b]	1.49 [a]	3.26 [b]	Zhang et al. (2022a)
Urban Birmingham, Alabama, USA	Summer, 2013	RPLC/ESI-MS	165 [c]	374 [d]	7.20 [c]	10.4 [d]	Rattanavaraha et al. (2016)
Urban Beijing, China	Spring, 2017	RPLC/ESI-MS	11.8 [d]	17.3 [b]	21 .5 [d]	7.2 [b]	Bryant et al. (2020)
Urban San Agustin, Mexico	Summer, 2018	HILIC/ESI-MS	20 [d]	40 [d]	/	/	Cooke et al. (2024)
Urban Manaus, Brazil	Winter, 2016	HILIC/ESI-MS	0.39 [d]	0.14 [d]	/	/	Cui et al. (2018)
Urban Guangzhou, China	Summer, 2018	HILIC/ESI-MS	62.8 [e]	60.5 [b]	13.8 [e]	2.9 [b]	Liu et al. (2025)
Urban Guangzhou, China	Fall, 2018	HILIC/ESI-MS	29.7 [e]	16.6 [b]	7.7 [e]	3.0 [b]	Liu et al. (2025)

Note: Concentrations of target compounds quantified by: [a]camphorsulfonate, [b]erythritol, [c]propyl sulfate, [d]authentic standard, and [e]ethyl sulfate.

4. When comparing to prior studies, the authors need to consider how similar or different methods may influence the comparison.

Response: Thanks for the reviewer's suggestion. The type of chromatographic columns used for quantification in prior studies are summarized in Table S6. When comparing the result in this work and previous measurements, the influence of similar or different methods have been considered (see response to #1c and #3).

5. The notation "HMML/MAE" implies the ratio of HHML / MAE. Is this intended? Or could this be HHML, MAE, or HHML & MAE?

Response: The notation "HMML/MAE" indicates the NOx-dominant pathway with HMML or MAE as the reaction intermediates. We have replaced it with "HMML & MAE" in the revised manuscript.

6. At least one of the studies mentioned at line 166 (Hettiyadura et al. 2015) did not use camphorsulfonic

acid as a surrogate standard. Please check and revise this thoroughly.

Response: Thanks for pointing out this. We have deleted this sentence and added the following statement regarding the use of surrogate standards in the revised manuscript.

Lines 162-163: “Use of surrogate standards would lead to uncertainties in measured concentrations of 2-MT-OS and 2-MG-OS (Bryant et al., 2021; Bryant et al., 2020), but not alter the inter-annual trend of iSOA OSs.”

7. At line 38, it is it a realistic recommendation to “regulate atmospheric oxidizing capacity”? Typically, regulations are either on emission sources or on ambient concentrations of hazardous pollutants. Please reconsider this closing statement in the abstract.

Response: Thanks for the reviewer’s comment. We have modified this sentence as “These findings highlight pathway-specific iSOA responses to emission reductions in a megacity and the importance of targeted anthropogenic emission reductions for mitigating biogenic SOA formation through regulating atmospheric oxidizing capacity and aerosol reactivity.”

8. Line 67, a symbol before 45 is appearing as a box.

Response: Thanks. We have modified this.

9. The logic at lines 98-104 needs improvement. The approach that “previous studies have mainly focused on the characterization of the particle-phase abundance of the iSOA tracers” is justified in that for iSOA to form it must be in the particle phase. Additionally, this paragraph implies that gas phase concentrations of tracers were measured in this study, whereas they appear only to be estimated by calculation and not measured.

Response: Thanks for the reviewer’s suggestion. We have modified the text for a clearer logic:

Lines 98-102: “Furthermore, while the iSOA polyol tracers are formed in the particle phase, they can actively partition between gas and particle phases due to their semi-volatile characteristics (Fan et al., 2020; Isaacman-Vanwertz et al., 2016; Nguyen et al., 2015). As a result, considering their particle-phase concentration only may bias our understanding of the atmospheric abundance and chemistry of iSOA.”

10. Can the authors validate their estimates of gas-particle distributions using experimental data?

Response: Thanks for the reviewer’s suggestion. However, currently we are not able to perform such validations due to the lack of the measured concentration of iSOA polyol tracers in the gas phase. Previous observational studies have determined a gas-phase fraction of 40-80% for 2-MG (Yee et al., 2020; Nguyen et al., 2015) and approximately 50% for 2-MTs (Yee et al., 2020; Isaacman-Vanwertz et al., 2016). Moreover, the gas-phase fraction of 2-MG exhibited a negative correlation with pH when partitioning between gas phase and bulk solution (Nguyen et al., 2015) or ambient $PM_{2.5}$ (Yee et al., 2020). When pH was lower than 3, over 50% of 2-MG partitioned into the gas phase in southeastern U.S. and central Amazon (Yee et al., 2020). In this study, the pH values ranged from 2 to 4, suggesting a substantial fraction of 2-MG in the gas phase.

11. Table S2, it appears that matrix effects were considered in only six samples, not eight as suggested by the caption.

Response: Thanks. The caption has been revised.

12. In Figure 1, is wind speed data missing from 2021 and 2022? It seems not to appear in the figure shown. In general, the resolution and the quality of this figure should be improved prior to publication.

Response: Yes, the wind speed data were not collected for 2021. We have added a statement on this to the figure caption. We have also replaced Figure 1 with a version of higher resolution.

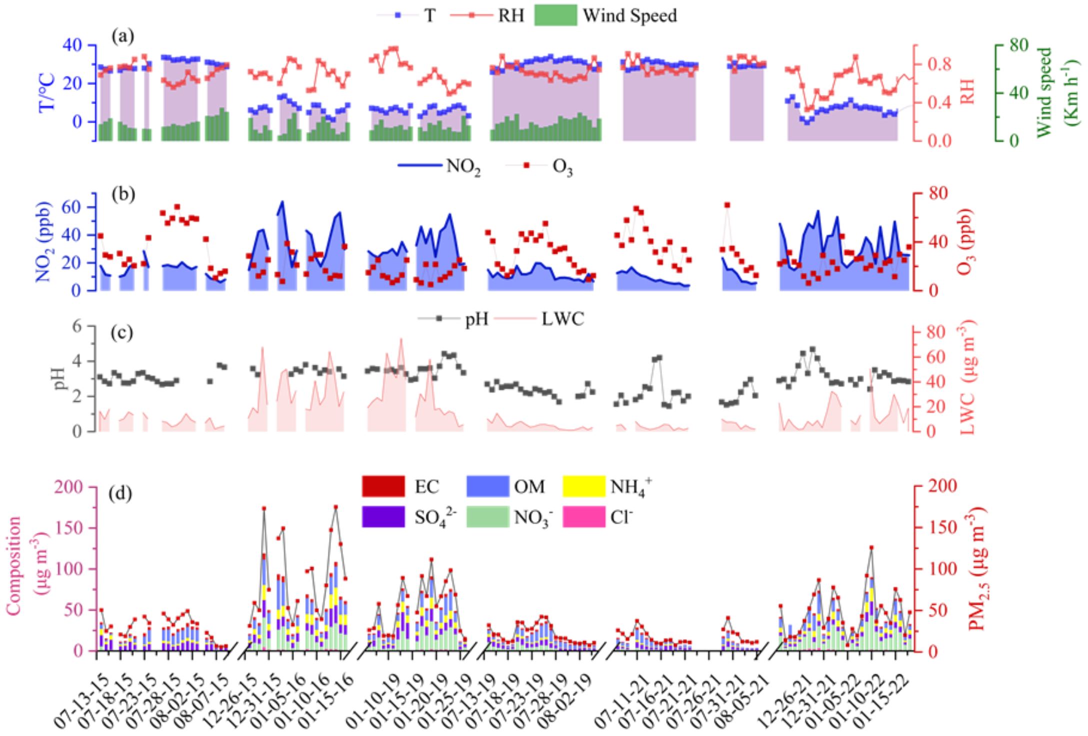

Figure 1. Temporal variations of (a) meteorological parameters (ambient temperature, relative humidity, and wind speed), (b) concentrations of NO_2 and O_3, (c) aerosol pH and liquid water content (LWC), and (d) concentrations of $PM_{2.5}$ and its major components (OM, EC, sulfate, nitrate, chloride, and ammonium) in urban Shanghai during the observation period. The wind speed data were not collected during the observations in 2021.

References:

Bryant, D. J., Elzein, A., Newland, M., White, E., Swift, S., Watkins, A., Deng, W., Song, W., Wang, S., Zhang, Y., Wang, X., Rickard, A. R., and Hamilton, J. F.: Importance of Oxidants and Temperature in the Formation of Biogenic Organosulfates and Nitrooxy Organosulfates, ACS Earth Space Chem., 5, 2291-2306, 10.1021/acsearthspacechem.1c00204, 2021.

Bryant, D. J., Dixon, W. J., Hopkins, J. R., Dunmore, R. E., Pereira, K. L., Shaw, M., Squires, F. A., Bannan, T. J., Mehra, A., Worrall, S. D., Bacak, A., Coe, H., Percival, C. J., Whalley, L. K., Heard, D. E., Slater, E. J., Ouyang, B., Cui, T., Surratt, J. D., Liu, D., Shi, Z., Harrison, R., Sun, Y., Xu, W., Lewis, A. C., Lee, J. D., Rickard, A. R., and Hamilton, J. F.: Strong anthropogenic control of secondary organic aerosol formation from isoprene in Beijing, Atmos. Chem. Phys., 20, 7531-7552, 10.5194/acp-20-7531-2020, 2020.

Chen, Y., Ng, A. E., Green, J., Zhang, Y., Riva, M., Riedel, T. P., Pye, H. O. T., Lei, Z., Olson, N. E., Cooke, M. E., Zhang, Z., Vizuete, W., Gold, A., Turpin, B. J., Ault, A. P., and Surratt, J. D.: Applying a Phase-Separation Parameterization in Modeling Secondary Organic Aerosol Formation from Acid-Driven Reactive Uptake of Isoprene Epoxydiols under Humid Conditions, ACS ES&T Air, 1, 511-524, 10.1021/acsestair.4c00002, 2024.

Cooke, M. E., Waters, C. M., Asare, J. Y., Mirrielees, J. A., Holen, A. L., Frauenheim, M. P., Zhang, Z., Gold, A., Pratt, K. A., Surratt, J. D., Ladino, L. A., and Ault, A. P.: Atmospheric Aerosol Sulfur Distribution and Speciation in Mexico City: Sulfate, Organosulfates, and Isoprene-Derived Secondary Organic Aerosol from Low NO Pathways, ACS ES&T Air, 1, 1037-1052, 10.1021/acsestair.4c00048, 2024.

Cui, T., Zeng, Z., dos Santos, E. O., Zhang, Z., Chen, Y., Zhang, Y., Rose, C. A., Budisulistiorini, S. H., Collins, L. B., Bodnar, W. M., de Souza, R. A. F., Martin, S. T., Machado, C. M. D., Turpin, B. J., Gold, A., Ault, A. P., and Surratt, J. D.: Development of a hydrophilic interaction liquid chromatography (HILIC) method for the chemical characterization of water-soluble isoprene epoxydiol (IEPOX)-derived secondary organic aerosol, Environ. Sci. Proc. Imp., 20, 1524-1536, 10.1039/C8EM00308D, 2018.

Fan, Y., Liu, C.-Q., Li, L., Ren, L., Ren, H., Zhang, Z., Li, Q., Wang, S., Hu, W., Deng, J., Wu, L., Zhong, S., Zhao, Y., Pavuluri, C. M., Li, X., Pan, X., Sun, Y., Wang, Z., Kawamura, K., Shi, Z., and Fu, P.: Large contributions of biogenic and anthropogenic sources to fine organic aerosols in Tianjin, North China, Atmos. Chem. Phys., 20, 117-137, 10.5194/acp-20-117-2020, 2020.

Frauenheim, M., Offenberg, J., Zhang, Z., Surratt, J. D., and Gold, A.: The C5–Alkene Triol Conundrum: Structural Characterization and Quantitation of Isoprene-Derived C5H10O3 Reactive Uptake Products, Environ. Sci. Technol. Lett., 9, 829-836, 10.1021/acs.estlett.2c00548, 2022.

Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., and Humphry, T.: Determination of atmospheric organosulfates using HILIC chromatography with MS detection, Atmos. Meas. Tech., 8, 2347-2358, 10.5194/amt-8-2347-2015, 2015.

Isaacman-VanWertz, G., Yee, L. D., Kreisberg, N. M., Wernis, R., Moss, J. A., Hering, S. V., de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Riva, M., Surratt, J. D., Viegas, J., Manzi, A., Edgerton, E., Baumann, K., Souza, R., Artaxo, P., and Goldstein, A. H.: Ambient Gas-Particle Partitioning of Tracers for Biogenic Oxidation, Environ Sci Technol, 50, 9952-9962, 10.1021/acs.est.6b01674, 2016.

Liang, S., Wang, Y., Chen, H., Chan, W., and Yu, J. Z.: Accurate Quantification of Multifunctional C2–3 Organosulfates in Atmospheric Aerosols Using Liquid Chromatography-Electrospray Ionization Mass Spectrometry: Overcoming Matrix Effects and Underestimation, Environ. Sci. Technol., 10.1021/acs.est.5c01846, 2025.

Liu, P., Ding, X., Li, B. X., Zhang, Y. Q., Bryant, D. J., and Wang, X. M.: Quality assurance and quality control of atmospheric organosulfates measured using hydrophilic interaction liquid chromatography (HILIC), Atmos. Meas. Tech., 17, 3067-3079, 10.5194/amt-17-3067-2024, 2024.

Liu, P., Ding, X., Bryant, D. J., Zhang, Y.-Q., Wang, J.-Q., Yang, K., Cheng, Q., Jiang, H., Wang, Z.-R., He, Y.-F., Li, B.-X., Zhao, M.-Y., Hamilton, J. F., Rickard, A. R., and Wang, X.-M.: Comparison of Isoprene-Derived Secondary Organic Aerosol Formation Pathways at an Urban and a Forest Site, ACS Earth Space Chem., 9, 1752-1767, 10.1021/acsearthspacechem.4c00398, 2025.

Nguyen, T. B., Bates, K. H., Crounse, J. D., Schwantes, R. H., Zhang, X., Kjaergaard, H. G., Surratt, J. D., Lin, P., Laskin, A., Seinfeld, J. H., and Wennberg, P. O.: Mechanism of the hydroxyl radical oxidation of methacryloyl peroxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere, Phys. Chem. Chem. Phys., 17, 17914-17926, 10.1039/c5cp02001h, 2015.

Piletic, I. R., Edney, E. O., and Bartolotti, L. J.: A computational study of acid catalyzed aerosol reactions of atmospherically relevant epoxides, Phys. Chem. Chem. Phys., 15, 18065-18076, 10.1039/c3cp52851k, 2013.

Pye, H. O. T., Murphy, B. N., Xu, L., Ng, N. L., Carlton, A. G., Guo, H., Weber, R., Vasilakos, P., Appel, K. W., Budisulistiorini, S. H., Surratt, J. D., Nenes, A., Hu, W., Jimenez, J. L., Isaacman-VanWertz, G., Misztal, P. K., and Goldstein, A. H.: On the implications of aerosol liquid water and phase separation for organic aerosol mass, Atmos. Chem. Phys., 17, 343-369, 10.5194/acp-17-343-2017, 2017.

Qin, M., Wang, X., Hu, Y., Ding, X., Song, Y., Li, M., Vasilakos, P., Nenes, A., and Russell, A. G.: Simulating Biogenic Secondary Organic Aerosol During Summertime in China, J Geophys Res-Atmos, 123, 11,100-111,119, https://doi.org/10.1029/2018JD029185, 2018.

Rattanavaraha, W., Chu, K., Budisulistiorini, S. H., Riva, M., Lin, Y. H., Edgerton, E. S., Baumann, K., Shaw, S. L., Guo, H., King, L., Weber, R. J., Neff, M. E., Stone, E. A., Offenberg, J. H., Zhang, Z., Gold, A., and Surratt, J. D.: Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM2.5 collected from the Birmingham, Alabama, ground site during the 2013 Southern Oxidant and Aerosol Study, Atmos. Chem. Phys., 16, 4897-4914, 10.5194/acp-16-4897-2016, 2016.

Yee, L. D., Isaacman-VanWertz, G., Wernis, R. A., Kreisberg, N. M., Glasius, M., Riva, M., Surratt, J. D., de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Liu, Y., Misztal, P. K., Artaxo, P., Viegas, J., Manzi, A., de Souza, R. A. F., Edgerton, E. S., Baumann, K., and Goldstein, A. H.: Natural and Anthropogenically Influenced Isoprene Oxidation in Southeastern United States and Central Amazon, Environ. Sci. Technol., 54, 5980-5991, 10.1021/acs.est.0c00805, 2020.

Zhang, Y.-Q., Ding, X., He, Q.-F., Wen, T.-X., Wang, J.-Q., Yang, K., Jiang, H., Cheng, Q., Liu, P., Wang, Z.-R., He, Y.-F., Hu, W.-W., Wang, Q.-Y., Xin, J.-Y., Wang, Y.-S., and Wang, X.-M.: Observational Insights into Isoprene Secondary Organic Aerosol Formation through the Epoxide Pathway at Three

Urban Sites from Northern to Southern China, Environ. Sci. Technol., 10.1021/acs.est.1c06974, 2022a.

Zhang, Y.-Q., Ding, X., He, Q.-F., Wen, T.-X., Wang, J.-Q., Yang, K., Jiang, H., Cheng, Q., Liu, P., Wang, Z.-R., He, Y.-F., Hu, W.-W., Wang, Q.-Y., Xin, J.-Y., Wang, Y.-S., and Wang, X.-M.: Observational Insights into Isoprene Secondary Organic Aerosol Formation through the Epoxide Pathway at Three Urban Sites from Northern to Southern China, Environ. Sci. Technol., 10.1021/acs.est.1c06974, 2022b.