RC2: 'Comment on egusphere-2023-1242', Anonymous Referee #2, 25 Jul 2023

The authors examined the role of HCHO in the formation of PM2.5 and ozone using integrated measurements in a coastal city of China. They conducted box model runs to illustrate the chemical role of HCHO in PM2.5 formation, ozone, as well as atmospheric oxidation capacity. Overall, I believe the topic of this study fits well with the scope of ACP. The manuscript is also easy-reading. I am happy to see its publication in due course. However, in current version, I think more discussion on HCHO should be added and its role in $PM_{2.5}$ needs to be further justified. Please find my comments below:

Response: Thank you very much for all the valuable comments and suggestions. We have addressed each comment in the following point by point and have revised the manuscript accordingly.

The authors highlight the important role of HCHO in $PM_{2.5}$, but HMS concentrations are very limited and I am also not convinced that HCHO plays very important role in inorganic sulfate formation. Please justify your argument.

Response: Thank you for your good suggestions. We are sorry about some unclear expressions in the original manuscript. Indeed, as the reviewer mentioned, HMS concentrations are very limited and their particulate sulfur molar percentage were relatively low. We just try to present the important role of HCHO on the formations of HMS (not for the formation of $PM_{2.5}$) and ROx radicals during the wintertime co-occurring ozone and $PM_{2.5}$ pollution. According to the reviewer's opinion, we revised the title of the manuscript.

"Exploring the amplied role of HCHO in the formation of HMS and O_3 during the co-occurring $PM_{2.5}$ and O_3 pollution in a coastal city of southeast China"

In addition, we have revised the related descriptions in all the manuscript comprehensively, as follows:

However, the molar ratio of HMS to sulfate were very low (Figure 4), suggesting the limited contributions of HMS concentrations to inorganic sulfate concentrations. Potential roles of HCHO in the HMS formation in coastal city of southeast China was differed from those in the megacities of China. Previous studies found that HCHO reacts with dissolved SO_2 (aq) to produce hydroxymethanesulfonate (HMS), which, upon oxidation with the hydroxyl radical (OH), forms sulfate (Ma et al., 2020; Moch et al., 2020). Ma et al. (2020) reported that heterogeneous formation of HMS accounted for 15% of OM, and resulted in 36% overestimates of sulfate during the winter haze in Beijing. The HMS concentration and the molar ratio of HMS to sulfate increased with the deterioration of winter haze, as well as from winter 2015 to winter 2016 with the growth in HCHO concentration. Meanwhile, Moch et al. (2018) and Song et al. (2019) reported the potential contribution of hydroxymethanesulfonate (HMS) to particulate sulfur during winter haze in Beijing.

The authors ran box model with and without the HCHO mechanism. But how was this conducted? E.g., disable the HCHO photolysis? The method should be well explained.

Response: Thank you for your comments.

To furtherly quantify the varieties in ROx chemistry and O_3 formation in response to HCHO chemistry, two parallel scenarios were conducted through the F0AM model. One scenario was run with all MCM mechanism defined as Input HCHO mechanism, and the other was run with the HCHO mechanism disabled in MCM mechanism defined as Non-input HCHO mechanism. Considering the numerous chemical formation reactions of HCHO, our study mainly disabled the HCHO loss pathways of HCHO photolysis, HCHO + OH, and HCHO + NO_3, which makes HCHO become a stable secondary pollutant that will not continue to react, thus the HCHO loss pathways were disabled in Non-input HCHO mechanism scenario. The differences in ROx levels and production pathways in the two model scenarios were analyzed to investigate the chain effect of HCHO on ROx cycling and O_3 formation. More details could be found in our previous studies (Liu et al., 2023).

The related sentences have been added into the revised manuscript, as follows:

To furtherly quantify the effects of HCHO on ROx chemistry and O_3 formation, we disabled the loss pathways of HCHO photolysis, HCHO + OH, and HCHO + NO_3 in MCM mechanism, defined as Non-input HCHO mechanism (Liu et al., 2023). Meanwhile, the other scenario was run with all MCM mechanisms, defined as Input HCHO mechanism.

Liu, T., Lin, Y., Chen, J.*, Chen, G., Yang, C., Xu, L., Li, M., Fan, X., Zhang, F., and Hong, Y.* Pollution mechanisms and photochemical effects of atmospheric HCHO in a coastal city of southeast China. Science of the Total Environment. 2023, 859:160210

I am very interested in where does HCHO come from? Secondary vs primary origin? How is the HCHO level compared with other studies?

Response: Thank you for your good suggestions. However, we didn't quantify their secondary and primary sources under different pollution stages using the PMF method, due to the limited data. By the way, we have another preparing manuscript that focused on the occurrence, seasonal variations of HCHO in the monitoring site, and would comprehensively quantify their secondary and primary sources based on the PMF method or the photochemical age-based parameterization method. Preliminary results showed that the contribution of secondary formation was the largest, followed by vehicle exhaust, biogenic and industrial emissions, and solvent usage. In this study, for the co-occurring ozone and $PM_{2.5}$ pollution cases, we just try

to emphasize the important role of HCHO on the formations of HMS and ROx radicals.

During the monitoring periods, the concentrations of measured HCHO ranged from 0.68 ppbv and 3.59 ppbv (Tabe S1). According to our previous studies (Liu et al., 2023), the average levels of the measured HCHO in spring and autumn in Xiamen were 2.9 ± 0.3 ppbv and 3.2 ± 1.4 ppbv, respectively. Totally, the HCHO level in Xiamen was lower than that in megacities (Table S2), such as Beijing (summer: 11.39±5.58 ppbv), Hongkong (summer: 8.07±1.94 ppbv), and Guangzhou (summer: 6.69±1.98 ppbv), while was comparable to the coastal cities, including Shenzhen (spring: 3.4±1.6 ppbv), Yantai (summer: 3.90±1.12 ppbv), and Shanghai (summer:3.31±1.43 ppbv). More details have been added in the revised manuscript, as shown in Table S2. Also, we have added the related descriptions in the revised manuscript.

Table S2 Comparisons of atmospheric HCHO in China

Location	Type	Seasons	Mean(±SD) (ppbv)	Range (ppbv)	Reference
Xiamen, China	Urban	Spring	2.9 ± 0.3	0.25-8.34	[12]
	Urban	Autumn	3.2 ± 1.4	0.38-7.56	[12]
	Urban	Winter	1.95±1.06	0.23-6.22	This study
Shenzhen, China	Urban	Spring	3.4±1.6	N.A.[a]	[2]
Hong Kong, China	Urban	Spring (2012)	3.02±0.91	N.A.	[6]
Shanghai, China	Suburban	Spring (2018)	6.7±3.6	N.A.-20.9	[4]
Shanghai, China	Suburban	Spring (2018)	5.01±3.80	N.A.-18.69	[10]
Beijing, China	Urban	Summer (2013)	11.39±5.58	N.A.	[5]
Shanghai, China	Urban	Summer (2018)	3.31±1.43	N.A.	[8]
Shenzhen, China	Urban	Summer	5.0±4.4	N.A.	[2]
Hong Kong, China	Urban	Summer (2011)	8.07±1.94	N.A.	[6]
Guangzhou, China	Urban	Summer (2010)	6.69±1.98	N.A.	[3]
Yantai, China	Urban	Summer	3.90±1.12	N.A.	[3]
Beijing, China	Suburban	Summer	11.17±5.32	3.14-35.08	[9]
Shanghai, China	Suburban	Summer	2.2±1.8	N.A.-9.4	[7]
Wuhan, China	Suburban	Summer	2.1±0.2	0.6-4.1	[1]
Hong Kong, China	Urban	Autumn (2011)	2.96±0.70	N.A.	[6]
Guangdong,China	Urban	Autumn	4.12±1.02	2.56-7.31	[11]
Beijing, China	Urban	Winter (2013)	7.39±5.26	N.A.	[5]
Shenzhen, China	Urban	Winter	4.2±2.2	N.A.	[2]
Hong Kong, China	Urban	Winter (2012)	2.70±1.20	N.A.	[6]
Guangzhou, China	Urban	Winter	3.35±1.38	N.A.	[3]

Note: (a) N.A. means no relevant data available.

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[12]Liu, T., Lin, Y., Chen, J.*, Chen, G., Yang, C., Xu, L., Li, M., Fan, X., Zhang, F., and Hong, Y.* Pollution mechanisms and photochemical effects of atmospheric HCHO in a coastal city of southeast China. Science of the Total Environment. 2023, 859:160210

L219-224: is this backward trajectory analysis necessary?

Response: Thank you for your kindly suggestions. Originally, backward trajectory analysis was used for sources apportionment of $PM_{2.5}$ under different pollution stages. So, we removed it to the SI.

L244: I suggest to replace “might be” with “are”.

Response: Corrected.

In Fig.1, it looks halogenated VOC contributed greatly to TVOCs. What are they coming from? Do you include HCHO concentrations in your TVOCs calculation?

Response: Thank you for your good comments. In the coastal cities of southeastern China, halogenated VOC is one of important VOC species, which originated from industrial emissions and solvent usage, according to our previous studies (Chen et al., 2022; Ji et al., 2022; Liu et al., 2022). In this study, during the monitoring period, backward trajectories showed air mass transport from the northeast, which brought pollutants from Quanzhou city, an industrial city adjacent to Xiamen. Similar to aromatics (2131±1236 pptv), the concentrations of halocarbons (1951±572 pptv) was higher than alkenes (1205±464 pptv) and acetylene (674±290 pptv), according to our previous studies (Liu et al., 2022). So, we have added the related descriptions in the revised manuscript.

In addition, we didn't include HCHO in the TVOCs calculation.

Chen, G., Liu, T., Ji, X., Xu, K., Hong, Y*., Xu, L., Li, M., Fan, X., Chen, Y., Yang, C., Lin, Z., Huang, W., and Chen, J.: Source Apportionment of VOCs and O3 Production Sensitivity at Coastal and Inland Sites of Southeast China, Aerosol Air Qual. Res., 22, 220289, 10.4209/aaqr.220289, 2022.

Ji, X., Xu, K., Liao, D., Chen, G., Liu, T., Hong, Y. *, Dong, S., Choi, S.-D., and Chen, J.*: Spatial-temporal Characteristics and Source Apportionment of Ambient VOCs in Southeast Mountain Area of China, Aerosol Air Qual. Res., 22, 220016, 2022.

Liu T.#, Hong, Y.#, Li, M., Xu, L., Chen, J.*, Bian Y., Yang C., Dan Y., Zhang Y., Xue L., Zhao M., Huang Z., Wang H., Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of Southeast China: Analysis of a typical photochemical episode by Observation-Based Model. Atmos. Chem. Phys. 22, 2173-2190, 2022

L300-301: "under different periods" refers to EP1 and EP2?

Response: Yes. We have clarified this sentence, as follows:

However, there was no significant difference in the existing form of SNA in $PM_{2.5}$ during EP1 and EP2.

L334: change "HCOH" to "HCHO"

Response: Corrected.