

Editor and Reviewer comments:

Response: We thank the editor and reviewers for good comments and suggestions. We have addressed each comment in the following point by point. In addition, we have adjusted our reference list according to the ACP guideline.

RC1: [Comment on egusphere-2023-1242](#), Anonymous Referee #1, 14 Jul 2023

The manuscript by Hong et al. investigated the synergistic mechanisms between fine particulate matter (PM_{2.5}) and surface ozone (O₃) in a coastal city of southeast China. Especially, the authors explore the influence mechanism of HCHO on co-occurring O₃ and PM_{2.5} pollution based on the observation-based model (OBM). They employed well established analytical techniques for identification and quantification of HCHO effects on hydroxymethanesulfonate (HMS) and O₃ formations. The obtained results are interesting and would be helpful for understanding the role of HCHO in photochemical pollution and secondary aerosol formation. I can recommend its publication in Atmospheric Chemistry and Physics (ACP) after addressing the 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.

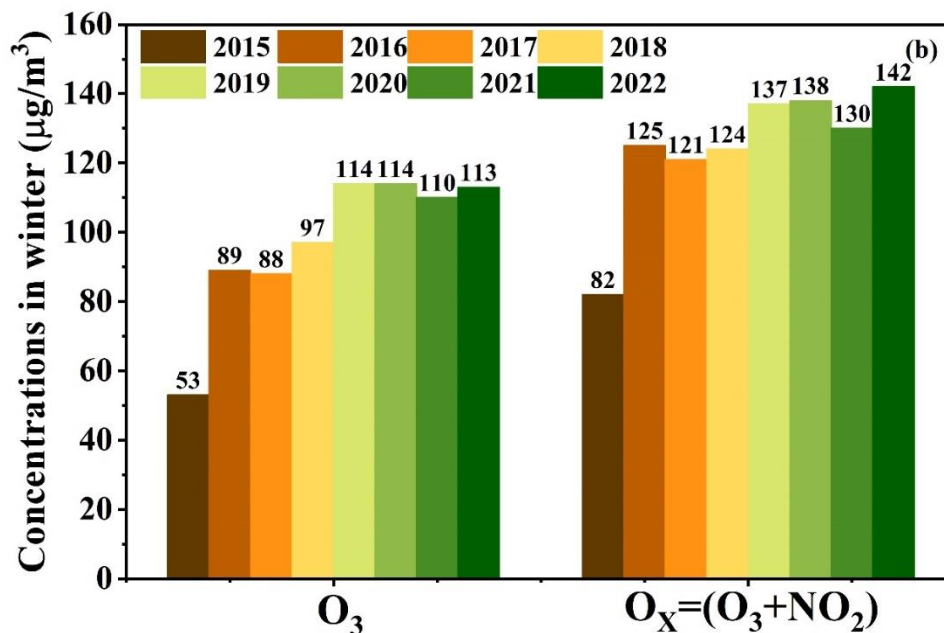
Line 37-38: the authors mentioned, “suggesting an increase in atmospheric oxidation capacity (AOC) during the cold seasons”. Could you elaborate why or provide more evidence to support it. This is not clear.

Response: Thank you very much for your suggestions. We provided the supporting data for atmospheric oxidation capacity (AOC) during the cold seasons. Inter-annual averaged concentrations of O₃ and Ox in winter has been added into Fig S3.

So, the related sentences have been added in the revised manuscript, as follows:

The results of this study revealed the characteristics of positively correlated PM_{2.5} and MDA8 O₃ concentrations, and an increase in atmospheric oxidation capacity (AOC) during the cold seasons.

Meanwhile, inter-annual averaged concentrations of O₃ and Ox in winter were shown in Fig S3 (b), suggesting an increase in atmospheric oxidation capacity (AOC) during the cold seasons.



Lines 79 to 90: Additional references about the effects of HCHO on HMS in the introduction are needed.

Response: Thank you for your good suggestions. We have added the details of the HMS in the revised manuscript, as follows:

Recent studies have shown that HCHO can react with hydrogen peroxide (H₂O₂) to produce hydroxymethyl hydroperoxide (HMHP), which rapidly oxidizes dissolved sulfur dioxide (SO₂, aq) to sulfate (Dovrou et al., 2022). Meanwhile, HCHO reacts with dissolved SO₂ (aq) to produce hydroxymethanesulfonate (HMS, HOCH₂SO⁻), which, upon oxidation with the hydroxyl radical (OH), forms sulfate (Ma et al., 2020; Moch et al., 2020). Totally, atmospheric HCHO contributes to sulfate formation in PM_{2.5} by producing HO₂ radicals and HMHP or HMS (Wu et al., 2023; Dovrou et al., 2022; Campbell et al., 2022). However, these studies highlight the necessity for more observation research to obtain evidence of the contributions of HCHO to HMS formation. HMS is an important organosulfur compound in the atmosphere, not only in cloud and fog but also in atmospheric aerosols (Munger et al., 1986; Dixon and Aasen, 1999). The misidentification of HMS as inorganic sulfate caused the overestimation of the observed particulate sulfate (Ma et al., 2020; Dovrou et al., 2022).

Munger, J. W., Tiller, C., and Hoffmann, M. R.: Identification of hydroxymethanesulfonate in fog water, *Science*, 231, 247–249, <https://doi.org/10.1126/science.231.4735.247>, 1986.

Dixon, R. W. and Aasen, H.: Measurement of hydroxymethanesulfonate in atmospheric aerosols, *Atmos. Environ.*, 33, 2023–2029, [https://doi.org/10.1016/s1352-2310\(98\)00416-6](https://doi.org/10.1016/s1352-2310(98)00416-6), 1999.

Lines 198 to 209: The methodology for HMS modeling needs to be presented in detail.

Response: Thank you for your kindly suggestions. We have added the descriptions in all the manuscript comprehensively.

To simulate the concentration of particulate HCHO and its role in the heterogeneous formation of hydroxymethanesulfonate (HMS), the observation-based zero dimensional multiphase chemical box model was used, of which the gas phase chemistry is described by the regional atmospheric chemistry mechanism version 2 (RACM2) and the aqueous phase part of the mechanism is represented by the chemical aqueous-phase radical mechanism version 3.0 (CAPRAM 3.0). The mass transfer processes between the gas and aqueous phases is also considered in current model according to Schwartz (1986). The Henry's law constant of HCHO was updated with a value of $0.31 \times 10^8 \text{ M atm}^{-1}$, as estimated by Mitsuishi et al. (2018). Sensitivity analysis was conducted to evaluate the uncertainties introduced by the Henry's law constant, details can be found in SI. For major production and loss paths of HMS, dissolved HCHO reacts with sulfite and bisulfite to form HMS (Eq (3-4)), which can be further oxidized by aqueous OH radicals (Eq (5)), details about the HMS mechanisms and the corresponding reaction kinetics are documented in CAPRAM website (<https://capram.tropos.de/>).



For detailed modeling steps of HMS, firstly, the observation data of gaseous NO, NO₂, O₃, SO₂, CO, NMHCs, HCHO and other ten carbonyls, particulate phase NO₃⁻, NH₄⁺, and Cl⁻, along with meteorological parameters were averaged or interpolated into a 1-h time resolution and classified into model recognized groups as model inputs, while the measured SO₄²⁻ was used as the initial conditions. Liquid water content (LWC) and aqueous H⁺ concentrations, calculated using the ISORROPIA-II model (Hong et al., 2022), were also used as model inputs. Then, model calculations were conducted using the commercial FACSIMILE software, the modeling period was from February 26 to March 16, 2022 and each day was regarded as an independent simulation case. The model was constrained every hour by the input observation data for integral calculation. For each case, The integration ran three times in series to steady the unconstrained species (e.g., radicals), which was initiated at 00:00 local time (LT), and had a step of 1 h and a duration of 24 h. Finally, the modeled HMS concentrations of the third run were outputted with a 1-hour time resolution for further analysis.

Line 348-355: The manuscript focused on the HCHO mechanisms, so it is suggested to discuss more about the effects of HCHO on HMS in PM_{2.5}.

Response: Thank you for your good suggestions. Indeed, as the reviewer mentioned, the effects of HCHO on HMS in PM_{2.5} were emphasized in this study. We have added the descriptions in all the manuscript comprehensively.

However, the molar ratio of HMS to sulfate were very low, suggesting the limited contributions of HMS concentrations to inorganic sulfate concentrations. Potential roles of HCHO in the HMS formation in coastal cities of southeast China was differed from those in the megacities of China. Previous studies found that HCHO reacts with dissolved SO₂ (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.

Line 313-314: The authors state " As shown in Fig. 3(b) and (c), a good correlation was found between SO₄²⁻ and Fe and Mn." The use of correlations is indeed a helpful tool to explore some specific trends; however, such data processing techniques are not sufficient to reach a definite conclusion on that the TMI-catalyzed oxidation contributed to the formation of SO₄²⁻.

Response: Thank you for your good comments. The reviewer raised a good point that the TMI-catalyzed oxidation contributed to the formation of SO₄²⁻. As shown in Figure 1, under low aerosol pH, the catalytic reaction of transition metal ions (TMIs), e.g., Fe(III) and Mn(II) plays an important role in the oxidation of S(IV). In this study, low aerosol pH ranged from 2 to 4 was observed, indicating the potential influence of TMI-catalyzed oxidation.

Previous studies found that Mn(III) was the intermediate product that could oxidize S(IV) (Wang et al., 2021). Meanwhile, SO₃⁻ can react with dissolved O₂ to generate SO₅⁻ radicals, which can oxidize Mn(II) to regenerate Mn(III) (Seinfeld and Pandis, 2016). Therefore, the Mn catalytic redox reaction could continue to produce sulfate while consuming only oxygen and SO₂, meaning that this reaction would occur even in the low concentration of Mn (Wang et al., 2021). The sulfate production rate was affected by many factors, including the aerosol surface, the aerosol acidity and ionic strength, and environmental conditions (temperature and relative humidity), along with various mixing ratios of SO₂, NO₂ and NH₃ (Zhang et al., 2020; Hung et al., 2018; Lee et al., 2019). Some findings demonstrated that there may be a massive gap in the reaction rate between air-liquid interface and bulk solution, and the mechanism of air-liquid interface rate enhancement effect may differ greatly in a distinct reaction system (Yan et al., 2017; Zhang et al., 2020; Lee et al., 2019). For aqueous phase oxidation to form sulfate processes, such as oxidization by NO₂, O₃, H₂O₂, are not only limited by the availability of oxidants in the atmosphere and the solubility of SO₂, these oxidants would also be consumed at the same order of magnitude as the

formation of sulfate. In the future, it is vital to further evaluate the interaction of sulfate formation and Fe/Mn, and to elucidate the main pathway of the S(IV) oxidation in the coastal areas.

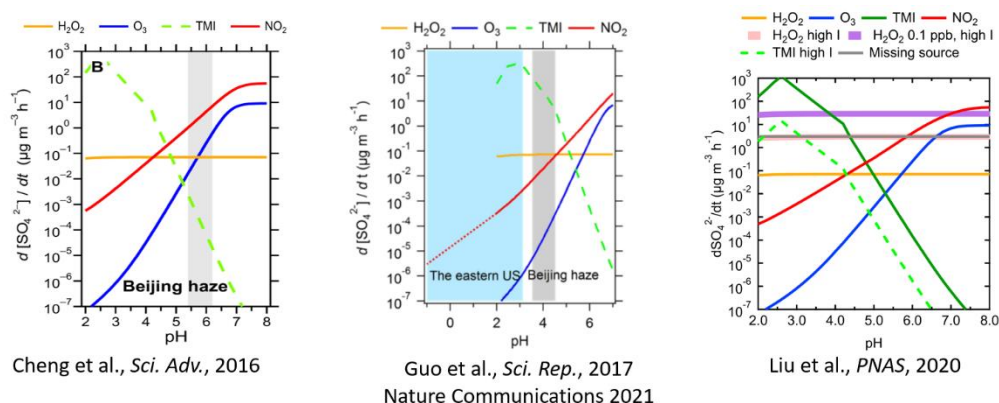


Figure1 The formation of SO_4^{2-} in fine particulate matter under different aerosol acidity conditions

Seinfeld, J. H. & Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (John Wiley & Sons, 2016).

Yan, X., Cheng, H. & Zare, R. N. Two-phase reactions in microdroplets without the use of phase-transfer catalysts. *Angew. Chem.* 129, 3616–3619 (2017).

Zhang, Y., Apsokardu, M. J., Kerecman, D. E., Achtenhagen, M. & Johnston, M. V. Reaction kinetics of organic aerosol studied by droplet assisted ionization: enhanced reactivity in droplets relative to bulk solution. *J. Am. Soc. Mass Spectrom.* 32,46–54 (2020).

Hung, H. M., Hsu, M. N. & Hoffmann, M. R. Quantification of SO_2 oxidation on interfacial surfaces of acidic micro-droplets: implication for ambient sulfate formation. *Environ. Sci. Technol.* 52, 9079–9086 (2018).

Lee, J. K. et al. Spontaneous generation of hydrogen peroxide from aqueous microdroplets. *Proc. Natl Acad. Sci. USA* 116, 19294–19298 (2019).

Y. Cheng, G. Zheng, C. Wei, Q. Mu, B. Zheng, Z. Wang, et al. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China.[J].*Science advances*.2016,(12).e1601530.

Wang, W., Liu, M., Wang, T., et al., 2021. Sulfate formation is dominated by manganese-catalyzed oxidation of SO_2 on aerosol surfaces during haze events. *Nat. Commun.* 12, 1993. <https://doi.org/10.1038/s41467-021-22091-6>.

We discussed the effects of metal oxidation on the sulfate production in the revised manuscript, as follows:

Under low aerosol pH conditions, the catalytic reaction of TMIs plays an important role in the oxidation of S(IV). In this study, low aerosol pH ranged from 2 to 4 was observed, indicating the potential influence of TMI-catalyzed oxidation. In the future,

it is vital to further evaluate the interaction of sulfate formation and Fe/Mn, and to elucidate the main pathway of the S(IV) oxidation in the coastal areas.