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 (O$_3$) in a coastal city of southeast China. Especially, the authors explore the influence mechanism of HCHO on co-occurring O$_3$ 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 O$_3$ 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 O$_3$ 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 O$_3$ concentrations, and an increase in atmospheric oxidation capacity (AOC) during the cold seasons.

Meanwhile, inter-annual averaged concentrations of O$_3$ and Ox in winter were shown in Fig S3 (b), suggesting an increase in atmospheric oxidation capacity (AOC) during the cold seasons.
Recent studies have shown that HCHO can react with hydrogen peroxide (H$_2$O$_2$) to produce hydroxymethyl hydroperoxide (HMHP), which rapidly oxidizes dissolved sulfur dioxide (SO$_2$, aq) to sulfate (Dovrou et al., 2022). Meanwhile, HCHO reacts with dissolved SO$_2$(aq) to produce hydroxymethanesulfonate (HMS, HOCH$_2$SO$^-$), 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 HO$_2$ 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).


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/).

\[
HCHO_{(aq)} + HSO_3^- = HOCH_2SO_3^- \tag{3}
\]

\[
HCHO_{(aq)} + SO_3^{2-} + H_2O = HOCH_2SO_3^- + OH^- \tag{4}
\]

\[
HOCH_2SO_3^- + OH^- \cdot = 2SO_4^{2-} + HCHO_{(aq)} + 3H^+ \tag{5}
\]

For detailed modeling steps of HMS, firstly, the observation data of gaseous NO, NO\(_2\), O\(_3\), SO\(_2\), CO, NMHCs, HCHO and other ten carbonyls, particulate phase NO\(_3^+\), NH\(_4^+\), 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 SO\(_4^{2-}\) 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.
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 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 authors state " As shown in Fig. 3(b) and (c), a good correlation was found between SO$_4^{2-}$ 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 SO$_4^{2-}$.

Response: Thank you for your good comments. The reviewer raised a good point that the TMI-catalyzed oxidation contributed to the formation of SO$_4^{2-}$. 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, SO$_3^-$ can react with dissolved O$_2$ to generate SO$_5^-$ 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 SO$_2$, 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 SO$_2$, NO$_2$ and NH$_3$ (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 NO$_2$, O$_3$, H$_2$O$_2$, are not only limited by the availability of oxidants in the atmosphere and the solubility of SO$_2$, 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.

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 TMI's 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.