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Reply on RC2

Taotao Liu et al.

Author comment on "Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of southeastern China: analysis of a typical photochemical episode by an observation-based model" by Taotao Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-764-AC2>, 2022

Reply on RC2

AOC is key to photochemical reactions and the formation of secondary components like O₃ and secondary organic aerosol. This study uses OBM to understand the AOC in a coastal city in China during a typical photochemical episode. It is well organized and suitable for publication in ACP. I have below comments for the authors.

Response: Thanks for your valuable comments and positive feedback. We have corrected this manuscript according to your suggestion.

- OBM is good for understanding the local photochemical formation of O₃, but it is not good to evaluate the transport, while back trajectories cannot quantify the contributions. Thus, it is important to show the method of how the regional transport contribution is determined. In this study, the differences between observed O₃ changes and local formation were treated as regional transport, which is very misleading. A better method representation should be physical processes instead of regional transport.

Response: Thanks for your suggestion, we strongly agree with your suggestions of R_{trans} representing physical processes. The in-situ ozone concentration change is a result of both physical and chemical processes. The O₃ concentration change rate (R_{meas}) can be determined by the observed O₃ concentration. The difference between R_{meas} and R_{chem} is caused by physical processes, including horizontal and/or vertical transportation, dry deposition, dilution mixing, and so on, and many studies showed that the impacts of dry deposition were minor. Hence, the differences between observed O₃ changes and local formation were mainly caused by the regional transport (note that the effect of atmospheric mixing was also included in this term). Anymore, the changes of near-surface winds were corresponding to the variation of the R_{trans} in our study. In some relevant studies, their results also suggested that this method can capture the variations in physical processes, thereby, this calculation method could reasonably quantify the contributions of regional transport at our observation site (Zhang et al., 2021; Xue et al., 2014; Tan et al., 2018; Chen et al., 2020). To avoid misleading, we have revised the relevant content in the manuscript.

"The physical processes (R_{tran}) were calculated by the equation of $R_{tran} = R_{meas} -$

Rchem, including horizontal and/or vertical transport, dry deposition dilution mixing, and so on. Many studies showed that the impacts of dry deposition were minor, thus the differences between observed O₃ changes and local O₃ production were mainly caused by the regional transport (note that the effect of atmospheric mixing was also included in this term), which could be treated as regional transport and could reasonably quantify the contributions of regional transport at our observation site (Zhang et al., 2021; Chen et al., 2020)."

- CO looks very important in OH reactivity, a quick search showed me that it is quite different from other countries, please add comparison or discussion why it is high in this study. (CalNex-LA, BEACHON-SRM08, DISCOVER-AQ)

Response: Thanks for your suggestion. About the relatively high fraction of CO in OH reactivity, which was mainly due to the high CO concentrations during the observation period. CO mainly comes from vehicle exhaust and the combustion of fossil fuels. The observation site is a city with high density vehicles, and the high values of observed CO in the morning and evening rush hour also verified the important effects of vehicle emissions. Meanwhile, this pollution event was under the influence of West Pacific Subtropical High, which carries favorable photochemical reaction conditions (high temperature, low RH, and stagnant weather conditions) and promotes the formation and accumulation of pollutants in the southeast coastal area. The relevant contents were discussed in our manuscript, and the main revisions are as follows.

"The high fraction of OVOCs and NO₂ in OH reactivity indicated the high aged degree of air mass and the intensive NO_x emissions during the observation period, respectively (Li et al., 2018). However, the fraction of CO to OH reactivity at our observation site was higher than that at an urban site in Los Angeles (Hansen et al., 2021), a rural site in Hong Kong (Li et al., 2018), and a mountain site in Colorado (Nakashima et al., 2014), comparable to that at the urban site of Shanghai (Zhang et al., 2021a), which could be attributed to the abundant CO in our observation site. CO mainly comes from vehicle exhaust and the combustion of fossil fuels, and the observation site is a city with high density vehicles. Meanwhile, this pollution event was under the influence of the WPSH, which promoted the formation and accumulation of pollutants."

- The episode is just one high O₃ event, thus, not necessarily the whole story of O₃-NO_x-VOCs relationship. It should be cautious when making policy implications.

Response: Thanks for your suggestion. As the episode is a typical pollution process in the coastal region, the research results might act as reference for the policy makers. It should be known that is necessary to adjust timely the reduction of VOC and NO_x policies as the O₃ sensitivity changed under the implementation of control measures. Based on your suggestions, we have revised the relevant content of the manuscript.

"As shown in Fig. 10b, achieving the 5% control target were 1) S(VOCs) is reduced by 15%, while S(NO_x) remains unchanged; 2) S(VOCs) is reduced larger than 35%; 3) S(NO_x) reduction is higher than 60%. The first scenario of just reducing VOCs emission was the most cost-efficient way for short-term or emergency control of O₃. However, NO_x, as important precursors of PM_{2.5}, need to be reduced according to the long-term multi-pollutant control air quality improvement plan in China, thus the second scenario is a more practical and reasonable way to control air pollution."

"As the episode is a typical pollution process in the coastal region, the research results might act as reference for the policy makers."

- From Figure 11, the Rtran is mostly opposite to the Rchem, which means local formation and so-called regional transport do not work together to cause high ozone events. The conclusion that “regional transport aggravated the pollution of ozone” is not accurate.

Response: Thanks for your suggestion. The regional transport of Rtran was divided into O₃ import and O₃ export, and the O₃ import bringing relatively high O₃ concentration caused high ozone events, so we mainly focus on the relationship between positive Rtran and Rchem values. In Figure 11, we found that the O₃ concentrations showed two peaks at around 15:00 and 17:00 LT, and O₃ concentrations rose slowly, or even decreased firstly and then increased between the two peaks. Under these circumstances, the O₃ change rates of Rmeas showed the “M” trend during the daytime. The first transient intense O₃ import happened in the early morning (at around 6:00-9:00), leading to a more rapid increase at around 6:00-9:00 LT in O₃ concentration than that at 9:00-15:00 LT, when the increase in O₃ concentration was mainly due to photochemical reactions. The second O₃ import happened at around 15:00-17:00, leading to the second peak of O₃ concentration. In conclusion, the first O₃ import of regional transport increased the O₃ production rate and ozone concentration, and the second O₃ import based on the intense photochemical conditions made O₃ concentration reaching the maximum peak to exceed the National Ambient Air Quality Standard. Hence, the combined effect of regional transport and local O₃ formation led to the pollution event, and the regional transport made the O₃ concentration exceeding the standard. We have revised the expression to make the conclusion accurate, and the revisions in the manuscript are as follows.

“The first transient intense O₃ import happened in the early morning (at around 6:00-9:00), leading to a rapid increase in O₃ concentration, which was mainly attributed to the residual ozone from the day before. The O₃ export was remarkable at around 10:00-16:00, indicating the potential impacts on air quality in downwind areas. Generally, the maximum daily value of O₃ at this observation site appeared at around 15:00 LT without regional transport (Wu et al., 2019). In Figure 11, we found that the O₃ concentrations showed two peaks at around 15:00 and 17:00 LT, and O₃ concentrations rose slowly, or even decreased firstly and then increased between the two peaks. Under these circumstances, the local photochemical production kept producing O₃, but the decreased O₃ concentrations could be attributed to the favorable atmospheric conditions in diluting pollutants (O₃ export). When the near-surface wind direction changed from northeast to southeast, the second O₃ import phenomenon occurred in the afternoon (16:00-19:00 LT) in four days (20, 25 27 and 29 Sep.). Due to the persistence of Rtran in the afternoon, the daily maximum O₃ values appeared at around 17:00 LT.”

“Overall, the results indicate that the three conditions of local photochemical production, synoptic situations, and regional transport played very important roles in the pollution event.”

- Some expresses are not in scientific mode, for example, 1) In Abstract, “were the important primary sources of RO_x”, O₃ and HCHO are not emission sources, so not proper to use primary. 2) how the uncertainties are calculated? OH contributed to 91±23%, at what cases, you have a larger than 100% contribution?

Response: Thanks for your suggestion. The answers to the questions were shown below.

1) The expression of the primary source of RO_x in our manuscript means chain initial reaction, a reaction that molecules rely on heat and light decomposing into free radicals,

and also means the major source. The RO_x chain initial reactions are uniformly expressed as primary sources in related researches (Zhang et al., 2021; Xue et al., 2014; Tan et al., 2018; Chen et al., 2020). For better understanding, I changed the expression as "Photolysis of nitrous acid (HONO, 33±14%), O₃ (25±13%), formaldehyde (HCHO, 20±5%), and other OVOCs (17±2%) were major RO_x sources, which played initiation roles in atmospheric oxidation processes".

2) About the uncertainties of the model simulation results, the index of agreement (IOA) can be used to judge the reliability of the model simulation results, and its calculation equation showed in the supplement (Liu et al., 2019). The IOA range is 0-1, and the higher the IOA value is, the better agreement between simulated and observed values is. In many studies, when IOA ranges from 0.68 to 0.89 (Wang et al., 2018a), the simulation results are reasonable, and the IOA in our research is 0.80. Hence, the performance of the OBM-MCM model was reasonably acceptable.

The value of ±23% here represents the standard deviation based on the samples, reflecting the degree of dispersion of the values. During the daytime, the OH contributing to AOC ranged from 13% to 99%, and there was no case where OH contribution was larger than 100%.

Reference□

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Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-764/acp-2021-764-AC2-supplement.pdf>