
Response to the editor

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1. The manuscript is of excellent technical quality, as pointed out by all reviewers. However, I would like to ensure the manuscript fits with the ACP author guidelines. Specifically the conclusions section is somewhat incomplete. I would like to ask the authors to provide a more detailed discussion of comparisons, context, limitations and broader implications. It would make the manuscript even stronger.

Reply: We appreciate your valuable comments and suggestions, which are very helpful for the improvement of our manuscript. Based on your suggestions, we have rephrased the conclusions section and provided more discussions on the context of our study, comparisons with previous works, implications for future studies on secondary air pollution, and the limitations of our study. [see P 19-20, L 484-524]

"*The inadequate vertical distribution data of volatile organic compounds (VOCs) poses a significant barrier to fully comprehending the mechanisms underlying photochemical ozone formation and devising effective mitigation strategies. To address this concern, we made vertical gradient measurements of VOCs, NOx, and ozone based on a 325 m tall tower in urban Beijing during the summer of 2021. This study offered more exhaustive and nuanced insights into the vertical variability of VOCs compared to previous studies. Our findings underscored that the vertical variations of VOCs were strictly regulated by the diurnal evolution of the PBL and chemical processes. In daytime, reactive NMHCs were rapidly oxidized when they were mixed upward along with the formation of OVOCs. As a result, concentrations of NMHCs decreased with height and many of OVOC species increased with height. OVOC species played more significant roles in regulating the photochemical ozone formation in urban regions aloft.*

Model simulations unveiled that the photochemical formation of ozone belongs to the transition regime in the lower PBL and became more sensitive to changes in the concentrations of AVOCs and OVOCs with height. With the further increase in height,

the photochemical formation of ozone may change to the NOx control regime due to the total OHR of VOCs decreased much slower than NOx concentrations. $P(O_3)$ exhibited decreasing tendencies with height due to coupled declines in concentrations of NOx and VOCs. $P(O_3)$ still remained large in high altitudes, likely driven by high OVOC concentrations. This implies that the bulk of ozone formation occurs within the middle and upper strata of the PBL rather than proximate to the ground surface. Therefore, regional ozone control strategies necessitate meticulous consideration of vertical gradients in $P(O_3)$ and the varying regimes of photochemical ozone formation throughout the entire PBL.

The vertical variations in concentrations and compositions of VOCs significantly influence ozone formation. In addition, the vertical changes in chemical reaction environments (e.g., temperature, humidity, and solar radiation) and concentrations of other chemicals (e.g., particulate matters, NOx, ozone) can also impact the degradation pathways of VOCs. These factors also affect the formation pathways and production yields of other secondary air pollutants, such as formic acid, isocyanic acid, and secondary organic aerosol. This is particularly crucial for the highly reactive NMHCs in urban areas with complex anthropogenic and biogenic emissions.

Limitations of our study include the confinement of measurements below 320 meters due to the tower's height, leaving the mid and upper daytime PBL's VOC distributions and chemistries unexplored. Additionally, the absence of measurements for some key chemical species like HONO, organic aerosol components, and reactive halogen species might have implications for the accuracy of our box model results. Future endeavors could integrate multiple observational techniques to capture a broader vertical scope and a more comprehensive suite of species, thereby enhancing our understanding of how vertical variations in VOC chemistry impact secondary pollution formation."