Reviewer #2

Comment [2-1]: General comments: The paper by He et al., investigated vertical distributions and process contributions of the nighttime boundary-layer ozone in Southern China using 3-year tower-based measurements. As indicated by the authors, the continuous gradient measurements of ozone in the lower boundary layer, particularly in urban regions, are very important for clarifying vertical exchange characteristics of ozone and thus elucidating the reasons that regulate surface ozone air quality. The paper is well written and organized. The analysis regarding vertical distributions and key drivers of ozone was reasonable and has been well supported in the literature. Therefore, I only have some small concerns that may be further explained by the authors before its publication.
Response [2-1]: We thank the reviewer for the positive and valuable comments. All of them have been implemented in the revised manuscript. Please see our itemized responses below.

Comment [2-2]: Specific comments: Line 115: How the wind information was measured on the tower? was it measured inside or outside the outer shell of tower? The structure of the tower may cause complicated and different turbulences affecting the measured winds on different altitudes.
Response [2-2]: Thank you for pointing it out. The wind speed at the lower altitude is obtained from an observation station beside the Canton Tower. The wind speed at the middle layers (118 m, 168 m) is measured inside the outer shell of the tower. The wind speed at the highest layer (488 m) is measured inside the hollow mast at the tip of the tower.

We agree that the structure of the tower may affect the measured winds on different altitudes. In our study, we find that the dependence of the nighttime 488 m ozone concentration on temperature vertical lapse rate does not show obvious difference under various wind speed condition over the 3-year measurements. According to the previous studies on measurements from the Canton Tower, we have added the following text within paragraph 2 of Section 2.1 as follows: <u>"The structure of the tower may cause complicated and different turbulences affecting the measured winds on different altitudes, however, the above previous studies have demonstrated the reliability of atmosphere components measured from the Canton Tower."</u>

Comment [2-3]: Line 205: The vertical gradients of ozone in the nighttime boundary were much stronger than in the daytime due to the inhibition of the vertical mixing. The authors also stated that the vertical gradients of O_x mixing ratios are much weaker than those of ozone. Therefore, the positive gradients of vertical ozone profiles were mainly determined by the gradually reduced NO titration effect. Were any vertical gradient measurements of NO on the tower that can be used to support this conclusion?
Response [2-3]: Thank you for pointing it out. Following your suggestion, we have

added Figure S3 to show the vertical gradient of measured NO_x. We find that vertical gradient measurements of NO_x can be used to support the vertical gradients of ozone between nighttime and daytime. We have added the following text in Section 3.1 as follows: <u>"We also find a larger vertical gradient of NO_x ($NO+NO_2$) concentrations in nighttime than daytime (Fig. S3), suggesting that the titration effect is an important factor shaping the ozone vertical structure."</u>

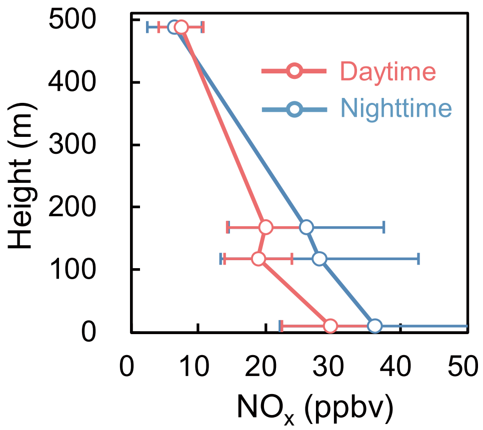

Figure S3. Mean NO_x ($NO+NO_2$) vertical structure in the lower boundary layer observed at the Canton Tower, October 2017. Blue and rosy lines denote nighttime (20:00-07:00 LT) and daytime (08:00-19:00 LT) mean NO_x profiles, respectively.

Comment [2-4]: Line 235-240: As highlighted by the authors, the discrepancies between modeled and measured ozone in urban regions aloft may be caused by many factors. In my opinion, a grid with a small spatial scale of 3×3 km^2 in the urban region may be not the dominant factor causing these significant differences. I suggest that the authors can provide a comparison between the modeled and measured vertical profiles of NO_x in the boundary layer to check whether exist significant discrepancies. In addition to the state of vertical mixing, the vertical distribution of NO_x is also an important factor to shape the vertical profile of ozone in the boundary layer. Furthermore, as reported in the literature, ambient NO_x concentrations declined rapidly in recent years in China and thus I am not sure whether the emission inventory of NO_x used in the model can well reflect these changes.
Response [2-4]: Thank you for your suggestions. The MEIC inventory used in this study provides anthropogenic emission in China for year 2017, which covers the simulation period of this study.

We compare the mean vertical profiles of NO_x in the lower boundary layer between the model simulation and measurement, as shown in Figure R2. The model mostly captures the observed magnitude and vertical structure of NO_x both in daytime and nighttime, but still has notable bias at the surface, suggesting uncertainties in emission inventory. We have added the following text in Section 2.3 to clarify the use of anthropogenic emission inventory in this study <u>"Anthropogenic emissions from MEIC in 2017 are downscaled from its original resolution of 25×25 km^2 to the model resolution of 3×3 km^2, using the Modular</u>

<u>Emission Inventory Allocation Tool for Community Multiscale Air Quality Model (MEIAT-CMAQ) v1.0 (Wang et al., 2023a)</u>", and in Section 3.1 for the model bias discussion <u>"The lack of high-resolution (e.g. ~3km or higher) anthropogenic emission inventory may cause bias for simulation of ozone precursors."</u>

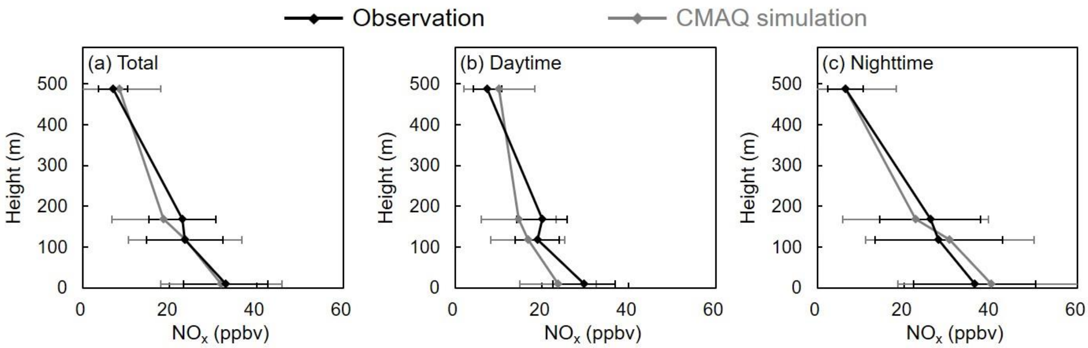

Figure R2. Mean NO_x vertical structure in the lower boundary layer of observation and CMAQ simulation.

Reference:

Wang, H., Qiu, J., Liu, Y., Fan, Q., Lu, X., Zhang, Y., Wu, K., Shen, A., Xu, Y., Jin, Y., Zhu, Y., Sun, J., and Wang, H.: MEIAT-CMAQ v1.0: A Modular Emission Inventory Allocation Tool for Community Multiscale Air Quality Model Version 1.0, EGUsphere, 2023, 1-33, https://doi.org/10.5194/egusphere-2023-1309, 2023a.

Comment [2-5]: Line 245-250 and Figure 4: These results and conclusions are quite confusing. In nighttime, process contributions of the change in ozone at different altitudes are plausible. However, process contributions of the change in ozone in daytime are confusing. As shown in Figure 4, the increase in surface ozone in daytime were mainly contributed by vertical diffusion and horizontal advection. The authors also highlight that chemistry is not a major source/sink of ozone at 488 m. According to these results, the boundary-layer ozone budget in urban Guangzhou was mainly contributed by transport from adjacent regions or from even higher altitudes? Local formation of ozone from photochemistry has negligible contributions to the increase in the boundary layer ozone in daytime?

Response [2-5]: Thank you for pointing it out. Our results of ozone budget diagnostics are consistent with previous study conducted in Hong Kong (Wang et al., 2015) and Guangzhou (Xu et al., 2023) using CMAQ model, all showing negative contributions of photochemistry to surface ozone concentrations and positive contribution at higher altitudes in urban area. This may reflect strong chemical loss by high NO_x at the surface once the ozone is produced. Here we additionally present the ozone vertical budget extending from surface to about 2 km ahead at noon when the ozone chemical production is the most intense, as depicted in Figure R3. We indeed find significant net ozone production in the boundary layer that contribute to ozone increase, and these ozone enhancements can be transported and/or diffused to surface level. We have added the following

text in Section 3.1 as follows: <u>"In noon when chemical production is intense, however, we find that the ΔCHEM exhibits positive contribution at ~200-1000 m, while ΔVDIF exhibits negative contribution at ~200-1000 m but positive at the surface. These budgets are consistent with the previous study conducted in Hong Kong (Wang et al., 2015) and Guangzhou (Xu et al., 2023), indicating that surface ozone is mainly contributed by vertical diffusion from local photochemistry in higher altitudes in urban Guangzhou."</u>

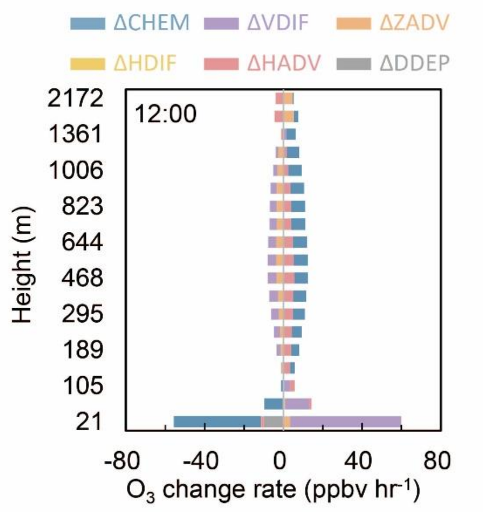

Figure R3. CMAQ model simulation of ozone budgets at the Canton Tower, October 2017. ΔCHEM represents change in chemistry, ΔVDIF represents change in vertical diffusion, ΔZADV represents change in vertical advection, ΔHDIF represents change in horizontal diffusion, ΔHADV represents change in horizontal advection, and ΔDDEP represents change in dry deposition.

Reference:

Wang, N., Guo, H., Jiang, F., Ling, Z. H., and Wang, T.: Simulation of ozone formation at different elevations in mountainous area of Hong Kong using WRF-CMAQ model, Sci. Total Environ., 505, 939-951, https://doi.org/10.1016/j.scitotenv.2014.10.070, 2015.

Xu, Y. F., Shen, A., Jin, Y. B., Liu, Y. M., Lu, X., Fan, S. J., Hong, Y. Y., and Fan, Q.: A quantitative assessment and process analysis of the contribution from meteorological conditions in an O_3 pollution episode in Guangzhou, China, Atmos. Environ., 303, https://doi.org/10.1016/j.atmosenv.2023.119757, 2023.

Comment [2-6]: Line 260-265: In daytime, the enhancement of air turbulence could drive the well mixing of ozone in the boundary layer. Therefore, the defined "nighttime ozone residual capacity" may be not suitable to assess the influence of the ozone at a certain height in the nighttime on the ozone budget at the same height in the daytime boundary layer.

Response [2-6]: We agree, thank you for correction. The defined "nighttime ozone

residual capacity" ignore the contribution from horizontal transportation and vertical mixing to ozone at a certain height. It only reflects the relative amount of ozone concentrations averaged over nighttime to that averaged over afternoon.

To prevent potential misleading to readers, we have replaced the definition of "nighttime ozone residual capacity" to "nighttime ozone residual ratio" in a mathematically manner. Specifically, we have made revisions to the statement in Section 3.2 as follows: "We note that this ratio at a certain height only quantifies the averaged level of nighttime ozone compared to afternoon when ozone concentrations typically reach the daily peak, and does not account for additional influence of horizontal transportation and vertical mixing. However, it can still serve as a useful metric to quantify to what extent ozone in the afternoon can be reserved in the nighttime."

Comment [2-7]: Line 340-344: How O_x changes at different altitudes during the NOE events?

Response [2-7]: During the NOE event, the observed O_x concentration becomes more consistent between the surface and the higher altitudes, as shown in Figure R4. It is a signal for the enhanced vertical mixing.

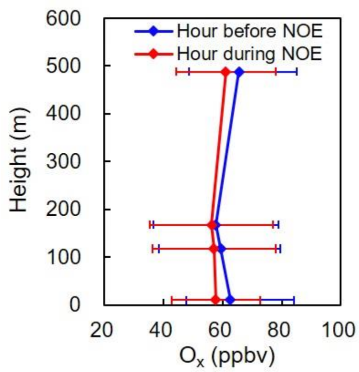

Figure R4. Characteristics of O_x profiles before (blue colored lines) and during (red colored lines) the occurrence of the NOE event.

Comment [2-8]: Line 370-375: I agree with the authors' opinion that the improvement of the model capability in simulating nighttime ozone in the RL is a key to decreasing errors of the modeling results. The timely update of the NO_x emission inventory may be another important approach to improve the accuracy of the ozone modeling results.

Response [2-8]: We agree. We have reflected this point in Section 3.1. Please kindly refer to Response [2-4].