Reviewer #3

Comment [3-1]: General comments: Nighttime ozone in the lower boundary layer and its influences on surface ozone: insights from 3-year tower-based measurements in South China and regional air quality modeling. This is an interesting manuscript on vertical structure of ozone in the lower atmosphere based on 3-year tower-based measurements in South China and air quality model analysis. The manuscript is clearly written and well organized.

Response [3-1]: 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 [3-2]: Specific comments: The title is confusing a little bit. "Nighttime ozone in the lower boundary layer" includes surface ozone, right? How to understand "its influences"?

Response [3-2]: Thank you for pointing it out. We have revised the title as follows: <u>"Nighttime ozone in the lower boundary layer: insights from 3-year tower-based measurements in South China and regional air quality modeling"</u>

Comment [3-3]: How many nighttime ozone enhancement (NOE) events occurred in the 3-year tower-based measurements? Does NOE happen at the same day in other air quality stations in Guangzhou? Are there seasonal differences in NOE? Authors stated that "During the surface nighttime…a typical feature of enhanced vertical mixing" (lines 32-34). Is there another way leading to NOE in Guangzhou, for example, horizontal advection. A period of 3 years is not short.

Response [3-3]: In our study, measurements are available in 2017-2019 for January, April, and October, but are only available in 2019 for July due to instrument malfunction in other summers. We find 75 NOE events which account for 24% among the available measurements.

We follow previous studies to define an NOE event if surface ozone concentration increases by more than 5 ppbv ($\Delta O_3/\Delta t > 5$ ppbv h^{-1}) in one of any two adjacent hours during nighttime. Accordingly, we analyze the measurements collected from 4 air quality stations near the Canton Tower. The results reveal that NOE events occur simultaneously in the Canton Tower and in other air quality stations in Guangzhou for 67% of the NOE episodes.

The frequency of NOE event exhibits seasonal differences, we have added the following text in Section 3.3 as follows: <u>"The frequency of NOE events follow the seasonal pattern of Autumn (37%) > Winter (32%) > Spring (11%) > Summer (3%), which consistent with Wu et al. (2023) for the period 2006-2019 in the Pearl River Delta region, which also shows a higher frequency in Autumn and a lower frequency in Summer."</u>

We have followed your suggestion to conduct two cases study and examine the factors leading to NOE in Guangzhou. We find the vertical mixing is the major impact factor for surface ozone enhancement in case I, while vertical mixing and horizontal advection contribute equally in case II. Please kindly refer to Response [3-6].

Reference:

Wu, Y. K., Chen, W. H., You, Y. C., Xie, Q. Q., Jia, S. G., and Wang, X. M.: Quantitative impacts of vertical transport on the long-term trend of nocturnal ozone increase over the Pearl River Delta region during 2006-2019, Atmos. Chem. Phys., 23, 453-469, https://doi.org/10.5194/acp-23-453-2023, 2023.

Comment [3-4]: "oxidation capacity" is not clearly defined in the abstract. How to understand "This indicates a persistent high ozone level and oxidation capacity aloft the surface" (line 23)?

Response [3-4]: Thank you for pointing it out. To avoid confusion, we have removed the sentence "This indicates a persistent high ozone level and oxidation capacity aloft the surface" from both the Abstract and Conclusions sections.

Comment [3-5]: What is the weather condition favoring "significant influences of nocturnal RL ozone on both nighttime and the following day's daytime surface ozone air quality"?

Response [3-5]: We have introduced the weather condition favoring "significant influences of nocturnal RL ozone on both nighttime and the following day's daytime surface ozone air quality" in Introduction section and paragraph 2 of Section 3.3 (e.g. "In nighttime, the ozone-rich air in the RL may mix down to surface and trigger a nocturnal ozone enhancement (NOE) event in favorable weather conditions such as the nocturnal low-level jets (Sullivan et al., 2017; He et al., 2022a; Wu et al., 2023)". However, due to word limitation, we do not expand it in detail in the abstract.

Reference:

He, C., Lu, X., Wang, H. L., Wang, H. C., Li, Y., He, G. W., He, Y. P., Wang, Y. R., Zhang, Y. L., Liu, Y. M., Fan, Q., and Fan, S. J.: The unexpected high frequency of nocturnal surface ozone enhancement events over China: characteristics and mechanisms, Atmos. Chem. Phys., 22, 15243-15261, https://doi.org/10.5194/acp-22-15243-2022, 2022a.

Sullivan, J. T., Rabenhorst, S. D., Dreessen, J., McGee, T. J., Delgado, R., Twigg, L., and Sumnicht, G.: Lidar observations revealing transport of O_3 in the presence of a nocturnal low-level jet: Regional implications for "next-day" pollution, Atmos. Environ., 158, 160-171, https://doi.org/10.1016/j.atmosenv.2017.03.039, 2017.

Wu, Y. K., Chen, W. H., You, Y. C., Xie, Q. Q., Jia, S. G., and Wang, X.

M.: Quantitative impacts of vertical transport on the long-term trend of nocturnal ozone increase over the Pearl River Delta region during 2006-2019, Atmos. Chem. Phys., 23, 453-469, https://doi.org/10.5194/acp-23-453-2023, 2023.

Comment [3-6]: Model performances are evaluated only on monthly bases, while NOE does not happen every day. How does the model capture typical NOE? I suggest two or three typical cases are analyzed in order to see its major impact factors.

Response [3-6]: Thank you for the suggestion. We follow previous studies to define an NOE event if surface (10 m) ozone concentration increases by more than 5 ppbv ($\Delta O_3/\Delta t$ > 5 ppbv h^{-1}) in one of any two adjacent hours during nighttime. We identified a total of 10 NOE events based on tower-based measurements during the model simulation period. Out of these 10 events, the model successfully captures 5 cases that matched the defined criteria.

We have followed your suggestion to conduct two typical cases and analyze the major impact factors on NOE events. Figure S5 have been added to Supporting Information. The detail analyses in the following text have been added to paragraph 6 of Section 3.3 as follows: "We zoom in the processes leading to NOE events in two episodes, October 24 (case I) and October 28-29 (case II) in 2017, as depicted in Figure S5. We quantify the physical and chemical influences on ozone budget at 02:00 LT and 00:00 LT when observed ozone concentration at 10 m increases by 17 ppbv and 18 ppbv in case I and case II, respectively. CMAQ model successfully capture the ozone enhancement in both two episodes. At the surface level, the ΔCHEM contributes significantly to ozone destruction, while ΔVDIF and ΔHADV positively contribute to ozone enhancement in both cases. The ΔVDIF is the major impact factor for surface ozone enhancement in case I, while ΔVDIF and ΔHADV contribute equally in case II. We find that in case II, horizontal advection also contributes significantly in the boundary layer. This is associated with the occurrence of a low-level jet, as evident by the high horizontal wind speed exceeding 12 m/s recorded in 950 hPa (from the ERA5 dataset) in the midnight at the location to the Canton Tower (Figure S6). The low-level jet not only brings air with rich ozone concentration from the north, but also enhances vertical mixing by producing turbulent kinetic energy and weakening the decoupling of the RL and the stable boundary layer (He et al., 2022a). This suggests a combined contribution of horizontal transport and vertical diffusion to the NOE event."

Reference:

He, C., Lu, X., Wang, H. L., Wang, H. C., Li, Y., He, G. W., He, Y. P., Wang, Y. R., Zhang, Y. L., Liu, Y. M., Fan, Q., and Fan, S. J.: The unexpected high frequency of nocturnal surface ozone enhancement events over China: characteristics and mechanisms, Atmos. Chem. Phys., 22, 15243-15261, https://doi.org/10.5194/acp-22-15243-2022, 2022a.

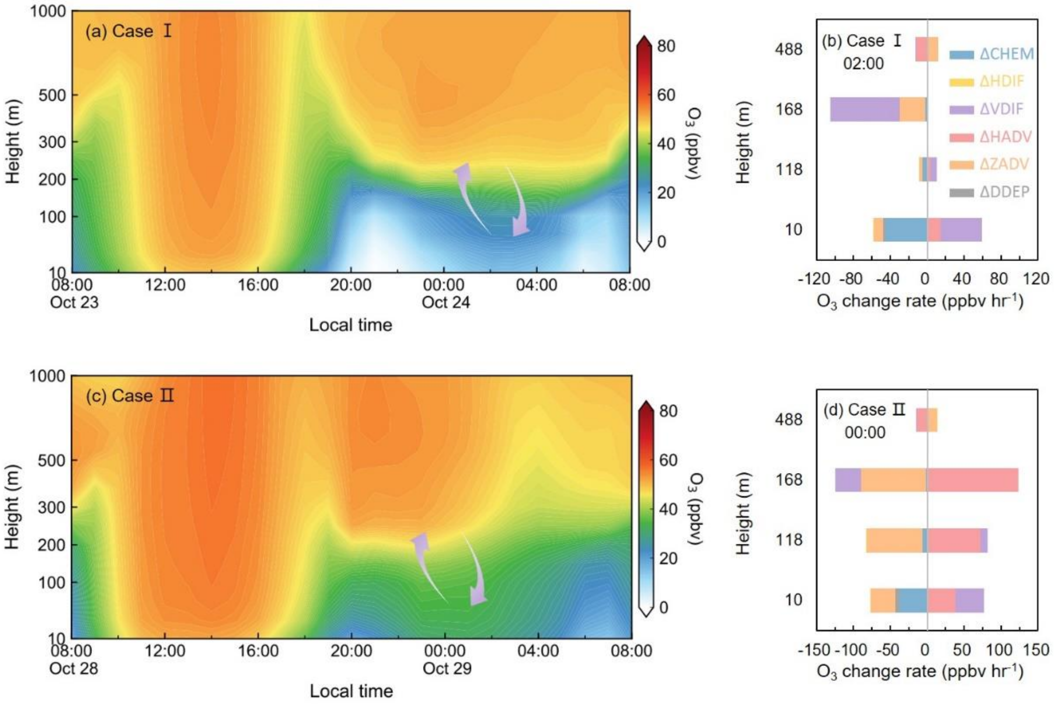

Figure S5. CMAQ model simulation of two NOE events. Panels (a) and (b) show the simulated ozone of case I from the surface to 1000 m at the Canton Tower and ozone budget terms diagnosed from the CMAQ IPR module at different measurement height. Panels (c) and (d) are the same as panels (a) and (b) but for case II. 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.

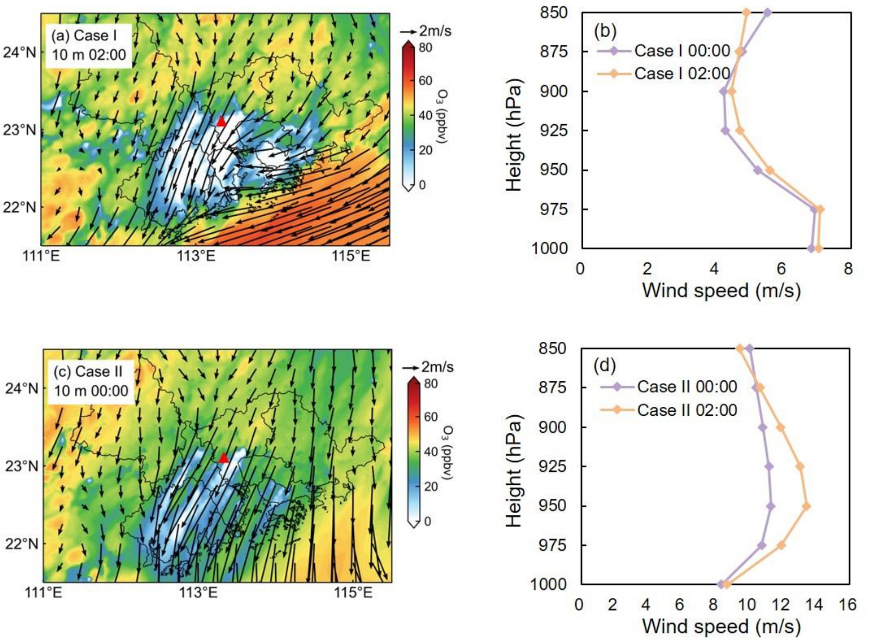

Figure S6. CMAQ model simulation of two NOE events. Panels (a) and (b) show

the simulated surface ozone and the horizontal and vertical wind from the ERA5 dataset of case I. Panels (c) and (d) are the same as panels (a) and (b) but for case II. The triangle marks the location of the Canton Tower.