Reviewer #1

Comment [1-1]: GENERAL: This paper focuses on the characteristics and mechanisms of nocturnal ozone enhancement (NOE) events. Cases with surface ozone enhancement of 5 ppbv/hour or greater in one of any two adjacent hours in 20:00-06:00 LT are defined as NOE events. Frequencies of NOE events are calculated for 814 sites in China, 762 sites in the US and 1880 sites in EU countries in 2014-2019. The annual frequency of NOE events over China is found unexpectedly high (41%+/-10%) and much higher than those over the US and EU. Higher afternoon ozone levels (as proxies of nocturnal ozone levels in the residual layer) are believed to be the precondition of NOE events. It is confirmed by cases studies that the NOE events in the surface layer is triggered by enhanced atmospheric mixing during processes like convective storms and low-level jets. More NOE events are found in warm season than in cold season. Distributions of NOE events of different magnitudes over China are presented and discussed as well as the timing of NOE events and nighttime variations of ozone, NO_2, CO, friction velocity and PBLH in NOE and non-NOE events in five Chinese cities.

NOE events have been found at some sites in different parts of the world and reported in the literature. Previous studies have already shown that the NOE events are caused mainly by convective storms, low-level jets, horizontal transport, etc. To the best of my knowledge, however, there has been no previous publication presenting nationwide statistics of NOE events over China or the comparison of NOE events over China with those over EU and the US. In this sense, this paper is original and within the scope of ACP. The methods applied in this paper are mostly valid. The results presented are interesting and generally sound. The paper is well structured and written. It can be improved by appropriately addressing the following issues. I recommend publication of this paper in ACP after revisions.
Response [1-1]: 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 [1-2]: MAJOR COMMENTS: In this study, a NOE event is defined as ozone increase by at least 5 ppbv/hour in one of any two adjacent hours in 20:00-06:00 LT. The selection of the threshold (5 ppbv/hour) for NOE seems to be arbitrary. As the threshold value substantially impacts not only the statistics of NOE events but also the results like the contrasts between regions and between warm and cold seasons, it should be determined based on scientific analysis and consideration. The observations of ozone and also other species are always fluctuating in a certain degree due to factors like turbulences, source/sink disturbances, transport, etc. The intensities of fluctuations related to different factors should vary in a large range and may be dependent of season and location. I think you may obtain a kind of fluctuation intensity spectrum for each site by plotting the frequencies against the delta[O_3]/delta(t) values. I do not know how the spectrum may look like but guess it might not be monotonic. If the spectrum is really not a monotonic curve, you may relatively easily determine your threshold based on your scientific considerations. Otherwise it might be difficult for you to determine the threshold and convince the readers of your threshold. I think the focus of this paper is the NOE event that is really caused by any particular atmospheric condition or process. The nocturnal ozone fluctuations occur daily under normal atmospheric conditions should not be included in the NOE statistics. In particular, when you are using "unexpected high frequency of" NOE in your title, the threshold definition must be supported by scientific analysis.

Response [1-2]: Thank you for pointing it out. We were hoping to be consistent with previous studies (Eliasson et al., 2003; Zhu et al., 2020) by defining the NOE event as ozone increase by >5 ppb hour^{-1} in one of any two adjacent hours in 20:00-06:00 local time. We agree that this threshold should be carefully examined.

We have followed your suggestion to derive the fluctuation intensity spectrum for each site by plotting the frequencies of the $\Delta O_3/\Delta t$ values. Results are shown in Figure R1. We find that the nocturnal ozone $\Delta O_3/\Delta t$ values generally follow the Gaussian distribution, based on observations at all Chinese sites in 2014-2019. About 70% of the $\Delta O_3/\Delta t$ values are negative, reflecting the expected dominant ozone decrease at nighttime. We find a possibility with $\Delta O_3/\Delta t$ >5 ppb hour^{-1} of 7.7%, which is mostly outside the two-sigma standard deviation at Gaussian distribution, suggesting that $\Delta O_3/\Delta t$ >5 ppb hour^{-1} cases are not likely "normal fluctuation" under normal atmospheric conditions. Using the threshold of $\Delta O_3/\Delta t$ greater than 4 or 6 ppb hour^{-1} does not change the spatial pattern of NOE frequency. We have also tried to define a NOE by considering the relative fluctuation of nocturnal ozone (i.e., nighttime ozone enhancement normalized by the corresponding afternoon ozone level), but we find that it much complicates the analyses by introducing low $\Delta O_3/\Delta t$ values when afternoon ozone level is low, which has weak implication. We thus prefer to stick to this threshold so that our results are comparable to existing studies.

We have added the following text in Section 2.3 for justification: "Following previous studies of Eliasson et al. (2003) and Zhu et al. (2020), we define a nocturnal ozone enhancement (NOE) event if ozone concentration at a site increases by more than 5 ppbv ($\Delta O_3/\Delta t$ > 5 ppb hour^{-1}) in one of any two adjacent hours in the nighttime period. We find that nocturnal $\Delta O_3/\Delta t$ values at Chinese sites generally follow the Gaussian distribution, and $\Delta O_3/\Delta t$ > 5 ppb hour^{-1} cases only account for 7.7% of the $\Delta O_3/\Delta t$ dataset, indicating that this definition should have effectively ruled out nocturnal ozone fluctuations occur under normal atmospheric conditions (Figure S2). We only define one NOE event if there are more than one hour with $\Delta O_3/\Delta t > 5\, ppb\, hour^{-1}$ at a specific night, and observations with maximum $\Delta O_3/\Delta t$ are used for statistical analyses."

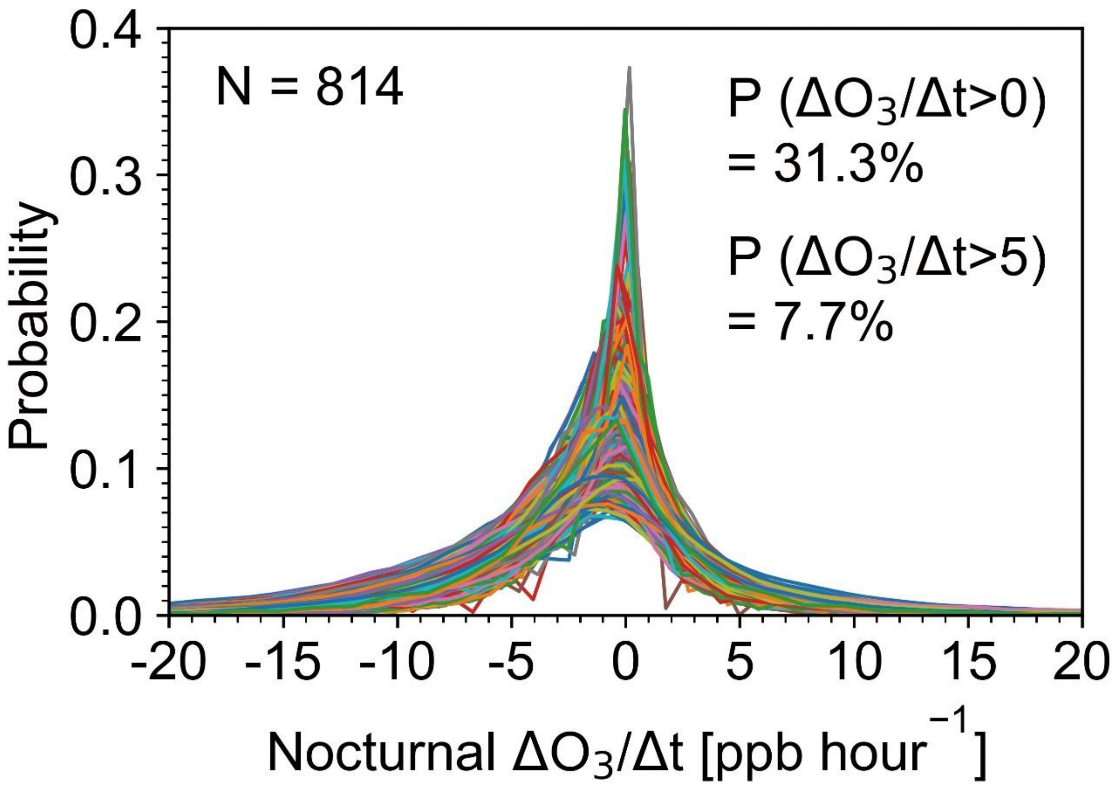

Figure R1 Probability density distribution of hourly nocturnal ozone fluctuation ($\Delta O_3/\Delta t$) at all Chinese sites (represented by each curve) in 2014-2019.

Reference:

Eliasson, I., Thorsson, S., and Andersson-Sköld, Y.: Summer nocturnal ozone maxima in Göteborg, Sweden, Atmospheric Environment, 37, 2615-2627, https://doi.org/10.1016/S1352-2310(03)00205-X, 2003.

Zhu, X., Ma, Z., Li, Z., Wu, J., Guo, H., Yin, X., Ma, X., and Qiao, L.: Impacts of meteorological conditions on nocturnal surface ozone enhancement during the summertime in Beijing, Atmospheric Environment, 225, 117368, https://doi.org/10.1016/j.atmosenv.2020.117368, 2020.

Comment [1-3]: The regional and seasonal differences in the NOE frequencies are all impressive. Data show that regions with higher frequencies of NOE events are associated with higher levels of afternoon ozone. However, the real cause of the regional and seasonal differences in the NOE frequencies is not clear. Are the NOE differences caused by the differences in atmospheric processes (convective storm, low-level-jet, etc.) or purely the ozone level differences or both? To answer this question, it is suggested to consider the relative fluctuation of nocturnal ozone (i.e., nighttime ozone enhancement normalized by the corresponding afternoon ozone level) as the metric of a NOE event (again, the threshold should be carefully determined).

Response [1-3]: Thank you for pointing it out. We have compared in Figure R2 the spatial and seasonal pattern of the NOE frequencies, afternoon ozone level, and the frequency of $\Delta U^*/\Delta t$ ($\Delta PBLH/\Delta t$) enhances by 30% in one of any two

adjacent hours in the nighttime period, as an indicator of enhanced nighttime atmospheric mixing. We can see that regions with relatively higher frequency of enhanced nighttime U* or PBLH are located in the Sichuan Basin, the Fenwei Plain (Shanxi Province), and Pearl River Delta. Coastal regions typically show lower frequency. This spatial pattern is clearly not consistent with the hotspots of NOE frequency as shown in Figure R2a and 2e, suggesting that the overall regional differences in the NOE frequencies are more likely to be driven by afternoon ozone than enhanced atmospheric mixing. However, for some regions such as the Sichuan Basin, atmospheric processes may be more important as indicated by the high frequency of enhanced ΔU*/Δt (ΔPBLH/Δt). We also find that the frequency of enhanced nighttime atmospheric mixing in warm season is indeed much higher than that in the cold season, indicating that atmospheric processes may also contribute to the seasonal difference of NOE patterns. We now state in the text <u>"We also find higher frequency of nighttime U* and PBLH enhancement in the warm season than that in the cold season, suggesting that seasonal difference in nighttime atmospheric mixing activity also contributes to that in NOE frequency as shown in Figure 2."</u> Here we do not use relative fluctuation of nocturnal ozone as a metric to define NOE. Please kindly find our response in [Response 1-2].

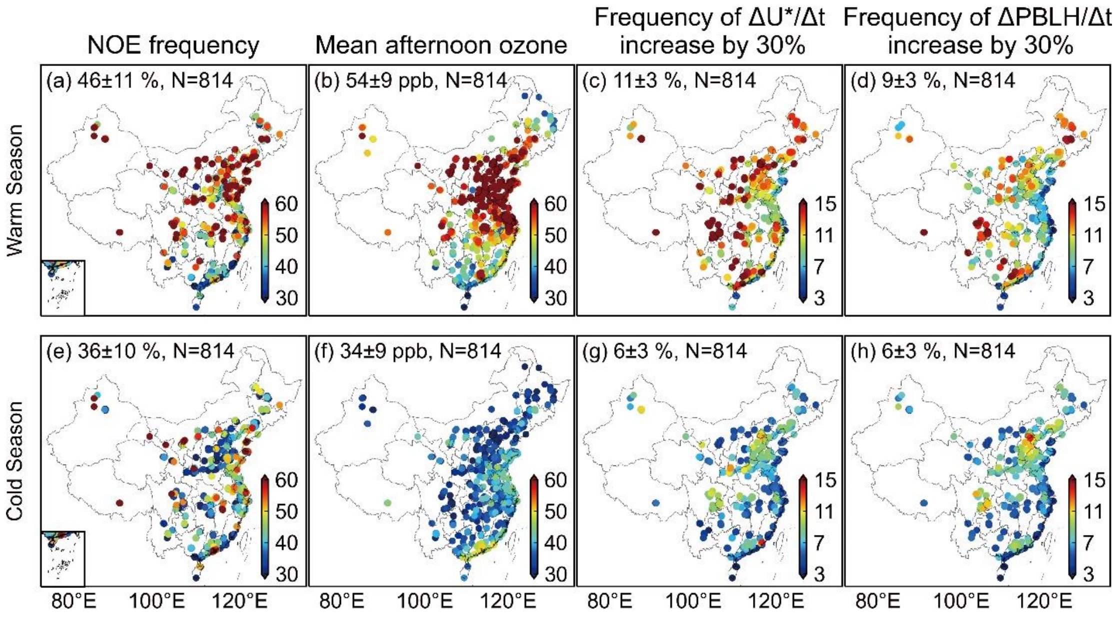

Figure R2. Comparison of the pattern of the NOE frequencies, afternoon ozone level, and the frequency of ΔU*/Δt (ΔPBLH/Δt) increase by 30% at nighttime period. The values of regional mean and standard deviations among the N sites are shown inset at the top of each figure (mean ± standard deviation).

Comment [1-4]: MINOR CONCERN/EDIT: L110: In the abstract section the NOE event is defined as ozone increase by at least 5 ppbv/hour, meaning equal to or greater than 5 ppbv/hour. This is not consistent with >5 ppbv/hour stated here. In addition, it is not clear which number is counted if two or more cases occur with enhancement

over the threshold during one night. In other word, can the NOE event in a day be more than one?
Response [1-4]: Sorry for the confusion. We have now clarified in the abstract "(NOE, defined as ozone increase by more than 5 ppbv hour^{-1} in one of any two adjacent hours in 20:00-06:00 local time)" This is now consistent with the statement in Section 2.3. We also state in Section 2.3 "We only define one NOE event if there are more than one hour with $\Delta O_3/\Delta t$ > 5 ppb hour^{-1} at a specific night, and the observations with maximum $\Delta O_3/\Delta t$ are used for statistical analyses"

Comment [1-5]: L176: what do you mean by "evenly distributed"? The statistics (Figure 4a) for this time period are 18%, 29%, and 19%.
Response [1-5]: We have revised the statement in the text to "In Beijing, the timing of NOE events is diversely distributed across 0:00-6:00 LT with a frequency ranging from 18 to 29%, resulting in a flat ozone change when averaging the ozone time series in all NOE events (Figure 4a)"

Comment [1-6]: L274: I think substantial differences in the absolute values of U* and PBLH between the NOE and NNOE events are required if the NOE is really caused by enhanced vertical mixing. The differences may have been masked by averaging effect, average over six years and different sites. Case studies using data from individual sites may make it clear.
Response [1-6]: We have plotted the absolute values of U* and PBLH between the NOE and NNOE events in Figure S4, and indeed find that the values are significantly higher in NOE than NNOE events for all the selected cities except for Beijing, but the plot is somewhat scattered because the values for each city differ a lot. As we focus more on the relative enhancement of U* and PBLH than mean values, we prefer to present the relative ratio to the 8 p.m. (LT) value in the main text and place the absolute value plot in the supplement. Case studies indeed support the large value and the enhancement of U* and PBLH with NOE event. We have revised the text to "We find that the absolute values of nighttime U* and PBLH are generally larger in NOE than NNOE events (Figure S4). More importantly, we see distinct differences in their temporal evolution. U* and PBLH typically show a steady decreasing trend throughout the nighttime during NNOE events, while the U* and PBLH show increase in at least a certain part of the nighttime period in NOE events, suggesting that atmospheric mixing is becoming more active (Figures 6a and 6c)."

Comment [1-7]: L280: FV or U*? Be consistent.
Response [1-7]: We have revised FV to U* in the text.

Comment [1-8]: L283: it is worth knowing which process is the most important one that causes the increasing atmospheric instability.
Response [1-8]: We agree. We attempt to shed some lights on specific processes

contributing to increasing atmospheric instability in the case studies, but much more work is required to quantify the relative contribution from each process (e.g. LLJs, convections) to the NOE events at different region. We have added the discussion in the Conclusion remark "We call for more direct observations of vertical structure of ozone and its evolution from daytime to nighttime (Kuang et al., 2011; Jia et al., 2015; Caputi et al., 2019; He et al., 2021), and more 3-D chemical modelling studies (Hu et al., 2013; Klein et al., 2014) to quantitatively explore the contribution of mixing and regional transport to NOE events (including the underlying synoptic processes such as low-level jets and convective storms), and to further analyze the impacts of NOE events on atmospheric chemistry, human health, and vegetation productivity. "

Reference

Caputi, D. J., Faloona, I., Trousdell, J., Smoot, J., Falk, N., and Conley, S.: Residual layer oz one, mixing, and the nocturnal jet in California's San Joaquin Valley, Atmos. Chem. P hys., 19, 4721-4740, 10.5194/acp-19-4721-2019, 2019.

He, Y., Wang, H., Wang, H., Xu, X., Li, Y., and Fan, S.: Meteorology and topographic influen ces on nocturnal ozone increase during the summertime over Shaoguan, China, Atmosp heric Environment, 256, 118459, https://doi.org/10.1016/j.atmosenv.2021.118459, 2021.

Hu, X.-M., Klein, P. M., Xue, M., Zhang, F., Doughty, D. C., Forkel, R., Joseph, E., and Fue ntes, J. D.: Impact of the vertical mixing induced by low-level jets on boundary layer ozone concentration, Atmospheric Environment, 70, 123-130, https://doi.org/10.1016/j.at mosenv.2012.12.046, 2013.

Jia, S., Xu, X., Lin, W., Wang, Y., He, X., and Hualong, Z.: Increased Mixing Ratio of Surfac e Ozone by Nighttime Convection Process over the North China Plain, J Appl Meteor Sci, - 26, - 280, - 10.11898/1001-7313.20150303, 2015.

Klein, P. M., Hu, X.-M., and Xue, M.: Impacts of Mixing Processes in Nocturnal Atmospheric Boundary Layer on Urban Ozone Concentrations, Boundary-Layer Meteorology, 150, 1 07-130, 10.1007/s10546-013-9864-4, 2014.

Kuang, S., Newchurch, M. J., Burris, J., Wang, L., Buckley, P. I., Johnson, S., Knupp, K., Hu ang, G., Phillips, D., and Cantrell, W.: Nocturnal ozone enhancement in the lower trop osphere observed by lidar, Atmospheric Environment, 45, 6078-6084, https://doi.org/10.1 016/j.atmosenv.2011.07.038, 2011.

Comment [1-9]: L359-370: the case with typhoon "Fung-wong" may be more complicated than just transport of ozone-rich air in the north to the PRD region". It is known that typhoon processes may strongly impact the surface ozone level in the periphery of typhoons. Descending air usually play a key role in these processes. Even ozone in the upper troposphere and lower stratosphere can be transported down to the surface (e.g., Jiang et al., Why does surface ozone peak before a typhoon landing in southeast China?, Atmos. Chem. Phys., 15, 13331–13338, https://doi.org/10.5194/acp 15-13331-2015,2015).

Response [1-9]: Thank you for pointing it out. We have added the following text in Line 394 "Descending air in the periphery of the typhoon can trigger vertical

transport of O_3-rich air from upper troposphere or even lower stratosphere to the surface, contributing to ozone enhancement (Jiang et al., 2015).”

Reference

Jiang, Y. C., Zhao, T. L., Liu, J., Xu, X. D., Tan, C. H., Cheng, X. H., Bi, X. Y., Gan, J. B., You, J. F., and Zhao, S. Z.: Why does surface ozone peak before a typhoon landing in southeast China?, Atmos. Chem. Phys., 15, 13331-13338, 10.5194/acp-15-13331-2015, 2015.

Comment [1-10]: L374-375: I think it depends highly on the timing and strength of the NOE event. Of course, it is not so simple considering the variations of ozone precursors and redistribution in the vertical direction.
Response [1-10]: We agree. We have revised the text: “However, it does not necessarily result in higher daytime ozone compared to the precedent day, which highly depends on the timing and strength of the NOE event and the variations of ozone precursors and redistribution in the vertical direction.”

Comment [1-11]: L390: the seasonal variation of surface ozone in the PRD region is much different from those in other Chinese regions. More of the NOE events in the PRD occur in cold season than in warm season. Perhaps it is better to point out this particularity.
Response [1-11]: Thank you for pointing it out. We have added the point in text: “The NOE frequency is higher in the warm (46% averaged for all sites) than the cold season (36%) in most regions, except for the PRD region where NOE events occur at higher frequency in the cold season than in the warm season, consistent with the seasonal evolution of ozone levels.”

Comment [1-12]: Figure 6: the temperature differences between NOE and NNOE events are very large. Why?
Response [1-12]: The differences between NOE and NNOE events in terms of the absolute values are small in all selected cities except for Urumqi. We find that this is because the NOE events in Urumqi are concentrated on May-August when temperature is significantly higher than April and September. In terms of the vertical profiles, the differences between the NOE and NNOE events reflect the more effective heat exchange between the land and near-surface atmosphere with active mixing in the NOE events, as stated in the text. We have now replaced this plot with the potential temperature following the other referee’s comment [Response 2-7]. The results are consistent. We have added the following text “The higher potential temperature in Urumqi in the NOE than NNOE events is due to the higher NOE frequency in May-August when temperature is significantly higher than April and September.”