

Review for: Measurement report: Vertical and temporal variability of near-surface ozone production rate and sensitivity in an urban area in Pearl River Delta (PRD) region, China.

We are grateful for the reviewer's comments and suggestions, which will help us to provide a more accurate description of our work. Our responses are given below in red, after the reviewer's comments, which are in black. The changes in the text are marked in yellow.

Summary:

This manuscript presents a detailed study of the vertical and temporal profile of ozone production, using both measurement data and chemical box modelling. Overall, the manuscript is well written with a good flow. However, there are some grammatical issues that should be addressed before publication. I really enjoyed reading this manuscript, and feel that it would be of great interest to the urban ozone community, therefore I recommend it for publication to ACP provided some important changes to the text have been made.

Of particular concern is the use of the phrase “statistically different/difference” throughout the text. When this phrase is used, I would expect it to be backed up by a statistical test(s). I don't think any further analysis is required, but the authors should re-think how they describe their findings and avoid this phrase when there is no statistical evidence to back up their claims. I would also recommend another detailed read-through of the document to check for grammatical errors that occur periodically. Please see below for more detailed comments.

Thank you for your careful review and useful suggestions. We have checked the grammar throughout the manuscript and addressed the grammatical issues. We have also improved the presentation of the results of the statistical analyses, avoiding the overuse of the phrase “statistically different/difference” throughout the text.

Detailed comments:

56 Replace “have” with “has”.

We have replaced “have” with “has” on page 2, line 56.

65 Check grammar.

We have checked the grammar and modified the sentence on page 3, lines 67-72 in the modified manuscript:

“Local O₃ concentrations can be further influenced by meteorological conditions and the regional transport of O₃ and its precursors (Gong and Liao, 2019; Chang et al., 2019). The Pearl River Delta (PRD) stands out as one of the most rapidly developing economic and urbanized regions in China, which currently is suffering from severe ground-level O₃ pollution (Lu et al., 2018; Yang et al., 2019).”

71 Check grammar.

We have checked the grammar and changed the sentence on page 3, lines 72-80 in the revised manuscript:

“Currently, many scholars have analyzed the relationship between tropospheric ozone pollution and its precursors and meteorological elements in the PRD region (Mao et al., 2022; Li et al., 2022a), which has greatly improved our understanding of the sources and formation processes of O₃ in the PRD region. However, the distribution of O₃ is highly variable at different altitudes (Wang et al., 2021), due to vertical differences in VOCs concentrations and sources, as well as the sensitivity of O₃ formation (Liu et al., 2023; Tang et al., 2017).”

75 Please explain why using only one height of measurements is of great limitation. Why is it important that this is done at multiple altitudes, when O₃ exposure occurs at ground level?

In the boundary layer, the surface heating leads to strong vertical mixing during daytime, so ozone formation at higher altitudes may also influence the O₃ budgets and its exposure at ground level. Additionally, the vertical gradients of O₃ precursors may drive the change in the photochemical formation regimes of ozone in vertical directions (Zhao et al., 2019). We have added the corresponding description on page 3, lines 80-85 in the revised manuscript:

“Due to the presence of strong vertical mixing driven by the surface heating effect in the daytime boundary layer, the budget of the ozone at the ground level and also at an arbitrary height in the daytime boundary layer is closely related to the formation and removal of ozone at other heights (Tang et al., 2017). In addition, the difference in vertical gradients of precursors may drive the vertical change in the photochemical formation regimes of ozone (Zhao et al., 2019).”

81 Check grammar.

We have checked the grammar and changed the sentences on pages 3, lines 89-94 in the revised manuscript:

“Currently, remote sensing techniques with high time resolution and real-time response, such as lidar and optical absorption spectroscopy, have been utilized to measure the vertical distribution of O₃ (Luo et al., 2020a; Wang et al., 2021). However, in situ measurements of VOCs at various heights primarily rely on offline methods combined with diverse techniques, including aircraft, tethered balloons, tall buildings and towers, unmanned aerial vehicles (UAVs or drones), and satellite observations”

85 This sentence is very long – check grammar and split into two after “VOC and NO_x measurements”.

We have checked the grammar and changed the sentence on page 3-4, lines 96-100 in the modified manuscript:

“Owing to the low time resolution of these monitoring techniques, achieving continuous vertical coverage of VOCs and NO_x measurements is challenging. Consequently, the vertical distribution structure of VOCs remains unclear, thus largely hindering our understanding of the vertical and temporal regional ozone formation mechanism.”

113 Misspelled “Asia”.

We modified the word of “Asia” on page 5, lines 123.

116 Check grammar.

We have checked the grammar and changed the sentence on page 4, lines 127-128 in the revised manuscript:

“The area is surrounded by a high density of vegetation, reservoir features, low-

rise buildings, and hills/mountains (Luo et al., 2020b).”

224 Please state in the text that a full list all 47 NMHCs s available in the supplementary (Table S2).

Thank you for the careful checking. We have found an error in this description, we actually measured 56 non-methane hydrocarbons (NMHCs), instead of 47 NMHCs. We have added this statement on page 8, lines 254-256 in the modified manuscript:

“A full list of all 56 non-methane hydrocarbons (NMHCs) can be found in the supplementary materials (Table S2).”

As well as page 9, lines 287-288:

“56 NMHCs (toluene, benzene, isoprene, styrene, etc., as listed in Table S2),...”

230 Please include in this section the dilution / ventilation approach you have included in the model.

Ok. We have added the description of the dilution factor throughout the modelling period on page 10, lines 292-296 in the revised manuscript:

“The effect of physical processes (such as vertical and horizontal transport) was considered by setting a constant dilution factor of $1/43200 \text{ s}^{-1}$ throughout the modelling period. Additionally, the dry deposition rate of O_3 was set to 0.42 cm s^{-1} and the background concentrations of O_3 , CO , and CH_4 were set to 30, 70, and 1800 ppbv, respectively.”

333 I advise that you should avoid using the word “statistically”, unless you have performed a statistical test. Please rephrase.

Thank you for your advice. We have changed “statistically” to “significantly” on page 13, line 393 in the revised manuscript.

346 Again, if you use the phrase “statistically different”, I would expect to see evidence of a statistical test showing this.

Ok, we changed the description on page 14-15, lines 404-406:

“The mean concentrations of O_3 precursors, including CO , NO , NO_2 , and the total VOCs measured by PTR-TOF-MS (shown as TVOC in Fig. 1 and Table 1), did not exhibit notable discrepancies between episodes and non-episodes.”

351 I would rephrase this. Are you saying that event and non-event OFP and $P(O_3)_{net}$ are not statistically different because they are within one standard deviation?

We apologize for the confusing description. We meant that the averaged OFP and $P(O_3)_{net}$ during O_3 pollution events and non-events showed no difference when considering $\pm 1\sigma$ obtained from their average calculation. In other words, the averaged $OFP \pm 1\sigma$ (or averaged $P(O_3)_{net} \pm 1\sigma$) obtained during episodes are not significantly different from those obtained during non-episodes, they fall in the same range within 1σ . We have changed this statement on page 15, lines 408-413, in the revised manuscript:

“Further comparison of the daytime mean O_3 formation potential (OFP) and the measured $P(O_3)_{net}$ during episodes and non-episodes showed no significant differences, ranging from $5.1E-4$ to $1.0E-3$ $g\ m^{-3}$ and 14.3 to 21.5 $ppb\ h^{-1}$, respectively, during non-episodes, whereas they are ranged from $4.1E-4$ to $4.7E-4$ $g\ m^{-3}$ and 5.6 to 18.9 $ppb\ h^{-1}$ respectively, during episodes.”

Further explanations are provided in the response to comments 352 and 644 below.

352 It is not clear to me how you have come to this conclusion (These findings indicate that...). Please clarify in the text.

We apologize for the confusing description. As shown in the response to comments 351 and 644, we meant to say that the daytime averaged O_3 formation potential (OFP) and the measured $P(O_3)_{net}$ ranged from $5.1E-4$ to $1.0E-3$ $g\ m^{-3}$ and 14.3 to 21.5 $ppb\ h^{-1}$, respectively, during non-episodes, whereas they are ranged from $4.1E-4$ to $4.7E-4$ $g\ m^{-3}$ and 5.6 to 18.9 $ppb\ h^{-1}$, respectively, during episodes. Although OFP during episodes was always higher during episodes than that during non-episodes, $P(O_3)_{net}$ during episodes can be higher or lower than that during non-episodes, as shown in Table 1. This demonstrates that the O_3 pollution episodes are not always due to local photochemical O_3 formation (represented as $P(O_3)_{net}$). For example, $P(O_3)_{net}$ is lower during episodes I and III than during non-episode II, which may be due to the much less stable weather conditions during episodes III (with lower wind

speed), favoring the accumulation of O₃ formed by local photochemical O₃ formation. While for non-episode II even higher $P(O_3)_{net}$ is processed, the average O₃ concentration is still lower than that during episodes I and III, which may be due to the outflow of O₃ from the observation site by physical processes. Therefore, we conclude that the O₃ pollution episodes are either due to significantly increased local photochemical O₃ formation (i.e., episode II), or to the accumulation of O₃ formed by moderate local photochemical O₃ formation under stable weather conditions (i.e., episodes I and II). To make the sentences clearer, we have added the following explanations on pages 15, lines 414-419 in the revised manuscript:

“Although OFP was always higher during episodes than during non-episodes, the mean $P(O_3)_{net}$ values during episodes I and III were even lower than during non-episodes II. The higher O₃ concentrations may be due to the more stable weather conditions during episodes I and III (with lower wind speed), which benefits the accumulation of O₃ formed by local photochemical O₃ formation. While for non-episode II, even it processes higher $P(O_3)_{net}$, the outflow of O₃ from the observation site by physical processes may be higher due to the higher wind speed. These findings indicate that the O₃ pollution episodes stem from either substantially elevated local photochemical O₃ formation (i.e., episode II), or the accumulation of O₃ formed by moderate local photochemical O₃ formation under stable weather conditions (i.e., episodes I and II).”

358 It is well known that O₃ pollution episodes are jointly affected by photochemical reactions and physical transport processes. It's unclear to be how what you have said previously has led you to this statement.

According to the similar $P(O_3)_{net}$ average values obtained on episode and non-episode days (as described above, they were not statistically different within one standard deviation), we concluded that the O₃ pollution episodes stem from either substantially elevated local photochemical O₃ formation (i.e., episode II), or the accumulation of O₃ formed by moderate local photochemical O₃

formation under stable weather conditions (i.e., episodes I and II). On the other hand, if there is an outflow of O₃ from the observation site (which can be considered as physical transport) due to favorable weather conditions, the intense local photochemical reactions may not lead to the O₃ pollution (i.e., non-episode II). Therefore, we have left to the statement that the O₃ pollution episodes in this study are jointly affected by the photochemical reactions and physical transport processes. We have changed this statement on page 15, lines 425-427 in the revised manuscript:

“These results indicate that O₃ pollution episodes are jointly affected by the photochemical reactions and physical transport processes, which we will discuss in more detail in Sect. 3.2.1.”

438 Remove word “besides” – not needed.

Ok, we removed the word “besides” accordingly.

476 Instead of saying “the results show”, be specific about which part of the figure you are referring to in the text. What is it in the figure that has led you to this conclusion?

Ok, thank you for your suggestion. We have changed this sentence on page 19-20, lines 531-535:

“ $R(\text{O}_x)_{\text{trans}}$ at 5 m ground level was derived from $\frac{d\text{O}_x}{dt}$ minus $P(\text{O}_x)_{\text{net}}$, according to Eq. (5) shown Sect. 2.3.2, their hourly averages and diurnal variations are shown in Figs. 4 and 5, respectively. From these figures, it is evident that the fluctuation of the O₃ concentration change rate ($d(\text{O}_3)/dt$) at ground level is typically small and primarily dominated by the physical processes during nighttime.”

478 How do you know this is attributed to physical transport? Is this just a suggestion based on knowledge of the atmosphere (please supply a reference), or is there something in the figure that provides evidence that increasing O₃ is due to vertical transport, and not early morning photochemistry? If it’s because you have not measured any $P(\text{O}_3)_{\text{net}}$ at this time, please state this in the text.

Sorry for the confusing description. We reached this conclusion because of the

diurnal variation of the contribution of chemical and physical transport to the O_3 changes at the ground level, as shown in Fig. 5. After a careful check, we realize that around 6:00-7:00 LT, O_3 concentrations increase for all episodes and non-episodes, mainly due to physical transport during episodes I and II and non-episodes I, while photochemical reactions and physical processes are equally important for episodes III and non-episode II. We have changed the description on page 20, lines 543-553 to make the description more accurate:

“Around 6:00-7:00 LT, O_3 concentrations increase for all episodes and non-episodes, mainly due to physical transport during episodes I and II and non-episodes I, while photochemical reactions and physical processes are equally important for episodes III and non-episode II. This could be due to short-term strong vertical turbulence in the early morning, which leads to an expansion of the boundary layer height and makes the residual layer “leaky”, allowing vertical transport. At the same time, O_3 precursors were also transported down from the residual layer, and with increasing sunlight, these O_3 precursors underwent rapid photochemical reactions that competed with the physical processes between 6:00-7:00 LT, leading to a sharp increase in $P(O_3)_{net}$ between 8:00 to 12:00 LT.”

483 Change “residue” to “residual”.

We have changed “residue” to “residual” on page 20, line 548.

644 “statistically difference” – see comments for lines 333 and 346

Thank you for the suggestions. We have added the Mann-Whitney tests, and found that the differences in the measured/modelled $P(O_3)_{net}$ during episodes and non-episodes are not statistically different, with the Mann-Whitney p -value=0.12 and 0.28 for measured and modelled $P(O_3)_{net}$, respectively. We have added such explanations on page 24-25, lines 692-695 in the modified manuscript:

“Consequently, the modelled $P(O_3)_{net}$ during episodes does not exhibiting a statistically significant difference from that during non-episodes (Mann-Whitney p -value=0.12), as shown in Fig. S5, which is in agreement with the measured $P(O_3)_{net}$ (Mann-Whitney p -value=0.28), as depicted in Sect. 3.1.1.”

659 In the text, please direct the reader to Table S2 which defines which VOCs are in each category (NMHC, AVOC, BVOC and OVOC).

Thank you for the suggestion. We have added a sentence on page 26, lines 734-737 to refer the reader to Table S2:

“including nonmethane hydrocarbons (NMHC), anthropogenic volatile organic compounds (AVOC), biogenic volatile organic compounds (BVOC), and oxygenated volatile organic compounds (OVOC) (as shown in Fig.8f). The VOCs species included in each category are listed in Table S2.”

698 Check grammar in this section.

We have checked the grammar in this section accordingly and corrected any errors.

816 Remove “proper” – not needed.

Ok, we have removed “proper” accordingly.

References:

Zhao, W., Tang, G., Yu, H., Yang, Y., Wang, Y., Wang, L., An, J., Gao, W., Hu, B., Cheng, M., An, X., Li, X., and Wang, Y.: Evolution of boundary layer ozone in Shijiazhuang, a suburban site on the North China Plain, J. Environ. Sci., 83, 152-160, 10.1016/j.jes.2019.02.016, 2019.