Response to reviewer #1's comments

Journal: Atmos. Chem. Phys

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Title: " O3-precursor relationship over multiple patterns of time scale: A case study in Zibo, Shandong Province, China"

Author(s): Zheng et al.

General comments:

Based on 5-month observation data of VOCs, CO, NO_x and meteorological factors at three sites in a major prefecture-level city of Zibo, Shandong province of China, this manuscript explored the relationship between O_3 and its two precursors (VOCs and NO_x) by using a 0-D box model. The results implied that diagnosis of photochemical O_3 formation regimes was better based on model simulations with constrain of the observation data on shorter time scales (e.g., daily or weekly scales), which would have a certain significance for developing O_3 control strategies in different pollution areas. To my knowledge, there are few studies to comparably investigate the difference of photochemical O_3 formation regimes diagnosed by model simulations with input of observation data treated on different time scales. Therefore, this reviewer recommends the manuscript to be published in the journal after considering the following specifics.

Reply: We appreciate the professional and positive comments by the reviewer, and we have addressed the proposed concerns in below point-by-point, with revised text in red.

Specifics:

There are many grammar mistakes, repetitive specifications and unclear descriptions thorough the whole manuscript, and thus an English native speaker is suggested to polish the manuscript.

The results and discussion seemed to be very confused for discussing the results at the three sites on the four-time scales. As the topic of this manuscript is "O_3-precursor relationship over multiple patterns of time scale", the investigation is better focused on the observation data at one sampling site, rather than at the three sampling sites.

Reply: Thanks for the careful review of our manuscript. We have carefully checked and revised to improve our manuscript, and this manuscript has been polished by an English native speaker during the revision.

Moreover, we agree with the reviewer that the investigation may be better focused on the observation data at one sampling site to illustrate this topic of timescale issue. In this study, the three observation sites are co-located within Zibo city of Shandong province, and the distances among them are around 50 km. The field measurement was simultaneously carried out at the three sites in Zibo City during the whole campaign, and the analysis together with the three sites can provide more comprehensive results with synchronous and informative O3-NOx-VOC sensitivity. For example, the results from the three sites jointly showed that the discrepancy of O3-precursor relationship would become larger along with the time scale changed from narrower (i.e., daily scale) to wider (i.e., five-month scale) pattern, which reinforces the fact that using narrower time scale to derive the O3-precursor relationship would be more reliable and robust.

Abstract:

Comment 1: Line 24-27, the subject of "reactivity" doesn't match the predicate of "were" in this sentence; "time scale" is better replaced by "time scales"; "varied from wider and narrower" is better moved before the parentheses. This sentence seemed to be vague, and thus is better to be rephrased.

Reply: This sentence has been rephrased in our manuscript as below.

Line 27-31: "It was found that the relative incremental reactivity (RIR) of major precursor groups (e.g., anthropogenic volatile organic compound (AVOC), NO_x) was overall consistent in the sign along with time scales changed from wider to narrower (four patterns: five-month, monthly, weekly, and daily) at each site, though the magnitudes of RIR varied at different sites."

Comment 2: Lines 28-30, "The time series of the photochemical regime" seemed not match "magnitude".

Reply: We have corrected the sentence as below.

Line 31-34: "The time series of the photochemical regime (using RIR_{NOx}/RIR_{AVOC} as indicator) in weekly or daily patterns further showed a synchronous temporal trend

among the three sites, while the magnitude of RIR_{NOx}/RIR_{AVOC} was site-to-site dependent."

Introduction:

Comment 1: Lines 52-54, "the non-linearity of ozone pollution and complex process involved in it" should be "the complex non-linear relationship between O_3 formation and its precursors (VOCs and NO_x)"; "challenges" doesn't match "lies".

Reply: Corrected as below.

Line 56-59: "Given the complex non-linear relationship between O_3 formation and its precursors (VOCs and NO_x), challenges in mitigating its severity lie primarily in comprehensively understanding of O_3-precursor relationship (Su et al., 2018a; Tan et al., 2018a)."

Comment 2: Lines 61-65, the large spatiotemporal variability of O_3-precursor relationship has been widely reported in literature, rather than a finding of your recent study. Therefore, this sentence is better to be rephrased.

Reply: We fully agree with the reviewer's comments, and this sentence have been rephrased as below.

Line 65-69: "Some previous studies (Li et al., 2021; Lu et al., 2010a; Sicard et al., 2020; Yu et al., 2020b) have reported a large variability of O_3-precursor relationship in spatiotemporal scales in many cities of China, which indicates great challenges in current O_3 pollution control (Wang et al., 2017a; Xue et al., 2014b)."

Reference:

Li, K., Wang, X., Li, L., Wang, J., Liu, Y., Cheng, X., Xu, B., Wang, X., Yan, P., Li, S., Geng, C., Yang, W., Azzi, M. and Bai, Z.: Large variability of O_3-precursor relationship during severe ozone polluted period in an industry-driven cluster city (Zibo) of North China Plain, J. Clean. Prod., 316, 128252, doi:https://doi.org/10.1016/j.jclepro.2021.128252, 2021.

Yu, D., Tan, Z., Lu, K., Ma, X., Li, X., Chen, S., Zhu, B., Lin, L., Li, Y., Qiu, P., Yang, X., Liu, Y., Wang, H., He, L., Huang, X. and Zhang, Y.: An explicit study of local ozone budget and NOx-VOCs sensitivity in Shenzhen China, Atmos. Environ., 224, 117304, doi:https://doi.org/10.1016/j.atmosenv.2020.117304, 2020a.

Lu, K., Zhang, Y., Su, H., Brauers, T., Chou, C. C., Hofzumahaus, A., Liu, S. C., Kita, K., Kondo, Y., Shao, M., Wahner, A., Wang, J., Wang, X. and Zhu, T.: Oxidant (O_3 + NO2) production processes and formation regimes in Beijing, J. Geophys. Res. Atmos., 115(7), 1–18, doi:10.1029/2009JD012714, 2010a.

Lyu, X. P., Chen, N., Guo, H., Zhang, W. H., Wang, N., Wang, Y. and Liu, M.: Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China, Sci. Total Environ., 541, 200–209, doi:https://doi.org/10.1016/j.scitotenv.2015.09.093, 2016a.

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z. and Wang, W. X.: Ground-level ozone in four Chinese cities: Precursors, regional transport and heterogeneous processes, Atmos. Chem. Phys., 14(23), 13175–13188, doi:10.5194/acp-14-13175-2014, 2014c.

Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L. and Zhang, L.: Ozone pollution in China: A review of concentrations, meteorological influences, chemical precursors, and effects, Sci. Total Environ., 575, 1582–1596, doi:10.1016/j.scitotenv.2016.10.081, 2017a.

Methods:

Comment 1: Lines 107-112; 119-127; 128-137, why did you describe the VOCs measurements in three paragraphs? The time resolution of VOCs measurements was repeated for three times. The description of "a FID detector is applied for quantification" is not correct. The FID detector can only detect the signal of target species, rather than quantification of the targets. Why did you respectively select Tenax GR to pre-concentrate C6-C12 VOCs and C2-C6 VOCs for the GC-FID and the GC/FID/PID? Could the Tenax GR effectively capture C2-C6 VOCs at room temperature? What's the role of PID for the GC/FID/PID? How about variations of the retention times of VOCs during the monthly calibration period?

Reply: Thank you for your good comments.

We have simplified the description of VOCs instruments into one paragraph and removed the repetitive contents, as shown in **Line 108-130**. We have removed the incorrect sentence "FID detector is applied for quantification" in this revision.

Note that we intentionally did not have the technical options for setting up the commercial GC systems (also known as PAMS system), and some technical features (e.g., selection of FID or FID/PID detector; Tenax GR for VOC capture) were mainly determined by their manufacturers. Nevertheless, we tried to address some technical details metioned by the reviewer based on our limited instrument knowledge. For example, Tenax GR is a composite of the TENAX-TA matrix whereby 23% graphitized carbon is used as an integral part of the material, which is widely applied as a column packing material for trapping VOCs from the air for the commercial VOC instruments. As shown in previous studies, the Tenax GR cartridges can capature most volatile compounds (Brown et al., 1996), such as C5-C8 hydrocarbons (Cao et al., 1993), C2-C9 aldehydes and C3-C9 ketones (Lomonaco et al., 2018). Also, the Tenax GR can effectively capture C2-C6 VOCs at room temperature, while C6-C12 VOCs were pre-concentrated by cooling trap (range form -10℃ to 10℃). Similar to FID, PID is another detector for target VOC species. We performed a single-point calibration (i.e., 6 ppbv) every month, and the retention times of measured VOCs remained overall consistent during the whole campaign.

Line 116-131: "Two online GC systems (gas chromatography–flame ionisation detector, GC-FID, Thermo Scientific GC5900) were deployed at TZ and BJ respectively to measure VOC species. For C_2-C_5 VOCs, desorption and separation were performed using a GC with pre-concentration on a combination of two columns, followed by a FID detector. For C_6-C_{12} VOCs, air sample was pre-concentrated on Tenax GR cartridges and subsequently separated by chromatographic column, then detected by another FID detector. Similarly, one online system (gas chromatography–flame ionisation detector/photoionisation detector, GC-FID/PID, Syntech Spectras GC 955-615/815) was deployed at XD site. For C_2-C_6 VOCs, the hydrocarbons were concentrated on a Tenax GR carrier, then thermally desorbed and separated on a DB-1 column, and finally detected by FID and PID detectors. For C_6-C_{12} VOCs, the air sample was concentrated on a Carbosieves SIII carrier at 5℃, then thermally desorbed and separated on a combination of two columns, and FID and PID detectors were employed for subsequent detection. These systems measured 55 VOC species at a 1-h resolution, and more detailed descriptions can be found elsewhere (Chien, 2007; Jiang et al., 2018; Xie et al., 2008)."

Reference:

Brown R H. What is the best sorbent for pumped sampling–thermal desorption of volatile organic compounds? Experience with the EC sorbents project[J]. Analyst, 1996, 121(9): 1171-1175.

Cao X L, Hewitt C N. Evaluation of Tenax-GR adsorbent for the passive sampling of volatile organic compounds at low concentrations[J]. Atmospheric Environment. Part A. General Topics, 1993, 27(12): 1865-1872.

Lomonaco T, Romani A, Ghimenti S, et al. Determination of carbonyl compounds in exhaled breath by on-sorbent derivatization coupled with thermal desorption and gas chromatography-tandem mass spectrometry[J]. Journal of Breath Research, 2018, 12(4): 046004.

Xie, X.; Shao, M.; Liu, Y.; Lu, S.; Chang, C.-C.; Chen, Z.-M. Estimate of Initial Isoprene Contribution to Ozone Formation Potential in Beijing, China. Atmos. Environ. 2008, 42 (24), 6000–6010.

Chien, Y.C. Variations in Amounts and Potential Sources of Volatile Organic Chemicals in New Cars. Sci. Total Environ. 2007, 382 (2), 228–239. https://doi.org/https://doi.org/10.1016/j.scitotenv.2007.04.022.

Jiang, M.; Lu, K.; Su, R.; Tan, Z.; Wang, H.; Li, L.; Fu, Q.; Zhai, C.; Tan, Q.; Yue, D. Ozone Formation and Key VOCs in Typical Chinese City Clusters. Chinese Sci. Bull. 2018, 63 (12), 1130–1141.

Comment 2: Lines 138-145, besides the calibration, field comparison for the VOCs measurements by using the two types of GCs at one of the three sites is most important for the QA/QC. Did you conduct the comparison?

Reply: We fully agree with the importance of inter-comparison for the VOCs measurements, which should be done by using the two types of GCs at one of the three sites. Unfortunately, we did not conduct such comparison in our campaign, as these VOC instruments were separately deployed for rountine operation at three different sites, and it is very difficult to relocate and maintain them in one site due to practical reasons. Nevertheless, these commercial GC systems were regarded as standard VOC instruments, and were regularly checked and maintained during the whole campaign to ensure good QA/QC. Besides, these VOC instruments were regularly calibrated by standard gases with 55 VOC species from the same cylinder (Linde Co., Ltd, USA). Therefore, we assume that the VOC datasets obtained at the three sites are overall reliable for subsequent analysis in this study.

Line 134-141: "Unfortunately, we did not conduct the inter-comparison between the GC-FID and GC-FID/PID instruments at the same site due to practical reasons, as these VOC instruments were separately deployed at the three different sites for continuous routine operation. To ensure the quality assurance / quantity control (QA/QC) of online VOC measurement, two five-point calibrations (i.e., 2, 4, 6, 8, 10 ppbv, dilution from one cylinder) for standard gases with 55 VOC species (Linde Co., Ltd, USA) were carried out in May and August of 2019 at the three sites."

Comment 3: Lines 163-165, "for the best reproduction of O_3" at the end of this sentence.

Reply: Done. (Line 169)

Comment 4: Lines 177-179, the subject of "dataset" doesn't match the predicate of "were"; Considering the repetition for classifying the four patterns of time scale, this sentence is suggested to "Specifically, the entire campaign data classified as four patterns of time scale were modeled as base runs."

Reply: Corrected. (Line 181-182)

Comment 4: Lines 211-216, to avoid confusing between the species of X and its concentration, POx(X) and POx(X-ΔX) are suggested to be POx(CX) and POx(CX-ΔCX); either "(ΔX, 10% of X in this study in accordance with the previous studies" or "Therefore, ΔC(X)/C(X) was 10% in this study" can be deleted to avoid repetition.

Reply: We have corrected this as below.

Line 215-221:

$$\mathrm{RIR(X)} = \frac{[PO_x(CX) - PO_x(CX - \Delta CX)]/PO_x(CX)}{\Delta CX/CX}$$

Here, X is a specific precursor (i.e., NO_x, CO or grouped / individual VOC species), CX is the measured concentration of precursor X, and ΔCX is the hypothetical concentration change (ΔCX/CX = 10% in this study in accordance with the previous studies (Lyu et al., 2016; Wang et al., 2018)). $PO_x(CX)$ represents the simulated O_x production rate in a base run, whereas $PO_x(CX–\Delta CX)$ is the simulated O_x production in a second run with a hypothetical concentration change of species X.

Results and discussion:

Comment 1: Line 245, “within” should be “among”.

Reply: Corrected. (Line 261)

Comment 2: Lines 247-250, the bracket is suggested to be moved after alkene*.

Reply: Corrected.

Comment 3: Lines 254-257, why were the nocturnal O_3 concentrations significantly underestimated by the model simulations (e.g., Fig. S3)?

Reply: The nocturnal ground O_3 concentrations are mainly influenced by the physical process, such as aggravating vertical mixing and horizontal transport from ozone-rich plumes (He et al., 2022), but not produced from atmospheric chemical process at nighttime due to no photochemical activities. Unlike the 3-D air quality model, 0-D box model usually simplifies the representation of the physical processes (i.e., deposition and advection), and focuses on modelling chemical process (Lu et al., 2010; Xu et al., 2021). Therefore, due to the lack of representing O_3 sources from physical tranport while maintaining the nighttime chemical consumption of O_3 (e.g., O_3+NO titration reaction), uncertainty is unavoidable in simulating nocturnal O_3 concentrations by box modelling to some extent, which may explain the O_3 underestimation in our study.

Line 273-278: “However, on some days the modeling results underestimated or overestimated the O_3 concentrations, particularly the underestimation of nocturnal O_3 concentrations. Such discrepancies between the simulated and observed O_3 were likely due to limitations in explicit representations of atmospheric and transport processes (i.e., the horizontal and vertical transport process of ground ozone) by 0-D modeling approach (Lyu et al., 2019; Yu et al., 2020b).”

Reference:

He, C., Lu, X., Wang, H., Wang, H., Li, Y., He, G., He, Y., Wang, Y., Zhang, Y., Liu, Y., Fan, Q., and Fan, S.: Unexpected high frequency of nocturnal surface ozone enhancement events over China: Characteristics and mechanisms, Atmos. Chem. Phys. Discuss. [preprint], https://doi.org/10.5194/acp-2022-310, in review, 2022.

Lu, K., Zhang, Y., Su, H., Brauers, T., Chou, C. C., Hofzumahaus, A., Liu, S. C., Kita, K., Kondo, Y., Shao, M., Wahner, A., Wang, J., Wang, X. and Zhu, T.: Oxidant

(O_3 + NO2) production processes and formation regimes in Beijing, J. Geophys. Res. Atmos., 115(7), 1–18, doi:10.1029/2009JD012714, 2010a.

Xu D, Yuan Z, Wang M, et al. Multi-factor reconciliation of discrepancies in ozone-precursor sensitivity retrieved from observation- and emission-based models. Environment International. 2022 Jan; 158:106952. DOI: 10.1016/j.envint.2021.106952.

Comment 4: Lines 280-287, why was the model performance for TZ better than for XD and BJ?

Reply: We applied an optimized dilution rate of 3/86400 s^{-1} for all simulated days, which is conductive to ensuring the rationality and comparability of modeled results at the three sites. We infer that this optimized dilution rate for non-constraint species in our model configuration may result in better model performance in TZ than the other two sites.

Line 297-300: "In summary, TZ showed the best performance of the box model simulation, followed by XD and BJ, regardless of any statistical metrics or different patterns of time scale, which may be associated with the optimized dilution rate for non-constraint species in our model configuration."

Comment 5: Line 292, alkenes* have been noted before, and thus the brackets in here can be deleted.

Reply: Done.

Comment 6: Lines 309-313, the relationship between the monthly variations of the species and the RIR is better to be discussed, or readers cannot understand why you present them in here?

Reply: Thank you for the good comments. In our revision, we have added some descriptions to illustrate the monthly variations of the measurements from these species as below.

Line 323-330: "Significant monthly variations of O_3, NO_x, CO, VOC reactivity and TVOC/NO_x ratios (in ppbC/ppbv, as a widely used simple metric to determine the photochemical regime) (National Research Council, 1991) were also observed from May to September (see **Figure S9** and **Table S3**) at the three sites. For example, the BVOC reactivity in TZ showed highest level among the three sites during the whole

campaign, and the AVOC reactivity in BJ showed more considerable variations in different months, which indicated spatial and temporal variations of local primary emission for O_3 precursors in Zibo city."

Comment 7: Lines 314-316, "two regimes (i.e., VOC-limited and NO_x-limited) or" can be deleted because the three regimes are prevailingly adopted.

Reply: Done.

Comment 8: Lines 326-328, the correlation between the monthly TVOC/NO_x and RIR_{NOx}/RIR_{AVOC} would become worse when only one sampling site was considered. Therefore, Fig. 5b could not well explain the considerable variation of monthly O_3 formation chemistry.

Reply: We agree with the reviewer's comments that the correlation between the monthly TVOC/NO_x and RIR_{NOx}/RIR_{AVOC} would vary when each site was considered individually. As shown in **Figure 5**, we added the correlation between TVOC/NO_x and RIR_{NOx}/RIR_{AVOC} for each individual site. It seems that the correlation between TVOC/NO_x and RIR_{NOx}/RIR_{AVOC} for each site was overall consistent with the result by merging all data points from the three sites. Hence, we suppose that the variations of O_3 formation chemistry can be elucidated by the variability of O_3 precursors at the three sites to some extent. This has been incorporated into our manuscript as below.

Line 336-339: "**Figure 5b** shows good consistency between monthly TVOC/NO_x and RIR_{NOx}/RIR_{AVOC}, suggesting that the changes of local emissions for O_3 precursors may partially explain the considerable variation of O_3 formation chemistry in different months."

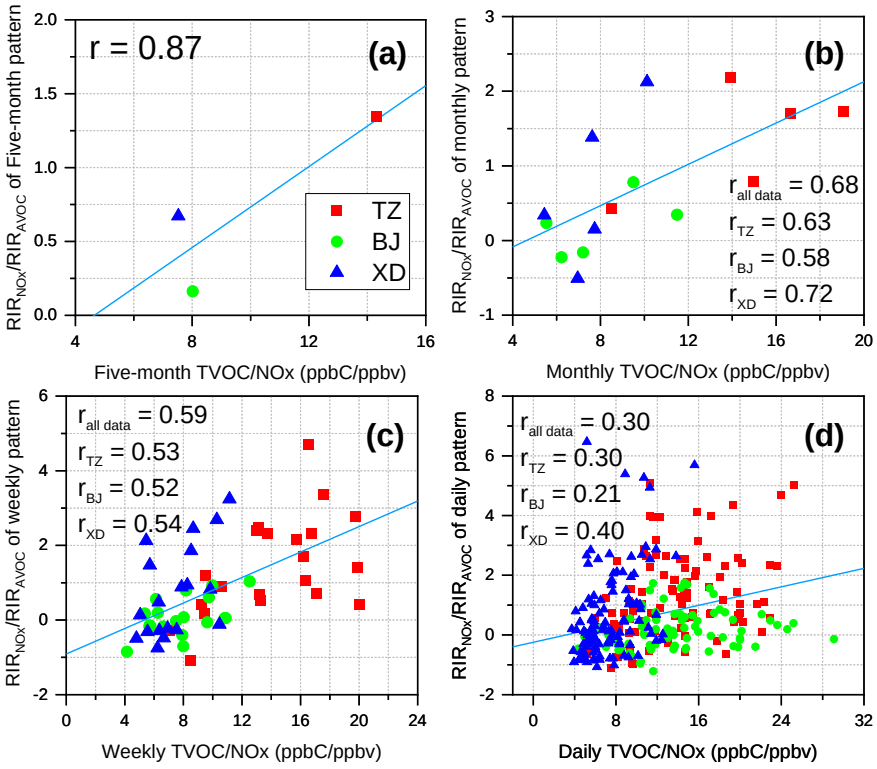

Figure 5. The correlations of TVOC/NO_x with RIR_{NOx}/RIR_{AVOC} at multiple patterns of time scale at the three sites in Zibo.

Comment 9: Lines 344-347, the correlation between the weekly TVOC/NO_x and RIR_{NOx}/RIR_{AVOC} at one sampling site (Fig. 5c) was also weak for explaining the weakly variation of O_3 formation chemistry. Additionally, the data point with TVOC/NO_x of zero for BJ in Fig. 5d is wrong, should be removed.

Reply: Thanks for your detailed review, and pointed out our mistake. The data point with TVOC/NO_x of zero for BJ in **Figure 5d** has been removed. In addition, the weekly correlation between TVOC/NO_x and RIR_{NOx}/RIR_{AVOC} at each site was slightly low but overall consistent with the result merged by three sites (see above **Figure 5** in **Comments 8**). This suggests that the weekly variation of O_3 formation chemistry can be partially explained by the variability of O_3 precursors. This has been incorporated into our manuscript as below.

Line 355-358: "Given the moderate correlation between weekly TVOC/NO_x and RIR_{AVOC}/RIR_{NOx} (**Figure 5c**), the temporal variations of RIR values and O_3 formation chemistry at the three sites may be partially elucidated by the emission changes of O_3 precursors."

Comment 10: Lines 361-363: "Additionally, the time series of daily RIR_{NOx}/RIR_{AVOC} (**Figure S11**) first increased and then decreased during the entire campaign, which was also consistent with that of weekly scale.", the description seemed not well reflect the time series of daily RIR_{NOx}/RIR_{AVOC} in Fig. S11 with irregular variations.

Reply: Thank you for careful review of our manuscript. This sentence has been rephrased in our manuscript as below.

Line 372-374: "Additionally, the time series of daily RIR_{NOx}/RIR_{AVOC} (**Figure S13**) showed more irregular variations in temporal trends during the entire campaign, though such temporal trends were overall consistent with that of weekly scale in **Figure 4 g-i**."

Comment 11: Lines 399-402, the model simulations with inputting the average values for the five-month scale would greatly mask the large temporal variations of species especially for meteorological factors (such as sunlight and temperature), which is the key reason for the discrepancy of RIR values between five-month scale and daily scale. It is not proper to explain the discrepancy of RIR by the uncertainty.

Comment 13: Line 460, besides the analyzed uncertainties, the uncertainty due variation of meteorological factors for the long period scales may play a more important role in the O_3 sensitive chemistry.

Reply to **Comment 11** and **Comment 13:** Thank you for the good comments. We agree that both precursor emissions and meteorological factors play a key role in O_3 formation over a long observational period. Indeed, the averaged dataset for model input will mask the temporal variations of O_3 precursors and meteorological factors, and the exent of which depends on the selected timescale pattern. We rephrased some discussions in the revised manuscript as below.

Line 478-480: "This averaging approach will conceal the temporal variations of O_3 precursors and meteorological factors, particularly for a long-term observational campaign."

Line 485-489: "In addition, meteorological factors such as temperature and irradiation also play an important role on O_3 formation, especially these meteorological parameters can vary greatly over a long observational period (Boleti et al., 2020; Liu et

al., 2019b; Weng et al., 2022). Therefore, the masked temporal variation of these meteorological factors behind the averaged input dataset would also result in model uncertainty."

Reference:

Boleti, E., Hueglin, C., Grange, S. K., Prévôt, A. S. H., and Takahama, S.: Temporal and spatial analysis of ozone concentrations in Europe based on timescale decomposition and a multi-clustering approach, Atmos. Chem. Phys., 20, 9051–9066, https://doi.org/10.5194/acp-20-9051-2020, 2020.

Weng, X., Forster, G. L., and Nowack, P.: A machine learning approach to quantify meteorological drivers of ozone pollution in China from 2015 to 2019, Atmos. Chem. Phys., 22, 8385–8402, https://doi.org/10.5194/acp-22-8385-2022, 2022.

Liu, X., Lyu, X., Wang, Y., Jiang, F., and Guo, H.: Intercomparison of O_3 formation and radical chemistry in the past decade at a suburban site in Hong Kong, Atmos. Chem. Phys., 19, 5127–5145, https://doi.org/10.5194/acp-19-5127-2019, 2019.

Comment 12: Lines 415-418, there is a repeated comparison.

Reply: Thank you for careful review of our manuscript, and we have removed the repeated comparision.