

We thank the referees for their insightful questions and comments, which helped to improve the quality of this paper. Our answers to all the concerns are listed in the following in red, after the reviewer's comments, which are in black. The changed parts in the modified manuscript are marked in yellow.

Anonymous Referee #1

This manuscript presents a comprehensive investigation of net ozone production rate ($P(O_3)_{net}$) and ozone formation sensitivity (OFS) through the integration of in situ field observations using a novel dual-channel reaction chamber system (NPOPR) and detailed box model simulations based on MCM v3.3.1. The study is of high relevance and scientific value, particularly in addressing long-standing issues of underestimation in modeled ozone production. The work also has practical implications for improving model-based OFS diagnosis and VOC pollution control strategies. However, several major issues must be addressed in the manuscript.

In your study, observed OVOC concentrations are used to constrain the box model. However, many OVOCs (e.g., formaldehyde, acetaldehyde, ketones) are not only emitted directly but also formed via secondary photochemical reactions from VOC precursors. Directly constraining their concentrations may mask deficiencies in the model's chemical mechanism and artificially suppress diagnostic signals of missing secondary formation pathways.

We fully appreciate your concern and recognize the potential issues that may arise from directly constraining OVOC concentrations. To investigate whether the model can reproduce secondary formation on its own, we added a modelling scenario without OVOC constraints based on Case D1 and output key OVOC species (as shown in Fig. S19). Results show that, Without additional constraints, the model overestimates some OVOCs (e.g., HCHO and CH₃CHO) yet adequately reproduces their secondary-formation pathways; in contrast, the observed diurnal cycle of CH₃COCH₃ shows no evident signature of secondary production. These results demonstrate that directly constraining the OVOC concentrations may mask deficiencies in the model's chemical mechanism and artificially suppress diagnostic signals of missing secondary formation pathways. However, refraining from any constraint would also falsely amplify the primary-source signal, especially those lacking clear secondary-generation signatures. Applying a constraint can better capture the influence of primary OVOCs. Furthermore, our analysis indicates that the $P(O_3)_{net}$ missing is not likely caused by unaccounted secondary production (see Sect. 3.3). Until such mechanistic gaps are resolved, observational nudging of OVOCs remains a pragmatic compromise: it preserves

concentration accuracy while curbing spurious chemical feedbacks. We have added such kind of discussion in lines 401-406 of the modified manuscript:

“The negligible (or even negative) change in $P(\text{O}_3)_{\text{net}}$ Mod when OVOCs are constrained in Cases D1-D4 may arise because the OVOC constraint masks deficiencies in the model’s chemical mechanism and artificially suppresses diagnostic signals of missing secondary formation pathways. Until the underlying chemical mechanisms are improved, observational nudging of OVOCs offers a practical compromise—it helps maintain concentration accuracy while limiting unrealistic chemical feedbacks (more details can be found in Supplementary Materials S5).”

And S5 in the Supplementary Materials:

S5. Impacts of OVOCs constraints in the model

To explore the impact of OVOCs constraint in the model, we further added a modelling scenario without OVOC constraints based on Case D1 and output key OVOC species (see Fig. S19). From Fig. S19, the model tends to overestimate some OVOC concentrations (i.e., HCHO, CH₃CHO), and their secondary-formation pathways are adequately captured, while the observed diurnal variation of CH₃COCH₃ does not exhibit clear secondary formation characteristics. These results show that directly constraining OVOC concentrations can fill the concentration gap in the model to match observed OVOC levels, but may mask deficiencies in the model’s chemical mechanism and artificially suppress diagnostic signals of missing secondary formation pathways (i.e., the RO₂-to-OVOC reaction pathways). This will lead to the underestimation of the entire HO_x-cycle oxidation rate, lowers the budgets of OH, O₃, and NO₃, and subsequently the $P(\text{O}_3)_{\text{net}}$ Mod. However, without any constraint, the model may overestimate the contribution from primary sources. Furthermore, our analysis indicates that the $P(\text{O}_3)_{\text{net}}$ missing is not likely caused by unaccounted secondary production (see Sect. 3.3). Until such mechanistic gaps are resolved, observational nudging of OVOCs remains a pragmatic compromise: it preserves concentration accuracy while curbing spurious chemical feedbacks.

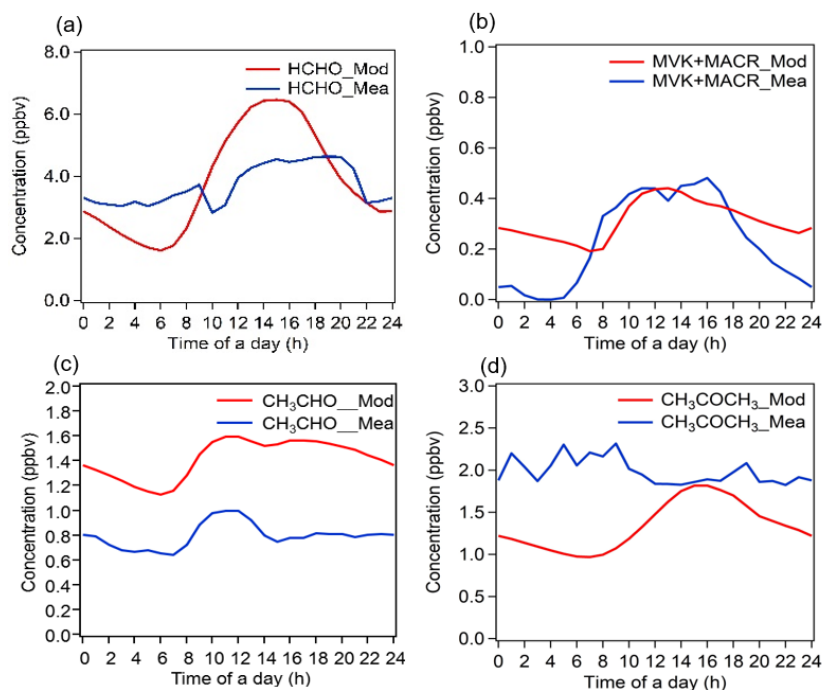


Figure S19: Comparison of measured OVOCs with modeled values from a no-constraint OVOC scenario based on Case D1."

Why were NO and NO_x changed between the two methods to diagnose O₃ sensitivity, respectively?

We measured ozone (O₃) formation sensitivity (IR index) directly using the NPOPR instrument, with NO as the NO_x indicator. This approach aligns with previous studies (Sklaveniti et al., 2018; Morino et al., 2023), which also used NO in their $P(O_3)_{net}$ measurement systems. By adding NO instead of NO_x, the CAPS-NO₂ instrument could eliminate NO₂ interference and directly quantify NO's contribution to O₃ production. When O₃ formation sensitivity is in the NO_x-limited regime, increasing NO enhances $P(O_3)_{net}$ because HO₂/RO₂ reacts more efficiently with NO to produce NO₂. Conversely, in the VOCs-limited regime, adding NO may reduce $P(O_3)_{net}$ because NO consumes OH to form HONO, weakening VOC oxidation chain reactions.

Our model's O₃ formation sensitivity (OFS) analysis is based on the absolute $P(O_3)_{net}$ sensitivity calculation, which directly evaluates how changes in NO_x (NO + NO₂) affect $P(O_3)_{net}$ while considering both the NO titration effect and the role of NO₂ photolysis in O₃ production.

The manuscript attributes the model – measurement discrepancy ($P(O_3)_{net_Missing}$) entirely to missing reactive VOCs or underrepresented chemical pathways. However, box models by design do not account for horizontal or vertical

transport, which may play a significant role in shaping the measured ozone production rate—especially during periods with strong advection or mixing layer evolution, such as early morning or late afternoon. You should clarify why transport processes are neglected and whether their influence is truly negligible.

We acknowledge that transport processes may influence O_3 distribution under specific conditions. However, this study primarily focuses on local photochemical O_3 production. By employing the NPOPR detection system with an extremely short residence time (0.15 h), we aimed to capture instantaneous in-situ photochemical reactions rather than O_3 accumulation effects over time and space. The modeling incorporated real-time meteorological conditions and pollutant concentration data. On such short timescales, the impacts of vertical mixing and horizontal advection become relatively minor. Moreover, this study compares measured and simulated net O_3 production rates ($P(O_3)_{net}$) rather than O_3 concentrations themselves. Our previous study also demonstrated that $P(O_3)_{net}$ more directly reflects the photochemical O_3 formation potential from local precursors and is less affected by transport processes compared to O_3 concentrations (Zhou et al., 2024b).

We added “The time resolution of the $P(O_3)_{net}$ measurement is 4 min. Our previous study demonstrated that $P(O_3)_{net}$ more directly reflects the photochemical O_3 formation potential from local precursors and is less affected by transport processes compared to O_3 concentrations (Zhou et al., 2024b).” in line 129-131 of the modified manuscript.

Although the manuscript includes substantial observation – model comparisons and compensatory mechanisms for missing reactivity, the concluding section does not clearly state what is new in this work compared to existing studies, please clearly emphasize the innovation points and boundaries of this study in the conclusion section and explain its promoting role in the research of the formation mechanism of ozone pollution.

We appreciate the reviewer's valuable suggestion to clarify the novel contributions of our study. The main innovation of this work is that we have successfully applied the NPOPR detection system to directly measure OFS in field observations. This approach enables us to quantitatively assess the impact of $P(O_3)_{net}$ simulation deficits on OFS determination. Previous studies in this field predominantly relied on model simulations without sufficient observational validation. While our earlier research (Zhou et al., 2024a) qualitatively analyzed the effects of different VOC species on $P(O_3)_{net}$ through model-observation comparisons, quantitative analysis was still lacking. This study makes significant advancements by employing direct measurement methods to quantitatively investigate the contributions of different VOC species to $P(O_3)_{net}$.

simulation deficits. Our findings address the critical scientific issue of model underestimation of $P(\text{O}_3)_{\text{net}}$ and quantify its impact on OFS determination. These results provide both a robust database and theoretical foundation for improving the accuracy of model-based OFS assessment and developing more effective O_3 pollution control strategies.

We have changed the sentence “In conclusion, improving the model's accuracy requires further expansion of the measurement of VOC species, particularly OVOCs, and the incorporation of relevant chemical mechanisms into the model. In future studies, continuing field observations based on direct measurement of $P(\text{O}_3)_{\text{net}}$ and accumulating more data will contribute to a better understanding of O_3 pollution formation mechanisms and make effective O_3 pollution control strategies.” to “In conclusion, we quantitatively assessed the $P(\text{O}_3)_{\text{net}}$ simulation deficits and their impact on OFS diagnosis by comparing the measured and modelled $P(\text{O}_3)_{\text{net}}$, and found that the unmeasured VOCs —rather than the secondary atmospheric formation — are the primary causative factor of $P(\text{O}_3)_{\text{net}}$ Missing. Furthermore, both direct measurements and model results reveal a diurnal OFS shift dominated by the morning regime; transition and VOC-limited conditions prevailed, so prioritizing VOCs while co-controlling NO_x is the most effective approach to O_3 pollution control in PRD region. Our results also demonstrate that the persistent model biases risk under-estimating the local photochemical formation contribution to O_3 pollution, thereby has weakening its perceived impact relative to physical transportation. Future studies should expanded VOCs measurements and combine direct $P(\text{O}_3)_{\text{net}}$ observations with regional transport model to separate local production from up-wind advection.” in lines 610-617 in the modified manuscript.

Lines 29-31: You mentioned “the only approach to fill the gap was to add unmeasured VOCs” appears too strong. It implies that no other explanations or methods could be relevant, which may not be justified. Consider softening this to reflect that unmeasured OVOCs were the most effective compensating factor in this study, rather than the only one possible.

Thanks for your suggestion. We have changed the sentence “The only approach to fill the gap between observation and computation was to add possible unmeasured reactive VOCs, ...” to “The results in this study reflected that unmeasured oxygenated VOCs (OVOCs) were the most effective compensating factor for the discrepancies between observed and computed $P(\text{O}_3)_{\text{net}}$ and OFS, ...” in lines 29-30 in the modified manuscript.

Line 43: “precursor” should be “precursors” .

We changed “precursor” to “precursors” in line 43 of the modified manuscript.

Line 46: “equation” should be “equations” .

We changed “equation” to “equations” in line 50 of the modified manuscript.

Lines 205-206: It is unclear what magnitude of precursor perturbation was applied, please provide a more explicit description of the model configuration used for the sensitivity analysis.

We thank the reviewer for this valuable comment. Regarding the calculation method for absolute $P(\text{O}_3)_{\text{net}}$ sensitivity in our model, we employed the analytical approach proposed by Sakamoto et al. (2019). This method does not require artificial perturbation of precursor concentrations in the simulations. Instead, it is defined as the change in $P(\text{O}_3)_{\text{net}}$ values caused by a percentage change in either $[\text{NO}_x]$ or $[\text{VOCs}]$ concentrations. To better clarify this methodology, we have revised the manuscript to explicitly state: “In this study, the analysis of absolute $P(\text{O}_3)_{\text{net}}$ sensitivity was conducted using the box model through an analytical calculation approach that does not involve artificial perturbation of precursor concentrations.” in line 233 of the modified manuscript.

Lines 278-281: The confidence interval of 68.3% is relatively conservative, please provide additional analysis.

Regarding the confidence interval selection, we initially chose the 68.3% interval as it corresponds to the $\pm 1\sigma$ range in Gaussian distribution, which represents a standard statistical measure. However, as suggested by the reviewer, we have conducted additional sensitivity analysis using a 90% confidence interval. The results show similar trends in both cases, confirming the robustness of our findings.

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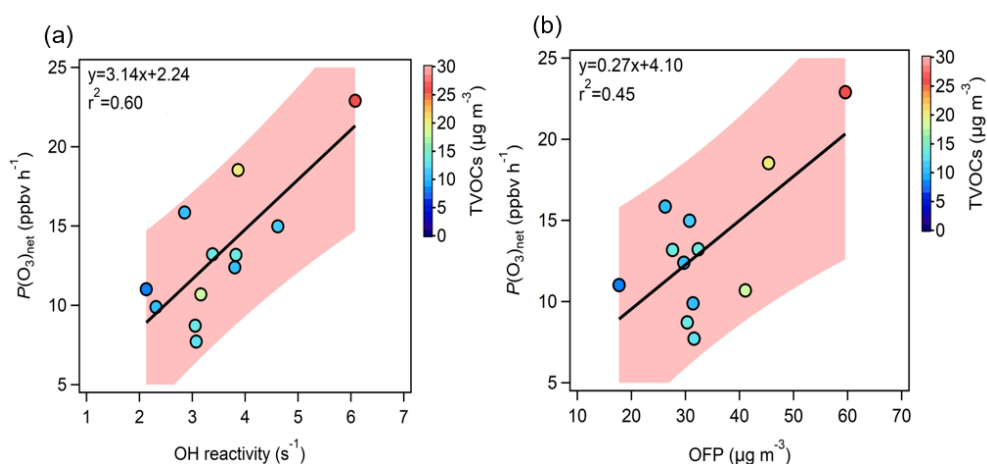


Figure 1: Correlation between measured $P(\text{O}_3)_{\text{net}}$ ($P(\text{O}_3)_{\text{net_Mea}}$) and (a) total OH reactivity (k_{OH}) and (b) O_3 Formation Potential (OFP). The shaded area in the figure represents the confidence interval (90 %) of the fitting line between $P(\text{O}_3)_{\text{net}}$ and k_{OH} , and between $P(\text{O}_3)_{\text{net}}$ and OFP.”

We have changed the sentence “The shaded area in the figure represents the confidence interval (68.3%) of the fitting line between $P(\text{O}_3)_{\text{net}}$ and k_{OH} , and between $P(\text{O}_3)_{\text{net}}$ and OFP.” to “The shaded area in the figure represents the confidence interval (90 %) of the fitting line between $P(\text{O}_3)_{\text{net}}$ and k_{OH} , and between $P(\text{O}_3)_{\text{net}}$ and OFP.” in line 309 in the modified manuscript.

Line 306: The reported p-value ($P < 0.5$) does not indicate statistical significance, and the analysis doesn't hold.

Thank you for catching this typographical error. We have carefully re-examined the statistical analysis comparing $P(\text{O}_3)_{\text{net_Missing}}$ between O_3 pollution days and normal days. The corrected results show a significant difference with $p = 0.03$ (< 0.05). We have changed the sentence “The median $P(\text{O}_3)_{\text{net_Missing}}$ values on O_3 pollution days were statistically higher than those on normal days (*t-test*, $P < 0.5$), ...” to “The $P(\text{O}_3)_{\text{net_Missing}}$ values on O_3 pollution days were statistically higher than those on normal days (*t-test*, $p < 0.05$), ...” in line 343 of the modified manuscript.

Lines 305-307: The statement that the mechanisms added in Case D1 “are not the main cause” of the bias may overstate the conclusion. The remaining discrepancy could still be partly due to uncertainties in those mechanisms, parameterization, site-specific variability and transportation etc. A more cautious wording would improve clarity and avoid giving a false sense of certainty.

Thanks for your suggestion. We have changed the sentence “The median $P(\text{O}_3)_{\text{net_Missing}}$ values on O_3 pollution days were statistically higher than those on normal days (*t-test*, $P < 0.5$), indicating that the supplementary mechanisms explored in the model, as mentioned above, are not the main cause of the $P(\text{O}_3)_{\text{net_Missing}}$.” to “The $P(\text{O}_3)_{\text{net_Missing}}$ values on O_3 pollution days were statistically higher than those on normal days (*t-test*, $p < 0.05$), suggesting that while the supplementary mechanisms explored in the model may contribute to some extent, they are unlikely to be the dominant cause of the $P(\text{O}_3)_{\text{net_Missing}}$.” in lines 343-344 in the modified manuscript.

Lines 328-329: The statement that “ $P(\text{O}_3)_{\text{net_Missing}}$ increases significantly at higher O_3 precursor concentrations” (based on $r^2 = 0.4-0.5$) may overstate the strength of the relationship. A moderate correlation should not be equated with a strong or significant increase unless supported by statistical testing.

We appreciate this constructive comment regarding the interpretation of our correlation results. Our additional analyses, including both Pearson correlation and t-tests, and found that $r = 0.24$ and 0.20 for TVOCs and NO_x , respectively. And the correlations are very weak, with $t = 1.6$ and 1.3 for VOCs and NO_x (*t-tests*), respectively. These t-test values for correlation significant are lower than the critical value of $t = 2.0$, confirming

that $P(O_3)_{\text{net_Missing}}$ shows weak relationships with VOCs and NO_x precursor concentrations.

We have changed the sentence “Under O_3 pollution days, $P(O_3)_{\text{net_Missing}}$ showed a positive correlation with VOCs and NO_x , with r^2 values of 0.4 and 0.5, respectively, indicating that $P(O_3)_{\text{net_Missing}}$ increases significantly at higher O_3 precursor concentrations. This phenomenon is consistent with previous studies (Whalley et al., 2021; Ren et al., 2013; Zhou et al., 2024a).” to “On O_3 pollution days, $P(O_3)_{\text{net_Missing}}$ exhibited a moderate positive correlation with VOCs ($r^2=0.4$, $R=0.2$, $t=2.9$) and NO_x ($r^2=0.5$, $R=0.2$, $t=3.8$), confirming that the $P(O_3)_{\text{net_Missing}}$ is larger at higher precursor concentrations/mixing ratios (both $t > \text{critical } 2.0$, $p < 0.05$), consistent with earlier box-model studies (Whalley et al., 2021; Ren et al., 2013; Zhou et al., 2024a). A moderate positive correlation is also found with J_{O_1D} on both O_3 pollution days and normal days, with r^2 values of 0.5 and 0.4, respectively. On normal days all correlations collapse ($r^2 < 0.2$, $p > 0.1$), implying that the model deficit is not tied to the measured precursors under low- NO_x conditions and may instead related to the missing mechanisms for unmeasured photolabile VOCs.” in lines 368-375 in the modified manuscript.

Lines 389-391: You use an empirical relationship between k_{OH} and $P(O_3)_{\text{net}}$ to get $k_{OH_Missing}$, and then adjust VOC concentrations to match this value. However, this method assumes a direct linear relationship without showing how real chemical reactions support this assumption. Please explain why this approach is reasonable, and whether it reflects actual atmospheric chemistry.

The method of estimating missing VOC concentrations through the empirical linear relationship between OH reactivity (k_{OH}) and $P(O_3)_{\text{net}}$ is used in this study, fundamentally based on the OH-driven nature of O_3 production. The scientific basis lies in the fact that $P(O_3)_{\text{net}}$ is closely related to the production rate of RO_x radicals ($P(RO_x)$), which are primarily formed through the reaction of OH with VOCs. Since $P(RO_x)$ is directly influenced by the OH reactivity (k_{OH}), $P(O_3)_{\text{net}}$ is consequently correlated with k_{OH} . Furthermore, previous study have shown that $P(O_3)_{\text{net}}$ exhibits a linear relationship with both $P(HO_x)$ and k_{OH} when O_3 formation is located in VOCs-limited regime (Baier et al., 2017), and this approach reflects nearly actual atmospheric chemistry if $P(O_3)_{\text{net}}$ missing is driven by VOCs reactivity missing (Wang et al., 2024).

To explore the influence of unconstrained secondary products to $P(O_3)_{\text{net}}$ missing (which may influence the linear relationship between $P(O_3)_{\text{net}}$ missing and k_{OH}), we checked the dependence of $P(O_3)_{\text{net}}$ missing on the ethylbenzene/m,p-xylene ratio. As the m,p-xylene has a larger reaction rate constant ($18.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) than ethylbenzene ($7.0 \times 10^{-12} \text{ cm}^3$

molecule⁻¹ s⁻¹) when reacting with OH radicals, the ratio of ethylbenzene to m,p-xylene was used to characterize the degree of air mass aging (de Gouw et al., 2005; Yuan et al., 2013), a higher ratio of ethylbenzene to m,p-xylene corresponds to a higher degree of air mass aging. We see that the $P(\text{O}_3)_{\text{net}}$ missing decreases with the increasing ratio of ethylbenzene to m,p-xylene (as added in Fig. S11f), which indicates that the $P(\text{O}_3)_{\text{net}}$ missing was not caused by unconstrained secondary products.

To make the description clearer, we have changed the sentence “We hypothesize that the remaining $P(\text{O}_3)_{\text{net}}$ Missing is caused by unknown VOCs that are not constrained in the box model. By quantifying the relationship between k_{OH} and $P(\text{O}_3)_{\text{net}}$...” to “We hypothesize that the remaining $P(\text{O}_3)_{\text{net}}$ Missing is caused by unknown VOCs that are not constrained in the box model. The method of estimating missing VOC concentrations through the empirical linear relationship between OH reactivity (k_{OH}) and $P(\text{O}_3)_{\text{net}}$ is used in this study, the scientific basis lies in the fact that $P(\text{O}_3)_{\text{net}}$ is closely related to the production rate of RO_x radicals ($P(\text{RO}_x)$), which are primarily formed through the reaction of OH with VOCs. Since $P(\text{RO}_x)$ is directly influenced by the OH reactivity (k_{OH}), $P(\text{O}_3)_{\text{net}}$ is consequently correlated with k_{OH} . Previous study have shown that $P(\text{O}_3)_{\text{net}}$ exhibits a linear relationship with both $P(\text{HO}_x)$ and k_{OH} when O₃ formation is located in VOCs-limited regime (Baier et al., 2017), and this approach reflects nearly actual atmospheric chemistry if $P(\text{O}_3)_{\text{net}}$ missing is driven by VOCs reactivity missing (Wang et al., 2024b). Furthermore, we examined whether unconstrained secondary products affect $P(\text{O}_3)_{\text{net}}$ missing—and thus the linear relationship between $P(\text{O}_3)_{\text{net}}$ missing and k_{OH} —by analysing its dependence on the ethylbenzene / m,p-xylene ratio. Because this ratio increases with the degree of air-mass aging (de Gouw et al., 2005; Yuan et al., 2013), the observed decrease in the $P(\text{O}_3)_{\text{net}}$ missing with increasing ratio (Fig. S11f) indicates that the $P(\text{O}_3)_{\text{net}}$ missing is not caused by unaccounted secondary production.” In lines 428-438 in the modified manuscript.

The corresponding references are also added in the reference list:

“de Gouw, J., Middlebrook, A., Warneke, C., Goldan, P., Kuster, W., Roberts, J., Fehsenfeld, F., Worsnop, D., Canagaratna, M., and Pszenny, A.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *Journal of Geophysical Research-Atmospheres*, 110, D16305, <https://doi.org/10.1029/2004JD005623>, 2005.

Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.: VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China, *Atmospheric Chemistry and Physics*, 13, 8815–8832, <https://doi.org/10.5194/acp-13-8815-2013>, 2013.”

The corresponding figure which plots the dependence of $P(\text{O}_3)_{\text{net_missing}}$ on the ethylbenzene/m,p-Xylene ratio is added in Fig. S11f:

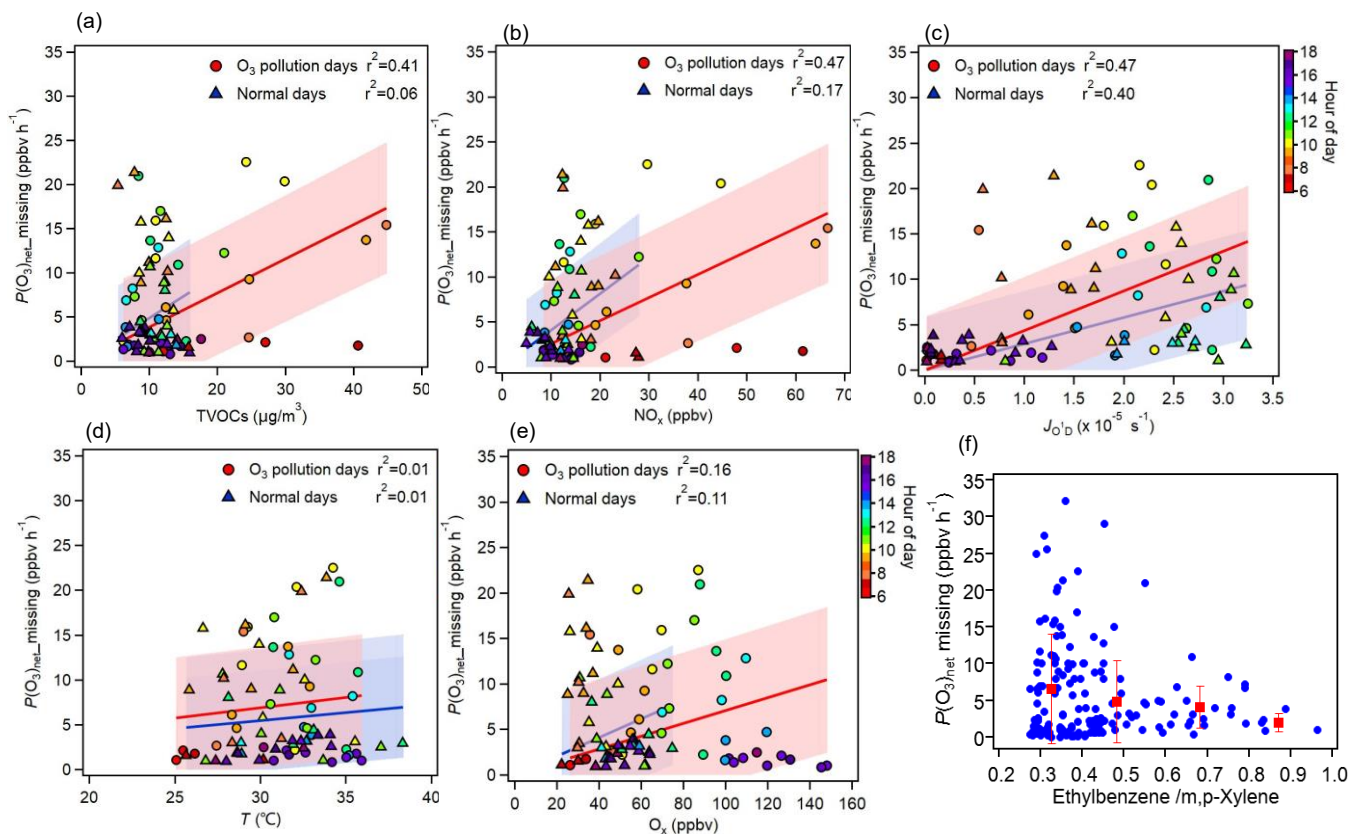


Figure S11: Correlations between $P(\text{O}_3)_{\text{net_missing}}$ and TVOCs, NO_x, $J_{\text{O}^1\text{D}}$, T , O_x (a–e), and the ethylbenzene/m,p-Xylene ratio (f, representing the air mass aging). Circles represent O₃ pollution days, triangles represent normal days, and the shaded area indicates the 68.3 % confidence interval of the fitting line.

Lines 396-397: In Case E2, ethylene was amplified to 5.9-85.6 times the original concentration, far exceeding the limit emission levels in the conventional urban atmosphere. The lack of emission inventories or observational data support may cause the simulation results to deviate from reality. More discussion on the rationality of these magnifications is required.

The purpose of these scenarios is to demonstrate the potential impact of this type of VOCs on $P(\text{O}_3)_{\text{net_Missing}}$. We have changed the sentence “...This value was then used to compensate for the unmeasured VOCs in the model (with a daytime k_{OH} compensation range of 1.2–2.4 s⁻¹). Based on the significant contribution of OVOCs to $P(\text{O}_3)_{\text{net_Missing}}$ mentioned earlier, we designed three modelling scenarios to compensate for $k_{\text{OH_Missing}}$, with the specific multiples varying each day: (1) Case E₁: by expanding the constrained overall VOCs concentrations in

Case D₁, the daily TVOC concentration was increased by 1.1 to 1.7 times; (2) Case E₂: according to k_{OH} ratio of NMHC to OVOCs in the constrained VOCs of Case D₁, the concentrations of ethylene (a representative NMHC species) and formaldehyde (OVOCs indicator) were expanded separately. The ethylene concentration was increased by 5.9 to 85.6 times, and the formaldehyde concentration was increased by 1.4 to 2.0 times; (3) Case E₃: by expanding only the formaldehyde concentration to compensate for $k_{OH_Missing}$, in this case, the daily formaldehyde concentration was increased by 1.8 to 9.2 times, to verify the role of OVOCs in compensating for $P(O_3)_{net_Missing}$ to “...This value was then used to compensate for the unmeasured VOCs in the model (with a daytime k_{OH} compensation range of 1.2–2.4 s⁻¹, approximately 27.6–45.1% of missing values). Based on the significant contribution of OVOCs to $P(O_3)_{net_Missing}$ mentioned earlier, we designed three modelling scenarios to compensate for $k_{OH_Missing}$, with the specific multiples varying each day. We note that these scenarios are idealized sensitivity tests to explore potential bounds of OVOCs’ contribution to $P(O_3)_{net_Missing}$ compensation, rather than realistic emission assumptions. Specifically, we tested how much the $P(O_3)_{net_Missing}$ could be accounted for if the k_{OH} were attributed to different VOCs categories. The specific scenarios include: (1) Case E₁: by expanding the constrained overall VOCs concentrations in Case D₁ (daily mean compensation range for TVOCs: 0.5–2.8 µg m⁻³), the daily TVOC concentration was increased by 1.1 to 1.7 times; (2) Case E₂: according to k_{OH} ratio of NMHC to OVOCs in the constrained VOCs of Case D₁, the concentrations of ethylene (a representative NMHC species) and formaldehyde (OVOCs indicator) were expanded separately. The ethylene concentration (daily mean compensation range for TVOCs: 0.5–2.8 µg m⁻³) was increased by 5.9 to 85.6 times, and the formaldehyde concentration (daily mean compensation range for TVOCs: 0.0–0.5 µg m⁻³) was increased by 1.4 to 2.0 times; (3) Case E₃: by expanding only the formaldehyde concentration to compensate for $k_{OH_Missing}$, in this case, the daily formaldehyde concentration (daily mean compensation range for TVOCs: 0.6–1.4 µg m⁻³) was increased by 1.8 to 9.2 times, to verify the role of OVOCs in compensating for $P(O_3)_{net_Missing}$.” in lines 445-459 in the modified manuscript.

Line 485: It is not necessary to add legends to every subgraph in Fig. 6. Simplification can be considered.

Okay, we have removed the redundant legends in Fig. 6. See lines 517–520 in the modified manuscript:

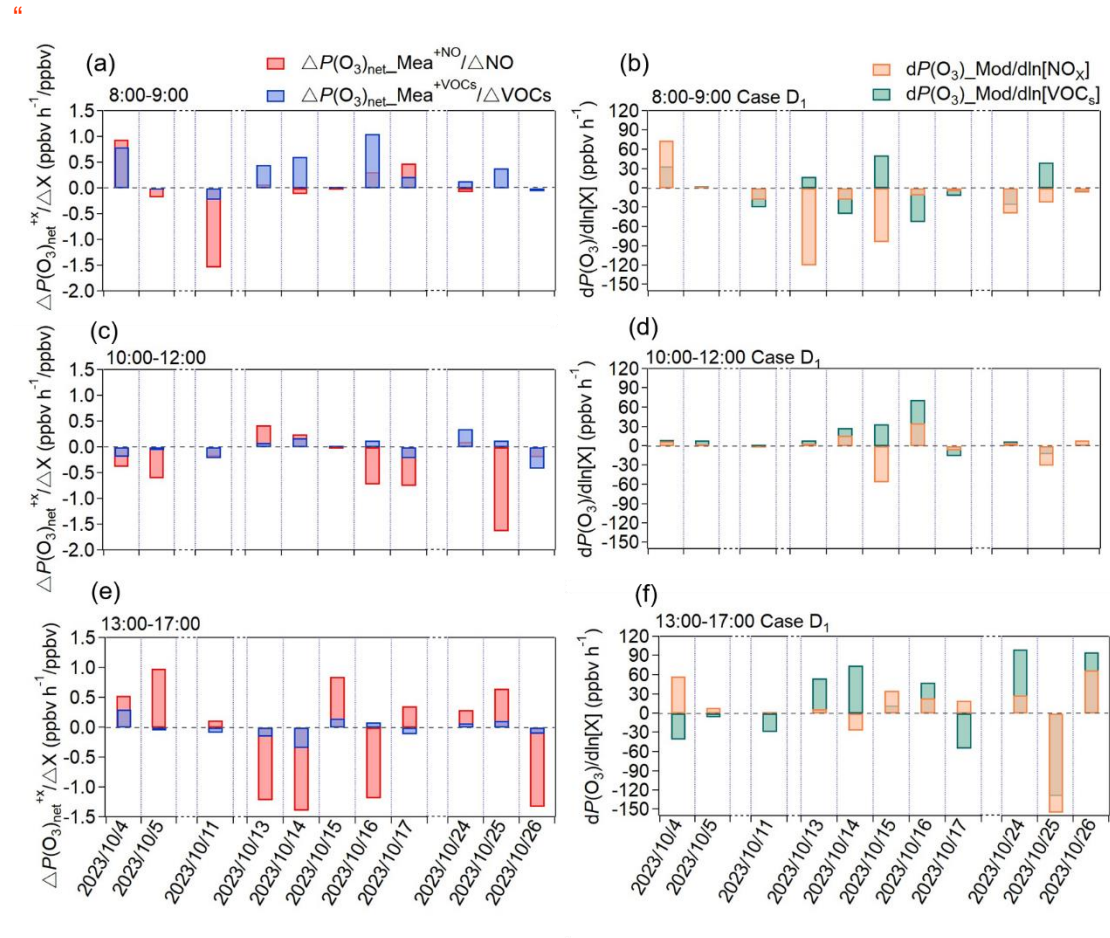


Figure 6: Average values of IR derived from the direct measurement data using the NPOPR detection system (e.g., $\Delta P(O_3)_{net}^{+NO}$ and $\Delta P(O_3)_{net}^{+VOCs}$) and absolute $P(O_3)_{net}$ sensitivity from the box model during (a)–(b) $P(O_3)_{net}$ rising phase (8:00–9:00) ; (c)–(d) $P(O_3)_{net}$ stable phase (10:00–12:00) (e)–(f) $P(O_3)_{net}$ declining phase (13:00–17:00)."

Lines 519-521: The conclusion repeatedly emphasizes the role of OVOCs in O₃ formation and compensation, yet it assumes these are mainly anthropogenic in origin. As noted earlier, many OVOCs are also formed secondarily. It is recommended that you should distinguish between primary and secondary OVOC contributions or clearly state the limitation of their current attribution.

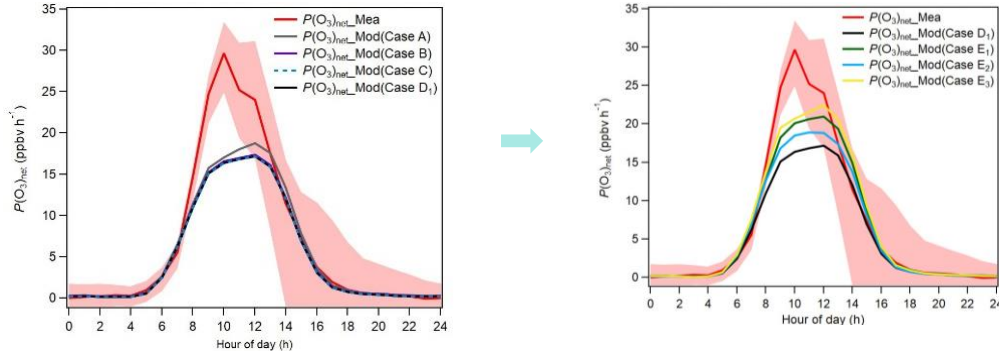
Thank you for your suggestion. We agree with the reviewer that it is not appropriate to say "These species are mainly emitted by anthropogenic emissions", as the OVOCs are also formed secondarily from both anthropogenic and natural emissions. Therefore, we have deleted this sentence and added the related discussion in lines 289-293 in the modified manuscript:

"As OVOCs arise from both direct (anthropogenic and natural) emissions and secondary atmospheric formation (Lyu et al., 2024; Yuan et al., 2012), precluding a direct quantification of their respective contributions to O₃ formation. Nevertheless, our previous work showed that

anthropogenic primary VOCs correlate most closely with instantaneous $P(O_3)_{net}$ on O_3 pollution days, and urban anthropogenic OVOC emissions markedly enhance both oxidative capacity and O_3 production (Qian et al., 2025; Wang et al., 2024b)."

Appendix:

- (1) We detected an error in Fig. 3b, therefore, we changed the diurnal variations of $P(O_3)_{net_Mea}$ and $P(O_3)_{net_Mod}$ (Case A–D₁) to diurnal variations of $P(O_3)_{net_Mea}$ and $P(O_3)_{net_Mod}$ (Case D₁–E₃) in Fig. 3b.



- (2) The calculation method of the absolute $P(O_3)_{net}$ is adapted from the logarithmic derivative approach of Sakamoto et al. (2019). Therefore, We have changed the sentence "We calculated the modelled OFS using the absolute $P(O_3)_{net}$ sensitivity method from Sakamoto et al. (2019). It is defined as the change in $P(O_3)_{net}$ induced by a percentage increase in O_3 precursors. This method facilitates the quantitative assessment of how reductions in O_3 precursors contribute to the overall reduction of $P(O_3)_{net}$ over a period or within a region. The formula is as follows:

$$\text{Absolute } P(O_3)_{net} = \frac{\delta P(O_3)}{\delta \ln[X]} = P(O_3) \frac{\delta P(O_3)}{\delta \ln[X]} \quad (10)" \text{ to}$$

"We calculated the modelled OFS using the absolute $P(O_3)_{net}$ sensitivity adapted from the logarithmic derivative approach of Sakamoto et al. (2019). It is defined as the change in $P(O_3)_{net}$ for the natural logarithm of O_3 precursor concentrations. This method facilitates the quantitative assessment of how reductions in O_3 precursors contribute to the overall reduction of $P(O_3)_{net}$ over a period. The formula is as follows:

$$\text{Absolute } P(O_3)_{net} = \frac{dP(O_3)_{net}}{d \ln[X]} \quad (10)"$$

in lines 224-228 in the modified manuscript.

References

- Baier, B. C., Brune, W. H., Miller, D. O., Blake, D., Long, R., Wisthaler, A., Cantrell, C., Fried, A., Heikes, B., and Brown, S.: Higher measured than modeled ozone production at increased NO_x levels in the Colorado Front Range, *Atmospheric Chemistry and Physics*, 17, 11273-11292, <http://doi.org/10.5194/acp-17-11273-2017>, 2017.
- de Gouw, J. A., Warneke, C., Parrish, D. D., Holloway, J. S., Trainer, M., and Fehsenfeld, F. C.: Emission sources and ocean uptake of acetonitrile (CH₃CN) in the atmosphere, *Journal of Geophysical Research-Atmospheres*, 108, 4329, <https://doi.org/10.1029/2002JD002897>, 2003.
- de Gouw, J., Middlebrook, A., Warneke, C., Goldan, P., Kuster, W., Roberts, J., Fehsenfeld, F., Worsnop, D., Canagaratna, M., and Pszenny, A.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *Journal of Geophysical Research-Atmospheres*, 110, D16305, <https://doi.org/10.1029/2004JD005623>, 2005.
- Lyu, X., Li, H., Lee, S.-C., Xiong, E., Guo, H., Wang, T., and de Gouw, J.: Significant Biogenic Source of Oxygenated Volatile Organic Compounds and the Impacts on Photochemistry at a Regional Background Site in South China, *Environmental Science & Technology*, 58, 20081-20090, <http://doi.org/10.1021/acs.est.4c05656>, 2024.
- Morino, Y., Sadanaga, Y., Sato, K., Sakamoto, Y., Muraoka, T., Miyatake, K., Li, J., and Kajii, Y.: Direct evaluation of the ozone production regime in smog chamber experiments, *Atmospheric Environment*, 309, 119889, <http://doi.org/10.1016/j.atmosenv.2023.119889>, 2023.
- Qian, H., Xu, B., Xu, Z., Zou, Q., Zi, Q., Zuo, H., Zhang, F., Wei, J., Pei, X., and Zhou, W.: Anthropogenic Oxygenated Volatile Organic Compounds Dominate Atmospheric Oxidation Capacity and Ozone Production via Secondary Formation of Formaldehyde in the Urban Atmosphere, *ACS ES&T Air*, <http://doi.org/10.1021/acsestair.4c00317>, 2025.
- Sakamoto, Y., Sadanaga, Y., Li, J., Matsuoka, K., Takemura, M., Fujii, T., Nakagawa, M., Kohno, N., Nakashima, Y., and Sato, K.: Relative and absolute sensitivity analysis on ozone production in Tsukuba, a city in Japan, *Environmental science & technology*, 53, 13629-13635, <http://doi.org/10.1021/acs.est.9b03542>, 2019.
- Sklaveniti, S., Locoge, N., Stevens, P. S., Wood, E., Kundu, S., and Dusanter, S.: Development of an instrument for direct ozone production rate measurements: Measurement reliability and current limitations, *Atmospheric Measurement Techniques*, 11, 741-761, <http://doi.org/10.1029/98jd00349>, 2018.
- Wang, W., Yuan, B., Peng, Y., Su, H., Cheng, Y., Yang, S., Wu, C., Qi, J., Bao, F., and Huangfu, Y.: Direct observations indicate photodegradable oxygenated volatile organic compounds (OVOCs) as larger contributors to radicals and ozone production in the

atmosphere, *Atmospheric Chemistry and Physics*, 22, 4117-4128, <http://doi.org/10.5194/acp-22-4117-2022>, 2022.

Wang, W., Yuan, B., Su, H., Cheng, Y., Qi, J., Wang, S., Song, W., Wang, X., Xue, C., and Ma, C.: A large role of missing volatile organic compound reactivity from anthropogenic emissions in ozone pollution regulation, *Atmospheric Chemistry and Physics*, 24, 4017-4027, <http://doi.org/10.5194/acp-24-4017-2024>, 2024.

Yuan, B., Shao, M., De Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., and Zhang, J.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, *Journal of Geophysical Research: Atmospheres*, 117, <http://doi.org/10.1029/2012jd018236>, 2012.

Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., Zeng, L. M., and Hu, M.: VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China, *Atmospheric Chemistry and Physics*, 13, 8815–8832, <https://doi.org/10.5194/acp-13-8815-2013>, 2013.

Zhou, J., Wang, W., Wang, Y., Zhou, Z., Lv, X., Zhong, M., Zhong, B., Deng, M., Jiang, B., and Luo, J.: Intercomparison of measured and modelled photochemical ozone production rates: Suggestion of chemistry hypothesis regarding unmeasured VOCs, *Science of The Total Environment*, 951, 175290, <http://doi.org/10.1016/j.scitotenv.2024.175290>, 2024a.

Zhou, J., Zhang, C., Liu, A., Yuan, B., Wang, Y., Wang, W., Zhou, J.-P., Hao, Y., Li, X.-B., and He, X.: Measurement report: Vertical and temporal variability in the near-surface ozone production rate and sensitivity in an urban area in the Pearl River Delta region, China, *Atmospheric Chemistry and Physics*, 24, 9805-9826, doi: 10.5194/acp-24-9805-2024, 2024b.