**A point-to-point response to referee #1**

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Title: "Reconstructed VOC emissions reveal hidden ozone precursors: Overlooked roles of primary OVOCs and unmeasured species"

Author(s): Sijia Yin, Gan Yang, Chuang Li, Qingyan Fu, Juntao Huo, Yuruo Fu, Rengqi Yan, Lei Yao, and Lin Wang

We sincerely thank referee #1 for his/her careful reading and constructive comments, which have helped us substantially to clarify and strengthen the manuscript. We address each comment in turn below. Reviewer's comments appear in *red italics*, our responses in black, and the revised manuscript text in blue. All changes are highlighted in the revised manuscript. Line numbers refer to those in the revised manuscript.

1. *In this study, the authors reconstruct VOC emissions at a suburban site in Shanghai and estimate ozone formation potential based on reconstructed results. The topic is within the scope of ACP. However, in my point of view, this study does not provide sufficient novel insights into VOC emissions for promoting the understanding of ozone pollution in China. The overall framework remains largely an extension of conventional OFP calculations based on MIR by Carter et al, while the observations are limited by discontinuous sampling and a single-site dataset.*

**Response:** We appreciate referee #1's recognition that the topic of our manuscript falls within the scope of ACP. We respectfully wish to clarify, however, that the contribution of this study is not a further application or extension of the MIR-based OFP framework, but rather **the explicit quantification of a systematic bias that stems from observation-based OFP analysis**. We summarize the core message and the major revisions we have made in this overall reply, with detailed responses to individual concerns.

Previous OFP studies in China have been carried out using observed (i.e., photochemically aged) VOC concentrations as a proxy for emissions. We show that this practice introduces a substantial and directional bias: it underestimates the OFP of NMHCs by 31.7% and overestimates the OFP of OVOCs by 42.6% for the Dianshan Lake supersite during the campaign period, while simultaneously hiding the role of (1) primary OVOCs, which we show contributed 33.2% of the initial total OFP, and (2) unmeasured VOCs as reflected by the missing OH reactivity, which contributed an additional 14.5%. These three key findings, i.e., the bias

itself, the importance of primary OVOCs, and the importance of unmeasured species, are not captured by conventional MIR-based analyses or by previously reported source apportionments of ambient OVOCs.

Major revisions are made in response to this and the subsequent comments:

(1) The framing of the manuscript has been sharpened to clearly show that the novelty of this study lies in quantifying an aging-induced bias that is *independent of the reactivity metric* used (Sect. 1 and Sect. 4).

(2) Additional discussion on the methodological limitations of the MIR metric has been added (Sect. 2.5), and policy implications have been toned down to emphasize on identification of key ozone ($O_3$) precursors rather than estimating actual $O_3$ production under ambient conditions (Sect. 4).

(3) The dataset coverage has been clarified. The apparent gaps in Fig. 1, i.e., shaded nighttime periods (18:00–07:00 LT) that are excluded as a prerequisite of photochemical aging, are not missing data (Sect. 2.2 and Fig. 1).

(4) The daytime VOCs detected by Vocus PTR-ToF-MS and OH-reactivity dataset has been deposited on Zenodo (https://doi.org/10.5281/zenodo.18932275) and Figshare (https://figshare.com/s/d42bb104b4329bad7ee2) for transparency.

Detailed point-by-point responses are provided after each comment.

2. *The most significant concern is that this work relies on MIR-based OFP estimation derived from Carter et al, which remains a highly simplified reactivity metric rather than a process-resolving representation of ozone production. In recent years, many studies in China have already highlighted the limitations of conventional MIR/OFP approaches and have proposed more localized or observation-constrained methods to diagnose ozone precursor importance under region-specific chemical regimes. Although the authors attempt to reconstruct initial VOC concentrations and correct biases arising from photochemical aging, the analysis still builds on a simple OFP framework rather than a more rigorous assessment.*

**Response:** We agree with referee #1 that the MIR-based OFP framework (Carter, 1994, 2010) is a simplified reactivity metric that does not resolve $O_3$ production chemistry under region-specific conditions, and we appreciate the referee's emphasis on this point. We respectfully note, however, that **the bias we quantify in this study is independent of the reactivity metric employed**. This bias propagates into every observation-based OFP study regardless of the metric chosen (Zheng and Xie, 2025), including those that adopt more localized or observation-constrained metrics mentioned by the referee (Ma et al., 2022b).

The root cause of the bias as discussed in our manuscript is not how reactivity is weighted, but which concentrations enter the calculation. If observed (i.e., photochemically aged) concentrations are used, i.e., alkenes and aromatics have already been depleted by OH radicals and OVOCs have already been produced, reactivity weighting (MIR, OH reactivity, and MCM-derived ozone production rate) will inherit the same directional bias. Thus, the key contribution of the present work is to quantify and correct this concentration-side bias, which is logically prior to the choice of reactivity metric.

We choose the MIR-based OFP for three practical reasons:

(1) MIR is transparent, fully documented (Carter, 1994, 2010), and species-resolved at the level needed for the present analysis (191 of the 321 measured VOCs possess documented MIR values).

(2) MIR remains the standard metric for identifying key $O_3$ precursors and therefore enables direct comparison with previous studies; notably, the most directly comparable recent study - Zheng and Xie (2025), published in *Atmos. Chem. Phys*. precisely on the question of emitted-versus-ambient concentrations - also employs the MIR-based OFP framework, indicating that it is an accepted and appropriate metric for this class of analysis.

(3) It remains an operative metric in current emission inventory and regulatory frameworks for $O_3$ precursor management in China (Gu et al., 2021; Huang et al., 2021; Ma et al., 2022a).

In other words, we adopt MIR not because we consider it as the most physically faithful metric, but because this practice isolates the concentration-side bias as the single variable under examination. A method that simultaneously changes both the concentrations and the reactivity metric would be hard to attribute the resulting differences to either factor unambiguously.

To address the reviewer's concern, we have added the following explicit caveat in the revised manuscript (Sect. 2.5, lines 196–199): "Additionally, it should be noted that MIR-based OFP represents a simplified reactivity metric under idealized conditions and does not explicitly account for region-specific chemical regimes. The OFP values reported in this study should therefore be interpreted as relative indicators of precursor reactivities, rather than direct representations of $O_3$ production under ambient conditions."

3. *Another major concern is the very short sampling period and the quality of the VOC observations. As shown in Figure 1, VOC observations contain substantial missing periods, especially during the first three weeks of August, where only intermittent measurements are available and the time series is highly discontinuous. I have serious concerns regarding the quality of the dataset and the robustness of the source apportionment as well as reconstruction*

*results. When the observational basis is fragmented to this extent, it becomes difficult to support strong quantitative statements regarding the relative contributions of OVOCs, NMHCs, and unmeasured species to ozone precursor budgets.*

**Response:** The campaign extended from 1 August to 15 September 2020 (46 days), during which VOC measurements from three state-of-the-art instrument systems were performed for more than 40 days. Considering that periods with a simultaneous availability of all measurements are required for photochemical age-based parameterization method (PAPM) fitting, the valid fitting data for each OVOC species ranges from 191 daytime hours (acetone) to 324 daytime hours (formaldehyde and acetaldehyde), with most OVOCs exceeding 300 hours. The robustness of our PAPM fits is reflected in the correlation coefficients R = 0.40–0.90 across the 208 OVOCs (Tables S3 and S4). The daytime concentrations of VOCs detected by Vocus PTR-ToF-MS has been deposited on Zenodo (https://doi.org/10.5281/zenodo.18932275) to enable an independent verification.

In addition, we would like to clarify that the apparent "gaps" in the concentration profiles do not represent missing VOC measurements, but correspond to nighttime periods (18:00–07:00 local time), which were intentionally excluded from the analysis and shown as shaded regions in the figure, because the PAPM is based on the assumption that VOC removal is dominated by OH radical reactions during daytime photochemical conditions (07:00–18:00 local time). Nighttime observations, during which $NO_3$ radical chemistry becomes important, fall outside the scope of the PAPM framework and are therefore not included in the reconstruction analysis.

4. *Another key issue is that the importance of OVOCs in Chinese urban and suburban atmospheres, including their sources, formation pathways, and contribution to ozone chemistry, has already been extensively investigated in previous studies, including many conducted in the Pearl River Delta, Yangtze River Delta, and other heavily polluted regions of China. Compared with prior studies, this analysis is based on a single suburban site with limited available data points. The authors rely on only approximately three weeks of available VOC observations for their analysis. It remains unclear whether the key conclusion regarding the contribution of directly emitted OVOCs would be changed if the sampling period were extended to a full season or even an annual scale.*

**Response:** We thank referee #1 for this important comment. We agree that OVOCs have been extensively studied in Chinese urban and suburban atmospheres, particularly in terms of their ambient concentrations and roles in $O_3$ chemistry (Huang et al., 2020; Hui et al., 2023).

However, we respectfully clarify that the present study addresses a distinct and previously underexplored problem that goes beyond characterizing ambient OVOCs.

The objective of this study is not to further characterize ambient OVOC concentrations or their general role in $O_3$ chemistry, but rather to evaluate the contribution of directly emitted (primary) OVOCs at the emission stage by reconstructing initial VOC compositions from ambient observations. This distinction is critical: **ambient OVOC concentrations measured at a receptor site inevitably contain a substantial secondary fraction generated during the atmospheric transport, meaning that OFP estimates derived directly from observed OVOC concentrations will systematically overestimate the true OFP of primary OVOCs.** To our knowledge, this overestimation bias has been explored, but not explicitly quantified across the broad range of OVOCs in prior studies, which represents a key target of the present work.

To clarify this point, we have added the following statement to the revised manuscript, which reads,

(Lines 44-46): "This bias has recently been demonstrated by reconstructing emitted concentrations from ambient observations, which revealed that observation-based OFP underestimates reactive NMHCs and overestimates OVOCs (Zheng and Xie, 2025)."

and (Lines 51-52): "However, this overestimation bias in the OFP of OVOCs has been previously explored, but not for a broad range of OVOCs detected by multiple state-of-the-art instruments.",

Regarding representativeness of this study, we agree that inherent limitations exist for a single summer campaign at one suburban site, and we now explicitly acknowledge this point in the "Atmospheric implications" section (Lines 434-438): "On the other hand, given that these findings are based on observations from a single suburban site in Shanghai during summer, the spatial and seasonal representativeness of these results is inherently limited. While the quantitative contributions may vary across seasons and regions, the bias identified here is driven by photochemical aging and is expected to be generally applicable. Future investigations across diverse geographical regions and seasons are therefore warranted to evaluate the broader applicability of these conclusions."

We would additionally note that summer represents the most policy-relevant season for ozone control in Shanghai, where $O_3$ exceedances are most frequent and severe, and where photochemical processing is most intense. The bias between observed and reconstructed VOC concentrations is expected to be largest under summertime conditions. While the quantitative results may vary across seasons, the directional conclusion that ambient observations

overestimate OVOC's OFP and underestimate NMHC's OFP is expected to hold under conditions where photochemical aging occurs during atmospheric transport. The reconstruction framework developed here is season-independent and broadly applicable to future multi-season investigations.

5. *In the Atmospheric implications section, the authors suggest that this work supports a shift toward reactivity-based VOC management. However, a critical issue is overlooked: how important are these OVOCs for ozone pollution? In other words, what is their contribution to ozone levels in Shanghai under ambient conditions? This is a central question that the study should address. A more rigorous analysis, such as using an MCM-based box model, is essentially needed to quantify and elucidate the contribution of OVOCs to ozone formation.*

**Response:** We fully agree with referee #1 that quantifying the absolute contribution of OVOCs to ambient $O_3$ levels requires process-based chemical modeling (e.g., an MCM box model constrained by the full set of observed precursors, radicals, and meteorology). We also agree that the original manuscript overstated the policy implications by suggesting a shift in VOC management strategies on the basis of an OFP analysis alone.

We have therefore (1) toned down the policy language, which reads (Sect. 4, lines 438–442): "Consequently, by clarifying the OFP of a broader range of VOCs at the emission stage, this work provides an integrated observational–diagnostic framework that bridges ambient measurements with source emissions, offering a more robust tool for identifying key $O_3$ precursors and informing the design of future process-based modeling studies."

and (2) added an explicit caveat distinguishing OFP from actual $O_3$ production, which reads (Sect. 4, lines 423–426): "It should be emphasized, however, that the OFP reported in this study represents a relative reactivity metric rather than an estimate of actual $O_3$ production under ambient conditions. Quantifying the contribution of primary OVOCs and unmeasured species to ambient $O_3$ levels at the DSL site will require future work integrating detailed chemical mechanism modeling."

Again, we would like reiterate the scope of this study. OFP is a relative reactivity metric for ranking precursors at the emission stage, not a predictor of ambient $O_3$ mixing ratios. Process-based modeling and OFP analysis answer two complementary questions: the former provides how much $O_3$ is produced from a given air mass, while the latter gives which precursors should be prioritized for emission reduction. Our reconstruction framework addresses the second question without claiming to address the first.

We fully endorse the use of MCM-based box modeling in a future work to translate the reconstructed initial OFP into absolute contributions to ambient $O_3$, and we believe the reconstructed daytime emission composition reported here, together with the deposited dataset, provides a useful input for such studies.

6. *In terms of the comprehensiveness of the data and the scientific insights presented in the manuscript, I think this paper does not qualify as a research article in its current form in ACP.*

**Response:** We respect the referee's overall judgment, and we have taken the opportunity offered by these comments to substantially revise and strengthen our manuscript. We respectfully hope that, in its revised form, the manuscript provides a clearly defined and quantitatively original contribution that meets the standards of an ACP research article.

We note that the scientific motivation of this work - that observation-based OFP systematically misranks $O_3$ precursors because it uses photochemically aged rather than emitted concentrations - was very recently recognized by a previous paper in *Atmos. Chem. Phys*.( Zheng and Xie 2025), which employed a similar MIR-based OFP framework used here, and established the validity and importance of the reconstruction approach, but only for a limited species set (86 NMHCs and 13 OVOCs measured by GC-MS/FID with no treatment of unmeasured VOCs). The present study advances substantially beyond that of Zheng and Xie (2025) study in both scope and conclusion:

(1) Extension of the PAPM source apportionment to 208 OVOCs, compared with the 3–13 species (e.g., formaldehyde, acetaldehyde, acetone) treated in previous PAPM applications in China.

(2) Using concurrent missing-OH-reactivity measurements, we attribute and reconstruct the initial concentrations of unmeasured species, showing that they contribute 14.5% of the initial total OFP - a fraction systematically omitted from conventional OFP analyses, including all prior reconstruction studies.

(3) Following (1) and (2), we find that primary OVOCs (33.2% of initial TOFP) and unmeasured species (14.5%) together rival NMHCs (52.3%) as $O_3$ precursors at the emission stage. This conclusion contrasts with that of prior reconstruction work, where the OFP was dominated by NMHC alkenes, aromatics, and isoprene - a difference that shifts the implied control priority from a few reactive NMHCs toward the previously overlooked oxygenated and unmeasured fractions.

To make this advance more explicit and to position our results transparently against the most directly comparable published work, we have added a dedicated quantitative comparison

with Zheng and Xie (2025), which reads (Lines 386-400): "Our results are qualitatively consistent with, yet quantitatively and conceptually distinct from, those of Zheng and Xie (2025), who compared reconstructed primary emitted versus ambient VOC concentrations at three sites in the Sichuan Basin. Both studies found that NMHCs, particularly alkenes and aromatics, were underestimated in OFP estimation when using observed rather than primary emitted concentrations, while OVOCs' OFP were overestimated. Specifically, Zheng and Xie (2025) found that OVOCs' OFP in Chengdu decreased from 171.9 to 88.4 μg $m^{-3}$ when emitted rather than ambient concentrations were used (~95% overestimation), consistent with the 42.6% overestimation identified here; conversely, the OFP of reactive NMHCs increased, mirroring the 31.7% underestimation for NMHCs at the DSL site. For individual species, isoprene, acetaldehyde, propylene, m&p-xylene, ethylene, toluene, and o-xylene were consistently identified as key $O_3$ precursors, reinforcing their priority status in $O_3$ control strategies. Notably, a key distinction is that our study covers a far broader range of VOC species, encompassing 321 measured VOC species (113 NMHCs and 208 OVOCs), together with $R_{OH}$ inferred unmeasured species, compared to the 99 species (86 NMHCs and 13 OVOCs) analyzed by Zheng and Xie (2025). This broader coverage enables us to attribute 33.2% and 14.5% of initial TOFP to primary emitted OVOCs and unmeasured species. The two studies are thus complementary rather than hierarchical: Zheng and Xie (2025) additionally resolved nighttime $NO_3/O_3$-driven alkene loss, whereas our reconstruction focuses on the daytime OH-dominated window to characterize a broader range of oxygenated and unmeasured species."

Again, we are very grateful to referee #1, whose critical reading has clearly improved both the framing and the rigor of the manuscript.

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