A point-to-point response to referee #2

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

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We sincerely thank referee #2 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. *The work presented by Yin et al., highlights the importance of chemical aging from primary emissions and the inconsistency of neglecting this in measurement based ozone formation potential studies and associated impacts on air quality management policies. By tracing the atmospheric composition back to primary emission mixtures that are aged chemically, they are able to associate the ozone formation potential to primary emitted compounds and asses their integrated impact on atmospheric chemistry.*

Results are obtained from a limited dataset obtained during summer in a suburban region. While this limits the overall implications and may introduce a bias in their interpretation, the authors do acknowledge this in their last section. I hope to see similar evaluations at different locations and seasons to see how results compare to the assessment made in the current publication.

The work is presented clearly and I appreciated the high quality of writing. However, one major concern about the data availability and some minor remarks should be resolved before I can recommend publication.

Response: We are grateful for this constructive evaluation from referee #2. We have carefully addressed all concerns in the following response, particularly regarding the data availability.

2. *According to the ACP data policy authors are required to provide a statement on how their underlying research data can be accessed. The data deposited in the doi reflect data shown in the figures from the paper and are not sufficient for reproducing the analysis. Please make the*

calculated concentrations from the measurement campaign available either here or through a separate paper submitted to ESSD in accordance to the ACP data policy suggestion.

Response: We fully accept the importance of data availability and, in line with the ACP data policy, have deposited the portion of the campaign dataset that we are permitted to release publicly. Specifically, the deposited dataset includes:

(1) Hourly-averaged measured concentrations of 252 unspecified VOC species (57 unspecified NMHCs and 195 unspecified OVOCs) detected by Vocus PTR-ToF-MS;

(2) Hourly-averaged reconstructed concentrations of these Vocus-detected species from emission sources; and;

(3) Hourly-averaged measured and calculated total OH reactivity;

We note, however, that the concentrations of the 56 Photochemical Assessment Monitoring Station (PAMS) compounds and 13 carbonyls measured by the GC-MS/FID and Kore PTR are part of a routine monitoring network and are not publicly available due to data privacy regulations. These data can be made available only with permission of the Shanghai Environmental Monitoring Center. The deposited Vocus-detected species nonetheless cover the majority of the analyzed compounds (252 of 321), and the data availability statement has been updated accordingly (Lines 445–450): "The measured and reconstructed concentrations of VOCs detected by Vocus PTR-ToF-MS are available at https://doi.org/10.5281/zenodo.18932275 (Yin, 2026). The measured and calculated OH reactivity are available at https://figshare.com/s/d42bb104b4329bad7ee2 (Yang et al., 2022). The concentrations of PAMS compounds and carbonyls measured by GC-MS/FID and Kore PTR are part of a routine monitoring network and are not publicly available due to data privacy regulations; these data can be made available from the corresponding author only with permission of the Shanghai Environmental Monitoring Center."

3. - *L 48-50; Traditional source apportionment methods like PMF do resolve secondary sources, though limitedly. E.g., source factors identified by PMF that are the dominant source of MVK/MACR are usually identified as a "secondary biogenic factor". The high simplification being that chemical ageing of primary emissions is assumed to be a linear combination of the primary and the secondary factor which does not allow for differences in chemical lifetime of primary compounds. Your analysis has the edge because it explicitly traces back the secondary source factors to the origins. Please be more precise in your discussion.*

Response: Referee #2 is absolutely correct that receptor-based methods such as PMF can identify secondary factors (e.g., a "secondary biogenic" factor dominated by MVK and MACR). Our original wording inadvertently overstated their limitation.

We would like to clarify that our original intention was not to suggest that receptor-based methods such as PMF cannot resolve secondary sources. Instead, we aimed to emphasize that these approaches rely on observed VOC concentrations as input and do not explicitly account for photochemical processing during atmospheric transport. As a result, the observed concentrations may deviate from the original emission composition, which can introduce uncertainties in source apportionment.

To avoid misunderstanding, we have revised our statement in lines 54-57: "Commonly used VOC source appointment approaches, including principal component analysis, positive matrix factorization, and chemical mass balance, generally rely on observed VOC concentrations as input without explicitly accounting for photochemical losses of VOCs during atmospheric transport, and thus could introduce uncertainties in source apportionment results."

4. - *L 199-203; Please make a clearer separation between your results (identification of an anthropogenic source), and discussion (which anthropogenic activities emit these compounds). As I understood the analysis, you cannot resolve sector based sources which is inconsistent with the formulation of most notably L 199-200.*

Response: We fully agree that our analysis does not resolve sector-specific anthropogenic sources. The original wording inadvertently suggested an application that our method cannot provide. We have therefore revised our statement in lines 241-247: "Specifically, $C_nH_{2n}O_2$ (n=2-8) were predominantly attributed to primary anthropogenic sources (34.7-84.4%). These compounds are likely alkanoic acids, which have been previously linked to emissions from traffic and agricultural activities (Mattila et al., 2018). Similarly, compounds such as $C_6H_{14}O_2$, $C_9H_{10}O$, $C_2H_3NO_2$, C_3H_7NO, C_5H_9NO, and $C_6H_5NO_3$ were also mainly associated with anthropogenic primary emissions (> 50%). These species are likely solvents and amides, with potential sources including industrial processes, volatile chemical products, and wildfire, as reported by previous studies (Salvador et al., 2024; Zhang et al., 2024)."

5. - *L 35; grammatical error, remove "the" before "smog chambers"*

Response: Corrected.

We note, in response to a related suggestion from Referee #3, that the phrase "added in the smog chambers or numerical simulations" is removed entirely (because the precise origin of the MIR values is not essential at this point of the introduction), which reads (Lines 37-40), "By definition, the MIR coefficient quantifies the mass of O_3 formed per unit mass of a freshly emitted VOC (i.e., before any photochemical processing) (Carter, 1994, 2010); a physically consistent OFP must therefore be evaluated from the initial emission concentrations rather than from ambient observations."

6. - *L 113; Please remain consistent in naming between the formula and the explanation (i.e., choose between NMHC or VOC here).*

Response: We have unified the notation as "NMHC" throughout Eq. (2) and its description, which reads (Lines 126-128): "

$$[\mathrm{NMHC}_{i,j}]_{\mathrm{source}} = [\mathrm{NMHC}_{i,j}]_{\mathrm{t}} \times \exp(k_i[\mathrm{OH}]\Delta \mathrm{t}_j) \quad (2)$$

where $[\mathrm{NMHC}_{i,j}]_{\mathrm{source}}$ is the initial concentration of NMHC species i from the j^{th} source; $[\mathrm{NMHC}_{i,j}]_{\mathrm{t}}$ is the observed concentration of NMHCs species i from the j^{th} source (including anthropogenic and biogenic sources);"

References:

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