

Reviewer 3

General comments:

Katz et al uses long-standing flux measurements at a site in Berkely California and couples them with intermittent mobile laboratory measurements throughout the broader region to identify OVOCs (ethanol, methanol, acetaldehyde) that contributed heavily to the molar flux and OH reactivity flux. The combined methodologies cover broad spatial and temporal scales and evaluates the results with current emissions inventories. This is a well-written manuscript, though, I have a few questions regarding the source attributions, assumptions, uncertainties, and spatial scale mismatches with the emissions inventories that should be addressed before publications. Overall, this is an impressive dataset and analysis, though limited in scope by the footprint representativeness.

We thank the reviewer for the thoughtful comments.

Specific comments:

Cooking ethanol:nonanal ratio: The derived cooking-specific ethanol:nonanal ratio was determined as 80 using a 10th percentile "lower edge" daytime flux fit. While this matches specific indoor stir-fry experiments (Arata et al., 2021: 75), it is more than double the regional, observationally constrained ratios of 37 utilized in recent Los Angeles chemical transport models (Zhu et al., 2025), which are based on LA airborne fluxes and integrated HOMEChem profiles (Arata et al., 2021: 40.2). It is also much higher than the values determined from PMF source apportionment that the GRAPES inventory was initially built upon (Coggon et al., 2024;11). These differences can really drive the conclusions of this work, significantly modifying the daytime ethanol flux attributed to cooking and the subsequent residual determinations of VCPs.

We thank the reviewer for pointing this out. While we were preparing this manuscript, we also noticed a large range of ethanol/nonanal ratios throughout the literature. We believe that the approach outlined in the manuscript and updated per the second reviewer's suggestions (see above) provides the most robust and representative ratio for this specific study domain. Other ratios may be more suitable for those specific studies. The ratio from Arata et al. also includes the Thanksgiving day experiment, which included many different cooking styles.

→Can you explain how these discrepant spatial scales reconcile (local high-density commercial tower footprint of 2.8 km² vs. integrated regional airborne flights).

In this manuscript, we did not directly compare our quantitative flux results to flight campaign results. However, comparing the spatial scales should not be an issue because fluxes are normalized to the surface area, i.e., the unit is nmol m⁻² s⁻¹ or similar (e.g., mg km⁻² h⁻¹). Since our flux footprint is more focused than flight campaigns, comparing e.g., campaign medians, should consider relevant metrics including population density, temperature, etc. Future analyses that involve such comparisons should consider comparing similar geographic areas. For instance,

a flight campaign that covers a dense commercial and residential city center could compare those specific geographical results to our results.

→Can you demonstrate that the 10th percentile fit isolated pure cooking rather than co-located, temperature-independent VCP solvent or mobile emissions, maybe color the scatter plot in Figure S9 by the benzene:ethanol ratio.

Thank you for the suggestion. We assess the lower edge of the ethanol/nonanal scatter plot in detail in our response to Reviewer 2.

→Can you provide a quantitative assessment showing how varying this ratio impacts the absolute molar flux distribution of ethanol.

We thank the reviewer for the question, but varying the ethanol/nonanal ratio would not impact the absolute molar flux we determined for ethanol.

→Can you confirm which specific ratio the GRA2PES inventory applies (i.e., is it PMF-based or scaled up using HOMEChem and flux measurements?).

The ratio we report from GRA2PES (ethanol/nonanal = 110) is directly from the inventory that we downloaded from NOAA (<https://csl.noaa.gov/groups/csl4/gra2pes/datasets/>). We apologize, but it is unclear how they go from the values reported by Coggon et al. (PMF-based) or Arata et al. (HOMEChem) to the value that is in the publicly available inventory.

Mobile and VCP tracers: It appears as though the total benzene flux is used as a mobile source scalar to establish an upper bound on vehicular ethanol emissions. However, the mobile data demonstrate that benzene co-emits with PCBTF and acetone, pointing to significant solvent/VCP sources of benzene in this urban footprint.

We thank the reviewer for the comment. We would like to clarify that the manuscript text does not state that benzene co-emits with PCBTF and acetone, the direct quote is “Acetone and PCBTF spike correlations were not observed with BTEX spikes, indicating at least two distinct solvent-based acetone sources were sampled: one that includes PCBTF and one that includes BTEX.” We made an adjustment to the language to ensure that correlations do not equal co-emission. It’s possible that solvent-related sources of acetone and PCBTF (e.g., construction) occur near BTEX sources (e.g., motor vehicles). Co-located sources could result in adjacent spike correlations in the maps of Figure 8.

To our knowledge, and following discussions with Brian McDonald, a key developer of the GRA2PES and FIVE-VCP inventories, benzene is not an ingredient in solvents in California. We suspect that the benzene mass used in the mobile data (C₆H₇) could be influenced by fragmentation of substituted aromatics. We added that note in Sect. 2.1.3.

“Also, C₆H₇⁺, the formula for protonated benzene used in the mobile dataset, may be influenced by fragmentation of substituted aromatic VOCs.”

We also added a clarifying note to Sect. 3.3.2 to further address the question.

“Acetone and PCBTF spike correlations were not observed with BTEX spikes, indicating at least two distinct solvent-based acetone sources were sampled: one that includes PCBTF and one that includes BTEX. Benzene is not an ingredient in solvents in California, so acetone correlations with BTEX could indicate that VCP sources were near on-road sources or that C₆H₇⁺, the ion used for benzene detection in the mobile dataset, was influenced by fragmentation of substituted aromatics.”

→Can you discuss how much urban solvent emissions inflate the local benzene flux and quantify how this might lead to a systematic overestimation of the 9% upper-bound on-road ethanol allocation.

We do not suspect that urban solvent emissions inflate the local benzene flux. Benzene is not an ingredient in solvents in California and the GRA2PES inventory does not include any benzene from VCPs.

→How much should we “trust” the GRAPES ethanol to benzene ratio for on-road sources and are there other studies that justify using this ratio for the mobile sector

Previous studies (e.g., Pfannerstill et al. 2023 <https://doi.org/10.1021/acs.est.3c03162>) including this one have shown that VOC emissions inventories like FIVE-VCP and GRA2PES are better at estimating motor vehicle emissions than non-traditional sources of VOCs like VCPs due to decades of previous work in that area. Therefore, we feel confident in the GRA2PES estimates of motor vehicle emissions.

Residual lumping to VCP+: VCPs are treated as a simple residual ("other") without explicit tracers, acting as a grab bag for everything from indoor-to-outdoor exchange to solvent evaporation. Because any uncertainty in the cooking ratio (80) or the vehicle fuel ratio (7.1) directly propagates to this residual...

→are there sector-specific tracers within VCPs that could further elucidate these sources?

Unfortunately, because VCPs are such a broad source category, there is not a specific tracer available. Following a suggestion from Reviewer 2, we decided to change the VCP+ category to be called “other” since we cannot isolate VCP sources using this dataset.

→Can mobile sampling data be leveraged to isolate specific ethanol plumes and associate them or their ratios with co-emitted industrial, construction, or cleaning tracers? Essentially using mobile measurements to “constrain” mobile sources, specific VCP sources, etc. Similar to how fingerprints can be used to constrain PMF.

We thank the reviewer for the thoughtful suggestion. We're focusing on similar ideas (mobile laboratory methodology for pinpointing direct VOC sources in urban areas) in a separate manuscript. Pinpointing precise sources and plume origins via the mobile laboratory is beyond the scope of this work. Instead, we chose to focus on source apportionment with the flux data and use the mobile laboratory to supplement our understanding of the broader urban area.

Biogenic emissions: It is assumed that biogenic emissions of ethanol, methanol, and acetaldehyde are negligible and can be ignored. However, biogenic inventories (MEGAN and BEIS) can systematically underestimate urban biogenic VOCs. Specifically urban biogenic emissions have been shown to be underestimated by MEGAN, do you have any localized tree coverage estimates within your footprint or can you justify whether assuming a strict zero contribution from biogenics is physically warranted. Can biogenics be integrated into the tracer methods for ethanol or methanol in any way? How does this vary in the surrounding regions?

In our previous manuscript, we estimated that the vegetation cover fraction was around 30 %. The predominant source of biogenic ethanol is decomposition, which we speculated was minor in the footprint relative to the other sources. We appreciate the reviewer's suggestion but performing a detailed evaluation of MEGAN and biogenic ethanol and methanol in urban environments is the subject of focused manuscripts and beyond the scope of the current study. We do not have data to directly answer the question of how this varies in surrounding regions.

Spatial scales and inventory evaluation: The flux footprint (2.8 km²) is compared to a much coarser inventory grid resolution (3 grids at 4×4 km). Can you justify the selection of 3 grids and were they renormalized to the footprint's area? Because the inventory distributes cooking emissions based on population density, *please discuss how population density compares to actual restaurant density in the area*. Can the authors downscale the inventory using restaurant density metrics to match the footprint, or scale up the flux measurements to match the grid?

We thank the reviewer for this comment. The three grid cells were chosen because they either contained the flux footprint or were the only adjacent grid cells with a large fraction of urban development (other adjacent grid cells contained a large fraction of water or forest). They were not renormalized to the footprint area. Surface fluxes could be compared directly to the inventory. In the manuscript, we acknowledge that the flux footprint area is small relative to the grid cell and that the measurements are representative of higher density urban residential and commercial zones. We also added a sentence in Sect. 3.1.1 to comment on spatial scales and inventory evaluation.

“This grid cell and flux footprint are unique in that they have a high restaurant density, high population density, and large influx of commuters and students during the week. The high population density of the flux tower could have contributed to the discrepancy with GRA2PES.”

We appreciate the suggestion but think that adjusting the inventory is beyond the scope of this study. Our goal was to focus on the source apportionment results from our measurements and

assess these results against the existing inventory. Future studies which focus on inventory development may choose to adjust the inventory following your suggestion.

Methanol:ethanol: Methanol flux correlates strongly with ethanol flux, which is attributed to VCPs and indoor-to-outdoor exchange. While this holds at a monthly scale, does this correlation persist at the high-frequency 30-minute or diurnal scale? Showing this high-frequency correlation is necessary to prove whether these compounds share immediate emission sources or if the correlation is merely a seasonal artifact of temperature and boundary layer dynamics.

We thank the reviewer for this suggestion. We examined the relationship between methanol and ethanol fluxes at 30-min resolution and found that the correlation was weak ($R^2=0.05$), in contrast to the stronger relationship observed for monthly median fluxes ($R^2=0.70$). This indicates that the monthly-scale correlation does not reflect strongly coupled short-term emission events. Instead, methanol and ethanol appear to exhibit similar longer-term temporal variability, which may reflect shared seasonal influences. We have revised the text to clarify that the monthly correlation alone does not provide evidence that methanol and ethanol share the same immediate emission sources.

“Methanol monthly median fluxes were correlated with ethanol ($R^2 = 0.70$), indicating similar long-term variability, however, the high frequency (30-min) correlation was low ($R^2 = 0.05$), suggesting that this relationship does not arise from coupled short-term emission events.”

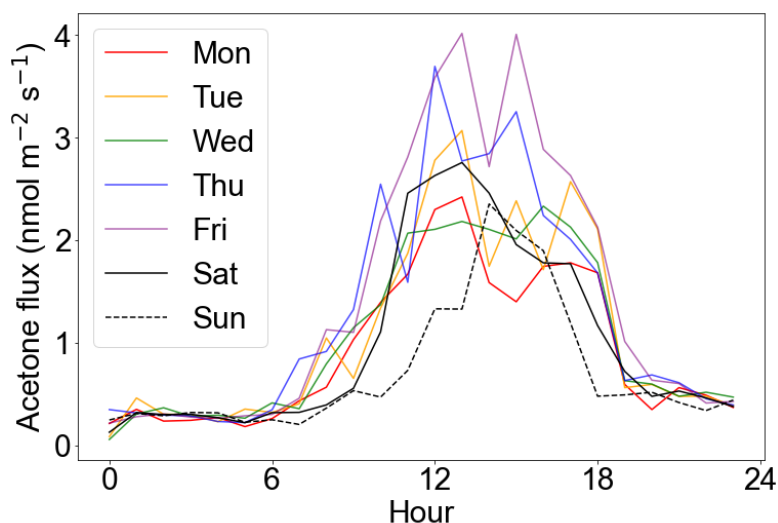
Grouping Saturday with weekdays (Monday–Friday) masks key differences, as commercial construction and industrial solvent use typically drop significantly on Saturdays compared to mid-week. What do you see when you separate Monday–Friday, Saturday, and Sunday in the acetone diurnal flux analysis.

We thank the reviewer for the suggestion. We wanted to clarify that acetone fluxes were significantly lower on Sunday when compared to every other day of the week individually, and we added text in Sect. 3.3.1 to clarify this.

“Day of week variability also suggests construction is a key source of acetone. Daytime acetone fluxes were significantly lower on Sundays than every other day of the week ($p<0.05$, significance was tested for each day individually).”

Below is a figure showing the median diurnal profile of acetone flux for each day of the week. The trend for Sunday is distinct from Saturday, while Saturday has a similar pattern as the weekdays. We added the figure to the SI and the following text to Sect. 3.3.1.

“Figure S18 shows the median diurnal flux of acetone for each day of the week; the trend for Sunday is distinct from all other days.”



If cooking occurs year-round and restaurant density is constant, why does the daytime ethanol flux decrease by nearly 50% in winter? Is this more driven by temperature-dependent indoor-to-outdoor exchange (e.g., closed windows suppressing ventilation transport) or physical deposition effects. I'd imagine the levels of cooking stay the same through all seasons.

We speculate that the seasonal difference is caused by changes in ethanol emissions associated with human activity. The change could be caused by lower indoor to outdoor emissions of both cooking and VCPs or lower VCP use (e.g., less construction activities) in the winter. Also, during colder months, the outdoor patios and restaurants in the footprint have fewer patrons due to the weather, so there are less evaporative ethanol emissions. We suspect that physical deposition is not a key driver of the changes, because the exchange velocity is lower in the winter, indicating a weaker source strength. (See Reviewer 2 response and Fig. S10).

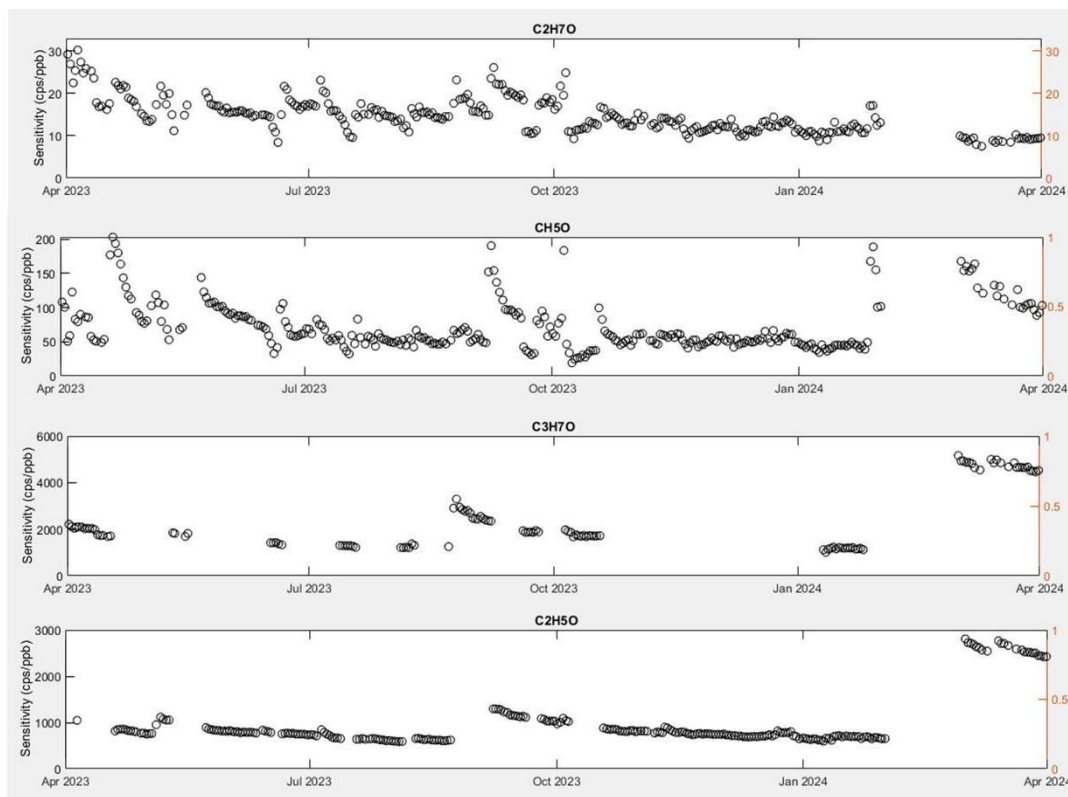
Minor Comments/Technical Corrections:

Report the exact instrument operational parameters (specifically E/N and FIMR voltages) and the stability of the calibration factors across different periods in the SI

We added the following text to Sect. 2.2.2.

“The mass to charge (m/z) range of the Vocus was 10 to 497. The sampling rate was 10 Hz. The FIMR was 100°C and 2.5 mbar. The reagent flow was 15 standard cubic centimeters per second, the electric field gradient was 590 V, and the radio frequency was 450 V. The E/N ratio was ~ 125 Td (1Td = 10–21 V m²). The big, segmented quadrupole (BSQ) voltage was 200 V.”

We added the figure below to the SI. The calibration factors were interpolated across the dataset. Jumps in sensitivity correspond to changes in drift tube tuning or instrument maintenance. We alternated between cylinders, which is why there are periodic breaks in the acetone sensitivity.



L118 Monoterpenoids are summed at the parent and major fragment mass, how is fragment overlap from monoterpenoids and monoterpene alcohols (such as eucalyptol, which fragments to m/z 137) accounted for?

In this line, we refer only to the calibrant gases which included monoterpenes (no monoterpenoids). In the ambient data, C10H17+ could be impacted by monoterpenoids and we did not correct for this. We added a sentence to Sect. 2.1.3 to clarify.

“C10H17+, the formula for protonated monoterpenes, could have been impacted by fragmentation of monoterpenoids.”

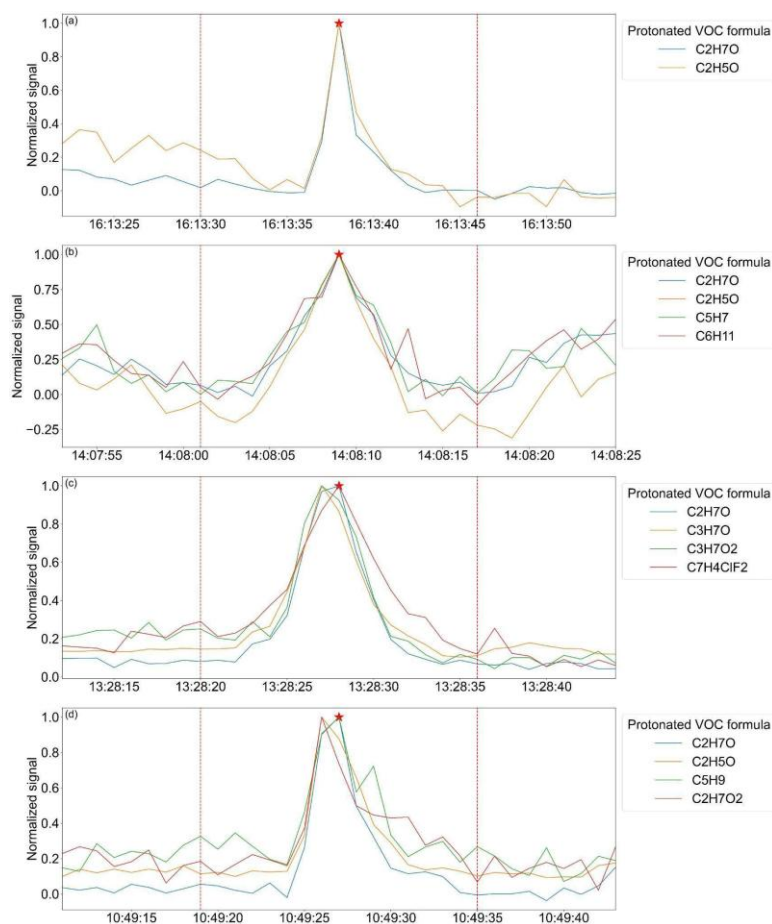
L119 Define what specific criteria are used to classify compounds as "well-behaved."

We define “well-behaved” in Sect. 2.1.2, and we added an additional sentence for clarification (see below).

“Well-behaved calibrants are those that do not fragment or those whose fragmentation products may be summed with confidence, such as monoterpenes ($C_{10}H_{17}^+ + C_6H_9^+$). Well-behaved calibrants have a linear relationship with the proton transfer reaction rate constant (kPTR).”

Can you explain further the physical or mathematical justification for choosing a 8 second window to determine co-emitted VOC spikes.

After visual examination, this window was selected because it encompassed short-term spikes in concentration that were sampled while driving past a source or group of sources. We modified Figure S4 to include more examples of spikes in concentration (see below).



L166 Please clarify the phrase "default calibration factor scaled by the fraction of parent ion detected." Does this refer to a calculated k-rate calibration factor adjusted for instrument-specific fragmentation?

Yes, that is correct. The calibration factor applied was the default sensitivity multiplied by the parent ion fraction, which accounts for instrument-specific fragmentation patterns. We added this sentence for clarity.

“Thus, these VOCs were calibrated using the default sensitivity accounting for instrument-specific fragmentation patterns.”

Are there any other known interferences at the propanol dehydration product ($C_3H_7^+$) given its low molecular weight?

Interference from fragmentation on $C_3H_7^+$ is possible. For this reason, we did not focus on this ion for further analysis. We added this text to Sect. 2.2.2.

“Fragmentation of larger VOCs could influence the signal at $C_3H_7^+$ in addition to propanol, so it was not the focus of further analysis.”

Were any corrections applied to acetaldehyde for ethanol and ethylene glycol interferences?

We did not correct for potential fragmentation from these VOCs.

L275 Tower ethanol fluxes in Berkeley were higher than those in Beijing. Given differences in cooking styles and oil usage, is this physically expected, or is it an artifact of Beijing's measurements representing a much broader regional scale?

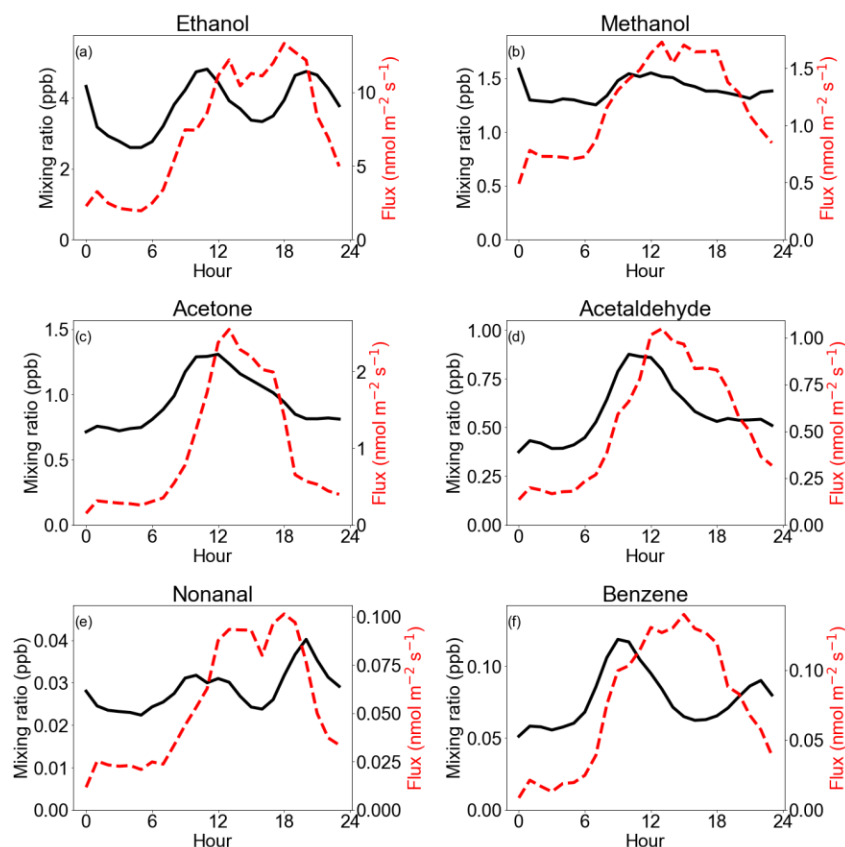
Our flux tower was located next to many restaurants, bars, and breweries, which likely contributed to the high ethanol fluxes we observed. Without knowing more about the Beijing flux footprint, it is challenging to compare the two.

Why was nonanal not quantified in the mobile laboratory?

We found that VOC fragmentation was sensitive to the skimmer voltage gradient in the drift tube (Katz et al., 2025 ACP, <https://doi.org/10.5194/acp-25-15281-2025>). At higher skimmer gradients, the nonanal fragmentation increased. During the mobile laboratory, our drift tube was not tuned sufficiently to allow for nonanal to be detected.

Show a diurnal profile comparing raw mixing ratios to fluxes to contrast nighttime boundary layer accumulation against active daytime venting (especially for nonanal and ethanol).

We thank the reviewer for the suggestion and added the following figure to the SI.



In Figure 6(a), shouldn't the measured ethanol flux be reached since VCP+ represents the full residual?

We thank the reviewer for pointing this out. The measured ethanol flux is slightly higher than the sum of each ethanol source. The residual (i.e., VCP+) was calculated for each 30-minute averaging interval after accounting for the other two sources, so slight differences were expected between the median sum of each source and the actual measured median flux. Further, some of the VCP+ (now called “other”) averaging intervals were negative, which explains why the sum doesn't exactly match the measured value.

Why not include nonanal spike co-occurrences in Figure 9?

Unfortunately, nonanal spike co-occurrences could not be included because nonanal was not quantified in the mobile dataset due to instrument parameters.