Peron et al. provide an analysis of VOC flux measurements conducted over multiple years during the spring and summer seasons in Innsbruck, Austria. The authors focus on quantifying the fluxes of isoprene, monoterpenes, and sesquiterpenes in order to assess the potential contribution of anthropogenic sources, such as motor vehicle emissions and VCPs. Some measurement periods include the COVID lockdown, which provides a unique opportunity to evaluate fluxes in the absence of traffic and pedestrians around the sampling site. The authors evaluate nighttime data, weekday / weekend differences, and seasonal differences to infer the contribution of anthropogenic and biogenic sources to these VOCs.

In general, I find the authors approach to apportioning monoterpenes, methanol, and sesquiterpenes fluxes very informative and an advance in research aimed at quantifying the effects of VCPs and other anthropogenic sources on VOCs that are traditionally biogenic. The weekday / weekend and COVID analyses show changes to the flux that provides bounds on the impact of anthropogenic sources.

My biggest concern relates to the isoprene apportionment. As outlined below in my comments, I am not yet convinced that PTR-ToF-MS measurements are reliable in determining anthropogenic isoprene fluxes. It is not clear to me if the authors correct for anthropogenic interferences to m/z 69.070, which have recently been shown to significantly degrade PTR-ToF-MS measurements of isoprene at night. Consequently, I hope to see more analysis and/or measurement validation that confirms the presence of nighttime isoprene.

Major Comments:

The authors use nighttime data to determine the anthropogenic contributions to isoprene emissions. The authors note the importance of fragmentation on the isoprene mass (m/z 69.070) and provide a brief discussion about the potential measurement inferences. As written, it is not clear if the authors corrected the isoprene mass for interferences, or if this discussion is intended to provide error bounds in the flux estimates. Ultimately, I believe a correction is needed, not a discussion of errors, since it is likely that anthropogenic interferences to isoprene overwhelm the signal associated with anthropogenic isoprene and impact the authors' conclusions about weekday/weekend effects, seasonality, and mobile source contributions to isoprene.

My concern is due to the significant contribution of fragmentation to m/z 69.070 previously observed in urban nighttime data. Coggon et al. (2023) showed that interferences to the isoprene mass in urban areas are highest at night and largely associated with the fragmentation from VOCs of anthropogenic origin – i.e., C5 – C9 aldehydes emitted from cooking and possibly other human activities. Coggon et al. show that, at night, the isoprene interference in four urban areas (Los Angeles, Las Vegas, Detroit, New York City) amounts to > 90% of the signal at m/z 69.070. Coggon et al. were able to determine nighttime isoprene mixing ratios after correcting the data, and this was only confirmed by comparison with GC-MS measurements.

Since the authors are using nighttime data to determine the anthropogenic component, I would like to see more discussion / analysis to confirm that indeed a nighttime interference has been removed. Currently, the authors quote a 30% measurement uncertainty. Is this over the entire day, or is this specific for nighttime measurements? Is there a strong correlation between m/z 69 and aldehyde water-loss products (e.g., m/z 111 + 125) at night that would be indicative of an anthropogenic interference? I believe that the authors need to remove the signals associated with these masses, as higher carbon aldehydes are more indicative of anthropogenic interferences than C5 compounds (e.g. m/z 87), which were attributed by Fall et al. (2001) to be associated with biogenic emissions of alcohols and aldehydes. Even with such an analysis, I would be wary of the isoprene signals at night unless there are GC-MS measurements available to cross-validate the PTR measurements.

Other Comments:

Lines 38 – 45: I think this section could be significantly shortened. While it's important to note that BVOCs globally important, I prefer the authors' focus on the impact of BVOCs on urban air quality.

Lines 46 – 48: It would be great if the authors could expand a bit more on the literature that has quantified the impact of BVOCs on urban OH reactivity, ozone formation, and SOA potential. This would be a good place to quantify the isoprene impacts on SOA in China from Wu et al. (2020). Other research could be highlighted as well. For example, Gu et al. examines the role of BVOCs on air quality in Los Angeles and how changing emissions due to urban greening programs might further degrade urban air quality. Pfannerstill et al. conducted aircraft flux measurements in LA and showed that over half of the OH reactivity and SOA formation potential was linked to terpenoids (some biogenic, some anthropogenic). The authors also show that biogenic inventories used in LA significantly underestimated the flux of isoprene – this highlights the importance of flux measurements, such as those presented here by the authors.

Lines 68 – 78: It would be worth noting Borbon et al. (2023) here as well. They show the ubiquity of urban monoterpenes and suggest that monoterpenes emitted in developing countries may have a traffic source. This also highlights the need for identifying mixed source contributions in urban areas.

Section 2.1: It would be useful to see a map of the location, wind direction, and footprint for measurement period, similar to what is shown by Kaser et al. (2022).

Lines 122 – 133: Here, it is not clear how the interferences were treated in the data (see main comment)

Lines 324 – 333: The mass attributed to GLV is potentially impacted by ketones used in VCPs (methyl isobutyl ketone and cyclohexanone, McDonald et al. 2018). It would be worth noting this here.

Section 3.3: There is a lot of great information in this section showing the effects of weekday/weekend, seasonality, and effects of the COVID lockdown period on monoterpene fluxes. At times, I had trouble keeping all of the points in order. I would find it helpful if this section were broken down a bit more into sub-sections (3.3.1, 3.3.2, etc) that focus on the weekday / weekend effect then the COVID lockdown. For example, at line 390, there could be a Section 3.3.2 that marks the discussion of the lockdown. It would be also helpful to separate the sesquiterpenes with their own sub-section.

Line 382-383: This sentence should be revised. Gkatzelis et al. used monoterpene / benzene ratios as a proxy to evaluate VCP / traffic ratios. The authors attribute monoterpene emissions to VCPs (personal care and cleaning products) rather than traffic emissions.

References

Borbon, A., Dominutti, P., Panopoulou, A., Gros, V., Sauvage, S., Farhat, M., et al. (2023). Ubiquity of anthropogenic terpenoids in cities worldwide: Emission ratios, emission quantification and implications for urban atmospheric chemistry. *Journal of Geophysical Research: Atmospheres*, 128, e2022JD037566. https://doi.org/10.1029/2022JD037566

Gu, S., Guenther, A., Faiola, C. Effects of anthropogenic and biogenic volatile organic compounds on Los Angeles Air Quality. *Environmental Science & Technology* **2021** *55* (18), 12191-12201 DOI: 10.1021/acs.est.1c01481

Eva Y. Pfannerstill, Caleb Arata, Qindan Zhu, Benjamin C. Schulze, Roy Woods, Colin Harkins, Rebecca H. Schwantes, Brian C. McDonald, John H. Seinfeld, Anthony Bucholtz, Ronald C. Cohen, and Allen H. Goldstein *Environmental Science & Technology* **2023** *57* (41), 15533-15545, DOI: 10.1021/acs.est.3c03162