Anonymous Referee #1

Received and published: 31 January 2024

We thank reviewer 1 for the constructive comments. Below is our point by point reply to specific comments.

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.

Reply: We thank the referee for pointing out this issue. In the manuscript we have attempted to assess the magnitude of this interference. As suggested by the reviewer we have significantly expanded the analysis as outlined by Coggon et al. and provide a better constraint on the isoprene interference. Overall our main conclusions do not change as outlined below.

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.

Reply: We thank the reviewer for pointing out this issue. We have investigated the interference patterns on m/z 69+ due to fragmentation of higher aldehydes ((e.g., m/z 111 + 125) in more detail. In our case, an analysis was performed both on concentrations, as in Coggon et al. and on fluxes, given the fact that a lot of the analysis in this paper is based on fluxes. In our case, the campaigns were analysed individually, reporting the measured m/z 69 values and those corrected by Coggon et al. With the exception of the spring 2018 campaign, where the measured and corrected values differ slightly from each other, the difference is generally found to be much smaller than that found in Coggon et al. For the other three campaigns, the difference between the two sets of values is negligible (see plots further below). In our study, therefore, we can assume that in the case of m/z 69 there was a comparably small interference with other masses. Three major reasons explain this finding. First, we typically operate the PTR-TOF-MS at lower E/N (ie. 108 Td) as compared to VOCUS type models, that are typically run at 140-160 Td, thus likely yielding a higher degree of fragmentation. Yesildagli et al. for example report almost complete fragmentation of nonanal (https://doi.org/10.1016/j.jhazmat.2023.131368) onto m/z 69. Under regular PTR conditions a fragmentation of 30-40% is observed at most. Second, on the reported aircraft campaigns also the PTR-TOF-MS was also run at higher E/N (e.g. 120 Td) than in this study. Third the average abundance of higher aldehydes as compared to the cited studies seems quite a bit lower. As suggested by the reviewer we provide uncertainty bounds for m/z69 for the assignment of isoprene due to these interferences.

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.

Reply: We have rephrased this section, to make it more clear, but still believe mentioning the global significance of BVOCs remains an important aspect worth mentioning in a couple of sentences.

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.

Reply: Thank you for this comment. We have expanded discussion on this issue and included the references of the relevant literature pointed out by the reviewer. (45-55).

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.

Reply: Thank you for this comment. Observations on the paper cited have been added to the text (80-85).

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).

Reply: Thank you for this comment. We added the footprint analysis in the supplement.

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.

Reply: we added the reference and a sentence to that issue. Since the correlation is poor (R^2=0.35), any potential influence of isobutyl ketone or cyclohxanone is likely small. However, please take into consideration the fact that the two masses (Methyl isobutyl ketone ($[C_6H_{12}O]H^+$, m/z 101.0966) and cyclohexanone ($[C_6H_{10}O]H^+$, m/z 99.081) reported by the reviewer are not distinguishable from other GLVs through the measurements with the PTR.

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.

Reply: Thank you for your suggestion. We have divided this part into monoterpenes and sesquiterpenes with subsections according to the type of analysis (weekday/weekend and lockdown).

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.

Reply: Yes, we confirm. We have therefore changed both the sentence in these lines and at 415.

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

Interference m/z 69

In our analysis we have taken into account the interference at m/z 69 caused by m/z 87, m/z 111, m/z 125, m/z 129 and m/z 143 detected in all the campaigns analysed in this study. The analysis was performed on both fluxes and concentrations for comparison with Coggon et al. 2023 (https://egusphere.copernicus.org/preprints/2023/egusphere-2023-1497/egusphere-2023-1497.pdf).

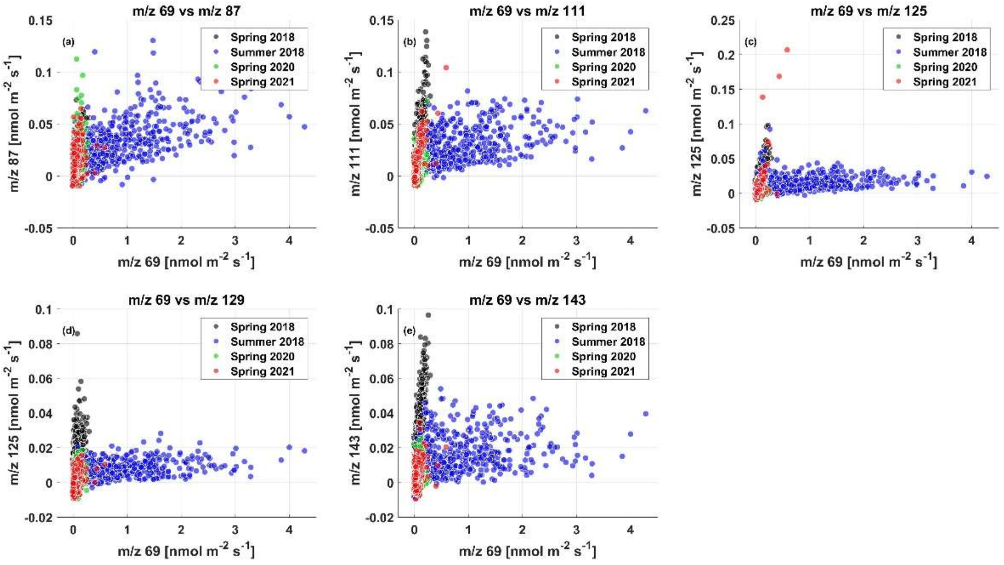

Figure 1: fluxes in [nmol m-2 s-1] of m/z 69 compared with those of m/z 87, m/z 111, m/z 125, m/z 129 and m/z 143 for all campaigns analysed without applying any filtering to the data.

Accordingly, we have applied the formula 1 proposed by Coggon et al, 2023:

m/z 69 $_{\text{Corrected}} = S_{69} - S_{111+125} \cdot f_{69/(111+125)}$ (Eq. 1)

S_{69} is the signal measured at m/z 69, $S_{111+125}$ is the signal of the isoprene interference (sum of m/z111 + m/z 125), and $f_{69/(111+125)}$ is the interference ratio determined at night.

For the determination of the interference ratio at night, only night data from 20 to 3 UTC were extracted. This was based on Coggon et al, 2023 to exclude biogenic sources of m/z 69.

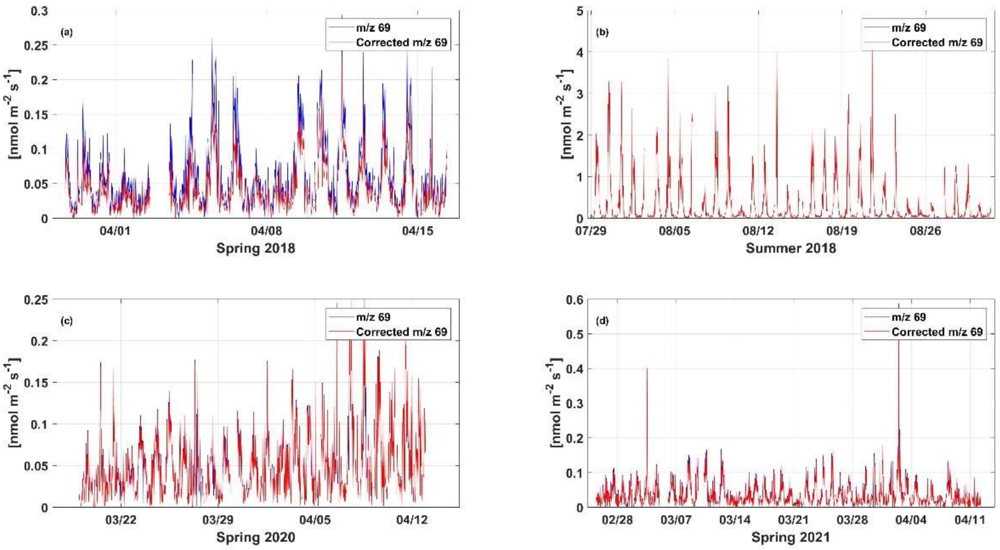

Figure 2: Fluxes in [nmol m^{-2} s^{-1}] measured by m/z 69 in blue and fluxes corrected by applying the correction given by Equation 1 of Coggon et al. 2023 in red.

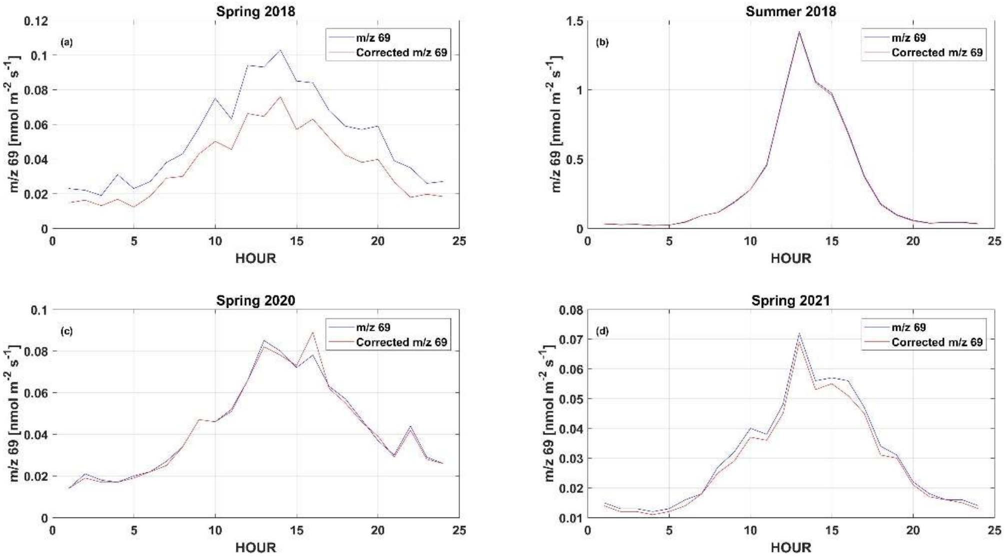

Figure 3: Measured fluxes (in blue) and corrected fluxes (in red) during the day.

Looking instead at concentrations:

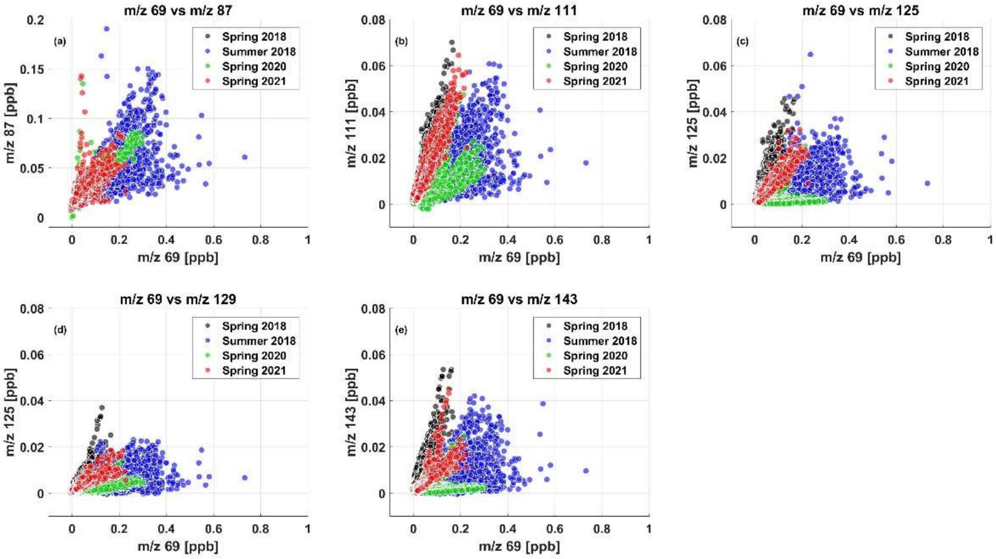

Figure 4: Concentrations in [ppb] of m/z 69 compared to those of m/z 87, m/z 111, m/z 125, m/z 129 and m/z 143 for all campaigns analysed without applying any filter to the data.

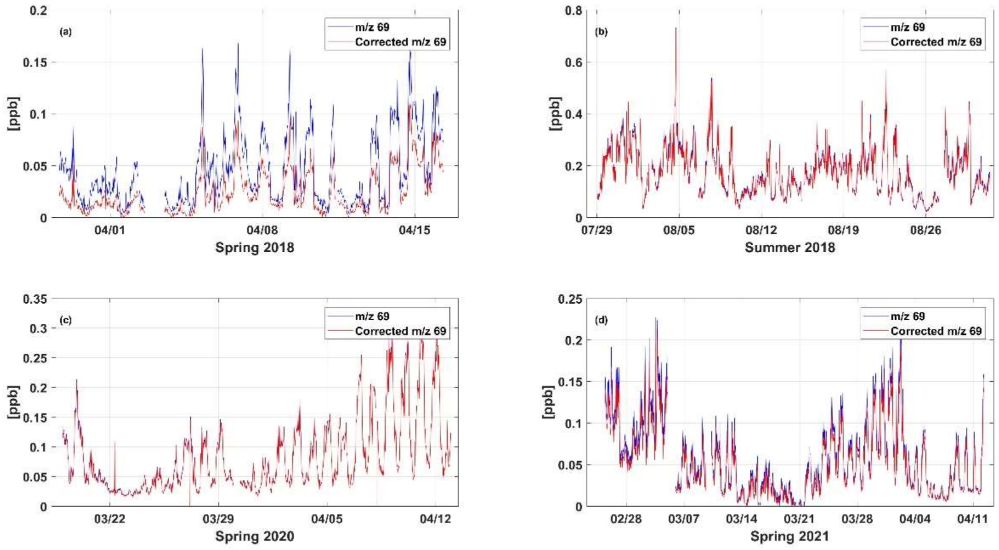

Figure 5: concentrations in [ppb] m/z 69 in blue and corrected concentrations using the correction given by Equation 1 of Coggon et al. 2023 in red. This is for each campaign.

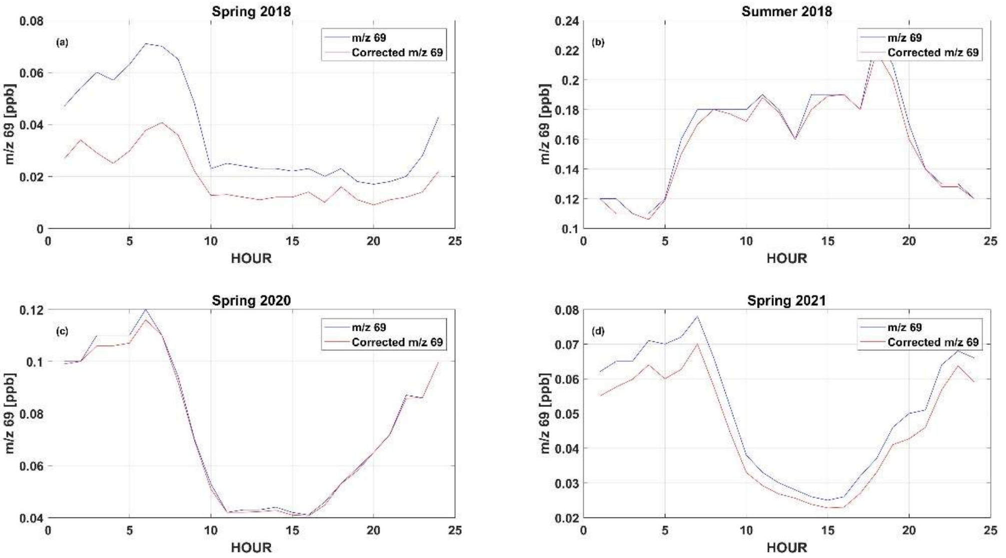

Figure 6: measured flows (in blue) and corrected flows (in red) during the day.

It can be seen that the values reported in Figure 6 follow a similar trend to that reported in Figure 4 in Coggon et al., 2023 for the Las Vegas site.

Coggon et al, 2023 report an $f_{69/(111+125)}$ of 3 for the city of Las Vegas. In our study the average $f_{69/(111+125)}$ is 0.35 for the spring period and 0.21 for the summer period. The nocturnal interference ratio found in the city of Innsbruck is therefore lower for all periods analysed, compared to that found by Coggon et al. 2023 in the city of Las Vegas.

This allowed us to consider the possible interference found by the PTR-MS at m/z 69 as small, and thus to consider the values measured at this m/z as those of isoprene emissions. Especially in the 2020 campaign, during the lockdown. As suggested by the reviewer, we now provide realistic bounds for assigning isoprene to m/z 69, based on upper limit interferences from m/z87, m/z111, and m/z 125.