Review of “Biogenic and anthropogenic contributions to urban terpenoid fluxes”

Summary

I enjoyed reading this paper. The authors put considerable effort into detailing sources of isoprene, monoterpenes, and sesquiterpenes as shown in one example by the 80% footprint-weighted flux maps. As the authors note, there are not many measurements of terpenoid fluxes in urban environments. These measurements are relatively labor-intensive and very useful. The authors quality control of the flux data and data treatment in statistical analyses are robust. Comparison of BWW fluxes to MEGAN demonstrate a missing emission source for monoterpene fluxes in the morning that is clearly observed when comparing weekday to weekend measurements. I have a major technical and a major conceptual comment. I have also provided other minor comments. As described in my major conceptual comment I am curious why the increase in monoterpene fluxes occurs so much earlier in the morning compared to what is measured at the BWW site. If this discrepancy between the early morning increase in monoterpenes predicted by FIVE-VCP and BWW is resolved, then would the temporal correlations shown in Figure S11 improve? Can the authors contribute information from their measurements to improve the VCP inventory?

Comments

(Major Technical: Page 4 Line 157) Use of the C6H11+ ion to do a correction for C5H9+ is interesting because the source, identity, and product ion distribution of C6H11+ is not known. There is a spreadsheet of product ion distributions we recently published (https://amt.copernicus.org/articles/18/1013/2025/) that contains product ion distributions measured on many different Vocus instruments (https://data.nist.gov/od/id/mds2-3582). One of the VOCs in Table S2 of this study is nonanal. When looking in the H3O+ PID library, nonanal produces both the C5H9+ (product ion fraction = 0.3) and C6H11+ (product ion fraction = 0.1) fragments. Did the authors refer to this study to identify what product ions to look for when doing the parent ion fraction calculation and when searching for possible sources of C5H9+ fragments? This may be a useful resource as all of the instruments in that study are Vocus PTR-ToF instruments. I am also unclear of how exactly a correction to the C5H9+ signal was applied from the C6H11+ signal. How much of the uncorrected C5H9+ signal was attributed to fragmentation of C9H17+, C8H15+, and C6H11+?

(Major Conceptual: Page 15 Line 516) I find it really interesting that when combining MEGAN and FIVE-VCP the correlation of MT fluxes with BWW data basically does not improve at all. As the authors note, for MEGAN the increase in MT and SQT fluxes are delayed by a couple hours compared to the weekday BWW indicating an anthropogenic source. However, the FIVE-VCP fluxes shown in Figure S10 seem to start to increase around 3am which is a few hours earlier than BWW measurements show. I have two questions: (1) I assume the answer is not good, but if you do a correlation (similar as shown in Figure S11) between FIVE-

VCP and BWW does that agree better? and (2) Is the reason for the disagreement of the temporal correlation between combined MEGAN + VCP and BWW MT fluxes driven by the delay of MEGAN increase in MT fluxes (compared to BWW) and the early start of the increase in VCP fluxes (compared to BWW)? In other words do the combined MEGAN+VCP fluxes agree reasonably with BWW fluxes between the hours of 11am and approximately 7pm?

(Page 3 Line 135) Could the authors add the units of Td to the statement of E/N values: "Pressure drops in the FIMR impacted the E/N ratio (increase from ~125 to ~135)…"?

(Page 3 Line 135) In reference to that same statement are the authors referring to a pressure drop induced by a high flowrate reduced pressure sample line or a pressure drop from a clogged capillary?

(Page 4 Line 145) Could the authors replace "second" in the following statement with "s": "kPTR of 2.25*10-9 cm3 molecule-1 second-1…"

(Page 4 Line 148) I don't see the fIMR voltage values in Table S2. It would be interesting if the authors found that the fIMR voltage affected product ion distributions because Li, et al. (2024) found that product ions were not affected by fIMR voltages between 200 V to 500 V.

(Page 4 Line 147) For the following statement I think instead of referencing Table S2 they maybe intended to reference Figure S1 or Table S1? "Some VOCs (nonanal, sesquiterpenes) were calibrated using the default kPTR scaled by the percentage of signal falling on the parent ion determined by laboratory calibrations (Table S2)."

(Page 4 Line 157) I don't think the reference supports the following statement. "While C6H11+ has been identified in areas with oil and natural gas extraction (Gueneron et al., 2015)…" Gueneron, et al. (2015) measured vapors from gasoline test mixtures in lab with no field measurement component to the study.

(Table S2) The parent ion fraction values for the terpenoids in this table are interesting because I am not aware of any published product ion distributions from these molecules. I would be interested to know what the authors measured for product ion distributions from the caryophyllene and cedrene.

(Figure S3) Can the authors add text to the figure describing what the quartile ranges are and the horizontal line versus triangles mean?

(Figure 1) It would be my preference to have the MEGAN and BWW flux values (left and right axes) to have the same range for panels b though d. The problem is that when I glanced at the figures initially it looks like the monoterpene fluxes agree in magnitude, but one of the major points of the paper is that there is an important anthropogenic component. Additionally, the seasonal differences for the fluxes looks to agree well making the seasonal comparison a less important point and the major difference between MEGAN and the measurements being the absolute value. I understand wanting to highlight the seasonality since that is a unique feature of this study so if the authors want to duplicate this figure with the y-axes adjusted such that left and right ranges agree for panels b though d, put it in the SI, and point to it with a reference in the main text I think that would be a reasonable action.

(Page 8 Line 307) Do the authors mean > 0.05% contribution to the molar flux in the following statement: "…with average flux contributions of over 0.05 % were included in Fig. 3."?

(Page 9 Line 323) Can the authors put (Figure S5) behind the following part of this sentence: "…increased with increasing temperature,…"? As it's written right now I was expecting to see a comparison to the Pfannerstill results in Figure S5.

(Page 11 Line 393) With respect to the following sentence: "…and the monoterpene lifetime is expected to be similar." Did the authors calculate/estimate a monoterpene lifetime? This statement is unusual as they go through the trouble of calculating an isoprene and cedrene lifetime.

(Page 12 Line 400) With respect to the following statement: "These differences are too low to produce the observed weekday versus weekend differences observed." What is the percent difference between weekday and weekend monoterpene and sesquiterpenes? Based on the differences shown in Figure 4 I'm a little surprised there is a statistically significant difference between weekends and weekdays. Although I see that the difference in fluxes in the morning hours is noticeable.

(Page 12 Line 402) Do the authors have any explanation for the agreement of BWW isoprene fluxes with MEGAN when comparing medians and IQRs compared to higher time resolution data?

(Page 14 Line 488) With respect to the following statement: "The total anthropogenic fraction of monoterpene emissions is expected to be higher, but it would be difficult to accurately estimate with this dataset." Could the authors provide more explanation for this statement? It is not clear to me why the total anthropogenic MT emissions are expected to be higher.

(Page 15 Line 550) With respect to the following statement: "The prevalence of other monoterpenes including alpha-pinene (35 %), beta-myrcene (16 %), (+)-3-carene (13 %), beta ocimene (12 %), and beta-pinene (4 %) indicate that biogenic emissions were the predominant source of monoterpenes on average." I don't think this is quite accurate. Other monoterpenes besides limonene are also present in cleaning and consumer products (see Figures S1 and S2 https://pubs.rsc.org/en/content/articlelanding/2024/em/d4em00144c and Figure S3 from https://www.science.org/doi/full/10.1126/sciadv.ads7908). These speciated measurements are interesting, but the presence of these different terpene isomers do not indicate a dominate biogenic emission source.

(Page 17 Line 631) Do the authors think that terpenoid emissions as a whole are a problem or could consumer products be reformulated to soften their impact on air quality?

The authors may consider at least editing the following statement: “Terpenoid emissions from fragranced consumer products may also be a target for emissions reductions.” to instead say “Decreased use of terpenoid compounds in fragranced consumer products would likely decrease terpenoid emissions from anthropogenic sources in urban environments.”

Similarly, the authors might consider editing the sentence following that one. “Further work on terpenoid source apportionment in urban environments would contribute to a better understanding of additional targets for reducing emissions.” to “Further work on terpenoid source apportionment in urban environments would contribute to a better understanding of pollutant formation associated with consumer product use.”.