Reviewer 1

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 comment 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 predicted by FIVE-VCP 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?

> Thank you! We appreciate the very thoughtful review. These suggestions strengthen the paper and will be addressed below. Regarding your question about our measurements improving the inventory, we modified this sentence in the conclusion section:
>
> "Comparing **direct observations of terpenoid fluxes like these** with bottom-up approaches in urban environments will contribute to more robust models, and therefore, **more accurate** air quality **predictions**."
>
> We also wanted to note that we updated our study name to URBAN-EC from BWW. That stands for Urban Research on Biogenic and ANthropogenic Emissions of Carbon. We changed every instance of BWW in the paper to URBAN-EC and added a sentence to the introduction to define the acronym.
>
> "**We introduce the URBAN-EC project (Urban Research on Biogenic and ANthropogenic Emissions of Carbon).**"

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+?

> Thank you for this important comment. We split up the response based on the questions you posed.

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?

> We analyzed the correlation of C5H9+ to other ions during periods when isoprene (calculated using the original method, i.e., C9H17+ and C8H15+) was over-corrected. C6H11+ was highly correlated with C5H9+ during those time periods, so we included C6H11+ in the correction and had good results. The literature suggested this ion could be produced along with isoprene, which was nice confirmation. We should reference your paper too. Updated text is below.

I am also unclear of how exactly a correction to the C5H9+ signal was applied from the C6H11+ signal.

> In Coggon et al. 2024, the correction factor is found using the slope of C5H9+ versus the sum of C9H17+ and C8H15+ overnight. We used this method except with the sum of C6H11+, C8H15+, and C9H17+ overnight instead of just the two ions suggested in the paper. We updated the text to be more descriptive about the method.

> Isoprene = C5H9 – C*(C9H17 + C8H15 + C6H11)

> C = overnight slope of C5H9 versus C9H17+C8H15+C6H11

> Coggon, M. M., Stockwell, C. E., Claflin, M. S., Pfannerstill, E. Y., Xu, L., Gilman, J. B., Marcantonio, J., Cao, C., Bates, K., Gkatzelis, G. I., Lamplugh, A., Katz, E. F., Arata, C., Apel, E. C., Hornbrook, R. S., Piel, F., Majluf, F., Blake, D. R., Wisthaler, A., Canagaratna, M., Lerner, B. M., Goldstein, A. H., Mak, J. E., and Warneke, C.: Identifying and correcting interferences to PTR-ToF-MS measurements of isoprene and other urban volatile organic compounds, Atmospheric Meas. Tech., 17, 801–825, https://doi.org/10.5194/amt-17-801-2024, 2024.

> Paragraph with updated text:

> Fragmentation can negatively impact the detection of isoprene, benzene, and other VOCs in the Vocus. The parent ion for isoprene detection ($C_5H_9^+$) has known interferences from fragmentation of aldehydes, substituted cycloalkenes, 2-methyl-3-buten-2-ol, and more (Buhr et al. 2002; Karl et al. 2012; Gueneron et al. 2015; Coggon et al. 2024b; Link et al. 2025). Coggon et al. developed a method to correct isoprene fragmentation using $C_9H_{17}^+$ (m/z 125) and $C_8H_{15}^+$ (m/z 111) (Coggon et al. 2024b). **_Briefly, the correction factor, C, is the slope of $C_5H_9^+$ versus the sum of interferences (e.g., $C_8H_{15}^+$ and $C_9H_{17}^+$) overnight when isoprene emissions are not expected. Isoprene is then calculated following Equation 1._** We utilized the method **_from Coggon et al. 2024b_** with the addition of $C_6H_{11}^+$ (m/z 83), a PTR fragment that can be produced with $C_5H_9^+$ **_during the ionization of nonanal, cycloalkenes, and more_** (Buhr et al., 2002; Gueneron et al., 2015; Link et al., 2025). **_$C_6H_{11}^+$ was added to the correction because it was highly correlated with $C_5H_9^+$ during time periods when isoprene was over-corrected (negative isoprene data) with the original method. This_** addition reduced the number of averaging intervals with over-correction and resulted in diurnal flux and

concentration profiles that agreed with theoretical expectations. $C_6H_{11}^+$ **has been identified as a fragment produced with $C_5H_9^+$ when sampling compounds found in gasoline** (Gueneron et al., 2015), and it has also been reported as a fragment in indoor environments from continuous emissions from building materials and other activities like cooking and cleaning (Arata et al., 2021; Liu et al., 2019). $C_6H_{11}^+$ had the fifth highest VOC emission rate for continuous indoor emissions at a normally occupied residence in the East San Francisco Bay Area, and was thought to be the product of alcohol dehydration in the PTR-MS (Liu et al., 2019). The corrected isoprene mixing ratio was validated against 2-dimensional gas chromatography mass spectrometry data for a portion of the sampling campaign (Figure S2). **Corrections to $C_5H_9^+$ caused an average reduction of ~75% in the mixing ratio, which is similar to the $C_5H_9^+$ product ion distribution reported by Ditto et al. (2025) for outdoor air in Maryland during spring.** Fragmentation onto the proton transfer product of benzene ($C_6H_7^+$) was avoided by calibrating benzene on its charge transfer product ($C_6H_6^+$).

$$Isoprene = C_5H_9^+ - C * \sum Interferences \qquad (1)$$

How much of the uncorrected C5H9+ signal was attributed to fragmentation of C9H17+, C8H15+, and C6H11+?

> Corrections to C5H9+ caused an average reduction of ~75% in the mixing ratio. This was added to the text (see above).

(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?

(1) Thanks for this suggestion. This is a bit tough to calculate because the format of FIVE-VCP emissions is one emission factor for each hour of the day (i.e., 24 data points). We considered two ways to calculate the correlation of our measurements with the inventory. Option A: Compare the median of BWW for each hour versus the FIVE-VCP emission rate for each hour. Result: Correlation of 0.70, but it isn't comparable to the MEGAN scatter plot which uses the whole dataset. Option B: create a FIVE-VCP time series that is the length of the BWW time series which is just the same repeating diurnal trend. Result: Correlation of 0.12. To clarify how we did this for the scatter plot in Figure S11, in the MEGAN+VCP case, we added the corresponding FIVE emission value based on the hour of the day.

(2) The BWW versus MEGAN+VCP from 11:00 to 19:00 R^2 is 0.05 (weaker than including all hours).

(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)…"?

Updated: "These parameters resulted in an E/N ratio of ~125 Td *(1 Td = 10⁻²¹ V m²)*."

(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?

We speculated the FIMR decreases were caused by a dirty inlet filter. This impacted the data for minimal time periods, mostly overnight.

(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…"

Fixed.

(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.

Fixed. Our FIMR was set to 450 V for each test.

(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)."

Table S2 shows the parent ion fraction for nonanal and sesquiterpenes from our laboratory calibrations, so we think this is the correct reference. Figure S1 shows how the default sensitivity was calculated so we will include that reference, too.

(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.

Thanks for catching that. Here is the updated text: "$C_6H_{11}^+$ *has been identified as a fragment produced with $C_5H_9^+$ when sampling compounds found in gasoline* (Gueneron et al., 2015), and it has also been reported as a fragment in indoor environments from continuous emissions from building materials and other activities like cooking and cleaning (Arata et al., 2021; Liu et al., 2019)."

(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.

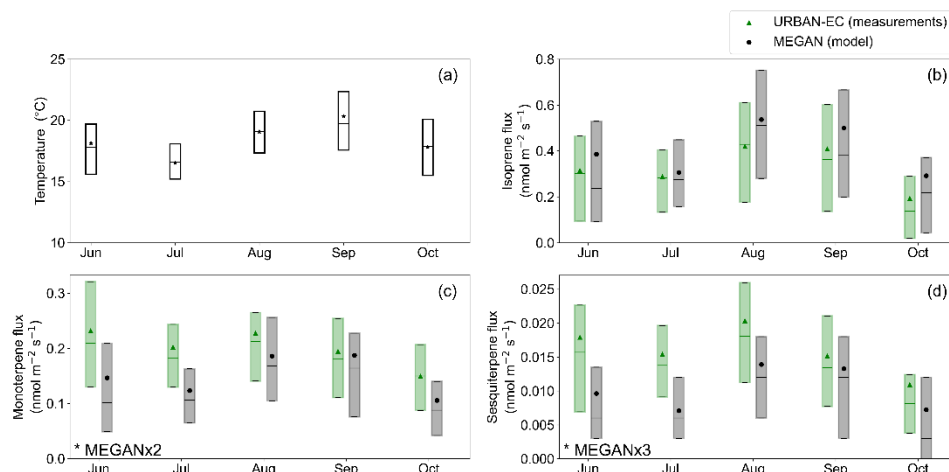
Thanks for the suggestion. We added this data to the supplemental information (Table S3 and Table S4) and updated text in the methods section:

"Some VOCs (nonanal, sesquiterpenes) were calibrated using the default k_{PTR} scaled by the percentage of signal falling on the parent ion determined by laboratory calibrations (Table S2). *The product ion distributions for the sesquiterpenes beta-caryophyllene and cedrene are shown in Table S3 and Table S4. The results* show that FIMR voltage settings can impact fragmentation despite similar E/N. *The parent ion ($C_{15}H_{25}^+$) fraction is 19-51% for cedrene and 13-32% for caryophyllene depending on the voltage setting.*"

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

The figure caption was modified: "Figure S3: Modeled isoprene fluxes (MEGAN) using different plant functional types: needle leaf, temperate broadleaf, tropical, and shrub. The default emission factor of 10 nmol/m2/s was used here. *The boxes represent the interquartile ranges, the horizontal lines in the box represent the medians, and the triangle icons represent the means*."

(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.

With MEGAN and BWW on the same axis, the difference is too large to see a trend in the MEGAN data. This revised figure compromises by clearly pointing out that MEGAN is multiplied by 2 or 3 in the case of monoterpenes and sesquiterpenes, while still showing the seasonal trend.

(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."?

> Yes. Modified text: "VOCs with average ***measured molar*** 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.

> Fixed: "The terpenoid fraction of the median total measured flux, calculated OH reactivity flux, and calculated SOAFP increased with increasing temperature ***(Figure S5),*** which agrees with observations from Pfannerstill et al. 2024."

(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.

> We inferred that monoterpene and isoprene lifetimes are similar because their emission velocities are close (6.3 cm s^{-1}, 6.5 cm s^{-1}). Since calculating isoprene lifetime is more straightforward than an uncertain mixture of monoterpene isomers (one rate constant versus many), we say the sum of measured monoterpene isomers has a lifetime like isoprene (2.6 hours). We updated the text for clarity.
>
> "The lifetime for isoprene was 2.6 hours using the measured ozone concentration (24 ppb) and an assumed OH concentration of $1.0*10^6$ molecules cm^{-3}, and the lifetime ***of the sum of measured monoterpene isomers*** is expected to be similar ***because of the similar emission velocities.***"

(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.

> % difference = (Weekday-Weekend)/Weekend * 100%
>
> % difference for 24-hour average: MT 24%, SQT 24%
>
> % difference for morning 06:00-12:00: MT 56%, SQT 55%
>
> Modified text in first paragraph of Sec. 3.2:
>
> "There was not a statistically significant difference in isoprene fluxes between weekdays and weekends (p>0.05), while monoterpenes and sesquiterpenes were significantly higher on weekdays compared to weekends (p<0.05). *Weekday fluxes of monoterpenes and sesquiterpenes were on average 24 % higher than weekend fluxes on a 24-hour basis, and larger differences were observed during the morning (55 % and 56 %, respectively). These morning enhancements are shown in Figure 4.*"

(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?

> The central tendency of the measurement followed the expected biogenic trend, but with considerable scatter due to the complexity of the real urban environment.

(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.

> The method which involves the Weekday – Weekend subtraction only describes anthropogenic emissions that are higher on weekdays compared to weekends. There are anthropogenic emissions present on weekends that are not accounted for with this subtraction. That is why our result is the 'lower bound' or 'weekday excess' anthropogenic emission, because it doesn't include weekend anthropogenic emissions.
>
> This is described in this line from the original manuscript:
>
> "This method provides the excess weekday anthropogenic monoterpene flux, or ΔF_{anth}, which is the lower bound of the anthropogenic monoterpene emission. It is not a measure of the total anthropogenic emission, as anthropogenic monoterpene emissions are expected on both weekdays and weekends which are not accounted for here."
>
> We modified the line you mention in this comment to be clearer:

"The total anthropogenic fraction of monoterpene emissions is expected to be higher, but it *cannot be calculated using this method.*"

(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.

> Agreed, this is a good comment and was brought up by another reviewer also. We modified that paragraph.
>
> "Limonene is considered a tracer for anthropogenic monoterpene emissions due to its prevalence in fragranced consumer products, though it is also emitted by plants (Geron et al. 2000; Steinemann et al. 2011; Gkatzelis et al. 2021a). *Other monoterpenes including alpha and beta pinene are also emitted by fragranced consumer products (Link et al., 2024; Zannoni et al., 2025).* Sorbent tubes and 2D GCMS analysis were deployed for three days in June of 2022 to provide a snapshot of the monoterpene speciation in Berkeley. Limonene accounted for 19 % of the monoterpene mixing ratio (Figure S14). 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 also an important source* of monoterpenes on average."

(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.".

> Great question. We are not really in a position to say whether or not the terpenoid emissions are a problem, but they certainly contribute meaningfully to the OH reactivity. We took your suggestions and modified the text.

"*Additionally, decreased use of terpenoid compounds in fragranced consumer products would likely decrease terpenoid emissions from anthropogenic sources in urban environments.*

Further work on terpenoid source apportionment in urban environments would contribute to a better understanding of *pollutant formation associated with consumer product use*."