Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-851-RC1, 2021

Comment on acp-2021-851

Anonymous Referee #1

Referee comment on "Interannual variability of terpenoid emissions in an alpine city" by Lisa Kaser et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-851-RC1, 2021

Review of acp-2021-851: Kaser et al "Interannual Variability of BVOC Emissions in an Alpine City"

General comments: The authors present a comparison between eddy covariance fluxes of isoprenoids (isoprene, monoterpenes and sesquiterpenes) measured from a flux tower located in the urban centre of an Alpine city (Innsbruck) during the peak growth seasons (July-Sept) in 2015 and 2018. The campaign period in 2018 corresponded to an extended heatwave accompanied by drought across most of Europe and previous studies have reported substantial increases in isoprenoid emissions and fluxes during this period.

By normalising the measured fluxes to standard conditions (30Ë□C and 1000 µmol m-2 s-1 PAR), they demonstrate that the observed increase in mono- and sesqui-terpene fluxes in 2018 compared to 2015 were attributable to the higher temperatures during the heatwave summer. Isoprene fluxes, however, were around 2.5x higher in 2018 than could be accounted for by the increase in air temperature. The authors explore a range of potential sources of these anomalously high isoprene emissions but are unable to reach a mechanistic understanding. They conclude that our knowledge of isoprene synthesis and emission under environmental stress is incomplete and call for further leaf-level measurements.

In general, the paper is well-written, but would benefit from further detail particularly with regard to methodology. While the authors point the reader to previous work in which various techniques are more fully described, elements of the data collection and analysis that are critical to their conclusions should be set out more clearly here.

The research presented here is of clear interest to the biogenic flux and urban emissions communities, fits centrally within ACP’s scope and I recommend publication following minor revisions and further explanation and clarification.

Specific comments:

The authors have attempted to delve deeper than a mere presentation of measured fluxes and correlation between variables. For example, they estimate emissions of the isoprenoids within the footprint of the flux tower using standard emissions algorithms and a detailed tree inventory, and attempt to attribute the anomalously high standardised isoprene emissions observed in 2018. However, their description of the methods used, and their interpretation and discussion of their results are at times surprisingly superficial, detracting from the important addition to real-world observational data and knowledge this paper should have provided.

Before this paper is accepted for publication in ACP, the authors should supply far greater detail of the measurements made and the calculations and analyses performed, rather than entirely relying on previous publications. The purpose of the methods section is to supply the reader with sufficient detail to fully understand what has been done, how and why; further detail required to enable replication of the study can be left to the previous studies conducted at this location.

2.1 Field site and instruments:

Please give details of the sampling frequency of the CPEC200, and any periods for which flux data are unavailable.

Likewise the PTR, and explain the significance of the acetone and isoprene sensitivities. Was the PTR operated in full mass scan or selective scan mode? How long was the inlet line from the tower to the PTR? What are the estimated wall and chemical losses of VOCs, particularly the sesquiterpenes and lower volatility and more reactive monoterpenes, in the inlet tube?

How reliable a measure of precipitation at the urban site is the tipping bucket gauge? Presumably this has been evaluated in previous studies. Likewise, the SMAP retrievals: at 9km resolution, how well do they capture the fine detail of heterogeneity in surface across an urban area? Also, it is not clear the purpose of the SMAP retrievals as the authors barely make reference to them and do not appear to make use of these data in their estimates of isoprenoid emissions or discussions of shortcomings in their study and areas of future research.

2.2 Eddy covariance fluxes

Why was the dataset reduced to daytime hours (although this is not apparent from the presented plots of diurnal profiles of fluxes)? Both monoterpene and sesquiterpene emissions are predominantly temperature controlled and hence continue throughout the night. Isoprene accumulation overnight has been reported on numerous occasions, with Millet et al (2016; doi: 10.1021/acs.est.5b06367) attributing an early morning burst of ozone formation in an urban area to isoprene emissions late the previous evening. It is more usual for nighttime fluxes to be filtered out by too low windspeed if and when a stable nocturnal boundary layer is established. Why have the authors not simply followed this established methodology?

How many measurements were excluded? What proportion of measurements were suitable for flux calculation and subsequent analysis in each year? Please explain more clearly the filter that was applied (L142-146).

While the footprint of the flux tower is shown in Fig 1, it would be more instructive to see the footprint density, which would benefit from a fuller explanation in the text. I assume that by density, the authors are referring to an estimation of the relative contribution of each point within the footprint to the air mass samples at the flux tower. How is the contribution determined? What weighting system is used? Simply by air mass or by proportion of CO_2 and H_2O flux?

The authors need to explain why the 2018 footprint is so much smaller than the 2015 footprint. To me that suggests that windspeeds were considerably lower in 2018 - yet the authors demonstrate that AVERAGE windspeeds were similar. I think Fig 1 would benefit from the inclusion of the a panel showing the footprint density and windrose plots for each year - this would considerably help understanding of these issues.

Why did the authors choose to use MEGANv2.0 to calculate isoprene emissions AND include only the light and temperature activity factors? The biggest limiting factor to photosynthesis and therefore availability of electrons and carbon for isoprenoid synthesis is water availability, which the authors have via the SMAP retrievals. Multiple studies have demonstrated the importance of accounting for soil moisture status (in addition to the observational studies the authors cite, Sinderalova et al (2014; doi:10.5194/acp-14-9317-2014), Emmerson et al (2019; doi: 10.1016/j.atmosenv.2019.04.038), Otu-Larbi et al (2021; doi: 10.1111/gcb.14963) have applied various models to show this, and Jiang et al (2018; doi: 0.1016/j.atmosenv.2018.01.026) have presented a new parameterisation of soil moisture impacts on isoprene emissions specifically for MEGAN). I can understand that the authors may wish to start with the "standard" algorithms, but why not use this in the subsequent exploration of "other factors" that may account for the 2018 anomaly?

Monoterpene and sesquiterpene emissions are very definitely NOT "known to be purely temperature dependent"! As early as 1995, Staudt & Seufer (Naturwissenschaften 82: 89–92) reported light-dependent emissions of monoterpenes and this is now well-accepted AND, importantly, is explicitly included in the emissions algorithms for mono- and sesqui-terpenes in MEGAN2.1 (Guenther et al, 2012; doi: 10.5194/gmd-5-1471-2012). Why have the authors not used these more recent formulations? (Even if this serves to support their later statement that at this location fluxes are solely temperature dependent)?

How were the effects of LAI and leaf age on emissions accounted for?

The authors state that the chemical lifetime of sesquiterpenes against oxidation primarily via ozonolysis is of a similar order of magnitude as turbulence timescales. The same will be the case for the more reactive monoterpenes, many of which could be expected to be emitted from the mix of tree species shown in Table 1. Why have the authors not also accounted for the chemical loss of a proportion of the monoterpenes? Also, while the authors have given an equation for the chemical loss, is not at all clear how and when this was applied to their estimation of sesquiterpene emissions and fluxes. Please elucidate. For example, the chemical loss rate will be highly dependent on the availability of atmospheric oxidants, particularly ozone in this case, but also the nitrate radical at night, and the concentration of the isoprenoid, What assumptions have the authors made in this regard, and how is this justified?

2.3 City tree inventory
What % of the trees are contained in private gardens? And how many trees would the authors estimate are unaccounted for in the inventory.

2.4 Emission potentials
Why did the authors not use the emission potentials, or parameterisations for calculating them, from Guenther et al (2012; doi: 10.5194/gmd-5-1471-2012)?

2.5 Relative emission ratio maps
Why choose such a coarse grid as 100m x 100m when a full tree inventory is available for the footprint of the tower (which was <1km x1km each year)?
What effect would the authors expect changes in leaf age and phenology, and differences between different tree species, to have on the estimated ratios? This does not appear to be discussed anywhere.

3.1 Flux footprint
Again, the authors refer to the footprint density but do not explain how this is derived (see previous comment).

While the authors do point out that they are unable to calculate absolute values of emissions as they do not have data for the leaf dry weight for the different trees and so focus on the ratios of the different terpenoids, I would expect to see further analysis of discussion of the robustness of this approach. For example, in this first paragraph, they discuss the contributions of the different tree species to absolute values of each isoprenoid without consideration of differences in total leaf mass of the different species, nor the potential for differences in leaf mass between years or over the course of the measurement period which extends into a time when some of the trees are likely starting to senesce.

How do the authors account for the strong horizontal heterogeneity of the flux footprint? A fundamental assumption required for applying EC techniques is that the fetch is homogeneous in all directions from the flux tower. This is very definitely not the case here. I would suggest that at the very least, they should split out the fluxes and bottom-up emissions by wind direction - this would provide a far more powerful analysis of the drivers of the potential emissions and observed fluxes.

3.2 Two summers of urban BVOC fluxes
The authors appear to use "flux" and "emissions" interchangeably throughout this and subsequent sections. The two are NOT equivalent and the authors should be explicit about this. While the fluxes can be taken as a good indicator of the pattern and magnitude of emissions in the footprint, they are not measuring leaf- or tree-scale emissions, particularly of the more reactive species.
Similarly, "footprint" and "footprint density".

Presumably the authors use the winter-time benzene/isoprene ratio in an attempt to exclude biogenic sources of isoprene. However, I would expect the sources of anthropogenic VOCs to differ between summer and winter, resulting in differences in magnitude but also ratios of different VOCs between seasons. It's not clear how the authors extrapolated from the winter-time ratio to deduce that 70-80% of the isoprene measured at the flux tower during the campaign was biogenic in origin.

While the authors highlight the discrepancies between predicted emissions and measured fluxes for lower temperature for mono- and sesqui-terpenes, particularly during 2018, they do not similarly highlight the over-estimation of isoprene emissions for these same temperatures in 2018. In fact, they state that measured isoprene fluxes closely followed estimated isoprene emissions. Furthermore, for the mono- and sesqui-terpenes, I would expect to see a more detailed discussion of why this might be the case, rather than the brief statement that perhaps other vegetation contributed. This is undoubtedly true: mono- and sesqui-terpene emissions from grasses and herbaceous plants such as those likely commonplace in urban areas can be expected to be high. Why do the authors not, at the very least, consider the proportion of the footprint density covered by short vegetation (shown in Fig 1) and attempt to estimate what proportion of the flux may be accounted for by this?

It's not entirely clear why the authors spend so much time comparing their standardized emission potentials to those measured at other urban sites, without a deeper analysis of the similarities and differences between the various studies. Why not simply give the range of previous fluxes and show that these are of a similar magnitude?

In their analysis and discussion of sesquiterpene fluxes, the authors refer back to their "correction factor" which they state puts an upper limit on actual fluxes up to 2.5 times those measured. Please see my previous comments regarding the calculation, application and appropriateness of this factor. In particular, neither turbulent nor chemical timescales remain constant over the course of a day or the 6-week plus observation period, and given the differences in temperatures, windspeeds (and possibly directions) between years, the inter annual variation is likely substantial. Have the authors considered these factors? In particular, the chemical climate of the urban atmosphere through the measurement periods should be carefully considered and discussed. What assumptions are the authors making with regard to the oxidant budget, reaction rates and turbulence?

It would be useful for the authors to present a measure of the goodness-of-fit between the observed and theoretical fluxes for each of the isoprenoids for each year. Does it vary by wind direction and/or speed?

3.3 Isoprene flux anomaly
The details of the temperature and light dependence (including 24h and 240h) should already have been fully introduced in the methods section, not here in the results. Furthermore, in L152 the authors state they are using the MEGAN 5-layer canopy approach but here in L285 they state they are using the big leaf approach. Which is it? They are very different in their formulation and capability. How appropriate is either canopy (5-layer or big leaf both assume horizontal homogeneity and a relatively uniform vertical structure) for modelling an urban canopy?

Figure 3 is barely referred to from the text yet it makes a critical point that the authors then go on to discuss in some depth. Far more analysis and insight is required here. Figure 3B shows that the anomaly (roughly) increases with temperature and PAR, not PAR alone.

It would be very useful to see the number of data points per T-PAR bin in Figure 3B. The authors should also take their analysis deeper and attempt to elucidate what other factors and conditions lead to the observed anomalies. Wind direction (and therefore synoptic-scale met conditions), wind speed, soil moisture, VPD, etc.

It was good to see that the authors attempted to find alternative explanations for the substantial anomalies in isoprene fluxes during 2018.

(a) While average wind speeds are relatively similar between the years, the median Obukhov lengths are very different (by nearly a factor of 2!). Please could the authors explain this difference and provide some insight into the likely effect on fluxes measured at the flux tower.

Again, it should be noted that mono- and sesqui-terpenes are considerably more reactive than isoprene and do not directly inform whether changes in isoprene emissions should be expected.

(b) It should be noted that LAI and leaf area density can vary for reasons other than pruning. For example, early senescence, difference in nutrient availability, herbivore or pathogen infestation, etc.

(c) It seems likely that the increased water fluxes in 2018 are due to surface evaporation from both the soil and the bare surfaces of the city if watering was increased during that summer. The similar SMAP retrievals for the 2 years further supports this. It should also be noted that, while useful, SMAP retrievals only provide moisture content of the top layers of soil and not the root zone which is critical for accessibility of water for trees. Is this why the authors appear to distinguish between soil water and soil moisture?

In fact, the authors are incorrect: mile drought has been shown from multiple measurement campaigns and modelling studies to INCREASE isoprene emissions (see previous reference list) and could in part explain the anomaly (Otu-Larbi et al, 2020 for example found emission potentials increased by a factor of 2.5 during mild drought in temperate deciduous forest). Otu-Larbi et al (2020) also reported an apparent burst of isoprene emissions on rewetting.

I suggest that the authors need to investigate more thoroughly whether the anomalies in isoprene fluxes occur at times of mild drought or in response to rewetting following drought conditions.

I would recommend that the authors split (c) into two sections: one dealing with soil moisture, drought and rewetting and the second with the parameterisation and specifically the choice of Topt as these are quite distinct.

It should be noted that both mono- and sesqui-terpene emissions are also controlled by stomatal conductance which could be expected to affect emission rates during drought periods (se e.g. Niinemets and Reichstein, 2003a & b; doi: 10.1029/2002JD002620 & 10.1029/2002JD002626).

How accurately does the MEGAN canopy (again the authors refer to the 5-layer version here) represent LEAF as opposed to air temperature? This is usually anomalously high during periods of drought and other abiotic stresses (Niinemets, 2010; doi: 10.1016/j.tplants.2009.11.008 & Potosnak et al, 2014; doi: 10.1016/j.atmosenv.2013.11.055).

3.4 Top-down and bottom-up BVOC flux ratios
Please see previous comments regarding the treatment of chemical loss of sesquiterpenes in the analysis of flux vs emission. To my mind, this is a substantial weakness of the authors' approach (assuming I have correctly understood how the correction factor is applied) as it appears to involve a gross and relatively unjustified assumption regarding the oxidative capacity of the urban atmosphere during the measurement periods.

The conclusion that more studies of sesquiterpene emission potentials are needed is weak. Much is still required to be understood about sesquiterpene synthesis, emission, dispersion and atmospheric reactions before fluxes and emissions can genuinely be compared.

Figure 5 is very poor - the colour scales are such that the panels provide very little useful information. Presumably the squares with apparently no overlay contain no vegetation at all, but why not white them out? Again, it would also be useful to see how many flux observations originated from each of the grid cells (this again comes back to the matter of the missing figure of footprint density).

4 Summary
This section is rather superficial and the conclusions weak.

In particular, the authors again refer to having ruled out the effect of severe drought, apparently unaware that in several of the studies they have cited, that isoprene emissions are substantially enhanced during periods of MILD drought. Possible causes of this are well discussed by both Potosnak et al (2014) and Ferraci et al (2020). Plus they have not attempted to analyse whether their observed anomalies coincided with officially recognised drought conditions in the city.

Their study certainly does not show that urban conditions are distinct from other ecosystems. The unexpectedly high isoprene concentrations during heatwave-droughts have been reported from woodlands as well.

Again, the final statement that more work is needed is weak. Precisely what lab- and field-based experiments and modelling is required in the authors' opinion?

Technical comments: While mostly clearly written and presented, the manuscript would benefit from English editing to clarify some statements and explanations. I have suggested replacement text only where the original meaning is unclear.

Abstract:
L17 (and throughout document): Standard scientific notation should be used, i.e. 3.0 x 10-3 rather than 3.0 . 10-3, etc.
L21 - please replace "explained" with "explain"
L21 - please replace "standard emission potentials" with "standardized isoprene emission potentials"

2 Material and methods
L128-129 - please give the conversion used to estimate PAR from short wave radiation.

L173 - What is meant by "overlapping"?
L178 - "IS" should read "ISO"
L186-7 - This is a little unclear. I suggest that the authors demonstrate the full calculation

specifically for ISOtile/MTtile.
L200, 205 & 208: The same 12, 19 & 38 trees in 2015 and 2018? (As the footprint does differ)
L213 - If the authors have discounted nighttime fluxes, it is not clear why they consider nighttime emissions (which I assume they do as they refer here to differences in nighttime temperatures).

Figure 1: The difference between dark green and light green for trees and short vegetation is not sufficiently distinct.

L225 - I would suggest replacing “BVOC” with “isoprenoid” as the authors do not report the fluxes of any other BVOC.
L226-228 - Why do the authors refer back to parameterisations developed in 1993 and 1994 rather than the ones they have actually used? (And see previous comments regarding the light-dependence of monoterpene emissions).

Figure 2A-C - Why have the authors presented a full diurnal cycle, when they explicitly state in the methods that they consider only “daytime” fluxes, which they further refine to 09:00-16:00 LT?

L415-6 - It’s not clear what the authors mean by “extrapolated to”. Do they simply mean assumed to be the same during the summer?
L433-434 - See previous comments regarding the superficial nature of the conclusion that the anomaly increased with increasing T and PAR. It would be far more useful if the authors could demonstrate that e.g. SMAP soil moisture content or VPD or … were not in fact the cause of the apparent correlation.
L434 - The authors have not considered water availability at root depth. Please replace this term with something more appropriate.
L447 - Is it big leaf or 5-layer?