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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ethene, propene, butene and isoprene emissions from a ponderosa pine forest measured by Relaxed Eddy Accumulation" *by* Robert C. Rhew et al.

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The paper presents studies of emissions of light alkenes from a pine forest. Since data on emissions of light alkenes from vegetation are rare and existing emission data have substantial uncertainty the presented information creates new, useful insight into the role of vegetation as source of volatile organic compounds (VOC), a subject that is highly relevant for ACP. The emission studies are based on state of the art methodology, Relaxed Eddy Accumulation (REA). The results are of very high quality, the methodology is clearly explained and overall the discussion is sound and the conclusions justified. The paper is well structured and written, the figures and tables overall of

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very good quality. Consequently, the paper merits publication in ACP, although I have a few suggestions for changes and additions to improve the paper.

The two main points are:

i) Gap-filling: I agree that gap-filling can provide a better estimate for averaged monthly or daily fluxes. However, gap-filling, independent of the interpolation procedure, has serious limitations.

- It cannot compensate for bias in the data set resulting from experimental limitations, for example flux data below the DL will be absent from the measured data and gap-filling cannot compensate for this. Indeed, in Figure 6 it seems that for ethene and propene the gap-filled data are always, even at night, above zero. In Figure 9 the PAR dependence of the fluxes predicts that the fluxes are zero for PAR=0.

- When using interpolated data, it is very difficult to derive meaningful statistical criteria. I assume that ± in Table 1 indicates the standard deviation σ. I am not sure how to interpret a standard deviation for an interpolated data set. Based on basic statistics the error of the mean can be calculated from σ and the number of data points N: Error of mean = σ/sqrt(N-1). Since there is no limit in the number of interpolated data points this would imply that the error of the mean interpolated flux is effectively zero. Strictly speaking the modeled flux is a calculated value and the error of a calculated value can be determined using (Gaussian) error propagation, which is close to impossible for an ANN interpolated data set.

- Independent of the interpolation procedure, the results of the interpolation can be biased by the assumptions required for the interpolation. Here the situation is especially complex due to the two step interpolation procedure. It is stated that for the ANN gap-filling “inputs were normalized”. This needs more explanation. Moreover, from page 9, line 17-18, it seems that the ANN input set was created by interpolation of measured data, although no detail of the interpolation procedure is given.

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- An interesting scientific question is: Do the ANN based fluxes provide a better fit to the measured fluxes than a calculation based on the T and PAR dependence developed in 5.5 (Figure 9). This could provide evidence that modeling alkene fluxes using T and PAR alone is insufficient.

ii) Statistics:

- The authors should provide a more detailed evaluation of the significance of the findings. For example, there are no error bars for the binned data in Figure 9. There are no uncertainties for the fitted parameters in Table 2. Based on the scatter of binned data in Figure 9 (especially for the PAR dependence) I would expect substantial uncertainty. This is mentioned in the discussion, but still does not allow an estimate of uncertainty for fluxes calculated from the models. It seems from Figure 6 that the night-time fluxes for ethene and propene are above zero, which is in contrast to the PAR dependence derived in 5.5, the fit parameters given in Table 2 and the fitted functions in Figure 9. Is this a real discrepancy between measured and modeled fluxes (which would indicate shortcomings in the modeled fluxes) or can this be explained by the uncertainty of averages, fits, and binned data, or is this a result of gap-filling?

- On Page 13, lines 27-29 it is mentioned that “The understory REA measurements showed detectable consumption overall for ethene, propene and butane. . .”. However, due to the large uncertainty of the negative fluxes and the small number of data points I am not sure if these fluxes are below zero at a meaningful significance level.

- From Figure 1S it is evident that the probability distribution of measured fluxes cannot be described by a Normal Distribution as implied by the mean values and standard deviations in Table 1. In this case non-parametric statistics (median, percentiles) provide a more realistic insight into the actual distributions than mean and standard deviation or error of mean.

- Correlations: Most of the correlations and linear regressions are for data sets with substantial seemingly random variability of y and x values. Standard linear regression does not consider uncertainty for the independent variable and an arbitrary identification of the independent variable may result in biased estimates of slope, intercept or R2. A better indicator for the quality of a correlation is the Pearson product moment correlation coefficient, which does not require distinction between a dependent and independent variable. I also think that correlations with R2 values of 0.5 or less do not qualify as good or high correlations. Figure 7 only shows the slopes (without errors) of the linear regressions, not intercepts. Are the axis intercepts zero (within their uncertainty) or was a regression used that did not allow a non-zero axis intercept?

Some details:

Introduction: This is a good, detailed overview of the role and sources of light alkenes in the atmosphere with emphasis on vegetation. I understand that the different estimates etc. represent the uncertainty in current emission inventories and differences between different studies. However, it is not easy for the reader to extract an overall perspective of the role of alkene emissions from vegetation in comparison to other sources of light alkenes or emissions of other VOC from vegetation. A table (or graph) summarising the emission rates of light alkenes from various sources would be very useful for the reader and make it easier for the reader to understand the potential importance of reducing uncertainties in emission rates of light alkenes from vegetation.

Page 5, line 5: “with a lapse between. . .” should be rephrased (gap?).

Page 6, line 19 and other occurrences: “sonic temperature” should be rephrased.

Page 8, line 3 and S, page 5, line 20-30: I accept that, due to the absence of an extreme change between consecutive measurements, alternating the sequence of analysis between the “up bags” and “down bags” allows excluding that storage has a dominating impact on measured fluxes. However, due to the substantial variability of the measured fluxes and the use of two sets of bags, it is not obvious that the flux measurements are entirely free from impact by storage. The authors should present some quantitative estimate at which level of “storage bias” the mentioned “seesaw” pattern (pages 5, line

27-28) would clearly be visible.

Page 8, line 15-25, Fig. S1: Quality control, detection limits and flagged data. “Quality control for each hourly REA flux measurement was checked against eight potential flags associated with the sample volumes, meteorological conditions or footprint analysis”. There is an explanation in the supplement. However, since 47% of used data were flagged for not strictly meeting all criteria some quantitative estimate should be given to which extent this may impact data quality. Data flagged with more than 4 flags or data not meeting specific footprint criteria are excluded. I am not sure about the rational for this specific threshold. Moreover, it seems that a large portion of very low fluxes were flagged or failed QC. How does this impact the overall averages and representativeness of the flux data? How were flux data below the lowest flux detection limit treated in further data evaluation? The way data below the LDL are used is important since this may create bias for averages, fits, modeling etc. It is also mentioned that some fluxes were negative. How were they used in the data set? From Figure 7 it seems that there are no negative fluxes, but it is mentioned that a small number of fluxes which met QC are negative.

Page 8, 9, S2, Understory REA fluxes: I understand that measuring the understory flux is very difficult, especially since it seems that the flux is small. Nevertheless, the very small fraction of measurements that passed QC raises the question of representativeness of the few good quality data. Since the main result of this study is that understory fluxes are (on average) small compared to the total flux, rejected data which could be used to provide meaningful upper limits of understory fluxes may strengthen this point.

5.2 and 5.3: Both subchapters present a comparison between literature and this study. Combining both chapters would allow a more consistent comparison. For example, in 5.2 the alkene fluxes are placed in context to CO2 and other VOC fluxes. However, in 5.3 this context is not considered. Yet, it would be very important to understand if some of the differences in alkene fluxes maybe related to differences in assimilation or respiration rates and so on.

Page 16, lines 25-27: “We utilized fluxes instead of concentrations to provide a measure of OH reactivity that is independent of elevated concentrations associated with pollution events and more representative of site specific sources.” This creates a distorted view of the importance of emissions. The atmospheric OH-reactivity of a VOC at a given concentration ([VOC]) is determined by [VOC] kOH, as mentioned in the previous sentence and the cited literature. In a simplified steady state [VOC] is proportional to the flux and inversely proportional the reactivity (kOH). Consequently, the overall relative impact of an emission is simply determined by the emission flux. The reactivity determines the temporal and spatial scales at which this happens. It should also be considered that alkenes also react with ozone, OH reactivity therefore only determines one part of the overall alkene reactivity.

Page 17, lines 11-12: Based on the uncertainties of averaged fluxes, extrapolation etc. I am not certain that a 20-60% difference is really significant. I also do not understand why the estimate of the seasonal flux average is based on such a simple extrapolation. The paper presents two more detailed models (gap-filling based on ANN and the T and PAR dependence presented in 5.4) which can be used to calculate averaged fluxes for comparison.

Combining subchapters 5.4 and 5.5 would allow streamlining the discussion of flux parametrizations and model predictions, for example how well MEGAN 2.1 parameterizations agree with the measured alkene (and not only isoprene) fluxes. Based on the current discussion it is not evident that (and why) “Modifying the light and temperature parameterizations for light alkenes in the vegetation emissions model will lead to a corresponding increase in estimated global emissions for these compounds”.

Conclusions: They are more or less a summary. I agree with the overall conclusions that the current understanding of alkene emissions from vegetation is insufficient and that alkene emissions from vegetation can be relevant for the chemistry of the atmosphere. However, based on the many interesting aspects presented and discussed in the paper I am a bit disappointed that the suggestions for tackling open questions

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and reducing uncertainties is basically a generic “more research needed” approach. Specifically, the very good correlation between ethene and propene fluxes is striking and raises questions about origin and the factors determining the emissions of these two alkenes.

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