acp-2017-363: Ethene, propene, butene and isoprene emissions from a ponderosa pine forest measured by Relaxed Eddy Accumulation

RESPONSE TO REVIEWER #1 (Anonymous Referee #1)

We thank reviewer 1 for the thorough and positive review of our manuscript and especially for the helpful comments, which we have incorporated in the revised manuscript. We believe that this revised manuscript is improved in quality and clarity. In the following text, we address each comment individually and highlight changes to the revised manuscript. Reviewer 1 comments appear in italics, and our responses are in bold type-face.

In this study, the authors measured and analysed the concentrations and fluxes of light alkenes (ethene, propene, butene), isoprene, acetylene and benzene above and within a ponderosa pine forest canopy during the summer in 2014. They concluded that these light alkenes were originated from local forest canopy, and the measured fluxes of them were about 1 to 3 times as large as the results in previous studies. The authors also found the strong responses of alkene fluxes to temperature and PAR, and then parameterized the responses with two fit functions which agreed well with the measured data.

This study provides a new dataset of measured net fluxes of light alkenes in the ambient air and new parameters to model the biogenic emissions of light alkenes. The measurement techniques are described in a clear and detailed way. The parameterization methods will improve or potentially increase the accuracy of biogenic emission models (e.g., MEGAN) in simulating light alkenes. In general, this study has provided a solid understanding of biogenic emissions of light alkenes. Therefore, I recommend to accept this manuscript after some minor revisions.

P6, L1: "in (Businger and Oncley, 1990)" –> "in Businger and Oncley (1990)"

Corrected.

P8, L7: "next Additional" –> "next. Additional"

Corrected.

P9, L26: "correlation coefficients" –> "coefficients of determination (rˆ2)" Here rˆ2 is usually named as the coefficient of determination which represents the percentage of explained variation.

We agree and adopted the proposed terminology.

P11, L27: The acronym of quality control QC is not defined before.

Rephrased to: "the reported quality-ensured fluxes"

P12, L9-10: The names of isoprene, acetylene, benzene need to be added in the table caption.

Corrected.

P12, L17-18: "Storage occurred at night (19-24 MST), offsetting for additional ~ 25% of measured nighttime respiration." This sentence is not clear and needed to be rephrased.

We thank Reviewer 1 for pointing this out. This has been rephrased to: "Storage occurred at night (19-24 MST), leading to an underrepresentation in measured night time respiration on the order of ~25 %."

P13, L16-22: The correlations of concentrations and fluxes for acetylene and benzene should be described here or at other places since they are also plotted in Fig. 7.

We have added a correlation analysis for acetylene and benzene in section 4.4 and have added text in section 5.1 as follows: "In contrast, no such diurnal patterns in concentration are observed for the primarily anthropogenic compounds (acetylene and benzene), and their fluxes are near zero (Table 1). Consequently, correlations between the light alkenes and either acetylene or benzene are poor (concentrations) or non-significant (fluxes)."

P14, L11: "BVOC models" –> "BVOC emission models"

Corrected.

*P18, L12: The equation 4 is not described clearly. Should the response equation be: F(T) = alpha*exp(beta*(T - 30)) ? Is the actual emission rate calculated as: F = F(T)*F_30? Here F_30 is from Table 2. But if this is true, the actual flux at T=30 [degC] for ethene is: 302.9 * 0.0325 = 9.84 [ug m-2 h-1], which is much lower than the measured flux shown in Table 1.*

Equation 4 was originally intended to be a normalization factor to the observed flux at 30°C. This would allow the curve fits for different gases to be compared more easily by being plotted on a single graph (i.e., temperature = 30°C and F(T) = 1 for all gases). For example:

>> 0.0325 x exp(0.1142 x 30) = 1

To scale to meaningful flux units (F), however, it was indeed necessary to multiply by the reference flux (F_{30}): F = F(T) * F_{30}. We see how this was unclear, so in the revised manuscript (eq.4 is now eq.5), the equation was changed slightly, to improve clarity and to conform better with the MEGAN nomenclature. The equation is now written as:

$$F(T_{LDIF}) = F_{ref} * \exp(\beta(T - T_{ref})) \qquad \text{(Eq 5)}$$

Here, $F(T_{LDIF})$ describes the light independent fraction of temperature response, where β is an empirical coefficient (Table 2), T is the ambient temperature (°C), T_{ref} is constant = 30 °C, and F_{ref} is the observed flux at 30 °C.

The normalization by F_{ref} is now included as part of the equation, and fitted coefficients from Table 3 can be plugged in to calculate fluxes in units [$\mu g\ m^{-2}\ hr^{-1}$]. For example, at 30°C with reference flux for ethene (table 3) being 316 [$\mu g\ m^{-2}\ hr^{-1}$]:

F(30°C) = 316 * exp(0.114*(30-30)) = 316, as expected.

*P18, L9: Is the actual emission rate calculated as: F = F(PAR)*F_1000? Here F_1000 is from Table 2. The same symbol "alpha" is used for both equations 4 and 5, but it represents different parameters. Two different symbols should be used here.*

The parameterization was indeed a normalization function to F_{1000}. We reassigned the Greek symbols in the equations so that each letter is now used only once. Similar to the temperature response function, we have clarified the PAR response equation (eq. 4) to improve clarity. Now the normalization by F_{1000} is included in the function, as follows:

$$\boldsymbol{F(PAR) = \frac{\alpha\, C_{L1}\, PAR}{\sqrt{1+\alpha^2 PAR^2}} * F_{1000}} \qquad \textbf{(4)}$$

P18, L29-30: "This is consistent with respect to the observed source of isoprene in the understory, which is partially shaded." The meaning of this sentence is not clear. Why the partially-shaded subcanopy should be a large emission source of isoprene?

We acknowledge that this sentence was unclear. The canopy consists almost entirely of mature ponderosa pine trees, which are considered to be low isoprene emitters. The plant composition in the understory includes juvenile coniferous trees, grasses and ferns, and a considerable amount of the ground surface is either bare ground or leaf and needle litter. During our understory case study, measured fluxes above the forest ground were a similar magnitude as, or larger than, fluxes measured above the forest canopy. Thus, we hypothesized that almost the entire isoprene source was below the forest canopy.

However, the PAR values that we used in the light-response curve computations were measured above the forest canopy. For compounds that are presumably produced by the canopy (e.g., ethene/propene/butene), the fluxes flatten out at PAR > 1000, whereas isoprene fluxes still increase with increasing light. This was what we sought to explain.

Since only a fraction of the light observed above the canopy penetrates to the forest ground, the forest ground experiences a muted sunlight intensity, and therefore the subcanopy may not experience the high sunlight intensity where fluxes start to asymptote.

We rephrased the sentence as follows (section 5.4):
"It should be noted that the PAR measurements employed to compute the light-response curves were measured above the canopy, while the observed source of isoprene appears to be in the vegetated understory, which experiences more diffuse light. In fact, PAR intensity measured near ground level (2 m a.g.l.) was on average 50 ± 30 % (standard deviation) of the measured PAR above the forest canopy. Hence, the subcanopy isoprene source(s) may experience an optimum quantum yield at much larger incident PAR (measured above canopy) than the light alkene source within the ponderosa pine canopy, explaining the different light response curve."

P18, L31: "... on average a factor of 3.4 smaller than tower-based ..." This is a bit confusing, maybe using percentage is better here.

We changed this to a percentage [%], see above.

P18-19: A general comment on section 5.4 and 5.5.
1. In section 5.4, you show the temperature response curves of light alkenes fit the measurement data more than the light response curves. Do you think the equation 4 can be used to simulate the alkene emission rates alone?

We explored this by predicting alkene fluxes in 5 different ways: a) only eq. 4 (PAR); b) only eq. 5 (temperature, light independent); c) only eq. 6 (T, light dependent); d) the weighted (according to the LDF in MEGAN) combination of eq 5 / 6; and e) our initial gap-filling method (Artificial Neural Networks). Here are the statistics as root mean square error (RMSE) and Pearson's correlation coefficient (ρ) of comparison between predicted and measured fluxe:

Q&A Table 1.

	ethene		**propene**		**butene**		**isoprene**	
	RMSE	**ρ**	**RMSE**	**ρ**	**RMSE**	**ρ**	**RMSE**	**ρ**
F(PAR)	**46.5**	**0.68**	**42.2**	**0.69**	**16.3**	**0.7**	**41.4**	**0.54**
F(T_LIDF)	**48.4**	**0.72**	**46**	**0.68**	**16.8**	**0.64**	**44.3**	**0.48**
F(T_LDF)	**45.7**	**0.72**	**48**	**0.69**	**16.9**	**0.65**	**41.2**	**0.56**
F(T_MEGAN)	**45.5**	**0.73**	**43.1**	**0.69**	**16.5**	**0.68**	**41.2**	**0.56**
ANN	**32.1**	**0.83**	**27.7**	**0.8**	**8.6**	**0.8**	**28.6**	**0.64**

Yes, fluxes can be reasonably predicted solely as a function of T or PAR. However, the combined approaches F(T_MEGAN) and ANN yield better predictions of fluxes. Since all studied light alkenes show a response to light, we believe light should be included in parameterizations. If one wanted to predict fluxes solely on one equation, one should use the temperature response function with best fitting results, and this is now presented in table 3 of the revised manuscript.

If so, LDF in MEGAN 2.1 for light alkenes should be set to 0, while currently LDF of ethene is 0.8 and LDF of propene and butene is 0.2. Could you make a solid conclusion in this section about what kind of parameterization methods are better to use in the emission models?

Our results demonstrate that ethene and propene fluxes are highly correlated, and we propose to change the LDF of propene to 0.8, matching ethene.

2. In section 5.5, you have compared several parameters between MEGAN 2.1 and the parameterization methods used in this study. Although this manuscript is mainly about measurement and data analysis, I still recommend to implement the new parameters into MEGAN 2.1 and show quantitatively how much more light alkenes are emitted compared to the old version, if this is not difficult to realize.

This is a very worthwhile exercise, but we feel this is more appropriate in the context of a modeling paper that can explore the implications of these new equations better. We prefer to keep the focus of this manuscript on the measurement techniques, novel

results, and improved flux parameterizations, all of which should set up a future modeling paper nicely.

P19, L9: "CL1 = 0.0007
α = 1.73 in this study, CL1 = 0.0007
α = 1.74 in MEGAN 2.1"
This is not consistent with the values shown in Table 2.

Thanks for spotting that mistake. The values in the text now correspond with values in table 3. The table version was correct and remained unchanged.

0: "compounds be" –> "compounds should be"

Corrected.

P31: Figure 4: What do the dots mean in the butene plot from day 215 to 220?

We had trouble locating any wayward dots. The acetylene and benzene subplot had a blue and red dot used in the legend, which were perhaps too subtle. We changed the legend and hope to have resolved the issue.

P34: Figure 7: The names of acetylene, benzene should be added the caption

Corrected.