

Response to Reviewer 1

The manuscript reports a very interesting and important research concerning the relationship between carbonyl sulfide and carbon dioxide fluxes on ecosystem level and their response to diffuse radiation and heat waves. Current literature lacks the flux measurements provided by this study. This study will help fill in some knowledge gaps needed for implementing carbonyl sulfide as a constrain for the gross primary production on larger scales. Although the author had good references concerning the methods it lacks some basic information. Is the used instrument capable of correcting for the any effects due to water broadening and equally important were the surfaces chamber fluxes executed correctly? If the flow that is sucking the air out of the chambers is too high, COS depleted air from lower soil layers could distort the measurements. Concerning the concentration gradient, I was wondering why no invers lagrangian modelling was done as this method could help determine the sinks or sources within the canopy.

We thank the reviewer for providing thoughtful and detailed feedback on the manuscript. We address comments about water broadening, surface measurements and Lagrangian modelling in this response.

30-33 This statement is a bit farfetched. On what basis do you make this statement? LRU varies in your study, not only between seasons, but also as a result of changing light conditions (fraction of diffuse downwelling shortwave radiation)

Thank you for pointing this out. We have changed these lines in the abstract (lines-25-29) to say “*OCS fluxes showed a pronounced diurnal cycle, with maximum uptake during mid-day. OCS uptake was found to scale with independent measurements of CO₂ fluxes over a 60-m-tall old-growth forest in the Pacific Northwestern U.S. (45°49'13.76" N; 121°57'06.88") at daily and monthly timescales under mid-high light conditions across the growing season in 2015.*”

48 This is not entirely true, under stressed conditions plants have been reported to emit COS.
Add:

Bloem, E., et al. (2012). "Sulfur Fertilization and Fungal Infections Affect the Exchange of H₂S and COS from Agricultural Crops." *Journal of Agricultural and Food Chemistry* 60(31): 7588-7596. or other stress related OCS publication, as a heatwave might change the ratio of OCS to CO₂ uptake.

Thank you for providing the reference. We have included this (line 49).

115 If related to plant stress and photosynthesis (108), water potential would be a much better parameter to reflect the plant available water (if the parameter is available). Plant available water strongly depends on soil type and structure.

We agree with the reviewer’s comment about water potential. Unfortunately, we were not able to measure this quantity at the time of measurement.

140 My knowledge about the Los Gatos instrument is limited, but as literature tells me, the build in water correction of the instrument might not able to fully compensate for the effect of water vapor in sample air. Have you done dependency curves of gas with a known OCS concentration

at levels of different water vapor to test your instrument and the analysis routine? If not, I would strongly suggest doing this to avoid or correct for measurement errors. For further information, I recommend reading: Bunk, R., et al. (2017). "Exchange of carbonyl sulfide (OCS) between soils and atmosphere under various CO₂ concentrations." *Journal of Geophysical Research-Biogeosciences* 122(6): 1343-1358. See section 2.3, where this problem has been tackled with!

Thank you for pointing this. This was a cause of concern, we worked with the manufacturer on this, and found that while there was a slight dependence of water vapour on OCS mixing ratios, the effect was very small and likely doesn't affect measurements in this study (Fig.1).

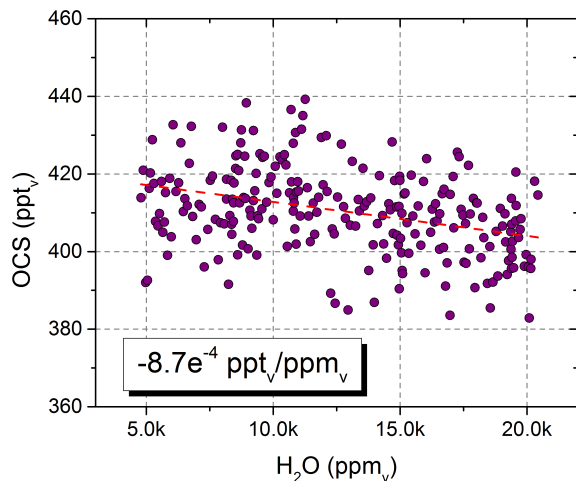


Figure 1. OCS water vapor cross-interference tested in the lab. The magnitude of this cross interference is negligible compared to observed canopy- atmosphere ecosystem exchange in this study

176 A reference suggesting only using mid-day hours would be appreciated. Didn't the cloud cover change from early morning to late evening?

Cloud cover does change during the day. However, the ratio of direct: diffuse light is also sensitive to solar zenith angles (such that the fraction of diffused light is always higher in the mornings and evenings). This is why we restrict our analyses with diffused radiation to mid-day.

181 Did you have problems applying the modified bowen ratio method? The publication cited in Commane et al. 2015 Meyers, T. P., et al. (1996). "Use of the modified Bowen- ratio technique to measure fluxes of trace gases." *Atmospheric Environment* 30(19): 3321-3329 States, that using this method might have issues when used within plant canopies. They state that "Infrequent but large energetic eddies are responsible for most of the exchange that occurs within canopies (Baldocchi and Meyers, 1991; Shaw et al., 1983). Transport by these coherent structures often leads to the counter-gradient flux structure frequently observed in crop and forest canopies." Also, why didn't you apply invers Lagrangian modelling like: Nemitz, E., et al. (2000). "Sources and sinks of ammonia within an oilseed rape canopy." *Agricultural and Forest Meteorology* 105(4): 385-404. and

Karl, T., et al. (2004). "Exchange processes of volatile organic compounds above a tropical rain

forest: Implications for modeling tropospheric chemistry above dense vegetation." *Journal of Geophysical Research: Atmospheres* (1984–2012) 109(D18).

You could even get the information about the source or sink strength of layers within your canopy.

Thank you for your suggestions and accompanying references. We have been trying to use an inverse Lagrangian/ Eulerian model to address this very problem. This is an ongoing project, we have had severe challenges in parametrizing a model that is able to estimate the wind profile and other parameters (such as eddy diffusivity) through the tall old-growth canopy. We hope to address this, and report these in a future study.

232 Even though you reference Falk et al. (2008) state that you are using a night time flux partitioning method that has been optimized to the field site. The LRU in this study will be used by modelers and I think the information from what the LRU is calculated is crucial.

We agree and have included this information (lines 228-229).

246 Are you using the Licor 8100 as flow through chamber with ambient air able to enter the chamber while you suck out the air at another end? If so, is the flowrate of 3 liters per minute not too much? How big were the openings of the chamber where ambient air was allowed to enter the chamber? If the flowrate is too high, air would be sucked out of the soil which would alter the fluxes you measure. Have you done differential pressure measurements like: Kitz, F., et al. (2017). "In situ soil COS exchange of a temperate mountain grassland under simulated drought." *Oecologia*: 1-10.

Yes, we agree with the reviewer on the issue of high flow rate. However, in contrast to other chambers, there is a vent on the top of the Li-Cor 8100 soil chamber that allows equalization of pressure between the inside and outside of the chamber. This consists of an always-open tube with a specially designed flow path to keep pressures stable even in windy conditions (Xu et al., 2006).

Xu, L., Furtaw, M. D., Madsen, R. A., Garcia, R. L., Anderson, D. J., & McDermitt, D. K. (2006). On maintaining pressure equilibrium between a soil CO₂ flux chamber and the ambient air. *Journal of Geophysical Research Atmospheres*, 111(8), 1–14. <https://doi.org/10.1029/2005JD006435>

251 Was it statistically indistinguishable, then write so.

Yes, thank you. We have included this (line 241).

286 Fig 2b-c instead of 2b

Changed accordingly.

307 Inverse lagrangian modelling could answer this question. Again, why not apply it?

Kindly see comment above.

311 Fig 2c add FCO₂ to ylabel

Changed accordingly.

346 There is no soil moisture in plot 4 which would help the reader see this correlation. Is there statistical evidence or just a trend?

We have included a figure (Fig. 3) that shows this relationship.

363 To make this statement you would have to compare the soil fluxes of your site with the publications. In your case, you have a combination of soil plus understory plants and mosses which could compensate for a soil emission. (As you stated in line 271: “The influence of the developed soil on site 1 is therefore considered minimal.”). I would use the citation you used to tell that no soil emissions are expected at your site.

We have included the relevant citation (lines 354-355).

373 In line 363 you write that you haven’t observed any OCS emission, I guess you meant uptake in line 373?

We mean to say that OCS uptake was correlated with CO₂ emissions.

388 Please state what the error bars stand for (I assume standard deviation).

Noted accordingly (line 371).

394 5b-c (a would be VPD)

Changed accordingly.

424 As NEE includes both, GPP and RECO, are you saying both components are increasing during the peak growing season, or did you want to refer to the CO₂ uptake only?

We have changed this to “increase in CO₂ uptake” (line 406).

123 mid-day VPDa (c) and soil moisture instead of Mid-day VPDa (c) and Soil moisture

Changed accordingly.

225 When this condition was not met (e.g. at nighttime), fluxes were calculated by integrating the rate of change in hourly OCS mixing ratios through the entire profile. — skip using

We have removed storage flux estimates from estimation of canopy-scale leaf OCS flux.

152 from instead of form

Changed accordingly.