

Interactive comment on “Observations of the uptake of carbonyl sulfide (COS) by trees under elevated atmospheric carbon dioxide concentrations” by L. Sandoval-Soto et al.

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j.kesselmeier@mpic.de

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Interactive comment on “Observations of the uptake of carbonyl sulfide (COS) by trees under elevated atmospheric carbon dioxide concentrations” by L. Sandoval-Soto et al.

Anonymous Referee #1

Authors: We greatly appreciate the extensive effort that referee 1 has spent in reviewing our manuscript and hope that our comments will help to answer all questions.

COMMENT 1 Referee: *The conclusions drawn by the authors don't appropriately represent the ambiguity in the results obtained. The authors approach this study with

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expectations on how the exchange between COS and plants should be affected by increased CO₂ concentrations. These expectations are reasonable given our understanding of this system, but the important question regarding this manuscript is whether the new data add to the evidence supporting those assertions and how those results are interpreted by the authors and conveyed to the reader. Unfortunately, the signals they measure in most respects are not robust so that the expected relationships do not appear to be generally confirmed by the new data. The authors' results do show that CO₂ depositional velocities increase by factors of 2-4 when the trees were grown for an extended period at 800 ppm vs 350 ppm CO₂ concentrations. The conductance data, however, only fit expectations half of the time (conductance reduced under elevated CO₂). Expectations suggest that enzyme activity (carbonic anhydrase only, as it is relevant for COS) should be important for interpreting trace gas results, but those measurements do not clarify the situation for CO₂ or COS (none of the measured activities were significantly different under the two CO₂ concentration environments). Finally, in the case of COS uptake, the difference signals are typically not significant ($p > 0.05$ in 4 of 6 measurement periods). Where the differences are significant it seems that they are on the order of a 15-20% increase in deposition velocity. As a result, the paper is full of discussions of differences that are explicitly stated as not being significant and the primary conclusions don't adequately reflect the ambiguity in the results. Comments regarding expectations and possibilities are included in the conclusions where the data don't robustly add support. I think an accurate conclusion section would convey the ambiguity in these results and their limitations in re-formulating our understanding of this plant-trace gas system. My takeaway thoughts: expected signals are small compared to unexplained variability. Some speculations are provided to explain the anomalous observations, but these explanations seem arbitrary and, in one case, not supported by other information the authors present.

Authors: Well, there are not simply “no” or “not robust” results. Coming to the conclusion that the hypothesis is not fully supported or missing “robust signal”, the results should be regarded as a result. To our knowledge, besides our manuscript, there is

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only one paper which is touching the issue of COS deposition to tree species under elevated CO₂, i.e. White et al. (2010). Therefore, we need more information to discuss these issues. Let me therefore shortly summarize what we found: 1. Significance of differences of the leaf conductances under the different regimes is indicated by p-values for *Fagus sylvatica* for all data and for *Quercus ilex* only June/August 1998. *Quercus ilex* is an evergreen oak species and some of the data were obtained in winter time (see remarks on seasonality below). 2. Significant differences of the CO₂ deposition velocities comparing growth under normal with elevated CO₂ were found in all cases. 3. Differences of COS deposition velocities were insignificant in all cases and CA activities also did not show significant changes but the latter might indicate a trend. 4. A response could be identified for *Quercus ilex* exhibiting a shift of the “virtual compensation point” or “substrate affinity” after one year of growth under the different growth regimes. What did we learn from this study? Firstly, the data do not contradict other studies of CO₂ exchange and stomatal behavior. Secondly, one plant species exhibited a response (*Q.ilex*). The hypothesis we started with, could not be generally confirmed, but we found one tree species which may have shown a response. This result should encourage us to perform experiments with more plant species and with “modern” techniques measuring online and allowing us to perform a faster screening. This would deliver a larger overview and would help to avoid a bias by seasonal developments.

COMMENT 2 Referee: *The use of the compensation point concept seems misleading. A non-zero compensation point implies emissions of COS, yet the authors explicitly state that there was no indication of COS emissions from these trees. How should the reader reconcile these conflicting points? Whether or not there are COS emissions from vegetation is an important point for budget considerations for this gas. The use of a new term "virtual compensation point" doesn't add to this discussion, in particular because it isn't clear what it represents and it isn't used consistently throughout the paper. Does the flux go to zero at lower COS concentrations because the outlet COS concentration in the chamber is zero? If so, I think the model for using this concept becomes inappropriate.

Authors: There was no problem of detection limits for COS; the outlet concentrations were always high enough. The term “virtual compensation point” was introduced as we could not find a compensation point because of missing COS emission. Of course it is important for budget considerations to check the potential for COS emissions. But with increasing technical quality of COS measurements during the last decade it became clear that there is no emission of this gas from vegetation under normal conditions. We do not want to exclude such an emission under “stress” conditions, but we simply did not find any such emission during our studies. Nevertheless, there is the strong relationship between COS uptake and ambient mixing ratios. Plotting this relation one gets an intersection of the regression line with the x-axis, thus demonstrating some relation to a potential compensation point, i.e. virtual compensation point. But according to the definition this is not a compensation point. Nevertheless it reflects an affinity of the plant towards the substrate COS and may help to discuss an acclimation to environmental changes. To make that clearer, we will rewrite some parts of the manuscript.

COMMENT 3 Referee: *How is it that the fluxes are influenced by seasonality when the plants were kept at 25 C, consistent light intensity with 12 hours of daylight and 12 hours of sunlight (section 2.1)? The influence of seasonality is used in places as a speculative explanation for anomalous observations. This potential influence and the issue of non-concurrent measurements make me question the usefulness of this new data even in a revised manuscript.

Authors: The referee picks up only “half of the truth”. As reported, the plants were grown in a greenhouse under “controlled” conditions. While the temperature is easier to control, the light is not. We supported the light by 12 hours of additional illumination with a light intensity of $600 \mu\text{mol m}^{-2} \text{s}^{-1}$ of photons (PAR). But of course the diurnal natural cycle could not be masked. Circadian and seasonal clocks of plants are well accepted and therefore seasonal effects are not used as “a speculative explanation for anomalous observations”. Such endogenous rhythms exist and can never be excluded. It is always a pleasure for me to demonstrate my students that photosynthetic rates

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and stomatal behavior are controlled by time of the day pushing light intensities into the second line. Hence, a potential seasonal behavior must be discussed.

COMMENT 4 Referee: *Indirect inferences made here regarding the potential for competitive uptake by vegetation between COS and CO₂ are in direct contrast to a study that explicitly measured this influence (Stimler et al). It is hard to determine if the data and analysis presented here add significantly to the discussion of this topic, though given the indirect nature of the approach taken here, my impression is that they do not.

Authors: As already answered to this concern as put forward by referee 2, we do not share this interpretation of the Stimler data. As long as we have to consider the same binding site for CO₂ and COS on the enzyme CA we must consider a competition. The data presented by Stimler do not really exclude an inhibition of the COS binding and consumption under high CO₂ values (see more information in the comments to referee 2.

COMMENT 5 Referee: Experimental details could be clearer. For example, how many individuals of each tree species were tested?

Authors: We will include this information in a revised version. We tested three individuals of each species.

COMMENT 6 Referee: How does seasonality influence the trees?

Authors: That is a good question and deserves more studies (see also above). Such studies can be performed with faster online techniques in future. For the existing studies we may discuss seasonality as a potential bias.

COMMENT 7

Referee: What do the 2nd and 3rd columns represent in Table 8, coefficients or p values?

Authors: We agree with the referee that this did not get clear only by regarding table 8.

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The 2nd and 3rd columns represent the p values. We will mention this in the legend in the revised version.

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