

## ***Interactive comment on “Carbonyl sulfide (OCS) exchange between soils and the atmosphere affected by soil moisture and compensation points” by Rüdiger Bunk et al.***

### **Anonymous Referee #2**

Received and published: 16 May 2018

The manuscript entitled “Carbonyl sulfide (OCS) exchange between soils and the atmosphere affected by soil moisture and compensation points” was submitted by Bunk, Yi, and coauthors for peer review to Biogeosciences. The authors present useful data on soils from four sites that help distinguish trends in simultaneous production and consumption processes that yield net OCS exchange in soils. The concept of the compensation point is used, which is not useful in the process-based sense, but can help identify soils that are more likely to be a source or sink to the atmosphere. While the results could be useful to a growing community of scientists studying OCS biosphere-atmosphere exchange processes, the paper and study design (as currently described) suffers from a number of significant flaws. Discussions of the implications regarding mi-

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Microbial drivers come across as forced and unsupported, the chemical measurements are underutilized, and many points require clarification. In this review, suggested improvements regarding organization, clarity, and pairing the scope main message to the scope of the study are given.

General comments:

Because the compensation point is a combination of multiple processes that each have different soil moisture dependencies, there is not a mechanistic reason that CP itself has a coherent moisture dependence. I would de-emphasize the CP relationship and focus more on what was learned independently about P and U.

A sign convention should be adopted and net or gross uptake fluxes should be indicated with a '-' sign throughout the text and net or gross emissions with a '+' sign.

State the time duration over which the experiments were performed for a given soil from wet to dry. How can one distinguish between changes in the moisture dependency from changes in microbial communities and their CA over that time period? What implication could that have for kocs?

Improvements could be made to the organization of the introduction. For example, three drivers of OCS fluxes are mentioned first, two are explained in one paragraph and the third in another. In the introduction it should be stated what the reason is for comparing the fresh and dry soil.

Discussion paragraphs should be made more concise and shortened quite a bit. I would hesitate to claim 'good agreement' between the field and lab studies, but certainly the values are within the same range, suggesting that mechanistic conclusions from the lab can inform processes that may occur in the field.

A problem with the discussion point on litter (in 4.1) is that no other horizons were tested at the forest sites, making it difficult to determine whether it was the litter or other characteristics of forest soils that drive higher uptake rates. This should be ac-

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knowledge. Add the horizon or litter designation to Table 1 for each sample, as it is difficult to determine from the methods which horizons were used for each sample.

It would be helpful to clearly state how this study differs from previous results and what new information is provided

Specific comments:

P1L16: Not clear how the QCL is 'new', or why it is relevant. Appears multiple times.

P1L20: The values given are a range, which would be better terminology than "of the order", the meaning of which I don't understand.

P1L28: How are emissions excluded under lowest CPs?

P2L11: The last two sentences of this paragraph are difficult to understand. It's not clear if GPP is what is estimated from OCS or if OCS is used to estimate GPP. The introduction topics should be better developed to connect the last sentence to where the field currently stands in terms of OCS sink strength estimates.

P2L16: Explain how OCS:CO<sub>2</sub> relationships are used to constrain the S cycle.

P2L22: Some orientation to which scale you are referring to would be helpful. Leaf, ecosystem, globe?

P2L29-P3L2: Not clear why it matters that early studies had artificially high OCS emissions because of measurement artifact unless you connect this explicitly to CPs for example.

P3L3: Is there a paper arguing the missing sinks early on that you could cite here?

P3L4: There is now a fair amount of literature on these drivers of OCS soil fluxes and mechanistic formulations representing them (see citations below). I'm sure this understanding can be tested in different soil, but is it fair to say the drivers are largely unknown? You cite additional papers to this point in the next few paragraphs, making

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that statement seem a bit contradictory.

1. Ogée, J.; Sauze, J.; Kesselmeier, J.; Genty, B.; Van Diest, H.; Launois, T.; Wingate, L. A new mechanistic framework to predict OCS fluxes from soils. *Biogeosciences* 2016, 13, 2221–2240, doi:10.5194/bg-13-2221-2016.
2. Sun, W.; Maseyk, K.; Lett, C.; Seibt, U. A soil diffusion–reaction model for surface COS flux: COSSM v1. *Geosci. Model Dev.* 2015, 8, 3055–3070, doi:10.5194/gmd-8-3055-2015.
3. Whelan, M. E.; Hilton, T. W.; Berry, J. A.; Berkelhammer, M.; Desai, A. R.; Campbell, J. E. Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon uptake. *Atmos. Chem. Phys.* 2016, 16, 3711–3726, doi:10.5194/acp-16-3711-2016.
4. Sun, W.; Maseyk, K.; Lett, C.; Seibt, U. Litter dominates surface fluxes of carbonyl sulfide in a Californian oak woodland. 2016, 438–450, doi:10.1002/2015JG003149.Received.
5. Kaisermann, A.; Ogée, J.; Sauze, J.; Wohl, S.; Jones, S. P.; Gutierrez, A.; Wingate, L. Disentangling the rates of carbonyl sulphide (COS) production and consumption and their dependency with soil properties across biomes and land use types. *Atmos. Chem. Phys. Discuss.* 2018, 1–27, doi:10.5194/acp-2017-1229.

P3L11: Cite also Whelan et al., 2016

P3L20: These are net sinks, but there can still be gross production in forest soils (Kasermann et al., 2018).

P3L23: Would be helpful to distinguish that you mean ‘atmospheric or headspace’ CO<sub>2</sub> mixing ratios is what was controlled in that study (not pore-scale mixing ratios)

P5L15-27: The methods for calculating CP are circular and are not clearly explained. Please rewrite. Add additional equation notation to indicate the values determined where  $E_{ocs}=0$ .

P5L28: I would clarify why the deposition velocity contains also the production term. This is for comparability to field measurements, correct?

P6L4: “Bourtsoukidis et al. (submitted)” is an unnecessary reference for this volumetric formulation. Please use a more suitable source. Define all terms in the equation (e.g.,  $t_i$ ,  $t_s$ ) P6L18: If based on instrument precision, why would the resolution threshold vary by soil type? How is this different from your reported precisions L21, that have similar values?

P6L21: How did you determine the absolute mole fraction for the permeation source standard and for the certified gas mixtures? Which OCS source was used for which OCS mole fractions? What were their precisions? A supplemental figure showing the calibration curve should be shown to indicate how two of three types of calibration gases had excellent instrument response matching, but that the most high precision standard at atmospheric values was off by 7%.

P7L13: Is this gross uptake reported at the soil moisture where net uptake is highest? Clarify for your readers. ‘Total uptake’ is not clear. Please pick a set of terms for each meaning and stick to them throughout, such as: net exchange, net source, net sink, gross uptake, and gross production. Currently many terms are used in the text and figures (e.g., net release, exchange rate, total uptake, etc. . .). P7L15: The confidence intervals or standard deviation on these average emissions (not ranges) can be given or statistical tests performed to show if they are different from zero.

P7L20-30: This paragraph could be condensed significantly to make the main point (intermediate OCS mixing ratios give intermediate fluxes, which indicate compensation points).

P9L24-31: The argument here about higher heterotroph abundance and activity being related to higher  $U_{ocs}$  is not well supported by the data in this study or any references listed. The cited literature is not referenced appropriately (e.g., Kato 2007 was looking at mycobacteria, which are heterotrophs). This is a poorly developed line of reasoning,

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and I would suggest sticking to the chemical data in Table 2 to discuss possible drivers. I feel that this discussion point relies too strongly on submitted manuscripts that can't be accessed by reviewers, inaccurately referenced studies, and statements without any references. Instead, the discussion should be de-scoped to accurately integrate published results alongside the data from this work.

P10L14-22: The scope of this discussion point regarding production is much more in line with the paper (in contrast to aforementioned uptake sections) and seems quite appropriate.

P11L8: The role of diffusion limitation of substrate at high soil moisture levels should be discussed. Enzymes are likely active, but substrate limited in that case. This statement is not supported: "We suspect these processes to be connected to autotrophic organisms, as discussed in Section 4.4."

P11L10: The relationship between Eocs (and correspondingly Uocs shifted by the magnitude of Pocs) does not seem linear with OCS mole fraction, but instead increases significantly between 50 and 500 ppt and then less so from 500 to 1000 ppt. Please show a plot of the fits. What is a 'true trend'? If the relationship is not linear, errors in estimating U at E=0 may lead to errors in estimated kocs from two-point measurements. Are you confident this was not the case? This will bear on the discussion in 4.4

P12L8: Is there a specific heterotrophic CO<sub>2</sub> fixation reference you can provide for the relation to OCS? The paper should focus on fluxes and CPs you observed without too much speculation on microbial metabolisms implicated. As stated by the authors, that activity was beyond the scope of the work.

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