

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

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REFeree: 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 study-

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ing 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 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.

AUTHORS: We thank the referee for the work he invested to improve our manuscript.

REFeree: 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.

AUTHORS: That depends on the view. If we look at the exchange with a view of an atmospheric scientist, the exchange is affected by a compensation point. At higher concentration it switches to an uptake and at lower concentration OCS is emitted. It is not simply variable. But we agree to rewrite to: OCS exchange exhibits a CP. Additional consideration how soil properties may affect UOCS will also be included. We agree with the referee that these considerations will represent a very useful complementation for the discussion of the compensation point. One main point of interest will be the difference in Ammonium content and how it may be linked to OCS uptake.

REFeree: 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.

AUTHORS: This is a tackling a basic discussion between meteorologists and physiologists. Do we need a positive or negative sign for example in case of photosynthetic uptake of CO₂? However, we fully agree that a sign and a term convention can be very helpful to foster understanding of our data. We will check our revised manuscript carefully.

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REFeree: 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?

AUTHORS: This point goes back to the beginning of the review, where the referee stated that the concept of CP is not useful in the process-based sense. We agree to that statement, but want to add, that indeed the disentangling of POCS and KOCS contain valuable information which allows interpretation with respect towards microbial metabolism. In a recent modelling study (Ogee et al., 2016) KOCS was modelled over various environmental conditions (eq. 11b) using k_{uncat} , and a temperature dependency for k_{cat}/KM (only one value is known in literature for certain pH and T: $2.39 \text{ s}^{-1} \mu\text{M}^{-1}$, which is used to parameterize the model for various pH and T), CA concentration [CA] (was kept constant over dry-out) expressed as fCA, the CA enhancement factor. Thus assuming that in our short incubations no major growth occurred, the difference in KOCS for Mainz soil/Finland needle soil versus Waldstein blueberry/Waldstein spruce could be explained by either different isoforms of CA (Sauze et al. 2017) having different k_{cat}/KM values (or assuming other enzymes such as RubisCO (Whelan et al., 2018) being involved, or that the enzyme concentration of CA (or others such as RubisCO) is not constant during drying-out as assumed by Ogee et al., 2016. Finally, we want to point out that the role of CA, RubisCO and PepCO in plants and soil is still not fully understood. Which effect was the dominant one, would need simultaneous molecular/enzyme analysis which was out of scope for this work.

REFeree: 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,

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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 acknowledged. 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

AUTHORS: We will rewrite and restructure to incorporate the proposals for an improvement of the manuscript. We will clarify and summarize what we regard as new.

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

AUTHORS: Its new in the sense that cavity ring down and cavity output laser instruments that can measure OCS concentrations online at normal atmospheric concentrations are a fairly new development (about 6 years now). Measurements as in this study would not have been possible with the older techniques, which required pre-concentration via cryo-trapping and could only produce one data point every 15 minutes or so (compared to a measurement rate of 1Hz and more).

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

AUTHORS: we agree and will replace "of the order" with "in the range"

REFeree: P1L28: How are emissions excluded under lowest CPs?

AUTHORS: These CP are far below normal atmospheric concentrations, so net emission could occur only under highly unusual conditions.

REFeree: 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.

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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.

AUTHORS: Both is possible and done according to the literature. We will clarify this a bit more.

REFEREE: P2L16: Explain how OCS:CO₂ relationships are used to constrain the S cycle.

AUTHORS: We agree this is a somewhat incomplete statement. The (atmosphere-biosphere) S Cycle is touched in the cited papers but OCS:CO₂ relationship is not directly exploited that way. But the approach of measuring OCS fluxes and deduct the CO₂ flux into vegetation from it can be reversed to estimate OCS uptake from CO₂ uptake. OCS and CO₂ are metabolized by the same enzymatic pathways. Hence, CO₂ assimilation can be regarded as a proxy for OCS deposition and vice versa. This view opens a window to the Sulphur cycle. The impact of OCS uptake on plant needs for sulfur on the other hand is most likely very low, at least for plants with roots which may take up sulfur compounds from the soil. Nevertheless, OCS which is metabolized to H₂S and fed into the plant sulfur cycle may be regarded to contribute, an assumption which has been discussed earlier for lichens with no connection to soil (Kuhn et al., 2000). Therefore, we think that the OCS:CO₂ relationship may be also exploited to contribute to our understanding of the sulfur cycle. This has been demonstrated using numbers of carbon uptake to estimate global OCS fluxes (see Sandoval-Soto et al., 2005).

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

AUTHORS: This sentence is a continuation of the statement of the sentence before, referring to leaf uptake. However, it is likewise true on an ecosystem scale. On that scale the exchange behavior of soils complicates the picture which is addressed later on. Soil exchange is considered so low in comparison to vegetation exchange that it

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is often considered negligible in these considerations. However, this is an uncertain assumption and may not be true under all conditions.

REFEREE: 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. AUTHORS: This bit of historic information was originally connected to a paragraph about the gap in the current budget between sources and sinks, which is much bigger than the observed changes in atmospheric OCS concentration. Therefore, it is generally assumed that either sources are under- or sinks overestimated. However, that paragraph was discarded before submission. Without this context, this piece of information, while interesting, is probably also not required here and can be removed.

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

AUTHORS: As R1 has correctly pointed out, this statement is incorrect. Therefore, it will be removed. (Budgets currently are missing sources or the sinks are overestimated.)

REFEREE: 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 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,

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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.

AUTHORS: We agree that statement is not accurate. We propose to remove the sentence stating that drivers are largely unknown. Instead, after the list of known drivers with their citation we propose to add: “Unfortunately, the mechanistic pathways by which these drivers influence the soil-atmosphere exchange and the quantity of their impact are not always fully understood and quantified yet. Problems exist in view of the mix of contributing enzymes and microbial groups as well as the chemical quality of the soil, for example ammonium content and metabolism.” As some of the soil samples we tested, contain high amounts of ammonium, we will specifically discuss the role of ammonium in our revised paper.

REFEREE: P3L11: Cite also Whelan et al., 2016

AUTHORS: Agreed, Whelan et al., 2016 should be cited here and will be added.

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

AUTHORS: While addressing a soil as a sink does not per se imply there is no production, it will be useful to include more details. We propose to change the sentence to (changes in bold): “Agricultural soils have been characterized as either a net OCS source or sink (Bunk, et al., 2017; Whelan et al, 2015; Maseyk et al., 2014), whereas forest soils have been characterized as net sinks (Sun et al., 2017; Steinbacher et al., 2004; Kaisermann et al., 2018).

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REFEREE: P3L23: Would be helpful to distinguish that you mean ‘atmospheric or headspace’ CO₂ mixing ratios is what was controlled in that study (not pore-scale mixing ratios)

AUTHORS: Strictly speaking the referee is right and we will add this information. However, we would like to point out that the soil layer was very thin (several mm) in order to have all soil (unless covered by a water film) exposed to headspace conditions.

REFEREE: 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 $E_{OCS}=0$.

AUTHORS: Agreed. Additional equations will be added for the CP and k_{OCS} as follows: $k_{OCS} = (EOCS_{1000} - EOCS_{50}) / (C_{1000} - C_{50})$ (R1) where $EOCS_{1000}$ is the net OCS exchange at 1000 ppt OCS mixing ratio, $EOCS_{50}$ is the net OCS exchange at 50 ppt OCS mixing ratio, C_{1000} is the exact OCS mixing ratio when 1000 ppt OCS mixing ratio were set and C_{50} is the exact OCS mixing ratio when 1000ppt OCS mixing ratio were set. The CP is reached when $EOCS$ is zero. This is the case when $U_{OCS} = P_{OCS}$. Derived from eq(3) and (4) this can be expressed as: $k_{OCS} * CCP = P_{OCS}$ (R2) where CCP is the OCS concentration at which the compensation point at a given soil moisture. Solved for CCP we get: $CCP = P_{OCS} / k_{OCS}$ (R3)

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

AUTHORS: Yes, we are always measuring the net exchange which is comprised by both terms

REFEREE: 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)

AUTHORS: The definition of the terms will be added where needed. Bourtsoukidis

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et al. is now published (Bourtsoukidis, E., Behrendt, T., Yañez-Serrano, A.M., Hellén, H., Diamantopoulos, E., Catão, E., Ashworth, K., Pozzer, A., Quesada, C.A., Martins, D. and Sá, M., 2018. Strong sesquiterpene emissions from Amazonian soils. *Nature Communications*). The deviation of the soil moisture equation we used can also be found in the supplement of Behrendt et al., 2014.

REFeree: 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?

AUTHORS: This noise is not purely dependent on the instrument precision. The experimental setup and scatter of the soil exchange also add to it. Therefore, it is a little higher than the precision in L21. The forest soils exhibited a stronger scatter, most likely because of their much higher activity (much higher uptake and emission rates).

REFeree: 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%.

AUTHORS: For the certified mixture the mixing ratio given by the manufacturer and the flow rate of the gas mixture and the synthetic air (both controlled by MFC) were used to calculate the expected mixing ratio. This commercial mixture has a higher uncertainty ($\pm 10\%$) than the NOAA standard, which may have masked an underestimation of 7% during our calibration measurements. For the permeation device, the permeation rate is calculated from the weight loss of the permeation container over a long observation time at closely monitored (and constant) air flow rate and temperature. The Forschungszentrum Jülich has established a setup for that purpose that is also cross checked against other methods. Marc von Hobe and his team kindly did a joint calibra-

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tion check and inter-comparison of instruments (they have three LGR OCS Analyzers of their own) together with us, using their very sophisticated permeation setup.

REFeree: 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...).

AUTHORS: Yes, this is gross uptake. We agree this should be clarified and a set of terms defined in the beginning applied strictly throughout the text without using any other. This will be added/changed for the revision

REFeree: 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.

AUTHORS: We will include a more detailed statistical discussion on that question in the revised manuscript.

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

AUTHORS: We will try to compress the paragraph without removing too much of the information.

REFeree: P9L24-31: The argument here about higher heterotroph abundance and activity being related to higher UOCS 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, 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

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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.

AUTHORS: Based on reviewer input and reconsiderations we have decided to remove the discussion about heterotrophs and autotrophs as well as strongly reducing most discussion of microbial communities. Instead, other options as physical and chemical soil properties shall be included in the discussion of the revised version. Especially a topic of diffusion limitation by high soil moisture and a brief discussion of the possible role of ammonium oxidizing organisms, as there are significant differences in ammonium content in the examined soils that coincide with curve shapes of UOCS and KOCS, will be included. Also, the section can be shortened as it is covered in our follow up study which is already under review. We propose a merger of the current sections 4.2 and 4.3 (as KOCS and EOCS are necessarily tightly related) by compressing the points discussed therein and adding additional points of view (chemical and physical soil properties, diffusion limitation). Kato et al. (2007) is indeed incorrectly referenced and all references in this section will be carefully rechecked.

REFEREE: 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.

AUTHORS: Thanks.

REFEREE: 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."

AUTHORS: a discussion about diffusion limitation will be added (see above). Section 4.4 will be reduced in scope and probably be fused with another section. However, we think the possibility should be mentioned.

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REFEREE: 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

AUTHORS: We agree that there are some problems with the CP calculation that will be thoroughly discussed in the revised version. Our reply to R1s concerns applies here too: We agree that the method used to derive compensation points in this study may be improved by investing much more measuring time and sample material. However, we can rely on older reports about the linearity of OCS exchange between 50-1000 ppt in soils and plants. More data points to fit a regression would certainly be helpful. But it will further our understanding to present the current data set, also in view of the different soil types and chemical properties, and use it for discussion and development of new approaches. The limitations will definitely be addressed in a revised manuscript. However, our large data set provides a consistency over the whole range of the investigated soil water content, which covers a much wider range of soil moisture than in previous reports. To address the uncertainties, we will add error estimations based on Gaussian error propagation for the net release (EOCS), uptake coefficient (KOCS), gross uptake (UOCS), gross production (POCS) and compensation points (CP). Of further importance is the question about linearity of the relationship between OCS concentration and exchange rates at higher OCS mixing ratios. Earlier reports demonstrate good linearity up to approximately 1500 ppt OCS ambient concentration in measurements with soil (Kesselmeier et al., 1999). Investigations performed with lichens (Kuhn and Kesselmeier, 2000), which are lacking any outer protective cell layers and seem to behave similarly as soils, exhibit a comparable linearity relating exchange rates and OCS concentrations. In both cases the authors report a saturation effect at higher OCS concentrations, which leads to an increasing uncertainty. The reasons are not

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investigated but can be understood as metabolic saturation (enzyme saturation) or different/additional biotic processes influencing the rate of OCS exchange. These uncertainties limit the reliability of the compensation points calculated, especially if those are >1500ppt or at soil moistures above 60 % WFPSlab. However, despite this uncertainty, the CPs show a clear and consistent trend that cannot be disregarded. It can clearly be seen that the uptake coefficient (slope of the regression) first increases and then decreases again with decreasing soil moisture. Setting the reliability of the absolute values aside, such coherent trends contain information that can be explored. Additionally, the calculated CPs have reasonable overlap with older data. An important aspect of the paper is the observation of CPs over soil moisture which has not been reported before. Even with relatively high uncertainties this data is worth to pursue and to plan future experiments accordingly. For the current revision we propose to test the significance of all trends in EOCS, KOCS and POCS by using the first data point of each measurement as control and perform a t-test to see if the next value is statistically different from the previous one. It would highlight the idea of monitoring a significant trend in OCS over drying out.

REFeree: P12L8: Is there a specific heterotrophic CO₂ 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.

AUTHORS: As said above, we agree that more room should be given to discussion of the physical and chemical factors that may influence the fluxes and CPs and will add this in the revised version. We have decided to abandon the discussion about autotrophy/heterotrophy.

Referenced Literature:

Ogée, J., Sauze, J., Kesselmeier, J., Genty, B., Van Diest, H., Launois, T. and Wingate, L., 2016. A new mechanistic framework to predict OCS fluxes from soils. *Biogeo-*

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Whelan, M.E., Lennartz, S.T., Gimeno, T.E., Wehr, R., Wohlfahrt, G., Wang, Y., Kooijmans, L.M., Hilton, T.W., Belviso, S., Peylin, P. and Commane, R., 2018. Reviews and syntheses: Carbonyl sulfide as a multi-scale tracer for carbon and water cycles. *Biogeosciences*, 15(12), pp.3625-3657.

Kaisermann, A., Ogée, J., Sauze, J., Wohl, S., Jones, S. P., Gutierrez, A., and 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.*, <https://doi.org/10.5194/acp-2017-1229>, in review, 2018

Kuhn, U. and Kesselmeier, J. (2000) Environmental variables controlling the uptake of carbonyl sulfide by lichens. *J. Geophys. Res.* 105 (22), 26783-26792. Bunk, R., Behrendt, T., Yi, Z., Andreae, M.O. and Kesselmeier, J., 2017. Exchange of carbonyl sulfide (OCS) between soils and atmosphere under various CO₂ concentrations. *Journal of Geophysical Research: Biogeosciences*.

Bourtsoukidis, E., Behrendt, T., Yañez-Serrano, A.M., Hellén, H., Diamantopoulos, E., Catão, E., Ashworth, K., Pozzer, A., Quesada, C.A., Martins, D. and Sá, M., 2018. Strong sesquiterpene emissions from Amazonian soils. *Nature Communications*

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