Biogeosciences
Discussions

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 #1

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General comments

The manuscript presents a laboratory study on two important drivers of soil OCS exchange—soil moisture and ambient OCS concentration. The authors collected four soil samples from the field, incubated them in the laboratory, and determined their OCS exchange patterns under varying conditions of soil moisture and OCS concentrations. The experimental design covered the full range of relative soil moisture, from 0% to 100% with a fine step. This allowed the construction of well-defined soil moisture response curves of OCS exchange. By measuring OCS exchange under different ambient OCS concentrations, this study was also able to separate OCS gross uptake

and production components from the net exchange and investigate their respective responses to soil moisture.

However, the experimental design to derive compensation points was seriously flawed and unable to produce robust estimates of the compensation points. As the authors noted, they used measurements at 1,000 ppt and 50 ppt to derive the compensation points. **This practice is essentially to fit a regression line with only two data points, and then extrapolate to somewhere up to 5,500 ppt!** The uncertainty would likely be huge. Yet they present no uncertainty measures of this derived quantity in the figures or the text. That is not to say that the data shouldn't be published, but the authors should quantify the uncertainties and properly acknowledge the limitations of their method.

The manuscript identified the compensation point as a driver of OCS exchange, as the title and some section titles implied. But a critical examination of the mechanisms governing OCS uptake and production processes suggests that this is a misinterpretation. Compensation point manifests the dynamic balance between uptake and production. It is not an intrinsic property of the soil, but a variable that depends on soil moisture, as the authors have demonstrated in Fig. 3. Therefore, it is inaccurate to say that OCS exchange is 'affected' by the compensation point.

The manuscript suffers from other flaws. The equations (Eqs 1 and 2) used to calculate the OCS exchange apply only to the **steady state** condition, which can be shown mathematically by solving a mass balance equation for chamber gas exchange. Yet, they did not assure the readers of the validity of the steady state assumption used in their measurements. In addition, the interpretations of data are insufficient, and sometimes superficial. I would suggest the authors to exploit their dataset for new understanding rather than confirmatory interpretations. The discussion is poorly organized and lacks novel insights. This part has to be rewritten for clarity and coherence. As a suggestion, please figure out the main point of each section and organize the paragraphs in a streamlined way that helps convey the main point and impart understanding to the

readers. Detailed comments on specific issues are listed below.

Specific comments

Abstract

> P1L24–26: "The OCS compensation points (CPs) were highly dependent on soil water content and extended over a wide range of 130 ppt to 1600 ppt for the forest soils and 450 ppt to 5500 ppt for the agricultural soil."

If OCS exchange was measured only at "50, 500, and 1000 ppt" (P1L18), how did you obtain a compensation point of 5,500 ppt for a certain sample? This has not been explained in the manuscript. Presumably, the only way would be to extrapolate a linear relationship between the net exchange and the concentration. The compensation points derived this way will inevitably have large uncertainties, since there were only three (and sometimes just two!) data points to fit a line. Please provide the uncertainty measures and address the limitations of this method.

Introduction

> P2L6: "In view of the potential role of OCS, . . ."

What kind of 'potential role'? Please clarify.

> P2L2–8: "Carbonyl sulfide (OCS) is . . . in the troposphere (Brühl et al., 2012)."

C3

I think the first paragraph of the Introduction can be shortened significantly without losing the sense.

> P2L16: "in both the carbon and sulfur cycles"

The 'sulfur cycle' is not a major concern of the studies cited here. I suggest removing it.

> P2L15–26: "The relationship between concentrations of OCS and gross primary production (GPP) . . ."

This paragraph is an elaboration on the use of OCS as a tracer for GPP. While broadly speaking this is a motive for many recent studies on soil OCS exchange, as plant uptake of OCS is not the topic of this study, having such a level of details in the Introduction seems excessive. I suggest cutting this paragraph down to three sentences or so.

> P3L3–4: "Although the understanding of soils as a major sink helps to explain the 'missing sinks' for OCS, soil uptake still shows a wide scatter among different environments."

Where does the "missing sink" come from, all of a sudden? Please explain.

> P3L4–5: "Also, the drivers of soil OCS fluxes and their dependences to environmental parameters (such as soil moisture, soil temperature, and OCS mixing ratio) are still largely unknown."

This is not an accurate statement. Actually, you have cited quite a few studies in the next few paragraphs to show that the drivers are not 'largely unknown.'

C4

> P3L5–6: "Uncovering the mechanisms for soil OCS fluxes would allow soil-atmospheric OCS exchange to be estimated on broader spatial scales."

I think that Berry et al. (2013) and Launois et al. (2015) have already estimated soil–atmosphere OCS exchange 'on broader spatial scales'. Please clarify what you mean by this statement.

> P3L12–17: "Furthermore, there is a strong evidence that the OCS exchange between soil and the atmosphere is dependent on the ambient OCS mixing ratio . . ."

What's missing from the introduction of the compensation point is the fundamental cause of it: OCS uptake is a pseudo first-order reaction and thus depends linearly on the ambient OCS concentration, whereas OCS production is independent of OCS concentration (Conrad, 1994).

> P3L24: "To deepen our understanding of source and sink characteristics . . ."

At the end of the Introduction it is still not clear to the readers what specific research questions this study aims to address. The authors should consider formulating research questions or hypotheses to better orient the readers.

Material and methods

> P4L3: "Soil samples were collected from four sites . . ."
> P4L9–10: "We tried to use the same method to collect all soil samples, but we cannot exclude the variability over time."

Can you provide information on **when** each sample was collected?

> P4L10–11: "Fresh subsamples of agricultural soil in Mainz were oven dried (at 40°C) for comparison."

Please specify how long they had been dried for in the oven.

Typically, using the gravimetric method to determine soil moisture would require samples to be oven dried at 105°C for 48 to 72 hours, but of course that temperature would not be desirable because microbial communities could be destroyed. I assume that the choice of 40°C had something to do with this concern, but at this temperature, how did you ensure that the samples were **dried completely** and the maximum soil moisture (θ_s) used in Eqn (6) was not biased by any remaining water?

> P4L16 and P4L26: "deionized water (R 18.2 MΩ)"

The unit of DI water resistivity is MΩ·cm, not MΩ.

> P5L21–23: "This is based on the linear relationship between OCS uptake and OCS mixing ratio shown by Kesselmeier et al. (1999) and the assumption that the ambient OCS mixing ratio does not influence OCS production (see 4.1)."

This sentence explains the theoretical basis of the 'compensation point' and should better be placed in the Introduction.

> P5L9, Eqn (1): $E_{OCS} = Q\Delta_{OCS}/m_{soil}$

This equation works only under a **steady state** condition. How did you ensure that OCS concentration in the chamber headspace reached a steady state? Please provide relevant details and reasoning.

Results

> P7L6–7: "OCS uptake at medium soil moisture was 20% stronger for the Waldstein soil with its young spruce understory than for the one with a blueberry understory."

What range is the "medium soil moisture"? Be quantitative.

Waldstein spruce soil showed a peak uptake of 23 pmol g^{-1} h^{-1} and Waldstein blueberry soil showed a peak uptake of 13 pmol g^{-1} h^{-1} (P7L11). This does not seem to be just "20% stronger". Please reassess the figure and revise this statement.

> P8L2: "The OCS compensation points were found to be variable in close dependence on the soil water content."

This is not the case of the Waldstein blueberry soil. This exception needs to be acknowledged in the text.

> P8L14–15: "The values of P_{OCS} were 2, 4, 7 and 30 pmol g^{-1} h^{-1} for Mainz soil, Waldstein soil with blueberry or young spruce understory, and Finland needle forest litter, respectively."

Which summary statistics are these numbers? Means or medians? Please specify.

> P8L20: "This might indicate involvement of multiple OCS uptake processes (see section 4.2)."

The observed OCS gross uptake vs. soil moisture patterns can be reproduced in model simulations even if there is just one OCS uptake process. See Sun et al. (2015) and

Ogée et al. (2016). This pattern can be explained as the result of two competing effects of soil moisture—inhibition on OCS diffusive transport and activation of microbial activity. In other words, it does not require the presence of multiple OCS uptake processes.

Discussion

The discussion sections, in general, are unnecessarily convoluted, cliché ridden, lack coherence, and fall short of offering novel insights. I struggle to find main points in a mixture of loosely connected statements. In each section, there is significant amount of superfluous or repeated information that needs to be pruned away to allow the point to get across.

4.1

> P8L24–25: "The OCS exchange from our laboratory measurements of the Finland litter layer soil is of the same magnitude as the field OCS exchange measurements performed by Sun et al. (2017) at the site where our samples were taken . . ."

The units are different (here, pmol g^{-1} h^{-1}, and pmol m^{-2} s^{-1} in the cited study). How did you make the comparison?

> P8L29–30: ". . . the deposition velocities of our lab measurements were corrected based on the temperature optimum curve presented in Kesselmeier et al. (1999) by a factor of 0.852 (the ratio of OCS uptake at 15°C to OCS uptake at 20°C in Kesselmeier et al., 1999)."

This correction implies that the temperature dependence of the Finnish soil follows the same relationship in Kesselmeier et al. (1999), which was originally derived from an

agricultural soil, with a temperature optimum around 18°C. However, Sun et al. (2017) has shown that the temperature optimum of the Finnish soil exists at a much lower temperature. Therefore, the correction applied to the deposition velocity is not justified.

> P9–P10: "All three organic forest soil samples were almost exclusively OCS sinks, . . ."

The rest of this section seems purely speculative, theorizing with little support from the data, and strays further from the main point. The discussion is not a place for literature review. Even if there is an abundance of literature on autotrophic and heterotrophic microbes, OCS exchange data alone can neither verify nor falsify a particular microbial mechanism. Please reconsider what you intend to mean in this section.

4.2

> P11L2: "Wet soils have shown to tend towards emission of OCS"

'Wet soils' is not accurate, I suppose you mean 'water-saturated soils'.

> P11L8–9: "We suspect these processes to be connected to autotrophic organisms, as discussed in Section 4.4."

This statement is too speculative. First, there is no data supporting the presence of OCS consuming autotrophs in your samples. Second, heterotrophs, too, may consume OCS.

> P11L12–13: "This is in clear accordance with the assumption of a linear dependence of U_{OCS} on the ambient OCS mixing ratio . . ."

This 'assumption' needs to be introduced in the Introduction first.

> P11L22–23: "Aside from that, only the experimental data obtained at 50 ppt and 1,000 ppt were used to calculate the compensation points."

This goes to the Methods, not the Discussion.

4.3

Rather than repeating what has been found in previous studies, more effort should be devoted to the interpretations of the compensation point results presented in this study.

4.4

The question why the 'k-coefficient' varies with soil moisture and shows an optimum remains unanswered.

4.5

> P13L23: "Samples had been stored 5 to 9 months."

This information should be provided in the Methods.

> P13L23–24: "For both, there was uptake of OCS at about 12% gravimetric soil water content, which was reduced when the soil contained a higher or lower amount of water, gradually switching to emission of OCS at wet and very dry states as demonstrated in Figure 7."

Why not just say that the **optimal** uptake of OCS occurs at 12% SWC?

> P14L1–3: "Some changes occur both over time and are induced by two different ways of sample treatment (storing 'fresh' or air drying the sample before storage), illustrating the importance of consistent treatment and storage of samples that are meant to be compared to each other."

Is there evidence that the differences in soil moisture response patterns arise from the "two different ways of sample treatment"?

4.6

This whole section should either be removed or reduced to two sentences. The point boils down to the first sentence that soil OCS exchange is a small fraction of the ecosystem OCS exchange; the rest is merely a lengthy digression (P14L12–30). Not only does the latter half of the paragraph lack relevance, but it philosophizes over leaf area index without any support from empirical data. The purpose of this section needs to be reconsidered.

Conclusion

The Conclusion is poorly structured and reads like a first draft. Please find out the meaning and rewrite it.

Figure 1 & 2

Both figures show the patterns of OCS exchange versus soil moisture. What is the reason to split the data into two figures? Why not show the 500 ppt data and the

"Mainz dry soil" data in Figure 1?

Figure 3

Please consider adding error bars on compensation points. The uncertainty in OCS exchange should propagate to the compensation point.

Figure 4

1. The unit of k_{OCS} is missing.

2. Net OCS flux is referred to as "net release" here, but "net exchange" in other parts. Please harmonize the terminology.

Technical comments

> P1L12: "Carbonyl sulfide (OCS) is a chemically quite stable gas in the troposphere (lifetime ~2-6 years) and consequently some of it is transported up to the stratosphere where it contributes to the stratospheric sulfate layer."

This sentence is verbose. In the second half you may just say ". . . and is a precursor of the stratospheric sulfate aerosols."

There are updated estimates of OCS lifetime from Campbell et al. (2008): 1.5 to 3 years. (I assume that you got the 2–6 years estimate from Khalil et al., 1984.)

> P1L13–14: "Due to the similarities in uptake mechanism between OCS and CO_2"

'uptake' → 'leaf uptake'

> P2L13: "Furthermore, changes of the sink strength of vegetation as a response to global change is a matter of discussion"

'is' → 'are'

> P3L4–5: "their dependences to environmental parameters . . ."

"their dependenc**e on** environmental parameters . . ."

> P7L23: "1000 ppm OCS"

I believe this should be "1,000 ppt OCS".