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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 #3

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This is an interesting study that investigates how the net carbonyl sulfide (COS) exchange between a set of soils (forest and agricultural) and the atmosphere is composed of two opposing component fluxes (a gross uptake flux of COS and a gross production flux of COS) that are regulated differently in response to variations in soil water filled pore space. They revisit the compensation point method of Conrad, 1994 and Lehmann & Conrad, 1996 to obtain estimates of COS production from observations of the net soil COS exchange measured under two different atmospheric COS concentrations of 50 and 1000 ppt. These concentrations are much lower than those used in Lehmann & Conrad, 1996 and likely more applicable to concentrations observed in the field. Although many studies have measured and modeled from theory the response of

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the net COS exchange to variations in soil moisture for a given soil and how differences in soil texture and bulk density play on the WFPS and subsequently the optimum net COS exchange (i.e. the maximum COS uptake rate measured), this is the first study to show that the COS production rate remains more or less constant over the entire range of %WFPS. Thus variations in the net COS exchange with WFPS are driven by the uptake component of the net COS flux. Between the different soils measured (3 spruce and 1 agricultural site) there were large differences in the magnitudes of the net COS flux and their component fluxes with largest fluxes for all components found in the Finnish forest and the lowest component fluxes observed in the agricultural soil in Germany. In addition a further experiment showed that after drying the agricultural soil for several months and re-humidifying, a very similar response of the net and component fluxes to % WFPS was observed, although no statistics were completed to test whether they were significantly different or not. In general there is some nice data in this study that is definitely worthy of publication.

Major comments

Throughout the manuscript there is very ambiguous application of terminology regarding the exact flux being presented. When the paper is expressly about partitioning the components of a net flux, one has to take care to be precise and state clearly which flux they are writing about. I thoroughly recommend that the authors go through the paper and clarify exactly what each flux is that they refer to, when they refer to it in the paper. Simply referring to COS exchange is too ambiguous, this paper must always refer to the net COS flux (EOCS), the COS emission rate or production rate (POCS) and the COS uptake rate (UOCS).

Furthermore, the partitioning approach taken in the current study does not completely isolate the two component gross fluxes, rather the uptake term measured at a constant temperature as presented by the authors is still regulated to some extent by diffusion (not strictly enzymatic uptake of COS) and the production term as presented still incorporates a COS deposition velocity (Vd0) that occurs even when the COS concentration = 0. These details are developed in the Ogee et al., 2016 paper https://www.biogeosciences.net/13/2221/2016/bg-13-2221-2016.pdf and more relevantly to the current study in a recent publication in Atmospheric Chemistry and Physics Discussions by Kaisermann et al. https://www.atmos-chem-phys-discuss.net/acp-2017-1229/acp-2017-1229.pdf that demonstrates within the current methodological framework that a small additional analysis is required to obtain the gross COS production rate when COS concentration = 0 that must be solved iteratively see Eqs 2, 3 and 4 of Kaisermann et al.

Another important point that was expressed several times in the paper is that the shape of the net COS exchange response to WFPS is unknown but probably caused by changes in the activity of the enzyme CA. However, this is not strictly true as in the past few years the community has made considerable progress in explaining the response of the net COS flux to variations in soil temperature, soil moisture, soil texture and soil microbial biomass collectively in the papers of Kesselmeier et al., 1999; Van Diest &Kesselmeier, 2007; Ogee et al., 2016 and Sun et al., 2016. From these papers it has been shown that the observed optimum with soil moisture content observed in the present study and many times in the literature can be modelled extremely well and is mostly caused by changes in the diffusion of OCS within the soil matrix that reduces the potential hydrolysis rate at a given temperature, microbial biomass and COS concentration. This can occur over the typically short time frames of these experiments and thus the net COS flux and the gross COS uptake rate does not need to be driven by changes in the intrinsic enzyme activity or size of the microbial population. Thus the discussion needs to take this in to account and furthermore considered in the interpretation of the data presented in the results. Subsequently, differences in soil texture can probably explain most of the differences in the absolute %WFPS values where the optimum net COS flux is observed. Unfortunately, no data is provided in the manuscript about the differences in texture between the sites, this should be added.

As described above the data in this study are interesting however the presentation of the results could definitely be improved and synthesised. I see no reason why figures 1 and 2 are not merged and a more synthetic analysis of the fresh vs dried/re-humidified soil results presented in a new Figure 2. This new figure could consist of 3 panels side by side. In panel (a) the authors would present the data from the 50ppt experiments, panel (b) the 500 ppt and panel (c) the 1000 ppt data. On the x-axis of each panel would be the net COS flux from the fresh soil against axis y the net COS flux from the same re-humidified dry soils. The authors could then colour the points by %WFPS (light blue = dry soils and dark blue = wet soils). Then they could also show the 1:1 line and do some regression statistics that way the audience can assess clearly and objectively the effect of the drying on the %WFPS response.

The authors also point out that the consumption rate coefficient (k) follows the same pattern with %WFPS as the net COS flux and the partitioned COS uptake rate (Uocs) and present the variability of k with %WFPS. However, U and k must vary with soil moisture and temperature . . ..etc as they are linearly related or even proportional if Vocs is always at the same COS concentration. Thus I would remove figure 5 and rewrite the discussion to address this point. Also the compensation point does not affect the COS exchange rate and thus the title of the manuscript should be corrected.

The authors state that the data from the Sun et al 2017 field study and this study are comparable and can be used to transfer the findings from the lab data to the field. However, the lab response to soil moisture content (green line) does not go through the middle of the points, but rather forms an upper envelope and there is no statistical test behind this statement. At the minimum the authors should calculate the mean deposition velocity for the relevant and comparable soil moisture values for their study and the Sun et al study and compare the means. Furthermore, I do not think it is appropriate to use the temperature optimum from the Mainz soil to make the field fluxes of the Finnish soil comparable. It has been demonstrated before that the net COS flux is strongly affected by the production rate and can cause a shift in the temperature optimum. As this study shows the Mainz and Finnish soils have extremely different production rates I do not think this is the most appropriate way to reconcile the two data sets and facilitate comparison.

Specific comments

Page 3 of the introduction lacks a number of citations that describe the theoretical advances the research community has made in describing the response of net COS exchange to soil water, texture, soil temperature etc... there is also some internal contradiction within the text.

Finally the introduction does not present any hypotheses on why they might expect shifts in sources and sinks relative to their experimental manipulation with COS concentration and soil moisture content.

The characteristics of the soils provided are partially useful. It would be better to provide the physical characteristics such as bulk density or texture rather than nitrate and ammonium fluxes taken from some other studies and not conducted on the soils at the same time as when measured. These values could be misleading as inorganic N concentrations are turned over rapidly and vary with season and management.

Pg 4 line 10 what exactly can the author not exclude variability in over time? Was there no fixed protocol for the collection, storage and handling of the soils?

Pg 4 line 14 length of sample storage should be provided here and was it the same for each soil?

Section 2.4 and description of %WFPS protocol should come just after Section 2.1

Pg4 line 20 state the temperature of the soil here and how constant.

Pg 4 Section 2.2 how many sample replicates are measured for each soil at a time and what do the error bars refer to in the figures?

Section 2.2 How long between wetting and gas exchange started? How long is the measurement sequence? How long is the airstream sampled? How do you check for steady-state? Information on when the soils were sampled would be useful e.g. time of year; before/after fetilisation?

Section 2.4 remove the citation Bourtsoukidis et al

Page 6 Line 24 is it the fluxes or absolute mixing ratios underestimated by 7%?

Page 7 line 12 I feel the last sentence of this paragraph is out of place and should appear later.

Section 3.2 really needs to be re-written. It is ambiguous, difficult to read and contains repetition. In places it is hard to work out what the authors are comparing.

Page 8 line 3 you should state that the soils had compensation points higher than the background atmosphere.

Section 3.3 again some repetition at the end of the paragraph.

Also the authors should point out that compensation points in themselves are not particularly useful as they are not intrinsic properties of a soil as their value will vary with temperature and COS concentration. They are only useful for establishing whether a soil is a source or sink of COS to the atmosphere.

Section 3.4 the figure 4 panel b production rate looks very strange. I am not sure why it has this appearance, but I am guessing maybe there is some interpolation being made between a limited number of measurements over the drying curve. It would be useful to explain what is going on here in the methods, results and the legend

Page 8 line 19-20 This statement as described above is redundant as is the figure 5 and is not linked to any of the things proposed in Section 4.2

Page 8 line 30 this correction may have some problems associated with it, if the authors insist on using it they should be more critical about why it is not ideal.

Page 9 Ln 3 the reason for the scatter is because many variables are changing at the

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same time, please be a bit more critical.

Page 9 Ln 8 I would not hold this graph up as evidence that your study can simulate what is happening in the field.

Page 9 line 11-22 This discussion is a little imaginative and is not so relevant to the results. The arguments do not follow a clear logic.

Page 10 Line 11-13 I don't understand these statements. What exactly has it's activity reduced? What is the different uptake process and what evidence in your data do you have for this?

Page 10 line 22 What about abiotic processes?

Page 10 line 28-30 ambiguous statements about exchanges and observed values without being precise about what they are referring to. Which exchanges and values exactly?

Page 11 section 4.2 lines 7-15 I don't think any of these arguments are relevant to the results they are discussing. The authors do not appreciate the role of diffusion within the soil matrix and it's affect on the ability of soils to take up COS or not as WFPS changes. This should be explored first before jumping to the conclusion that autotrophic organisms have some role to play in explaining this pattern, especially as the authors have no evidence to support this hypothesis.

Section 4.2 last paragraph should be in the results section it is not discussion.

Page 12 line 3 also mention the other factors that will alter the compensation point.

Page 12 line 14-16 your experimental data does not support this statement about the two compensation points of Lehmann & Conrad please modify the sentence.

Page 13 Ln 2-19 this discussion again contains a lot of conjecture and fails to mention that the differences in texture between the spruce sites is probably important and should be accounted for before attributing differences in COS uptake rates to other

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factors

Page 13 line 23 I think this is important info that should appear in the methods section.

Page 13 line 28-30 don't you think this is because fundamentally the soil texture did not change over the 6 years at the Mainz site and thus you observe a similar pattern when you wet and dry the soil 6 yrs later?

Page 13 line 18 LAI of 15? I don't believe this is possible

Section 4.6 I think this is a bit long and not so useful in the end I think it could be summarized in a sentence or two in the conclusion

Conclusions are currently based on conjecture and not the results. Statement 1 The experiment was not designed to test and cannot prove that COS is driven by the litter layer. Statement 2 There are no data presented about fungi in this paper so again this statement seems redundant. Statement 3 They do not prove that COS uptake is driven by different enzymatic processes. Statement 4 Is an introduced error of 1% really significant? Statement 5 No evidence in this study that the correlation coefficient k is linked to the presence or absence of auto- or heterotrophic organisms. Statement 6 I agree trying to understand compensation point variability without a model that accounts for how it varies with T, moisture and COS concentration is frustrating. We should use the theory and models that now exist to address this issue. Statement 7 they did not demonstrate statistically that the storage issues introduced significant differences in the fluxes and what level of uncertainty is introduced.

Merge Fig 1 and 2

Recommend a synthetic figure 2 with some statistical analysis.

Figure 3 should there not be some estimation of error on these points?

Figure 4 panel b looks weird also can you show that the inlet is constant during each of the experiments and that steady state was attained

Figure 5 redundant

Figure 6 not sure this is necessary either

Figure 7 not sure this figure is explicitly referred to in the text or necessary in the paper.

Table should state explicitly which nitrate and ammonium data are relevant to the gas exchange measurements taken during the actual present study experiment.

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