Anonymous Referee #1

This is a salient and timely contribution to our understanding of COS ecosystem exchange. Methods to use COS measurements are presently being developed to understand biosphere carbon uptake on ecosystem and continental scales. Uncertainty in estimates of global photosynthetic carbon assimilation are large; studies incorporating COS observations suggest that this uncertainty can be reduced (e.g. Hilton et al., Tellus B, 2015). While it has been demonstrated that plant foliar uptake is the largest terrestrial sink for COS, soil-atmosphere interactions can confound what would otherwise be a straightforward proxy for gross primary production. To my knowledge, this paper is the first thorough effort to represent soil COS exchange mechanistically, therefore predictively.

The careful treatment of Henry's Law relationship to temperature, effective diffusivity of COS, and catalyzed COS uptake processes are much needed additions to the COS soil modeling arsenal.

General Comments

It's not clear why advective fluxes can be dispensed with, but mechanical dispersion is still important. One of the first stated assumptions is one of equilibrium. If advective fluxes are negligible after an hour, how are mechanical dispersion fluxes still important after 2 hours?

Answer: The reviewer questions our statement on p. 15698 line 12 that mechanical dispersion can be important even when advective fluxes are negligible. This can be explained by the fact that advection is proportional to the flow velocity of the carrier fluid (q_l for water and q_a for air) while mechanical dispersion is proportional to the absolute value of that flow velocity, because dispersion happens in both directions and is always positive (see for example Eq. 1 in Maier et al. 2012 or Eq. 21 in Massman et al. 2006). Thus, when averaged on a long enough timescale (several minutes) the mean advective flux can be zero (because the mean flow velocity is zero) while the dispersion flux remains positive (because the mean absolute flow velocity is not zero).

Massman, W. J.: Advective transport of CO2 in permeable media induced by atmospheric pressure fluctuations: 1. An analytical model, J. Geophys. Res, 111(G3), G03004, doi:10.1029/2006JG000163, 2006.

Maier, M., Schack-Kirchner, H., Aubinet, M., Goffin, S., Longdoz, B. and Parent, F.: Turbulence Effect on Gas Transport in Three Contrasting Forest Soils, Soil Science Society of America Journal, 76(5), 1518, doi:10.2136/sssaj2011.0376, 2012.

For some of the important components of the soil fluxes described here, equations were based off of one or two studies. The important and as of yet unexplained process of aerobic soil COS production was discarded though there is plenty of evidence for it. There are several studies with empirical evidence of exponential COS production in dry soils, increasing with temperature rather than Eh. Liu et al., 2010, and Whelan et al., 2015 demonstrated this in incubation studies, and Maseyk et al., 2014 found exponential COS production during a field study in aerobic agricultural soils. This model could be improved by taking into account this process, even if its drivers are not entirely known.

Answer: The reviewer considers that the "process of aerobic soil COS production was discarded" in our model and calls for more references to studies reporting strong OCS production rates from dry (oxic) soils, and their response to temperatures. We will argue that our OCS production term is quite general as it responds to both temperature (an important trigger in oxic soils) and redox potential (an important trigger in anoxic soils). We agree however that, in the process of building our model, we did not refer explicitly to some important studies on oxic soils that showed the exponential increase of OCS production with temperature (apart from Whelan and Rhew 2015). We also agree that, although both temperature and Eh are important triggers, they should not act multiplicatively. Indeed studies on anoxic soils have shown Eh or tidal movements to affect the OCS production rate, but not temperature, while studies on oxic soils have shown that OCS responded exponentially to a temperature increase but did not report any change with Eh (probably because of the difficulty to measure Eh in non-flooded conditions). To address the reviewer's *comment we decided to modify slightly our model formulation by splitting the production rate P into an oxic (unsaturated) and an anoxic (saturated) component:*

$$P = P_{ref,dry} Q_{10,dry}^{((T-Tref)/10} + P_{ref,wet} y_P(E_h)$$

We also refer explicitly to Liu et al. 2010, Whelan et al. 2013 and Maseyk et al. 2015 for the dry component of the production term. These changes have absolutely no consequence on the results shown in the manuscript (including those shown in Fig. 7 that would then relate to the dry component of the production rate).

The overall model being presented needs more detail to reproduce. There are some missing connections that could be easily remedied with, perhaps, a supplement with all of the variable/constants defined and a tree of equations.

Answer: The reviewer suggests adding a supplement with all the variables/constants and a tree of equations to help the reader on how to implement the model. Because we derived an analytical solution of the transport equation, the soil OCS deposition rate can be calculated from one single equation (Eq. 16b or Eq. 17 if it is field conditions) but it is true that there are terms in this equation that are themselves computed from other variables. We thus included a sentence in section 2.7 explaining all the variables and the tree of equations that are needed to compute all the terms in Eqs. 16b or 17. There were also typos in Eq. 12b (a minus sign was missing) and Eqs. 13 and 15 (the subscripts "disp" should be replaced by "eff") that are now corrected.

Specific comments

15695 The tortuosity discussion would be aided by having the equations in a table.

Answer: a table that summarises the different parameterisations of the tortuosity factor has been added.

15696 It is unclear how the variables introduced here relate to the later discussion, particularly equation 17. It's clear that diffusivity and tortuosity are included in the analysis in Section 3.1, but this section and the actual equation given need to be better linked.

Answer: a sentence has been added at the beginning of the paragraph explaining why we needed estimates of $D_{0,a}$ and $D_{0,l}$.

15700 18-23 The exercise to show that COS membrane diffusion and CO2 competition is negligible is left for the reader. It would be helpful to do the calculation or, in the case of membrane diffusion, quote the numbers used as well as the citation.

Answer: these calculations are now explained in more detail in this section with the numbers used for membrane diffusion.

15701 5-15 I had to read this a couple of times to figure it out. The Protoschill-Krebs work was based on extracts of CA from pea shoots, which is also β-CA. Burnell et al. 1988 is the only work that looked at temperature and β-CA. Sun et al. 2015 used Km directly from Protoschill-Krebs and then calculated kcat using the Protoschill-Krebs data set. The Sun et al. work is the only work to report kcat and Km for OCS and β-CA. And now this study is reporting a relationship based on the empirical temperature-response data from the Burnell study. The paragraph makes it sound like Protoschill-Krebs might be a theoretical work or examines a different family of CA. Some minor re-phrasing would make everything clear.

Answer: We agree that this paragraph needs rephrasing, because obviously the statements were unclear. The only study that reports kcat and Km for OCS and β-CA is the one of Protoschill-Krebs et al., not Sun et al., and it is from Protoschill-Krebs et al. that we derived the values of Km and kcat used in this study, not from Sun et al. (2015). Sun et al. (2015) used a kcat value that was empirically fitted to their field dataset and a Km value from a table in Ogawa et al. (2013), which seemed inappropriate to use in our context as it corresponds to an α-CA from the coleopter Tribolium castaneum (Herbst). Similarly the temperature response reported here was derived from Burnett et al. on a study of β-CA, while Sun et al. used a theoretical formulation that they also fitted to their field dataset. To clarify statements in this paragraph we slightly rephrased the sentence that refers to the study of

Sun et al. and moved it to the end of the paragraph.

Ogawa, T., Noguchi, K., Saito, M., Nagahata, Y., Kato, H., Ohtaki, A., Nakayama, H., Dohmae, N., Matsushita, Y., Odaka, M., Yohda, M., Nyunoya, H., and Katayama, Y. (2013) Carbonyl sulfide hydrolase from Thiobacillus thioparus strain THI115 is one of the β-carbonic anhydrase family enzymes, J. Am. Chem. Soc., 135, 3818–3825.

15703 2 There is field data (Maseyk et al, 2014) that also reports production above ~25 C for drier soils.

Answer: The study of Maseyk et al. 2014 is now cited here too.

15703 12-14 It is unclear that the availability of sulfate will affect either the uptake or production of COS.

Answer: We agree that at this stage the role of sulphate ions on OCS production rate is a hypothesis based on the possibility that the abundance of sulphate ions is an important trigger for OCS production in anoxic soils.

15705 Section 2.7. Only some of the variables defined in the preceding equations have actual numbers assigned to them. For example, the moving water and air fields (ql and qa)– how are they calculated for this incubation data?

Answer: To interpret the laboratory experiments we neglected advection fluxes. This is now stated in this section. We also added a sentence explaining the tree of equations required to apply our steady-state model to compare to these datasets.

15713 21-29 If the turbulent mixing would increase dispersion, could there be a data set that was collected without turbulent mixing? In other words, should the dispersive fluxes always be included? It would be good to include a further justification of why they were neglected here.

Answer: This is an important question. We believe that in all experiments where air mixing is imposed by fans at the soil surface, dispersion should be accounted for. In our case we had to neglect it because we had no information on turbulence intensity at the soil *surface in the experiments of Van Diest and Kesselmeier (2008). As discussed in this paragraph we believe that this could lead to an overestimation of soil CA activity by a factor two at least. We now included a sentence explaining why we had to neglect dispersion for our study.*

Van Diest, H. and Kesselmeier, J. (2008) Soil atmosphere exchange of carbonyl sulfide (COS) regulated by diffusivity depending on water-filled pore space, Biogeosciences, 5, 475–483.

15714 paragraph starting at line 20 This paragraph makes it sound like lab data cannot be extrapolated to the field, answering the question in the title of section 4.2. Perhaps moving this paragraph up to the top of the section, then describing previous work in that context would work better. It reads now like a discussion of previous lab-based modeling efforts, but ends by dismissing this work as problematic.

Answer: yes, our aim is exactly to point out that lab data cannot be (directly) extrapolated to the field, because of the soil treatments (sieving, repacking…) prior to the lab experiments that strongly affect the diffusivity properties of the soil. On the other hand applying our model with a soil diffusivity formulation applicable to undisturbed soils should work for the field. A sentence has been added at the end of the paragraph to clarify this point.

Technical corrections

15692 17-18 introduces Ksw but then 15693 line 4 starts a discussion about Ksl

It was a typo that is now corrected.

15692 25 the Henry's law equation is difficult to parse and might benefit from formatting as an Equation rather than a line of text.

Done.

15694 Not sure why some units have "m2 soil" and some others are just "m2. If this is a fine distinction, it needs to be explained a little further.

The distinction between soil and air is made only when needed (i.e. m^3 air m^{-1} soil s^{-1} instead of simply m^2 s^{-1} for soil diffusivity).

15695 17, Is Camindu Deepagoda the full name of the researcher? In the Bibliography, it suggests the first name begins with T.

Chamindu is the first name. It is now removed from the text.

15697 Equation 6a, hl does not appear to be defined.

Done.

15700 17 I'm not sure what co-limination means. Co-limitation is meant here?

Corrected.

15701 20 The text and Figure 2b suggest that you're using the equation from Rowlett et al., 2002. Is there a reason to plot the equation twice? Or is it a slightly different equation in the figure?

No, it is the exact same equation but the dotted line show the pH range over which the equation has been derived.

15703 10 "oxydants".

Yes "oxydants" is the right word.

15704 10 z units are probably meters.

Yes SI units are used throughout the manuscript.

15704 Eq. 16a is z12 supposed to be (z1)2? Or is this another variable?

Same variable.

15710 12 do you mean Equation 16b?

Corrected.

15710 14 "asymetric"

Corrected.

15714 21 and 15715 5 there are two parenthetical comments with "…".

Should we replace them by "etc."?

15715 21 "mistmatch".

Corrected.