

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: Mechanical dispersion can be important even when advective fluxes are negligible because advection is proportional to the flow velocity of the carrier fluid (q_l for water and q_a for air) while mechanical dispersion, happening in both directions and being always positive, is proportional to the absolute value of that flow velocity (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: We agree that the OCS production term in our model is mostly relevant for anoxic conditions while several studies have also reported strong OCS production rates from dry (oxic) soils, at least at high temperatures. In that sense, Eq. 12a would probably need to be adapted to capture the range of OCS production rates observed in dry soils. For example rather than a response to E_h , we would probably need to include a response to light, and whether we should use UV light only or total solar radiation could also be debated. The only trigger that seems common to all conditions is soil temperature and this is the reason why we decided to focus on the temperature response, making our analysis valid for all conditions, provided that the other important factors (E_h , light...) remain constant.

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: 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 have been 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 (Table 1, now referred to in the text in section 2.3 and elsewhere).

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 details in the text and in an appendix (Appendix A).

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 K_m directly from Protoschill-Krebs and then calculated k_{cat} using the Protoschill-Krebs data set. The Sun et al. work is the only work to report k_{cat} and K_m 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 k_{cat} and K_m for OCS and β -CA is the one of Protoschill-Krebs et al., not of Sun et al., and this is from Protoschill-Krebs et al. that we derived the values of K_m and k_{cat} used in this study, not from Sun et al. (2015). Sun et al. (2015) used a k_{cat} value that was empirically fitted on their field dataset and a K_m 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 on 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 moved the sentence that refers to Protoschill-Krebs et al. in a separate paragraph below.*

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 pure speculation. However we wanted to point out 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 (q_l and q_a)– 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, we wanted 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 (e.g. Mol03u or Deepa11) 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 typesetting mistake 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. m³ air m⁻¹ soil s⁻¹ instead of simply m² s⁻¹ for gas diffusivity).

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

Camindu 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-limitation 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".

Corrected to "oxidants".

15704 10 z units are probably meters.

Yes SI units are used throughout the manuscript.

15704 Eq. 16a is z^{12} supposed to be $(z^1)^2$? Or is this another variable?

Same variable.

15710 12 do you mean Equation 16b?

Corrected.

15710 14 "asymmetric"

Corrected to "asymmetric".

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

Should we replace them by "etc."?

15715 21 "mismatch".

Corrected.

Anonymous Referee #2

General comments

Overall, this paper, and the model framework it describes, represents a significant advance in our theoretical understanding of soil-atmosphere OCS fluxes. The derivation of the model is thorough and well thought out, and the sensitivity tests give a good sense of the model behavior. The ability of the model to reproduce (qualitatively, if not quantitatively) a wide range of laboratory and field results, including both net production and consumption of OCS, is impressive. Without a doubt, this should be published in BG.

That said, there are a few issues that need to be dealt with first: 1. Considering that you say “For this study we thus consider that Eh is the primary driver of OCS production, independently of pH:” and that “The soil redox potential (Eh) is a very dynamic variable that is not easily measured in the field ...”, there does not seem to be proportionate attention paid to E_h in the Discussion and Perspectives regarding how to make progress with its specification in the future. For example, no sensitivity tests regarding V_d and E_h seem to have been performed.

Answer: We agree that more emphasis could be put on redox potential in the discussion. With the current model formulation, a sensitivity test on Eh would however be a bit useless as Eh acts simply as an on/off trigger for OCS production (i.e. OCS production occurs only below a certain Eh threshold of -100mV). Also, as explained in our answer to the second general comment of referee #1, the redox potential may be the trigger of only a fraction of the OCS source term and could also not be a trigger at all in some situations (e.g. oxic soils). We thus feel that a better understanding of the exact mechanisms leading to OCS production by soils is needed before performing sensitivity tests on the different parameters related to this process. A first step would be to measure, together with the soil OCS flux, the speciation of soil S (i.e. the percentages of reduced (inorganic and organic) and oxidized S).

2. In the same vein, what is the prognosis for specifying f_{CA} in ‘real-world’ applications of the model? That is, while f_{CA} was tuned to give good matches with laboratory data, how would one choose values of CA to apply the model at regional (or global) scales? Fig. 6 shows a substantial difference between f_{CA}=10,000 and f_{CA}=100,000, which (more or less) bounds the range of plausible f_{CA} values.

Answer: This is a very important point that will clearly need to be addressed in future work. In the current study we mostly explored whether the f_{CA} values that we derived for OCS were compatible with f_{CA} values reported in CO₂ oxygen isotope studies and with microbial community size. Our analysis seems to indicate that such compatibility was plausible and that soil microbial biomass could be an important trigger for changes in f_{CA} across soils or season. Unfortunately the datasets available for this paper did not have microbial data to test further this hypothesis. It should definitely be tested in future work as it is a necessary step to upscale our model to larger scales.

3. [Minor] Given that the paper title includes the word 'flux', deposition velocity is used extensively. Wouldn't it be better to convert the observed V_d values to fluxes to conform to the derived theory?

Answer: We agree that the notion of deposition velocity is more appropriate for one-way fluxes, while our model includes both OCS source and sink terms. We thus added a second axis on Figs. 3-4 and 6-8 to display the corresponding range of OCS fluxes.

For both (1) and (2) please suggest a way forward and also indicate how these uncertainties might manifest themselves under various conditions.

Answer: For (1) we added a few lines at the end of the Perspectives that explain in more details the limitations of the proposed model with regard to the OCS emission term and the way forward to improve this aspect. For (2) we also added some suggestions in the second paragraph of the Perspectives.

Specific comments

p 88, l2: 'is' to 'are'

Corrected.

p 88, l27: 'evoked' to 'invoked'

Corrected.

p 89, l25: 'interconverted' to 'converted'

Corrected.

p 90 l20: 'with also' to 'but with'

Changed.

p92 l2: 'specificity' is not clear to me; could this be replaced with 'rate constant'?

Changed to 'affinity'.

p92 l9: For symmetry with other subscripts, could you use ' C_a ' instead of ' C '?

No because C_a is the OCS concentration in the air above soil surface (see p104 l9).

p92 l18: to be consistent with earlier notation, change K_{sw} to K_{sl} .

Done.

p92 l22: 'was' to 'is'

Changed.

p93 l4: not sure here what is meant by 'organic'. OCS is certainly not an organic compound.

We agree and we make this point on p93 l13, saying that what was found for organic vapours (e.g. VOCs...) is not necessarily true for inorganic gas such as OCS.

p93 l12: Sentence starting with "However": if these relationships are not applicable to OCS, then why discuss?

In the original version we almost dropped this paragraph but decided to leave it for completeness. Ideally we should cite studies relevant for OCS but we could not find such studies in the literature.

Also note here and elsewhere that ‘However’, ‘Interestingly’, etc. should generally be followed by a comma when starting a sentence.

My impression is that it is a question of writing style. I used to put commas after these adverbs and had several editors asking me to remove them, which I now do.

P93 117: ‘rather large’ is a bit vague. Can you be more specific?

We agree but we found it difficult to relate to this study in a quantitative manner because they were using pure, perfectly dry metal oxides. In real soils we believe that competition of water molecules would minimize by several orders of magnitude the adsorption capacity of soil particles. This is explained on p93 118-20.

P93 123: ‘reaction occurs and continuously remove’ to ‘reactions occur and continuously remove’

Changed.

P94 16: in Eq 1, consider using C_a instead of C.

We could not for the reason explained above (C_a is OCS concentration in the air just above the soil surface).

P94 17: I’m a bit confused here. In the definition of eps_{tot} , why is the third term included if you earlier say “In the following we will neglect adsorption of OCS on solid surfaces..”

This was for completeness. The third term is now removed to stay coherent with what we say above.

P95 117: strike ‘Camindu’

Done.

P98 13: Incidentally ‘a change in the air composition...’ is going to be overwhelmingly dominated by water vapour fluctuations.

This is probably true, or by temperature gradients, but as explained, “the resulting flux [would be] significant only in highly permeable (i.e. fractured) soils”.

P98 116: ‘a diffusive’ to ‘diffusive’

Corrected.

P98 123: ‘plan’ to ‘plane’

Corrected.

P100 17: more efficient to say ‘low concentrations of OCS’

Changed.

P100 124: insert comma after ‘reaction’

Done.

P101 l3: earlier 'S' is used for sink; here S_d is completely different. Could you substitute a different letter (Greek?)

We now use ΔS_d (and ΔH_a and ΔH_d) to be consistent with more common notations in thermodynamics.

P101 l16: 'monotonic decrease function' to 'monotonically decreasing function'

Changed.

P103 l10: 'oxydants' to 'oxidants'

Changed.

P104 l4: when saying 'uniform' do you mean 'horizontally uniform'?

Equation 13 is already assuming horizontally uniform conditions. Here we mean vertically uniform conditions in terms of soil moisture and porosity. This is now clarified.

P106 l15: make the RHSs of theta formulations consistent so they are easy to compare. I would define all as $\theta_{opt} = 0.xx \cdot \phi$.

Done.

P106 l26: comma after 'In contrast'

Added.

P108 l4: would it be clearer to add 'by observations' after 'constrained'?

Added.

P108 l8: 'direction' to 'directions'

Changed.

P109 l15: 'really' is vague. Perhaps replace with 'measurably' or say that the impact on V_d is (e.g.) only a 1% change.

Changed to 'significantly'.

P109 l22: It's not clear to me what justifies setting the source term to zero. Couldn't V_d being positive just be the result of larger uptake than production fluxes?

This is true and having a source term would result in a higher soil moisture optimum and a lower temperature optimum (Fig. 7) and this could explain some discrepancies between the model and observations on Figs. 9 or 11 for example.

P110 l4: be consistent about soil moisture units (cm³/cm³ vs. m³/m³)

This is now changed throughout the manuscript.

P111 l7: insert semicolon after 'dry' or change 'this' to 'which'.

Done.

P111 l24: 'CA's' to 'CAs' (apply 's only to possessives)

Changed.

P112 l6: insert 'which is' before 'of the order...'

Done.

P112 l11: please provide a citation for the microbial population size.

Done.

P112 l14: change 'Any' to 'With any'

Done.

P112 l18: It's not clear to me whether identical CA enzymes apply to CO₂ and OCS. Thus, is this test valid?

All CAs react with CO₂ and OCS but their affinity for these two gases can change from one CA to another. This caveat is discussed in the following paragraph.

P113 l3: Consider striking 'at least' given that the following discussion gives reasons to think that f_{CA} values may indeed be reasonable.

This sentence has been moved at the end of the following discussion and the "at least" has been removed from it.

P114 l7: On p110 l8, '12% of soil weight' is used, but here the 12% is a volumetric ratio. Am I missing something?

This is correct. We now changed the unit and added a sentence on paragraph 4.2 to discuss the correspondence between the two and show that our model clearly indicates that the 12% of soil weight should not be taken for granted for any soil type.

P115 l18: 'by a factor of two at least', but as mentioned earlier, you also argue that CA contents could well be realistic.

This sentence has been entirely reformulated.

Figures:

2. insert 'normalized' after 'Response of the'?

Done.

3. In Figs 3, 4, 6, 7, 8, change 'thick line in left panel' to 'right panel'

Done.

5. Could you overplot the data that the dotted line is fit to?

Unfortunately no because the plot of the actual data was not shown in the referred study and the dataset was too hard to retrieve (over 15 years old).

Anonymous Referee #3

Summary

This manuscript presents a rigorous and much needed framework for modeling OCS fluxes in soils. This contribution will aid in the re-analysis of existing data sets and will prompt new experimental undertakings to clarify processes that Ogee et al identify as data poor.

Comments

- The discussion of diffusivity terms that go into the final model could be clarified. How does one determine the input values for D in eqn 15? The rationale for moving forward with D (eqn 15) depending only on dispersive and not effective diffusion could be discussed in more detail. Situations where one would use the dispersion flux instead of the diffusive flux and vice versa could be explained. Relatedly, in p. 15698 l. 21: values or example values for the terms going into equations 7a and 7b would help facilitate model utilization (i.e., longitudinal dynamic dispersivities (α), dispersive diffusivities (D_{disp}), velocity fields (q)) as these values are used in expression 15. Similarly, p. 15713 l. 21, which diffusive terms were used if dispersion fluxes were neglected?

Answer: This comment arises mostly from a typo in Eq. 15 that resulted in writing twice the dispersive diffusivities (once explicitly and once with their approximate formulations with longitudinal dynamic dispersivities) and from the fact that we did not clearly state that we were neglecting advection and dispersion fluxes in all the model results shown. The typo in Eq. 15 is now corrected and a sentence has been added to explain that advection and dispersion fluxes are neglected to compare to the datasets available. We also added a sentence explaining the tree of equations required to apply our steady-state model to compare to these datasets.

- p. 15698 l. 8: details on the measurements used to test the model would be useful to include (e.g. measurement time, z_{max} , repacking) that are relevant to the assumptions made in the model description (e.g., neglecting advective fluxes). This could be done in Sec 3.5.

Answer: A sentence has been added in section 2.7 to explain the tree of equation and list all the measurements required to test the model.

- p. 15700 l. 16: The k_{cat} and K_m may not only be spatially averaged at the organism level, but also the microbial community or population level.

Answer: This is what we meant but the expression was obviously misleading. We corrected the text to "volume-averaged parameters for the entire soil microbial community".

- The production model includes drivers of emissions that are not tested in this study. Is there any way to assess the proposed model with extant data in terms of the temperature or Eh sensitivity? Production assumed to be zero in model tests,

although agricultural soils have been found to have large emission components. Can the value of Q_{10} be estimated?

Answer: This is a good point that we cannot address directly with the current datasets. Our intent was to show the influence of a source term on the temperature and moisture response curves, but the exact processes leading to OCS emissions are still too poorly understood to derive a fully-mechanistic model for this process. On-going work is being conducted to test the model on other datasets collected at higher temperatures (>35°C) with strong OCS emissions and extract nominal OCS emission rates (S_{25}) in order to identify potential drivers for this model parameter. It is however out of the scope of this study to include such analysis.

- p. 15709 section 3.4 on sensitivity to soil pH could use a summarizing sentence to tie it all together.

Answer: A sentence has been added.

- p. 15711: Regarding the discussion of possible impacts of the treatment of soils over the long period that the temperature and moisture responses were measured. The soil microbial community and its activity could have very likely changed by these treatments, and a citation could be included to point to a case where the size and diversity of the microbial population would be sensitive to this. As this is a pivotal part of the data interpretation, e.g., how can such large changes in fCA be justified, the justification might be made more quantitative. This could be done by indicating which measurements were made within a short time period versus those that were separated by long periods. In addition, it could be noted which measurements were done at the same site, but using soils from a different time of sampling. If the differences in fCA are aligned with soil age or different samples, it could strengthen the argument.

Answer: This is a very important point. Very good care was taken to minimise possible biases between soil samples, i.e. soils samples were stored at 5°C shortly after sampling and remained stored in the refrigerator until measured. The storage at 5°C is a commonly-used method to limit changes of microbial activity during storage, but of course there is no guarantee and we cannot exclude changes in microbial activities. Nevertheless, measurements from wetting to drying out (1-2 days) at a given temperature were reproducible when using samples taken from the same stock. Our only explanation is that the incubation temperature just before and during the measurements and/or the time of sampling (some samples for the German soil come from different seasons) are the main cause of the variations in fCA. This is now explained in the manuscript.

Minor comments

p. 15692 l. 25: K_H off by factor of 100?

Yes because the value of 0.021 has unit of $M \text{ atm}^{-1}$, not the official SI unit of $\text{mol m}^{-3} \text{ Pa}^{-1}$, and the conversion factor is 101.325. We now changed the value of 0.021

to its SI value. For information, this conversion was done in all the simulations done, it is only in the manuscript that this unit conversion factor was missing.

p. 15695 l. 1: what is meant by "binary" diffusivity.

Binary diffusivity is the term used to describe the diffusivity of compounds in a binary system (OCS in water in this case).

p. 15696 l. 16: the wording in this sentence is a bit unclear. Was the value of $D_{0,a}$ derived from these values (diffusivity of water vapor in air, CO₂/OCS diffusivity, etc...)? Or are those provided as justification for why the $D_{0,a}$ is reasonable? Using "derived from" if the former is the case would clarify.

We changed "based on" to "derived from".

p. 15698 l. 23: do you mean "plane" instead of "plan"?

Changed.

p. 15699 l. 3: what is meant by "drift velocity"?

The definition is given in the text ($F_{diff,a}/C$). We added "defined as the ratio" to clarify this point.

p. 15700 l. 17: "limitation" instead of "limination"

Changed.

p. 15700 l. 22: values illustrating the point that OCS uptake is not limited by diffusion could be given in the sentence, as they were in the previous sentence to prove the point.

Following referee #1's suggestion this sentence has been extended with numerical values to better describe our calculations (see Appendix A).

p. 15703 l. 10: "oxidants" instead of "oxydants"

Changed.

p. 15710 l. 13: the terminology "almost exactly" could be changed, especially since there were differences in some of the data-model fit for soil moisture responses, eg Fig 12, and the summary of goodness of fit could be more descriptive.

The terminology "almost exactly" has been removed.

throughout: Should cite "Van Diest" and not "VanDiest"?

Changed.

p. 15711 l. 27: It's not clear to me that OCS emissions are the result of enzymatic processes. They could be abiotic, right?

Correct it could be biotic or abiotic. The word "enzymatic" has been removed to stay more open.

p. 15712 l. 7: I think it's fair to assume this CA concentration in microbial cells, but I would note that the same concentrations do not necessarily need to be maintained

in microbes with different metabolisms that might require very different levels of CA. The examples of known CA concentrations seem to all come from phototrophs.

We agree and it is just a working hypothesis right now. We could not find estimates of CA concentrations in microbes from the literature.

- p. 15715 l. 20: "could have greatly" instead of "could greatly"

Changed.

all figures: There appears to be a black outline on all text in the figures (even on black text) that makes the text look grainy. This also contributes to making the text highly compressed and difficult to read in figures 9-12. Perhaps removing the outline or changing the fonts would help.

This happened during the submission process (fonts have been changed and the file format has been changed). Hopefully this will disappear in the final version.

figure 5 caption: It would be easier to read this sentence if it were converted to a serial list instead of the "respectively" framework: Soil column depth is also converted into soil weight assuming a soil surface area of 165.1 cm² and a soil bulk density and pH of 0.85 kg m³ and 7.2, respectively, to be comparable with the experimental setup used in Kesselmeier et al. (1999) to derive the observed response curve.

Changed.

1 **A new mechanistic framework to predict OCS fluxes from**
2 **soils**

3

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12

1 **Abstract**

2 | Estimates of photosynthetic and respiratory fluxes at large scales are needed to improve our
3 predictions of the current and future global CO₂ cycle. Carbonyl sulphide (OCS) is the most
4 abundant sulphur gas in the atmosphere and has been proposed as a new tracer of
5 photosynthesis (GPP), as the uptake of OCS from the atmosphere is dominated by the activity
6 of carbonic anhydrase (CA), an enzyme abundant in leaves that also catalyses CO₂ hydration
7 during photosynthesis. But soils also exchange OCS with the atmosphere which complicates
8 the retrieval of GPP from atmospheric budgets. Indeed soils can take up large amounts of
9 OCS from the atmosphere as soil microorganisms also contain CA, and OCS emissions from
10 soils have been reported in agricultural fields or anoxic soils. To date no mechanistic
11 framework exists to describe this exchange of OCS between soils and the atmosphere but
12 empirical results, once upscaled to the global scale, indicate that OCS consumption by soils
13 dominates over production and its contribution to the atmospheric budget is large, at about
14 one third of the OCS uptake by vegetation, with also a large uncertainty. Here, we propose a
15 new mechanistic model of the exchange of OCS between soils and the atmosphere that builds
16 on our knowledge of soil CA activity from CO₂ oxygen isotopes. In this model the OCS soil
17 budget is described by a first-order reaction-diffusion-production equation, assuming that the
18 hydrolysis of OCS by CA is total and irreversible. Using this model we are able to explain the
19 observed presence of an optimum temperature for soil OCS uptake and show how this
20 optimum can shift to cooler temperatures in the presence of soil OCS emissions. Our model
21 can also explain the observed optimum with soil moisture content previously described in the
22 literature as a result of diffusional constraints on OCS hydrolysis. These diffusional
23 constraints are also responsible for the response of OCS uptake to soil weight and depth
24 observed previously. In order to simulate the exact OCS uptake rates and patterns observed on
25 | several soils collected from a range of biomes, different CA activities had to be invoked in
26 each soil type, coherent with expected physiological levels of CA in soil microbes and with
27 CA activities derived from CO₂ isotope exchange measurements, given the differences in
28 affinity of CA for both trace gases. Our model can also be used to help upscale laboratory
29 measurements to the plot or the region. Several suggestions are given for future experiments
30 in order to test the model further and allow a better constraint on the large-scale OCS fluxes
31 from both oxic and anoxic soils.

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1 1 Introduction

2 The terrestrial biosphere is, with the ocean, the largest sink in the global atmospheric CO₂
3 budget, with a very large year-to-year variability (e.g., Gurney and Eckels, 2011). Yet there is
4 a scarcity of observations on how photosynthesis (GPP) and respiration over land respond
5 individually to warmer temperatures, increasing atmospheric CO₂ mixing ratios and changes
6 in water availability (Beer et al., 2010; Frankenberg et al., 2011; Welp et al., 2011; Wingate
7 et al., 2009). Obtaining new observational constraints of these two opposing land CO₂ gross
8 fluxes at large scales is key to improve our models of the land C sink and provide robust
9 projections of the atmospheric CO₂ budget and future climate (Friedlingstein et al., 2006; Piao
10 et al., 2013).

11 In this context, additional tracers such as carbonyl sulphide (OCS), an analogue of CO₂ in
12 many respects, could be very useful (Berry et al., 2013; Campbell et al., 2008; Kettle et al.,
13 2002; Montzka et al., 2007). Indeed, the uptake rate of OCS by foliage is strongly related to
14 GPP (Sandoval-Soto et al., 2005; Stimler et al., 2010), or more generally to the rate of CO₂
15 transfer into foliage (e.g., Seibt et al., 2010; Wohlfahrt et al., 2011). This is because both OCS
16 and CO₂ molecules diffuse into foliage through the same stomatal pores and through
17 mesophyll cells where they get rapidly hydrated in an enzymatic reaction with carbonic
18 anhydrase (CA) (Protoschill-Krebs and Kesselmeier, 1992). However, unlike CO₂ that is
19 reversibly hydrated and converted into bicarbonate, OCS molecules are irreversibly
20 hydrolysed (Elliott et al., 1989) and are not expected to diffuse back to the atmosphere, given
21 the high affinity of CA towards OCS and the high activity of CA usually found in leaves
22 (Protoschill-Krebs et al., 1996; Stimler et al., 2012).

23 Carbonic anhydrase is also widespread in diverse species from the Archaea, Bacteria, Fungi
24 and Algae domains (Smith et al., 1999), so that OCS uptake can theoretically take place in
25 soils. Several field studies provide support for this by showing that soils generally act as an
26 OCS sink when measured at ambient concentrations (Castro and Galloway, 1991; Kuhn et al.,
27 1999; Liu et al., 2010a; Steinbacher et al., 2004; White et al., 2010; Yi et al., 2007) and that
28 the uptake rate is reduced when the soil is autoclaved (Bremner and Banwart, 1976).
29 Kesselmeier et al. (1999) also observed a significant (>50%) reduction of the OCS uptake rate
30 in soil samples after adding ethoxzolamide, one of the most efficient known CA inhibitors
31 (e.g., Isik et al., 2009; Syrjänen et al., 2013). This finding strongly supports the idea that OCS
32 uptake by soils is dominated by soil CA activity.

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1 Soils can also emit OCS into the atmosphere as reported in some agricultural fields (Maseyk
2 et al., 2014; Whelan and Rhew, 2015) or in anoxic soils (Devai and Delaune, 1995; Mello and
3 Hines, 1994; Whelan et al., 2013; Yi et al., 2008) but the exact mechanisms for such
4 emissions are still unclear (Mello and Hines, 1994; Whelan and Rhew, 2015). At the global
5 scale, OCS consumption by soils seems to dominate over production and its contribution to
6 the atmospheric budget is large, at about one third of the OCS uptake by vegetation, but with
7 a large uncertainty (Berry et al., 2013; Kettle et al., 2002; Launois et al., 2015).

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8 This large uncertainty in the OCS exchange rate from soils is partly caused by the variety of
9 approaches used to obtain a global estimate of this flux. Kettle et al. (2002) assumed soil OCS
10 fluxes responded to soil surface temperature and moisture only and used a parameterisation
11 derived by Kesselmeier et al. (1999) from incubation measurements performed on a single
12 agricultural soil in Germany. They recognised the limitation of such parameterisation and also
13 noted the important role of some intrinsic properties of the soil and particularly its redox
14 potential (Devai and Delaune, 1995) but did not account for it in their analysis. More recent
15 approaches have assumed that the OCS flux from soils is proportional to other soil-air trace
16 gas fluxes, such as heterotrophic (microbial) respiration (Berry et al., 2013) or the H₂
17 deposition rate (Launois et al., 2015). Experimental evidence that supports such scaling
18 between different trace gas fluxes is however scarce and with mixed results. In summary, all
19 the approaches to estimate soil OCS fluxes at large scales remain essentially empirical or
20 based on hypotheses that are largely un-validated. Given the supposedly important
21 contribution of soils in the global OCS atmospheric budget, it becomes apparent that a deeper
22 understanding of this flux and its underlying mechanisms is urgently needed. Until then
23 estimating global GPP using OCS as an additional tracer of the carbon cycle remains elusive.

24 A plethora of process-based models exist that describe the transport and fate of trace gases in
25 porous media (Falta et al., 1989; Olesen et al., 2001). Transport processes are fairly well
26 understood and similar between different trace gases. On the other hand the processes
27 responsible for the emission or destruction are usually quite unique, i.e., specific to each trace
28 gas. The main difficulty then resides in understanding these emission and destruction
29 processes. Very recently Sun et al. (2015) proposed parameterisations of OCS emission and
30 destruction in soils. However their parameterisations remain largely empirically-based and
31 lack important drivers such as soil pH or redox potential. In this paper we propose a
32 mechanistic framework to describe OCS uptake and release from soil surfaces, based on our

1 current understanding of OCS biogeochemistry in soils. Our model includes OCS diffusion
2 and advection through the soil matrix, OCS dissolution and hydrolysis in soil water and OCS
3 production. Soil microbial activity contributes to OCS hydrolysis, through a pseudo first order
4 CA-catalysed chemical reaction rate that varies with soil temperature and moisture, pH and
5 CA concentration. OCS production, either abiotic or biotic, is also accounted for using a
6 simple Q_{10} -type temperature response modulated by the soil redox potential. Using the model
7 we explore the theoretical response of OCS fluxes to soil water content, soil temperature, soil
8 depth and soil pH. We also evaluate our model against observed soil OCS uptake rates and
9 patterns from the literature and discuss how the CA-catalysed reaction rates for each soil type
10 can be reconciled with those typically observed for CO_2 hydration, given the differences in
11 affinity of CA for OCS and CO_2 .

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12 **2 Model description**

13 **2.1 Partitioning of OCS in the different soil phases**

14 Carbonyl sulphide, like any other trace gas, can be present in the soil matrix in three forms:
15 (1) vaporised in the air-filled pore space, (2) dissolved in the water-filled pore space or (3)
16 adsorbed on the surface of the soil matrix (mineral and organic matter solid particles). The
17 total OCS concentration C_{tot} (mol m^{-3} soil) is thus the sum of the OCS concentration in each
18 phase weighted by their volumetric content: $C_{\text{tot}} = \epsilon_a C + \theta C_1 + \rho_b C_s$ where ϵ_a (m^3 air m^{-3} soil)
19 is the volumetric air content, θ (m^3 water m^{-3} soil) is the volumetric water content, ρ_b (kg m^{-3})
20 is soil bulk density, C (mol m^{-3} air) and C_1 (mol m^{-3} water) denote OCS concentration in soil
21 air and liquid water respectively and C_s (mol kg^{-1} soil) denotes the OCS concentration
22 adsorbed on the soil matrix.

23 In the following we will assume full equilibrium between the three phases. We will also
24 assume linear sorption/desorption behaviour (a fair assumption at ambient OCS
25 concentrations), so that C_1 and C_s can be linearly related to C : $C_1 = BC$ where B (m^3 water m^{-3}
26 air) is the solubility of OCS in water and $C_s = (K_{\text{sg}} + BK_{\text{sw}})C$ where K_{sg} (m^3 air kg^{-1} soil) and
27 K_{sw} (m^3 water kg^{-1} soil) are the solid/vapour and solid/liquid partitioning coefficients,
28 respectively (Olesen et al., 2001). The solubility B is related to Henry's law constant K_{H}
29 ($\text{mol m}^{-3} \text{Pa}^{-1}$): $B = K_{\text{H}} RT$ where $R = 8.31446 \text{ J mol}^{-1} \text{ K}^{-1}$ is the ideal gas constant and T (K) is
30 soil water temperature. It has been shown that K_{H} is fairly independent of pH (at least for pH
31 below 9, see De Bruyn et al., 1995; Elliott et al., 1989) but decreased with temperature and

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1 salinity (De Bruyn et al., 1995; Elliott et al., 1989). In the following we will use the
2 parameterisation of Wilhelm et al. (1977) assuming low salinity levels in the soil:

3
$$K_H = 0.021 \exp[24900/R (1/T - 1/298.15)].$$

4 We preferred this expression rather than the more recent expression proposed by DeBruyn et
5 al. (1995) that was based on one single dataset rather than a compilation of multiple datasets.
6 The difference between the two expressions is shown in **Fig. 1a**.

7 Expressions of K_{sg} and K_{sw} for OCS are currently not available. For organic vapours it has
8 been shown that K_{sw} is well correlated with soil characteristics such as C content (Petersen et
9 al., 1995), specific surface area or clay content (Yamaguchi et al., 1999), and that K_{sg} is
10 usually significant at soil water contents corresponding to less than five molecular layers of
11 water coverage (Petersen et al., 1995). In this range of soil moisture, direct chemical
12 adsorption onto dry mineral surfaces dominates and can increase the adsorption capacity of
13 soils by several orders of magnitude. For these organic vapours the relationship of K_{sg} with
14 soil moisture can be related to soil specific surface area (Petersen et al., 1995) or clay content
15 (Yamaguchi et al., 1999). However these relationships obtained for organic vapours are
16 unlikely applicable for OCS because the adsorption mechanisms may be completely different.
17 Liu and colleagues have estimated OCS adsorption capacities of several mineral oxides and
18 found that quartz (SiO₂) and anatase (TiO₂) did not adsorb OCS but other oxides with higher
19 basicity adsorbed, reversibly or not, rather large quantities of OCS (Liu et al., 2008; 2010b;
20 2009). They also recognised that these estimates of the adsorption capacity of the minerals
21 were an upper limit owing to the competitive adsorption of other gases such as CO₂, H₂O and
22 NO_x that occur in the real Earth's atmosphere (Liu et al., 2009; 2010b) and the somewhat
23 lower OCS partial pressure in ambient air compared to that used in their experimental setup.
24 Also, at steady state, adsorption should have little influence on the soil-air OCS exchange
25 rate, unless heterogeneous (surface) reactions occur and continuously remove OCS from the
26 adsorbed phase (Liu et al., 2010b). In the following we will neglect adsorption of OCS on
27 solid surfaces but we recognise that this assumption might be an over-simplification.

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28 **2.2 Mass balance equation**

29 The transport of OCS through the soil matrix occurs by either pressure-driven (advective-
30 dispersive) or concentration-driven (diffusive) fluxes. Carbonyl sulphide can also be

1 destroyed or emitted, owing to abiotic and/or biotic processes. The general mass balance
 2 equation for OCS in a small soil volume can then be written:

$$3 \quad \frac{\partial \epsilon_{\text{tot}} C}{\partial t} = -\nabla F_{\text{diff}} - \nabla F_{\text{adv}} + P - S, \quad (1)$$

4 | where $\epsilon_{\text{tot}} = \epsilon_a + \theta B + \rho_b(K_{\text{sg}} + BK_{\text{sw}}) \approx \epsilon_a + \theta B$ (m^3 air m^{-3} soil) is total OCS soil porosity,
 5 F_{diff} ($\text{mol m}^{-2} \text{s}^{-1}$) represents the diffusional flux of OCS through the soil matrix, F_{adv}
 6 ($\text{mol m}^{-2} \text{s}^{-1}$) is the advective flux of OCS, P ($\text{mol m}^{-3} \text{s}^{-1}$) the OCS production rate and S
 7 ($\text{mol m}^{-3} \text{s}^{-1}$) the OCS consumption rate and $\nabla = \partial/\partial x + \partial/\partial y + \partial/\partial z$ denotes the differential
 8 operator, i.e., the spatial gradient in all three directions x , y and z .

9 If the soil is horizontally homogeneous (that is, the soil properties are independent of x and y)
 10 and the soil lateral dimensions are much larger than its total depth (minimal edge effects), the
 11 OCS concentration is only a function of soil depth z and time t and Eq. (1) simplifies to:

$$12 \quad \frac{\partial \epsilon_{\text{tot}} C}{\partial t} = -\frac{\partial F_{\text{diff}}}{\partial z} - \frac{\partial F_{\text{adv}}}{\partial z} + P - S. \quad (2)$$

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13 2.3 Diffusive fluxes

14 Diffusion in the gas phase is commonly described by Fick's first law (Bird et al., 2002;
 15 Scanlon et al., 2002):

$$16 \quad F_{\text{diff,a}} = -D_{\text{eff,a}} \frac{\partial C}{\partial z}, \quad (3)$$

17 | where $F_{\text{diff,a}}$ ($\text{mol m}^{-2} \text{s}^{-1}$) is the diffusive flux of gaseous OCS and $D_{\text{eff,a}}$ (m^2 air m^{-1} soil s^{-1}) is
 18 the effective diffusivity of gaseous OCS through the soil matrix. The latter is commonly
 19 expressed relative to the binary diffusivity of OCS in free air $D_{0,a}$ (m^2 air s^{-1}): $D_{\text{eff,a}}/D_{0,a} = \tau_a \epsilon_a$
 20 where τ_a is the so-called air tortuosity factor that accounts for the tortuosity of the air-filled
 21 pores, as well as their constrictivity and water-induced disconnectivity (e.g., Moldrup et al.,
 22 2003). The air-filled porosity (ϵ_a) appears in this equation to account for the reduced cross-
 23 sectional area in the soil matrix relative to free air, although the effective porosity for
 24 diffusion could be smaller if the soil contains small pores that do not contribute to the overall
 25 transport such as dead end or blind pores. Expressions for τ_a differ depending on whether the
 26 soil is repacked or undisturbed (Moldrup et al., 2003). For undisturbed soils the most
 27 commonly used equations are those of Penman ((1940); $\tau_a = 0.66$, hereafter referenced as

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1 Pen40) and Millington and Quirk ((1961); $\tau_a = \epsilon_a^{7/3}/\phi^2$, where ϕ is total soil porosity, hereafter
 2 referred to as MQ61). For repacked soils, equations proposed by Moldrup et al. ((2003);
 3 $\tau_a = \epsilon_a^{3/2}/\phi$, hereafter referred as Mol03r) are preferred. For undisturbed soils with high
 4 porosity such as volcanic ash, the expression proposed by Moldrup et al. ((2003);
 5 $\tau_a = \epsilon_a^{1+3/b}/\phi^{3/b}$, where b is the pore-size distribution parameter) seems a better predictor
 6 (Moldrup et al., 2003). Recently a new density-corrected expression for undisturbed soils has
 7 also been proposed by Deepagoda et al. ((2011); $\tau_a = [0.2(\epsilon_a/\phi)^2 + 0.004]/\phi$) that seems to be
 8 superior to previous formulations and has the advantage of not requiring knowledge of the
 9 pore-size distribution parameter b . [A summary of these different formulations of the](#)
 10 [tortuosity factor and their range of application is given in Table 1.](#)

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11 Diffusion in the liquid phase is described in a similar fashion to the gas phase (Olesen et al.,
 12 2001):

$$13 \quad F_{\text{diff},l} = -D_{\text{eff},l} \frac{\partial C_l}{\partial z} = -D_{\text{eff},l} \left\{ B \frac{\partial C}{\partial z} + C \frac{dB}{dT} \frac{\partial T}{\partial z} \right\}, \quad (4)$$

14 where $F_{\text{diff},l}$ (mol m⁻²s⁻¹) is the diffusive flux of dissolved OCS in soil water and $D_{\text{eff},l}$ (m³
 15 water m⁻¹ soil s⁻¹) is the effective diffusivity of dissolved OCS through the soil matrix. As for
 16 gaseous diffusion $D_{\text{eff},l}$ is commonly expressed relative to the binary diffusivity of OCS in
 17 free water $D_{0,l}$ (m² water s⁻¹): $D_{\text{eff},l}/D_{0,l} = \tau_l \theta$ where τ_l is the tortuosity factor for solute
 18 diffusion. [Different expressions for \$\tau_l\$ can also be found in the literature \(Table 1\).](#)

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19 Diffusion of OCS in the adsorbed phase can also theoretically occur and can be described in a
 20 similar fashion to other trace gases (e.g., see Choi et al., 2001 for ozone). However we will
 21 neglect such a diffusion flux in the adsorbed phase because it is expected to be orders of
 22 magnitude smaller than in the two other phases. Also the binary diffusivity of any trace gas is
 23 several orders of magnitude higher in the air than it is for its dissolved counterpart in liquid
 24 water so that, in unsaturated (oxic) soils, $F_{\text{diff}} = F_{\text{diff},a} + F_{\text{diff},l}$ is dominated by the gas-phase
 25 OCS diffusion flux $F_{\text{diff},a}$. The role of $F_{\text{diff},l}$ in the OCS transport equations becomes
 26 significant only when the soil is water-logged.

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 ({*Penman:1940wa}; $\tau_l = 0.66$), Millington
 and Quirk ({*Millington:1961wv}; $\tau_l = \theta^{7/3}/\phi^2$)
 and Moldrup et al. ({*Moldrup:2003cd};
 $\tau_l = \theta^{b/3}/\phi^{b/3-1}$)

27 The binary diffusivity $D_{0,a}$ depends on pressure and temperature and is assumed here to follow
 28 the Chapman-Enskog theory for ideal gases (i.e., Bird et al., 2002):
 29 $D_{0,a}(T,p) = D_{0,a}(T_0,p_0) (T/T_0)^{1.5} (p_0/p)$. A value for $D_{0,a}(25^\circ\text{C}, 1\text{atm})$ of $1.27 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$ is used
 30 and [derived from](#) the value for the diffusivity of water vapour in air at 25°C ($2.54 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$,

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1 see Massman (1998)) and the CO₂/OCS diffusivity ratio of 2.0±0.2 derived from the
 2 Chapman-Enskog theory and the difference in molar masses of OCS and CO₂ (Seibt et al.,
 3 2010). The binary diffusivity $D_{0,1}$ also depends on temperature (Ulshöfer et al., 1996).
 4 Because the Stokes-Einstein equation only applies to spherical suspended particles we
 5 preferred to use an empirical equation that works well for both the self-diffusivity of water and
 6 the diffusivity of dissolved CO₂ in liquid water (Zeebe, 2011): $D_{0,1}(T) = D_{0,1}(T_0) (T/T_0 - 1)^2$,
 7 with $D_{0,1}(25^\circ\text{C}) = 1.94 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Ulshöfer et al., 1996) and $T_0 = 216\text{K}$. This value of T_0 was
 8 chosen to be intermediate between the value used for water (215.05K) and dissolved CO₂
 9 (217.2K) (Zeebe, 2011) and results in a temperature dependency of $D_{0,1}$ for OCS in water in
 10 very good agreement with relationships found in other studies (**Fig. 1b**).

11 2.4 Advective fluxes

12 Advection of OCS can occur in both the liquid and gas phases when the carrier fluid (water or
 13 air) moves relative to the soil matrix:

$$14 \quad F_{\text{adv},l} = q_l C_l = q_l B C, \quad (5a)$$

$$15 \quad F_{\text{adv},a} = q_a C, \quad (5b)$$

16 where q_l (m s^{-1}) and q_a (m s^{-1}) are the velocity fields for liquid water and air respectively. If
 17 the flow in the porous soil is laminar these velocity fields are given by Darcy's law (Massman
 18 et al., 1997; Scanlon et al., 2002):

$$19 \quad q_l = -\frac{k_l}{\mu_l} \frac{\partial \Psi_l}{\partial z} = -K_l \left(\frac{\partial h_l}{\partial z} + 1 \right), \quad (6a)$$

$$20 \quad q_a = -\frac{k_a}{\mu_a} \left(\frac{\partial p_a}{\partial z} + \rho_a g \right), \quad (6b)$$

21 In Eqs. (6a) and (6b) k_l and k_a (m^2) denote soil permeabilities for liquid water and air
 22 respectively, μ_l and μ_a ($\text{kg m}^{-1} \text{ s}^{-1}$) are water and air dynamic viscosities, $\Psi_l = \rho_l g(h_l + z)$ is
 23 total soil water potential (Pa), ρ_l is water density (1000 kg m^{-3}), h_l (m) is matric potential
 24 height, g is gravitational acceleration (9.81 m s^{-2}), ρ_a is air density (ca. 1.2 kg m^{-3}) and p_a (Pa)
 25 is air pressure. We also defined the soil hydraulic conductivity K_l (m s^{-1}): $K_l = k_l \rho_l g / \mu_l$. In
 26 practice p_a can be expressed as the sum of the hydrostatic pressure ($p_{\text{ah}} = -\rho_a g z$) and a
 27 fluctuating (non-hydrostatic) part: $p_a = -\rho_a g z + p'_a$ so that Eq. (6b) can be replaced by:

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$$q_a = -\frac{k_a}{\mu_a} \frac{\partial p'_a}{\partial z} \quad (6c)$$

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From Eq. (6c) we can see that advection in the gas phase can result from pressure fluctuations, caused by, e.g., venting the soil surface (according to Bernoulli's equation) or turbulence above the soil surface. Typical air pressure fluctuations are of the order of 10 Pa (Maier et al., 2012; Massman et al., 1997). Pressure fluctuations can also result from non-hydrostatic density fluctuations caused by a change in the air composition with gas species of different molar mass as air or by temperature gradients, but the resulting flux is significant only in highly permeable (i.e. fractured) soils.

When averaged over a long enough timescale (>1h) the advective flux starts to become negligible compared to the diffusive flux (e.g., Massman et al., 1997). Integration timescales of a few minutes were already assumed to allow liquid-vapour equilibration in Eq. (5a). In the following we will thus neglect advective fluxes in the OCS budget equation, keeping in mind that such an assumption is valid only for time scales of about 1h or longer.

Even when advective fluxes are negligible, advection through porous media generates a diffusive-like flux called mechanical dispersion that reflects the fact that not everything in the porous medium travels at the average water or gas flow speed. Some paths are faster, some slower, some longer and some shorter, leading to a net spreading of the gas or solute plume that looks very much like diffusive behaviour. Since mechanical dispersion depends on the flow, it is expected to increase with increasing flow speed and is usually expressed as:

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$$F_{\text{disp,l}} = -D_{\text{disp,l}} \frac{\partial C_l}{\partial z} = -\alpha_l |q_l| \frac{\partial BC}{\partial z}, \quad (7a)$$

$$F_{\text{disp,a}} = -D_{\text{disp,a}} \frac{\partial C}{\partial z} = -\alpha_a |q_a| \frac{\partial C}{\partial z}, \quad (7b)$$

where α_l (m) and α_a (m) are the longitudinal dynamic dispersivity of liquid water and air flow respectively and $D_{\text{disp,l}}$ ($\text{m}^2 \text{s}^{-1}$) and $D_{\text{disp,a}}$ ($\text{m}^2 \text{s}^{-1}$) are the corresponding dispersive diffusivities. Transverse dispersion (i.e. in a plane perpendicular to the flow) can also occur but will be neglected here.

In practice, because of advective-dispersive fluxes, we must know the liquid water and air velocity fields q_l and q_a in order to solve the trace gas OCS mass budget Eq. (2). This requires solving the total mass balance equations for liquid water and air separately. However, except

1 during rain infiltration and immediate redistribution, q_1 rarely exceeds a few mm per day
 2 while the drift velocity, defined as the ratio $F_{\text{diff,a}}/C_2$, is typically of the order of a few mm per
 3 minute. For this reason, advection fluxes are generally neglected in soil gas transport models.
 4 Dispersive fluxes can still be accounted for as a correction factor to true diffusion, provided
 5 we have parameterisations of the dispersion diffusivities that are independent of the advective
 6 flux (e.g., expressions for $D_{\text{disp,a}}$ independent of q_a). For example Maier et al. (2012) proposed
 7 expressions of $D_{\text{disp,a}}/D_{0,a}$ that rely on the air-filled porosity (ϵ_a) and permeability (μ_a) of the
 8 soil and the degree of turbulence above the soil surface (characterised by the friction velocity
 9 u^*).

10 2.5 Consumption and production rates

11 The processes of consumption or production of OCS in a soil are not fully understood.
 12 Carbonyl sulphide can be consumed through hydrolysis in the bulk soil water at an un-
 13 catalysed rate k_{uncat} (s^{-1}) that depends mostly on temperature T and pH (Elliott et al., 1989). In
 14 the following we will use the expression proposed by Elliott et al. (1989) because it covers the
 15 widest range of temperature and pH :

$$16 \quad k_{\text{uncat}} = 2.15 \cdot 10^{-5} \exp\left(-10450\left(\frac{1}{T} - \frac{1}{298}\right)\right) + 12.7 \cdot 10^{-pK_w + pH} \exp\left(-6040\left(\frac{1}{T} - \frac{1}{298}\right)\right), \quad (8)$$

17 where pK_w is the dissociation constant of water. Other expressions are available in the
 18 literature and compared to Eq. 8 for both temperature (**Fig. 1c**) and pH (**Fig. 2a**)
 19 responses. Using Eq. 8 the uncatalysed OCS uptake rate is then computed as
 20 $S_{\text{uncat}} = k_{\text{uncat}} B \theta C$. The volumetric soil water content θ appears in this equation to convert the
 21 hydration rate from $\text{mol m}^{-3} \text{ water s}^{-1}$ to $\text{mol m}^{-3} \text{ soil s}^{-1}$.

22 This uncatalysed rate is rather small and cannot explain the large OCS uptake rates observed
 23 in oxic soils (Kesselmeier et al., 1999; Liu et al., 2010a; Van Diest and Kesselmeier, 2008).
 24 The main consumption of OCS is thought to be enzymatic and governed by soil micro-
 25 organisms' CA activity (Kesselmeier et al., 1999; Liu et al., 2010a; Van Diest and
 26 Kesselmeier, 2008). We will assume that such a catalysed reaction by CA-containing
 27 organisms can be described by Michaelis-Menten kinetics, as was observed for OCS in
 28 several marine algae species (Blezinger et al., 2000; Protoschill-Krebs et al., 1995) and one
 29 flour beetle (Haritos and Dojchinov, 2005). Because of the low concentrations of OCS in
 30 ambient air (500ppt) and the comparatively high values of the Michaelis-Menten coefficient

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1 for OCS (K_m , see Ogawa et al., 2013; Protoschill-Krebs et al., 1995; 1996) the catalysed
 2 uptake rate S_{cat} ($\text{mol m}^{-3} \text{s}^{-1}$) can be approximated:

$$3 \quad S_{\text{cat}} = \theta k_{\text{cat}} [CA] \frac{BC}{K_m + BC} \approx \frac{k_{\text{cat}}}{K_m} [CA] B\theta C, \quad (9)$$

4 where k_{cat} (s^{-1}) and K_m (mol m^{-3}) are the turnover rate and the Michaelis-Menten constant of
 5 the enzymatic reaction, respectively and $[CA]$ (mol m^{-3}) is the total CA concentration in soil
 6 water. We recognise that Eq. 9 is an over-simplification of the reality in the sense that k_{cat} and
 7 K_m are not true kinetic parameters but rather volume-averaged parameters for the entire soil
 8 microbial community. Also Eq. 9 neglects the competition for CA by CO_2 molecules and the
 9 co-limitation of the uptake by diffusional constraints. Given the Michaelis-Menten constant of
 10 CA for CO_2 (K_{m,CO_2} , of the order of 3mM at 25°C and pH 8-9) and the range of CO_2 mixing
 11 ratios encountered in soil surfaces (300-5000 ppm or 0.01-0.15 mM at 25°C and 1atm) we can
 12 conclude that the competition with CO_2 is negligible (*i.e. the denominator in Eq. 9 would*
 13 *need to be multiplied by a factor $1 + [\text{CO}_2]/K_{m,\text{CO}_2}$ which would be less than 5%*). We
 14 recognise that the CO_2 concentration inside microbial cells (*i.e. at the CA sites*) must be
 15 somewhat larger than in the surrounding soil water but certainly not to an extent to justify
 16 accounting for competition between the two substrates. Also, using typical values of transfer
 17 conductance across cell wall and plasma membrane (Evans et al., 2009), we can show that the
 18 limitation of OCS uptake by diffusion into the microbial cells is negligible for calculating the
 19 OCS uptake rate (see Appendix A for a derivation). In the following we will therefore assume
 20 Eq. 9 to be valid.

21 As found for any enzymatic reaction, k_{cat} and K_m depend on temperature and internal pH
 22 (pH_{in}). In the following we will assume that the ratio k_{cat}/K_m has a temperature dependency
 23 that can be approximated as:

$$24 \quad \frac{k_{\text{cat}}}{K_m} \propto x_{\text{CA}}(T) = \frac{\exp(-\Delta H_a/RT)}{1 + \exp(-\Delta H_d/RT + \Delta S_d/R)}, \quad (10a)$$

25 where ΔH_a , ΔH_d and ΔS_d are thermodynamic parameters. In the following we will take
 26 $\Delta H_a = 40 \text{ kJ mol}^{-1}$, $\Delta H_d = 200 \text{ kJ mol}^{-1}$ and $\Delta S_d = 660 \text{ J mol}^{-1} \text{ K}^{-1}$, that leads to a temperature
 27 optima $T_{\text{opt,CA}} = 25^\circ\text{C}$ and reproduces well the temperature response of β -CA found on maize
 28 leaf extracts observed in the range 0-17°C by Burnell et al. (1988) (**Fig. 1d**). To our
 29 knowledge this is the only study that reports the temperature response of β -CA, the dominant

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1 CA class expected in soils (Smith et al., 1999). Interestingly our parameterisation of $x_{CA}(T)$,
2 based on direct measurements on β -CA from Burnell et al. (1988), is very different from the
3 one used by Sun et al. (2015), especially at temperatures above 20°C (Fig. 1d).

4 The pH response of CA activity for OCS hydrolysis was described by a monotonically
5 decreasing function towards more acidic pH_{in} , as observed in plant β -CA for both OCS
6 (Protoschill-Krebs et al., 1996) and CO₂ (Rowlett et al., 2002). In the following we will use
7 the expression proposed by Rowlett et al. (2002) for CO₂:

$$8 \quad \frac{k_{cat}}{K_m} \propto y_{CA}(pH_{in}) = \frac{1}{1 + 10^{-pH_{in} + pK_{CA}}} \quad (10b)$$

9 A value of $pK_{CA} = 7.2$ was used that corresponds to the CA response of the wild-type
10 *Arabidopsis thaliana* (Rowlett et al., 2002). The shape of the function y_{CA} is shown in Fig. 2b.

11 A β -CA K_M value for OCS (39 μ M at 20°C and pH 8.2) was estimated on pea (*Pisum*
12 *sativum*) by Protoschill-Krebs et al. (1996). From a re-analysis of the same dataset we also
13 estimated a k_{cat} of 93 s^{-1} at the same temperature and pH , leading to a k_{cat}/K_m value of
14 2.39 $s^{-1} \mu M^{-1}$. To our knowledge this is the only report of k_{cat} and K_m values for OCS in β -CA.

15 The breaking of water film continuity that occurs at low soil water content leads to a
16 reduction in microbial activity owing to the spatial separation of the microbes and their
17 respiratory substrates (Manzoni and Katul, 2014). In our case soil water discontinuity should
18 not affect OCS supply as gaseous OCS should be equally available in all soil pores. On the
19 other hand different organisms may have different k_{cat}/K_m values so that the spatially-averaged
20 k_{cat}/K_m could vary with drought-induced changes in microbial diversity. However our
21 knowledge of how k_{cat}/K_m for OCS varies amongst different life forms is too scarce to know if
22 it should increase or decrease during drought stress. We will therefore assume that soil water
23 discontinuity does not affect k_{cat}/K_m directly. CA concentration ($[CA]$) could also vary during
24 drought stress, although it is not clear in which direction. During water stress microbial
25 activity such as respiration or growth is usually reduced, but slow growth rates and heat stress
26 have been shown to cause an up-regulation of CA-gene expression in *Escherichia coli*
27 (Merlin et al., 2003), probably because of a need of bicarbonate for lipid synthesis. For this
28 study we thus make the simplifying assumption that CA concentration does not vary with soil
29 water content. The catalysed OCS uptake rate S_{cat} is then simply proportional to soil water
30 content (Eq. 9).

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1 Destruction of OCS can also occur in the solid phase and was observed on pure mineral
 2 oxides with high basicity (Liu et al., 2008; 2009; 2010b). However, such catalytic reaction
 3 should be significant only in very dry soils (with only a few molecular layers of water) and in
 4 the absence of other competitive adsorbants such as CO₂ (Liu et al., 2008; 2010c) and is
 5 therefore neglected in our model. The total soil OCS uptake rate is thus computed as
 6 $S = kB\theta C$ with:

$$7 \quad k = k_{\text{uncat}}(T, pH) + \frac{x_{\text{CA}}(T)}{x_{\text{CA}}(20^\circ\text{C})} \frac{y_{\text{CA}}(pH_{\text{in}})}{y_{\text{CA}}(8.2)} 2390 [\text{CA}] \quad (11a)$$

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8 Following common practice in the CO₂ literature we will also express k with respect to the
 9 uncalysed rate at 25°C and pH 4.5, i.e.:

$$10 \quad k = f_{\text{CA}} k_{\text{uncat}}(25^\circ\text{C}, pH = 4.5) \frac{x_{\text{CA}}(T)}{x_{\text{CA}}(25^\circ\text{C})} \quad (11b)$$

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11 where f_{CA} is the so-called soil CA enhancement factor. We can see from Eqs. (11a-b) that f_{CA}
 12 is not an intrinsic property of the soil and will vary with temperature, and pH , even at constant
 13 CA concentration. In the case where the catalysed rate dominates k in Eq. (11a) and the
 14 internal pH is close to 8.2 we have: $f_{\text{CA}} \approx 127 [\text{CA}]$, where $[\text{CA}]$ is in nM.

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15 In some situations the OCS uptake rates can be overridden by OCS production. This is the
 16 case when soil temperature rises above 25°C (Maseyk et al., 2014; Whelan and Rhew, 2015)
 17 or soil redox potential falls below -100mV (Devai and Delaune, 1995). Light has also been
 18 proposed as an important trigger of OCS production, assuming photoproduction processes
 19 similar to those observed in ocean waters can occur (Whelan and Rhew, 2015). However the
 20 literature and data on this possible mechanism is still too scarce and not quantitative enough
 21 to be accounted for in our model.

22 The soil redox potential (E_h) is a very dynamic variable that is not easily measured in the
 23 field, especially in unsaturated soils (e.g., van Bochove et al., 2002). Although E_h and pH are
 24 linked, their relationship is not unique and depends on the set of oxidants and reductants
 25 present in the soil solution (e.g., Delaune and Reddy, 2005). Also the soil redox potential is
 26 probably a more direct trigger for OCS production as it defines when sulfate ions start to
 27 become limiting for the plants or the soil microbes (Husson, 2012). For this study we thus
 28 consider that, for anoxic soils at least, E_h is the primary driver of OCS production,
 29 independently of pH :

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$$30 \quad P = P_{\text{ref}} y_p(E_h) Q_{10}^{(T-T_{\text{ref}})/10} \quad (12a)$$

1 where P_{ref} ($\text{mol m}^{-3} \text{s}^{-1}$) is the production rate at temperature T_{ref} (K) and low E_h
 2 (typically -200mV) and Q_{10} is the multiplicative factor of the production rate for a 10°C
 3 temperature rise. ~~Because soil OCS emission, when observed in oxic soils, usually occurs at~~
 4 ~~temperature around 25°C or higher, we will set $T_{\text{ref}} = 25^\circ\text{C}$ and thus $P_{\text{ref}} = P_{25}$.~~ According to
 5 results from Devai and DeLaune (1995), the function $y_p(E_h)$ may be expressed as:

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$$6 \quad y_p(E_h) = \frac{1}{1 + \exp(-(E_h - 100\text{mV})/20\text{mV})}, \quad (12b)$$

7 ~~For oxic soils, Eq. 12a would probably need to be modified to incorporate the effect of light~~
 8 ~~on the OCS production rate (Whelan and Rhew, 2015) and the function $y_p(E_h)$ given by~~
 9 ~~Eq. 12b may not hold and in any case would be difficult to evaluate. Whether we should use~~
 10 ~~UV light only or total solar radiation could also be debated. For all these reasons we decided~~
 11 ~~for this study to only look at the effect of temperature on the OCS production rate and its~~
 12 ~~consequences on the total OCS deposition rate.~~

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13 2.6 Steady-state solution

14 The one-dimensional mass balance equation (Eq. (2)) can be re-written as:

$$15 \quad \frac{\partial \varepsilon_i C}{\partial t} = \frac{\partial}{\partial z} \left\{ (D_{\text{eff},a} + \alpha_a |q_a|) \frac{\partial C}{\partial z} + (D_{\text{eff},l} + \alpha_l |q_l|) \frac{\partial BC}{\partial z} \right\} + P - kB\theta C \quad (13)$$

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16 Assuming steady-state conditions and isothermal and uniform ~~soil moisture and porosity~~
 17 ~~through the soil column~~, this simplifies to:

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$$18 \quad D \frac{d^2 C}{dz^2} - kB\theta C = -P, \quad (14)$$

19 with:

$$20 \quad D = D_{\text{eff},a} + \alpha_a |q_a| + (D_{\text{eff},l} + \alpha_l |q_l|) B \quad (15)$$

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21 Boundary conditions are $C(z=0) = C_a$, the OCS concentration in the air above the soil column
 22 and $dC/dz(z=z_{\text{max}}) = 0$, i.e., zero flux at the bottom of the soil column, located at depth z_{max}
 23 (the case for laboratory measurements). With such boundary conditions, the solution of
 24 Eq. (14) is:

$$25 \quad C(z) = z_1^2 P + (C_a - z_1^2 P) \frac{e^{-z/z_1} + \xi^2 e^{+z/z_1}}{1 + \xi^2}, \quad (16a)$$

1 with $z_1^2 = D/kB\theta$ and $\xi = e^{-z_{\max}/z_1}$. This leads to an OCS efflux at the soil surface:

$$2 \quad F = \sqrt{kB\theta D} \left(C_a - \frac{z_1^2 P}{D} \frac{1 - \xi^2}{1 + \xi^2} \right), \quad (16b)$$

3 from which we can deduce the deposition velocity $V_d = -F/C_a$.

4 For field datasets, the condition at the lower boundary should be modified to $dC/dz(z \rightarrow \infty) = 0$
5 and the production rate P should be positive and uniform only over a certain depth z_p below
6 the surface. In this case the steady-state solution becomes:

$$7 \quad F = \sqrt{kB\theta D} \cdot \left(C_a - \frac{z_1^2 P}{D} (1 - \exp(-z_p/z_1)) \right), \quad (17)$$

8 We can verify that both equations give the same results if $z_{\max} \rightarrow \infty$ and $z_p \rightarrow \infty$, and also that
9 Eq. (17) leads to $F \rightarrow -Pz_p$ when $k \rightarrow 0$.

10 2.7 Soil incubation datasets used for model validation

11 The steady-state OCS deposition model presented here (Eq. (16b)) was evaluated against
12 measurements performed on different soils in the laboratory. For this purpose we revisited the
13 dataset presented in Van_Diest and Kesselmeier (2008). Volumetric soil moisture content (θ ,
14 in $\text{m}^3(\text{H}_2\text{O}) \text{m}^{-3}(\text{soil})$) was converted from gravimetric soil water content data ($M_{w,\text{soil}}$, in
15 $\text{g}(\text{H}_2\text{O}) \text{g}(\text{soil})^{-1}$) by means of the bulk density of the soil inside the chamber (ρ_b , in g cm^{-3}):
16 $\theta = M_{w,\text{soil}} \rho_b / \rho_w$, where $\rho_w = 1 \text{ g cm}^{-3}$ is the density of liquid water. The soil bulk density was
17 itself estimated from the maximum soil moisture content after saturation
18 ($\theta_{\max} = M_{w,\text{soil,max}} \rho_b / \rho_w$), assuming the latter corresponded to soil porosity ($\phi = 1 - \rho_b / 2.66$),
19 i.e., $(\rho_b = 1 / (M_{w,\text{soil,max}} / \rho_w + 1/2.66))$. Soil thickness (z_{\max}) was further estimated using ρ_b , soil
20 dry weight (200g for the German soil, 80g for the other soils) and soil surface area
21 (165.1 cm^2) assuming soil density was uniform. Air porosity was calculated as:
22 $\epsilon_a = \phi - \theta$. These estimates of θ , ϕ , and ϵ_a were then used to compute D (Eq. 15, assuming
23 $|q_a| = |q_l| = 0$) and F (Eq. 16b, with $P = 0$ and k estimated using Eq. 11b, with different f_{CA}
24 values for each soil temperature incubation). Note that, in these experiments, the air in the
25 chamber headspace was stirred with fans above the soil surface so that dispersion fluxes may
26 be large (i.e. $|q_a|$ may not be zero). Without any more information about turbulence intensity
27 at the soil surface in these experiments we had to neglect this possible complication. We will

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1 | [discuss below how this simplification may affect the results of our simulations of these](#)
2 | [experiments.](#)

3 | 3 Results

4 | 3.1 Sensitivity to diffusivity model

5 | Given the large diversity of expressions for the air tortuosity factor (τ_a) used to compute the
6 | effective diffusivity of OCS through the soil matrix, we felt it important to perform a
7 | sensitivity analysis of the model to different formulations available in the literature for τ_a . In
8 | **Fig. 3** we show how the steady-state soil OCS deposition velocity model (Eq. (16b)) responds
9 | to soil moisture or soil temperature for three different formulations of τ_a : Pen40 ($\tau_a = 0.66$),
10 | MQ61 ($\tau_a = \epsilon_a^{7/3}/\phi^2$) and Mol03r ($\tau_a = \epsilon_a^{3/2}/\phi$). We also indicate the optimal soil moisture (θ_{opt})
11 | and temperature ($T_{opt,Vd}$) for each formulation.

12 | We found that the optimal temperature and the general shape of the response to temperature
13 | were not affected by the choice of the diffusivity model (**Fig. 3**, right panel). On the other
14 | hand the optimal soil moisture and the general shape of the response to soil moisture strongly
15 | depended on the choice made for τ_a (**Fig. 3**, left panel). In particular the model of Penman
16 | (1940) gives a perfectly symmetric response to soil moisture with an optimal value at
17 | $\theta_{opt} = 0.50\phi$, unlike other formulations: $\theta_{opt} \approx 0.23\phi$ for Millington and Quirk (1961) and
18 | $\theta_{opt} \approx 0.29\phi$ for Moldrup et al. (2003).

19 | It is also noticeable on the right panel of **Fig. 3** that the optimal temperature for V_d ($T_{opt,Vd}$) is
20 | actually lower than the prescribed optimal temperature for the catalysed OCS hydrolysis rate
21 | ($T_{opt,CA} = 25^\circ\text{C}$ in this case), even in the absence of an OCS source term. This is because
22 | $T_{opt,Vd}$ integrates other temperature responses, from the total effective diffusivity (D) and the
23 | OCS solubility (B). Although these variables do not exhibit a temperature optimum, their
24 | temperature responses affect the overall value of $T_{opt,Vd}$. It can be shown analytically that this
25 | leads to $T_{opt,Vd} < T_{opt,CA}$.

26 | 3.2 Sensitivity to soil depth

27 | Laboratory-based measurements of soil-air OCS fluxes are generally performed on small soil
28 | samples whose thickness are no more than a few centimetres. In contrast flux measurements
29 | performed in the field account for the entire soil column beneath the chamber enclosure. In

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1 order to see whether results from laboratory measurements could be directly applied to field
2 conditions we performed a sensitivity analysis of the model to soil thickness (**Fig. 4**). We
3 found that the responses to both soil moisture and soil temperature were affected by
4 maximum soil depth (z_{\max}), at least when z_{\max} was below a few centimetres. Thin soils lead to
5 lower maximum deposition rates but higher values of θ_{opt} and T_{opt,V_d} . In **Fig. 4** this is true
6 mostly for $z_{\max} = 1$ cm, and as soon as z_{\max} reaches values above or equal to 3 cm, the
7 response curve becomes almost indistinguishable from that obtained with $z_{\max} = 100$ cm.

8 However this threshold on z_{\max} also depends on soil CA activity. Results shown in **Fig. 4** were
9 obtained with an enhancement factor for OCS hydrolysis f_{CA} of only 10000. An even smaller
10 enhancement factor would have led to a deeper transition zone (e.g. about 10 cm with f_{CA} of
11 1000). This is because in Eq. (16b), the steady-state model of OCS deposition is proportional
12 to $\tanh(z_{\max}/z_1)$. Given the shape of the hyperbolic tangent function, we expect our steady-
13 state OCS deposition velocity model to become insensitive to z_{\max} as soon as $z_{\max}/z_1 \geq 2$. With
14 $z_1 = \sqrt{D/kB\theta}$ and because k is proportional to f_{CA} we can see that this condition on z_{\max}/z_1 will
15 depend on f_{CA} . At $f_{CA} = 1000$, we have $z_1(\theta_{\text{opt}}) \sim 5$ cm while at $f_{CA} = 10000$ we have
16 $z_1(\theta_{\text{opt}}) \sim 1.5$ cm.

17 This response to soil depth was already observed by Kesselmeier et al. (1999) who reported
18 measurements of OCS deposition velocity that increased linearly with the quantity of soil in
19 their soil chamber enclosure up to 200g of soil and then reached a plateau at around 400g.
20 Because their soil samples were evenly spread inside the soil chamber, an increase in the
21 quantity of soil directly translates into an increase in soil thickness. Using an enhancement
22 factor f_{CA} of 27000 we were able to reproduce their saturation curve with soil weight using
23 our steady-state model (**Fig. 5**). A lower f_{CA} value would have reduced the curvature of the
24 model but would have also lowered the maximum V_d (not shown, but see **Fig. 6**). A value for
25 f_{CA} of 27000 was the best compromise to match the observed saturation curve. Because
26 different soil weights were measured at different times with new soil material each time, it is
27 possible that they would correspond to slightly different f_{CA} values and this could explain the
28 slight mismatch between the model and the fitted curve on the observations.

29 3.3 Sensitivity to soil CA activity and OCS emission rates

30 Our model has two main parameters that need to be constrained by observations: these are the
31 CA concentration (or conversely the CA enhancement factor f_{CA}) and the OCS production rate

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1 at 25°C (P_{25}). A sensitivity analysis of our steady-state OCS deposition model to these two
2 parameters is shown in **Fig. 6** and **Fig. 7**. Both parameters affect the maximum deposition
3 rates but in opposite directions, with high f_{CA} values leading to higher V_d and high P_{25} values
4 leading to lower V_d . This was expected from Eq. (16b) as V_d is proportional to $\sqrt{f_{CA}}$ and is
5 linearly and negatively related to P_{25} .

6 Interestingly, the optimal soil moisture is not modified by changes in f_{CA} (**Fig. 6**, left panel)
7 and only slightly by P_{25} (**Fig. 7**, left panel). This means that, provided that z_{max} is known
8 precisely (or larger than $2z_1$, see section 3.2), the overall shape of the response to soil
9 moisture (as typically measured during a drying cycle) and the exact value of θ_{opt} are
10 indicative solely of the diffusivity model to be used (**Fig. 3**). This result is important and
11 should help us to, at least, decide whether the Pen40 formulation for τ_a must be used instead
12 of a more asymmetrical one (the Mol03r and MQ61 formulations are harder to distinguish,
13 see **Fig. 3**).

14 The value of $T_{opt,Vd}$ is also insensitive to changes in f_{CA} (**Fig. 6**, right panel) but diminishes
15 when P_{25} increases (**Fig. 7**, right panel). This means that very low optimal temperature values
16 $T_{opt,Vd}$ (i.e. unusually low compared to expected values for enzymatic activities and $T_{opt,CA}$)
17 should be indicative of an OCS emission term, even if the values of V_d remain positive (i.e.
18 the soil acts as a sink) in the temperature range explored. Of course at higher temperature, and
19 because in our model the OCS source term responds exponentially with temperature (Q_{10}
20 response) while k exhibits an optimal temperature ($T_{opt,CA}$), the V_d should reach negative
21 values if the value of P_{25} is large and f_{CA} is low. In some extreme cases where P_{25} fully
22 dominates over f_{CA} , our model could even predict OCS fluxes close to zero at temperatures
23 below $\sim 10^\circ\text{C}$ that would increase exponentially at warmer temperatures, as it has been
24 observed in some agricultural soils (Liu et al., 2010a; Maseyk et al., 2014; Whelan and Rhew,
25 2015).

26 **3.4 Sensitivity to soil pH**

27 The sensitivity of our model to different soil pH was also tested. Because the effect of soil pH
28 is mostly to modify the hydration rate k , we could not set a constant value of f_{CA} . Instead we
29 fixed the CA concentration in the soil (330nM) and also adjusted the internal pH assuming
30 partial homeostasis with changes in soil pH , as observed in bacteria (Krulwich et al., 2011):
31 $pH_{in} = 6 + 0.25pH$ (**Fig. 8**). By assuming pH_{in} to vary with changes in soil pH we changed k_{cat}

1 (Eq. (11a)) and this was equivalent to changing f_{CA} . Indeed results shown in **Fig. 8** are very
2 similar to those shown in **Fig. 6** where low pH (and pH_{in}) correspond to low f_{CA} values. If we
3 had assumed that pH_{in} was not modified by soil pH (and fixed at 8.2) no change in k_{cat} would
4 have been observed and the change in k would have only been caused by the effect of soil pH
5 on k_{uncat} (Eq. 11a). Unless the soil contains very little CA or the soil pH moves to very
6 alkaline values (**Fig. 2**), this change in k_{uncat} would have been too small to significantly affect
7 V_d . Indeed at a CA concentration of 330nM and with a pH_{in} maintained at 8.2 our model
8 Eq. (16b) gives exactly the same values for soil pH ranging from 4 to 9. In summary, within
9 the range of soil pH found in nature, the response of V_d to this environmental factor is only
10 happening through its influence on pH_{in} and hence on k_{cat} (Eq. 10b and Fig.2 b).

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11 **3.5 Model evaluation against lab-based drying curves**

12 Our steady-state OCS deposition model was further evaluated against experimental data from
13 Van Diest and Kesselmeier (2008) and results are shown in **Figs. 9-12** for different soils.
14 Because OCS deposition values observed by Van Diest and Kesselmeier (2008) were all
15 positive we set the source term to zero ($P_{25} = 0$) although we recognise that this may be an
16 oversimplification. We also set the optimum temperature for the catalysed OCS hydration rate
17 to 25°C. A value for f_{CA} was then manually adjusted for each soil and each temperature,
18 between 21600 and 336000, depending on the soil origin and temperature (**Figs. 9-12**). Once
19 this adjustment on f_{CA} was done, our model, with the diffusivity formulation of Moldrup et al.
20 (2003), was able to reproduce most observed response curves to soil drying (**Figs. 9-12**, left
21 and middle panels). The model was also able to reproduce, within the measurement
22 uncertainties, the temperature dependency of V_d at a soil moisture level of $0.12 \text{ m}^3 \text{ m}^{-3}$ (far
23 right panels in **Figs. 9-12**).

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24 **4 Discussion**

25 **4.1 Can the proposed model explain observations realistically?**

26 Many studies have clearly demonstrated that soil moisture strongly modulates OCS uptake by
27 soils, with an optimal soil moisture content usually around 12% of soil weight (Kesselmeier et
28 al., 1999; Liu et al., 2010a; Van Diest and Kesselmeier, 2008). As noted in some of these
29 studies, such a bell-shape response is indicative of reactional and diffusional limitations at
30 low and high soil moisture contents, respectively. Using our steady-state formulation for

1 | shallow soils (Eq. (16b)) we were able to reproduce the soil moisture response observed
2 | experimentally (Fig. 9-12). We also found that the observed asymmetric response to soil
3 | moisture was best captured by the soil diffusivity model of Moldrup et al. (2003) or
4 | Millington and Quirk (1961) and showed that the optimum soil moisture could be related to
5 | soil porosity: $\theta_{opt} = 0.3\phi/1.3$ for MQ61 and $\theta_{opt} = 2\phi/7$ for Mol03r. Using our model we were
6 | also able to explain the response of OCS uptake to soil weight (i.e. soil thickness) observed by
7 | Kesselmeier et al. (1999) (Fig. 5).

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8 | We also tested our model against observations of the temperature response of V_d . Empirical
9 | studies showed that, for a given soil, the maximum OCS uptake rate was modulated by
10 | incubation temperature, with an optimal temperature ranging from 15°C to 35°C (Kesselmeier
11 | et al., 1999; Liu et al., 2010a; Van Diest and Kesselmeier, 2008). This temperature response
12 | was interpreted as an enzymatically catalysed process, governed by soil micro-organisms' CA
13 | activity (Kesselmeier et al., 1999; Liu et al., 2010a; Van Diest and Kesselmeier, 2008). To
14 | reproduce this response of V_d to incubation temperature using our steady-state model, we had
15 | to manually adjust f_{CA} for each incubation temperature. We will argue here that using
16 | different f_{CA} values on the same soil is justified given the way measurements were performed.
17 | Van Diest and Kesselmeier (2008) wanted to characterise the V_d response to soil drying at a
18 | set temperature and for this, they saturated a soil sample with water and acclimated it to a
19 | given temperature (between 5°C and 35°C), they then recorded the OCS exchange
20 | immediately and continued to measure until the soil was completely dry, which usually lasted
21 | 1 to 2 days. The same soil sample, or a different one from the same geographical location,
22 | was then re-watered and re-acclimated to a different temperature and another cycle of
23 | measurements started. Sometimes several months separated measurements at two different
24 | temperatures but storage time (at 5°C) did not seem to affect the soil CA activity
25 | (measurements on the same soil and incubation temperature were reproducible). On the other
26 | hand incubation temperature clearly differ and, at least for the German soil, samples were not
27 | collected all at the same season. This means that, for a given soil origin, the microbial
28 | community was experiencing different environmental conditions and history between each
29 | drying curve. Thus, the size and diversity of the microbial population were likely different for
30 | each incubation temperature, thus justifying the use of different enhancement factors at each
31 | temperature. Interestingly f_{CA} tends to increase with incubation temperature, as we would
32 | expect for the microbial biomass. Only the German soil has a higher f_{CA} at low temperature

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1 (15°C) and this corresponds to a soil sampled at a different period (March) than the other two
2 incubation temperatures (June).

3 Following this argument it seems that the optimum temperatures observed by Van Diest and
4 Kesselmeier (2008) for different soil types are not a good proxy for the optimal temperature
5 of CA activity ($T_{opt,CA}$). Using our model we already showed that the optimum temperature
6 for V_d ($T_{opt,Vd}$) was different from $T_{opt,CA}$, at least for deep soils (Fig. 4). A closer inspection of
7 the results shown in Figs. 9-12 also show that the adjusted f_{CA} values closely follow the
8 patterns of the maximum V_d at θ_{opt} (see right panels in Figs. 9-12). This means that the
9 optimum temperature observed by Van Diest and Kesselmeier (2008) is a better indicator of
10 maximum f_{CA} or equivalently maximum CA concentration (assuming all the CAs in the soil
11 have similar k_{cat}/K_M as the pea extracts measured by Protoschill-Krebs et al. (1996). This
12 could explain why the optimum for the German soil was so low (around 15°C), i.e., lower
13 than expected for $T_{opt,CA}$. The presence of a competing enzymatic process, such as OCS
14 emission, could have explained this low $T_{opt,Vd}$ value (Fig. 7) but it is more likely that the soil
15 sample studied at 15°C contained more CA than those used for other incubation temperatures.
16 Measurements on microbial biomass could have helped confirm this hypothesis but were
17 unfortunately not made.

18 Because f_{CA} is a fitting parameter in our model, it is important to see if the values that we
19 derived for the different soils are realistic. There are two ways to do so. First, we have a
20 relatively good idea of how much CA is needed inside the cytosol of leaf mesophyll cells or
21 in unicellular algae, which is of the order of 100 μM (Tholen and Zhu, 2011). Assuming this
22 CA concentration value is also applicable to microbial cells, and using estimates of the soil
23 microbial population size we can convert this physiological CA concentration ($[CA]_{in}$) into a
24 CA concentration in the soil matrix ($[CA]$): $[CA]\theta = [CA]_{in}\rho_{mic}$, where ρ_{mic} ($\text{m}^3 \text{ microbes m}^{-3}$
25 soil) denotes the volumetric microbial content of the soil. Using a typical microbial
26 population size of $3 \cdot 10^9 \text{ cm}^{-3}$ and an average cell size of $1 \mu\text{m}^3$ (Wingate et al., 2009), we
27 obtain a microbial content of $\rho_{mic} = 0.003 \text{ m}^3 \text{ m}^{-3}$ and a soil CA content of about 1000 nM (we
28 used $\theta = 0.3$). Using this value of $[CA]$ and the k_{cat}/K_M value for OCS ($2.39 \text{ s}^{-1} \mu\text{M}^{-1}$ at 20°C
29 and $pH_{in} 8.2$) this leads to an f_{CA} value of about 127000 for OCS, which is in the same order
30 of magnitude as those found for the different soils in this study (between 21600 and 336000,
31 with a median value at 66000). From this crude calculation we can conclude that our f_{CA}
32 estimates are physiologically meaningful.

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1 Another way of checking if our f_{CA} estimates are meaningful is to convert them into f_{CA}
2 equivalents for soil CO₂ isotope fluxes, for which we have a better idea of what the expected
3 values should be (Seibt et al., 2006; Wingate et al., 2009; 2010; 2008). The k_{cat}/K_M value for
4 CO₂ in pea extracts has been measured for a pH range of 6-9 and at 25°C (Bjorkbacka et al.,
5 1999). The pH response described a similar pattern as the one found for *Arabidopsis* by
6 Rowlett et al. (2002) (Fig. 2) with a pK_a of 7.1. Using $x_{CA}(T)$ and $y_{CA}(pH_{in})$ to convert those
7 values to pH_{in} 8.2 and 20°C, we obtain a k_{cat}/K_M value for CO₂ of 50 s⁻¹ μM⁻¹, i.e., about 20
8 times greater than the k_{cat}/K_M for OCS. Given the difference in uncatalysed hydration rates
9 between the two gas species (12000 μs⁻¹ for CO₂ and 21.5 μs⁻¹ for OCS at 25°C and $pH = 4.5$)
10 this means that at equal soil CA concentration, the f_{CA} for CO₂ should be about 30 times
11 smaller than that derived for OCS. This corresponds to a median f_{CA} value of 2200 for CO₂,
12 | i.e., at the higher end of values observed in different soils (Wingate et al., 2009).^v

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Deleted: We can therefore draw the same conclusion as above, which is that the f_{CA} values obtained here for OCS are compatible with CO₂ studies, but may be overestimated, by a factor two at least.

13 The calculation above considers only β-CA kinetic parameters to relate the soil CA
14 enhancement factor for OCS to the f_{CA} for CO₂. However other enzymes can catalyse OCS
15 hydrolysis and not have a strong affinity to CO₂. For example Smeulders et al. found a carbon
16 disulphide hydrolase from an acido-thermophilic archaeon that was very efficient at
17 catalysing OCS hydrolysis but did not have CO₂ as one of its substrates (Smeulders et al.,
18 | 2012). More recently, Ogawa et al. (2013) found in *Thiobacillus thioparus*, a sulfur-oxidizing
19 bacterium widely distributed in soils and freshwaters, an enzyme that shared a high similarity
20 with β-CAs and was able to catalyse OCS hydrolysis with a similar efficiency ($K_M = 60\mu\text{M}$,
21 $k_{cat} = 58\text{ s}^{-1}$ at pH 8.5 and 30°C) but whose CO₂ hydration activity was 3-4 orders of
22 magnitude smaller than that of β-CAs. For this reason they called this enzyme carbonyl
23 sulphide hydrolase (COSase). The carbon disulphide hydrolase identified by Smeulders et al.
24 (2012) may only be present in extremely acidic environments such as volcanic solfataras, but
25 the COSase found in *T. thioparus* may be more ubiquitous in soils. If this was the case this
26 would imply that the f_{CA} ratio of OCS to CO₂ is not unique and could, in some soils, be higher
27 than the same ratio derived from β-CA kinetic parameters only. This could partly explain the
28 highest f_{CA} values obtained here for OCS.

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29 | Higher-than-expected values of f_{CA} could also be explained by the fact that we neglected
30 dispersion fluxes when we compared the model against observations. Indeed dispersion fluxes
31 would enhance OCS diffusion (Eq. (15)) and result in larger deposition velocities (Eq. (16b))
32 for the same level of CA concentration. Results from Maier et al. (2012) show that the

1 diffusivity D could be easily doubled by the presence of turbulence above the soil surface,
2 which would be equivalent to a doubling of k (D and k appear as a product in the sink term of
3 Eq. (16b)). This means that, if dispersion occurred in the experiments (a possibility that we
4 cannot rule out), the f_{CA} values that we derived from them may be overestimated by a factor
5 two, bringing them closer to values compatible with CO_2 studies.

6 To conclude, the f_{CA} values derived here for OCS seem compatible with physiological CA
7 contents and also compatible with f_{CA} values reported in CO_2 isotope studies, given possible
8 affinity differences of some CAs towards OCS and CO_2 and possible artefacts of mechanical
9 dispersion caused by fans in some laboratory experiments.

10 4.2 Can we transpose laboratory data to field conditions?

11 Response curves of OCS deposition rates to soil moisture and temperature have been derived
12 from laboratory experiments similar to those presented here (Kesselmeier et al., 1999) and the
13 derived equations have been used to estimate the OCS uptake by soils at the global scale
14 (Kettle et al., 2002). Also Van Diest and Kesselmeier have proposed that the optimum
15 (gravimetric) soil moisture content for OCS deposition was around 0.12 g g^{-1} , independently
16 of soil type (Van Diest and Kesselmeier, 2008). Our model allows us to verify if such
17 simplification or extrapolation is justified, on a theoretical point of view at least. For semi-
18 infinite soil columns we showed that θ_{opt} varied with soil porosity from 0.23ϕ to 0.5ϕ ,
19 depending on the soil diffusivity model used. Assuming soil bulk density is $2.66(1 - \phi)$, this
20 leads to gravimetric soil moisture contents of between $0.61\phi(1 - \phi)$ and $1.33\phi(1 - \phi)$, which is
21 clearly dependent on soil type. Also from Fig. 4 we can see that the general shape of the soil
22 moisture response and θ_{opt} strongly depend on the exact soil depth used during the
23 experiment, at least for soil less than 3cm thick (or more if the CA activity is lower). For
24 thicker soils the deepest soil layers do not contribute to the exchange and we reach the
25 saturation point with soil weight shown in Fig. 5. However in both aforementioned studies
26 (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008), care was taken not to reach the
27 saturation point (using soil weights of about 80g). From our model results we can see that this
28 would lead to an overestimation of θ_{opt} and an overall underestimation of V_d (Fig. 4). Thus
29 based on this observation we would recommend to use soil depths of at least 5-6 cm in future
30 studies so that the results can be more readily extrapolated to field conditions.

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1 Another difficulty when we want to extrapolate laboratory data to the natural environment is
2 that soil disturbance prior to the experiment (sieving, repacking...) strongly modifies the gas
3 diffusivity properties of the soil. Our results show that OCS deposition rates can be extremely
4 sensitive to the choice of the diffusivity model used (**Fig. 3**). In highly compacted, highly
5 aggregated soils the gas diffusivity response to soil moisture content can even become bi-
6 modal (Deepagoda et al., 2011) that would certainly have a strong impact on the V_d - θ
7 relationship. Even without such a complication our results suggest that deposition rate
8 measurements on repacked soils may not be representative of field conditions because the soil
9 treatment would modify the diffusivity properties of the soil and alter the soil moisture
10 response of the OCS deposition rate. On the other hand applying our model (Eq. 17, for semi-
11 infinite soil column) with a soil diffusivity formulation applicable to undisturbed soils (i.e.
12 Mol03u or Deepa11, see Table 1) should work for interpreting field measurements.

13 5 Perspectives

14 Our model so far has been tested under steady state conditions and with fairly uniform soil
15 properties (temperature, moisture, pH ...). In the natural environment such conditions are the
16 exception rather than the rule. The model has not been tested either on true temperature
17 response curves as happens in nature with strong diurnal variations of temperature at nearly
18 constant soil moisture content. Indeed data from Van Diest and Kesselmeier (2008) have been
19 collected at constant incubation temperatures and are therefore more indicative of the range of
20 f_{CA} and V_d values one would expect over a growing season for a given soil type. Suprisingly
21 we could not find published laboratory measurements of V_d where soil temperature was varied
22 diurnally.

23 Another point that should be addressed in future studies is the characterisation of the soil
24 microbial community size and structure, that should be done systematically with the soil OCS
25 deposition measurements. This would allow us to test whether our upscaling of CA activity to
26 the soil level (Eq. (11a)) is correct or not, and compatible with physiologically realistic CA
27 contents in soil microbes. Our results so far suggest that the CA contents that we derive seem
28 physiologically meaningful and also compatible with CO₂ isotope studies, given the
29 uncertainties in the k_{cat}/K_M values of different CAs for the two substrates and in the
30 diffusivity model formulation for different experimental setup (see above). Concurrent
31 microbial data on the soil samples could have greatly constrained our downscaling exercise
32 and lead to a more precise picture of possible mismatch between our model and the

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1 observations. When combined with both OCS and CO₂ isotope gas exchange measurements,
2 it could also help identify the microbial communities that are more prone to express specific
3 CAs which favor OCS uptake such as the COSase found in *T. thioparus*.

4 Finally our study mostly focused on the temperature response of the OCS production term,
5 but there is a growing body of evidence that other environmental variables trigger OCS
6 production from soils, independently of temperature. In oxic soils, light-induced OCS
7 emissions have been observed (Whelan and Rhew, 2015) whereas in anoxic soils, redox
8 potential seems to be the main trigger (Devai and Delaune, 1995). The mechanisms leading to
9 these OCS emission rates should be better understood before we can incorporate them into a
10 modelling framework and estimate OCS fluxes at large scales. For this reason we strongly
11 suggest to systematically report measurements of light and soil redox potential (and/or S
12 speciation), in future soil OCS flux studies.

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Deleted: Interestingly one study on boreal acidic soils reported higher rates of OCS uptake in water-logged plots compared to unsaturated plots {Simmons:1999tf}. This result seems to contradict most studies on anoxic soils that usually report OCS emissions {e.g., Hines:1992ug, Mello:1994wo, Fried:1993vq, Whelan:2013fj}, but our model may help explain this apparent contradiction. Indeed, provided that the saturation of the soil in the study by Simmons et al. {Simmons:1999tf} was only recent (the experimental campaign lasted only 22 days and dry and wet conditions had been observed over that period), water logging could have induced a temporary rise in *pH*, thus enhancing CA activity (**Fig. 2**) and OCS uptake (**Fig. 8**). Had the water logging started several weeks before, the *pH* would have risen even further and may have reached more neutral conditions, but anoxic conditions would have also lowered the redox potential, leading to strong emissions of OCS, as observed in most other studies on anoxic soils. Our model can qualitatively explain this result and more generally how acidic soils can change from a sink to a source of OCS during water logging. It would be important in future studies to test whether the model is also good at describing this dynamic pattern quantitatively. This would open new possibilities to estimate OCS fluxes at large scales from both oxic and anoxic regions

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17 reviewers for their constructive comments on an earlier version of this manuscript.
18

Appendix A

Here we derive an equation for the catalysed OCS sink term (S_{cat}) that accounts for the co-limitation between the enzymatic reaction that takes place inside the micro-organisms (at pH_{in} and with an OCS concentration C_{in}) and the OCS diffusion through the cell wall of the microbes. In this situation, Eq. 9 needs to be re-written as:

$$S_{\text{cat}} = \theta k_{\text{cat}} [CA] \frac{BC_{\text{in}}}{K_m + BC_{\text{in}}} \approx \frac{k_{\text{cat}}}{K_m} [CA] B\theta C_{\text{in}} \quad (\text{A1})$$

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The OCS uptake can also be written in terms of transport across the cell wall and the plasma membrane of the microbial cell (see for example Tholen and Zhu (2011), their Eqs. 8-9):

$$S_{\text{cat}} = G_{\text{wall}} V_{\text{mol}} (C - C_{\text{in}}) S_{\text{wall}} \quad (\text{A2})$$

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where G_{wall} ($\text{mol}(\text{air}) \text{m}^{-2} \text{wall s}^{-1}$) is the cell wall and plasma membrane aggregated conductance to OCS, V_{mol} ($\text{m}^3 \text{air mol}(\text{air})^{-1}$) is the molar volume of air and S_{wall} ($\text{m}^2 \text{wall m}^{-3} \text{soil}$) is the microbial cell wall surface density in the soil. Combining Eqs. A1-2 we can eliminate C_{in} and express S as a function of C only:

$$S_{\text{cat}} = \frac{B\theta k_{\text{cat}} [CA]}{K_m + B\theta k_{\text{cat}} [CA] r_{\text{wall}}} C \quad (\text{A3})$$

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where we defined $1/r_{\text{wall}} = G_{\text{wall}} V_{\text{mol}} S_{\text{wall}}$. Equation A3 simplifies to Eq. 9 under the condition that:

$$B\theta k_{\text{cat}} [CA] r_{\text{wall}} \ll K_m \quad (\text{A4})$$

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Accounting for the dilution of CA in soils, i.e. $[CA]\theta = [CA]_{\text{in}} \rho_{\text{mic}}$, where ρ_{mic} ($\text{m}^3 \text{microbes m}^{-3} \text{soil}$) is the volumetric density of the soil microbes (that can be expressed as $n_{\text{mic}} V_0$ in which n_{mic} is the number of microbes per soil volume and V_0 the volume of a single microbial cell), the condition (A4) also writes:

$$\frac{Bk_{\text{cat}} [CA]_{\text{in}} V_0}{G_{\text{wall}} V_{\text{mol}} S_{\text{wall0}}} \ll K_m \quad (\text{A5})$$

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where S_{wall0} is the single cell wall surface area. If the microbes are spherical with diameter D_0 , we have $V_0/S_{\text{wall0}} = D_0/6$. With typical values of $D_0 = 1 \mu\text{m}$, $B = 0.5 \text{m}^3 \text{m}^{-3}$, $V_{\text{mol}} = 0.025 \text{m}^3 \text{mol}^{-1}$, $k_{\text{cat}} = 93 \text{s}^{-1}$ and $G_{\text{wall}} = 0.14 \text{mol m}^{-2} \text{s}^{-1}$ (i.e. 0.35cm s^{-1} , see the note under Table 2 in Evans et al. (2009)) the left-hand side of Eq. (A5) equals $0.22 \mu\text{M}$, which is

1 much smaller than K_m (39 μM at 20°C, Protoschill-Krebs et al., 1996). In this situation the
2 transport of OCS through the membrane is not a co-limiting factor to the OCS uptake (for
3 CO_2 it is less true because the left-hand side of Eq. A5 is around 0.57 mM for a K_m around
4 3 mM). Note also that CA is not spread in the entire cell volume so that the cell volume
5 appearing in Eq. A5 should be somewhat smaller. Although there are large uncertainties on
6 the value of cytoplasmic CA concentration or k_{cat}/K_M , our derivation indicates that these
7 parameter would need to be much higher (by two orders of magnitude) to justify the need to
8 account for the transport of OCS into the cell during microbial consumption. In this study we
9 assumed Eq. 9 to be valid, bearing in mind that the CA concentration we derived from it
10 remains sensitive to the k_{cat}/K_M value we use.

11

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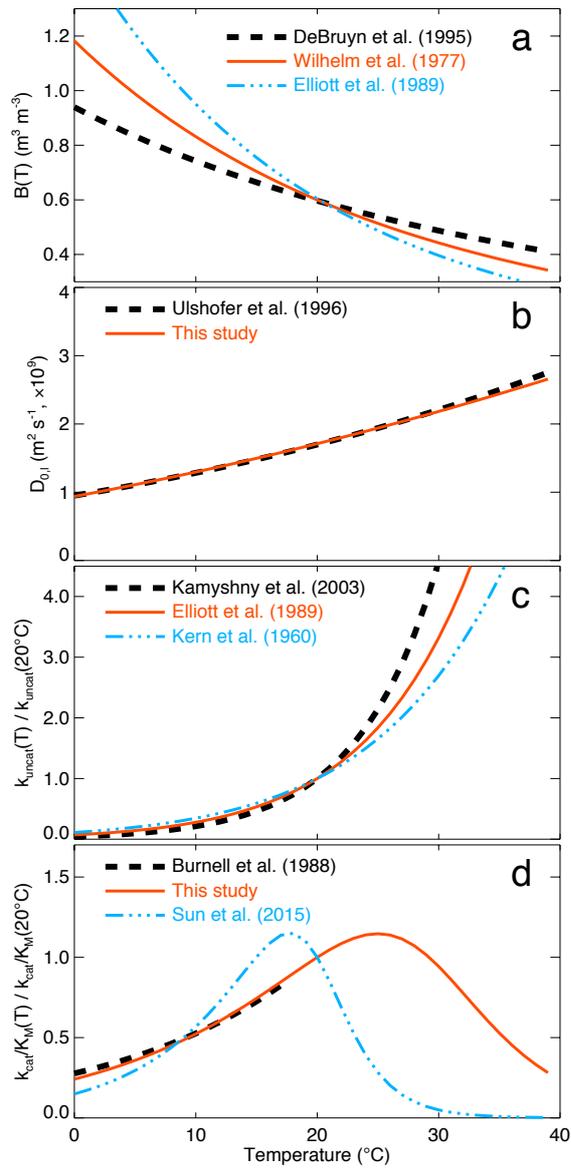
<u>Notation</u>	<u>τ_a</u>	<u>τ_l</u>	<u>Soil treatment</u>	<u>Reference</u>
<u>Pen40</u>	<u>0.66</u>	<u>0.66</u>	<u>n/a</u>	<u>(Penman, 1940)</u>
<u>MQ61</u>	<u>$\epsilon_a^{7/3}/\phi^2$</u>	<u>$\theta^{7/3}/\phi^2$</u>	<u>n/a</u>	<u>(Millington and Quirk, 1961)</u>
<u>Mol03r</u>	<u>$\epsilon_a^{3/2}/\phi$</u>	<u>$\theta^{b/3}/\phi^{b/3-1}$</u>	<u>repacked</u>	<u>(Moldrup et al., 2003)</u>
<u>Mol03u</u>	<u>$\epsilon_a^{1+3/b}/\phi^{3/b}$</u>	<u>$\theta^{b/3}/\phi^{b/3-1}$</u>	<u>undisturbed</u>	<u>(Moldrup et al., 2003)</u>
<u>Deepa11</u>	<u>$[0.2(\epsilon_a/\phi)^2 + 0.004]/\phi$</u>	<u>n/a</u>	<u>undisturbed</u>	<u>(Deepagoda et al., 2011)</u>

1 Table 1. Summary of tortuosity factor formulations for gaseous (τ_a) and liquid (τ_l) diffusion
2 from the literature. ϵ_a : air porosity; ϕ : total porosity; θ : soil water content; b : pore-size
3 distribution parameter; n/a: data not available.

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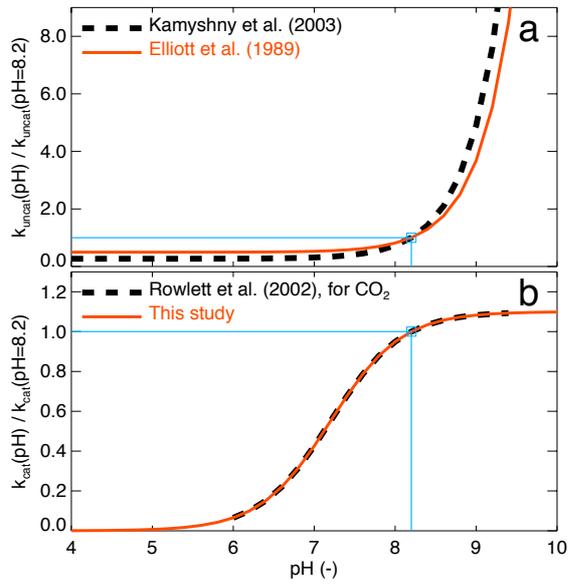
1 Figure 1. Temperature response of (a) the OCS solubility in water, (b) the OCS diffusivity in
 2 liquid water and (c) the uncatalysed and (d) CA-catalysed OCS hydrolysis rates. Red lines
 3 indicate the parameterisation used for this study.

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1 | Figure 2. Response of the normalised (a) uncatalysed and (b) CA-catalysed OCS hydrolysis
2 | rates to changes in soil *pH*. Red lines indicate the parameterisation used for this study. The
3 | blue lines indicate the normalisation at *pH* = 8.2.
4

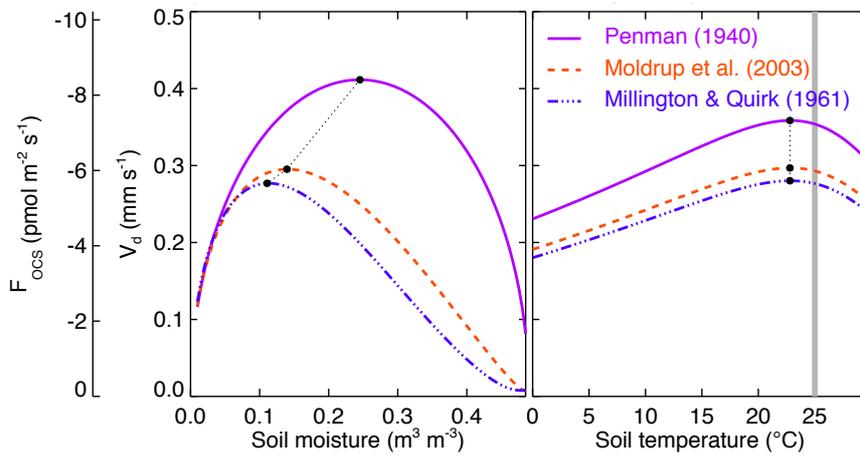


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1 | Figure 3. Sensitivity of the modelled OCS flux (F_{OCS}) and deposition velocity (V_d) to the
 2 | formulation used to describe gaseous and solute diffusion. The soil moisture and temperature
 3 | response curves shown here were obtained assuming no source term, a soil depth and pH of
 4 | 1m and 7.2 respectively and a CA enhancement factor for OCS hydrolysis of 30000. Closed
 5 | circles indicate the temperature or soil moisture optimum of each response curve and the grey
 6 | thick line in **right** panel indicates the set optimal temperature for CA activity (25°C in this
 7 | case).

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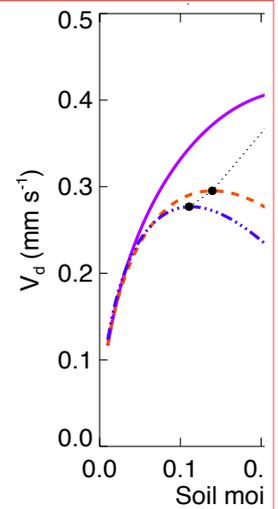


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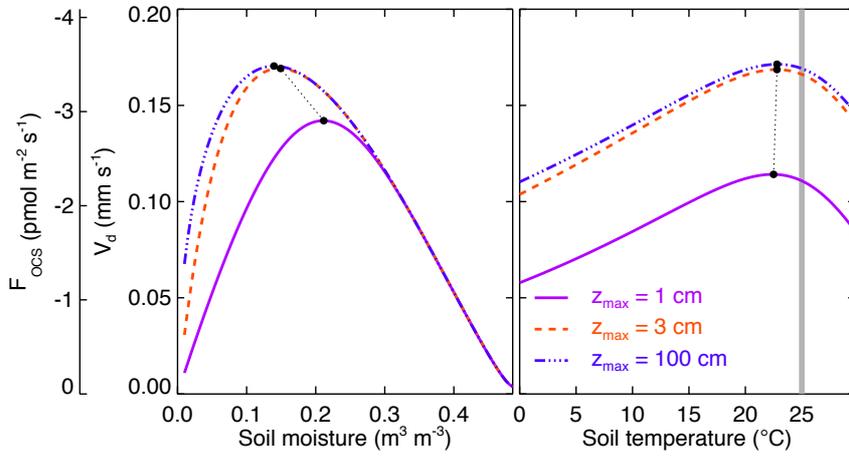


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1 | Figure 4. Sensitivity of the modelled OCS flux (F_{OCS}) and deposition velocity (V_d) to soil
 2 | column depth. The soil moisture and temperature response curves shown here were obtained
 3 | using the diffusivity model of Moldrup et al. (2003) and assuming no source term, a soil pH
 4 | of 7.2 and a CA enhancement factor for OCS hydrolysis of ~~10000~~. Closed circles indicate the
 5 | temperature or soil moisture optimum of each response curve and the grey thick line in right
 6 | panel indicates the set optimal temperature for CA activity (25°C in this case).

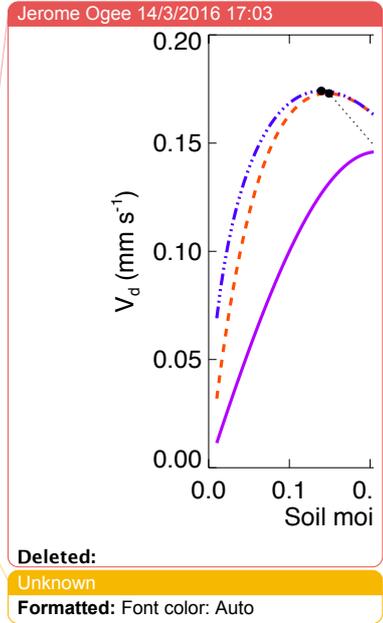
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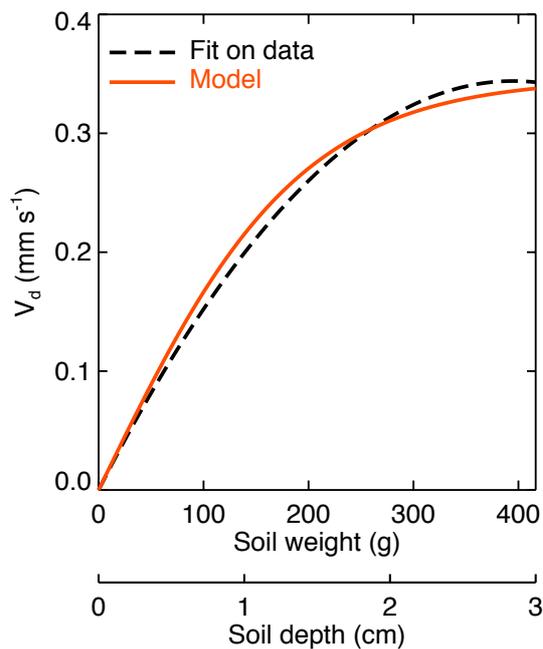
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1 Figure 5. Modelled (solid line) and observed (dotted line) response of the modelled OCS
2 deposition velocity (V_d) to soil column depth. Soil column depth is also converted into soil
3 weight assuming a soil surface area of 165.1 cm² and a soil bulk density and pH of 0.85 kg m³
4 and 7.2, respectively, to be comparable with the experimental setup used in Kesselmeier et al.
5 (1999) to derive the observed response curve. Model results shown here were obtained using
6 the diffusivity model of Moldrup et al. (2003) and assuming an enhancement factor and an
7 optimum temperature for OCS hydrolysis of 26000 and 25°C, respectively and no source
8 term. Soil water content and temperature were also set to 11% weight and 17°C, respectively,
9 to be comparable with the experimental data, while the fit on observed uptake rates that was
10 originally reported were converted into deposition velocities assuming a constant mixing ratio
11 of 600 ppt (Kesselmeier et al., 1999).

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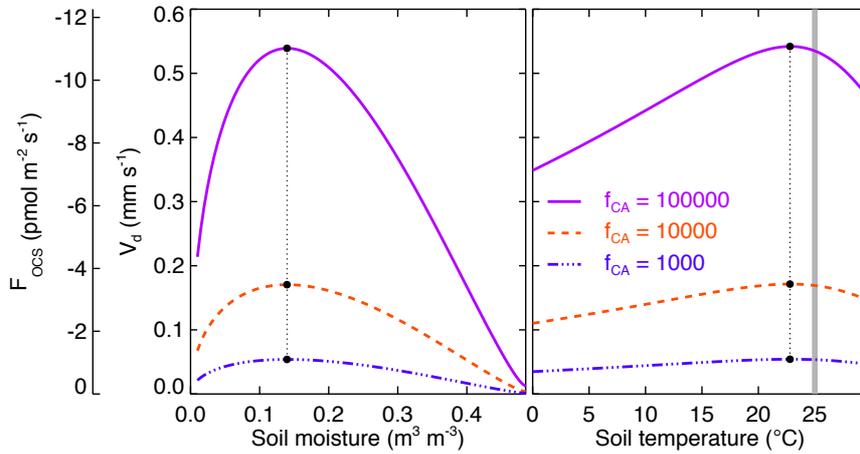
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1 | Figure 6. Sensitivity of the modelled OCS flux (F_{OCS}) and deposition velocity (V_d) to soil CA
 2 | activity. The soil moisture and temperature response curves shown here were obtained using
 3 | the diffusivity model of Moldrup et al. (2003) and assuming no source term, a soil pH of 7.2
 4 | and a soil depth of 1 m. Closed circles indicate the temperature or soil moisture optimum of
 5 | each response curve and the grey thick line in right panel indicates the set optimal temperature
 6 | for CA activity (25°C in this case).

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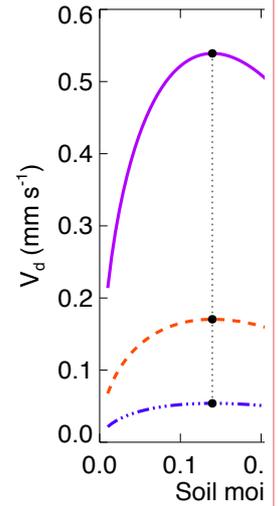


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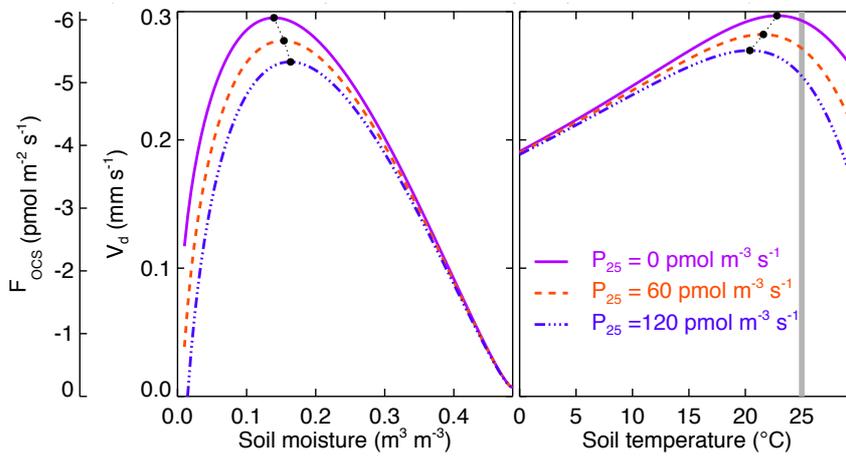


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1 | Figure 7. Sensitivity of the modelled OCS flux (F_{OCS}) and deposition velocity (V_d) to soil
 2 | OCS emission rate. The soil moisture and temperature response curves shown here were
 3 | obtained using the diffusivity model of Moldrup et al. (2003) and assuming a CA
 4 | enhancement factor of 30000, a soil pH of 7.2 and a soil depth of 1 m. OCS source is assumed
 5 | to occur only in the top 5 cm. Closed circles indicate the temperature or soil moisture optimum
 6 | of each response curve and the grey thick line in **right** panel indicates the set optimal
 7 | temperature for CA activity (25°C in this case).

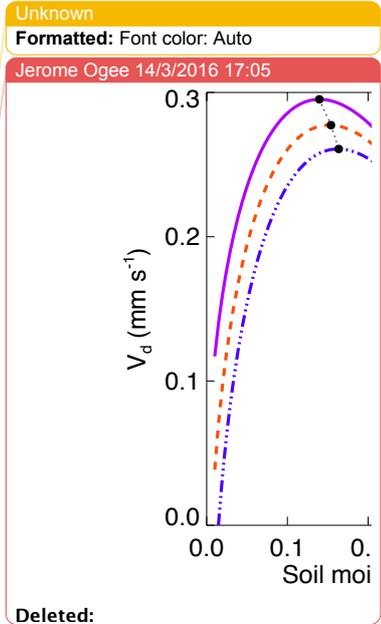
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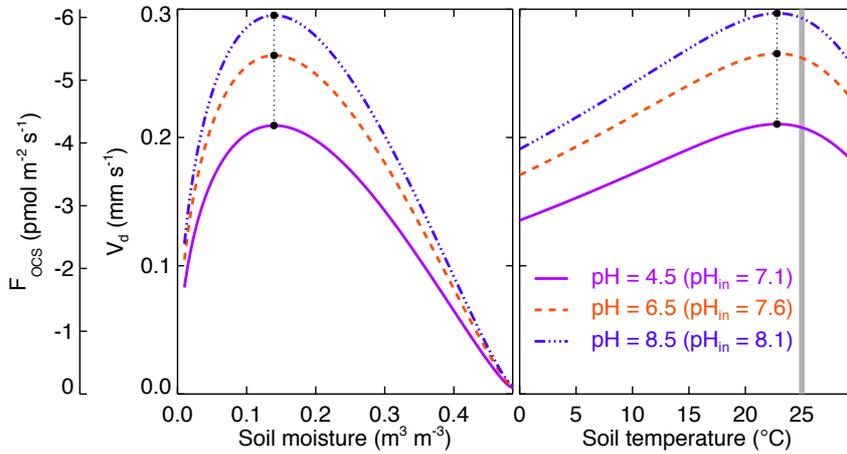


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1 | Figure 8. Sensitivity of the modelled OCS flux (F_{OCS}) and deposition velocity (V_d) to soil pH.
 2 | The soil moisture and temperature response curves shown here were obtained using the
 3 | diffusivity model of Moldrup et al. (2003) and assuming no source term, a CA concentration
 4 | in the soil of 330nM and a soil depth of 1 m. Closed circles indicate the temperature or soil
 5 | moisture optimum of each response curve and the grey thick line in **right** panel indicates the
 6 | set optimal temperature for CA activity (25°C in this case).

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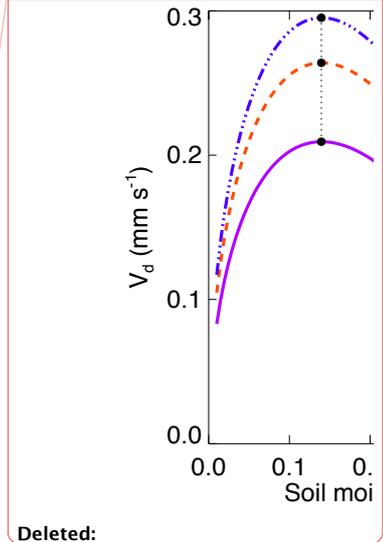


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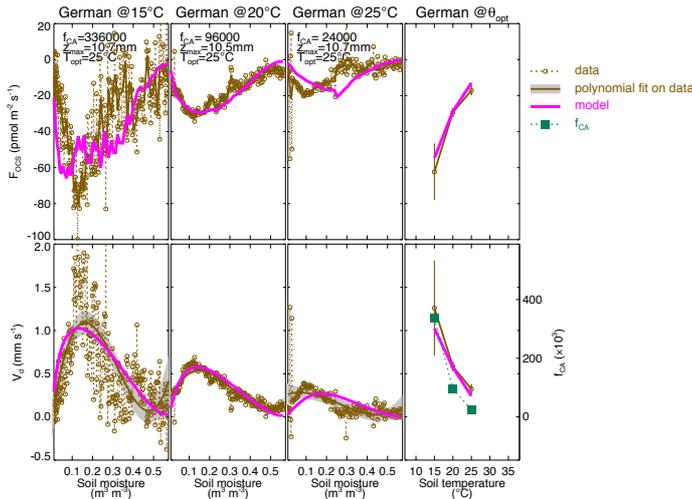


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1 | Figure 9. Observed and modelled soil-air OCS flux (F_{OCS}) and deposition velocity (V_d) during
 2 | soil drying at different incubation temperatures (indicated above each panel) and their value at
 3 | a soil moisture content $W_{opt} = 0.12 \text{ m}^3 \text{ m}^{-3}$ (far right panels). The soil moisture and
 4 | temperature response curves shown here were recalculated from data of Van_Diest and
 5 | Kesselmeier (2008) (open circles and brown line) or computed with our model (thick pink
 6 | line) using the diffusivity model of Moldrup et al. (2003). For each incubation temperature, a
 7 | different set of model parameters (f_{CA} , z_{max} , T_{opt}) was used as indicated in each panel. The data
 8 | shown here are representative of an agricultural soil near Mainz in Germany (soil weight is
 9 | 200g).

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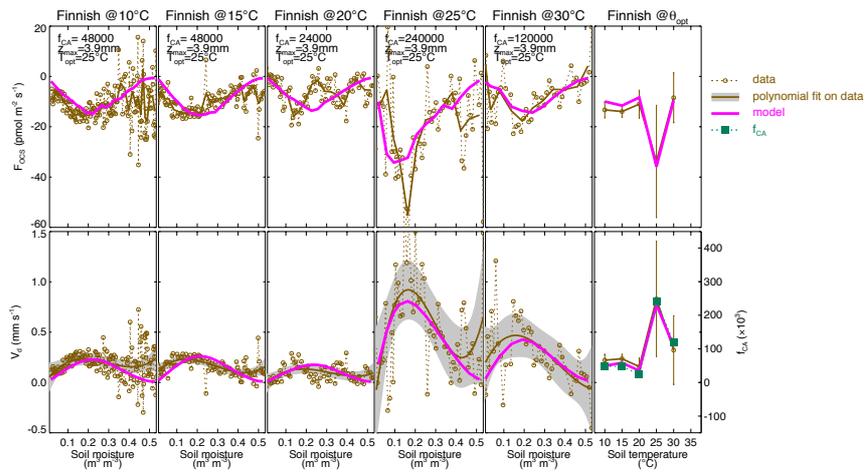


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1 Figure 10. Same as Fig. 9 but for an agricultural soil near Hyytiala in Finland (soil weight is
2 80g).

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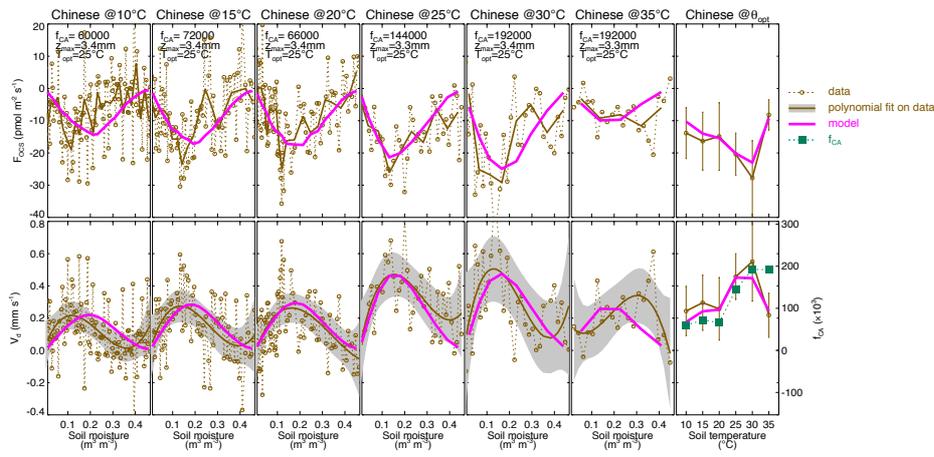


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1 Figure 11. Same as Fig. 9 but for an agricultural soil from north-eastern China (soil weight is
2 80g).

3



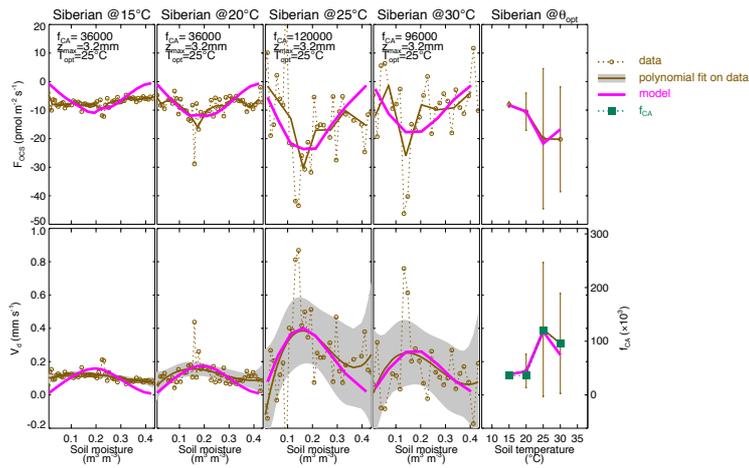
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1 Figure 12. Same as Fig. 9 but for an agricultural soil from Siberia (soil weight is 80g).

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