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Interactive comment on "Soil-atmosphere exchange of carbonyl sulfide in Mediterranean citrus orchard" *by* F. Yang et al.

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Dear Dr. Yang and others,

This study presents a good, field-based approach to characterizing OCS soil fluxes. Observations of OCS in the soil profile will do well to inform the process-based OCS soil modeling that has been framed in the past (Ogée et al., 2015; Sun et al., 2015).

At the same time, I have two methodological concerns about the profile measurements (L118-123). One is that decabon tubing might be unsuitable for "static" measurements. In other words, you might get some production or absorption from the tubing itself when put in contact with an air sample for long periods. For applications where the tubing is flushed, it appears to be fine. Within our own QCL, we replaced the decabon tubing

for static applications, where an air sample had to be contained within the sample cell and associated tubing for several minutes. Roisin Commane also reported similar issues. One possibility is that the decabon tubing you used was of a different age or a different formulation of plastic and doesn't have these problems. Reporting a simple blank experiment, which you've probably already performed, would clear things up. Perhaps trapping a sample of known OCS concentration in a few coils of tubing, waiting a day, then measuring it again, will show whatever uncertainty might be introduced by using this material.

The second concern I have is one about drawing air samples out of a soil profile. Unless a small volume (e.g. a stainless steel cup with a screen on the bottom) is buried at each depth, there is not that much volume of air to draw out. The methods suggest 400 mL/min for 5 min at each depth, with repeated measurements every 40 minutes for 5 total measurements at each depth. It's difficult to tell what is actually being sampled here: the soil depths start at 2.5 cm. If we think of the air as being drawn from a sphere around the sampling point, it seems like each 2L sample will end up drawing ambient air from the above-soil atmosphere. So, essentially you end up looking at ambient air that has been very recently drawn through different soil volumes. Is this impression accurate?

The introduction needs some touching up to be more useful for the reader. There is some vagueness with the wording and the literature reviewed could be better situated. The non-leaf fluxes are not "unknown" (L42) but poorly characterized. The word "significant" (L43, L47, L160, L170) is vague unless a level of significance is defined, as in L184 and L246.

The narrative presented regarding the changing ideas around OCS soil fluxes starting on L45 is slightly misleading: "exchanges were often considered small compared to plant uptake". The Whelan (2013) paper cited there showed a huge OCS emission from wetland soils that far exceeded any plant uptake. Most of the first work on OCS exchange was from wetlands, where large emissions were considered worthy of study and relatively easier to measure. At any rate, I'm providing a perspective here to help clarify your own structure, without expecting to include all or even any of this in your introduction. There are many studies that have furthered our understanding of OCS soil exchange. For your agricultural study site, you could focus the discussion on the curious problem of high OCS production in agriculturally managed soils. The progression of our understanding of soil OCS exchange moves forward like this:

(1) At first, wetlands are considered a huge source of OCS, though most of the data collected from pre-1992 have methodological problems detailed in (Castro and Galloway, 1991). OCS production is linked to redox potential. Our set of valid wetlands measurements to date are summarized in Whelan et al. (2018) Figure 4.

(2) Kesselmeier et al. (1999) performs the first thorough set of measurements on a single, oxic, agricultural soil and finds only OCS uptake with a soil moisture and temperature optimum. Adding a carbonic anhydrase inhibitor reduced uptake. This study produced a model of soil OCS exchange with a maximum of 10 pmol/m2/sec and suggested that oxic soils are entirely a sink, probably biotic. This idea was revisited with 4 soils in Van Diest and Kesselmeier (2008).

(3) Watts (2000) is a review paper that clarified the thinking of the time: anoxic soils are a large OCS source and oxic soils are a small sink.

(4) This view was challenged in the literature when Maseyk et al. (2014) dragged a QCL laser into a wheat field in Oklahoma. They installed an automated soil chamber which enabled near continuous observations of oxic soil OCS fluxes in the field. I think the Liu paper was a lab-based experiment, and not enough of a big deal was made over how surprising it was for dried rice paddy soil to produce OCS.

(5) The authors of the Maseyk study sent me a soil sample from the Oklahoma site, which I did a series of laboratory incubations with. I used a GC/MS, the more traditional measurement approach, to confirm that the Maseyk findings weren't the result of some sort of methodological problem. We sterilized the soil and subjected it to full spectrum

light, and demonstrated that OCS production was linked to both light and temperature and was probably abiotic (Whelan and Rhew, 2015).

(6) We then got soil samples from many, many sites and repeated the approach with a QCL in Whelan et al. (2016). We showed that air-dried soils in all biomes except deserts exhibit net OCS production, increasing exponentially with temperature. If one subtracts this curve from measurements made at other soil moistures, a curve resembling the initial Kesselmeier (1999) model can be recovered. This showed that abiotic OCS production and biotic consumption were occurring, probably in most soils. No one knew at this point why agricultural soils had such large magnitude emissions with temperature.

(7) Kitz et al., (2017) was the first field study to make conclusions about the effect of light in the field. It should be noted that this was an agriculturally managed soil, not a natural grassland. This is something to keep in mind in your discussion of it (L293/4).

(8) Finally, Kaisermann (2018) showed that nitrogen suppresses OCS consumption, providing a path to solve the mystery of why some agricultural soils appear to have such large OCS production compared to other oxic soils.

The discussion on L283 to L326 could be improved, too. In particular, the role of carbonic anhydrase is introduced multiple times. Also, I invite you to revisit the solubility/hydrolysis figures in Whelan et al., (2018) and calculate the proportion of OCS that might be dissolved then lost to hydrolysis considering your soil moisture content and OCS within-soil concentrations. The mention of the CO and $MgSO_4$ is an interesting idea that I wish we could explore more. While I know that your QCL is capable measuring CO, the ambient standards are tricky to maintain. Was CO measured? Is it possible to pull out any interesting relationships with CO concentration and temperature? Related, were the water vapor measurements mentioned in L79 calibrated? If so, how? It doesn't look like you used these, except indirectly for a water vapor correction on the other two gases.

Section 4.2 focuses on SRU values. Often the point of understanding soil OCS exchange is to "correct" ecosystem level exchange so that a more accurate GPP estimate can be made. A possible motivation for comparing soil OCS exchange and soil CO2 fluxes would be to try and estimate OCS soil fluxes from soil respiration model output. Otherwise, I'm not clear on what we gain by using SRU. In short, more justification is needed for this section.

Overall, this is an important and interesting study. Your ability to predict most OCS soil fluxes using only two variables is a great achievement and also heartening for other modeling efforts. Soil profiles would be very useful to support process-based soil OCS exchange modeling. I look forward to seeing this paper in its final form.

Sincerely,

Mary Whelan

References Castro, M. S. and Galloway, J. N.: A comparison of sulfur-free and ambient air enclosure techniques for measuring the exchange of reduced sulfur gases between soils and the atmosphere, J. Geophys. Res., 96(D8), 15427–15, 1991.

Kaisermann, A., Jones, S., Wohl, S., Ogée, J. and Wingate, L.: Nitrogen Fertilization Reduces the Capacity of Soils to Take up Atmospheric Carbonyl Sulphide, Soil Systems, 2(4), 62, 2018.

Kesselmeier, J., Teusch, N. and Kuhn, U.: Controlling variables for the uptake of atmospheric carbonyl sulfide by soil, J. Geophys. Res., 104(D9), 11577–11584, 1999.

Kitz, F., Gerdel, K., Hammerle, A., Laterza, T., Spielmann, F. M. and Wohlfahrt, G.: In situ soil COS exchange of a temperate mountain grassland under simulated drought, Oecologia, 183(3), 851–860, 2017.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M. and Seibt, U.: Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains, Proc. Natl. Acad. Sci. U. S. A., 111(25), 9064–9069, 2014.

Ogée, J., Sauze, J., Kesselmeier, J., Genty, B., Van Diest, H., Launois, T. and Wingate, L.: A new mechanistic framework to predict OCS fluxes from soils, Biogeosci. Discuss., 12(18), 15687–15736, 2015. Sun, W., Maseyk, K., Lett, C. and Seibt, U.: A soil diffusion–reaction model for surface COS flux: COSSM v1, Geosci. Model Dev., 8(10), 3055–3070, 2015.

Van Diest, H. and Kesselmeier, J.: Soil atmosphere exchange of carbonyl sulfide (COS) regulated by diffusivity depending on water-filled pore space, Biogeosciences, 5(2), 475–483, 2008.

Watts, S. F.: The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, Atmos. Environ., 34(5), 761–779, 2000.

Whelan, M. and Rhew, R.: Carbonyl sulfide produced by abiotic thermal and photodegradation of soil organic matter from wheat field substrate, J. Geophys. Res. Biogeosci., 2014JG002661, 2015.

Whelan, M. E., Min, D.-H. and Rhew, R. C.: Salt marshes as a source of atmospheric carbonyl sulfide, Atmos. Environ., 73, 131–137, 2013.

Whelan, M. E., Hilton, T. W., Berry, J. A., Berkelhammer, M., Desai, A. R. and Campbell, J. E.: Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon uptake, Atmos. Chem. Phys., 16(6), 3711–3726, 2016.

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., Kooijmans, L. M. J., Hilton, T. W., Belviso, S., Peylin, P., Commane, R., Sun, W., Chen, H., Kuai, L., Mammarella, I., Maseyk, K., Berkelhammer, M., Li, K.-F., Yakir, D., Zumkehr, A., Katayama, Y., Ogée, J., Spielmann, F. M., Kitz, F., Rastogi, B., Kesselmeier, J., Marshall, J., Erkkilä, K.-M., Wingate, L., Meredith, L. K., He, W., Bunk, R., Launois, T., Vesala, T., Schmidt, J. A., Fichot, C. G., Seibt, U., Saleska, S., Saltzman, E. S., Montzka, S. A., Berry, J. A. and Campbell, J. E.: Reviews and syntheses: Carbonyl sulfide as a multi-scale tracer for carbon and water cycles, Biogeosciences, 15(12), 3625–3657, 2018.

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