

We would like to thank the two reviewers for their helpful comments on this work. We fully addressed all the reviewer's comments, as described below. We believe the revisions improved the paper, while there is no change in any of the results or conclusions. The track corrected version of the manuscript is attached at the end.

### **Referee #1**

In this study, the authors present soil fluxes of COS from a Mediterranean soil and examined the spatial and temporal variation of those fluxes. The authors find substantial differences in space and time, from emissions to uptake of COS, of which the variability is predominantly driven by soil moisture. Although the English grammar can be improved, this is a well-structured paper with a good discussion of the results. This study is a nice contribution to understanding the COS exchange at different ecosystems, of which the Mediterranean soil was still missing. Below are general and specific comments:

**Response:** Thanks for your kind comments.

#### General comments

1) In the discussion on the different COS soil fluxes at the different sites it would be very helpful to visualise in Fig. 2, 3 and 6 to which site each data point belongs (e.g. use a color per site). This would make it easier to understand how soil moisture varied between the different sites, instead of referring to the numbers in Table 1. Also, the result sections 3.1 and 3.2 could be better readable if the data are discussed while referring to the figures, instead of referring to Table 1. If the data points from the different sites are visualised in the figures I think that Table 1 would be unnecessary (could be an appendix?), as all the information is then presented in the figures.

**Response:** As suggested, we now both refer to the Figures, and marked the points by site. Since Table 1 contain additional data and is cited many times throughout other sections we also left Table 1 in the main text.

2) The discussion focusses a lot on the variability of SRU, and I miss some statements on the importance and application of SRU earlier in the text. Moreover, the difference in size between SRU and LRU is used to discuss the implications of the soil COS fluxes for the use of COS as tracer for GPP, which I do not find very intuitive. Instead, I would compare the size of soil COS fluxes directly with that of ecosystem scale COS exchange, not that of the ratios of COS to CO<sub>2</sub> fluxes. Comparing the size of soil COS exchange with ecosystem COS exchange would also make a very nice link with the results from the parallel study (Yang et al., 2018, Glob. Change Biol.), which has now only been little discussed.

**Response:** Point is well taken. We added a full paragraph in the Introduction about SRU and a paragraph in the Discussion reintroducing the comparison of the soil and fluxes to canopy from Yang et al. 2018.

3) It would also strengthen the message of the paper if the variability of the soil COS uptake in space and time is discussed in light of using COS as tracer for GPP. The soil COS exchange is relatively small compared to the ecosystem COS exchange, but the variability in space and time seems significant and may still complicate the COS tracer method? It would be good to discuss the implications of the variability of the soil COS exchange on the COS tracer method.

**Response:** This is to a significant extent covered by in the previous comment above. We also note that this discussion is provided in detail in the Yang et al 2018 paper where both soil and canopy fluxes are reported, which we don't think should be repeated here. Instead, here we focus on providing more data that could help characterize and forecast the soil component, and validate it.

### **Specific comments**

Abstract

P2L19: what do you mean with “exposed”? Exposed to the sun?

**Response:** Changed so ‘sun-exposed’.

P2L20: “weighted mean uptake values”? Do you mean simply the average? Or what is it weighted by?

**Response:** corrected (‘weighted’ deleted).

Introduction:

P3L60: “In spite of these efforts, more field measurements of soil COS exchange are clearly needed”. It would be good to mention here that also contrasting ecosystems need to be studied. Previous studies have focused on agricultural soils (Maseyk et al., 2014), wetlands (Whelan et al., 2013), boreal forest soils (Sun et al., 2018), grasslands (Kitz et al., 2017), but several ecosystems are understudied, and the Mediterranean soil is a highly needed addition to this.

I like that the soil profiles of COS have now also been measured (for the first time?). It can be mentioned that the soil profile measurements will also be useful for validation of soil models of COS exchange (Sun et al., 2015.).

**Response:** Thank you. The suggested text was added.

Materials and methods:

One of the first questions I got while reading the manuscript was what the role is of photoproduction on the soil COS emissions, and only later I read that dark soil chambers were used. It would be good to mention already in the methods section that the chambers were dark and that photoproduction is not expected to play a role in the results.

**Response:** Done.

It was shown by Kooijmans et al. (2016, AMT), that measurements of COS made with the QCL can be biased at high H<sub>2</sub>O. Were the measurements corrected for the effect of water vapour?

**Response:** Yes, correction was made. This is now indicated in the Method and the

reference cited.

If available, it would be good to add more soil characteristics for this site, like pH and soil porosity.

**Response:** More information added (but we don't have soil porosity data).

Results:

P6L146: What do you mean with “interactions between microsite and season”?

**Response:** The confusing term was deleted.

P7L 178-179: “The response of soil COS fluxes to soil temperature varied among the three measurement sites (Fig. 3)”. This can only be judged from Fig. 3 when the data points in Fig. 3 get marked by site.

**Response:** Marked as suggested.

Discussions:

P11L289: “Temperatures did change over the daily cycle. . .”. Soil temperature?

**Response:** Changed to “Soil temperature”.

P13L334-335: “We use SRU values also to assess the relative importance of the soil COS flux compared with the canopy.”. I don't find this approach very intuitive. Why not simply compare the size of the soil COS flux with that of the ecosystem COS flux?

**Response:** See response to main comment 2.

P13L336: “. . . the absolute value of SRU. . .”. The sign of SRU shifts from negative to positive due to change in sign of the COS flux. So I would say that referring to the absolute value is not appropriate here.

**Response:** Text improves as noted for main comments 2. Note that either positive or negative, a small SRU, below 1, is indicative of “suppressed” COS flux compared to CO<sub>2</sub>, as opposed to LRU where the reverse is true.

P13L337: Reference to the pine forest soil (Sun et al., 2018) is missing.

**Response:** Added.

P13L342: A reference to Whelan et al. 2018 is given with LRU 1.7, which is the average over a large range of plant species. Why not refer to Yang et al. 2018 with LRU = 1.6 (at high light) that is specific for this site?

**Response:** Done.

Conclusions:

P15L393: “we provide constraint, and validation of the closed chamber measurements . . . by the additional gradient approach”. What do you mean with “constraint”? I would just call it validation.

**Response:** Done.

P15L397: This hypothesis on root distribution is introduced only very late in the manuscript, and it would be good to describe the different root distribution for the different sites already in the methods section.

**Response:** In fact, root distribution was briefly discussed in the Discussion, section 4.1. We now added a comment on this also in the Methods. Our data are only on distance from the trees, so we could comment on this “hypothesis” as a logical possibility.

Tables and figures:

Information in Table 1 is presented in Figures 2, 3 and 6, and the results section 3.1 and 3.2 could be better readable if it refers to the figures rather than the table.

**Response:** Done.

Fig. 2, 3 and 6 would benefit from having the data points marked by site.

**Response:** Done.

Figure 4 does not provide more information than Fig. 5, and I would consider removing it.

**Response:** It is true the two figures refer to the same data, but we they are complementary: with Fig. 4 showing the “integrated” response with rather dominant patterns, which is the main message. But Fig. 5 shows that behind these patterns there are interesting variations that could be open for interoperations by the readers. Since these profile data are rather unique, we feel that showing the entire picture is justified.

Technical corrections

-Be consistent throughout the text in the sign convention of fluxes. E.g. uptake of +2.5 pmol m<sup>-2</sup> s<sup>-1</sup>, or a flux of -2.5 pmol m<sup>-2</sup> s<sup>-1</sup>.

**Response:** Done.

-Be consistent with the number of digits of fluxes. E.g. P9L222: -1.0 +/- 0.26 pmol m<sup>-2</sup> s<sup>-1</sup>, which is -1.02 +/- 0.26 pmol m<sup>-2</sup> s<sup>-1</sup> in the abstract.

**Response:** Done.

-CO<sub>2</sub> flux units are missing the micro sign.

**Response:** Done.

-mositure = moisture (both in text and figure axis labels).

**Response:** Done.

Some textual corrections:

P3L42: “non-leaf contributions to the net ecosystem COS flux”.

**Response:** Done.

P3L50: Event = Even

**Response:** Done.

P4L83: “described by Asaf et al. (2013).

**Response:** Done.

P5L109: “. . .from the normalized ratio of CO<sub>2</sub> respiration to COS uptake (negative values) or emission (positive values) fluxes”.

**Response:** Done.

P6L125: “soil COS and CO<sub>2</sub> fluxes were estimated based on Fick’s first law: . . .”

**Response:** Done.

P6 Eq4: Ts is not defined in the text, but later T is defined. If Ts and T are the same then make it consistent throughout the text.

**Response:** Corrected.

P6L146: “both the spatial (microsites) and temporal (seasonal) scale”.

**Response:** Corrected.

P7L157: “In the UT site. . .”

**Response:** Done.

P7L176: “The fit to the data. . .”

**Response:** Done.

P8L206: Reference to Fig. 4 should be Fig. 5?

**Response:** Done.

P11L279: induced = induce.

**Response:** Done.

P11L288: remove “on”.

**Response:** Done.

P12L315: maybe = may be

**Response:** Done.

P12L319: Lab incubation results also indicated thermal production of COS in soil. . .”

**Response:** Done.

P15L391: “Our detailed analysis...”

**Response:** Done.

**P21L569-571: caption of Figure 3, this sentence doesn’t flow logically.**

**Response:** Revised.

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**Referee #2**

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).

**Response:** Thanks for the positive comments.

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.

**Response:** As now clarified, samples were not static and were not kept inside closed-off tubing before analysis. Tubing were flushed for several turnovers of tubing volume before used for analysis. Note that even the longest 20 cm deep tubing had a volume of ca 10 ml requiring few sec flushing, and other connecting tubing were flushed with atmospheric air before soil sampling.

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?

**Response:** Thank you for noting the confusing part, and hopefully things are clearer now: The flow rate was in fact 80 ml/min for 5 min (total volume of 400 ml pumped), and data used only from the 3rd min window. For soil tube volumes of 3-12 ml, depending on depth, 2-minute flush was more than sufficient. The QCL sampling cell (500 ml) was setup at 15 torr and therefore another 1 min at 80 ml/min sufficiently flush the cell (~8 turnovers). The main cause of atmospheric leaks in preliminary trials was leaks around the outside of the tubes (but fixed). In addition, the five sampling cycles per site were never consecutive and were, in fact, hours apart (sometime the following day). And the soil tubes to different depths were not in bundles, but rather spread to avoid communication between sampling points during sampling. (There is no way that

we could consistently observed thousands of ppm of CO<sub>2</sub> above ambient, and hundreds of ppt of COS below ambient a few cm below the surface if the system was leaking from the atmosphere).

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.

**Response:** Changed as suggested.

The word “significant” (L43, L47, L160, L170) is vague unless a level of significance is defined, as in L184 and L246.

**Response:** “significant” was replaced.

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.

**Response:** Indeed, we contrasted references on small and large soil fluxes, noting wetlands. But we nevertheless revised the language as suggested to avoid any ‘misleading’ (e.g. changed to, “in some cases small fluxes...”, and “Substantial soil COS emission...”)

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.

**Response:** Thank you for the nice perspective. One of the benefits of the open discussion format is that this is now available to the public. Our paper is not a review, and luckily we have the 2018 Whelan review out, but we now checked and adjusted our

citations are consistent with this narrative, including the addition of the recent reference of Kaisermann et al 2018.

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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/m<sup>2</sup>/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.

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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<sub>4</sub> 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.

**Response:** The relevant part and the CA issue was streamlined. We appreciate some suggestions for the follow-up studies (unfortunately, we were not geared for CO

measurements, and water vapor fluxes and soil moisture are tricky business and part of separate study).

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 CO<sub>2</sub> 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.

**Response:** Indeed, this is part of the motivation. This overlaps with comment of Ref 1 was addressed also there by better introducing the point up front in the Introduction.

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.

**Response:** Thanks.

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1 **Soil-atmosphere exchange of carbonyl sulfide in Mediterranean**  
2 **citrus orchard**

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11

12 **Abstract:**

13 Carbonyl sulfide (COS) is used as a as a tracer of CO<sub>2</sub> exchange at the ecosystem  
14 and larger scales. The robustness of this approach depends on knowledge of the soil  
15 contribution to the ecosystem fluxes, which is uncertain at present. We assessed the  
16 spatial and temporal variations of soil COS and CO<sub>2</sub> fluxes in the Mediterranean citrus  
17 orchard combining surface flux chambers and soil concentration gradients. The spatial  
18 heterogeneity in soil COS exchange indicated net uptake below and between trees of  
19 up to  $+4.6 \text{ pmol m}^{-2} \text{ s}^{-1}$ , and net emission in sun exposed soil between rows, of up to  
20  $+2.6 \text{ pmol m}^{-2} \text{ s}^{-1}$ , with a mean uptake value, of  $+1.10 \pm 0.10 \text{ pmol m}^{-2} \text{ s}^{-1}$ . Soil COS  
21 concentrations decreased with soil depth from atmospheric levels of ~450 to ~100 ppt  
22 at 20 cm depth, while CO<sub>2</sub> concentrations increased from ~400 to ~5000 ppm. COS  
23 flux estimates from the soil concentration gradients were, on average,  $-1.02 \pm 0.26 \text{ pmol}$   
24  $\text{m}^{-2} \text{ s}^{-1}$ , consistent with the chamber measurements. A soil COS flux algorithm driven  
25 by soil moisture and temperature (5 cm depth) and distance from the nearest tree, could  
26 explain 75% of variance in soil COS flux. Soil relative uptake, the normalized ratio of  
27 COS to CO<sub>2</sub> fluxes was, on average -0.37 and showed a general exponential response  
28 to soil temperature. The results indicated that soil COS fluxes at our study site were  
29 dominated by uptake, with relatively small net fluxes compared to both soil respiration  
30 and reported canopy COS fluxes. Such result should facilitate the application of COS  
31 as a powerful tracer of ecosystem CO<sub>2</sub> exchange.

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33 **Keywords:**

34 Carbonyl sulfide; COS; OCS; soil gas exchange; ecosystem gas exchange; tracer of  
35 carbon fluxes.

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40 **1. Introduction**

41 Carbonyl sulfide (COS) is a Sulphur-containing analogue of CO<sub>2</sub> that is taken up  
42 by vegetation following a similar pathway to CO<sub>2</sub>, ultimately hydrolyzed in an  
43 irreversible reaction with carbonic anhydrase. It therefore holds great promise for  
44 studies of photosynthetic CO<sub>2</sub> uptake (Asaf et al., 2013; Berry et al., 2013; Wehr et al.,  
45 2017; Whelan et al., 2018). One of the difficulties in the application of COS as a tracer  
46 for photosynthetic CO<sub>2</sub> uptake is that the non-leaf contributions to the net ecosystem  
47 COS flux are poorly characterized. There are reports of substantial soil fluxes,  
48 indicating both uptake and emissions (Kesselmeier et al., 1999; Kuhn et al., 1999;  
49 Masaki et al., 2016; Seibt et al., 2006; Yang et al., 2018; Yi et al., 2007). Although soil  
50 COS exchanges were in some cases small compared to plant uptake (e.g., Yang et al.,  
51 2018; Berkelhammer et al., 2014), this was not always the case. Substantial soil COS  
52 emissions have been found in wetlands and anoxic soils (Li et al., 2006; Whelan et al.,  
53 2013), and in senescing agricultural fields and high temperatures (Liu et al., 2010;  
54 Maseyk et al., 2014), or under drought conditions and in response to UV radiation (Kitz  
55 et al., 2017). Even for the same soil, COS fluxes could show large variations and both  
56 uptake and emission with sensitivities to soil moisture, and ambient COS  
57 concentrations (Bunk et al., 2017; Kaisermann et al., 2018). These studies also assessed  
58 the response of COS exchange to environmental controls, e.g. soil moisture and  
59 temperature and solar radiation. For COS application as a tracer of ecosystem CO<sub>2</sub>  
60 exchange characterizing the relationships between COS and CO<sub>2</sub> fluxes is important.  
61 This is done by assessing the 'relative uptake' (RU) of the COS/CO<sub>2</sub> flux rate ratio,  
62 normalized by the ambient atmospheric concentrations (that differ for the two gases by  
63 a factor of about 10<sup>6</sup>), as done at the leaf, (LRU) or ecosystem (ERU; e.g. Asaf et al.,  
64 2013). It was similarly applied to soil as SRU (Berkelhammer et al., 2014).  
65 Conservative, or predictable, SRU values reflect systematic relationships between  
66 process influencing CO<sub>2</sub> and COS, could help identification of the dominant process,  
67 and support the application of COS as tracer. Small, SRU values compared to LRU  
68 could also indicate reduced effect of soil on ecosystem fluxes. For example,  
69 Berkelhammer et al. (2014) reported mean SRU of -0.76, which are about half of the

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77 leaf values of about +1.7 indicating that compared to CO<sub>2</sub>, leaf COS is enhanced, and  
78 soil COS uptake is suppressed, which provide additional robustness to the COS-GPP  
79 approach. Note also that as soil CO<sub>2</sub> respiration measurements and modeling are  
80 much more common at flux sites, and knowledge of SRU could help derive soil COS  
81 fluxes and, for example, improve the partitioning of canopy COS flux from NEE<sub>COS</sub>  
82 measurements.

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83 Soil COS exchange has often been measured by incubations in the lab (e.g., Bunk  
84 et al., 2017;Kesselmeier et al., 1999;Liu et al., 2010;Van Diest and Kesselmeier, 2008),  
85 and by static or dynamic chambers in the field (e.g., Berkelhammer et al., 2014;Kitz et  
86 al., 2017;Sun et al., 2018;Yi et al., 2007;Mseyk et al., 2014), and using models (e.g.,  
87 Ogée et al., 2016;Sun et al., 2015;Whelan et al., 2016). In spite of these efforts, more  
88 field measurements of soil COS exchange are clearly needed as a basis for elucidating  
89 underlying mechanism, as well as obtaining better quantitative record of the possible  
90 range of soil COS fluxes under natural conditions. Note also that previous studies have  
91 focused on agricultural soils (Maseyk et al., 2014), wetlands (Whelan et al., 2013),  
92 boreal forest soils (Sun et al., 2018), and grasslands (Kitz et al., 2017), but several  
93 ecosystems are understudied, such as in the Mediterranean. Furthermore, soil profile  
94 measurements will also be useful for validation of soil models of COS exchange (Sun  
95 et al., 2015). The objective of this study was to apply dynamic chambers measurements,  
96 constrained by simultaneous soil gradient method to assess the spatial and temporal  
97 variations soil COS and CO<sub>2</sub> fluxes in a citrus orchard ecosystem where contrasting soil  
98 microsite conditions occur.

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100 **2. Materials and methods**

101 **2.1 Field site**

102 The experiment was conducted in an orchard in Rehovot, Israel (31°54' N, 34°49'  
103 E, 50 m, asl) in 2015 and 2016. The orchard is a plantation of lemon trees (*Citrus*  
104 *limonia Osbeck*), with 5 m distance between rows and 4 m between trees. Mean annual  
105 air temperature at the site is 19.7 °C, and mean annual precipitation is 537 mm. Most  
106 of the precipitation (82%) falls in November to February with no rain during June to

111 October. A trickle irrigation system was used from May to September with the standard  
112 irrigation plan of the orchard management. The soil in the area is ~~brown red~~ sandy soil  
113 (~~hamra soil~~) with an average bulk density of  $1.6 \text{ kg m}^{-3}$  ~~and pH of 6.5~~ (Singer, 2007).  
114 ~~Although root distribution was not measured we noted that roots were concentrated~~  
115 ~~mainly within about 50 cm of the tree trunks, as could be expected due to drip irrigation~~  
116 ~~installed around the trunk.~~

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## 118 2.2 Quantum cascade laser measurements

119 We used the commercially available quantum cascade laser (QCL) system  
120 (Aerodyne Research, Billerica, MA) with tunable laser absorption spectrometer (Model:  
121 QC-TILDAS-CS) to measure COS, CO<sub>2</sub>, and water vapor concentrations  
122 simultaneously. The device was installed in a mobile lab, described ~~by~~ Asaf et al. (2013).  
123 COS is detected at  $2050.40 \text{ cm}^{-1}$  and CO<sub>2</sub> at  $2050.57 \text{ cm}^{-1}$  at a rate of 1 Hz. The  
124 instrument was calibrated using working reference compressed air tank that was used  
125 for inter-comparison with the NOAA GMD lab (Boulder CO). ~~Corrections for water~~  
126 ~~vapor were made using the TDLWINTTEL software installed in the QCL (Kooijmans et~~  
127 ~~al. 2016)~~

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## 129 2.3 Soil chamber flux measurements

130 Custom-made stainless-steel cylindrical chamber of  $177 \text{ cm}^2$  directly inserted into  
131 the soil ( $\sim 5 \text{ cm}$ ) was used, as previously described (Berkelhammer et al., 2014; Yang et  
132 al., 2018). ~~The chambers were opaque and photoproduction was not considerate in this~~  
133 ~~study.~~ The chamber air and ambient air flows were pumped to the QCL analyzer through  
134 two 3/8-inch diameter Decabon tubing. Flow rate was maintained at  $1.2 \text{ L min}^{-1}$  and  
135 repeatedly cycled with 1 min instrument background (using N<sub>2</sub> zero gas), 9 min ambient  
136 air flow, and 10 min chamber air sample. Three different soil sites were used with  
137 distance of 3.20, 2.00 and 0.25 m away from a tree trunk, that represented sampling  
138 sites between rows (BR), between trees (BT) and under tree (UT). Each sampling site  
139 was measured continuously for 24 hours and cycled between sites for the duration of  
140 the campaign. Four measurement campaigns were carried out during 5th~9th August

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148 2015; 25th~28th December 2015; 5th~9th May 2016; 28th~31th July 2016.

149 Gas exchange rates,  $F_c$ , were calculated according to:

150 
$$F_c = \frac{Q}{A} \times (\Delta C_{sample} - \Delta C_{blank}) \quad (1)$$

151 where  $Q$  is the chamber flush rate in mol s<sup>-1</sup>;  $A$  is the enclosed soil surface in m<sup>2</sup>;  $\Delta C$  is  
152 the gas concentrations difference between chamber air and ambient air in pmol mol<sup>-1</sup>  
153 for COS and  $\mu\text{mol mol}^{-1}$  for CO<sub>2</sub> under sampling, and blank reference treatments (using  
154 the same chamber placed above a sheet of aluminum foil before and after measurement  
155 at each site. Hereafter, the soil fluxes are reported in pmol m<sup>-2</sup> s<sup>-1</sup> and  $\mu\text{mol m}^{-2}$  s<sup>-1</sup> for  
156 COS and CO<sub>2</sub>, respectively. Soil relative uptake (SRU) is used to characterize the  
157 relationship between soil CO<sub>2</sub> and COS fluxes, was estimated from the normalized ratio  
158 of CO<sub>2</sub> respiration to COS uptake (negative values) or emission (positive values) fluxes,  
159 (Berkelhammer et al., 2014):

160 
$$SRU = \frac{F_{COS_{soil}}}{[COS]} \Big/ \frac{F_{CO_2_{soil}}}{[CO_2]} \quad (2)$$

161

## 162 2.4 Soil concentration profile measurements

163 Four campaigns of soil concentration profile measurements were carried out  
164 during 1st~2nd March; 20th~26th April; 10th May; 22nd~28th June of 2016. The trace  
165 gas at five soil depths of 0, 2.5, 5.0, 10, 20 cm was sampled at each of the three  
166 microsites, BR, BT and UT.

167 Four individual Decabon tubes were inserted at adjacent but different points into  
168 the soil (to avoid communication between tubes during sampling), to the different  
169 depths indicated above and connect directly to the QCL positioned nearby in the mobile  
170 lab. At least one day after insertion and insuring sealing between tubing and soil, soil  
171 air was sampled with flow rate of 80 ml min<sup>-1</sup>, in a 10 min cycle of 1 min instrument  
172 background, 3 min surface air (depth 0; used initially to flush all above ground tubing),  
173 5 min sampling of a depth point in the profile (first two minutes for flushing the tubing,  
174 third minute used for data; total of 400 ml extracted from the soil), ending with 1 min  
175 surface air. Five complete sets of cycles including the four soil depths and surface air

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187 were repeated for each site (time gaps between cycles of hours, and in some cases  
188 completed the following day). The pressure in the 500 ml QCL sample cell was kept at  
189 15 torr to insure sufficient turnovers (~8 per minute using the chosen flow rate) before  
190 data were recorded.

191 Assuming that in the selected measurement sites, soil trace gas is only  
192 transported by diffusion, soil COS and CO<sub>2</sub> fluxes were estimated based on the Fick's  
193 first law:

$$194 \quad F = -D_s \frac{dC}{dz_{soil}} \quad (3)$$

195 where  $F$  is the upward or downward gas flux (pmol m<sup>-2</sup> s<sup>-1</sup> for COS and μmol m<sup>-2</sup> s<sup>-1</sup>  
196 for CO<sub>2</sub>);  $D_s$  is the effective gas diffusion coefficient of the relevant gas species in the  
197 soil (m<sup>2</sup> s<sup>-1</sup>);  $C$  the trace gas concentration (mixing ratio, converted from the measured  
198 mole fractions);  $z_{soil}$  is the soil depth (m).

199 The Penman (1940) function was used to describe the soil diffusion coefficient  
200 ( $D_s$ ) as in Kapiluto et al. (2007):

$$201 \quad D_s = D_a (\theta_s - \theta) \sqrt{\frac{T_s + 273.15}{298.15}} \quad (4)$$

202 where  $\theta_s$  is the soil saturation water content and  $\theta$  is the measured soil volumetric water  
203 content.  $D_a$  is the trace gas diffusion coefficient in free air, which varied with  
204 temperature and pressure, given by

$$205 \quad D_a = D_{a0} \left( \frac{T_s + 273.15}{293.15} \right)^{1.75} \left( \frac{P}{101.3} \right) \quad (5)$$

206 where  $D_{a0}$  is a reference value of trace gas diffusion coefficient at 293.15 K and 101.3  
207 kPa, given as  $1.24 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup> for COS (Seibt et al., 2010) and  $1.47 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup>  
208 for CO<sub>2</sub> (Jones, 1992);  $T_s$  is soil temperature (°C), and  $P$  is air pressure (kPa).

### 210 3. Results

#### 211 3.1 Variations in soil COS flux

212 Soil COS fluxes showed significant heterogeneity at both the spatial (microsites)  
213 and temporal (seasonal) scale, (Fig. 1). Overall, the hourly soil COS flux varied from -

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220 4.6 to +2.6 pmol m<sup>-2</sup> s<sup>-1</sup>, with mean value of -1.10 ± 0.10 pmol m<sup>-2</sup> s<sup>-1</sup>. On the spatial  
221 scale, the COS fluxes showed systematically uptake under trees (UT), moderate uptake  
222 and some emissions between trees (BT) and relatively more emission in the exposed  
223 area between rows (BR), with diurnal mean values across seasons of -3.00 ± 0.10, -0.43  
224 ± 0.13 and 0.13 ± 0.11 pmol m<sup>-2</sup> s<sup>-1</sup>, respectively.

225 On the diurnal time-scale, soil COS flux were generally higher in the afternoon  
226 (peaking around 15:00~16:00 hours), declining at night and early morning (Fig. 1). On  
227 the seasonal time scale, soil COS fluxes showed both changes in rates and shifts from  
228 net uptake to net emission, with interactions between site and season (Fig. 1). In the UT  
229 site, where only COS uptake was observed, the highest rates were observed in winter  
230 and peak summer (December and August) with diurnal mean rates of nearly +4 pmol  
231 m<sup>-2</sup> s<sup>-1</sup>, and more moderate uptake rates, around +2 pmol m<sup>-2</sup> s<sup>-1</sup>, in spring and early  
232 summer (May and July; Fig. 1). In the BT sites, significant COS uptake of ~+2.5 pmol  
233 m<sup>-2</sup> s<sup>-1</sup> was observed in winter, but net fluxes were near zero in other times, with some  
234 afternoon emission in summer. In the exposed BR sites, minor uptake (less than +1  
235 pmol m<sup>-2</sup> s<sup>-1</sup>) was observed in spring and early summer, but consistent emission in peak  
236 summer, with diurnal mean values of nearly +2 pmol m<sup>-2</sup> s<sup>-1</sup>.

237

### 238 3.2 Effects of moisture and temperature

239 During the hot summer (August 2015 and July 2016), differences in microsite soil  
240 water content ( $\theta$ ) were most distinct, with  $\theta$  of nearly 30% in the UT sites (associated  
241 with drip irrigation), but ~19% and ~12% in the BT and BR sites. Correspondingly, the  
242 UT sites had significant COS uptake of about -3 pmol m<sup>-2</sup> s<sup>-1</sup> while the other sites  
243 showed emission of about +1 pmol m<sup>-2</sup> s<sup>-1</sup> (Table 1). In winter (December),  $\theta$  in the  
244 three sites was similar ~25% and all sites showed soil COS uptake, but with clear  
245 gradient of +3.9, +2.5 and +0.7 pmol m<sup>-2</sup> s<sup>-1</sup> in the UT, BT and BR sites, respectively  
246 (Fig. 1). On average, soil COS fluxes showed non-linear increase in uptake with  
247 increasing  $\theta$ , but it seems that this response may saturate at about  $\theta$  of 25% and uptake  
248 rates of ~+3.9 pmol m<sup>-2</sup> s<sup>-1</sup> (Fig. 2). The fit to the data, presented in Fig. 2 also indicate  
249 that in dry soil with  $\theta < 15\%$  soil COS emission can be expected.

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258 The response of soil COS fluxes to soil temperature varied among the three  
259 measurement sites (Fig. 3). The BT and BR sites showed a near linear response with a  
260 shift from uptake to emission around 25 °C. In the shaded and moist UT site, COS uptake  
261 was always significant ranging between  $\pm 4$  to  $\pm 1$  pmol m<sup>-1</sup> s<sup>-1</sup> with relatively low  
262 temperature sensitivity, and with lowest mean uptake rates around 20 °C.

263 Pearson product-moment correlation analysis results showed that hourly soil COS  
264 flux was significantly related to soil moisture and temperature (at the 0.001 level), and  
265 the soil moisture had a stronger environmental controls on the soil COS flux ( $r=-0.77$ ),  
266 compared with soil temperature ( $r=+0.45$ ).

267 Comprehensive assessment of the effects of soil moisture ( $\theta$ ), temperature ( $T_s$ ) and  
268 distance away from tree trunk ( $d$ ), hourly soil COS flux ( $F_{COS}$ ) could be fitted to a three  
269 parameters exponential model, which could explain 75% of the variation in soil COS  
270 flux (Eq. 6).

$$271 \quad F_{COS} = 8.91 \exp(0.01T_s - 0.01\theta + 0.09d - 0.33) - 8.86, R^2 = 0.75 \quad (6)$$

272

### 273 3.3 COS flux estimates from soil concentration gradients

274 The average soil concentration gradient of COS and CO<sub>2</sub> for the four campaigns  
275 is shown in Fig. 4. COS concentrations decreased with soil depth, with the opposite  
276 trend for CO<sub>2</sub>, consistent with the results reported above of soil surface COS uptake  
277 and CO<sub>2</sub> emission at our orchard site. COS concentrations at depth of 2.5 cm was on  
278 average 314 ppt, and about one-third lower than the mean surface, ambient, value of  
279 460 ppt. The lowest COS concentration at depth of 20 cm (166 ppt) was almost one-  
280 third of that at the soil surface. An exponential and a linear equations provided  
281 reasonable fit to the changes in soil COS and CO<sub>2</sub> concentrations, respectively, as a  
282 function of depth ( $z_{soil}$ ):

$$283 \quad \begin{aligned} [COS] &= 283.5 \exp(-0.2z_{soil}) + 169.9, R^2 = 0.99 \\ [CO_2] &= 122.2z_{soil} + 558.5, R^2 = 0.99 \end{aligned} \quad (7)$$

284 In terms of individual site and campaign, all profiles except for BR in summer  
285 (June) showed the general trend of decreasing [COS] and increasing [CO<sub>2</sub>] with depth,

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291 with the steepest gradient at the top 5 cm (Fig. 5). In the BR microsite in summer, CO<sub>2</sub>  
292 profile was shallow, consistent with the low respiration (see July BR in Table 1). But a  
293 decrease in COS concentration toward the surface, with surface value lower than the  
294 next two soil depth points (Fig. 5J), was consistent with COS emission at that time (July  
295 BR in Table 1).

296 As noted above, the profile data generally exhibited the steepest gradient at the top  
297 few cm of the soil, indicating that the dominating COS sink (and likely also the CO<sub>2</sub>  
298 source) was located at shallow depth. We therefore used the gas concentration  
299 difference at two shallowest depths ( $z_{soil1} = 0$  and  $z_{soil2} = 2.5$  cm) to provide an  
300 approximation of the fluxes to and from the soil, to constrain the more extensive  
301 chamber measurements. The COS diffusion coefficient,  $D_s$ , was estimated for each  
302 campaigns (see Methods), indicating low  $D_s$  value in the UT site in June and July ( $D_s =$   
303  $2.55 \text{ mm}^2 \text{ s}^{-1}$ ), associated with the drip irrigation and the high soil water content, and  
304 high values in the dryer soils ( $D_s = 5.57 \text{ mm}^2 \text{ s}^{-1}$ ), with an average COS diffusion  
305 coefficient of  $4.40 \pm 0.29 \text{ mm}^2 \text{ s}^{-1}$ . The soil COS flux estimates using the gradient  
306 method is reported in Table 2. COS flux varied between  $-2.10$  to  $+1.55 \text{ pmol m}^{-2} \text{ s}^{-1}$   
307 with a mean value of  $-1.02 \pm 0.26 \text{ pmol m}^{-2} \text{ s}^{-1}$  during the measurement periods,  
308 consistent with the mean value of  $-1.10 \pm 0.10 \text{ pmol m}^{-2} \text{ s}^{-1}$  reported above for the  
309 chamber measurements. Also in agreement with the chamber measurements, fluxes at  
310 UT and BT always showed COS uptake, with generally higher values in spring (March)  
311 than in summer (May-June), while the BR data indicated change from uptake in spring  
312 (March-April, with  $+1.3$  to  $+1.6 \text{ pmol m}^{-2} \text{ s}^{-1}$ ) to emission in June ( $+1.6 \text{ pmol m}^{-2} \text{ s}^{-1}$ ).

313

### 314 3.4 Soil relative uptake

315 Soil was always a source of CO<sub>2</sub> due respiration (combined autotrophic and  
316 heterotrophic respiration). Soil CO<sub>2</sub> flux rates varied both spatially and temporally in  
317 similar patterns to those of COS, and with overall range of  $0.3$  to  $14.6 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$   
318 (Table 1). The highest soil respiration values were observed in the UT sites in summer  
319 (July, August; Table 1), with intermediate ( $1\sim 3 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) and low values ( $< 1 \text{ } \mu\text{mol}$

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328  $\text{m}^{-2} \text{s}^{-1}$ ) in the BT and BR sites, respectively. Generally, soil COS exchange varied from  
 329 release to increasing uptake with increasing  $\text{CO}_2$  production in a non-linear way (Fig.  
 330 6a). The normalized ratio of COS to  $\text{CO}_2$  fluxes (SRU; Eq. 2) varied from -1.92 to +1.85  
 331 with an average value of  $-0.37 \pm 0.31$ , with negative values indicating COS uptake  
 332 linked to  $\text{CO}_2$  emission. SRU values showed response to both soil temperature (Fig. 6b)  
 333 and soil moisture (Fig. 6c), although with relatively low  $R^2$  values. Respiration  
 334 increased with temperature while COS uptake declined and at temperature above about  
 335  $25^\circ\text{C}$  SRU turned positive when both COS and  $\text{CO}_2$  are emitted from the soil. SRU  
 336 exhibited inverse relationships with soil moisture, with positive values in dry soil and  
 337 increasingly negative values with increasing soil moisture (Fig. 6c). Based on its  
 338 combined temperature ( $T_s$ ) and moisture ( $\theta$ ) response, SRU could be forecasted by the  
 339 following algorithm, which explained 67% of the observed variations (Eq. 8):

$$340 \quad \text{SRU} = 0.01 \exp(0.17T_s) - 0.02\theta - 1.00, R^2 = 0.67 \quad (8)$$

341 ANOVA analysis results indicated that SRU was not significantly different among  
 342 the three observation microsites (BR, BT, and UT;  $P > 0.05$ ). Between the seasonal  
 343 campaigns, however, SRU values peaked in summer ( $0.53 \pm 0.66$ ) with highest  
 344 averaged soil temperature ( $29^\circ\text{C}$ ) and was significantly higher than winter SRU ( $-1.44$   
 345  $\pm 0.59$ ) when soil temperature was lowest ( $11^\circ\text{C}$ ;  $P < 0.05$ ), and with no significant  
 346 difference in SRU among the other campaigns ( $P > 0.05$ ).

347

## 348 4. Discussions

### 349 4.1 Heterogeneity in soil COS exchange

350 The observed soil-atmosphere COS exchange rates observed in this study (both  
 351 mean and range; Fig. 1, Table 1) are consistent with values reported in a range of other  
 352 ecosystems ( $-1.4$  to  $-4.9 \text{ pmol m}^{-2} \text{ s}^{-1}$ ; Steinbacher et al., 2004; Kitz et al., 2017; White  
 353 et al., 2010; Berkelhammer et al., 2014), but lower than  $-11.0$  to  $-11.8 \text{ pmol m}^{-2} \text{ s}^{-1}$  in a  
 354 riparian and subtropical forests (Berkelhammer et al., 2014; Yi et al., 2007). Soil COS  
 355 emissions were also observed in summer and spring campaigns, with maximal COS  
 356 emission consistent with the values of  $+1.8$  to  $+2.6 \text{ pmol m}^{-2} \text{ s}^{-1}$  observed in a riparian

357 and alpine forests (Berkelhammer et al., 2014), but significantly lower than reported in  
358 the senescing agricultural ecosystem ( $\sim \pm 30$  pmol m<sup>-2</sup>s<sup>-1</sup>; Maseyk et al., 2014).

359 The observed range in the soil-atmosphere exchange fluxes reflected significant  
360 heterogeneity on both the spatial and the temporal scales. The spatial scale  
361 heterogeneity clearly reflected the contrasting microsite conditions with lower  
362 temperatures and higher moisture under the trees (UT sites), compared with the higher  
363 temperatures and lower moisture in exposed soil between rows (BR sites), with  
364 intermediate, partially shaded, conditions between trees (BT sites). Indeed, a large  
365 fraction of the variations in the COS flux ( $\sim 75\%$ ) could be explained by a simple  
366 algorithm as a function of these two variables, temperature and moisture. Note that  
367 while temperature and  $\theta$  co-varied in general, with high temperatures associated with  
368 drier soil, under the wet UT conditions, sensitivity to temperature was significantly  
369 reduced. In the dry soil conditions, emission was associated with high temperature, and  
370 in the BR sites also with high solar radiation. However, all measurements were made  
371 in dark chambers and could not involve photochemical production, which was also  
372 demonstrated in agricultural soil by Kitz et al. (2017). Apparently even under dark  
373 conditions, high temperature can induce high emission rates, as also noted when the  
374 thermal insulation on the soil chamber in the BR site was incidentally removed and a  
375 large spike in temperature (52 °C) and emission of 11.4 pmol m<sup>-2</sup> s<sup>-1</sup> was observed.

376 Temporal variations were observed both on the daily and seasonal time scales.  
377 Diurnal changes were, however, minor compared to the changes from winter to summer  
378 in all microsites. Shifts from uptake to emission were observed essentially only on the  
379 seasonal time scale (Fig. 1). This likely reflected the dominance of soil moisture on the  
380 COS flux rates. This is because  $\theta$  did not change noticeably on the daily scale, while it  
381 did changed considerably across seasons (between 10.0 and 35.5% overall). Soil  
382 temperatures did change over the daily cycle (e.g. 26.0 to 42.4 °C in the BR site during  
383 summer), although such changes are still smaller compared with the seasonal changes  
384 in soil temperature (e.g. 10.5 to 31.8 °C in the BR site). A dominant role of soil moisture  
385 in explaining the variations in COS uptake is consistent with the results of Van Diest  
386 and Kesselmeier (2008), but less so with the negligible  $\theta$  effects in grassland under

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396 simulated drought (Kitz et al., 2017).  
 397 COS uptake is thought to be related to carbonic anhydrase activity in soil  
 398 (Kesselmeier et al., 1999), which could via microorganisms (Piazzetta et al., 2015),  
 399 such as Bacteria (Kamezaki et al., 2016; Kato et al., 2008), or fungi (Bunk et al., 2017;  
 400 Li et al., 2010; Masaki et al., 2016). CA activity is also influenced by soil moisture  
 401 (Davidson and Janssens, 2006; Seibt et al., 2006), although soil moisture can directly  
 402 influence soil gas diffusion rates (Ogée et al., 2016; Sun et al., 2015). The effect of CA  
 403 on COS exchange can also be related to root distribution and the effects of CA activity  
 404 within plant roots (Seibt et al., 2006; Viktor and Cramer, 2005; Whelan and Rhew,  
 405 2015). This could influence the spatial variations and soil moisture effects on COS  
 406 exchange in this study as most of the roots were distributed around the restricted trees'  
 407 drip irrigation zone at UT sites, and was sparse in the dryer areas, such as BR and BT  
 408 sites (un-quantified observations).

409 At least part of the variations in soil COS fluxes could also reflect the differential  
 410 effects of environmental conditions on COS uptake and production process (Ogée et al.,  
 411 2016). Solubility in soil water (with COS solubility of 0.8 ml ml<sup>-1</sup>; Svoronos and Bruno,  
 412 2002) could also be significant, especially in the UT microsites, influenced by the drip  
 413 irrigation from May to September that could involve water percolation to deeper soil  
 414 layers. The drivers of soil COS production are still unclear. COS could be produced by  
 415 chemical processes in the lab (Ferm, 1957), but can also be produced by biotic process  
 416 in soils such as by hydrolysis of metallic thiocyanates (Katayama et al., 1992) with  
 417 thiocyanate hydrolase (Conrad, 1996; Svoronos and Bruno, 2002) and hydrolysis of  
 418 CS<sub>2</sub> (Cox et al., 2013; Smith and Kelly, 1988). Fungi are also reported to be the source  
 419 of COS (Masaki et al., 2016). Additionally, abiotic thermal degradation of organic  
 420 matter leading to COS production may be supported by the temperature sensitivity of  
 421 COS emission in the BR microsite where biotic processes can be expected to be  
 422 minimized. Similar high temperature-dependent soil COS emissions were reported in  
 423 midlatitude forest (Commane et al., 2015) and agricultural field (Maseyk et al., 2014).  
 424 Lab incubation results also indicated thermal production of COS in soil, with increasing  
 425 temperature (Liu et al., 2010; Whelan et al., 2016; Whelan and Rhew, 2015).

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Moved up [1]: COS uptake is thought to be related to carbonic anhydrase activity in soil microorganisms (Piazzetta et al., 2015), such as Bacteria (Kamezaki et al., 2016; Kato et al., 2008), or fungi (Bunk et al., 2017; Li et al., 2010; Masaki et al., 2016).

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444 Photochemical production of soil COS was also proposed (Sun et al., 2015; Whelan and  
445 Rhew, 2015), and assumed to be driven by ultraviolet fraction of incoming solar  
446 radiation (Kitz et al., 2017). Note, however, that all measurements in the present study  
447 were made in the dark. In addition, the chemical reaction of CO and MgSO<sub>4</sub> under  
448 heating could also produce COS (Ferm, 1957). Note that MgSO<sub>4</sub> has been reported in  
449 our study soil (Singer, 2007), and we observed relatively high CO concentration in our  
450 field site. [Finally, we note the recent study that indicate that the balance between the](#)  
451 [uptake \(likely biotic dominated\) and emission \(likely abiotically dominated\) are](#)  
452 [influenced by soil nitrogen \(Kaisermann et al., 2018\).](#)

453

#### 454 4.2 Soil relative uptake

455 [We use SRU values also to assess the relative importance of the soil COS flux](#)  
456 [compared with the canopy. On average, the value of SRU at our site was smaller than](#)  
457 [reported for riparian or pine forests \(-0.37 vs -0.76 and -1.08; Berkelhammer et al.,](#)  
458 [2014; Sun et al., 2018\).](#) This may reflect the contribution of COS emissions at BR and  
459 BT in summer, that were not observed in the forest study. Overall, the mean SRU values  
460 observed here indicated that the soil COS uptake flux was proportionally less than 40%  
461 of the soil respiration flux. In contrast with the canopy fluxes where the COS uptake  
462 flux is, proportionally, nearly twice as large as the CO<sub>2</sub> assimilation flux (LRU~1.6; [at](#)  
463 [our site, Yang et al., 2018; 1.7 across vegetation types, Whelan et al., 2018\).](#) In contrast  
464 to leaves with robust LRU value that tend toward a constant, SRU at our site varied  
465 between -1.92 and +1.85. However, this range was observed only in the dryer and  
466 exposed BR sites, while in the shaded and moist UT sites, it was much narrower, -0.13  
467 to -0.79. Furthermore, it seems that the high SRU values (both positive and negative)  
468 represented conditions where the actual fluxes were small (COS uptake was on average  
469 -3.0 in the UT but only 0.1 pmol m<sup>-2</sup> s<sup>-1</sup> in the BR sites. It seems that the large SRU  
470 values in the BR microsites, were also associated with low soil respiration, 0.5  $\mu$ mol  
471 m<sup>-2</sup> s<sup>-1</sup> in BR sites, compared to 10  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> in the UT sites. It is therefore possible  
472 that the low SRU values are the more significant for ecosystem scale studies and

**Deleted:** For COS application as a tracer of ecosystem CO<sub>2</sub> exchange quantifying the relationships between COS and CO<sub>2</sub> fluxes is important. This is done by assessing the 'relative uptake' (RU) of the COS/CO<sub>2</sub> flux rate ratio, normalized by the ambient atmospheric concentrations (that differ for the two gases by a factor of about 10<sup>6</sup>), as done at the leaf, (LRU) or ecosystem (ERU; e.g. Asaf et al., 2013). It was similarly applied to soil as SRU (Eq. 2; Berkelhammer et al., 2014). ...

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488 indicate a much smaller contribution to overall ecosystem fluxes than that of the canopy  
489 (SRU~0.4 vs LRU~1.7).

490 Differential effects of changing environmental conditions on production and  
491 uptake processes were reflected in relatively large spatial and temporal heterogeneity  
492 observed in the soil COS exchange at our site. However, the contrasting effects of  
493 production and emission may explain both the sharp increase in SRU values at high  
494 temperatures as the effects of production counteract uptake (Fig. 6b), and the much  
495 lower sensitivity to temperature of COS flux compared to that of CO<sub>2</sub> (Fig. 6a). Such  
496 contrasting consumption/production effects may, in fact, reduce the magnitude of the  
497 net flux of soil COS, and may explain the relatively narrow range of SRU values.

498 [Application of COS as a tracer for canopy CO<sub>2</sub> exchange requires the accounting](#)  
499 [for the soil effects and while knowledge of SRU can help predicting it, ultimately we](#)  
500 [need to quantify the fluxes. Note in that respect, that in our recent canopy scale study](#)  
501 [at the same site \(Yang et al., 2018\) indicated that in spite of the considerable variations](#)  
502 [in soil COS fluxes, the soil COS uptake fluxes were equivalent to less than 1% of the](#)  
503 [daytime foliage flux across seasons, and reached 3% in the spring peak season \(but](#)  
504 [larger proportions were observed during more stressful periods when fluxes were](#)  
505 [overall small\).](#)

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### 507 **4.3 Soil COS profiles**

508 Complementing our chamber measurements with soil profile measurements of  
509 COS and CO<sub>2</sub> concentrations provided constrain on the relatively new surface soil COS  
510 measurements and provided additional information on the possible location of the  
511 source/sink in the soil. Using the near surface gradient yielded flux estimates  
512 comparable to chamber measurements, providing a useful and rare quantitative  
513 validation. For example, in May, the chamber and profile measurements were made at  
514 about the same time (5th~9th May for chamber and 10th May for profile) and the  
515 differences between chamber (all microsites) and gradient flux estimates, was  
516 negligible (~0.2-0.6 pmol m<sup>-2</sup> s<sup>-1</sup>). However, the profile results indicated in addition that  
517 the sink/source activities concentrated at top soil layers, probably at around 5 cm depth,

518 as reflected in the minimum or maximum in gas concentrations (indicating also the need  
519 for high vertical resolution in employing the profile approach). The variable profiles  
520 observed below these points must reflect temporal dynamics in the sink/source  
521 activities across the profile. The near surface peak activity makes it particularly  
522 sensitive to variations in temperature and moisture, as indeed observed (Figs. 2, 3). Low  
523 COS concentration in the lower parts of the profile may result from continuous removal  
524 of soil COS and may indicate distribution of CA activity beyond the litter layer and the  
525 soil surface (Seibt et al., 2006). COS production, however, seems to occur only near the  
526 soil surface with no indication for production in deeper layer, consistent with its high  
527 temperature sensitivity, and possibly also radiation (e.g. Kitz et al., 2017).

528 Note that the gradient method based on Fick's diffusion law have its own  
529 limitations (Kowalski and Sánchezcañete, 2010; Sánchez-Cañete et al., 2017; Bekele et  
530 al., 2007). However, it is simple low-cost approach and can help diagnose the  
531 magnitude of soil fluxes, which can also help in identifying below ground processes  
532 and their locations.

533

## 534 **5. Conclusions**

535 Our detailed analysis of the spatial and temporal variations in soil-atmosphere  
536 exchange of COS provided new information on a key uncertainty in the application of  
537 ecosystem COS flux to assess productivity. Furthermore, we provide validation of the  
538 close chamber measurements that are generally in use, by the additional gradient  
539 approach. Our results show that both microsites and seasonal variations in COS fluxes  
540 were related to soil moisture, temperature, and the distance from the tree (likely  
541 reflecting root distribution), but we suggest that soil moisture is the predominant  
542 environmental control over soil COS exchanges at our site. A simple algorithm was  
543 sufficient to forecast most of the variations in soil COS flux supporting its incorporated  
544 into ecosystem scale applications, as we recently demonstrated in a parallel study at the  
545 same site (Yang et al., 2018).

546 Clearly, uncertainties are still associated with soil processes involving COS, the  
547 differential effects of soil moisture, temperature, and communities of microorganisms

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549 and are likely to contribute to both the spatial and temporal variations in soil net COS  
550 exchange and require further research.

551

552 **Author contributions:**

553 DY designed the study; FY, RQ, FT, RS and DY performed the experiments. FY  
554 and FT analysed the data. DY and FY wrote the paper with discussions and  
555 contributions to interpretations of the results from all co-authors.

556

557 **Acknowledgements**

558 We are grateful to Omri Garini, Madi Amer, and Boaz Ninyo-Setter for their help. This work  
559 was supported by the Minerva foundation, a joint NSFC-ISF grant 2579/16; Israel Science  
560 Foundation (ISF 1976/17), the German Research Foundation (DFG) as part of the CliFF  
561 Project, and the JNF-KKL. FY is supported by the National Natural Science Foundation of  
562 China (41775105), and the Natural Science Foundation of Gansu Province (17JR5RA341).

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710 **Figure captions:**

711 **Figure 1.** Spatial variability of soil COS flux at three sites, between trees (a), between  
712 rows (b), and under tree (c). Each figure shows the diurnal cycling of soil COS flux in  
713 the four campaigns. Each data point was the hourly mean  $\pm$  1 S.E. (N=3).

714 **Figure 2.** Relationship of soil COS flux and soil moisture. Each data point represents  
715 the diurnal average (n=24) for each microsite and season (measurement campaign).  
716 Error bars represent  $\pm$ 1 S.E. around the mean; errors for flux are about the size of the  
717 symbols.

718 **Figure 3.** Soil COS fluxe as a function of temperature and its linear regression line,  
719 Each data point represents the diurnal average (n=24) for each site and season  
720 (campaign), Error bars represent  $\pm$ 1 S.E. around the mean. The data point marked in  
721 black cirble, were collected during irrigation cycle (enhanced uptake) and were excluded  
722 from the regression.

723 **Figure 4.** Mean COS and CO<sub>2</sub> concentrations at different soil depth. The COS  
724 concentration decreases exponentially with soil depth. The data point is the mean of the  
725 combined data at each of the four measurement campaigns (N=4;  $\pm$  1 S.E.).

726 **Figure 5.** Soil COS and CO<sub>2</sub> concentration profiles at the three microsities in four  
727 measurement campaigns. The data points are the mean of all measurements in a  
728 campaign (N=4,  $\pm$  1 S.E.)

729 **Figure 6.** The relationships between soil COS and CO<sub>2</sub> flux rates (chamber  
730 measurements; a). The response of soil relative uptake (SRU; normalized ratio of COS  
731 to CO<sub>2</sub> fluxes) to soil temperature (b) and to soil water content (c). The data points  
732 represent the diurnal average (N=24) of each site and season (measurement campaign).  
733 Error bars represent  $\pm$  1 S.E. around the mean (often the size of the symbol).

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748 **Table 1.** Mean values of soil COS and CO<sub>2</sub> flux rates across sites (BR, between rows;  
749 BT, between trees; UT, under tree), and seasons, together with the normalized ratio of  
750 COS/CO<sub>2</sub> fluxes (SRU), and the mean soil temperature at 5 cm depth ( $T_s$ ) and soil water  
751 content (% by wt;  $\theta$ ).

Campaigns	Sites	COS flux ( $\text{pmol m}^{-2} \text{s}^{-1}$ )	CO <sub>2</sub> flux ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ )	SRU	$T_s$ (°C)	$\theta$ (%)
August, 2015	BR	1.83±0.08	0.77±0.04	1.85	31.66±1.01	9.98±0.28
	BT	0.06±0.05	3.33±0.05	0.01	29.09±0.20	19.77±0.02
	UT	-3.64±0.13	10.79±0.12	-0.26	28.80±0.26	24.03±0.40
December, 2015	BR	-0.74±0.07	0.30±0.02	-1.92	10.50±0.17	23.33±1.89
	BT	-2.52±0.10	1.21±0.03	-1.62	11.20±0.19	24.22±0.94
	UT	-3.87±0.08	3.81±0.07	-0.79	12.17±0.16	26.11±1.01
May, 2016	BR	-0.77±0.02	0.32±0.02	-1.88	21.67±0.32	15.56±0.38
	BT	-0.05±0.04	1.31±0.05	-0.03	22.20±0.34	15.70±1.03
	UT	-1.80±0.11	10.78±0.54	-0.13	20.35±0.38	22.11±1.44
July, 2016	BR	0.21±0.04	0.79±0.05	0.21	29.66±0.60	14.73±0.57
	BT	0.76±0.09	1.97±0.04	0.30	26.68±0.15	17.49±0.70
	UT	-2.67±0.09	14.58±0.40	-0.14	27.83±0.34	35.47±3.47

752

753 **Table 2.** Estimates of soil COS and CO<sub>2</sub> fluxes from soil concentration gradient measurements (*T<sub>s</sub>*, soil temperature; *θ*, soil water content; BR,  
754 between rows; BT, between trees; UT, under tree.)

Campaigns	Sites	COS flux (pmol m <sup>-2</sup> s <sup>-1</sup> )	CO <sub>2</sub> flux (μmol m <sup>-2</sup> s <sup>-1</sup> )	CO <sub>2</sub> diffusion coefficient (mm <sup>2</sup> s <sup>-1</sup> )	COS diffusion coefficient (mm <sup>2</sup> s <sup>-1</sup> )	<i>T<sub>s</sub></i> (°C)	<i>θ</i> (%)
March, 2016	BR	-1.31	2.34	5.21	4.40	17.9	19.4
	BT	-1.15	2.21	4.80	4.05	16.2	21.8
	UT	-2.10	5.89	4.76	4.02	17.3	22.4
April, 2016	BR	-1.55	1.07	6.66	5.62	23.0	11.0
	BT	-0.89	1.14	6.44	5.43	20.4	11.6
	UT	-1.74	4.73	6.01	5.07	22.4	15.2
May, 2016	BR	-0.98	2.21	5.68	4.79	21.9	17.4
	BT	-0.51	1.24	5.06	4.27	22.0	21.6
	UT	-1.20	11.36	3.11	2.63	20.1	34.5
June, 2016	BR	1.55	2.63	6.61	5.57	35.9	15.5
	BT	-1.17	2.60	5.20	4.39	26.3	21.7
	UT	-1.19	11.85	3.02	2.55	22.9	35.6

755

Figure 1

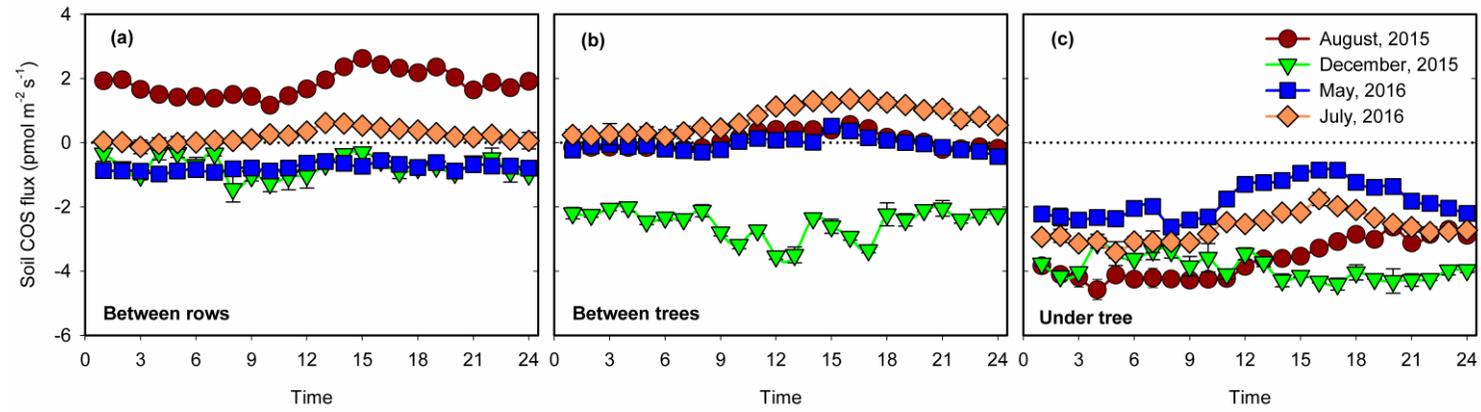
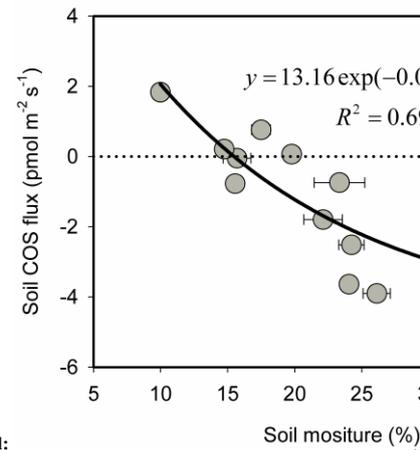
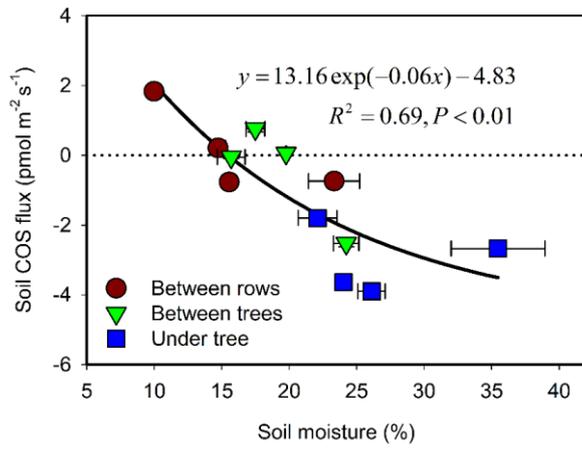
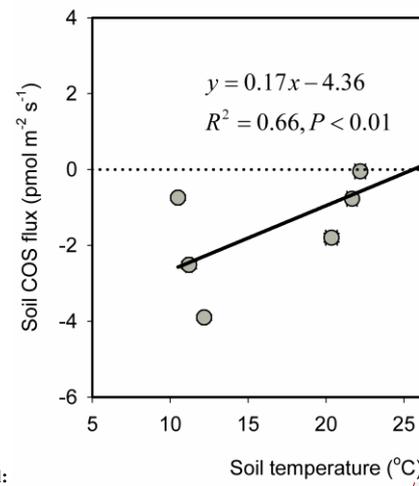
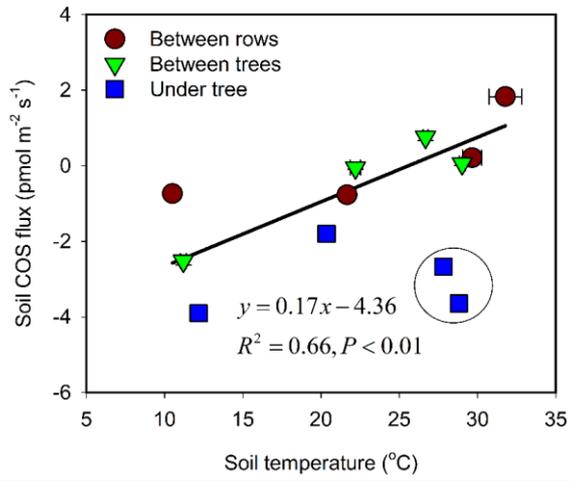


Figure 2



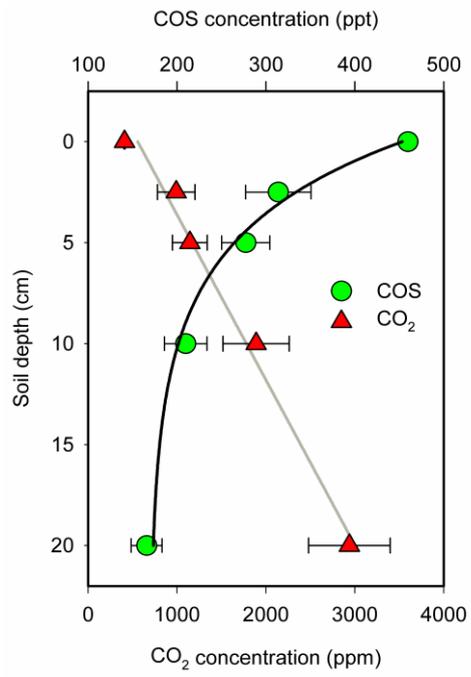
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Figure 3



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Figure 4



**Figure 5**

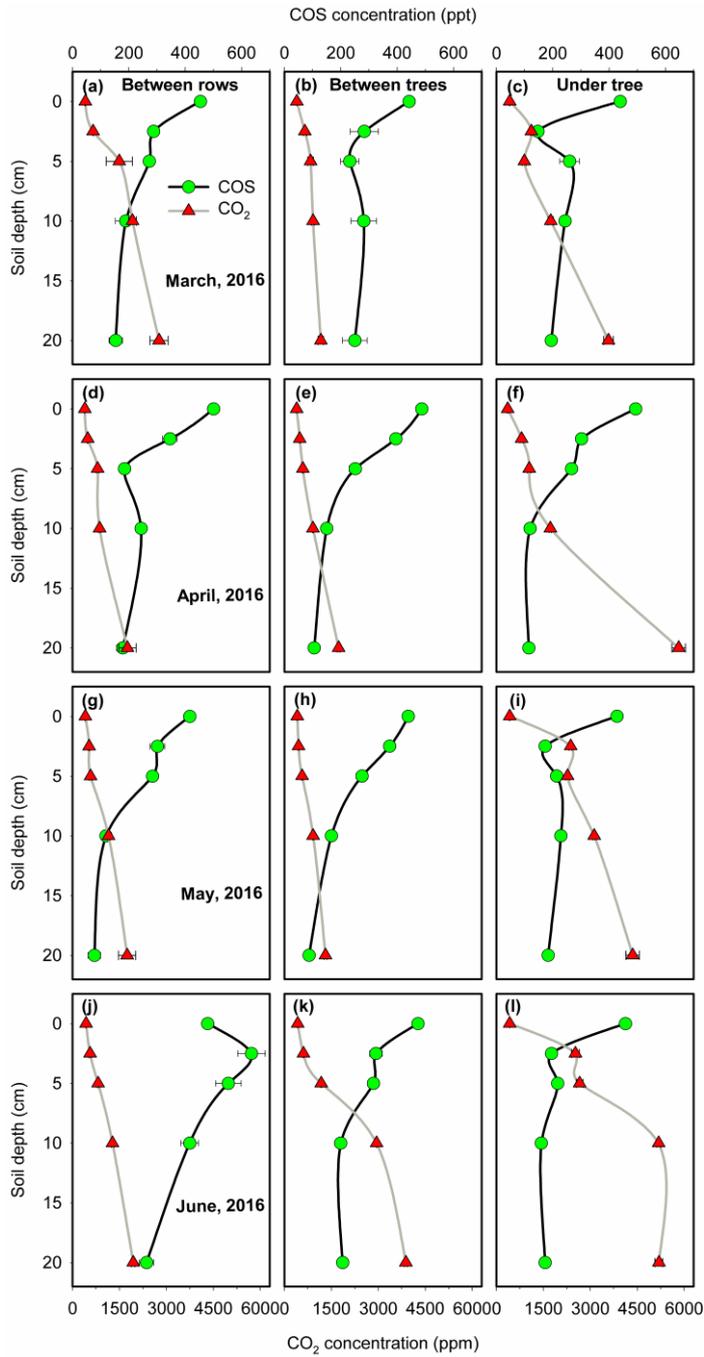


Figure 6

