

Response to the review comments on “Soil fluxes of carbonyl sulfide (COS), carbon monoxide, and carbon dioxide in a boreal forest in southern Finland”

Anonymous Referee #1

General comments:

Gas exchange processes at the atmosphere-soil interface play a key role in regulating both atmospheric chemistry and soil ecosystem. As in this paper, the exchange behaviors of three important gas species including COS, CO, and CO₂ at a representative boreal forest floor are investigated and, their potential implications are further discussed. Under the measured soil temperature and moisture ranges, soil more likely acts as a sink for COS and CO. The effects of biotic and abiotic factors on the uptake/exchange mechanism are usually closely combined under natural conditions and are difficult to be distinguished, unless the soil samples undergo specific pre-treatments (e.g., soil sterilization). The coexistence of both factors makes the analysis of uptake/exchange mechanism even more complicated. However, the results proposed in this paper, to some extent, emphasize one important point that, both the biotic processes and the abiotic processes can have crucial influences on gas uptake/exchange and their relative importance depends on the soil conditions. For clarity of the context of this paper, some more detailed elucidation and several minor corrections are further needed, as shown in the following specific comments and technical corrections.

We thank the referee for the constructive comments that helped to improve the manuscript. We have made clarifications and corrections to the issues raised here. Please see the detailed response below.

Specific comments:

Page 2, line 4: “Earth’s radiative balance”, how do the concentrations and distributions of COS and CO affect the Earth’s radiative balance? Please give an explanation for easier understanding.

We have provided examples to elaborate on this issue. COS is a precursor to the stratospheric sulfate aerosols and also a greenhouse gas (GHG), and its net radiative forcing is negative, while CO regulates concentrations of CH₄ and other GHGs through chemical reactions. See Line 5–10 on Page 2 in the revised version.

Page 2, line 14: “are geographically separated from the terrestrial sinks of COS” how do the terrestrial sinks of COS affect the COS emissions from the ocean? To what extent the plant and soil can be the sources of COS?

This statement was to emphasize that ocean emissions and terrestrial uptake are geographically separated, and merely that. Globally, leaf uptake is the dominant COS sink and there is no evidence of COS re-emission from leaves (see Line 16–17 on Page 2 in the revised version). Soil emissions of COS do exist and are treated in details in the paragraph that follows this one. But globally, the soil is still a major sink of COS second only to leaf uptake. We have made revisions in Line 21–27 on Page 2 to clarify this argument.

Page 3, line 14: “As the uptake of CO and COS is due to microbial activity” the uptake of CO and COS can also be related to physical or chemical processes (abiotic processes), it is better to add “possibly” or “partly” in front of “due to”.

We have added “mainly” before “due to”. We agree with the referee on the existence of abiotic uptake of COS and CO. However, abiotic uptake is unlikely to play a substantial role for soil COS or CO flux, as is repeatedly confirmed by sterilization and selective enzyme inhibition experiments. We have added references in Line 1–2 on Page 4 to support such claim.

Page 5, line 1: “air was sampled for 9-10 minutes” what is the gas residence time in the chamber? The sampling time period should be larger than the residence time. What is the chamber outlet position? Please provide more detailed information about the chamber configuration.

We have added these details on the chamber configuration as requested by the referee. The sam-

pling period was indeed much larger than the residence time. See Line 12–13 on Page 6 for the calculated residence time, and Line 5 on Page 6 for the chamber outlet position.

Page 5, line 15: “To prevent pressure-related flux biases, . . .” according to this sentence, a vent at the top of the chamber exists during the sampling time period, then how to keep the mass balance inside the chamber, please give a further explanation while interpreting the Eq. (1) (Page 5, line 24).

In Eq. (1) the flow rate is always the flow rate at the inlet (clarified on Line 29 on Page 6). The residual flow that is dissipated at the top vent carries the same concentration as the outlet flow, both equal to the mean headspace concentration within the chamber. Therefore, this residual flow does not affect the mass balance as long as the inlet flow rate is used in flux calculation. We have explained this on Line 19–20 on Page 6.

Page 24: For Figure 6, why the flux ratios come to a plateau at higher temperature bins? Does this ratio to some extent reflect the relative effects between biotic and abiotic processes in COS/CO fluxes? Please give explanations about the meanings/implications of the flux ratios.

The asymptote values of flux ratios may reflect the uptake to respiration sensitivity behavior of the microbial groups that are active at higher temperature. We have now devoted one paragraph to explain what this feature could mean and what its cause could be. In addition, we have acknowledge the possible influence from abiotic production. See Line 19–33 on Page 11.

Technical corrections:

Page 2, line 4: Please add “the” before “Earth’s radiative balance”.

Corrected. (Line 9 on Page 2)

Page 2, line 17: Please change “over” to “from”.

This sentence has been completely rewritten to address an issue raised previously. (Line 25–27 on Page 2)

Page 2, line 30: It seems that the sentence “These phenomena have presented . . .” needs to be further edited as it reads awkwardly.

The sentence has been rewritten. (Line 4–6 on Page 3)

Page 3, line 15: Please re-edit this part of “as CO and COS are consumption processes” to make it more clear to be understood.

We have rewritten the whole sentence and the previous one to improve clarity. See Line 1–4 on Page 4.

Page 4, line 1: What does “(ibid)” mean?

It literally means “in the same reference (aforementioned)”. We have replaced it with the proper citation entry. See Line 21 on Page 4.

Page 6, line 15: Please change “in” to “of”.

Corrected. (Line 19 on Page 7)

Page 7, line 7: Please add “, respectively.” after “SC2”.

Added. (Line 22 on Page 8)

Anonymous Referee #2

This study provides much-needed in situ measurements of the soil fluxes of COS and CO. Both are important trace gases for chemistry & climate impacts and as tracers for photosynthesis and anthropogenic activity, respectively. The data set is relatively rich, despite some significant gaps, and interesting trends in diurnal and seasonal patterns and relationships with environmental drivers are observed. The study has the potential to make a good contribution to the scant literature on the soil-atmosphere exchange of these trace gases. The paper suffers from a lack of specific language that is well supported by references and data. Specific instances of this are mentioned here and highlighted in the specific comments below. The paper would benefit from a greater analysis of the data at hand and less conjecture at mechanistic drivers that are not well tested by the analysis. The paper requires revisions before acceptance.

We thank the referee's critical comments on our manuscript. These comments have been very helpful in improving the quality and clarity of our manuscript.

General comment:

The paper should be more careful about the discussion and conclusions regarding the role of microbial activity in the COS and CO soil sink. While this is supported by the extant literature, this study is not capable of resolving respiration due to microbial activity from plant-derived respiration. Furthermore, both COS and CO can have significant production terms. Therefore, ratios of COS and CO to CO₂ are not necessarily a simple measure of the ratio of the COS or CO-consuming microbiota to the total microbial activity. I would suggest the text is revised to acknowledge the limitations early on.

We have revised the manuscript to confront with the limitations in the interpretation of results early on. We have addressed the existence of autotrophic respiration but noted that it is unlikely to be a large fraction since vegetation was removed from the soil plots. We have also acknowledged influences from COS or CO production on the patterns of flux ratios. Please find specific changes in the detailed response below.

Specific comments:

P2L5: what does actively engaged mean for a gas?

We have rephrased it to clarify its meaning: 'engaged actively' -> 'participates'. See Line 11 on Page 2.

P2L7: appropriate references for soil microbes should be included here such as:

- 1. Saito, M., Honna, T., Kanagawa, T. & Katayama, Y. Microbial Degradation of Carbonyl Sulfide in Soils. Microbes Environ. 17, 32–38 (2002).*
- 2. Ogawa, T. et al. Carbonyl sulfide hydrolase from thiobacillus thioparus strain THI115 is one of the β -carbonic anhydrase family enzymes. J. Am. Chem. Soc. 135, 3818–3825 (2013).*
- 3. Kato, H., Saito, M., Nagahata, Y. & Katayama, Y. Degradation of ambient carbonyl sulfide by Mycobacterium spp. in soil. Microbiology 154, 249–255 (2008).*

We have added these references as requested. We thank the referee's suggestion. (Line 13–14 on Page 2)

P2L19: I don't find "plant + soil" to be written clearly enough.

It means that the total ecosystem COS flux is the sum of leaf and soil COS fluxes. The sentence has been revised for clarity. (Line 27–29 on Page 2)

P2L22: essential with regards to what?

Revised: “. . . essential to the prediction of soil COS fluxes”. See Line 10 on Page 3.

P2L33: would be useful to give a clearer idea of the importance of soil uptake with respect to photosynthesis (explored in Whelan et al., 2016)

We have clarified the importance of accounting soil COS uptake for accurate photosynthesis estimates. See Line 11–14 on Page 3.

P3L3: How is this statement justified: “The microbial types, enzymes, and metabolic pathways involved are, however, much more diverse than those of COS uptake”? The references only relate to CO.

We agree that the claim that microbial types involved in CO uptake are more diverse than those in COS uptake is not backed by evidence. And the classification of enzymes can be subjective and does not warrant a straightforward comparison of the diversity of enzymes involved in COS and CO uptake. We can only be certain that the metabolic pathways involved are more diverse for CO uptake. We have therefore corrected the sentence and added the reference Ogawa et al. (2013) for COS uptake.

“Soil CO uptake is primarily due to microbial activity (Inman et al., 1971; Conrad and Seiler, 1980; Whalen and Reeburgh, 2001) and involves more diverse metabolic pathways compared with those in COS uptake (Mörsdorf et al., 1992; King and Weber, 2007; Ogawa et al., 2013).” (Line 17–19 on Page 3)

P3L6: I wouldn't suggest that CO and COS uptake are similar here because of their broad optima. That is quite common. Would be more useful to state what optima are and how different this site is. For example, temperatures are likely well below optima for both gases.

Agreed. This clause has been removed.

P3L8: Is there a reference to say most soils are above their optimal moisture levels in the average? Otherwise this statement seems very subjective and unsupported. Seems entirely unnecessary to make this statement in any case.

We agree that this statement was inaccurate. It has now been corrected. See Line 23–24 on Page 3.

P3L11: Should indicate whether biotic or abiotic or unknown.

This is attributed to the abiotic production. This has been clarified in Line 29–31 on Page 3 in the revised version.

P3L15–24: The expectations for COS and CO consumption and their link to CO₂ respiration could be clarified and supported by citations.

We have clarified this and added supporting references. See Line 2–3 and Line 24–26 on Page 3, and Line 2–3 on Page 4.

P4L1: is it really necessary to use “ibid” and not just spell out what you mean?

This has been spelled out. (Line 21 on Page 4)

P4L27: add citation for CO photochemical production

Added. (Line 15 on Page 5)

P4L29: COS emission from blank chamber. Was the temperature dependence of this tested? Can you be confident that accounting for it in the blank experiments (should be described in more detail) is sufficient? Was this only evaluated for one chamber, or both?

1. We did not find temperature dependence of the blank chamber COS flux at this site. Note that daily air temperature variation was small, but the same chamber was previously used at a southern Californian site with strong diurnal temperature variations and we did not find the blank chamber to show temperature-dependent emissions. See Line 28–32 on Page 5 and Sun et al. (2016) cited therein.

2. When accounting for the blank chamber COS effect, we have also added the uncertainty of the

blank chamber COS flux to that of soil COS flux following the Gaussian error propagation. See Line 33 on Page 5.

3. The blank tests were conducted with soil chamber 1 only. We assumed chamber 2 to have the same effect as chamber 1 because they had identical chamber materials. See Line 1–2 on Page 6.

We have rewritten the description of the blank tests with more relevant details. See from Line 22, Page 5 to Line 2, Page 6.

P4L30: define what you mean by “effect”

The “effect” has been defined as “apparent fluxes . . . from the blank chamber”. (Line 25 on Page 5)

P5L33: Comment on whether the issue could have been due to condensation cycles driven by A/C

Air conditioning was not used in the instrument room. And we did not find these issues to be related to condensation in the chamber either. We have added these details to the text. See Line 6 on Page 5 and Line 3–4 on Page 7.

P7L5: Diurnal trend in CO, could it be from CO production during day? I do see a diurnal trend in COS, at least SC1, that is weaker than CO, but not insignificant. This is brought up on P9L1, but should be brought up before any discussion of processes (eg microbial activity) driving net fluxes is undertaken (eg page 8). The possibility of the diurnal CO source conflicts with the statements made in P8L6 about steady if any production rates.

1. We have made revisions to acknowledge the possibility of daytime CO production early on in the Results. See from Line 32, Page 8 to Line 2, Page 9.

2. We did not find any statistically significant difference between daytime and nighttime mean soil COS uptake for each month. In the diurnal trends of COS flux, there may be a few spikes deviating from the background trend that are statistically significant according to the *t*-test for equal means, but the overall diurnal trends remain too weak to be declared concrete.

However, we have acknowledged that there was a weak diurnal trend in COS deposition velocity. See Line 10–12 on Page 8.

3. The statement made in Line 6 on Page 8 in the previous version has been corrected. See Line 27–29 on Page 9.

P7L18: One cannot necessarily conclude that microbes control CO flux through correlation with CO₂.

This was only suggestive. We now consider this point to be better addressed in the Discussion than in the Results. We have revised the sentence to give only a factual account without making any speculation. See Line 5–7 on Page 9.

P7L28: What does “late growing season” refer to here? What statistical test was used to assess this and over which periods? It appears that there is a trend in increasing net COS uptake flux/deposition velocity over the time period.

1. “late growing season” refer to the whole campaign period (July to November). This has been revised in Line 9 on Page 9.
2. We have carried out two-sample *t*-tests for equal means to test the difference between night-time and daytime fluxes. The differences do not pass a significance level of 0.05 for all months except July. The peculiar pattern of daytime dip in CO₂ flux in July is actually statistically significant according to the *t*-test. This has been corrected in Line 20–24 on Page 9 in the manuscript.

To support the lack of strong temperature dependence of CO₂ flux at the daily timescale, we refer to the daily Pearson correlation values between soil CO₂ flux and soil temperature. A histogram of the correlation values has been added to the Supplement. See Line 17–20 on Page 9, and Fig. S8 in the supplement.

3. We have acknowledged that there was a weak increasing trend in COS uptake over the time period of the campaign. See Line 3–5 on Page 8.

P7L29: Ecosystem fluxes of CO₂ on seasonal timescales have non-negligible contributions of photosynthetically derived contributions of plants through the rhizosphere. How does this study account for soil respiration derived from forest photosynthates (microbial, but often different communities than “bulk” soils) and root respiration? There is an extensive literature on hysteresis in diurnal patterns in soil respiration that should be cited as one possible explanation for the observations here.

We are unable to quantify autotrophic contribution to soil respiration with the data we have.

However, because the soil plots were removed of any ground vegetation (see Line 17 on Page 5), we assumed the autotrophic components to be a much smaller fraction than soil plots that had understory plants. This notion is also supported by the smaller August soil respiration ($4 \mu\text{mol m}^{-2} \text{s}^{-1}$) in our study compared with the higher August soil respiration ($6 \mu\text{mol m}^{-2} \text{s}^{-1}$) in Pumpanen et al. (2015). Even though there could be remnant roots of the understory plants in the soil, respiration activities from them would rely on photosynthate input from a tree in a distance and would likely be small.

We have added relevant discussion in section 4.2. See Line 19–25 on Page 12.

P7L29: Statements of significance should be accompanied by relevant statistics throughout the text.

Here we have corrected this statement to acknowledge that the daytime dip in CO_2 flux in July is actually a statistically significant feature according to the t -test. See Line 20–24 on Page 9.

P7L18: Possibility that daytime production caused reduction in apparent daytime deposition velocity could be brought up here and addressed instead of waiting until discussion.

Agreed. We have now addressed this point in the Results. See from Line 32, Page 8 to Line 2, Page 9.

P8L3: I'm not sure what 'coexist' means here. Soils are sources and sinks of both, but this makes it sound like there is a connection, when that is not what these papers necessarily show.

We did not intend to suggest a connection between sources and sinks with the word “coexist”. We have revised the sentence for clarity. See Line 27 on Page 9.

P8L27: Only references to data, not models should be given for citations of temperature optima.

Agreed. The citations that refer to models have been removed. See Line 14–16 on Page 10.

P8L31: Is this a given? “and that temperature and moisture co-vary in natural conditions”

We have removed this sentence.

P9L13 & Figure 5/6: The steep decline in F_{CO_2}/R and F_{CO}/R are driven by Oct/Nov declines in R that occur at that low temperature (Fig 4 shows that only R is temperature dependent and is thus driving Fig 6 trends). The possibility that plant-derived inputs are significantly reduced at that time, causing R to fall, must be addressed before suggesting any shifts in CO_2 - and COS -consuming microbial groups. Even in a system without plants, it would be hard to argue that modest increases in CO and COS uptake and large decreases in CO_2 emissions were the result of a less active microbial community but at the same time a significant increase in activity of strong CO and COS consumers. These points are alluded to in the P10 Pumpanen reference, but should play a more central role in the data interpretation as “autotrophic” contributions to soil respiration may be the most important factor in the gas ratios (instead of soil microbial activity).

We agreed with the referee on the possibility of this pattern been partially attributed to the reduction in autotrophic respiration. However, as being stated before, autotrophic respiration was likely a small fraction at our soil plots because there was no ground vegetation, and also the fluxes in our study were consistently smaller than those reported in Pumpanen et al. (2015). We have added relevant discussion on this in Line 19–25 on Page 12.

P10L23: R may not be a mechanistic predictor for COS soil uptake, but can state that in this study does a well enough without resolving the drivers

Agreed. We used the word ‘predictor’ in its statistical sense. To avoid confusion we have clarified it as ‘statistical predictor’. See Line 5 on Page 13.

P11L20: I would hesitate to draw conclusions about microbial drivers from the data generated in this study.

The sentence has been revised. See Line 2–4 on Page 14.

Table 2: Units are needed, especially because it is unclear if columns COS and CO are mole fractions or fluxes. What does n/a mean here?

Units have been added to the quantities shown on rows and columns as suggested. For pairs which we do not expect a mechanistic reason for their correlation, for example, COS flux and CO concentration, the correlation values were originally masked with “n/a”. We have decided to show these values in the revised version but added a caveat for their interpretation in the table

footnote.

Figure 2: soil temperature plots should all be on same y axis

The figure has been changed as requested.

Figure 2-3: trends would be easier to see if averaging in 1-2 hour bins. The current averaging shows large variability on the 30-min scale that does not look physically meaningful, especially in Oct/Nov

We indeed averaged the trends in one-hour bins. This has been clarified in the captions of both figures. We did not choose two-hour averaging because it would weaken the diurnal trends in CO fluxes but do little to help with the wiggling random noise in the Oct/Nov trends.

Figure 5: What is the take-away message here?

The relationships between COS and CO₂ fluxes and between CO and CO₂ fluxes are modulated by soil temperature. Changes in the soil temperature shifts the slope and forms different branches. This figure is necessary and without which the meaning in Figure 6 cannot be properly conveyed.

Table S1: which rows to columns 1-6 correspond to?

Columns 1-6 corresponded to all rows. To avoid confusion, we have filled the values in all rows.

Figure S1: not clear how figures to right and left relate to each other. Caption should be more descriptive. What is a blank chamber test? Explain. The explanation of units is not sufficient.

We have made the following changes to improve the readability of this figure:

1. The figure has been rearranged as top and bottom panels to better distinguish between the blank chamber fluxes and moss layer fluxes.
2. For each panel, units have been added under the descriptions of flux terms on the y-axes.
3. A blank chamber test is for testing the apparent fluxes from chamber materials. This has been explained in the caption.
4. We have made the caption more elaborate as suggested.

Figure S2: use statistics to describe extent of correlation instead of statements like “relatively well correlated”

We have added the Pearson correlation values and 2-tailed p -values in parentheses for statistical descriptions. However, we think the description in plain words (rephrased to “weakly correlated”) makes it easier for the readers to assimilate the message, and hence, should be retained. The sentence has been revised to:

“COS uptake do not show a correlation with COS concentration ($r = 0.005$, $p = 0.738$), whereas CO uptake is weakly correlated with CO concentration ($r = -0.468$, $p < 1 \times 10^{-16}$).”

Additional revisions

1. The study has received support from the NOAA contract NA13OAR4310082 (to H.C.). This funding source was accidentally missed out in the Acknowledgements in the previous version. It has now been added.
2. These parts have been improved for clarity and readability without changing the messages (unless otherwise noted in the response above):
 - Abstract
 - Introduction
 - Results
3. Due to a recent update of the plotting software `matplotlib`, the blue color on some figures may differ from the previous version. However, the figure contents remain the same unless otherwise noted in the response above.

Soil fluxes of carbonyl sulfide (COS), carbon monoxide, and carbon dioxide in a boreal forest in southern Finland

Wu Sun¹, Linda M. J. Kooijmans², Kadmiel Maseyk³, Huilin Chen^{2,7}, Ivan Mammarella⁴, Timo Vesala^{4,5}, Janne Levula^{4,5,6}, Helmi Keskinen^{4,5,6}, and Ulli Seibt¹

¹Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA 90095-1565, USA

²Centre for Isotope Research, University of Groningen, Nijenborgh 6, 9747 AG Groningen, The Netherlands

³School of Environment, Earth and Ecosystem Sciences, Open University, Milton Keynes MK7 6AA, United Kingdom

⁴Department of Physics, P.O. Box 68, FI-00014, University of Helsinki, Finland

⁵Department of Forest Sciences, P.O. Box 27, FI-00014, University of Helsinki, Finland

⁶Hyytiälä Forestry Field Station, University of Helsinki, 35500 Korkeakoski, Finland

⁷Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO, USA

Correspondence to: W. Sun (wu.sun@ucla.edu) and U. Seibt (useibt@ucla.edu)

Abstract. Soil is a major contributor to the biosphere–atmosphere exchange of carbonyl sulfide (COS) and carbon monoxide (CO). COS is ^[.1]a tracer to quantify terrestrial photosynthesis based on the ^[.2]coupled leaf uptake of COS and ^[.3]CO₂, but ^[.4]such use requires separating soil COS flux^[.5], which is unrelated to photosynthesis, from ecosystem COS uptake. For CO, soil is a ^[.6]significant natural sink that influences the tropospheric CO budget. ^[.7]In the boreal forest, magnitudes and variabilities of soil COS and CO fluxes remain poorly understood. We measured hourly soil fluxes of COS, CO, and CO₂ ^[.8]over the 2015 late growing season (July to November) in a Scots pine forest in Hyytiälä, Finland. The soil acted as a net sink of COS and CO^[.9], with average uptake rates around 3 pmol m^{−2} s^{−1} for COS ^[.10]and 1 nmol m^{−2} s^{−1} for CO, respectively. Soil respiration showed seasonal dynamics controlled by soil temperature, peaking ^[.11]at around 4 μmol m^{−2} s^{−1} ^[.12]in late August and September and dropping to 1–2 μmol m^{−2} s^{−1} in October. In contrast, seasonal variations of COS and CO fluxes were weak and mainly driven by soil moisture changes through diffusion limitation. COS and CO fluxes did not appear to respond to temperature, although they both correlated well with soil respiration in specific temperature bins. ^[.13]However, COS : CO₂ and

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⁴removed: this use requires the

⁵removed: to be well quantified

⁶removed: main sink in natural environments

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¹¹removed: in late August and September with fluxes

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¹³removed: We found that COS:CO₂ and CO:CO₂ flux ratios were modulated by temperature, possibly indicating

CO : CO₂ flux ratios increased with temperature, suggesting possible shifts in active COS and CO-consuming microbial groups. Our results show that soil COS and CO ^[..¹⁴]fluxes do not have strong variations over the late growing season in ^[..¹⁵]this boreal forest, and can be ^[..¹⁶]represented with the fluxes during the photosynthetically most active period. Well characterized and relatively invariant soil COS fluxes strengthen the case for using COS as a ^[..¹⁷]photosynthetic tracer in boreal forests.

1 Introduction

^[..¹⁸]

Soil is a significant sink of the trace gases carbonyl sulfide (COS) and ^[..¹⁹]carbon monoxide (CO) (Conrad, 1996; Schlesinger and Bernhardt, 2013), contributing to 26–33% of the ^[..²⁰]global COS sink (Berry et al., 2013; Launois et al., 2015b), and 10–15% of the ^[..²¹]global CO sink (Conrad and Seiler, 1985; Khalil and Rasmussen, 1990; King and Weber, 2007). ^[..²²]In the atmosphere, COS is a major precursor to the stratospheric sulfate aerosols that exert a negative radiative forcing (Brühl et al., 2012; Kremser et al., 2016), with the cooling effect greater than the warming potential of anthropogenic COS, and CO affects concentrations of methane and other important greenhouse gases by regulating their sinks through the OH radical (Daniel and Solomon, 1998). Soil fluxes influence the mean concentrations and distributions of COS and CO ^[..²³]in the atmosphere, and consequently atmospheric chemical processes and the Earth’s radiative balance.

COS ^[..²⁴]participates in land carbon cycle processes due to its chemical similarities to CO₂ ^[..²⁵](Kettle et al., 2002; Montzka et al., 2007; Berry et al., 2013). In leaf chloroplasts and soil microbes, COS as a substrate of carbonic anhydrase is hydrolyzed irreversibly to CO₂ and H₂S ^[..²⁶](Protoschill-Krebs and Kesselmeier, 1992; Protoschill-Krebs et al., 1996; Stimler et al., 2010, 2011; Kesselmeier et al., 1999; Saito et al., 2002; Kato et al., 2008; Ogawa et al., 2013). The hydrolysis occurs in parallel to CO₂ hydration^[..²⁷], the main physiological function of carbonic anhydrase (Badger and Price, 1994; Henry, 1996). Because of the ^[..²⁸]irreversible COS hydrolysis in leaves, COS is taken up

¹⁴removed: uptake

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¹⁸removed: Soil is an important contributor to the atmospheric budgets of many bioactive trace gases , including

¹⁹removed: CO (Conrad, 1996; Schlesinger and Bernhardt, 2013). Globally, soil acts as a significant sink of COS and CO, with recent estimates at

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²⁴removed: is a reduced sulfur gas engaged actively in land biogeochemical

²⁵removed: (Kettle et al., 2002; Montzka et al., 2007; Berry et al., 2013)

²⁶removed: as a substrate of carbonic anhydrase (Protoschill-Krebs and Kesselmeier, 1992; Protoschill-Krebs et al., 1996; Stimler et al., 2010, 2011; Kesselmeier et al., 1999), a ubiquitous family of enzymes catalyzing

²⁷removed: (Badger and Price, 1994; Henry, 1996)

²⁸removed: parallel uptake of COS and

concurrently with CO₂ through [..²⁹] stomata and is not emitted back from leaves (Sandoval-Soto et al., 2005; Stimler et al., 2010). This allows COS to serve as a tracer to quantify terrestrial photosynthesis independently from respiration
5 [..³⁰](Montzka et al., 2007; Campbell et al., 2008; Seibt et al., 2010; Wohlfahrt et al., 2012; Asaf et al., 2013; Berry et al., 2013; Billesbach et al., 2014; Maseyk et al., 2014).

Globally, the largest COS sink is leaf uptake, followed by soil uptake (Berry et al., 2013), whereas the major COS sources include ocean emissions from biogenic and photochemical processes [..³¹](Ferek and Andreae, 1984; Launois et al., 2015a), and anthropogenic emissions from industrial activities and biomass burning (Campbell et al., 2015). Since ocean
10 COS emissions are geographically separated from the terrestrial [..³²] COS sinks (leaf and soil), [..³³] and anthropogenic emissions are usually concentrated as point sources, [..³⁴] the spatial separation of dominant COS sources and sinks enables us to constrain land COS fluxes, and hence photosynthetic carbon uptake, from atmospheric COS observations (Campbell et al., 2008; Berry et al., 2013; Hilton et al., 2015). However, [..³⁵] for the use of COS as a photosynthetic tracer, soil COS flux, which is unrelated to photosynthesis, needs to be understood and separated from the [..³⁶] ecosystem
15 COS flux that is the sum of leaf and soil fluxes (Maseyk et al., 2014; Commane et al., 2015; Wehr et al., 2017).

Soils vary from COS sinks to sources depending on physical and biogeochemical conditions [..³⁷](Maseyk et al., 2014; Whelan and Rhew, 2015; Whelan et al., 2016; Devai and DeLaune, 1995). Aerated upland soils are primarily weak COS sinks, whereas anoxic wetland soils are COS sources (Whelan et al., 2013). In unmanaged upland soils, the uptake rates range from 0 to 12 pmol m⁻² s⁻¹ in field studies [..³⁸](e.g., Steinbacher et al., 2004; Yi et al., 2007;
20 Berkelhammer et al., 2014). Soil COS uptake depends nonlinearly on soil temperature and moisture, with optimal conditions that maximize the uptake [..³⁹](Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008; Whelan et al., 2016). Soil COS uptake also correlates positively with soil respiration (Yi et al., 2007; Berkelhammer et al., 2014; Sun et al., 2016), suggesting a link through microbial activity between them.

It has been assumed that soil COS flux is a minor component in the total COS budget of non-wetland ecosystems when using COS for photosynthesis measurements (e.g., Asaf et al., 2013). However, recent discoveries challenge this

²⁹removed: leaf stomata , COS has emerged as a promising

³⁰removed: (Sandoval-Soto et al., 2005; Montzka et al., 2007; Campbell et al., 2008; Stimler et al., 2010; Seibt et al., 2010; Wohlfahrt et al., 2012; Asaf et al., 2013; Berry et al., 2013).

Among the major sources of COS ,

³¹removed: (Ferek and Andreae, 1984; Launois et al., 2015a) are the largest but are

³²removed: sinks of COS (plant

³³removed: whereas anthropogenic emissions and biomass burning (Campbell et al., 2015) are smaller and

³⁴removed: which can be constrained with emission inventory data. This premise enables photosynthesis to be inferred from surface COS fluxes over regional to global scales (Campbell et al., 2008; Berry et al., 2013; Hilton et al., 2015)

³⁵removed: soil COS fluxes that are unrelated to photosynthetic uptake of CO₂ need to be quantified,

³⁶removed: surface (plant + soil) COS flux (Maseyk et al., 2014; Billesbach et al., 2014; Commane et al., 2015)

³⁷removed: (Maseyk et al., 2014; Whelan and Rhew, 2015; Devai and DeLaune, 1995), and including both production and consumption processes in soil-atmosphere exchange models is essential (Sun et al., 2015; Ogée et al., 2016)

³⁸removed: (e.g., Steinbacher et al., 2004; Yi et al., 2007; Berkelhammer et al., 2014). The uptake activity

³⁹removed: (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008; Whelan et al., 2016). However, strong

assumption. Strong net emissions of COS have ^[..⁴⁰] been observed from cropland soils at high ^[..⁴¹] temperature (Maseyk et al., 2014; Whelan et al., 2016) and in an alpine grassland under solar radiation (Kitz et al., 2017), ^[..⁴²] highlighting the crucial role of abiotic COS production in soil COS flux. In semi-arid ecosystems, the rewetting of leaf litter after rainfall can stimulate pulses in COS uptake that temporarily overwhelm leaf COS uptake (Sun et al., 2016). ^[..⁴³] Understanding the factors that control soil COS flux ^[..⁴⁴] variability is therefore essential to the prediction of soil COS fluxes. In ecosystems where soil COS flux makes up a potentially significant and variable fraction of the ecosystem COS budget, failure to account for soil COS flux may lead to significant biases in the photosynthesis estimates from the COS approach (Whelan et al., 2016). Ensuring accurate photosynthesis measurements from the COS approach requires understanding how soil COS flux is controlled by soil temperature, moisture, and biotic factors^[..⁴⁵].

^[..⁴⁶] Soil CO flux is also the net balance between ^[..⁴⁷] concurrent uptake and production activities ^[..⁴⁸] (Conrad and Seiler, 1980, 1985; Sanhueza et al., 1998; King, 1999; King and Crosby, 2002; Bruhn et al., 2013; van Asperen et al., 2015; Pihlatie et al., 2016). Soil CO uptake is primarily due to microbial activity ^[..⁴⁹] (Inman et al., 1971; Conrad and Seiler, 1980; Whalen and Reeburgh, 2001) and involves more diverse metabolic pathways compared with those in COS uptake (Mörsdorf et al., 1992; King and Weber, 2007; Ogawa et al., 2013). The key environmental factors controlling CO uptake rates ^[..⁵⁰] include soil moisture and temperature (Conrad and Seiler, 1985; King, 1999; Yonemura et al., 2000a). Similar to COS uptake, there can exist an optimal condition of soil moisture and temperature ^[..⁵¹] that maximizes the soil CO uptake (Moxley and Smith, 1998; King, 1999), but this feature has not been evaluated ^[..⁵²] extensively on different soil types. The moisture optimum can sometimes be lower than the annual ^[..⁵³] soil moisture range in natural conditions (e.g., King, 1999), and thus may not be well defined in field observations. Soil CO uptake has also been shown to correlate with soil respiration in the laboratory (Hendrickson and Kubiseski, 1991), but such correlation is yet to be investigated in field conditions.

⁴⁰removed: also

⁴¹removed: temperatures

⁴²removed: though the mechanisms are little understood

⁴³removed: These phenomena have presented challenges to the simplifying assumption that

⁴⁴removed: is small compared with leaf COS uptake (Asaf et al., 2013). Determining

⁴⁵removed: is needed when using COS to infer photosynthesis

⁴⁶removed: Soil-atmosphere exchange of CO

⁴⁷removed: coexisting

⁴⁸removed: (Conrad and Seiler, 1980, 1985; Sanhueza et al., 1998; King, 1999; King and Crosby, 2002; Bruhn et al., 2013; van Asperen et al., 2015; Pihlatie et al., 2016). Soil uptake of CO

⁴⁹removed: . The microbial types, enzymes, and metabolic pathways involved are, however, much more diverse than those of COS uptake (Mörsdorf et al., 1992; King and Weber, 2007). Field studies and laboratory experiments have identified soil moisture and temperature as key

⁵⁰removed: (Conrad and Seiler, 1985; King, 1999; Yonemura et al., 2000a). Soil CO uptake may exhibit an optimum condition of

⁵¹removed: (Moxley and Smith, 1998; King, 1999), a feature broadly similar to that of soil COS uptake . However,

⁵²removed: with extensive measurements on different soils. In field conditions, the optimum moisture can

⁵³removed: range of soil moisture , thus higher moisture more likely inhibits soil CO uptake . Soil may also show net emissions of CO

. The production of CO in soil was

Soil can show net CO emissions. CO production in soils has been considered largely abiotic ^[..⁵⁴] (Conrad and Seiler, 1985; Zepp et al., 1997), but microbes on fine roots have also been ^[..⁵⁵] reported to contribute significantly to CO production in the laboratory (King and Crosby, 2002). Soil CO ^[..⁵⁶] emissions generally increases with temperature and solar radiation ^[..⁵⁷] in field conditions (King, 1999; Yonemura et al., 2000a; Zepp et al., 1997; van Asperen et al., 2015), indicating dominant contributions from photochemical and thermal production. It remains poorly understood how environmental factors control the variability of soil CO flux in the field, because most studies on soil CO flux are laboratory incubations of altered soil samples or short-term, sporadic field experiments.

^[..⁵⁸] In general, soil fluxes of COS and CO ^[..⁵⁹] are controlled by gas transport in the soil column that responds to soil moisture (e.g., Sun et al., 2015; Yonemura et al., 2000a), and by in situ reactions including uptake and production. Both COS and CO uptake processes are mainly due to microbial activity ^[..⁶⁰] (Kesselmeier et al., 1999; Kato et al., 2008; Bartholomew and Alexander, 1979; Whalen and Reeburgh, 2001) and may correlate with soil respiration through microbial activity (Yi et al., 2007; Berkelhammer et al., 2014; Hendrickson and Kubiseski, 1991), whereas their production processes are predominantly abiotic and should respond to physical drivers. ^[..⁶¹] Similar to other ecosystems, we hypothesize ^[..⁶²] that soil temperature, moisture, and microbial activity ^[..⁶³] are the main drivers of soil COS flux in boreal forests, but also with responses unique to this type of ecosystem. Despite limited knowledge ^[..⁶⁴] of soil CO processes, we expect similarities in the responses of soil CO flux to soil physical variables and microbial activity compared to the responses of COS flux, based on the reactive transport mechanism in the soil column ^[..⁶⁵] (Sun et al., 2015; Ogée et al., 2016; Yonemura et al., 2000b). Here we report continuous field measurements of soil COS, CO, and CO₂ fluxes in a Scots pine forest in southern Finland over the late growing season (July to November). We explore diurnal and seasonal variabilities of the fluxes and ^[..⁶⁶] identify the major physical and biological drivers of the variabilities.

⁵⁴removed: (Conrad and Seiler, 1985; Zepp et al., 1997), but later,

⁵⁵removed: found

⁵⁶removed: production

⁵⁷removed: (King, 1999; Yonemura et al., 2000a; Zepp et al., 1997; van Asperen et al., 2015).

⁵⁸removed: This study aims to quantify soil

⁵⁹removed: fluxes in a boreal forest and identify the major physical and biological drivers of these fluxes. As the uptake of CO and COS is

⁶⁰removed: , these processes may also be linked to the production of CO₂ by microbial respiration

⁶¹removed: However, as CO and COS are consumption processes they may also share similarities in their response to environmental drivers that differ from CO₂ production. Based on previous studies

⁶²removed: soil COS flux to respond to soil

⁶³removed: indicated by heterotrophic respiration. Understanding soil COS fluxes will help determine the role of soil in ecosystem COS budget in support of COS-based estimates of gross primary productivity in the boreal forest

⁶⁴removed: on

⁶⁵removed: (e.g., Sun et al., 2015)

⁶⁶removed: their responses to soil environmental parameters

2 Materials and methods

2.1 Site description

25 Field measurements were made at the SMEAR II site (Station for Measuring Forest Ecosystem–Atmosphere Relations) at Hyytiälä Forestry Field Station of the University of Helsinki (61.845°N, 24.288°E, 181 m above sea level). The station features a largely homogeneous stand of Scots pine (*Pinus sylvestris*) planted in 1962 (Suni et al., 2003; Vesala et al., 2005). The forest floor is covered by mosses (*Dicranum polysetum*, *Hylocomium splendens*, and *Pleurozium schreberi*) and understory herbs including bilberry (*Vaccinium myrtillus*) and lingonberry (*Vaccinium*
5 *vitis-idaea*) (Kulmala et al., 2011). The climate is boreal, with 30-year average January and July temperatures of −7.2°C and 16.0°C, respectively (Pirinen et al., 2012). The average annual precipitation is 711 mm, with summer and fall receiving somewhat more than winter and spring [..⁶⁷] (Pirinen et al., 2012). Meteorological and ancillary data such as surface pressure, air temperature, relative humidity, radiation, precipitation, and soil temperature and moisture are continuously monitored at the SMEAR II site (see Hari and Kulmala, 2005 for description of the site
10 infrastructure). These data are available online at <http://avaa.tdata.fi/web/smart/smea/>.

Soils at the site are podzols of depths varying from 0.5 to 1.6 m, developed from glacial deposits. The O horizon is a porous mor-humus layer laden with fine roots and mycorrhizae, distinct from the mineral soil underneath. [..⁶⁸
]The thickness of the O horizon varies from 1 to 5 cm (Pihlatie et al., 2007; Pumpanen et al., 2008), [..⁶⁹]the bulk density is 0.10 g cm^{−3}, and [..⁷⁰]the porosity is 0.67 m³ m^{−3} (Pumpanen and Ilvesniemi, 2005). The O horizon is
15 highly acidic (pH = 2.9 to 3.6) and rich in carbon content (31–45 wt%). The mineral soil underneath is of sandy loam texture, but also has a high fraction of gravels and stones (Haataja and Vesala, 1997). The A horizon is 4–8 cm thick, and has [..⁷¹]the porosity of 0.61 m³ m^{−3} and a carbon content of 3–6 wt%. Beneath the A horizon, porosity and carbon content decrease with depth. The mineral soil is less acidic than the humus layer, with pH around 4 to 5.

20 2.2 Experimental setup

A quantum cascade laser spectrometer (QCLS, Aerodyne Research Inc., Billerica, MA, USA) was used to measure concentrations of COS, CO, CO₂, and H₂O at 1 Hz. The instrument has overall uncertainty (1 s.d.) of 7.5 ppt (parts per trillion) for COS, 3.3 ppb for CO, and 0.23 ppm for CO₂ (Kooijmans et al., 2016). An oil-free dry scroll pump (Varian TriScroll) was connected to the QCLS to pull the sampling air through the analyzer. The QCLS was
25 housed inside a small cabin that was not air conditioned. An automatic background correction was performed every

⁶⁷removed: (ibid.).

⁶⁸removed: Thickness

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⁷⁰removed: its

⁷¹removed: total

6 hours with an ultrahigh-purity ([..⁷²] > 99.999%) nitrogen cylinder to remove the curvature effect in the baseline spectra. An air purifier (Gatekeeper CE-500K-I-4R) was used to scrub trace amounts of CO from the cylinder air. The instrument was calibrated against three working standards that had been calibrated to the NOAA or WMO scale in the laboratory (Kooijmans et al., 2016).

Soil fluxes were measured in two automated soil chambers (LI-8100A-104, LI-COR Biosciences, Lincoln, NE, USA) modified to avoid COS emission artifacts from chamber materials and operated in a flow-through configuration (Maseyk et al., 2014). These modifications included replacing the chamber bowl and soil collar with stainless steel components, and removing or replacing other small COS-producing parts. Dark chambers were selected to prevent photochemical production of COS (e.g., Whelan and Rhew, 2015) or CO (e.g., van Asperen et al., 2015) at the soil surface during chamber measurements. The two chambers were placed in similar environments, about 10 m apart. The moss layer or any other vegetation was removed to expose the humus layer inside the chambers.

[..⁷³]

The sampling system used a multi-position valve (Valco Instruments Co., Inc.) to sample each soil chamber once per hour. Air was sampled from the open chamber for 3 minutes, then the chamber was closed and the headspace air was sampled for 9–10 minutes, followed by sampling from the open chamber for 2 minutes. Soil chamber 2 was added to the sampling system on 30 July 2015. Prior to this date, soil chamber 1 was measured twice per hour.

To ensure that the chamber materials do not show apparent fluxes that bias the measurements, we conducted blank chamber tests with soil chamber 1 at the start of the campaign. The chamber footprint was sealed off with a Teflon FEP film to exclude soil fluxes and measure only the fluxes from chamber materials. We found that the apparent fluxes of CO and CO₂ from the blank chamber were $0.00 \pm 0.10 \text{ nmol m}^{-2} \text{ s}^{-1}$ and $-0.05 \pm 0.15 \text{ } \mu\text{mol m}^{-2} \text{ s}^{-1}$, respectively (Fig. S1, Supplementary Information (SI)), and hence were not statistically different from zero. However, we found a small positive COS flux ($0.66 \pm 0.48 \text{ pmol m}^{-2} \text{ s}^{-1}$) that was statistically different from zero in a one-sample *t*-test ($t = 3.40$ and $p = 0.02$). We did not observe the blank chamber COS emissions to depend on temperature as in Maseyk et al. (2014), since daily temperature changes were small at the site. Because the same chamber was previously used at a site with strong diurnal temperature variations but did not show temperature-dependent COS emissions (Sun et al., 2016), we assumed the blank chamber COS flux to be constant throughout the campaign period. We therefore subtracted the mean blank chamber COS flux from the measured COS fluxes in both chambers, and included the uncertainty term from the blank chamber COS flux into the calculation of the overall flux uncertainty. In doing so, we also assumed soil chamber 2 to have the same blank chamber COS flux as soil chamber 1, since the chamber materials were the same.

⁷²removed: 99.99999

⁷³removed: In blank chamber tests at the start of the campaign, we found no significant effect in CO or CO₂ (Fig. S1, Supplement) but a small positive COS flux ($0.66 \pm 0.48 \text{ pmol m}^{-2} \text{ s}^{-1}$) that was statistically different from zero in a one-sample *t*-test ($t = 3.40$ and $p = 0.02$). We therefore subtracted this blank chamber COS effect from measured COS fluxes, and included the uncertainty term from the blank chamber.

The tubing connecting the chambers to the QCLS (Synflex 1/4") was flushed continuously to minimize wall effects for the sampled gases. The segment of inlet tubing inside the chambers was perforated to enhance the mixing of chamber air. The outlet tubing was pushed into the center of the chamber bowl, with a filter attached to it. Airflow into the chambers was provided by a diaphragm pump (KNF N811) with inlet at 0.5 m height in the vicinity of the chambers. The air flowing through the pump did not show enhanced COS or CO concentrations. The flow rates into the chambers were set to 1.5 standard liter per minute (slm) before, and 2.1 slm after 19 August 2015. Flow rates at the chambers, and pressure and flow rate at the pump inlet were checked during regular site visits. To correct for drifts, we interpolated the time series of chamber flow rate linearly from a set of discrete field measurements, including the measured flow rate values and the estimated values derived from linear correlations with pump flow rates and inlet pressure. The residence time of the air in the chamber was 3–4 minutes, as calculated from the chamber effective volume (6.1 L) and the flow rate.

In flow-through chambers, any imbalance between inlet and outlet flows creates pressurization in the chamber headspace that drives vertical advection in the soil column, leading to biases in measured fluxes (Lund et al., 1999). For soil fluxes, underpressure seems more problematic than overpressure, because it would siphon up the soil pore air that is usually enriched in CO₂ by a few orders of magnitude. To prevent pressure-related flux biases, we set the inlet flow slightly higher than the outlet flow, with the small residual flow (approx. 0.1 slm) equilibrated through the vent at the top of the chamber [..⁷⁴](Xu et al., 2006). The residual flow that was dissipated would not affect the mass balance calculation, because fluxes were always calculated using the flow rates measured at the inlet.

2.3 Flux calculation

Fluxes were calculated from the mass balance equation of chamber headspace concentrations during chamber closure. Assuming the chamber air is well mixed, the rate of change of headspace concentration of a gas species is the balance of the inlet flux, the outlet flux, and the soil flux. The inlet concentration is assumed to be the ambient concentration measured before chamber closure, and the outlet concentration is what the analyzer measures during chamber closure. We therefore obtain an equation of mass balance in the chamber,

$$V \frac{dC}{dt} = q(C_a - C) + FA \quad (1)$$

where C [mol m⁻³] is the chamber headspace concentration, C_a [mol m⁻³] is the ambient concentration, q [m³ s⁻¹] is the inlet flow rate, V [m³] and A [m²] are the chamber volume and footprint area, respectively, and F [mol m⁻² s⁻¹] is the flux rate to determine. By solving the differential equation of mass balance, the soil flux rate F is then obtained from least square fit of the chamber headspace concentration versus time.

We implemented a baseline correction to account for changes in ambient concentrations during chamber closure and instrument drift. The inlet concentration was interpolated between the two opening periods before and after

⁷⁴removed: .

chamber closure. This zero-flux baseline was subtracted from chamber concentrations before calculating the flux from least square fitting. Some measurement periods had wavelike [..⁷⁵]noise in all measured gas concentrations, likely due to instrument instability, which prevented the calculation of reliable fluxes. Causes of the instrument instability were unclear and we did not find it to be related to condensation in the chamber. The affected flux data points were filtered out by diagnosing the concentration versus time plots, and conspicuous outliers were also removed (Table S1, SI).

2.4 Treatment of soil moisture data

5 Soil moisture data were measured with the Campbell TDR100 time-domain reflector (Campbell Scientific, Logan, UT, USA) and provided by the SMEAR II database. Sensors were in close proximity to the chambers (~ 5 m). Since soil moisture measurements were associated with high-frequency random [..⁷⁶]noise, we ran a Savitzky–Golay filter with a one-day window to smooth [..⁷⁷]the data while retaining the daily trends. After early September 2015, soil moisture measurements had frequent gaps. A more complete time series was available from soil profile measurements
10 about 30 m north from the chamber site. Soil A horizon moisture at this site in August was highly correlated with both the A horizon ($r^2 = 0.88$) and humus layer ($r^2 = 0.93$) moisture measurements near the chambers. We reconstructed the missing measurements at our soil plots from the linear regressions using August data. The gapfilled soil moisture data of both layers generally [..⁷⁸]agreed well with the intermittent measurements during that period (RMSE = $0.042 \text{ m}^3 \text{ m}^{-3}$ for the humus layer and $0.015 \text{ m}^3 \text{ m}^{-3}$ for the A horizon, respectively).

15 2.5 Statistical analysis

To extract smooth patterns of temperature and moisture dependence [..⁷⁹]of soil fluxes, we ran a 2D local regression (LOESS) on COS, CO, and CO₂ fluxes against humus layer temperature and moisture (predictors). Unlike linear regression, LOESS is a non-parametric method that does not require any analytical expression of the underlying relationships. At each data point, a low-degree polynomial is fitted to all its neighboring points, weighted by distances,
20 to give a smoothed estimate at the current point (Cleveland et al., 1992).

3 Results

3.1 COS flux

[..⁸⁰]

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⁷⁶removed: noises

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⁷⁹removed: in

⁸⁰removed: Soil

Soils in both chambers behaved as COS sinks, with average fluxes of $-2.8 (\pm 1.0)$ and $-2.5 (\pm 1.2)$ $\text{pmol m}^{-2} \text{s}^{-1}$ for SC1 and SC2, respectively (Fig. 1a; Table 1). The two chambers exhibited broadly similar ^[..⁸¹] patterns of COS fluxes (Figs. 1a and 2a–d). COS emissions were rare, accounting for only 0.1% cases of SC1 and 1.5% cases of SC2, respectively. Most emission cases were not statistically different from zero, and the few large emissions appeared to be transient and isolated cases unrelated to temperature or moisture change. Overall, soil COS fluxes at this site were comparable to reported values in similar ecosystems, for example, $-2.5 \text{ pmol m}^{-2} \text{s}^{-1}$ from a Swedish boreal forest soil in Simmons et al. (1999).

^[..⁸²] There was a weak increasing trend in soil COS uptake (or decreasing net COS flux) throughout the campaign (Table 1). This increasing trend was not significant during the peak growing months (July and August), but became stronger towards the end of the growing season (September and October). Such trend in COS uptake appeared to coincide with the decreasing trends in soil temperature and moisture (Fig. 1d, e).

No significant diurnal trend was observed in COS fluxes (Fig. 2a–d), although surface (0.5 m) COS concentration often changed from around 300 pmol mol^{-1} at night to 400 pmol mol^{-1} at midday. Surprisingly, we found no correlation between COS fluxes and ambient COS concentrations ($r = 0.005$; Fig. S2, SI), indicating that COS uptake was not concentration limited at the daily timescale. The deposition velocity of COS (uptake normalized by concentration) ^[..⁸³] showed a weak diurnal variability (Fig. 3^[..⁸⁴] a, b), as a result of the depleted canopy COS concentration at night due to the stable boundary layer conditions and nocturnal canopy COS uptake (Kooijmans et al., 2017).

Smoothed 2D patterns of soil COS uptake ^[..⁸⁵] as a function of soil temperature and moisture were constructed with the LOESS method (sect. 2.5). Soil moisture rather than temperature was the dominant physical driver of soil COS uptake, with uptake rates decreasing with increasing moisture (Fig. 4^[..⁸⁶] a). There was only a weak tendency of increasing COS uptake with decreasing temperature. Soil COS uptake was positively correlated with soil respiration (Fig. 5), consistent with previous observations (Yi et al., 2007; Berkelhammer et al., 2014; Sun et al., 2016). However, the relationship between soil COS uptake and respiration seemed to divide into different branches delimited by soil temperature bins (Fig. 5).

3.2 CO flux

^[..⁸⁷]

⁸¹removed: COS fluxes. COS emissions happened rarely

⁸²removed: We found no significant changes in COS fluxes across the late growing season, although daily mean soil humus layer temperature dropped from 15 to 3°C during early July to late October of 2015. Moreover, there was no clear diurnal trend

⁸³removed: also did not show significant

⁸⁴removed:). The strongest physical driver

⁸⁵removed: was soil moisture

⁸⁶removed:). Soil COS flux is relatively well

⁸⁷removed: In both chambers,

CO was also taken up by ^[.88]soils in both chambers, with average fluxes of $-1.00 (\pm 0.43)$ and $-0.76 (\pm 0.43)$ $\text{nmol m}^{-2} \text{s}^{-1}$ in SC1 and SC2, ^[.89]respectively (Table 1). Although the two chambers were placed in similar conditions, SC1 always had slightly stronger uptake than SC2, ^[.90]indicating small scale heterogeneity. Both chambers had only a few ^[.91]and very weak CO emission cases (0.1% of SC1 and 0.5% of SC2).

5 In contrast to soil COS flux, there was clear diurnal variability in CO flux, ^[.92]consistent across all months (Fig. 2). CO uptake was significantly ^[.93]lower during the daytime ^[.94]than at night, with up to $0.5 \text{ nmol m}^{-2} \text{s}^{-1}$ difference (30–50% of nighttime CO uptake). ^[.95]We found weak correlations between soil CO flux and ambient CO concentration ($r = -0.590$ and -0.317 for SC1 and SC2, respectively, Table 2; Fig. ^[.96]S2, SI). However, the relative diurnal amplitudes of CO concentration were too small (less than 10% in monthly-mean diurnal trends; not shown) to explain the diurnal
10 variability in CO uptake. Significant diurnal variability was also present in CO deposition velocity (Fig. ^[.97]3c, d), with the midday values about 40% smaller than those around midnight. The diurnal variability in CO uptake was also unrelated to soil temperature, since it was out of phase with soil temperature variations (Fig. ^[.98]2). Instead, CO uptake was weakly correlated with the below-canopy radiation (rank correlation = 0.51 and 0.35 for SC1 and SC2, respectively^[.99]; Fig. ^[.100]S6, SI)^[.101], which varied diurnally, suggesting that the midday reduction
15 in CO uptake might be partially due to photochemical CO production at the soil surface.

During the campaign period, soil CO uptake was the highest in September compared with other months (Table 1; Fig. 2). The increase of CO uptake in September appeared to result from the decrease of soil moisture rather than changes in soil temperature (Fig. ^[.102]4). CO ^[.103]uptake was also weakly correlated with CO₂ flux (Fig. 5; Table 2), ^[.104]branching into different clusters depending on temperature bins. Such pattern resembled the relationship between
20 COS and CO₂ fluxes (Fig. 5).

3.3 CO₂ flux

⁸⁸removed: soil. Average fluxes were

⁸⁹removed: ,

⁹⁰removed: larger at night than

⁹¹removed: This diurnal pattern was consistent across all months (

⁹²removed: 2). No significant seasonal pattern of CO flux can be identified. From August to September 2015, CO uptake in both chambers increased slightly (Table 1 and

⁹³removed: 2). The increase appeared to be related to the drop in soil moisture rather than seasonal changes in soil temperature

⁹⁴removed: 4).

⁹⁵removed: CO flux was relatively well correlated with surface CO concentration ($r = -0.590$ and -0.317

⁹⁶removed: , Table 2; see also

⁹⁷removed: S2

⁹⁸removed: . However, diurnal changes in CO concentration were small compared with those in CO flux.

Thus, the deposition velocity of CO also shows a clear diurnal signal, with the midday deposition velocity about 40% smaller than that of the midnight

⁹⁹removed: 3

¹⁰⁰removed: flux was also negatively

¹⁰¹removed: indicating a prominent microbial control over soil CO₂ exchange.

The average CO₂ fluxes during the campaign period were 3.2 (\pm 1.3) and 3.8 (\pm 1.9) $\mu\text{mol m}^{-2} \text{s}^{-1}$ for SC1 and SC2, respectively. Soil respiration showed strong seasonal variations that [..¹⁰²] correlated with soil temperature changes (Table 2 and Fig. 4; Fig. S3 and S4, SI). [..¹⁰³] Monthly mean soil respiration in SC1 increased from 3.0 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in July to 4.1 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in August, the warmest month. As soil temperature began to decrease in September, soil respiration dropped to 3.2 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in SC1 but increased in SC2, indicating possible small-scale differences between the two chamber locations. [..¹⁰⁴] There was no well-defined relationship between soil moisture and respiration (Fig. 4).

We did not see [..¹⁰⁵] strong temperature-driven diurnal trends in soil respiration (Fig. 2), mainly because daily temperature [..¹⁰⁶] variations were small (2–3°C diurnal amplitude in the humus layer). [..¹⁰⁷] Temperature dependence of soil respiration at the daily timescale was generally weak since most of the days had low correlations between CO₂ flux and temperature (see Fig. S8, SI for a histogram of the corresponding daily r^2 -values), despite the correlation between soil respiration and temperature over the campaign period (Table 2 and Fig. 4). Interestingly, a small decrease in respiration at midday was found in the July diurnal trend [..¹⁰⁸] of CO₂ flux in SC1 (Fig. 2i). [..¹⁰⁹] Daytime CO₂ flux in July was on average 0.44 $\mu\text{mol m}^{-2} \text{s}^{-1}$ lower than nighttime CO₂ flux, and such difference was statistically significant ($p = 1 \times 10^{-8}$ in a two-sample t -test). The slightly higher nighttime respiration in July might be related with A horizon temperature that peaked at midnight. Other months did not show such pattern.

4 Discussion

4.1 [..¹¹⁰]

[..¹¹¹]

¹⁰²removed: were well

¹⁰³removed: There was no significant effect of soil moisture on respiration (Fig. 4). Mean soil respiration

¹⁰⁴removed: The average CO₂ fluxes over the observed late growing season were 3.2 (\pm 1.3) and 3.8 (\pm 1.9) $\mu\text{mol m}^{-2} \text{s}^{-1}$ for SC1 and SC2, respectively.

¹⁰⁵removed: significant diurnal changes

¹⁰⁶removed: changes

¹⁰⁷removed: A very

¹⁰⁸removed: , but was not statistically significant

¹⁰⁹removed: Thus, we could not detect temperature dependence of soil respiration at the daily timescale even though there was a significant correlation across the seasonal timescale.

¹¹⁰removed: Physical and biological factors controlling COS and CO fluxes

¹¹¹removed: Source and sink activities coexist in soils for COS (?Maseyk et al., 2014; Whelan et al., 2016) and for CO (Conrad and Seiler, 1985; King, 1999; Yonemura et al., 2000a). Since both COS and CO productions in upland soils depend strongly on temperature (Maseyk et al., 2014; Conrad and Seiler, 1985), the consistent net uptake of COS and CO and the lack of temperature correlation (Table 2) indicated steady (if any) production rates. Thus, with a negligible or largely invariant production term,

5 4.1 Physical and biological factors controlling COS and CO fluxes

The net soil flux of COS or CO is generally the balance of concurrent sink and source activities. Here we explore how physical and biological factors drive the variability in ¹¹²the net fluxes of COS and CO¹¹³, and infer their effects on the gross uptake of COS and CO¹¹⁴.

Soil moisture is the key determinant ¹¹⁵of the net soil COS flux (Fig. 4a¹¹⁶), reflecting the variability of ¹¹⁷the gross COS uptake, since COS production is controlled mainly by temperature (Whelan et al., 2016). Due to the fact that net uptake dominates soil COS flux, and that soil temperature does not show a strong variability (Fig. ¹¹⁸2a–d), COS production, if present at all, is likely a minor and constant component. The moisture dependence of COS uptake ¹¹⁹activity typically manifests as a bell-shaped curve with a moisture optimum (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008; Whelan et al., 2016). Below ¹²⁰the moisture optimum, microbial uptake of COS is limited by water availability, ¹²¹whereas above it, COS uptake is limited by the diffusional supply of COS from the atmosphere ¹²²because soil gas diffusivity decreases with moisture content ¹²³(Sun et al., 2015; Ogée et al., 2016). In this study, the decrease of COS uptake with increasing soil moisture (Fig. 4a) is characteristic of the diffusion-limited ¹²⁴regime in COS uptake. The diffusion-limited regime indicates that the moisture optimum for COS uptake was likely below the observed ¹²⁵soil moisture range and that most COS ¹²⁶uptake happened beneath the surface humus layer¹²⁷.

¹¹²removed: observed net

¹¹³removed: fluxes should reflect the variability in gross uptake rates

¹¹⁴removed: rather than an influence of production rates

¹¹⁵removed: for soil COS and CO uptake. The smoothed 2D patterns of temperature and moisture dependence of soil COS and CO fluxes, constructed from the LOESS method (section 2.5), show that uptake rates decrease with increasing soil moisture (

¹¹⁶removed: , b)in the natural ranges of temperature and moisture

¹¹⁷removed: S5, SI). Previously, laboratory incubations have identified nonlinear

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¹¹⁹removed: this

¹²⁰removed: and

¹²¹removed: , since gas diffusivity in soil

¹²²removed: . The moisture dependence of soil CO uptake, though not mathematically well-defined, is qualitatively similar to that of soil COS uptake based on limited observations (Moxley and Smith, 1998; King, 1999).Hence, the decrease in soil COS and CO uptakeat higher soil moisture in this study indicate that soil uptake of COS and CO was

¹²³removed: and moisture optima are

¹²⁴removed: range of soil moisture . The diffusion-limited regime suggests

¹²⁵removed: and CO uptake happens below

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To detect whether most COS and CO uptake happens in the lower humus layer or in the A horizon would require additional data, for example, vertical profiles of COS and CO concentrations in the soil.

[¹²⁷] There is only a weak tendency of [¹²⁸] decreasing net COS uptake with [¹²⁹] increasing temperature (Fig. 4a[¹³⁰]). The lack of strong temperature dependence is not surprising given that 90% of the data were measured [¹³¹] in the narrow temperature range of 8.3–16.4°C ([¹³²] humus layer). A temperature optimum for COS uptake cannot be identified within the observed temperature range, but likely exists below this range since COS uptake here tends to increase slightly with decreasing temperature (Fig. 4a). The low temperature optimum would differ from previous laboratory studies that report temperature optimum values of around 20° [¹³³] (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008), suggesting a need to constrain such parameter under field conditions.

Soil CO flux variability is also dominated by moisture dependence and did not show [¹³⁴] any significant temperature dependence (Fig. 4b). Previous studies show that the moisture dependence of CO uptake also follows a bell-shaped curve with a moisture optimum, which qualitatively resembles that of soil COS uptake (Moxley and Smith, 1998; King, 1999). Because CO uptake in the soil is subject to the same reactive transport mechanism as in COS uptake, the decrease of CO uptake with increasing soil moisture indicates that CO uptake is also diffusion-limited and the majority of uptake activity should happen below the surface humus layer. The absence of temperature-driven [¹³⁵] [¹³⁶] variability in net CO uptake suggests the lack of significant abiotic thermal production of CO, yet other production activity may still exist.

A unique feature of soil CO flux is the diurnal cycle showing reduced daytime net uptake (Fig. 2e–h), contrasting with [¹³⁷] soil COS flux that shows no significant diurnal [¹³⁸] variability. The correlation between CO uptake and below-canopy radiation ([¹³⁹] sect. 3.2; Fig. [¹⁴⁰] S2, SI) [¹⁴¹] implies that there might be photochemical production at the surface humus layer [¹⁴²] during the campaign. Although opaque chambers were used to prevent photochemical

¹²⁷removed: We found

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¹²⁹removed: decreasing temperature , whereas CO uptake shows negligible temperature dependence

¹³⁰removed: , b). Since soil COS uptake is mediated by carbonic anhydrases and other related enzymes, it typically shows a temperature dependence characteristic of enzymatic reactions, i.e., a bell-shape function with a temperature optimum (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008; Sun et al., 2015; Ogée et al., 2016). However, a temperature optimum for COS uptake cannot be identified for our site. This

¹³¹removed: at humus layer temperature in the

¹³²removed: below the optimum temperature of ca.

¹³³removed: C, for example, observed by Kesselmeier et al., 1999), and that temperature and moisture co-vary in natural conditions.

This also explains why soil CO uptake, which is mainly due to enzymatic reactions mediated by CO dehydrogenases (CODH),

¹³⁴removed: appreciable temperature dependence . We conclude that in this boreal forest,

¹³⁵removed: variability in soil COS and CO uptake is not significant within the observed temperature range.

¹³⁶removed: The CO flux exhibits a clear diurnal cycle , with weakened net uptake in the daytime

¹³⁷removed: COS fluxes showing

¹³⁸removed: cycle. The strong variability in CO uptake cannot be explained with changes in ambient CO concentration, because such diurnal variability is also present in the deposition velocity of CO (Fig. 3). Hence, a daytime source of CO probably exists in the soil.

¹³⁹removed: rank correlation = 0.51 and 0.35 for SC1 and SC2, respectively

¹⁴⁰removed: S6

¹⁴¹removed: suggests that photochemical production was likely present

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20 production of CO [..¹⁴³] during measurements (sect. 2.2), when the chamber [..¹⁴⁴] was open and not being measured, the soil surface [..¹⁴⁵] was exposed in the sun and photochemical production [..¹⁴⁶] might happen. CO production at the surface [..¹⁴⁷], if present, may alter the vertical CO profile and consequently affects surface flux measurements, because gas transport in the soil column is a slow process. Strong diurnal variability in soil CO flux due to photochemical production has [..¹⁴⁸] previously been reported in a boreal forest (Zepp et al., 1997), a temperate mixedwood plain (Constant et al., 2008), and a reed canary grass cropland [..¹⁴⁹] (Pihlatie et al., 2016). Hence, photochemical production is a possible daytime source of CO that can be responsible for the diurnal cycle of net CO flux. Future studies on soil CO flux will need to operate the chamber in constant darkness to confirm or falsify the existence of photochemical CO production.

5 Both COS and CO fluxes appear to correlate well with [..¹⁵⁰] soil respiration when divided into specific temperature bins (Fig. 5). [..¹⁵¹] To characterize the sensitivities of COS and CO fluxes to respiration, mean flux ratios ($F_{\text{COS}} : F_{\text{CO}_2}$ and $F_{\text{CO}} : F_{\text{CO}_2}$ [..¹⁵²]) are calculated in each temperature bin, approximated by the slope of the zero-intercept linear regression (Fig. 6). The sensitivity of COS or CO uptake to respiration is stronger at lower temperature, as indicated by the more negative $F_{\text{COS}} : F_{\text{CO}_2}$ or $F_{\text{CO}} : F_{\text{CO}_2}$ ratio (Fig. 6). The [..¹⁵³] temperature dependence of the $F_{\text{COS}} : F_{\text{CO}_2}$ ratio

10 shows an asymptotic feature at higher temperature, which corresponds well with [..¹⁵⁴] the temperature dependence of the concentration-normalized COS to CO₂ flux ratio ([..¹⁵⁵] also known as soil relative uptake, SRU) reported from temperate forest soils (Berkelhammer et al., 2014). Note that the normalization by ambient concentrations usually shrinks SRU by a factor of 1 to 1.15 [..¹⁵⁶] with respect to the flux ratio, but does not change its temperature dependence feature. The range of SRU values (−1.8 to −0.5) in Berkelhammer et al. (2014) is therefore comparable to the range

15 of $F_{\text{COS}} : F_{\text{CO}_2}$ ratio in SC2 but significantly smaller than that in SC1 (Fig. 6). The qualitative similarity in the [..¹⁵⁷] temperature dependence of [..¹⁵⁸] the $F_{\text{COS}} : F_{\text{CO}_2}$ ratio from different sites suggests that such relationship can be a generalizable feature for soils. Interestingly, the transition from linear increase to constant ratio occurs around 10°C at our site (Fig. 6) compared to 30°C in the temperate sites (Berkelhammer et al., 2014), indicating a soil or

¹⁴³removed: is a transient process and ceases immediately when the opaque chamber closes during measurements

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¹⁴⁷removed: alters the soil vertical profile of CO which affects subsequent flux measurements because diffusional transport

¹⁴⁸removed: also

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¹⁵⁰removed: respiration (Table 2), but the relationships vary by temperature

¹⁵¹removed: When flux data are binned by soil humus layer temperature, the

¹⁵²removed: ratios are greater in absolute magnitude (more negative) in the lower temperature bins

¹⁵³removed: asymptotic nature of the

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¹⁵⁵removed: termed the soil uptake ratio, SRU, which differs from the flux ratio by

¹⁵⁶removed:) reported from a temperate forest (Berkelhammer et al., 2014). This

¹⁵⁷removed: form of the response suggests this

¹⁵⁸removed: COS to CO₂ flux ratio may be a common

site-specific ^[..¹⁵⁹]feature for further investigation. ^[..¹⁶⁰]In addition, the newly discovered relationship between the $F_{CO} : F_{CO_2}$ ratio and temperature can be used to simulate soil CO uptake empirically.

There remains a question why the relationship between COS or CO uptake and respiration divides into different branches defined by soil temperature (Fig. 5), despite the observation that COS or CO uptake does not show strong temperature dependence (Fig. 4). Since microbial activity underpins COS or CO uptake, each branch in the uptake–respiration pattern may represent the behavior of a distinct microbial group. The temperature dependence of flux ratios hence may indicate shifts in active COS and CO-consuming microbial groups ^[..¹⁶¹]caused by temperature. For example, microbial groups that have optimal uptake at a lower temperature may have a stronger sensitivity of COS (or CO) uptake to respiration than groups active at higher temperature. The asymptote values of $F_{COS} : F_{CO_2}$ and $F_{CO} : F_{CO_2}$ (Fig. 6) hence would reflect the uptake to respiration sensitivity behavior of microbial groups active at higher temperature. Collectively, the sum of COS uptake (or CO uptake) contributions from the ensemble of microbial groups may not show a well-defined temperature response like that in respiration. Although we cannot rule out the possibility that the flux ratio vs. temperature pattern is ^[..¹⁶²]influenced by divergent temperature responses of ^[..¹⁶³]microbial uptake and abiotic production (e.g., Whelan et al., 2016; King, 1999; van Asperen et al., 2015), abiotic production is unlikely to correlate with respiration. A mechanistic explanation for the temperature dependence of flux ratios requires a clear-cut separation of uptake and production processes and further understanding on the microbial communities involved in COS uptake or CO uptake.

4.2 Variations of soil fluxes over the late growing season

^[..¹⁶⁴]Neither COS flux nor CO flux exhibits strong seasonality, mainly because soil temperature ^[..¹⁶⁵]variation was not strong and ^[..¹⁶⁶]soil moisture was not low enough to severely limit microbial activity. For example, Whelan et al. (2016) has shown that COS uptake is inhibited when soil moisture is below around $0.10 \text{ m}^3 \text{ m}^{-3}$ ^[..¹⁶⁷]in incubation experiments, yet in this campaign soil moisture was above this threshold most of the time. From August to October, ^[..¹⁶⁸]monthly mean net soil uptake of COS increased slightly from 2.7 to $3.8 \text{ pmol m}^{-2} \text{ s}^{-1}$ ^[..¹⁶⁹], and that of CO increased from 1.0 to $1.2 \text{ nmol m}^{-2} \text{ s}^{-1}$ ^[..¹⁷⁰], despite a significant drop in humus layer temperature from 13.5

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¹⁶⁰removed: The correlation between respiration and COS and CO uptake that emerges when the fluxes are binned by temperature might

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¹⁶²removed: partly due to contrasting

¹⁶³removed: biotic and abiotic (mainly production) processes (e.g., Kesselmeier et al., 1999; Maseyk et al., 2014). We suggest that the newly discovered relationship between temperature and the $F_{CO} : F_{CO_2}$ ratio can be used to simulate soil CO uptake empirically

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to 5.5°C. As discussed previously, the increase was ¹⁷¹ due to increased gas diffusivity caused by declining soil moisture. Soil microbial activities for COS and CO uptake at this site ¹⁷² appeared tolerant of low temperature at the end of the growing season (October/November). Given the lack of temperature-related seasonality in COS ¹⁷³ or CO uptake, it is possible that a shift in active microbial groups might have acted to stabilize the overall uptake ¹⁷⁴ against changes in soil physical variables.

Soil respiration in SC1 increased significantly from July to August (3.0 to 4.1 $\mu\text{mol m}^{-2} \text{s}^{-1}$), concurrent with a slight increase in the mean soil temperature (12.8 to 13.5°C). As shown in Pumpanen et al. (2008), soil respiration at the site is not only controlled by temperature but also by gas diffusivity and photosynthate input from the vegetation. Since soil moisture dropped greatly after July (Fig. 1), the increase in respiration was more likely driven by the aeration of soil than by just a slight increase in soil temperature. In early October, soil respiration was suppressed by the abrupt decrease in soil temperature, and gradually dropped to below 1 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (Fig. 1). In addition, the declining ecosystem photosynthetic activity after August (Vesala et al., 2010) would reduce photosynthate input to the soil, and therefore might also contribute to the decrease in respiration. However, since the soil plots in both chambers were cleared of understory vegetation before the campaign, autotrophic respiration would rely on photosynthate supply from trees in a distance and should therefore make up a much smaller fraction in the total soil respiration than at a vegetated soil plot. The smaller contribution of autotrophic respiration is also supported by the lower August soil respiration of around 4 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in our campaign compared with the August soil respiration of around 6 $\mu\text{mol m}^{-2} \text{s}^{-1}$ in Pumpanen et al. (2015) from a vegetated area at the same site. Overall, the seasonal pattern of CO₂ flux is mainly driven by soil temperature and moisture, and to a lesser extent, photosynthate input.

4.3 Implications on using COS as a photosynthetic tracer

The ¹⁷⁵ soil at this boreal forest site (podzol) was consistently a weak sink of COS ¹⁷⁶ during the late growing season. Soil uptake of COS was around 10–20% of the daytime mean ecosystem uptake ¹⁷⁷ of 20.8 $\text{pmol m}^{-2} \text{s}^{-1}$ (Kooijmans et al., 2017, with daytime defined as the period with solar elevation angle > 20° therein). Soil COS uptake did not show strong diurnal and seasonal variations, ¹⁷⁸ nor did it show any abrupt increase induced by rain events (cf. Sun et al., 2016; Whelan and Rhew, 2016). Moreover, soil COS uptake ¹⁷⁹ variability was well explained by changes in soil moisture and respiration, and it ¹⁸⁰ would be possible to construct an empirical model for soil COS

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¹⁷⁷removed: (with daytime defined as solar elevation angle above 20°). However, soil

¹⁷⁸removed: and we did not observe any significant pulse of soil COS uptake

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flux based on its ¹⁸¹relationship with soil moisture, temperature, and CO₂ flux (Figs. 4 and 5). Hence, we expect that soil COS uptake can be ¹⁸²reliably accounted for when using COS as a photosynthetic tracer at this site.

20 Since soil COS uptake ¹⁸³did not show a ¹⁸⁴well-defined response to soil temperature or moisture but correlates well with respiration ¹⁸⁵when divided into specific temperature bins (Figs. 4 and 5), simulating soil COS uptake in ¹⁸⁶this boreal forest will rely on using soil respiration as an important statistical predictor. In this case, the parameterization scheme used in Berry et al. (2013) and the empirical relationship based on soil relative uptake ratio (COS uptake to CO₂ emission ratio normalized by their concentrations) as in Berkelhammer et al. (2014) will
 25 be useful in predicting COS uptake, provided that diffusion in the soil column is ¹⁸⁷properly resolved (e.g., Sun et al., 2015; Ogée et al., 2016).

4.4 Implications on soil–atmosphere CO exchange

The global soil CO budget remains uncertain due to limited field observations and the lack of modeling studies. Our results from ¹⁸⁸a boreal forest site help bridge the gap in the understanding of soil CO exchange ¹⁸⁹in this important biome. CO uptake by soil is usually characterized by the deposition velocity of CO, because ambient CO concentration varies spatially. At this site, CO deposition velocity lies in the range of 0.1–0.35 mm s^{−1} (Fig. 3), similar to previous studies in boreal forests (Zepp et al., 1997; Kuhlbusch et al., 1998) and slightly less than those in
 5 temperate forests (Sanhueza et al., 1998; Yonemura et al., 2000a). CO deposition velocity shows a weak decreasing trend with increasing soil moisture (Fig. S7, SI), which is broadly similar to the negative correlation found in Yonemura et al. (2000a), indicating a prominent diffusional control on CO uptake.

Globally, soils contribute to a significant but poorly constrained CO sink. The current estimate of global soil CO uptake ($\sim 300 \text{ Tg yr}^{-1}$ in King and Weber, 2007) is equivalent to a global mean uptake of $2.3 \text{ nmol m}^{-2} \text{ s}^{-1}$,
 10 averaged over the total land area ($1.49 \times 10^8 \text{ km}^2$). This global mean value is significantly higher than the mean CO uptake ($\sim 1 \text{ nmol m}^{-2} \text{ s}^{-1}$) observed at this boreal forest in the late growing season. Recent field observations of soil CO uptake in temperate ecosystems are also smaller than this global mean, for example, less than $1 \text{ nmol m}^{-2} \text{ s}^{-1}$ in a grassland in Italy (van Asperen et al., 2015), and $0.78 \text{ nmol m}^{-2} \text{ s}^{-1}$ in a grassland in Denmark (Bruhn et al., 2013). If we assume ¹⁹⁰the soil from this site is representative of boreal forest soils, it ¹⁹¹follows that temperate

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15 and tropical soils must have higher CO uptake capacity to compensate for the relatively low soil CO uptake in the boreal forest compared with the global mean, or the current estimate of global soil CO uptake needs to be revisited.

5 Conclusions

The boreal forest soil studied here behaves consistently as a sink of COS and CO during the late growing season. Soil COS and CO uptake appear to be largely insensitive to temperature, at least within the narrow temperature (3–
20 16°C) and moisture range (0.10–0.38 m³ m⁻³) at this site. In contrast to laboratory experiments, controls on fluxes can be difficult to identify in field conditions due to concurrent changes in temperature, moisture, and microbial community. We find that soil moisture is the dominant physical driver for soil COS and CO uptake, and the uptake rate generally decreases with soil moisture, suggesting that microbial uptake is limited by the diffusional supply of COS and CO into the soil column. [..¹⁹²]The relationship between COS uptake and respiration and that between CO uptake and respiration are regulated by soil temperature, leading to the temperature dependence of COS : CO₂ and [..¹⁹³]CO : CO₂ flux ratios. In future studies, measuring soil vertical profiles of COS and CO will help resolve the interplay between physical transport and biological uptake. Furthermore, studies on microbial dynamics are needed to shed light on the mechanisms relating COS and CO uptake with respiration.

Compared with total ecosystem uptake of COS, soil COS uptake is a small fraction (10–20%). Soil COS uptake
5 does not show significant diurnal or [..¹⁹⁴]long-term variability in the peak growing season [..¹⁹⁵](July and August), and thus will not be a dominant source of uncertainty when inferring photosynthesis from COS [..¹⁹⁶]measurements.

Soil CO uptake shows reduced midday uptake rate and deposition velocity, possibly related to the photochemical production of CO at the surface organic layer. [..¹⁹⁷]A comparison of soil CO uptake [..¹⁹⁸]in this boreal forest [..¹⁹⁹]with the estimated global mean shows that boreal forest soils [..²⁰⁰]have relatively low CO uptake activity. Similar
10 studies on soil CO fluxes are needed in other biomes to better constrain the magnitude and distribution of global biosphere–atmosphere CO exchange.

¹⁹²removed: Both COS

¹⁹³removed: CO uptakes correlate with soil respiration in specific temperaturebins, indicating that microbial activity is a main control of uptake rates

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6 Data availability

Data presented here can be found in the University of California Curation Center (UC3) Merritt data repository at <http://n2t.net/ark:/c5146/r39p4r> with doi:10.15146/R39P4R, or in Zenodo with doi:10.5281/zenodo.322936.

- 15 *Author contributions.* U.S., K.M., H.C., and T.V. designed the research. L.M.J.K., K.M., I.M., J.L., and H.K. conducted field experiments. W.S. and L.M.J.K. performed data analysis. W.S. and U.S. wrote the paper with contributions from all co-authors.

Competing interests. The authors declare no conflict of interest.

- Acknowledgements.* This study was supported by the European Commission’s Seventh Framework Programme (FP7/2007–
20 2013) in the InGOS project (284274), the Academy of Finland projects Centre of Excellence (118780), Academy Professor (284701 and 282842) and CARB-ARC (286190), [²⁰¹] ICOS-Finland (281255), and the NOAA contract NA13OAR4310082. We acknowledge support at the SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations) Hyytiälä field station, Finland. W.S. was supported by the University of California Institute for the Study of Ecological and Evolutionary Climate Impacts (ISEECI) GSR fellowship.

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Table 1. A statistical summary of fluxes from the two soil chambers.

	mean	s.d.	1st quartile	median	3rd quartile	Jun/Jul mean	Aug mean	Sep mean	Oct/Nov mean
SC1									
F_{COS} ($\text{pmol m}^{-2} \text{s}^{-1}$)	-2.83	1.01	-3.38	-2.75	-2.17	-2.55	-2.74	-3.25	-3.76
F_{CO} ($\text{nmol m}^{-2} \text{s}^{-1}$)	-1.00	0.43	-1.27	-0.93	-0.69	-0.78	-1.02	-1.39	-1.18
F_{CO_2} ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	3.18	1.29	2.29	3.12	4.02	2.97	4.13	3.23	1.10
SC2									
F_{COS} ($\text{pmol m}^{-2} \text{s}^{-1}$)	-2.47	1.18	-3.12	-2.38	-1.75	n/a [†]	-2.15	-2.80	-2.79
F_{CO} ($\text{nmol m}^{-2} \text{s}^{-1}$)	-0.76	0.43	-1.01	-0.69	-0.44	n/a	-0.64	-0.94	-0.72
F_{CO_2} ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	3.84	1.92	2.42	3.58	5.23	n/a	3.73	5.12	1.94

[†] “n/a” means “not available”.

Table 2. Pearson correlations between fluxes and environmental variables for the two soil chambers. $T_{\text{soil,O}}$ and $T_{\text{soil,A}}$ are soil temperatures in the humus layer and in the A horizon, respectively. Similarly, $w_{\text{soil,O}}$ and $w_{\text{soil,A}}$ are soil moistures ($\text{m}^3 \text{m}^{-3}$) in the humus layer and in the A horizon.

	COS (pmol mol^{-1})	CO (nmol mol^{-1})	$T_{\text{soil,O}}$ ($^{\circ}\text{C}$)	$T_{\text{soil,A}}$ ($^{\circ}\text{C}$)	$w_{\text{soil,O}}$ ($\text{m}^3 \text{m}^{-3}$)	$w_{\text{soil,A}}$ ($\text{m}^3 \text{m}^{-3}$)	F_{CO_2} ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
SC1							
F_{COS} ($\text{pmol m}^{-2} \text{s}^{-1}$)	0.022	[.. ²⁰⁹]-0.096 [†]	0.327	0.307	0.308	0.293	-0.212
F_{CO} ($\text{nmol m}^{-2} \text{s}^{-1}$)	[.. ²¹⁰]0.592 [†]	-0.590	0.254	0.180	0.560	0.555	-0.205
F_{CO_2} ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	[.. ²¹¹]-0.204 [†]	[.. ²¹²]0.249 [†]	0.462	0.524	-0.007	-0.033	[.. ²¹³]1
SC2							
F_{COS} ($\text{pmol m}^{-2} \text{s}^{-1}$)	0.019	[.. ²¹⁴]-0.060 [†]	0.163	0.161	0.184	0.178	-0.491
F_{CO} ($\text{nmol m}^{-2} \text{s}^{-1}$)	[.. ²¹⁵]0.531 [†]	-0.317	0.075	0.041	0.231	0.226	-0.474
F_{CO_2} ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	[.. ²¹⁶]-0.223 [†]	[.. ²¹⁷]0.373 [†]	0.388	0.399	-0.041	-0.038	[.. ²¹⁸]1

[†]For pairs which we do not expect an underlying mechanistic reason for their correlations, for example, CO flux and COS concentration, the correlation values are labeled with a dagger symbol.

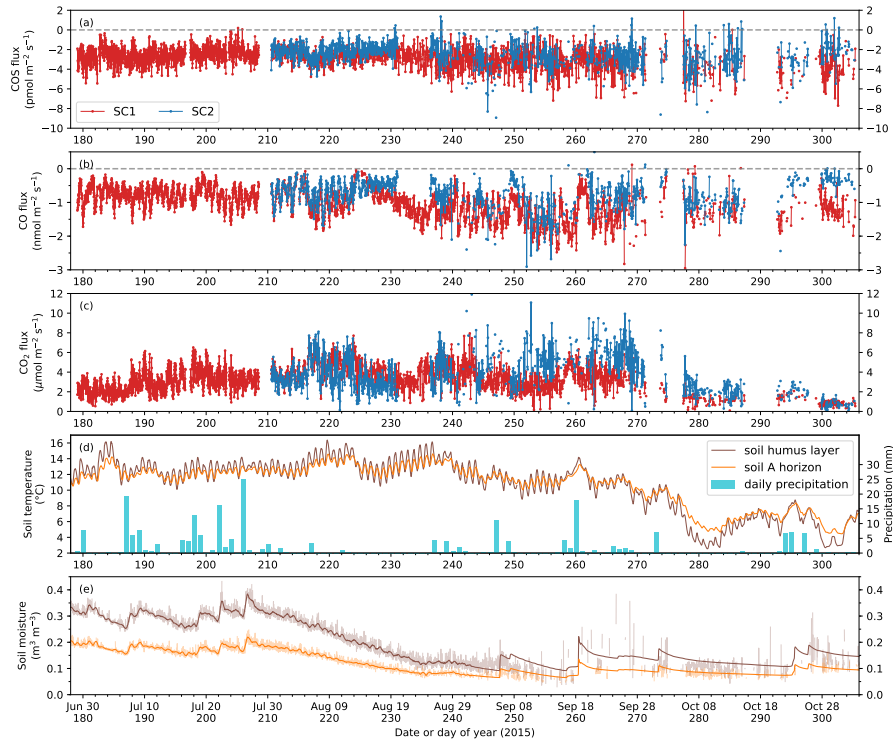


Figure 1. Soil fluxes of (a) COS, (b) CO, and (c) CO₂ from two chambers in a pine forest in southern Finland in summer and fall 2015. Also shown are (d) soil humus layer (1 to 5 cm) and A horizon (2 to 5 cm below the humus layer) temperatures (lines) and daily precipitation (bar plot), and (e) gapfilled and smoothed soil moistures in the humus layer and A horizon. Frequent gaps in raw soil moisture data (shown in transparent colors) from September 2015 onwards were gapfilled (solid lines) based on the correlation with soil moisture from a nearby location (see [..²¹⁹]sect. 2.4 for details).

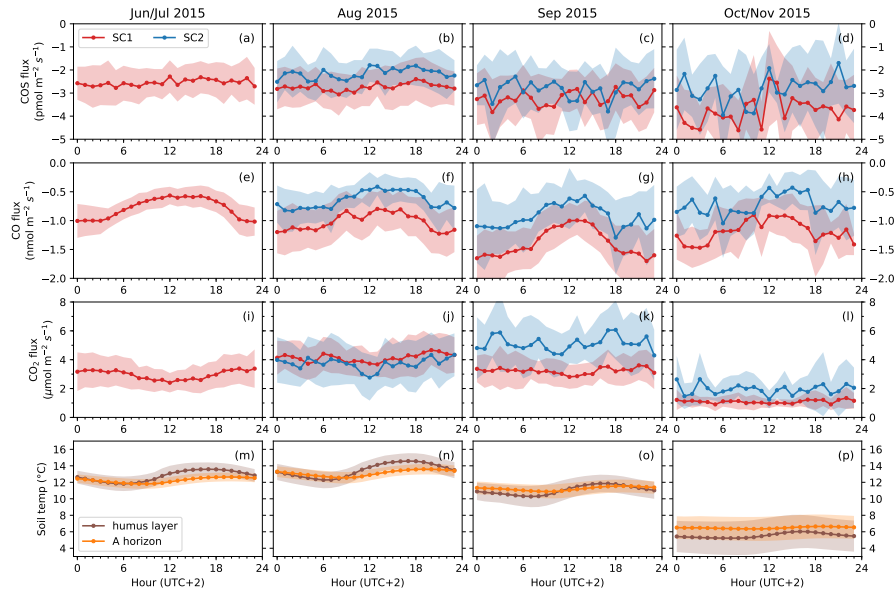


Figure 2. Monthly-mean diurnal trends of soil chamber fluxes of COS (a–d), CO (e–h), and CO₂ (i–l), and temperature in the humus layer and in the A horizon (m–p), **averaged in one-hour bins**. The x -axes are local winter time (UTC+2). Red and blue curves are mean diurnal trends of SC1 and SC2, respectively (a–l). Brown and orange represent temperature in the humus layer and in the A horizon, respectively (m–p). All shaded areas indicate standard deviations (± 1 s.d.). Note that for soil temperature the y -axis ranges change by month. The July 2015 subset includes two days of data from June, and the October 2015 subset includes two days from November.

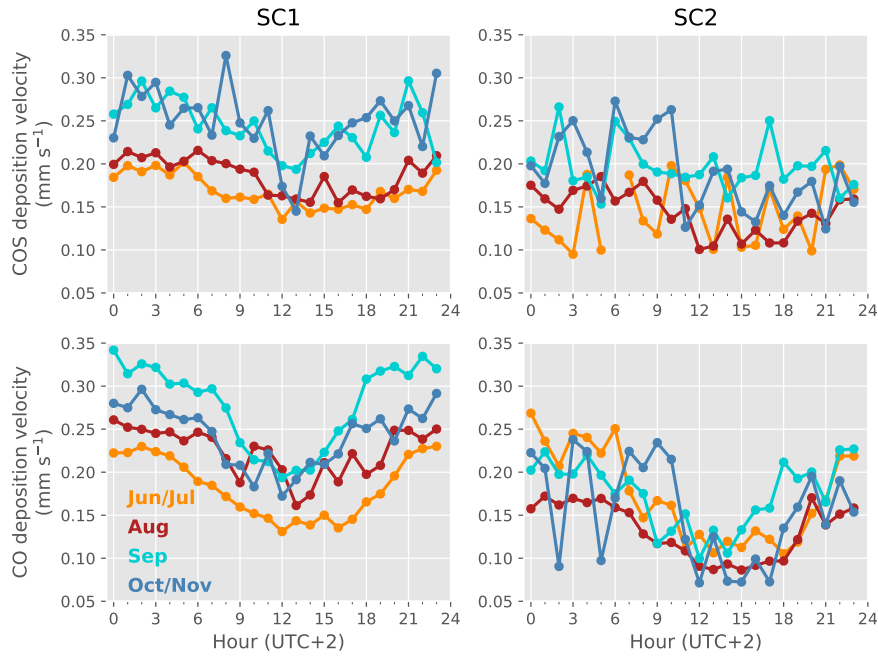


Figure 3. Monthly-mean diurnal trends of apparent deposition velocities of COS and CO ($-F_{\text{COS}}/[\text{COS}]_{0.5 \text{ m}}$ and $-F_{\text{CO}}/[\text{CO}]_{0.5 \text{ m}}$) in the two chambers, averaged in one-hour bins. Different monthly periods are color-coded.

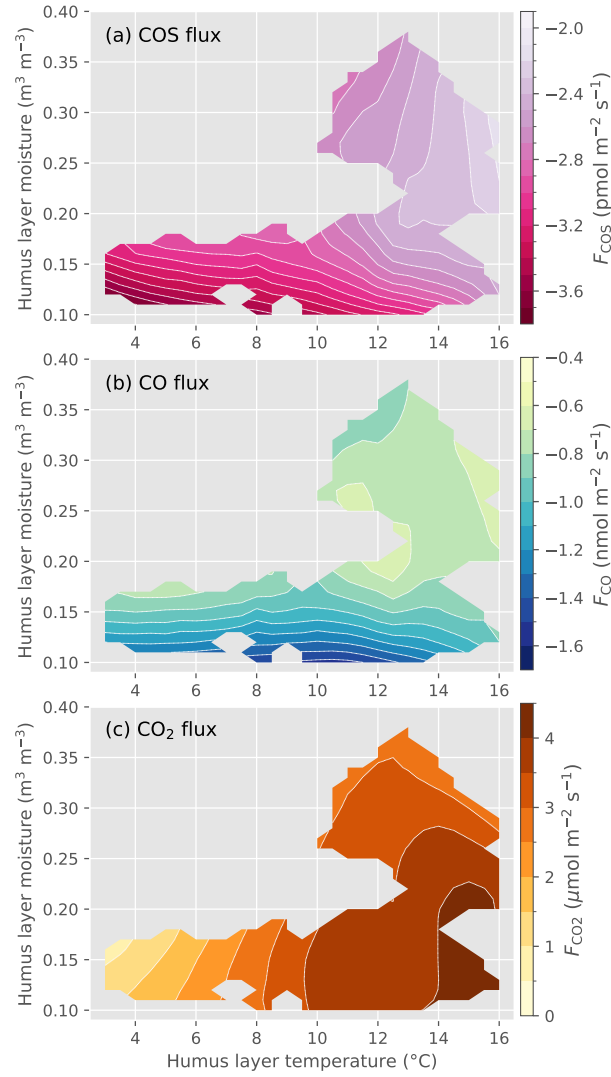


Figure 4. Smoothed patterns of soil COS (a), CO (b) and CO₂ (c) fluxes as functions of soil humus layer temperature and moisture, constructed using 2D local regression. Darker colors indicate stronger COS or CO uptake, or stronger CO₂ emission.

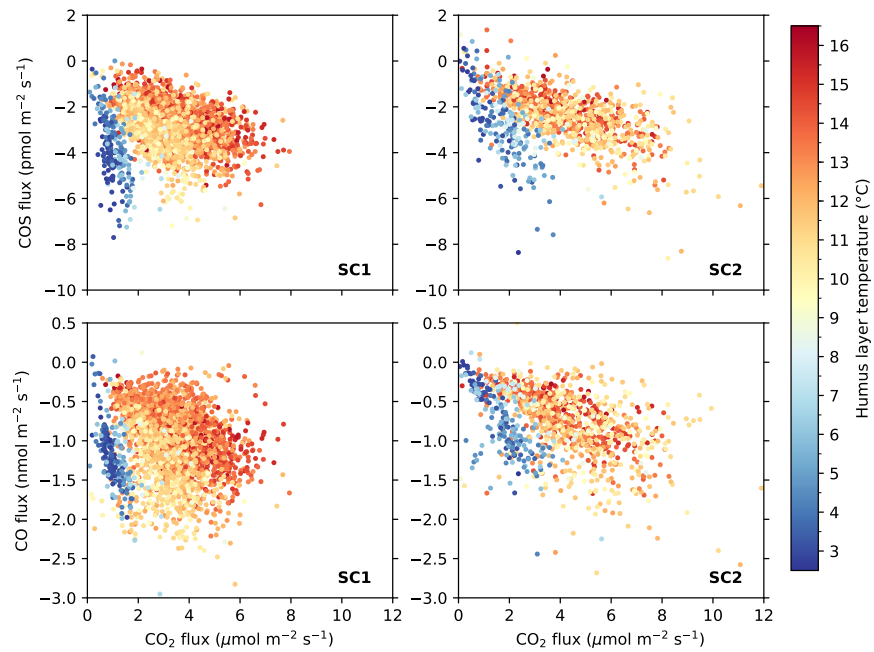


Figure 5. Relationships between COS and CO₂ fluxes (top row) and that between CO and CO₂ fluxes (bottom row). The slopes are modulated by soil humus layer temperatures (colored).

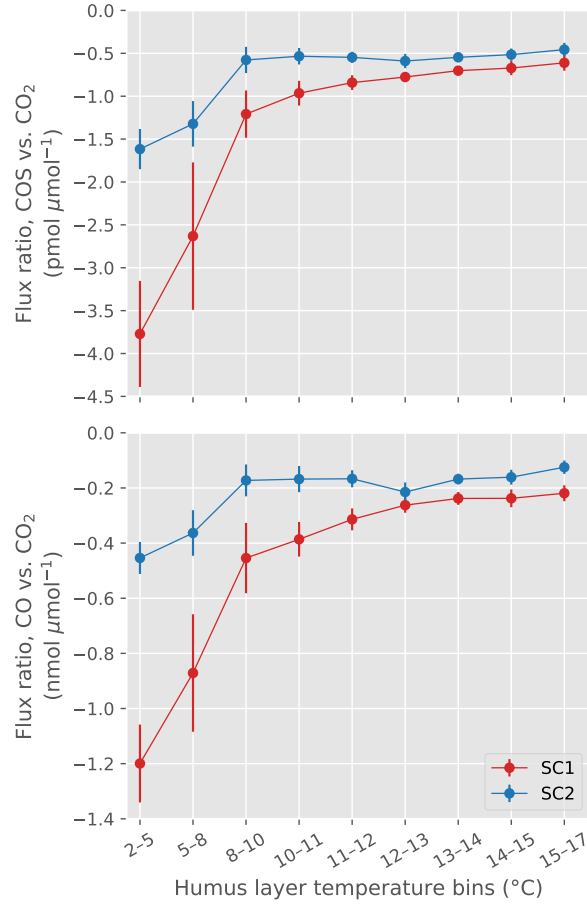


Figure 6. Ratios of COS vs. CO₂ and CO vs. CO₂ fluxes determined from [..²²⁰]zero-intercept linear regressions across soil temperature bins. Error bars are showing ± 2 standard errors (or 95.5% C.I.). Flux ratios are generally smaller in SC2 because of higher CO₂ fluxes.