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Atmospheric Chemistry and Physics Discussions

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

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Abstract. Soil is a major contributor to the biosphere–atmosphere exchange of carbonyl sulfide (COS) and carbon monoxide (CO). COS is used to improve constraints on terrestrial photosynthesis based on the link between leaf uptake of COS and of CO_2, but this use requires the soil COS flux to be well quantified. For CO, soil is a main sink in natural environments that influences the tropospheric CO budget. We measured soil fluxes of COS, CO, and CO_2 hourly over the 2015 late growing season in a Scots pine forest in Hyytiälä, Finland. The soil acted as a net sink of COS and CO. Average uptake rates were around 3 pmol m^{-2} s^{-1} for COS, and 1 nmol m^{-2} s^{-1} for CO, respectively. Soil respiration showed seasonal dynamics controlled by soil temperature, peaking in late August and September with fluxes around 4 µmol m^{-2} s^{-1} 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. We found that COS:CO_2 and CO:CO_2 flux ratios were modulated by temperature, possibly indicating shifts in active COS and CO-consuming microbial groups. Our results show that soil COS and CO uptake do not have strong variations over the late growing season in the boreal forest, and can be well described during the photosynthetically most active period. Well characterized and relatively invariant soil COS fluxes strengthen the case for using COS as a tracer for photosynthesis in this globally important biome.

1 Introduction

Soil is an important contributor to the atmospheric budgets of many bioactive trace gases, including carbonyl sulfide (COS) and CO (Conrad, 1996; Schlesinger and Bernhardt, 2013). Globally, soil acts as a significant sink of COS and

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Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

CO, with recent estimates at 26–33% of the total COS sink (Berry et al., 2013; Launois et al., 2015b), and 10–15% of the total CO sink (Conrad and Seiler, 1985; Khalil and Rasmussen, 1990; King and Weber, 2007). Soil fluxes thus exert strong influences on the atmospheric concentrations and distributions of COS and CO, and affect atmospheric chemical processes and Earth's radiative balance.

COS is a reduced sulfur gas engaged actively in land biogeochemical processes due to its chemical similarities to CO_2 (Kettle et al., 2002; Montzka et al., 2007; Berry et al., 2013). In leaf chloroplasts and soil microbes, COS is hydrolyzed irreversibly to CO_2 and H_2S 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 CO_2 hydration (Badger and Price, 1994; Henry, 1996). Because of the parallel uptake of COS and CO_2 through leaf stomata, COS has emerged as a promising tracer to quantify terrestrial photosynthesis independently from respiration (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, ocean emissions from biogenic and photochemical processes (Ferek and Andreae, 1984; Launois et al., 2015a) are the largest but are geographically separated from the terrestrial sinks of COS (plant and soil), whereas anthropogenic emissions and biomass burning (Campbell et al., 2015) are smaller and usually concentrated as point sources, 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). However, soil COS fluxes that are unrelated to photosynthetic uptake of CO_2 need to be quantified, and separated from the surface (plant + soil) COS flux (Maseyk et al., 2014; Billesbach et al., 2014; Commane et al., 2015).

Soils vary from COS sinks to sources depending on physical and biogeochemical conditions (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). Aerated upland soils are primarily 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 (e.g., Steinbacher et al., 2004; Yi et al., 2007; Berkelhammer et al., 2014). The uptake activity depends nonlinearly on soil temperature and moisture, with optimal conditions that maximize the uptake (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008; Whelan et al., 2016). However, strong net emissions of COS have also been observed from cropland soils at high temperatures (Maseyk et al., 2014; Whelan et al., 2016) and in an alpine grassland under solar radiation (Kitz et al., 2017), though the mechanisms are little understood. 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). These phenomena have presented challenges to the simplifying assumption that soil COS flux is small compared with leaf COS uptake (Asaf et al., 2013). Determining how soil COS flux is controlled by temperature, moisture, and biotic factors is needed when using COS to infer photosynthesis.

Soil–atmosphere exchange of CO is also the net balance between coexisting uptake and production activities (Conrad and Seiler, 1980, 1985; Sanhueza et al., 1998; King, 1999; King and Crosby, 2002; Bruhn et al., 2013;

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Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

van Asperen et al., 2015; Pihlatie et al., 2016). Soil uptake of CO is primarily due to microbial activity. 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 factors controlling CO uptake rates (Conrad and Seiler, 1985; King, 1999; Yonemura et al., 2000). Soil CO uptake may exhibit an optimum condition of moisture and temperature (Moxley and Smith, 1998; King, 1999), a feature broadly similar to that of soil COS uptake. However, this feature has not been evaluated with extensive measurements on different soils. In field conditions, the optimum moisture can be lower than the annual 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 considered largely abiotic (Conrad and Seiler, 1985; Zepp et al., 1997), but later, microbes on fine roots have also been found to contribute significantly to CO production (King and Crosby, 2002). Soil CO production generally increases with temperature and solar radiation (King, 1999; Yonemura et al., 2000; Zepp et al., 1997; van Asperen et al., 2015).

This study aims to quantify soil COS and CO fluxes in a boreal forest and identify the major physical and biological drivers of these fluxes. As the uptake of CO and COS is due to microbial activity, these processes may also be linked to the production of CO_2 by microbial respiration. However, as CO and COS are consumption processes they may also share similarities in their response to environmental drivers that differ from CO_2 production. Based on previous studies, we hypothesize soil COS flux to respond to soil temperature, moisture, and microbial activity 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. Despite limited knowledge on 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 (e.g., Sun et al., 2015). Here we report continuous field measurements of soil COS, CO, and CO_2 fluxes in a Scots pine forest in southern Finland over the late growing season. We explore diurnal and seasonal variabilities of the fluxes and their responses to soil environmental parameters.

2 Materials and methods

2.1 Site description

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 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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

and fall receiving somewhat more than winter and spring (ibid.). Meteorological and ancillary data such as surface pressure, air temperature, relative humidity, radiation, precipitation, soil temperature and moisture are continuously monitored at the SMEAR II site (see Hari and Kulmala, 2005 for description of the site infrastructure). These data are available online at http://avaa.tdata.fi/web/smart/smear/.

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. Thickness of the O horizon varies from 1 to 5 cm (Pihlatie et al., 2007; Pumpanen et al., 2008), its bulk density is 0.10 g cm^{-3}, and its porosity is 0.67 m^3 m^{-3} (Pumpanen and Ilvesniemi, 2005). The O horizon is 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 total porosity of 0.61 m^3 m^{-3} and 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.

2.2 Experimental setup

A quantum cascade laser spectrometer (QCLS, Aerodyne Research Inc., Billerica, MA, USA) was used to measure concentrations of COS, CO, CO_2, and H_2O 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 CO_2 (Kooijmans et al., 2016). An oil-free dry scroll pump (Varian TriScroll) was connected to the QCLS to pull sampling air through the analyzer. The QCLS was housed inside a small cabin. An automatic background correction was performed every 6 hours with an ultrahigh-purity (99.99999%) 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 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 at the soil surface during chamber measurements. The two chambers were placed in similar environments, about 10 m apart. The moss layer was removed to expose the humus layer inside the chambers. In blank chamber tests at the start of the campaign, we found no significant effect in CO or CO_2 (Fig. S1, Supplement) but a small positive COS flux (0.66 ± 0.48 pmol m^{-2} 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 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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

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.

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. 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.

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 CO_2 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.

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,

$$V\frac{\mathrm{d}C}{\mathrm{d}t} = q(C_\mathrm{a} - C) + FA \tag{1}$$

where C [mol m^{-3}] is the chamber headspace concentration, C_a [mol m^{-3}] is the ambient concentration, q [m^3 s^{-1}] is the flow rate, V [m^3] and A [m^2] 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 chamber closure. This zero-flux baseline was subtracted from chamber concentrations before calculating the flux from least square fitting. Some measurement periods had wavelike noises in all measured gas concentrations, likely due to instrument instability, which prevented the calculation of reliable fluxes. The affected flux data points were

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

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

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 noises, we ran a Savitzky–Golay filter with a one-day window to smooth them 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 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 of both layers generally agrees well with the intermittent measurements during that period (RMSE = 0.042 m^3 m^{-3} for the humus layer and 0.015 m^3 m^{-3} for the A horizon, respectively).

2.5 Statistical analysis

To extract smooth patterns of temperature and moisture dependence in soil fluxes, we ran a 2D local regression (LOESS) on COS, CO, and CO_2 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, to give a smoothed estimate at the current point (Cleveland et al., 1992).

3 Results

3.1 COS flux

Soil in both chambers behaved as COS sinks, with average fluxes of -2.8 ($\pm$ 1.0) and -2.5 ($\pm$ 1.2) pmol m^{-2} s^{-1} for SC1 and SC2, respectively (Fig. 1; Table 1). The two chambers exhibited broadly similar COS fluxes. COS emissions happened rarely, accounting for only 0.1% cases of SC1 and 1.5% cases of SC2. Most emission cases were not statistically different from zero, and the few large emissions appeared to be 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 pmol m^{-2} s^{-1} from a Swedish boreal forest soil in Simmons et al. (1999).

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 in COS fluxes (Fig. 2), although surface (0.5 m) COS concentration often changed from around 300 pmol

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

mol^{-1} at night to 400 pmol mol^{-1} at midday. The deposition velocity of COS (uptake normalized by concentration) also did not show significant diurnal variability (Fig. 3). The strongest physical driver of soil COS uptake was soil moisture rather than temperature (Fig. 4). Soil COS flux is relatively well correlated with soil respiration (Fig. 5), consistent with previous observations (Yi et al., 2007; Berkelhammer et al., 2014; Sun et al., 2016).

3.2 CO flux

In both chambers, CO was also taken up by soil. Average fluxes were −1.00 (± 0.43) and −0.76 (± 0.43) in SC1 and SC2 (Table 1). Although the two chambers were placed in similar conditions, SC1 always had slightly stronger uptake than SC2. Both chambers had only a few, and very weak CO emission cases (0.1% of SC1 and 0.5% of SC2).

In contrast to soil COS flux, there was clear diurnal variability in CO flux (Fig. 2). CO uptake was significantly larger at night than during the daytime, with up to 0.5 nmol m^{-2} s^{-1} difference (30–50% of nighttime CO uptake). This diurnal pattern was consistent across all months (Fig. 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 Fig. 2). The increase appeared to be related to the drop in soil moisture rather than seasonal changes in soil temperature (Fig. 4).

CO flux was relatively well correlated with surface CO concentration ($r = -0.590$ and −0.317 for SC1 and SC2, respectively, Table 2; see also Fig. S2, SI). 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 (Fig. 3). CO flux was also negatively correlated with CO_2 flux (Fig. 5; Table 2), indicating a prominent microbial control over soil CO exchange.

3.3 CO_2 flux

Soil respiration showed strong seasonal variations that were well correlated with soil temperature changes (Table 2; Fig. S3 and S4, SI). There was no significant effect of soil moisture on respiration (Fig. 4). Mean soil respiration in SC1 increased from 3.0 µmol m^{-2} s^{-1} in July to 4.1 µmol m^{-2} s^{-1} in August, the warmest month. As soil temperature began to decrease in September, soil respiration dropped to 3.2 µmol m^{-2} s^{-1} in SC1 but increased in SC2, indicating possible small-scale differences between the two chamber locations. The average CO_2 fluxes over the observed late growing season were 3.2 (± 1.3) and 3.8 (± 1.9) µmol m^{-2} s^{-1} for SC1 and SC2, respectively. We did not see significant diurnal changes in soil respiration (Fig. 2), mainly because daily temperature changes were small (2–3°C amplitude in the humus layer). A very small decrease in respiration at midday was found in the July diurnal trend, but was not statistically significant (Fig. 2i). 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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

4 Discussion

4.1 Physical and biological factors controlling COS and CO fluxes

Source and sink activities coexist in soils for COS (Conrad and Meuser, 2000; Maseyk et al., 2014; Whelan et al., 2016) and for CO (Conrad and Seiler, 1985; King, 1999; Yonemura et al., 2000). 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, the variability in observed net COS and CO fluxes should reflect the variability in gross uptake rates of COS and CO rather than an influence of production rates.

Soil moisture is the key determinant 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 (Fig. 4a, b) in the natural ranges of temperature and moisture (Fig. S5, SI). Previously, laboratory incubations have identified nonlinear moisture dependence of COS uptake, described with a bell-shape function featuring a moisture optimum for uptake (Kesselmeier et al., 1999; Van Diest and Kesselmeier, 2008; Whelan et al., 2016). Below this moisture optimum, microbial uptake of COS is limited by water availability, and above it, COS uptake is limited by the diffusional supply of COS from the atmosphere, since gas diffusivity in soil decreases with moisture content. 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 uptake at higher soil moisture in this study indicate that soil uptake of COS and CO was diffusion-limited and moisture optima are likely below the observed range of soil moisture. The diffusion-limited regime suggests that most COS and CO uptake happens below the surface humus layer, but does not constrain their exact depth. 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.

We found a weak tendency of increasing COS uptake with decreasing temperature, whereas CO uptake shows negligible temperature dependence (Fig. 4a, 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 is not surprising given that 90% of the data were measured at humus layer temperature in the range of 8.3–16.4°C (below the optimum temperature of ca. 20°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), did not show appreciable temperature dependence. We conclude that in this boreal forest, temperature-driven variability in soil COS and CO uptake is not significant within the observed temperature range.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

The CO flux exhibits a clear diurnal cycle, with weakened net uptake in the daytime (Fig. 2), contrasting with COS fluxes showing no significant diurnal 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. The correlation between CO uptake and below-canopy radiation (rank correlation = 0.51 and 0.35 for SC1 and SC2, respectively; Fig. S6, SI) suggests that photochemical production was likely present at the surface humus layer. Although photochemical production of CO is a transient process and ceases immediately when the opaque chamber closes during measurements, when the chamber is open and not being measured, the soil surface is exposed to the sun and photochemical production can happen. CO production at the surface alters the soil vertical profile of CO which affects subsequent flux measurements because diffusional transport is a slow process. Strong diurnal variability in soil CO flux due to photochemical production has also been reported in a boreal forest, a temperate mixedwood plain, and a reed canary grass cropland (Zepp et al., 1997; Constant et al., 2008; Pihlatie et al., 2016).

Both COS and CO fluxes correlate well with respiration (Table 2), but the relationships vary by temperature (Fig. 5). When flux data are binned by soil humus layer temperature, the $F_{COS} : F_{CO_2}$ and $F_{CO} : F_{CO_2}$ ratios are greater in absolute magnitude (more negative) in the lower temperature bins (Fig. 6). The asymptotic nature of the temperature dependence of $F_{COS} : F_{CO_2}$ ratio corresponds well with that of the concentration-normalized COS to CO_2 flux ratio (termed the soil uptake ratio, SRU, which differs from the flux ratio by a factor of 1 to 1.15) reported from a temperate forest (Berkelhammer et al., 2014). This similarity in the form of the response suggests this temperature dependence of COS to CO_2 flux ratio may be a common 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, indicating a soil or site-specific parameter for further investigation. The correlation between respiration and COS and CO uptake that emerges when the fluxes are binned by temperature might indicate shifts in active COS and CO-consuming microbial groups. However, considering that both production and consumption processes can exist in soil for COS and CO, we cannot rule out the possibility that the flux ratio vs. temperature pattern is partly due to contrasting temperature responses of 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.

4.2 Variations of soil fluxes over the late growing season

Soil COS and CO fluxes did not exhibit strong seasonality, mainly because soil temperature change was not strong and moisture was above the threshold of severe water limitation (around 0.10 m^3 m^{-3} from soil incubations in Whelan et al., 2016) most of the time. From August to October, mean COS and CO uptake increased slightly (2.7 to 3.8 pmol m^{-2} s^{-1} for COS uptake and 1.0 to 1.2 nmol m^{-2} s^{-1} for CO uptake, in SC1), despite a significant drop in humus layer temperature from 13.5 to 5.5°C. As discussed previously, the increase was likely due to increased gas diffusivity caused by declining soil moisture. Soil microbial activities for COS and CO uptake at this site appear

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

tolerant to low temperature. The lack of seasonality in COS and CO uptake may indicate that a shift in active microbial groups acted to stabilize the overall uptake fluxes against changes in soil physical variables.

Soil respiration in SC1 increased significantly from July to August (3.0 to 4.1 µmol m^{-2} s^{-1}), concurrent with a slight increase in 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 µmol m^{-2} 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. Overall, the seasonal pattern of CO_2 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 boreal forest soil in this study (podzol) was consistently a weak sink of COS. As daytime mean ecosystem COS uptake was about 24 pmol m^{-2} s^{-1} at this site (Kooijmans et al., 2017), soil uptake was around 8–16% of the daytime mean ecosystem uptake (with daytime defined as solar elevation angle above 20°). However, soil COS uptake did not show strong diurnal and seasonal variations, and we did not observe any significant pulse of soil COS uptake induced by rain events. Moreover, soil COS uptake is well explained by changes in soil moisture and respiration, and it is possible to construct an empirical model for soil COS flux based on its relationships with soil moisture, temperature, and CO_2 flux (Figs. 4 and 5). Hence, we expect that soil COS uptake can be well constrained and reliably accounted for when using COS as a photosynthetic tracer at this site.

Since soil COS uptake does not show a clearly defined response to soil temperature or moisture but correlates well with respiration in different temperature bins (Figs. 4 and 5), simulating soil COS uptake in a boreal forest will rely on using soil respiration as an important 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 CO_2 emission ratio normalized by their concentrations) as in Berkelhammer et al. (2014) will be useful in predicting COS uptake, provided that diffusion in the soil column is resolved.

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 the boreal forest site help bridge the gap in the understanding of soil CO exchange. Usually CO uptake by soil is 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 in temperate forests (Sanhueza et al., 1998; Yonemura et al., 2000). CO deposition velocity shows a weak decreasing trend with increasing soil moisture (Fig. S7,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

SI), which is broadly similar to the negative correlation found in Yonemura et al. (2000), 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 (~ 300 Tg yr^{-1} in King and Weber, 2007) is equivalent to a global mean uptake of 2.3 nmol m^{-2} s^{-1}, averaged over the total land area (1.49×10^8 km^2). This global mean value is significantly higher than the mean CO uptake (~ 1 nmol m^{-2} 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 nmol m^{-2} s^{-1} in a grassland in Italy (van Asperen et al., 2015), and 0.78 nmol m^{-2} s^{-1} in a grassland in Denmark (Bruhn et al., 2013). If we assume soil at this site is representative of boreal forest soils, it then indicates that temperate 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 (3–16°C) and moisture range (0.10–0.38 m^3 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. Both COS and CO uptakes correlate with soil respiration in specific temperature bins, indicating that microbial activity is a main control of uptake rates. 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. Soil COS uptake does not show significant diurnal or seasonal variability in the peak growing season. Thus, soil COS uptake in a boreal forest will not be a dominant source of uncertainty when inferring photosynthesis from COS fluxes. Soil CO uptake shows reduced midday uptake rate and deposition velocity, possibly related to photochemical production of CO at the surface organic layer. Comparison of soil CO uptake at this boreal forest site and the estimated global mean shows that boreal forest soils are relatively low in CO uptake activity. Similar studies on soil CO fluxes are needed in other biomes to better constrain the magnitude and distribution of global biosphere–atmosphere CO exchange.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

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.

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Competing interests. The authors declare no conflict of interest.

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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

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Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

Atmospheric Chemistry and Physics Discussions

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} (pmol m^{-2} s^{-1})	−2.83	1.01	−3.38	−2.75	−2.17	−2.55	−2.74	−3.25	−3.76
F_{CO} (nmol m^{-2} s^{-1})	−1.00	0.43	−1.27	−0.93	−0.69	−0.78	−1.02	−1.39	−1.18
F_{CO_2} (µmol m^{-2} s^{-1})	3.18	1.29	2.29	3.12	4.02	2.97	4.13	3.23	1.10
SC2									
F_{COS} (pmol m^{-2} s^{-1})	−2.47	1.18	−3.12	−2.38	−1.75	n/a	−2.15	−2.80	−2.79
F_{CO} (nmol m^{-2} s^{-1})	−0.76	0.43	−1.01	−0.69	−0.44	n/a	−0.64	−0.94	−0.72
F_{CO_2} (µmol m^{-2} s^{-1})	3.84	1.92	2.42	3.58	5.23	n/a	3.73	5.12	1.94

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

	COS	CO	$T_{soil,O}$	$T_{soil,A}$	$w_{soil,O}$	$w_{soil,A}$	F_{CO_2}
SC1							
F_{COS}	0.022	n/a	0.327	0.307	0.308	0.293	−0.212
F_{CO}	n/a	−0.590	0.254	0.180	0.560	0.555	−0.205
F_{CO_2}	n/a	n/a	0.462	0.524	−0.007	−0.033	n/a
SC2							
F_{COS}	0.019	n/a	0.163	0.161	0.184	0.178	−0.491
F_{CO}	n/a	−0.317	0.075	0.041	0.231	0.226	−0.474
F_{CO_2}	n/a	n/a	0.388	0.399	−0.041	−0.038	n/a

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 April 2017

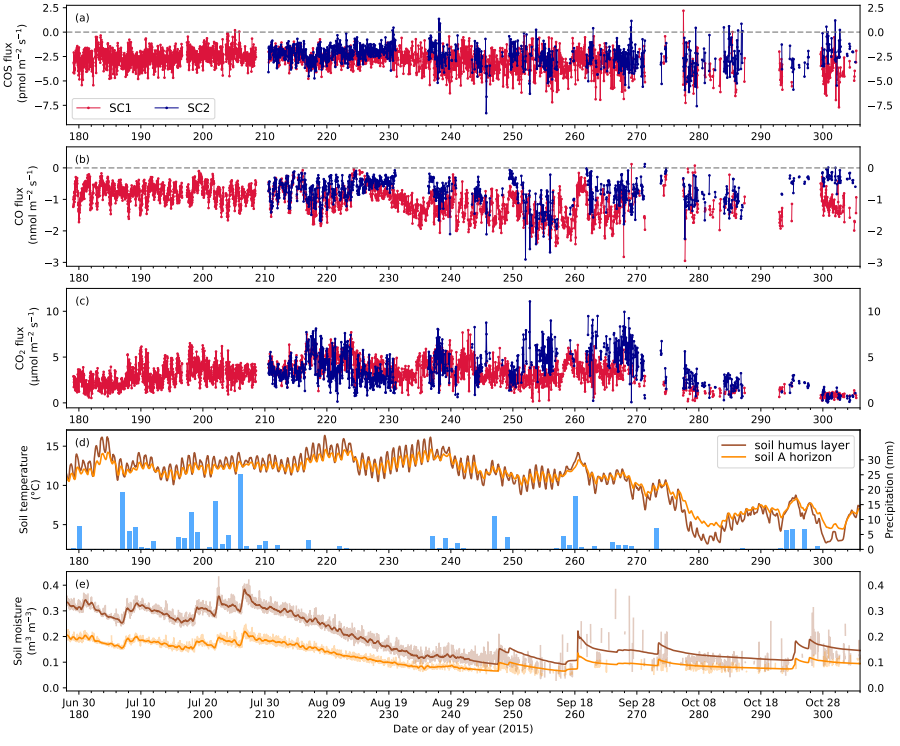

Figure 1. Soil fluxes of (a) COS, (b) CO, and (c) CO_2 from two chambers in a pine forest in southern Finland in summer and fall 2015. Also shown are (d) soil humus layer (1 to 5 cm) and A horizon (2 to 5 cm below the humus layer) temperatures (lines) and daily precipitation (bar plot), and (e) gapfilled 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 section 2.4 for details).

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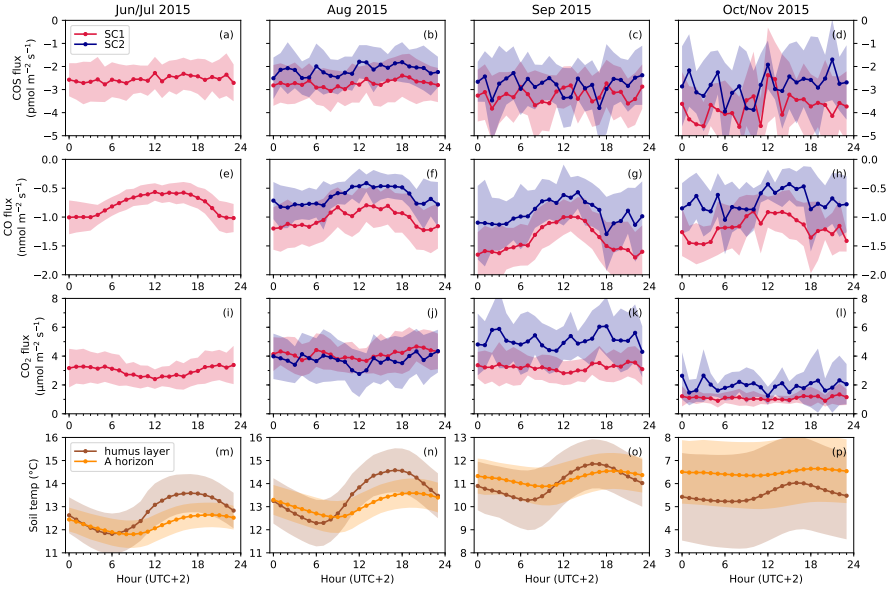

Figure 2. Monthly-mean diurnal trends of soil chamber fluxes of COS (a–d), CO (e–h), and CO_2 (i–l), and temperature in the humus layer and in the A horizon (m–p). The x-axes are local winter time (UTC+2). Red and blue curves are mean diurnal trends of SC1 and SC2, respectively (a–l). Brown and orange 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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
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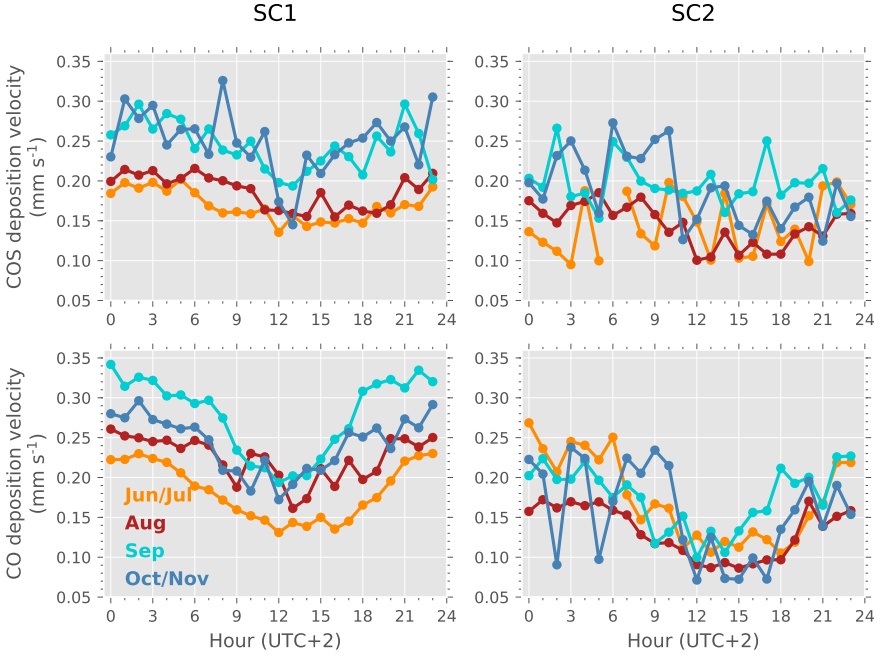

Figure 3. Monthly-mean diurnal trends of apparent deposition velocities of COS and CO ($-F_{\mathrm{COS}}/[\mathrm{COS}]_{0.5\ \mathrm{m}}$ and $-F_{\mathrm{CO}}/[\mathrm{CO}]_{0.5\ \mathrm{m}}$) in the two chambers. Different monthly periods are color-coded.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
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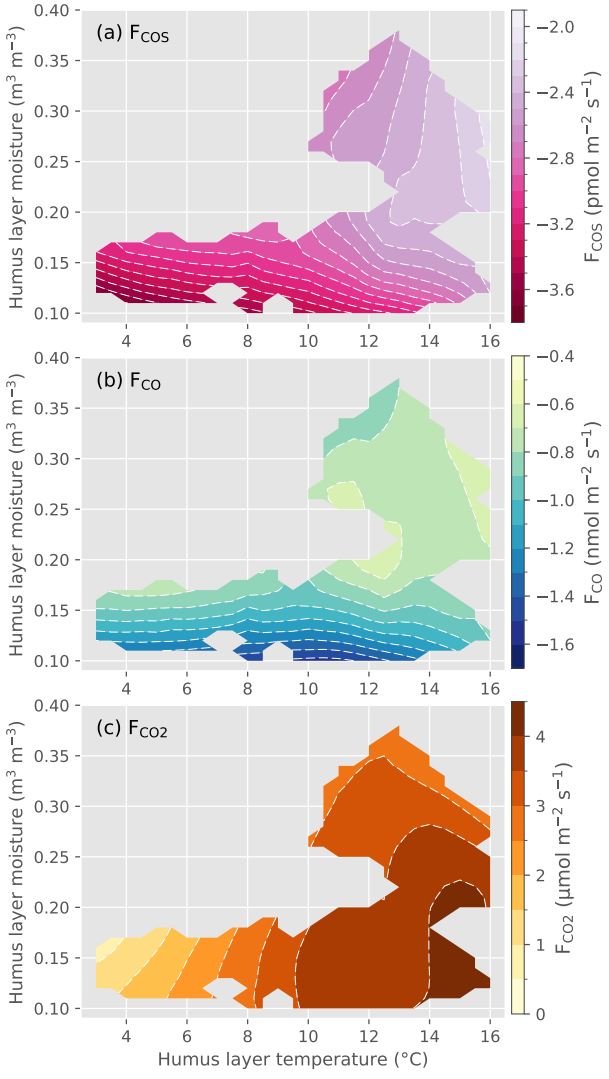

Figure 4. Smoothed patterns of soil COS (a), CO (b) and CO_2 (c) fluxes as functions of soil humus layer temperature and moisture, constructed using 2D local regression. Darker colors indicate stronger COS or CO uptake, or stronger CO_2 emission.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
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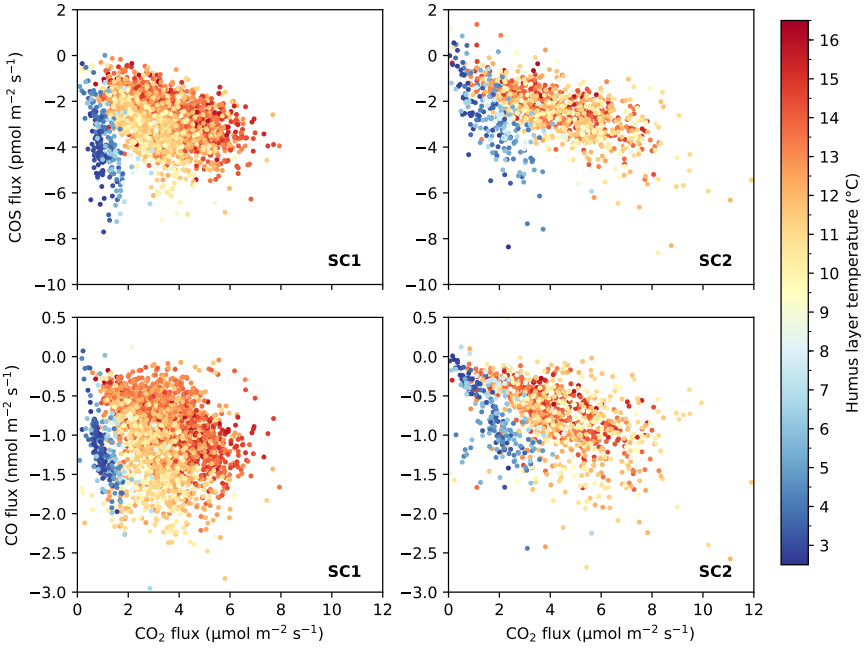

Figure 5. Relationships between COS and CO_2 fluxes (top row) and that between CO and CO_2 fluxes (bottom row). The slopes are modulated by soil humus layer temperatures (colored).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-180, 2017
Manuscript under review for journal Atmos. Chem. Phys.
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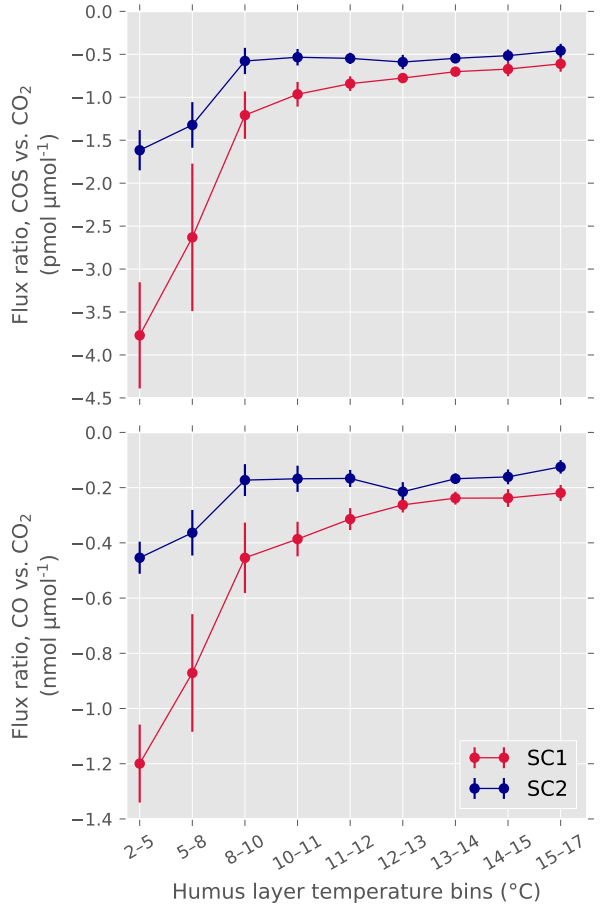

Figure 6. Ratios of COS vs. CO_2 and CO vs. CO_2 fluxes determined from no-intercept linear regressions across soil temperature bins. Error bars are showing ± 2 standard errors (or 95.5% C.I.). Flux ratios are generally smaller in SC2 because of higher CO_2 fluxes.