Supplement of Atmos. Chem. Phys., 16, 3711–3726, 2016
http://www.atmos-chem-phys.net/16/3711/2016/
doi:10.5194/acp-16-3711-2016-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon uptake

Mary E. Whelan et al.

Correspondence to: M. E. Whelan (marywhelan@gmail.com)

Supplemental Material

Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon uptake

M. E. Whelan[1,2], T. W. Hilton[1], J. A. Berry[2], M. Berkelhammer[3], A. R. Desai[4] and J. E. Campbell[1]

[1]{University of California, Merced, Merced, California}

[2]{Carnegie Institution for Science, Stanford, California}

[3]{University of Illinois Chicago, Chicago, Illinois}

[4]{University of Wisconsin, Madison, Wisconsin}

Correspondence to: M.E. Whelan (marywhelan@gmail.com)

1 COS ambient mixing ratios and COS net fluxes

Previous studies have shown interaction between net fluxes and ambient concentration of COS is linear (e.g. Conrad, 1994; Kesselmeier et al., 1999). COS soil fluxes have a demonstrated "compensation point", the atmospheric concentration of COS where the net flux of a specific system is 0. At concentrations below the compensation point, net emission to the atmosphere is observed; net consumption is observed when ambient concentrations are higher than the compensation point.

The COS in laboratory air during the experiments observed by this method was 510 ± 80 parts-per-trillion (ppt). The air actually present in the well-mixed soil incubation chamber, the mixing ratio observed at the outlet, was 470 ± 95 ppt COS. To calculate the maximum anticipated effect of this range, we used the maximum slope observed for the linear relationship described in Kesselmeier et al., (1999) for soils at 17 °C at a specific volumetric water content: $F_{uptake} = 0.006 \times [COS] - 0.32$, where soil COS uptake F_{uptake}, is reported in pmol gram dry soil^{-1} hour^{-1} and [COS] is the mixing ratio of COS in parts-per-trillion (ppt). The variability of COS mixing ratios in the soil chamber calculated by this method would cause a variability of ± 0.019 pmol gram dry soil^{-1} min^{-1}. By our simplified scaling presented in Section 2.2, this translates to 4.1 pmol m^{-2} sec^{-1}.

1.2 Discussion of variability in Figure 6

We believe that the variability in fluxes due to changes in soil moisture in Fig. 6 mask the effect of changes in COS chamber mixing ratios. The experiment depicted in Figure 6 aimed to qualitatively describe what happens to COS fluxes after water is added to soil at a constant temperature. Transitions in soil moisture are difficult to characterize: some soil samples show little change in COS fluxes after water addition, while others exhibit a COS "pulse" (see Figure 7 in the manuscript). In Kesselmeier et al., (1999), the authors used the mole fraction of COS exiting the incubation chamber as a measure of the well-mixed ambient environment actually experienced by the soil. The relationship between the observed soil COS fluxes after soil moisture change and COS mixing ratio exiting the chamber is depicted in Figure S1; all incubations depicted took place at 20 °C.

If the controlling variable of the net fluxes in Figure S1 was ambient COS, one would expect a strong inverse linear relationship, where higher concentrations of COS result in higher uptake of COS at a particular soil moisture state. Instead, at first glance, we see a positive relationship between COS mole fraction and COS flux. This is not surprising because higher soil COS production leads to more COS leaving the chamber. Perhaps there is a dampening effect on COS fluxes, where net COS production by soils increases soil COS consumption, but the overall effect is overwhelmed by high COS production. In other words, the net production reported here may be in reality higher at the lower ambient COS mixing ratios that would be encountered by unenclosed soils in the field.

High COS production does not appear to obscure the relationship between COS ambient mixing ratios and COS uptake. As a thought exercise to demonstrate this, we separated out the COS production component from fluxes of soy field soil, shown in Figure 7 in the main text. When soils were air-dried then incubated, a net COS emission was observed with an exponential relationship to temperature ranging from 10 to 40 °C for all the samples except the desert soil.

$$F_{production} = A \times \exp[B \times T] \qquad \text{(S2)}$$

$F_{production}$ is the production of COS in the assumed absence of COS consumption, T is the incubation temperature in °C, while A and B are fitting parameters found using least squares regression. This curve was generated for all soil types investigated other than the desert soils, though we did not generate enough data for savannah soils, shown in Figure S3 and Table S1.

Correcting for COS production in this way does not change the overall relationship between incubation COS mole fraction and observed COS fluxes. The production of COS is assumed to be insensible to the concentration of COS the soil experiences, depending here only on temperature. Examining Fig. S2, the correction for abiotic production at 20 °C is a small portion of the overall magnitude of the fluxes. Using this purposefully simple model (Eq. S1) to subtract out the effects of COS production vertically shifts the data and does not change the slope of the relationship, shown in Fig. S3.

2 COS mixing ratios and COS production

To explore the sensitivity of COS uptake to chamber COS mole fractions further, we performed a series of incubations with a freshly collected soil from near the original soy field site (Fig. S4). The soil was air-dried to approximately 2% VWC then incubated with ambient sweep air, as before, and COS-free zero air containing 300 ppm CO_2 and no detectable COS. The difference between the two treatments characterizes the effect of COS concentration on observed COS fluxes. If the response is linear, only two points are needed to extrapolate the appropriate curve.

The difference between the two exponential curves in Fig S5a suggests that some of the COS produced when the very dry soil was heated got taken up by other processes in the soil. With this simple experiment, it is impossible to confirm whether an adsorption/desorption mechanism is responsible.

The slopes of the linear regression lines in Fig. S4b and Fig. S5a represent the change in COS flux divided by the change in ambient COS. Slopes are all negative and become monotonically steeper as temperature increases. Under ambient and zero air treatments, the soil sample showed exponentially higher net COS emissions with temperature. Apparent uptake increased with more available COS in the headspace. In Kesselmeier et al., (1999), a similar relationship was found with soils that generally exhibited net COS uptake; however, the maximum slope occurred at 17 °C rather than at the maximum incubation temperature.

The linear regression intercepts in Fig S5b and graphed separately in Fig. S6b represent the theoretical flux we would expect if there were no COS in the chamber at all. This soil sample exhibited net emissions of COS at all temperatures, so the headspace always contained some small amount. We would expect the intercepts to have an exponential relationship with temperature, just as soil observations have exponentially increasing production as the incubation chamber was heated.

3 Conclusions

Understanding soil COS uptake processes still requires considerable work. The soil samples in this study were incubated under flowing . The soil and headspace air were assumed to be in equilibrium after 30 minutes. If that were true, adsorption and desorption should no longer contribute to the soil flux: equal amounts of COS should adsorb and desorb. The uptake difference between the zero air and ambient air treatments in Fig. S4 indicate that some uptake process was affecting net soil fluxes, even in a very dry soil.

References

Conrad, R.: Compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere, Biogeochemistry, 27(3), 155–170, doi:10.1007/BF00000582, 1994.

Kesselmeier, J., Teusch, N. and Kuhn, U.: Controlling variables for the uptake of atmospheric carbonyl sulfide by soil, J. Geophys. Res., 104(D9), 11577–11584, doi:10.1029/1999JD900090, 1999.

Table S1. The fitting parameters for air-dried soils versus temperature, found by least squares regression curve fitting to Eq. 2.

Soil ID	Parameter A	Parameter B
Soy field	-6.12	0.096
temperate forest	-7.77	0.119
savannah	-9.54	0.108
rainforest	-8.2	0.101

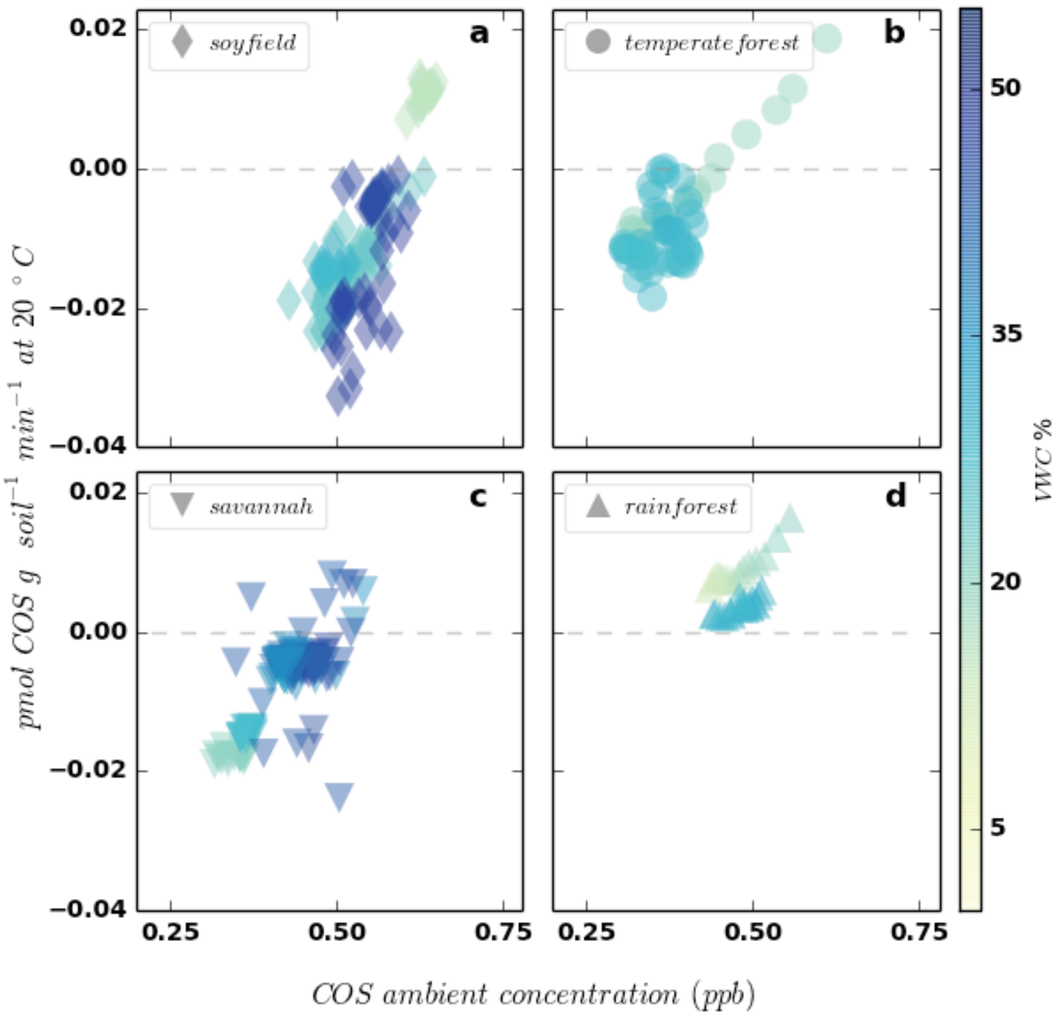

Figure S1. The concentration of COS exiting the incubation chamber versus COS fluxes after water addition at 20 °C.

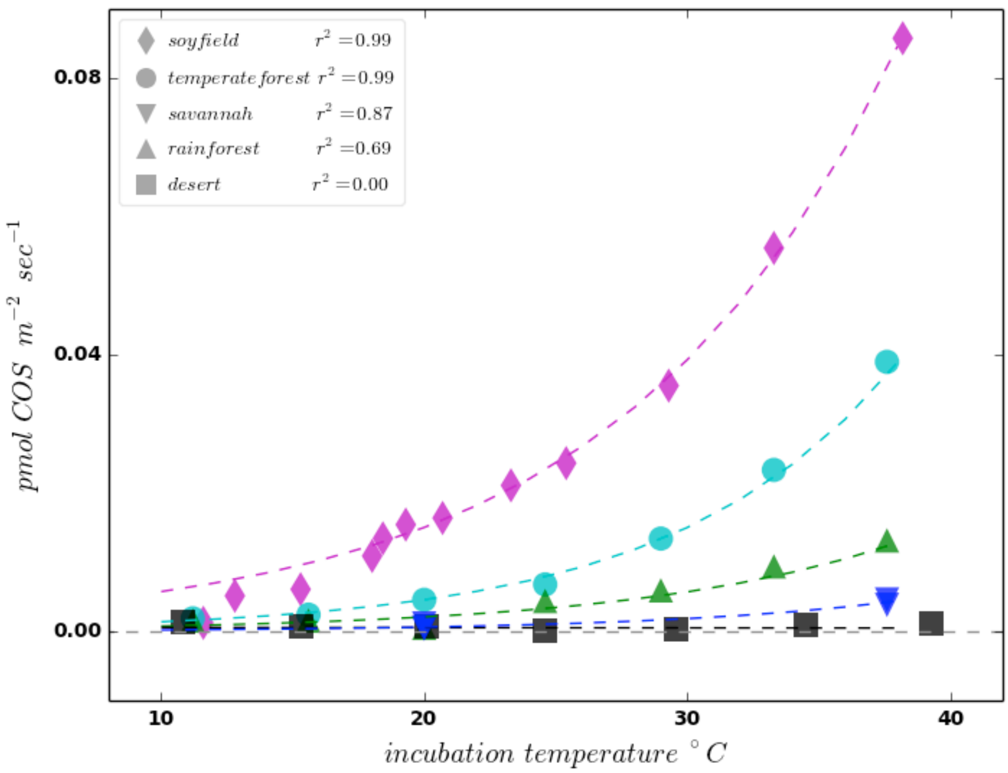

Figure S2. Observations of COS fluxes from air-dried soils over a range of temperatures. Air-dried soils are assumed to experience negligible COS uptake, the net fluxes here assumed to be soil COS production only. Eq. 2 was used to curve-fit the relationship between temperature and soil COS production. The r^2 values of this attempt are shown in the figure legend.

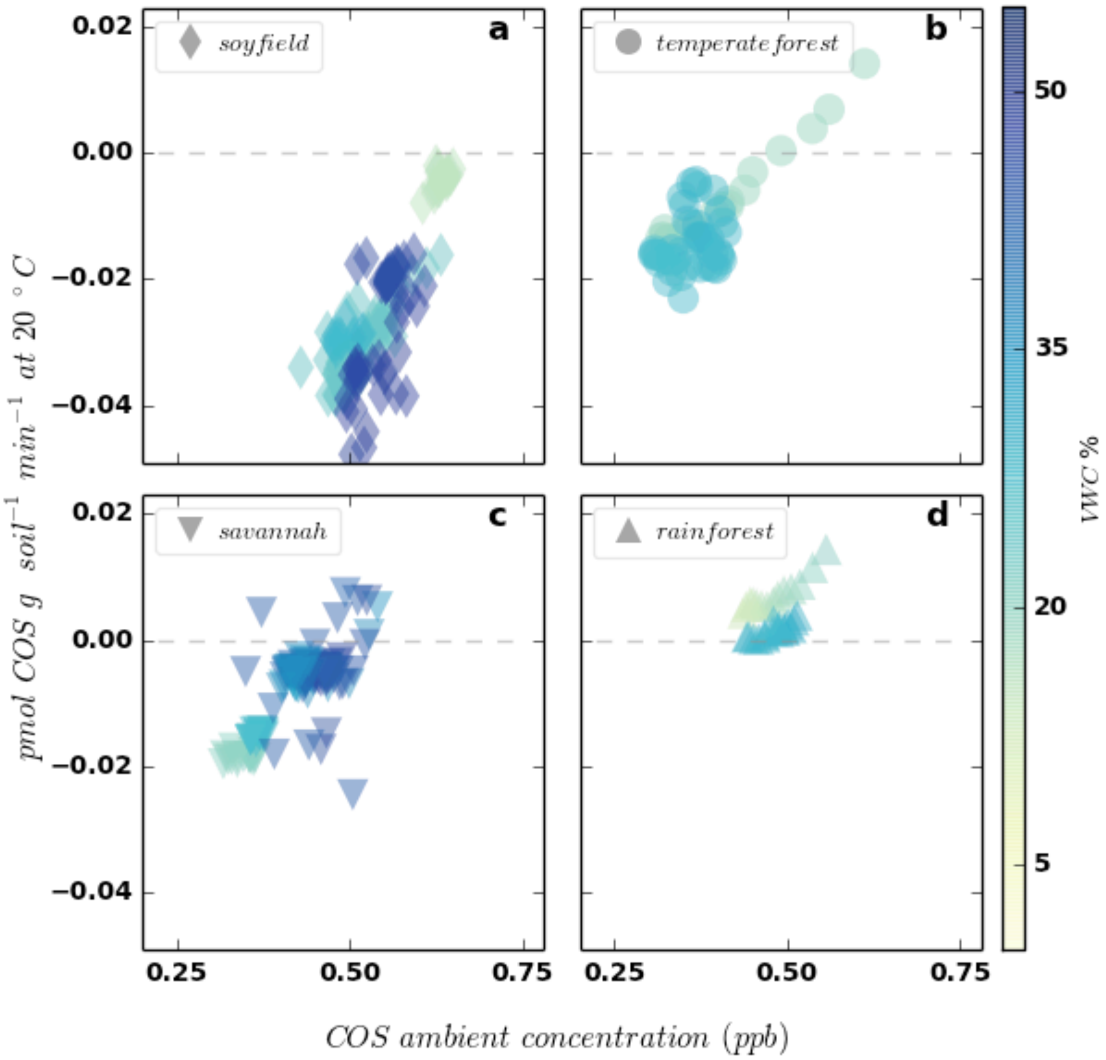

Fig. S3. Soil COS mole fractions and soil COS flux after water addition at 20 °C subtracted by anticipated COS production from Fig. S3.

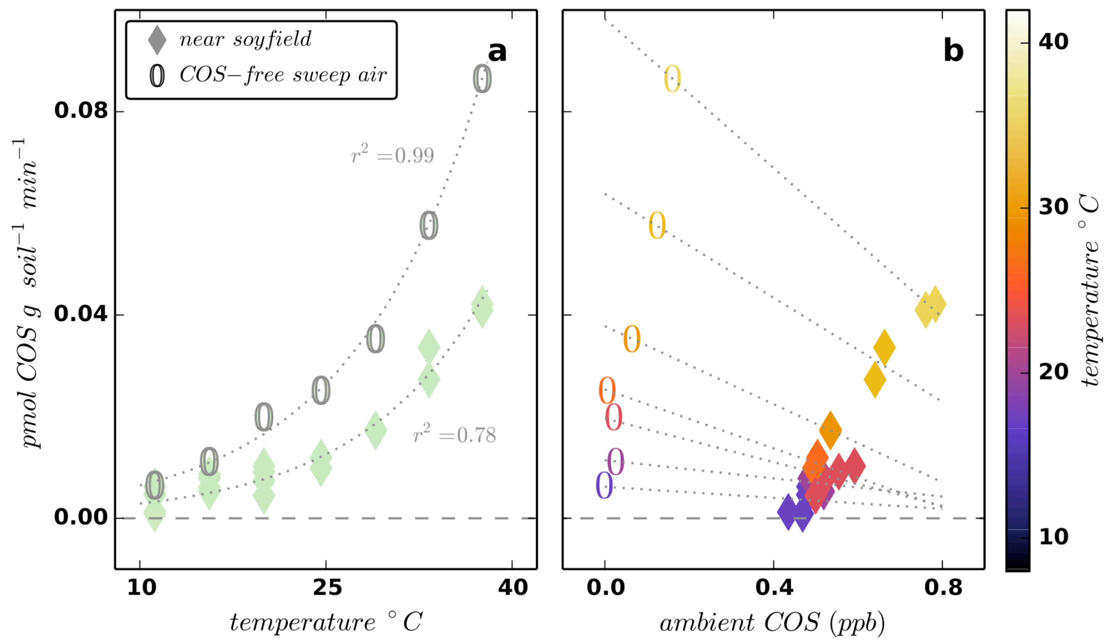

Fig. S4. Net COS exchange over temperature from a soil sample taken near the original soy field site: fluxes observed under ambient sweep air and COS-free sweep air conditions with exponential least squared regression lines (a); the relationship between ambient chamber COS concentrations and observed fluxes with linear least squared regression lines (b).

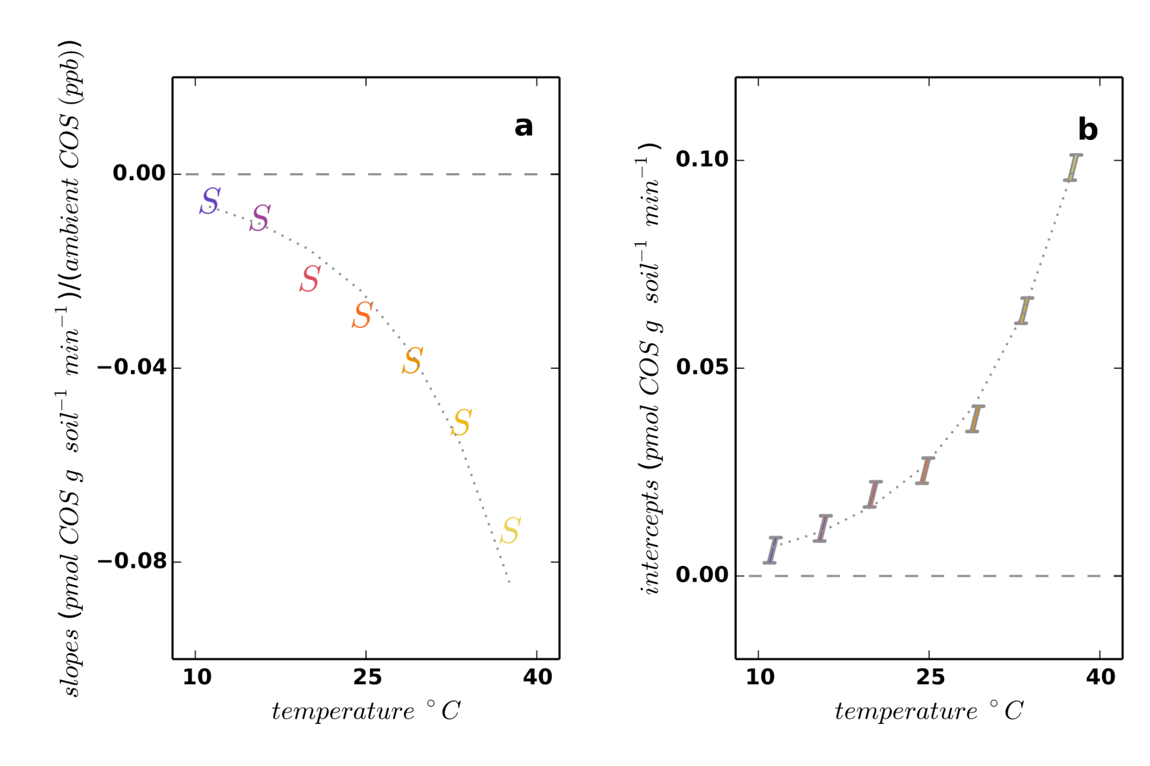

Figure S5. Slopes (a) and intercepts (b) of the linear least squared regression lines in Fig. S5b and their exponential linear least squared regression relationship with incubation temperature.