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Key Points:
- Net COS production in wheat field soil and roots scaled linearly by temperature
- Sterilized wheat field soil demonstrated abiotic COS production mechanism
- Lab observations of COS fluxes from soil confirmed previous field measurements

Correspondence to:
M. E. Whelan,
mary.whelan@gmail.com

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Carbonyl sulfide produced by abiotic thermal and photodegradation of soil organic matter from wheat field substrate

Mary E. Whelan[1] and Robert C. Rhew[2]

[1]Sierra Nevada Research Institute, University of California, Merced, California, USA, [2]Department of Geography, University of California, Berkeley, California, USA

Abstract Carbonyl sulfide (COS) is a reduced sulfur gas that is taken up irreversibly in plant leaves proportionally with CO_2, allowing its potential use as a tracer for gross primary production. Recently, wheat field soil at the Southern Great Plains Atmospheric Radiation Measurement site in Lamont, Oklahoma, was found to be a measureable source of COS to the atmosphere. To understand the mechanism of COS production, soil and root samples were collected from the site and incubated in the laboratory over a range of temperatures (15–34°C) and light conditions (light and dark). Samples exhibited mostly COS net uptake from the atmosphere in dark and cool (<22–25°C) trials. COS emission was observed during dark incubations at high temperatures (>25°C), consistent with field observations, and at a lower temperature (19°C) when a full spectrum lamp (max wavelength 600 nm) was applied. Sterilized soil and root samples yielded only COS production that increased with temperature, supporting the hypothesis that (a) COS production in these samples is abiotic, (b) production is directly influenced by temperature and light, and (c) some COS consumption in soil and root samples is biotic.

1. Introduction

Over the last decade, the relationship between concentrations of carbonyl sulfide (COS) gas and gross primary production (GPP) has been explored as a tool for constraining estimates of fluxes in both the carbon and sulfur cycles [*Asaf et al.*, 2013; *Berry et al.*, 2013; *Billesbach et al.*, 2014; *Blonquist et al.*, 2011; *Campbell et al.*, 2008; *Montzka et al.*, 2007; *Sandoval-Soto et al.*, 2005; *Seibt et al.*, 2010; *Suntharalingam et al.*, 2008]. CO_2 and COS diffuse through plant stomata; while CO_2 is simultaneously released through autotrophic respiration, generally COS is not produced by leaves [see *Wohlfahrt et al.*, 2012]. When the ratio of CO_2 to COS uptake by ecosystem vegetation is known, gross primary production could be calculated from measurements of COS and CO_2 concentrations [*Seibt et al.*, 2010]. This approach becomes complicated if there are other large sources or sinks of atmospheric COS in the ecosystem.

COS is well-mixed in the atmosphere with an average concentration of 476 ± 4 parts-per-trillion (ppt) in the Northern Hemisphere [*Montzka et al.,* 2007]. The primary source of COS is thought to be from the oceans, whereas the largest tropospheric sink is terrestrial vegetation [*Chin and Davis,* 1993; *Kettle et al.*, 2001, 2002; *Montzka et al.*, 2007]. COS is also destroyed in the stratosphere, contributing to the persistent sulfate aerosol layer; however, this indirect cooling effect of COS is approximately canceled out by its direct global warming potential [*Brühl et al.*, 2012]. In the global budget, the anthropogenic source fraction has been estimated to be 34–43%, based on ice core records which show an increase in atmospheric COS since 1850, perhaps from a combination of industrial emissions and deforestation [*Montzka et al.*, 2004].

Soils were originally treated as a source of COS because early observations were often made in chambers with an initially sulfur-free headspace. This led to artificially high COS emissions compared to measurements in ambient air [*Castro and Galloway*, 1991; *de Mello and Hines*, 1994]. Using accurate but sparse data, *Watts* [2000] divided soils into two categories: anoxic soils that produce COS and oxic soils that are a sink for COS, suggesting that redox potential alone drives net fluxes of COS. There are few in situ soil-only field experiments, many involving plots that simply had plants removed by above ground cutting or whole plant extraction before measurements commenced [*Fried et al.*, 1993; *Geng and Mu*, 2004; *Yi et al.*, 2008]. The parameterization of the soil sink in the modeling effort by *Kettle et al.* [2002] relied on a laboratory-based study by *Kesselmeier et al.* [1999], using sieved soils in a climate-controlled chamber. The soil uptake

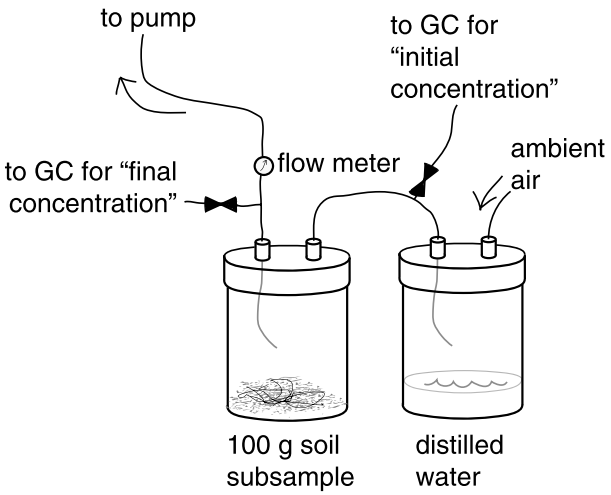

Figure 1. Subsample incubation setup. Two perfluoroalkoxy (PFA) chambers arranged in series and partially submerged in a constant temperature water bath were flushed with ambient air at 0.1 to 0.5 L min^{-1}. Air subsamples were analyzed from the outlet of the blank jar to establish the initial concentration and the outlet of the jar containing the subsample to quantify the final concentration of COS.

mechanism is thought to be enzymatic [*Conrad and Meuser,* 2000; *Kesselmeier et al.*, 1999; *Lehmann and Conrad*, 1996; *Van Diest and Kesselmeier*, 2008], probably due to carbonic anhydrase, the same enzyme that destroys COS in plant cells [*Protoschill-Krebs and Kesselmeier*, 1992; *Protoschill-Krebs et al.*, 1996].

The production of COS in soils is partially understood. In a laboratory-based redox manipulation experiment, more COS evolved from more anoxic salt marsh sediments, attributed to microbially mediated degradation of soil organic matter [*Devai and DeLaune*, 1995]. Field experiments in similarly anoxic wetlands showed that these soils tend to act as a net COS source to the atmosphere [*Fried et al.*, 1993; *de Mello and Hines*, 1994; *DeLaune et al.*, 2002; *Yi et al.*, 2008; *Whelan et al.*, 2013]. Under *aerobic* conditions, COS production was stimulated when rice paddy soils were incubated with organic sulfur (e.g., cysteine) [*Minami and Fukushi*, 1981].

The drivers of terrestrial COS production are still largely unknown. Uncovering mechanisms for soil COS production would allow soil-atmospheric COS exchange to be estimated on broader spatial scales. This ability would benefit both atmospheric sulfur cycle studies and efforts to estimate ecosystem GPP using COS as a proxy of CO_2 uptake. In a recent field outing investigating COS exchange over a wheat field, aerobic agricultural soil was shown to be a quantifiable source of COS to the atmosphere at high temperatures and a sink at low temperatures [*Billesbach et al.*, 2014; *Maseyk et al.*, 2014]. Using soil and root samples from this field site, here we investigate further the mechanism of COS production in aerobic soils.

2. Methods

2.1. Sample Collection

Samples were obtained from a wheat field in the Southern Great Plains Atmospheric Radiation Measurement site (36°36′18.0″N, 97°29′6.0″W), 3 m from where soil exchange measurements were previously performed [*Billesbach et al.*, 2014; *Maseyk et al.*, 2014]. Samples were collected from the top 15 cm of the soil column and sealed in polyethylene bags, then mailed overnight for analysis at University of California, Berkeley.

2.2. Quantification of COS

COS was quantified using an Agilent 7890A gas chromatograph outfitted with an Agilent 355 sulfur chemiluminescence detector (Agilent Technologies, Santa Clara, CA, USA) with a custom inlet (described in *Khan et al.* [2012]). A five-point calibration curve was generated by injecting different volumes of a whole air standard containing 543 ppt COS, calibrated to the NOAA-Scripps Institution of Oceanography provisional scale. An aliquot of the standard was injected between every four unknown samples to correct for instrument drift. The inlet and outlet of the incubation chamber were directly plumbed to the gas chromatograph (Figure 1) with stainless steel tubing coated in amorphous silica (Sulfinert coating, Restek, Bellefonte, PA, USA).

2.3. Flux Measurements

Flux measurements were made with a dynamic, flow-through chamber method similar to the cuvette system used by *Kuhn and Kesselmeier* [2000]. Soil and root matter subsamples of 100 g were enclosed in individual 1 L solid PFA incubation chambers (Savillex, Eden Prairie, MN, USA). Another 1 L PFA chamber containing 100 mL

Table 1. Bulk Density and Gravimetric Water Content by Sample[a]

Sample	Bulk Density, Dry (g/cm^3)	Soil Water Content (water g/dry soil g)
Soil_Only	0.99	16%
Soil+Fine_Roots	1.01	14%
Soil+Roots	0.99	15%

[a]Water content was maintained during the experiment by approximately weekly water additions. The uncertainty of soil water content is ± 0.2%.

ofdistilled water was attached in series to the inlet of each chamber before analysis (Figure 1). Both chambers were then partially submerged in a constant temperature water bath maintaining a temperature between 15 and 34°C. For the temperature manipulated in foil to prevent complications from ambient light reacting with subsamples. The second chamber was used both to mitigate moisture loss in subsamples and to act as a buffer volume allowing incoming air to equilibrate with the temperature of the water bath. Air was pumped downstream of the chambers with a microdiaphragm pump (model UNMP830, KNF Neuberger Inc., Trenton, NJ).

For the light/dark experiment, the sample chamber lid was replaced by transparent polytetrafluoroethylene (PTFE) film, affixed in place with a hose clamp. The edges of the film were further affixed to the chamber by tightly wrapping with clear adhesive tape. The flux measurement was performed either with the sample chamber covered in aluminum foil for the dark condition or illuminated with an incandescent light bulb. Light at soil level had a maximum intensity wavelength 600 nm and an intensity of photosynthetically active radiation (PAR) 380 microeinsteins m^{-2} s^{-1}, or about 0.2 the intensity of solar PAR. To correct for the additional warming caused during the light condition, self-contained thermocouple data loggers (iButtons, Maxim Inc., Sunnyvale, CA, USA) covered in PTFE were placed in the subsamples during initial trials. The constant temperature water bath was then adjusted so that both light and dark experiments proceeded with subsamples at 19°C.

Fluxes were calculated using the formula $F = V/m(C_f - C_0)$ [*Livingston and Hutchinson*, 1995], where V is the moles of air flushing through the chamber per minute, m is the mass of the subsample, C_0 is the initial concentration of COS entering the chamber in parts-per-trillion (ppt), C_f is the concentration of COS leaving the chamber in ppt, and F is the flux of COS reported in pmol min^{-1} per 100 g of soil. At least two flux measurements were made for each sample and treatment. To assess method uncertainty, COS fluxes from an empty chamber were quantified alongside chambers containing soil and root matter subsamples.

2.4. Sample Processing

Three field samples were used in this study, denoted "Soil_Only" collected from between wheat rows with little root matter, "Soil + Fine_Roots" from soil adjacent to wheat plants, and "Soil + Roots" containing a higher fraction of roots with some interspersed soil. Seven 100 g subsamples were taken from these three field sample bags and placed in incubation chambers. Letters were used to distinguish between samples from the same bag, e.g., Soil_Only-A and Soil_Only-B were subsampled from the same initial field sample. Subsamples were allowed to equilibrate with the chamber for 2 days before analysis. Field moisture was maintained during the course of the experiment by daily weighing and the addition of distilled water approximately once per week. To investigate the influence of abiotic processes versus microbial processes, three subsamples were sterilized at 121°C in a Steris Amsco Century autoclave (Steris Corporation, Mentor, OH, USA). Sterilization at this temperature should be sufficient to denature cellular and extracellular carbonic anhydrase. The sterilized subsamples were then incubated as before. Volumetric water content and bulk density were determined using standard gravimetric methods (Table 1).

A few previous studies involved processing soil samples with a 2 mm mesh sieve, extracting rocks or large pieces of litter, before lab incubations to quantify COS exchange [*Kesselmeier et al.*, 1999; *Van Diest and Kesselmeier,* 2008]. One soil-only subsample, Soil_Only-C-Sieved, was sieved to compare with other studies using this technique.

3. Results

3.1. Temperature Manipulation Experiments

3.1.1. Live Subsamples

Live subsamples consistently demonstrated net uptake between 15°C and 19°C, transitioning to COS production at higher temperatures (Figure 2). Every soil exhibited a positive linear relationship with soil

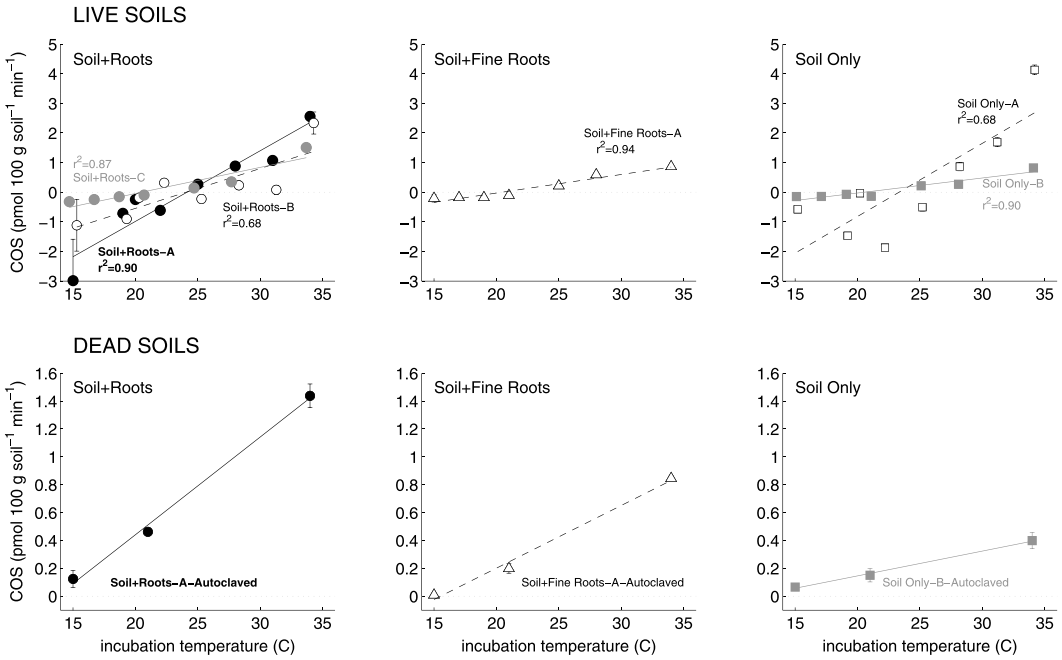

Figure 2. Net COS fluxes versus soil incubation temperature, with least squares linear regressions for each separate soil sample. Error bars represent the standard deviation (1 sigma, some error bars are smaller than the symbols). The soil sample name is near its associated symbol. For "Dead" soil data, the same soil used in the "Live" soil incubations was autoclaved and then incubated a second time. For these individual samples, we have reused the symbols from their live incubations in the panel above.

temperature with correlation coefficients greater than 0.8 (Table 2). Each subsample showed small variability in repeated measurements with much larger variation between subsamples, with the exception of the Soil + Roots subsample fluxes at 15°C. The Soil + Roots subsamples were the first measurements performed in this study and showed the highest variability, suggesting that these subsamples had not yet equilibrated after 2 days.

3.1.2. Autoclaved Subsamples

Incubations of sterilized dead soils resulted in solely net COS production for the temperature range investigated (15 to 34°C). Compared to observations of the same soil samples before sterilization, autoclaved soil samples produced a reduction in slope for temperature versus COS flux for all three trials (Figure 2). For the Soil + Roots-A-Autoclaved and Soil + Fine_Roots-A-Autoclaved samples, sterilization yielded a reduction in maximum COS flux at 34°C; however, at 34°C Soil_Only-B-Autoclaved (0.4 pmol min^{-1} per 100 g soil) exhibited larger net COS production compared to COS flux observations of Soil_Only-B (0.2 pmol min^{-1} per 100 g soil) before sterilization.

Table 2. Slope and Correlation Coefficient From Least Squares Linear Regressions of Mean COS Flux and Temperature

Sample Name[a]	r^2	Slope
Soil+Roots-A	0.90	0.24
Soil+Roots-A-Autoclaved[b]	0.99	0.070
Soil+Roots-B	0.68	0.13
Soil+Roots-C	0.87	0.088
Soil+Fine_Roots-A	0.94	0.063
Soil+Fine_Roots-A-Autoclaved[b]	0.99	0.045
Soil_Only-A	0.68	0.25
Soil_Only-B	0.90	0.050
Soil_Only-B-Autoclaved[b]	0.99	0.018
Soil_Only-C-Sieved	0.94	0.053

[a]Suffix letters refer to different subsamples from the same sample bag (A, B, or C). Soil+Roots-A, Soil+Fine_Roots-A, and Soil_Only-B were incubated at seven temperature conditions, autoclaved, and incubated a second time.
[b]Fluxes from the autoclaved samples and sieved sample were only measured at 15, 21, and 34°C.

3.2. Light and Dark Experiments

Exposing soil samples to light-induced net COS production and/or inhibited COS consumption in all cases except for the sterilized

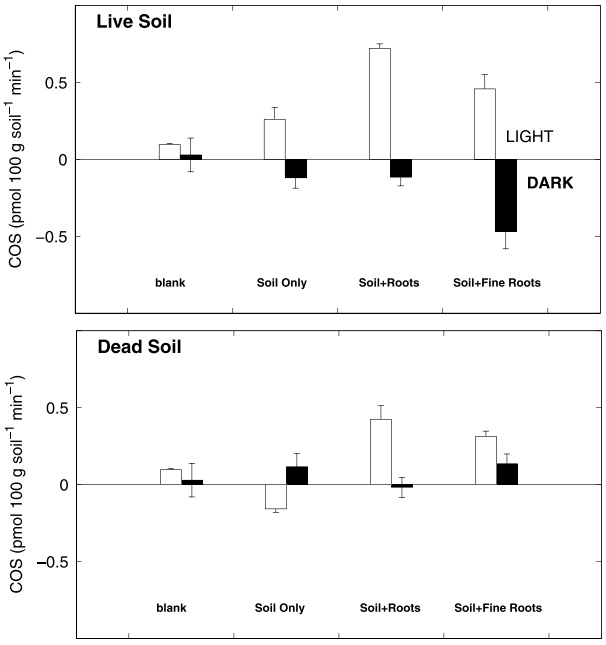

Figure 3. COS fluxes from subsample incubation experiments under light and dark conditions. Error bars indicate the standard deviation of repeated measurements. All measurements were performed with incubation temperature at 19°C.

Soil_Only-B-Autoclaved. The largest production rate with light exposure was from the wheat root samples (Soil + Roots-B and Soil + Roots-C) at 0.7 ± 0.03 pmol min^{-1} per 100 g soil (Figure 3). The empty "blank" incubation chamber had a measureable flux of COS of 0.09 ± 0.006 pmol min^{-1} soil under light conditions. Comparing fluxes measured with a clear PTFE versus the opaque PFA lid used in the temperature manipulation experiments (Figure 3 to Figure 2), most dark flux measurements were within the bounds of uncertainty of the corresponding temperature manipulation flux measurements at 19°C. The exception is sample Soil + Fine_Roots-A, which exhibited a dark uptake value closer to the COS flux estimate at 15°C.

3.3. Sieved Soil Treatment

The sieved subsample Soil_Only-C-Sieved was incubated at 15, 21, and 34°C and compared to Soil_Only-B, a different 100 g subsample taken from the same sample bag (Figure 4). The variability of COS fluxes from Soil_Only-B and Soil_Only-C-Sieved were comparable. Though Soil_Only-C-Sieved was incubated at only three temperatures, the overall slope of the relationship between COS flux and temperature is similar to Soil_Only-B (Table 2).

4. Discussion

These agricultural field soils and root matter converted from net sinks of COS to net sources when they were exposed to any of the following three conditions: higher temperatures (with a threshold between 20 and 25°C), strong light (at 19°C), and sterilization. Taken together, these results strongly suggest that production of COS by abiotic thermal/photodegradation of soil organic matter is sufficient to overwhelm the observation of simultaneous enzymatic consumption of COS in aerobic soil. This could explain two surprising patterns in COS fluxes that *Billesbach et al.* [2014] found over the Southern Great Plains Atmospheric Radiation Measurement (SGP-ARM) site, where the samples for this study were collected. First, during the wheat growing season, there was nighttime net COS uptake which could not be completely accounted for by a small nighttime stomatal conductance. Second, after the wheat harvest, *Billesbach et al.* [2014] observed large COS fluxes to the atmosphere with maximum net

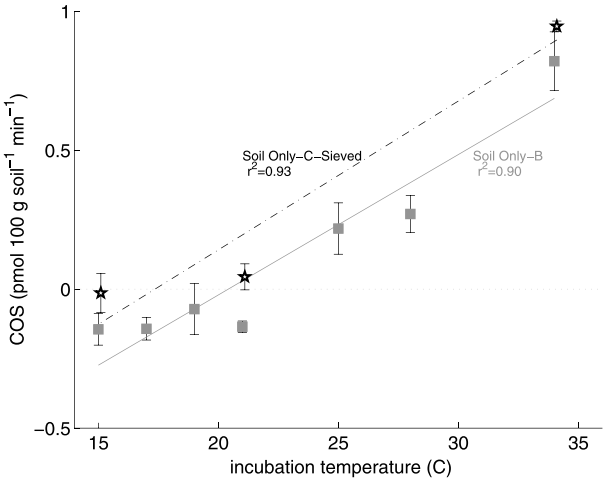

Figure 4. COS fluxes at different temperatures from two soil subsamples: Soil_Only-C-Sieved was processed with a 2 mm mesh sieve and Soil_Only-B was not.

production during the day. *Maseyk et al.* [2014] in a simultaneous experiment at the same site found that net COS production coincided with very high soil chamber temperatures. The mechanism behind these observations could be explained by variations in soil temperature and light leading to the degradation of soil organic matter.

4.1. Temperature and COS Fluxes

Prior work identified the importance of temperature in regulating the magnitude of COS uptake in soils; however, these studies report soil COS uptake exclusively. COS flux observations necessarily reflect the balance between production and consumption. *Kesselmeier et al.* [1999] and *Steinbacher et al.* [2004] modeled soil COS uptake in terms of temperature and soil water content, with the former study also relating COS uptake to ambient COS concentration. Over an overlapping range of temperatures, *Van Diest and Kesselmeier* [2008] and *Kesselmeier et al.* [1999] found that COS uptake had a distinct temperature maximum followed by declining uptake rates at higher temperatures, corresponding to presumed enzyme destruction. In contrast, soil and root matter COS fluxes in this study had a linear relationship to temperatures from 15 to 35°C, sustaining net COS uptake when incubated below 19°C and net COS production above 25°C.

The differences in sign of COS flux was not due to differences in processing the samples as in previous studies. One sample, Soil_Only-C-Sieved, was sieved as described in *Van Diest and Kesselmeier* [2008] and *Kesselmeier et al.* [1999]. The COS fluxes measured with Soil_Only-C-Sieved showed uptake at 15°C and production at 21 and 34°C (Figure 4).

One important variable that was largely unexplored in this study was the intentional variation of soil moisture. The water content of the subsamples decreased during incubations before more water was added, returning the sample to field moisture. The uncertainty of measurements depicted in Figure 2 would include the influence of this drying over time, since repeated incubations of the same subsample at a given temperature were sometimes made hours or days apart. In studies of other oxic soils, COS *uptake* varied with soil moisture by a second-order polynomial relationship [*Steinbacher et al.*, 2004] or a more complicated ratio of exponential functions [*Kesselmeier et al.*, 1999; *Van Diest and Kesselmeier*, 2008]. Correlations between soil moisture and soil COS *production* may be similarly robust [*Maseyk et al.*, 2014]. However, the objective of this study was to investigate the mechanisms of soil COS production that were first observed under field conditions.

In the case of observations from the SGP-ARM site, some in-soil process(es) resulted in COS production that overwhelmed COS consumption [*Billesbach et al.*, 2014; *Maseyk et al.*, 2014]. Two approaches were taken to determine if the COS production was primarily biological or abiotic. The first approach was to autoclave the subsamples to see if production would cease. This study found that autoclaved subsamples still generate COS, indicating abiotic production, confirming results by *Kato et al.* [2008]. Compared to live subsamples, autoclaved subsamples had a shallower slope when regressed with temperature, resulting in a small net production of COS at the minimum experiment temperature of 15°C. The change in slope could be attributed to the changes in functional groups in soil organic matter brought on by autoclaving as shown by *Berns et al.* [2008].

The second approach was to incubate the subsamples at increasing temperatures to see if results resembled abiotic or biological temperature response curves [*Conrad*, 1996]. Results from the range of incubation temperatures from 15 to 34°C did not show a temperature optimum within this range, such as that noted by *Van Diest and Kesselmeier* [2008] and *Kesselmeier et al.* [1999] for other agricultural soils. Instead, emissions increased seemingly linearly with temperature, supporting an abiotic production mechanism. It is possible that adsorption on soil surfaces could explain a portion of COS uptake and subsequent release under higher temperatures. If this is the case, some of the additional nonstomatal nighttime soil uptake during the *Billesbach et al.* [2014] study may be accounted for by this interaction. However, we have yet to be able to discern abiotic adsorption from the well-documented consumption of COS by carbonic anhydrase [*Protoschill-Krebs et al.*, 1996; *Kesselmeier et al.*, 1999].

4.2. Light and COS Fluxes

Live subsamples exhibited net consumption of COS in the dark and net production under light conditions at the same temperature. This suggests that photoproduction of COS is occurring in the soil. Alternatively, though more unlikely, light may somehow inhibit consumption, revealing an underlying and persistent

production of COS. In any case, the results here could explain the high daytime COS production after the wheat was harvested at the SGP-ARM site [*Billesbach et al.*, 2014; *Maseyk et al.*, 2014]. Harvesting wheat both removed the proportionally large COS sink and caused the remaining soil and litter to be subjected to direct sunlight. We did not vary the intensity of light, and it is unclear whether more intense light would cause greater production. Along with variation in soil temperature, these circumstances could contribute to the variable COS production rates and roughly diel behavior.

Prior studies considered the influence of light on terrestrial COS fluxes, using the relationship between PAR and photosynthesis to infer a relationship between the COS uptake by plants and available light [*Geng and Mu,* 2006; *Kesselmeier and Merk*, 1993; *Kuhn et al.*, 1999]. To our knowledge, this is the first study that has considered the influence of light on soil fluxes outside of the indirect effect on temperature.

Outside of terrestrial ecosystems, observations of COS photoproduction in ocean and rain water have been linked to the intensity of UV light [*Mu et al.*, 2004; *Weiss et al.*, 1995; *Zepp and Andreae*, 1994]. Rates of COS production were further correlated with concentrations of chromophoric dissolved organic matter [*Uher and Andreae*, 1997], organosulfur compounds [*Zepp and Andreae*, 1994], and humic acid with cysteine [*Flöck et al.*, 1997]. Considering the soil organic matter content in the wheat field soil and roots in this study, COS photoproduction could be related to a comparable process suggested by *Flöck et al.* [1997] for ocean water, where humus photosensitizes COS precursors, e.g., cysteine. In the study by *Minami and Fukushi* [1981], adding cysteine and a number of other organic sulfur compounds to soil samples resulted in aerobic COS production; light controls during their experiment were unspecified.

Although the soils and root matter studied here exhibited similar overall patterns in COS exchange and temperature, there remains unexplained variability in the magnitude of fluxes between subsamples. This may be accounted for by the heterogeneity in the overall quality and form of soil organic matter. In a future experiment, subsets of litter (roots and leaves) and soil could be incubated separately to assess the COS contribution of various types of litter, previously found to exhibit COS uptake [*Kesselmeier and Hubert*, 2002].

5. Conclusion

COS exchange rates can be used to approximate carbon assimilation rates in plants. In order to implement this technique on a larger, ecosystem scale, soil exchange of COS must be characterized to distinguish plant consumption from interactions with soils. In the wheat field investigated by *Billesbach et al.* [2014], soil COS flux observations had to be included to explain overall ecosystem COS exchange. Using soil and root matter samples from the same wheat field site, this study showed that some of the net COS release to the atmosphere could be attributed to abiotic thermal degradation and photodegradation of soil organic matter. These results suggest an approach for assessing soil influence on COS exchange in other ecosystems: isolating ecosystem soil components and investigating relationships between overall COS fluxes with temperature and radiation. Since the latter two variables are routinely measured, this may lead to a robust method of correcting the COS-derived GPP estimates for soil COS exchange. Reducing the potentially large uncertainty in GPP estimates will bolster this powerful proxy in investigating carbon-climate dynamics.

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