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ABSTRACT TITLE: COS Flux Measurements: New Instrumentation and Eddy Flux Observations for a Carbon Cycle Tracer at One-Millionth the Concentration of CO2

ABSTRACT: Atmospheric carbonyl sulfide (COS) is a promising new tracer for measurement-based approaches to constrain biosphere-atmosphere carbon and water exchange. As the uptake of COS and CO_2 by vegetation is closely coupled during photosynthesis, concurrent COS and CO_2 measurements have been proposed to separately quantify the terrestrial gross fluxes of photosynthesis and respiration at ecosystem to continental scales. We have explored the dynamics of COS ecosystem-atmosphere exchange in a wheat field at the Southern Great Plains ARM site using newly available instrumentation for trace gas research. Using Quantum Cascade laser technology and high resolution Tunable Infrared Laser Differential Absorption Spectroscopy (QC-TILDAS), the COS analyzer (Aerodyne Research) is capable of measuring COS concentrations at 10 Hz and with a 1 sec accuracy of < 5 ppt, as well as CO_2 and H_2O. This enabled us to make near continuous eddy covariance (EC) measurements of COS fluxes within a background atmospheric concentrations of ~ 500 ppt, which represent successful EC measurements from the lowest ambient concentration trace gas yet made. In addition, we coupled the QC-TILDAS to an automated soil chamber on a two-hourly cycle, providing us with unparalleled information on in situ soil COS flux behavior.

Measurements were made over a two-month period that covered the growing season, senescence and post-harvest periods. We found that during the growing season, there was a strong uptake of COS by the canopy of between ~ 10 and 40 pmol m^{-2} s^{-1}, with a strong diel signal. Ecosystem COS sink strength diminished as the plants approached the grainfilling period, and after senescence and over the harvested field, we observed a strong source of COS to the atmosphere of up to +40 pmol m^{-2} s^{-1}. Contrary to what is commonly assumed, we observed that overall the soil was a net source of COS, but both sink and source behaviour was observed in a strongly temperature dependent response. However, during the peak growing period, soil COS fluxes were only a few percent of the canopy COS uptake, and therefore not a significant source of error for using COS as tracer of gross carbon fluxes. Further investigations into the soil COS fluxes indicate that roots, not soil microbes, appear to be responsible for the COS production. We also observed COS production from grain heads. Therefore it seems processes associated with senescence and plant internal reallocation of resources underlie the interesting seasonal pattern of COS fluxes we observed. This information is now being incorporated into regional scale modelling and interpretation of boundary layer atmospheric COS concentration measurements. In this study, we have shown how these high-resolution COS measurements at high precision are opening up new opportunities for exploring and constraining carbon cycle processes. In addition they are providing new insight into system biogeochemistry and plant responses as revealed through trace gas production. Observations in a range of ecosystems are needed to compare and contrast these responses and identify the relevant parameters to include into terrestrial COS analyses and models.