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Scaling up carbonyl sulfide (COS) fluxes from leaf and soil to the canopy

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Carbonyl sulfide (COS) with atmospheric concentrations around 500 ppt is an analog of CO_2 which can potentially serve as powerful and much needed tracer of photosynthetic CO_2 uptake, and global gross primary production (GPP). However, questions remain regarding the application of this approach due to uncertainties in the contributions of different ecosystem components to the canopy scale fluxes of COS. We used laser quantum cascade spectroscopy in combination with soil and branch chambers, and eddy covariance measurements of net ecosystem exchange fluxes of COS and CO_2 (NEE) in citrus orchard during the driest summer month to test our ability to integrate the chamber measurements into the ecosystem fluxes. The results indicated that:

1) Soil fluxes showed clear gradient from continuous uptake under the trees in wet soil of up to -4 pmol m-2s-1 (CO_2 emission of $\sim$0.5 umol m-2s-1) to emission in dry hot and exposed soil between rows of trees of up to +3 pmol m-2s-1 (CO_2 emission of $\sim$11 umol m-2s-1). In all cases a clear correlation between fluxes and soil temperature was observed.

2) At the leaf scale, midday uptake was $\sim$5.5 pmol m-2s-1 (CO_2 uptake of $\sim$1.8 umol m-2s-1). Some nighttime COS uptake was observed in the citrus leaves consistent with nocturnal leaf stomatal conductance. Leaf relative uptake (LRU) of COS vs. CO_2 was not constant over the diurnal cycle, but showed exponential correlation with photosynthetically active radiation (PAR) during the daytime.

3) At the canopy scale mid-day summer flux reached -12.0 pmol m-2s-1 (NEE $\sim$6 umol m-2s-1) with the diurnal patterns of COS fluxes following those of CO_2 fluxes during the daytime, but with small COS uptake fluxes maintained also during the night when significant CO_2 emission fluxes were observed. The canopy-scale fluxes always indicated COS uptake, irrespective of the soil emission effects. GPP estimates were consistent with conventional indirect estimates based on NEE and nocturnal measurements. Scaling up from soil and leaf chamber to canopy scale was possible by estimating LAI, and differential consideration of soil surface components (shaded vs. exposed fractions).

4) Diurnal changes in the atmospheric concentrations of COS and CO_2 above the canopy showed complex patterns with opposite trends after sunrise that could be explain by the development of the planetary boundary layer

5) COS-based estimate of GPP can be improved by adopting light dependent LRU, around the mean value of $\sim$1.6, and correcting for soil COS fluxes based on soil temperature and canopy cover estimates, and coupled COS/CO_2 concentration measurements provide useful information on boundary layer dynamics.