The Potential of Carbonyl Sulfide as a Tracer for Gross Primary Production at Flux Tower Sites

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Abstract: Regional and continental scale studies of the seasonal dynamics of atmospheric carbonyl sulfide (OCS) mole fractions and leaf-level studies of plant OCS exchange have shown a close relationship with those for carbon dioxide (CO_2). CO_2 has sinks and sources within terrestrial ecosystems, but the primary terrestrial exchange for OCS is thought to be leaf uptake, suggesting potential for OCS uptake as a tracer for gross primary production (GPP). We examined the utility of OCS uptake as a GPP tracer in micrometeorological studies of biosphere-atmosphere CO_2 exchange. Theoretical concepts from earlier OCS studies were combined to relate vertical mole fraction gradients of CO_2 and OCS to GPP at the Harvard Forest AmeriFlux site during the 2006 growing season. Relative CO_2 and OCS vertical gradients were correlated with each other, consistent with previous OCS studies and indicating similar mechanisms controlled CO_2 and OCS vertical gradient dynamics. GPP estimates from temperature-based NEE partitioning (Reichstein et al., 2005) were similar to those derived with an OCS-based NEE partitioning model that used either daily or seasonal gradients, providing evidence that OCS uptake can potentially serve as a tracer for GPP in micrometeorological studies. OCS mole fraction and flux measurements at flux tower sites are rare, so an analysis was performed based on CO_2 mole fractions to evaluate potential OCS signals that might be found at five other AmeriFlux sites. Vertical CO_2 mole fraction gradients were used to project vertical OCS mole fraction gradients. At the three forest sites evaluated, projected OCS gradients were similar in magnitude to those at Harvard Forest and small compared to current OCS measurement uncertainty. At the two sites evaluated with short canopies (C_4 grassland and soybean crop), projected OCS gradients were greater than those in forests, indicating a stronger possible OCS signal and greater potential for use of OCS uptake as a GPP tracer at sites with short canopies.

Theory: The following requirements **R1-R4** should be met for OCS to be used as a GPP tracer at the flux tower scale (10^2-10^6 m^2 area):

R1. OCS must follow the same physical pathway as CO_2 into leaves (Stimler et al., 2010).

R2. OCS exchange must be a one-way flux (no OCS compensation point) (Stimler et al., 2010).

R3. OCS and CO_2 cannot directly or indirectly interact (no inhibitory or toxicity effects) (Stimler et al., 2010).

R4. All OCS fluxes must be negligible compared to plant uptake (Montzka et al., 2007; Campbell et al., 2008).

Leaf-level studies have indicated R1-R3 are met, and flux tower scale studies have provided some support for R4. When R1-R4 are accepted, OCS measurement can be used to estimate GPP at the flux tower scale via one of two methods: (1) OCS flux measurements or (2) simultaneous OCS and CO_2 gradient measurements.

Flux measurements (Sandoval-Soto et al., 2005):

$$GPP = F_{OCS}\left(\frac{C_{aCO2}}{C_{aOCS}}\right)\left(\frac{1}{LRU}\right) \quad (1)$$

Gradient measurements (Campbell et al., 2008):

$$GPP = NEE \cdot ERU\left(\frac{1}{LRU}\right) \quad (2)$$

where F_{OCS} is OCS flux [pmol m^{-2} s^{-1}], C_{aCO2} is ambient CO_2 mole fraction [μmol mol^{-1}], C_{aOCS} is ambient OCS mole fraction [pmol mol^{-1}], and LRU is leaf relative uptake (normalized leaf-level OCS flux divided by normalized leaf-level CO_2 flux; calculated from leaf uptake model proposed by Seibt et al., (2010)) in Eq. 1; NEE is net ecosystem exchange [μmol m^{-2} s^{-1}] measured with eddy covariance and ERU is ecosystem relative uptake in Eq. 2. ERU is calculated via OCS and CO_2 gradient measurements (G_{OCS} and G_{CO2}):

$$ERU = \frac{G_{OCS}/C_{aOCS}}{G_{CO2}/C_{aCO2}} \quad (3)$$

Methods: We used Eqs. 2 and 3 to estimate GPP from OCS mole fraction measurements made at the Harvard Forest AmeriFlux site (direct measurements of OCS flux were not available). The CO_2 gradient was calculated from mole fraction measurements at 29 m and 18 m; NEE was measured with eddy covariance instrumentation. OCS mole fraction measurements were only made at two heights, 29 m and 2 m. Rather than assume a linear OCS profile, **measured ozone (O_3) mole fraction profiles were used to estimate the OCS mole fraction at 18 m using the OCS measurements at 29 m and 2 m**:

$$OCS_{18m} = OCS_{29m} - \left(OCS_{29m} - OCS_{2m}\right)\left(\frac{O_{3\text{-}29m} - O_{3\text{-}18m}}{O_{3\text{-}29m} - O_{3\text{-}2m}}\right) \quad (4)$$

Estimation of OCS mole fractions with Eq. 4 assumes that the OCS profile has the same shape as the O_3 profile. We compared OCS-derived GPP estimates from Eq. 2 to GPP estimates from temperature-based NEE partitioning (Reichstein et al., 2005). OCS flux was also estimated from Eq. 1 using GPP estimates from temperature-based NEE partitioning and used to further evaluate R4. To estimate potential OCS signals at other AmeriFlux sites, where OCS mole fractions were not measured, we projected OCS gradients from measured CO_2 gradients using Eq. 3 and assuming ERU = 5 and C_{aOCS} = 400 pmol mol^{-1}.

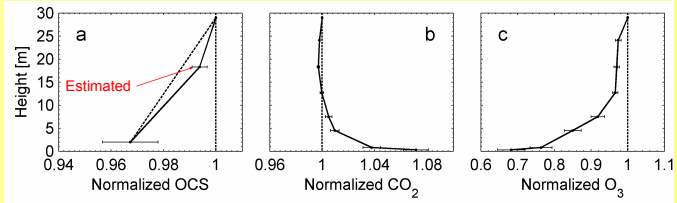

Figure 1: Mean normalized CO_2, OCS, and O_3 mole fraction profiles, calculated by dividing all mole fractions by the mole fraction at 29 m; error bars are one standard error of the mean. OCS mole fractions were only measured at 29 m and 2 m, thus **OCS mole fraction was estimated at 18 m using Eq. 4, based on the shape of the O_3 profile**. OCS and CO_2 gradients between 29 m and 18 m were used to calculate ERU from Eq. 3.

Results: Harvard Forest

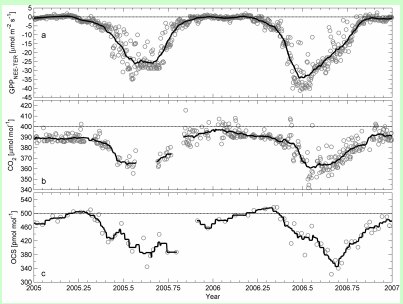

Figure 2: GPP estimated from the method of Reichstein et al. (2005) ($GPP_{NEE\text{-}TER}$), C_{aCO2} above the canopy, and C_{aOCS} above the canopy. **Seasonal trends were similar**, but OCS lagged behind CO_2 and further behind GPP.

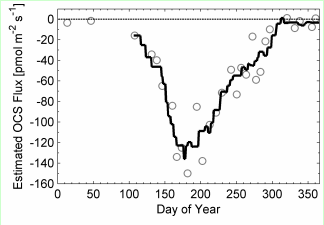

Figure 3: OCS flux estimates from 2006, calculated with Eq. 1 using GPP estimated from the method of Reichstein et al. (2005) and C_{aCO2} and C_{aOCS} measured above the canopy. Assuming literature values of soil OCS flux from other sites are reasonable soil OCS flux estimates for Harvard Forest, **canopy uptake was likely the dominant OCS flux**.

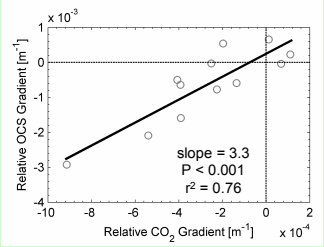

Figure 4: Relationship between relative OCS gradients (calculated from the numerator in Eq. 3) and relative CO_2 gradients (calculated from the denominator in Eq. 3). Each datum was used to calculate ERU (from Eq. 3) to provide **daily ERU values** and the slope of the line (3.3) provided a **seasonal ERU value**; ERU values were used to estimate GPP.

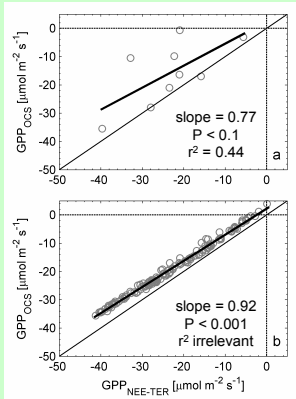

Figure 5: GPP from OCS measurements (GPP_{OCS}), calculated from Eq. 2, versus GPP estimated from the method of Reichstein et al. (2005) ($GPP_{NEE\text{-}TER}$). GPP_{OCS} was calculated using (a) individual, daily ERU values and (b) a constant, seasonal ERU value. **GPP_{OCS} was lower than $GPP_{NEE\text{-}TER}$**, but provided reasonable GPP estimates.

Results: Five Additional AmeriFlux Sites

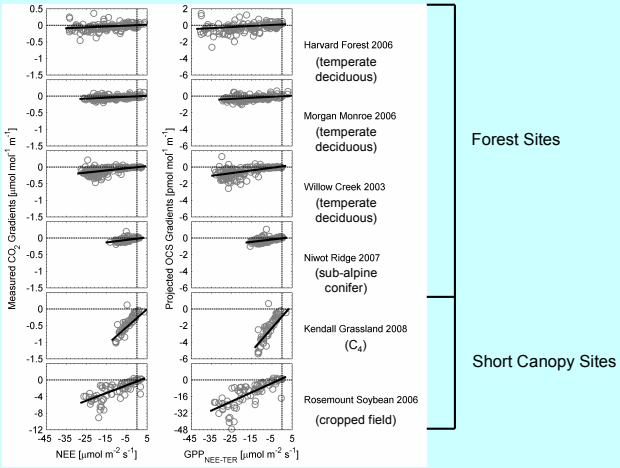

Figure 6: Relationship between measured CO_2 gradients and NEE, and projected OCS gradients and GPP estimated from method of Reichstein et al. (2005) ($GPP_{NEE\text{-}TER}$), at four forested AmeriFlux sites and two sites with short canopies. **Gradients were much larger at sites with short canopies**, indicating the potential of stronger OCS signals.

Conclusions:

- Despite limited data, results indicate potential for OCS as GPP tracer at Harvard Forest.
- Potential of stronger OCS signals at sites with short canopies.
- More flux tower scale OCS studies are warranted.
- Characterization of OCS fluxes other than plant uptake is required.

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