Geophysical Research Abstracts
Vol. 20, EGU2018-12437, 2018
EGU General Assembly 2018


# Flux partitioning plus – joint constraints by carbon dioxide and carbonyl sulfide increase inferred gross primary productivity estimates

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The trace gas carbonyl sulfide (COS) has been proposed as a tracer for canopy gross primary production (GPP) in the last few years. COS enters the plant leaf through the stomata and diffuses through the intercellular space, the cell wall, the plasma membrane and the cytosol like carbon dioxide ($CO_2$). It is then catalyzed by the enzyme carbonic anhydrase in a one-way reaction to hydrogen sulfide and $CO_2$. Studies show, that the leaf relative uptake (LRU), which is the ratio of the deposition velocities of COS to $CO_2$ on leaf level, are fairly constant across multiple species with a median of about 1.68. Although non-plant COS sources and sinks e.g. soils complicate the implementation of COS as a tracer for GPP on ecosystem level, the one-way flux into the leaf makes COS a promising GPP constraint.

The overarching objective of this study was to evaluate the potential of COS as a tracer for GPP, improve current flux partitioning (FP) models by implementing COS as an additional constraint for the plant canopy $CO_2$ exchange. To obtain our goal, we conducted field campaigns at different field sites across Europe. These sites included a managed temperate mountain grassland (AUT), a savanna (ESP), a temperate beech forest (DEN) and a soy bean field (ITA). On each of these sites we conducted ecosystem scale eddy covariance and manual soil chamber measurements of COS and $CO_2$ which resulted in daily hourly mean maximum ecosystem uptakes between -36 pmol m-2s-1 (ITA) and -85 pmol m-2s-1 (DEN). The soil COS flux reached emissions of up to 11 pmol m-2s-1 during daytime at grass dominated ecosystems. During nighttime we observed fluxes close to zero or as small as -3.8 pmol m-2s-1. Since the magnitude of the soil fluxes, which was strongly correlated to incoming shortwave radiation, could not be neglected, these were subtracted from the ecosystem flux to derive the actual canopy COS fluxes for all the measurement sites.

Our data confirm previous studies showing that the LRU is a light dependent variable and can therefore not be used as a constant in models. Incorporating this relationship and using synthetic data, we show that the implementation of COS as an additional constraint outperforms classical FP methods using only $CO_2$. In a last step we applied the new FP model to the 4 field sites. The joint constraint by both $CO_2$ and COS resulted in higher values for GPP which suggests that GPP estimates derived from current FP models are likely to underestimate the magnitude of GPP.