



From uptake to emission: Daily to seasonal COS soil and ecosystem fluxes and their correlation with CO₂ above a highly dynamic managed temperate mountain grassland

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In the last few years the trace gas carbonyl sulfide (COS) has been proposed as a tracer for canopy gross primary production (GPP). 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 (CO₂). It is then metabolized by the enzyme carbonic anhydrase (CA) in a one-way reaction. Studies show, that the leaf relative uptake (LRU), which is the ratio of the deposition velocities of COS to CO₂ 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.

Between May and November 2015 we conducted an intensive measurement campaign above a temperate mountain grassland in Austria to evaluate the potential of COS as a proxy for ecosystem scale GPP. Due to the highly intensive management, i.e. multiple cuts of the aboveground biomass during the growing season, we were able to observe multiple growing cycles of the grassland within one season.

We quantified the soil COS flux by using UV-transparent soil chambers, while the ecosystem scale COS and CO₂ fluxes were measured using the eddy covariance technique. A random forest regression analysis of the soil data allowed us to model the soil COS fluxes on half hourly basis and revealed a positive correlation between incident radiation reaching the soil surface and COS emission. At lower leaf area indices (LAI) classes the mean diurnal soil flux contributed up to 18 % of the mean diurnal ecosystem COS flux with reaching the highest ratios during midday. Right before the cuts, at a LAI above three, the midday ratio decreased to about 1 %, but stayed elevated during dusk and dawn. We subtracted the soil COS from the ecosystem flux to retrieve the canopy COS flux and consequently compared the COS to CO₂ deposition velocities. This revealed strong differences in their ratio, the ecosystem relative uptake (ERU), during midday shortly after cuts (> 8) and at high LAI classes (1-2), indicating variations in LRU throughout the season. During dusk and dawn the ERU increased, reflecting the dependency of photosynthesis on light compared to the light independent uptake of COS by CA.

To evaluate the variability of the LRU, we used a modified flux partitioning model to include the canopy COS fluxes as additional constrain on GPP, while keeping LRU a light dependent and variable parameter. Our model results for 15 day windows showed that the LRU at the field site varied between 0.8 and 1.7 over the course of the season.

Taken together our results suggest that COS as a tracer for canopy CO₂ is more complex than we hoped, LRU is not only susceptible to changes in light, but also to seasonal changes.