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Sources and sinks of carbonyl sulfide in a mountain grassland and relationships to the carbon dioxide exchange

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The trace gas carbonyl sulfide (COS) has been proposed as a tracer for canopy gross primary production (GPP), canopy transpiration and stomatal conductance of plant canopies 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 CO_2. It is then catalyzed by the enzyme carbonic anhydrase (CA) in a one-way reaction to H2S and CO_2. This one-way flux into the leaf makes COS a promising tracer for the GPP. However there is growing evidence, that plant leaves aren't the only contributors to the ecosystem flux of COS. Therefor the COS uptake of soil microorganisms also containing CA and abiotic COS production might have to be accounted for when using COS as a tracer at the ecosystem scale.

The overarching objective of this study was to quantify the relationship between the ecosystem-scale exchange of COS, CO_2 and H_2O and thus to test for the potential of COS to be used as a tracer for the plant canopy CO_2 and H_2O exchange. More specifically we aimed at quantifying the contribution of the soil to the ecosystem-scale COS exchange in order to understand complications that may arise due to a non-negligible soil COS exchange.

In May 2015 we set up our quantum cascade laser (QCL) (Aerodyne Research Inc., MA, USA) at a temperate mountain grassland in Stubai Valley close to the village of Neustift, Austria. Our site lies at the valley bottom and is an intensively managed mountain grassland, which is cut 3-4 times a year. With the QCL we were able to measure concurrently the concentrations of COS, CO_2, H_2O (and CO) at a frequency of 10 Hz with minimal noise. This allowed us to conduct ecosystem-scale eddy covariance measurements.

The eddy covariance flux measurements revealed that the COS uptake continues at night, which we confirmed was not caused by soil microorganisms, as the soil exchange was close to neutral during nighttime. Instead, the nocturnal COS uptake appears to be caused by incomplete stomatal closure and continuing catalytic CA activity in the absence of light. The resulting data also revealed a weaker correlation between COS- and CO_2-fluxes than expected, which hints to further COS-exchange mechanisms at our site. To disentangle sources and sinks within and below the canopy, we measured vertical within-canopy profiles of COS and CO_2 and inferred the vertical distribution of sources and sinks by means of an inverse Lagrangian analysis. The resulting data confirmed that soils at our site are sources for COS during daytime and close to neutral during nighttime and place the major COS/CO_2 sink in the central part of the canopy, where a large amount of leaf area still receives enough light.

Taken together our results suggest that using COS as a tracer for canopy CO_2 and H_2O exchange may be less straight forward than previously thought and that further work is required to better understand the ecosystem-scale COS exchange and its drivers.