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# [Constraining gross carbon fluxes using ecosystem flux and atmospheric concentration measurements of carbonyl sulfide (COS) and CO2, COSMOS]


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## Introduction and motivation

Carbonyl sulfide (COS) has been suggested as a useful tracer for Gross Primary Production (GPP) as it is taken up by plants in a similar way as $CO_2$, with plants being the dominant sink for COS. However, significant uncertainties remain in the processes of the uptake of COS and $CO_2$ by plants and other minor sinks, such as soil, and of major sources in the ocean and in the relationship between the uptake of COS and GPP, which limits the successful use of COS to constrain GPP on regional to global scales (Campbell et al., 2008; Stimler et al., 2010; Maseyk et al., 2014; Launois et al., 2015). Furthermore, atmospheric concentration measurements of COS have already been employed to improve regional to global GPP estimates, even though the available COS measurements are very sparse, and are only available from the analyses of discrete flask samples from the NOAA cooperative sampling network (Montzka et al., 2007). To this end, high-accuracy in situ atmospheric measurements of COS could potentially provide additional constraints on the use of COS for GPP estimates (Belviso et al., 2013; Kooijmans et al., 2017).

The ENVRI plus access opportunity made it possible for an international group of scientists from University of Groningen in the Netherlands, the Open University in UK, University of California Los Angeles in the US to work closely with local Finnish collaborators at the SMEAR site. We performed both leaf and soil chamber measurements of trace gases of COS, $CO_2$, and CO, in addition to the existing eddy covariance measurements from the University of Helsinki. It was wonderful and indispensable for the team to meet at the SMEAR site from both technical and scientific perspectives. We identified and solved the flow rate issues that are the major part of the uncertainties of the soil and leaf fluxes. We made blank chamber tests, and soil incubation tests, which are important to obtain accurate measurements, and to interpret the measurement results. Besides these, we have also worked out a detailed plan of publishing the results, and an opportunity to work together on a future project.

## Scientific objectives

The objective of this study is to improve our knowledge about the fluxes of COS and CO2 on ecosystem scales, and to derive a better GPP estimate of northern high latitude boreal forests than we are able to achieve with the current knowledge. Specifically, we will: 1) observe the leaf-scale uptake of COS and CO2, and make accurate in situ atmospheric concentration measurements of COS for a whole growing season at a boreal forest site; 2) Verify the use of COS as a tracer for GPP on the ecosystem scale 3) improve the parameterization of a biosphere model (SiB4) COS simulations; 4) derive an improved GPP estimate of northern high latitude boreal forest.

## Methodology and experimental set-up

Ecosystem COS flux measurements have been made at the SMEAR site using the eddy covariance (EC) technique for three years, and it is one of only a few sites worldwide making these measurements. The EC fluxes are calculated based on the 10 Hz measurements from a quantum cascade laser spectrometer (QCLS). Furthermore, a second frequently calibrated QCLS will be used to make high-accuracy 1 Hz COS concentration measurements from a tall tower, soil and branch chambers. The atmospheric concentration measurements will be analyzed for air from the top of the tall tower at 125 m and 4 m above ground. Two soil chambers (Licor LI-8100) have been modified for COS measurements, including using an inert stainless-steel chamber, removal


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and replacement of COS-producing material, and operation in open-flow configuration. Three branch chambers have been full tested, under both normal laboratory (20 °C, 0.6 lux) and additional growing light/heated conditions (40 °C, 150 W/m$^2$), and components that emit COS have been eliminated. The whole system has been automated, sampling each of the tower and chamber lines every 1.5 hours. The profile measurements from the tower and the soil and branch chambers will be used to calculate the storage fluxes. Below is a summary of equipment and the measurements for the campaign and some photos of the system setup.

Table 1. A list of equipment planned for the campaign

| Equipment | Measurements |
|---|---|
| COS analyzer #1 | Eddy covariance measurements |
| COS analyzer #2 | Concentration measurements of a tall tower, soil and branch chambers |
| Two soil chambers | Soil fluxes |
| Three branch chambers | Branch fluxes |
| Three cylinders | For calibrations |

Fig.1 The soil chamber (topleft); the branch chamber (top right); the two QCLS COS analyzers in a wooden hut (bottomleft); 125 m tall tower (bottomright).

**Preliminary results and conclusions**

The preliminary results of the measured leaf-scale fluxes of COS and $CO_2$ are shown in Figure 2, along with the recorded flow rates from April to November 2016. The measured fluxes of both COS and $CO_2$ before August were abnormally low, and were likely caused by an artifact due to the low flow rate. After a readjustment of the flow rate in August, we have obtained successful measurements of COS and $CO_2$ leaf-scale fluxes.

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The averaged diurnal cycles of COS and $CO_2$ fluxes of pine needles show that COS and $CO_2$ uptakes have a similar shape, and both peak at local noon. The measured leaf-scale relative uptake ratios are light dependent, and are rather constant when PAR is larger than 500 µmol $m^{-2}s^{-1}$, with a mean value of 1.4.

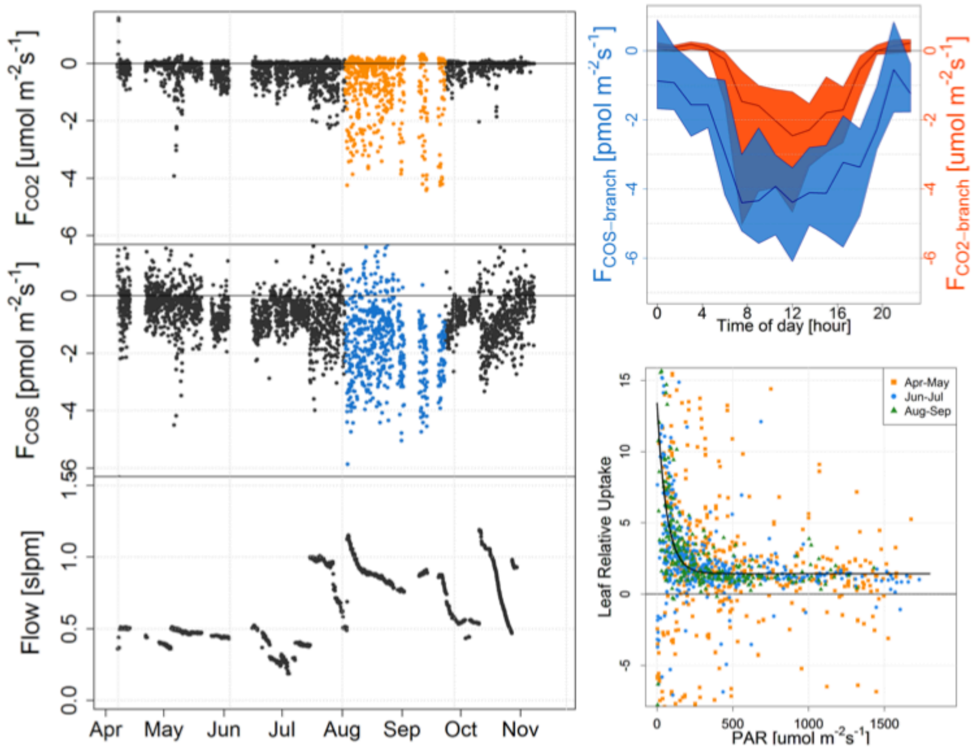


Fig.2 The time series of $CO_2$, COS, and flow rate measurements of one leaf chamber(left, from top to bottom); the averaged diurnal cycles of COS and CO2 fluxes, with uncertainties shown in shaded areas (topright); The leaf-scale relative uptake ratios as a function of PAR (bottomright).

**Multidisciplinary approach**

The SMEAR II - HYYTIÄLÄ site was chosen based on the fact that biosphere and atmosphere studies are well integrated at this site. In addition to the existing eddy-covariance flux, soil flux, and atmospheric concentration measurements of COS and $CO_2$, we performed leaf chamber measurements for the whole growing season, bridging the gap between the ecosystem COS fluxes and the estimate of GPP on the ecosystem scale, and further on the regional scale.

**Outcome and future studies**

The major outcome of the TNA campaign will be peer-reviewed publications. Here below a list of manuscripts in prep is shown:

Kooijmans, L.M.J., Maseyk, K., Seibt U., Sun W., Vesala T., Mammarella I., Aalto J., Erkkilä, K.M., Chen, H.: Branch fluxes of Carbonyl Sulfide (COS) and CO2: linking COS ecosystem fluxes to gross primary productivity, in prep. 2017

Sun W., Kooijmans, L.M.J., Maseyk, K., Chen, H., Vesala T., Mammarella I., Aalto J., Erkkilä, K.M., Seibt U.: Upscaling the fluxes of COS and $CO_2$ from the soil and leaf-scale scale to the ecosystem scale, in prep. 2017

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Vesala T., Sun W., Kooijmans, L.M.J., Maseyk, K., Chen, H., Mammarella I., Aalto J., Erkkilä, K.M., Seibt U.: Multiple-year eddy covariance measurements of COS in a boreal forest, in prep. 2017

After the TNA campaign in 2016, the established good cooperation between University of Helsinki and University of Groningen continued to work together on a joint campaign “From Chlorophyll fluorescence to photosynthesis: upscaling the link” in the spring of 2017, where both fluorescence and COS fluxes are being measured with a common goal to understand the photosynthetic uptake of $CO_2$.

The results learned from the TNA campaign are very useful to the understanding of GPP estimates, and will be used to improve the model simulations, e.g. MuSICA (Ogée et al., 2016) and SiB (Berry et al., 2013). The study was performed at a boreal forest, however, the findings shed lights on other ecosystems.

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Launois, T., Belviso, S., Bopp, L., Fichot, C. G., and Peylin, P.: A new model for the global biogeochemical cycle of carbonyl sulfide – Part 1: Assessment of direct marine emissions with an oceanic general circulation and biogeochemistry model, Atmos. Chem. Phys., 15, 2295-2312, doi: 10.5194/acp-15-2295-2015, 2015.

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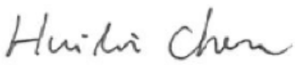

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