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CARBONYL SULFIDE FLUXES AND RELATION TO PHOTOSYNTHESIS IN THE BOREAL REGION

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Academic dissertation

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Kukka-Maaria Kohonen
University of Helsinki, 2022

Abstract

The global carbon cycle is changing due to human impact. Terrestrial ecosystems absorb approximately one third of the annual anthropogenic carbon dioxide (CO_2) emissions, which makes them the largest CO_2 sink together with oceans. The terrestrial net CO_2 sink is, however, a two-way process consisting of uptake by plant photosynthesis (gross primary production, GPP) and emission by plant and soil respiration. Traditionally ecosystem scale photosynthesis and respiration are determined by partitioning the flux tower based net ecosystem exchange (NEE). Ecosystem respiration is usually defined from temperature-dependent regressions that are based on nighttime NEE measurements. GPP is estimated then by subtracting NEE from respiration during daytime. This method assumes that respiratory processes would be the same under solar radiation as during nighttime, which may not be a valid assumption. Due to these uncertainties, other methods for determining GPP are needed.

Carbonyl sulfide (COS) has been suggested to be a useful proxy for GPP as it shares the same diffusional pathway with CO_2 in the leaf stomata but, in contrast to CO_2, is not respired back to the atmosphere. However, COS flux measurements are more complex than CO_2 flux measurements and standardized processing protocols are missing, reducing the comparability of previous COS flux studies. In addition, in order to calculate GPP from COS flux measurements, an accurate definition of the leaf-scale uptake ratio of COS and CO_2 (leaf relative uptake, LRU) is essential.

This thesis presents the longest time series (5 years) of COS flux measurements so far in a boreal forest using the eddy covariance (EC) flux measurement technique. Recommendations for COS EC flux processing and a new gap-filling function for COS fluxes are presented. A simple COS flux parameterization is also developed for boreal evergreen needleleaf forests. In addition to EC fluxes, branch chamber measurements of COS and CO_2 were done allowing to develop better LRU formulations: one with a simple radiation relation fit to measurements, and one based on stomatal conductance theories. Both LRU functions lead to higher COS-based GPP estimates than the traditional CO_2 partitioning. The COS flux parameterization agreed well with measurements and captured the seasonal COS flux variation. However, it was not able to simulate COS uptake reduction in dry conditions. The new LRU formulations advance the COS-based GPP estimates and the developed parameterization aims to help future land surface model development.

Keywords: carbonyl sulfide, eddy covariance, flux measurements, photosynthesis, gross primary production, leaf relative uptake

Contents

List of publications

This thesis consists of an introductory review, followed by four research articles. In the introductory part, these papers are cited according to their roman numerals. It is to be noted that the family name of the candidate has changed from Erkkilä to Kohonen during the process.

I Kohonen, K-M., Kolari, P., Kooijmans, L. M., Chen, H., Seibt, U., Sun, W., & Mammarella, I.: Towards standardized processing of eddy covariance flux measurements of carbonyl sulfide. *Atmospheric Measurement Techniques*, 13(7), 3957–3975, 2020.

II Vesala, T., Kohonen, K-M., Praplan, A. P., Kooijmans, L. M., Foltýnová, L., Kolari, P., Kulmala, M., Bäck, J., Nelson, D., Yakir, D., Zahniser, M. & Mammarella, I.: Long-term fluxes of carbonyl sulfide and their seasonality and interannual variability in a boreal forest. *Atmospheric Chemistry and Physics*, 22, 2569–2584, 2022.

III Kooijmans, L. M., Sun, W., Aalto, J., Erkkilä, K-M., Maseyk, K., Seibt, U., Vesala, T., Mammarella, I. & Chen, H.: Influences of light and humidity on carbonyl sulfide-based estimates of photosynthesis. *Proceedings of the National Academy of Sciences*, 116(7), 2470–2475, 2019.

IV Kohonen, K-M., Dewar, R., Tramontana, G., Mauranen, A., Kolari, P., Papale, D., Kooijmans, L.M., Vesala, T. & Mammarella, I.: Intercomparison of methods to estimate GPP based on CO_2 and COS flux measurements. *Biogeosciences Discussions*, 2022.

1 Introduction

The global climate is changing due to anthropogenic emissions of carbon dioxide (CO_2). The annual CO_2 emissions from fossil fuel combustion and cement production exceed 9.5 GtC yr^{-1} (IPCC, 2021). Of the cumulative emissions 23% is taken up by the oceans and 31% by terrestrial ecosystems, while rest of the emitted CO_2 is accumulated in the atmosphere (Friedlingstein et al., 2020). Due to the higher global CO_2 source than its sinks, the atmospheric CO_2 concentration is rising, which causes a stronger greenhouse gas effect, in turn warming the atmosphere (IPCC, 2021). The net CO_2 uptake by terrestrial vegetation is, however, a two-way process that consists both of the photosynthetic carbon uptake (gross primary production, GPP) and CO_2 emission by plant and soil respiration (R). Under warming climate, both of these processes are enhanced (Dusenge et al., 2019). However, it is not known how much they are changing relative to one another.

During last decades, flux towers, equipped with eddy covariance (EC) system, have been extensively used to measure the surface exchange of energy and gas at ecosystem scale. The EC method provides non-intrusive and direct method for continuous measurements of these fluxes at 30 minutes time scale (Aubinet et al., 2012). It is, however, only able to measure the net exchange. CO_2 fluxes measured with the EC technique have to be thus partitioned into ecosystem respiration and photosynthesis for analysing these two processes individually. Traditionally this is done by making temperature response curves to nighttime CO_2 flux data (that is only respiration in the absence of solar light) and assuming this response is valid also during daytime (Reichstein et al., 2005). Daytime respiration can then be calculated from air and soil temperature measurements, and subtracted from the net CO_2 exchange to get the CO_2 assimilation rate due to photosynthesis. However, it is not known if the respiration responses are similar during daytime and nighttime, and whether there is photorespiration (oxidation process competing with carboxylation under radiation, Heskel et al., 2013) or the Kok effect (that is leaf respiration inhibition under radiation, Kok, 1949, Yin et al., 2020, Keenan et al., 2019) or both influencing respiration under solar radiation.

In recent years, carbonyl sulfide (COS) has proven to be a possible proxy for photosynthetic CO_2 uptake, since it is taken up by the leaves through the same pathway as CO_2 through plant stomata but is totally destroyed at the chloroplast surface by the enzyme carbonic anhydrase (CA) in a hydrolysis reaction (Protoschill-Krebs and

Kesselmeier, 1992; Sandoval-Soto et al., 2005; Wohlfahrt et al., 2012). COS fluxes can thus be used as a proxy for stomatal conductance and gas transport into the leaves (Commane et al., 2015; Wehr et al., 2017; Sun et al., 2018b). There is no back-flux of COS to the atmosphere and thus measuring COS flux with EC technique gives directly its uptake as a net flux, if there are no other sources or sinks of COS in the ecosystem or if those sinks or sources are known. However, the soil has been found to act both as a sink and a source of COS complicating the ecosystem scale measurements (Maseyk et al., 2014; Sun et al., 2018a). Furthermore, the EC measurements of COS are complicated because they have a low signal-to-noise ratio and small fluxes, thus requiring some special attention for measurement maintenance and during flux data processing for ensuring good data quality. In addition, GPP estimates from COS fluxes rely on the knowledge of the leaf relative uptake (LRU), that is, the ratio of COS to CO_2 uptake rates at the leaf level. In many earlier studies, this ratio has been assumed to be a constant value varying mainly by tree species (Stimler et al., 2010; Asaf et al., 2013; Berkelhammer et al., 2014). While this assumption could be valid at daily and longer timescales (Yang et al., 2018), there is substantial sub-daily variation in LRU due to diurnal variation in COS and CO_2 fluxes. In the nighttime, leaves take up COS if stomata are open while CO_2 flux is zero during night. During daytime, both fluxes are affected by stomatal regulation but CO_2 flux also depends on RuBisCO activity that catalyzes the carbon fixation, which is controlled by solar radiation. The ratio of these fluxes is thus expected to have a diurnal variation as well and depend on radiation (Sun et al., 2018b; Yang et al., 2018).

At the global scale, COS is mainly produced by oceans but also emitted by anthropogenic sources (Kettle et al., 2002; Whelan et al., 2018). The main sink is the terrestrial vegetation (Sandoval-Soto et al., 2005). Recent global estimates of biospheric COS uptake vary from -739 GgS yr^{-1} (Kooijmans et al., 2021) to -756 GgS yr^{-1} (Maignan et al., 2021) and -851 GgS yr^{-1} (Ma et al., 2021), and recent studies by Ma et al. (2021) and Remaud et al. (2021) reported a missing sink in the boreal region. Ecosystem scale COS flux measurements are needed to understand the underlying processes of COS exchange and to improve the global sink estimates, but they are still scarce and especially long-term measurements are missing. These ecosystem scale flux measurements and flux dependencies on environmental factors are thus also needed, without tying the COS fluxes to stomatal conductance or GPP.

The general aim of this thesis is to refine the COS-based GPP estimate and analyze its uncertainties from sub-daily to interannual time scales. This thesis introduces a unique five-year data set of COS flux measurements in a boreal forest at the ecosystem scale and seven months at leaf level. With these data we are able to tackle several aspects related to COS EC fluxes and use all the newly gained information in a new COS-based GPP estimate. The contents of the thesis are illustrated in Fig. 1. More specifically, the aims of this thesis are to:

1) develop recommendations and standard protocols for COS EC flux measurements and data processing (**Paper I**),

2) determine the seasonal and interannual variability of COS fluxes in a boreal forest (**Paper II**),

3) create a simple parameterization for COS flux at the forest level and in the boreal region (**Paper II**),

4) constrain the drivers and temporal variability of LRU for more precise GPP estimates (**Papers III, IV**), and

5) evaluate different GPP estimates from COS and CO_2 flux measurements at annual, seasonal and daily scales (**Paper IV**).

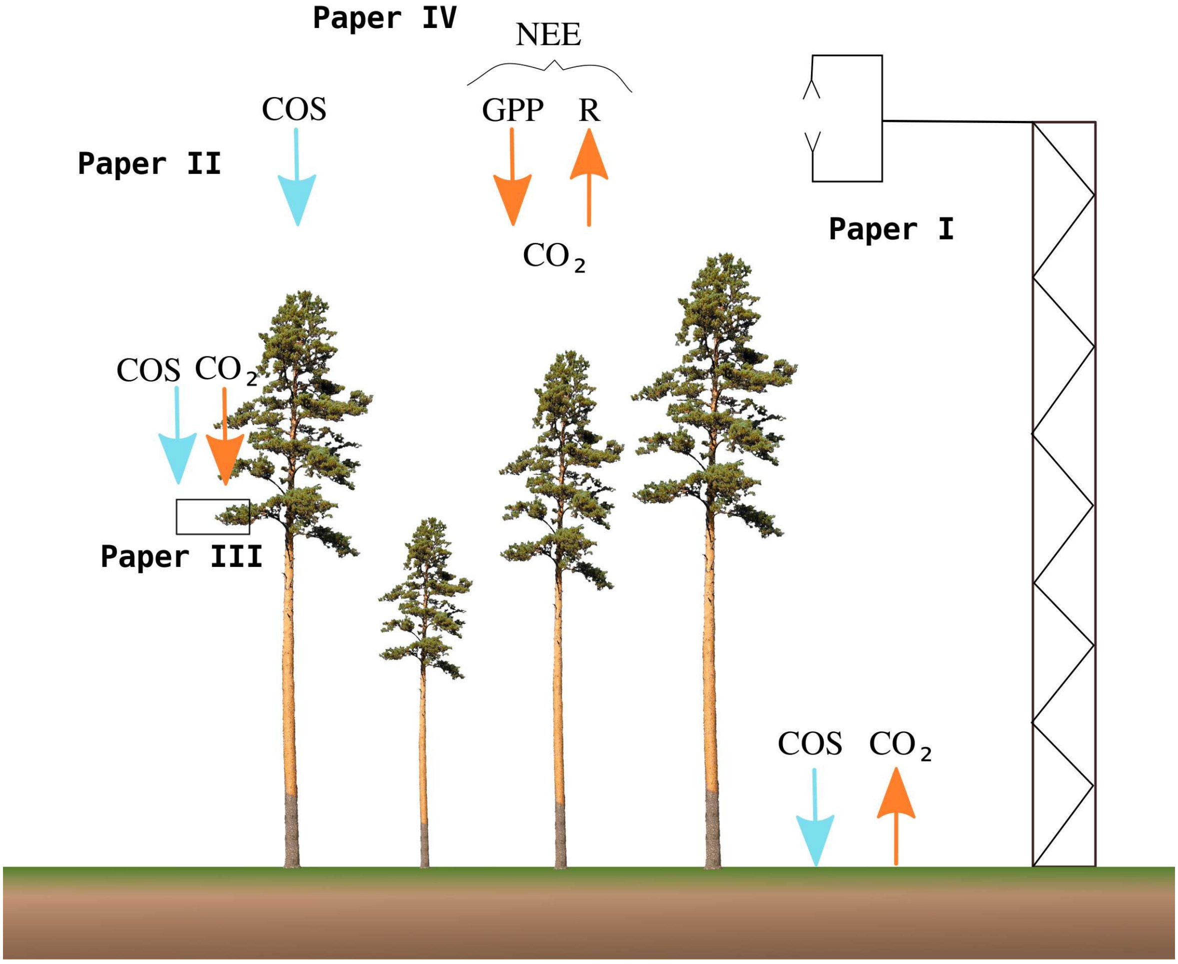

Figure 1: COS and CO_2 exchange processes in a boreal, pine dominated forest. **Paper I** focuses on COS EC flux measurements and processing. **Paper II** studies the COS exchange in a boreal forest from sub-daily to seasonal and interannual scales and introduces a simple parameterization for COS fluxes in the ecosystem level and the boreal region. **Paper III** introduces a new parameterization for leaf relative uptake based on leaf scale measurements of COS and CO_2 fluxes. **Paper IV** combines the information gathered in **Papers I-III** and compares four GPP estimates based on COS and CO_2 flux measurements from hourly to annual scales. Soil flux measurements of COS are used as background information in **Paper IV**. Photo of the pine tree by Juho Aalto.

2 Ecosystem scale carbon dioxide and carbonyl sulfide exchange

2.1 Basics of eddy covariance flux measurements

The EC technique is widely used for estimating the net exchange (source and sink) of energy and gas at the ecosystem scale. It is based on measuring the turbulent fluctuations of gas concentration and vertical wind speed at high frequency. Measurement setups consist of a sonic anemometer and a gas analyzer mounted above the ecosystem of interest. Measurements, with typically 10 Hz sampling frequency, have to be made in the atmospheric surface layer, where vertical fluxes are nearly constant with height (Aubinet et al., 2012). In addition, EC measurements need the assumption of homogeneity of the underlying surface and a stationary turbulent flow in the atmosphere (Foken and Wichura, 1996). EC flux measurements are continuous with low labour requirements after instrument installation and have a large footprint (source area), but are quite expensive and need extensive data processing.

The link between EC flux measurements and net ecosystem exchange is in the scalar conservation equation, which describes the conservation of any quantity in the atmosphere (Aubinet et al., 2012). Scalar conservation equation is written as:

$$\frac{\partial \rho_a c}{\partial t} + \nabla \cdot (\overrightarrow{u} \rho_a c) = S_c, \tag{1}$$

where the first term represents the rate of change of the quantity c (e.g. molar mixing ratio of a gas), the second is the atmospheric transport of c and the last term, S_c, is the source/sink strength of the quantity c. ρ_a is the dry air density and $\overrightarrow{u}$ the wind vector. By traditionally applying Reynold's averaging rules (Stull, 1988), Eq. (1) can be rewritten as

$$\overline{\rho_a} \overline{\frac{\partial c}{\partial t}} + \overline{\rho_a \overrightarrow{u}} \cdot \nabla(\overline{c}) + \nabla \cdot (\overline{\rho_a} \overline{\overrightarrow{u}' c'}) = \overline{S_c}, \tag{2}$$

where it is assumed that ρ_a is constant with time and the term S_c equals to the sum of the rate of change of the quantity c, advection in the atmosphere, and flux divergences (Aubinet et al., 2012). This equation is further simplified by integrating over a control volume extending from the surface to the measurement height h and assuming horizontal homogeneity, constant flux layer and zero turbulent flux at the ground level ($z = 0$), to get NEE:

$$\mathrm{NEE} = \frac{1}{h}\int_0^h \overline{\rho_a}\frac{\partial \overline{c}}{\partial t}dz + \frac{1}{h}\int_0^h \left(\overline{w\rho_a}\frac{\partial \overline{c}}{\partial z}\right) dz + \overline{\rho_a}\,\overline{w'c'}(h), \tag{3}$$

where NEE indicates the sum of biological sources/sinks at the surface and w is the vertical wind velocity. On the right-hand side, the first term represents the atmospheric storage change flux of the scalar (F_{sto}), second the vertical advection (F_A) and last term is the EC flux (F_{EC}) at height h. Further, assuming fully developed turbulence F_A can be neglected and this results to

$$\mathrm{NEE} = F_{sto} + F_{EC}. \tag{4}$$

Although F_{sto} changes the diurnal dynamics of NEE (**Paper I**), it is negligible in daily scale and long term budgets integrating to zero (Montagnani et al., 2018).

2.2 Eddy covariance data processing, flux calculation and corrections

Processing of EC flux data is rather complex and follows several steps. However, with careful consideration of each processing step, systematic biases – that stem from the limitations set by the measurement devices, setup and underlying assumptions – can be minimized.

Processing raw EC data into fluxes includes the following steps: spike removal and raw data filtering, rotating the coordinate system to align with the prevailing streamlines, detrending to separate the turbulent fluctuations from the mean trend, adjusting for a time lag between the sonic anemometer and the gas analyzer signals, calculating covariances, and correcting for flux losses at high and low frequencies (Aubinet et al., 2012; Aubinet et al., 2000; Rannik and Vesala, 1999). Fluxes are then quality-filtered and flagged according to atmospheric turbulence characteristics and stationarity (Foken, 2006). Coordinate system rotation, detrending, time lag determination and spectral corrections all have multiple options that require careful selection based on the measurement setup and measured gas. The different options and all processing steps are summarized in Fig. 2.

Time lag correction is done because there is usually a delay between the time series of the wind components and the time series of the scalar due to spatial separation between sensors or air travel through sampling tubes to gas analyzers. It is important to account for this time lag and shift the time series accordingly in order to maintain the timely turbulent fluctuations in the data and thus avoid a bias in flux calculation. Time lag is often determined from the maximum cross-covariance of w and the measured gas mixing ratio. This may, however, be difficult when dealing with fluxes with small signal-to-noise ratio due to noisy cross-covariance and may result in a "mirroring effect", i.e. fluxes close to zero are not detected correctly (Langford et al., 2015). Thus other methods for time lag determination have been suggested for fluxes with low signal-to-noise ratios (Nemitz et al., 2018). Accurate time lag determination is essential to minimize biases in flux estimates.

Spectral corrections are needed because air transport through sampling tubes, sensor separation and inadequate frequency responses cause losses both at high and low frequencies, leading to underestimated cospectral densities. High frequency spectral correction highly influences the final fluxes and increases the flux magnitude (Mammarella et al., 2016). Low frequency corrections, on the other hand are needed to correct for the losses caused by detrending the turbulent time series (Rannik and Vesala, 1999). However, the effect of the low frequency correction on the final flux is not as large as that of the high frequency spectral correction. Similar to time lag determination, the standard spectral corrections may be difficult to implement for flux measurements with low signal-to-noise ratios (Aubinet et al., 2000; Nemitz et al., 2018).

Processed fluxes still need post processing to ensure good data quality. This includes correcting for storage change fluxes (Montagnani et al., 2018), filtering out fluxes measured during low turbulence, traditionally using friction velocity (u_*) filtering with a site-specific u_* threshold (Papale et al., 2006), and calculating flux uncertainties. After these post-processing steps the fluxes are finally gap-filled (i.e. missing data replaced by either models, interpolation or mean diurnal variation).

While the Integrated Carbon Observation System (ICOS) research infrastructure has come up with standardized processing protocols for CO_2, methane (CH_4) and nitrous oxide (N_2O) fluxes (Sabbatini et al., 2018; Nemitz et al., 2018), the COS EC flux measurements do not have such standard protocols, and previous COS EC studies have used a variety of combinations of the different processing options as well as different measurement setups. Most studies have calculated the COS time lag from the maximum cross-covariance of COS and w (Asaf et al., 2013; Billesbach et al., 2014; Maseyk et al., 2014; Gerdel et al., 2017; Spielmann et al., 2019), although the cross-covariance function may be very noisy and having multiple peaks, making such approach very challenging. Commane et al. (2015) defined the COS time lag using H_2O measurements of the same analyzer, even though it has been noted that H_2O easily sticks to the sampling tube walls and may have higher time lag than other gases especially if the tubes are old or dirty (Mammarella et al., 2009). Gerdel et al. (2017) reported the effects of different detrending methods, high-frequency spectral correction, time lag determination, and u_* filtering, but did not compare different methods for defining the time lag or spectral corrections. The aim of **Paper I** is to find the optimal step chain for COS EC flux processing, to formulate recommendations for future COS studies, and to provide a gap-filling strategy for COS fluxes.

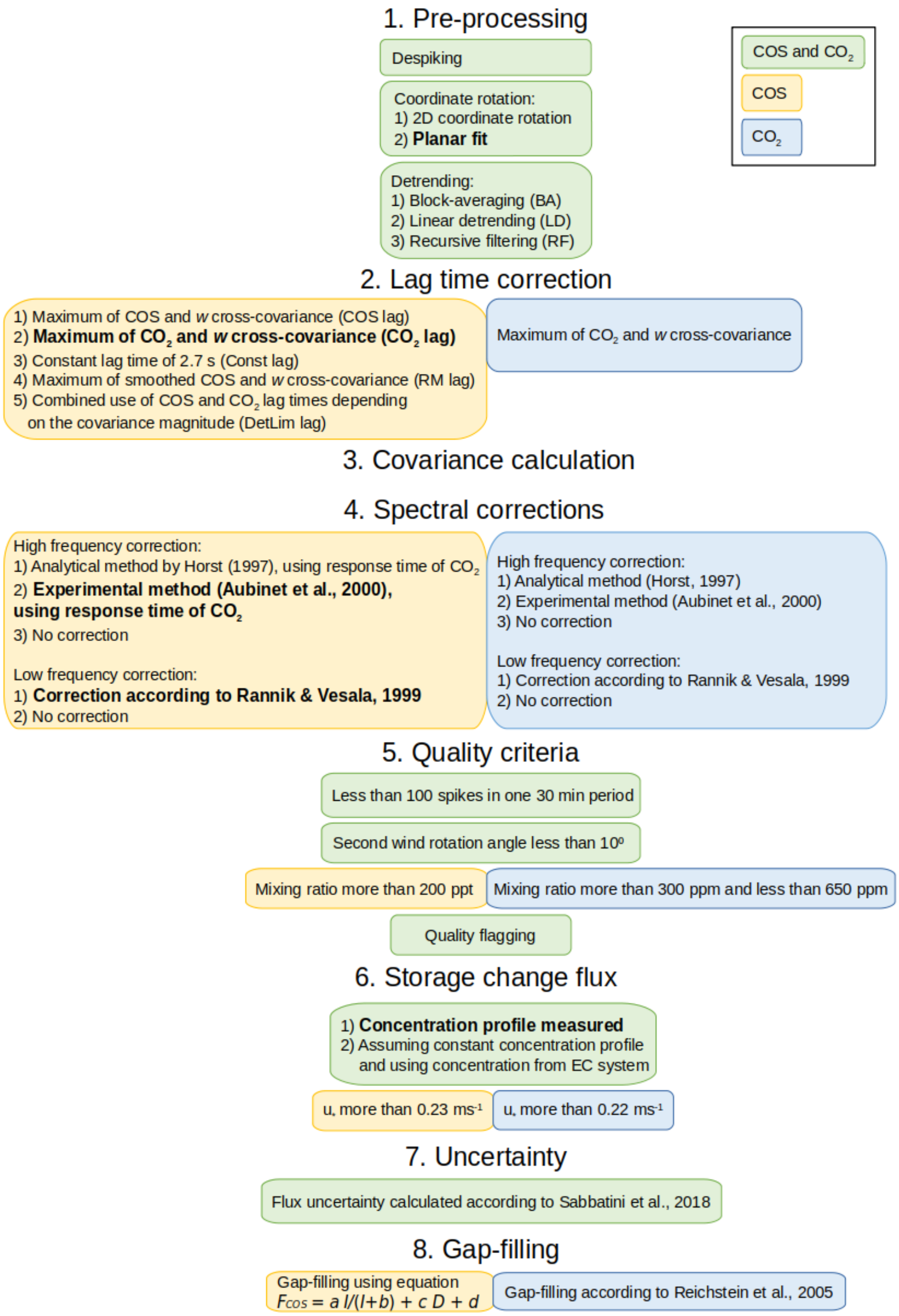

Figure 2: Different EC processing steps summarized. Yellow boxes refer to steps only used for COS data processing, blue boxes to steps used only for CO_2 data, and green boxes to steps that are relevant for both gases. Recommended options in **Paper I** are written in bold. Some options are site-specific and thus no recommendation is given for all steps. The abbreviations most commonly used throughout the text are written in parentheses. Thresholds for u_* filtering are site-specific to Hyytiälä forest. Figure adapted from **Paper I**.

2.3 Sources and sinks of carbonyl sulfide

COS is emitted from the oceans both directly and indirectly through carbon disulfide (CS_2) and dimethyl sulfide (current estimate 265±210 GgS y^{-1}, Lennartz et al. (2017)), and from anthropogenic activities (400±180 GgS y^{-1}) such as rayon production and biomass burning (60±37 GgS y^{-1}) (Stinecipher et al., 2019). The largest sinks are forests (-430 to -370 GgS y^{-1}) and grasslands (-500 to -200 GgS y^{-1}) (Whelan et al., 2018). In addition, COS is destroyed by OH radicals in the troposphere (-130 to -82 GgS y^{-1}, Berry et al. (2013), Kettle et al. (2002), and Watts (2000)). However, there is an imbalance in the global COS budget, with either an overestimated sink by terrestrial ecosystems or an underestimated source by oceans in global COS models (Montzka et al., 2007; Whelan et al., 2018; Ma et al., 2021). Recent land surface modelling efforts by Ma et al. (2021) and Remaud et al. (2021) further suggest that there is a missing COS sink at the Northern latitudes. The underestimated COS sink in the boreal region is addressed in **Paper II**.

Terrestrial COS uptake is mainly by the canopy (Berry et al., 2013; Hu et al., 2021), with COS being taken up by leaves via their stomata through the same diffusional pathway as CO_2. Inside the leaves, COS is destroyed by the hydrolysis reaction at the chloroplast surface. The COS hydrolysis reaction into CO_2 and hydrogen sulfide (H_2S) is catalyzed by the CA enzymes, that are present in all plant leaves in different cellular locations and in general catalyze the interconversion of CO_2 and bicarbonate ions. The COS hydrolysis follows the one-way chemical reaction (Protoschill-Krebs and Kesselmeier, 1992):

$$\mathrm{COS} + \mathrm{H_2O} \xrightarrow{\mathrm{CA}} \mathrm{HCOOS^-} + \mathrm{H^+} \longrightarrow \mathrm{CO_2} + \mathrm{H_2S}.$$

It has been found that the availability of atmospheric COS is the limiting factor of this reaction, rather than CA activity (Protoschill-Krebs et al., 1996). Because of the one-way reaction and same diffusional pathway with CO_2, COS has been used as a proxy for GPP (Asaf et al., 2013; Sandoval-Soto et al., 2005, **Paper III**, **Paper IV**, Sect. 2.4.2). Unlike GPP, however, the COS hydrolysis reaction does not depend on radiation. The ratio of CO_2 and COS uptake is thus radiation dependent and non-constant (Commane et al., 2015, **Paper III**, **Paper IV**).

2.4 Gross primary productivity

2.4.1 CO_2 flux partitioning

Ecosystem scale GPP from EC measurements is traditionally estimated by partitioning NEE into GPP and ecosystem respiration (R). It can be assumed that NEE consists only of ecosystem respiration during nighttime dark conditions preventing photosynthesis. Temperature response curves can be fitted on nighttime NEE data to acquire a function for R. Parameter estimation for this temperature response should be done every 15 days to introduce less bias in GPP estimation compared to parameter estimation done over longer time periods (Reichstein et al., 2005). This temperature response is assumed to be applicable to daytime data as well and thus daytime respiration may be estimated from temperature measurements (Lloyd and Taylor, 1994). Then NEE can be partitioned into respiration and GPP as

$$\mathrm{NEE} = \mathrm{R} - \mathrm{GPP}. \tag{5}$$

This method, however, relies heavily on nighttime EC measurements that may not be reliable due to suppressed turbulence and advective fluxes not measured by the EC system (Aubinet, 2008). In addition, it is not known if respiration responses really are the same during daytime and nighttime, and Keenan et al. (2019) suggested that respiration is inhibited under radiation. Another method has been developed to infer GPP directly from daytime NEE measurements by fitting radiation response curves (Kolari et al., 2009; Lasslop et al., 2010) and combining with the temperature response of respiration ($\mathrm{GPP}_{\mathrm{NLR}}$, NLR referring to non-linear regressions). Both of these methods, however, assume that respiration solely depends on temperature and that there is no plant respiration inhibition under radiation (Wehr et al., 2016; Keenan et al., 2019).

Lately, machine learning and artificial neural networks (ANN) have been used as an independent method for estimating GPP ($\mathrm{GPP}_{\mathrm{ANN}}$) purely based on data-driven empirical relationships without prescribed driver-output relations (Tramontana et al., 2020). These methods are, however, computationally demanding and have higher sensitivity to the uncertainty of the flux data and meteorological drivers, especially in the case there are long gaps in the data. **Paper IV** compares the traditional CO_2 flux partitioning to that given by the ANN method.

2.4.2 COS as a GPP tracer

As COS shares the same diffusional pathway with CO_2 but has no back-flux to the atmosphere, COS can be closely linked to gas transport into the leaf and COS-based GPP ($\mathrm{GPP_{COS}}$) may be calculated from ecosystem COS flux (FCOS) measurements as

$$\mathrm{GPP_{COS}} = -\frac{FCOS}{\mathrm{LRU}}\frac{[CO_2]}{[COS]} \tag{6}$$

where LRU is the leaf relative uptake ratio, that is the ratio of COS to CO_2 deposition velocities at leaf level (Sandoval-Soto et al., 2005), and $[CO_2]$ and $[COS]$ are the atmospheric mixing ratios of CO_2 and COS, respectively. LRU may be determined directly from branch scale measurements of COS and CO_2 fluxes as

$$\mathrm{LRU} = \frac{F_{COS,branch}}{F_{CO2,branch}}\frac{[CO_2]}{[COS]} \tag{7}$$

while the theoretical presentation, following Wohlfahrt et al. (2012) is

$$\mathrm{LRU} = \frac{1}{1-\frac{c_i}{c_a}}\frac{\frac{1}{1.21}+\frac{1}{1.14}\frac{g_s^s}{g_b^s}}{1+\frac{g_s^s}{g_b^s}+\frac{g_s^s}{g_i^s}}, \tag{8}$$

where $g_x^s (x = b, s, i)$ are the boundary layer, stomatal and mesophyll conductances for COS, respectively, c_a is the atmospheric CO_2 molar mixing ratio (mol $\mathrm{mol^{-1}}$) and c_i is the leaf intercellular CO_2 molar mixing ratio (mol $\mathrm{mol^{-1}}$), and numerical factors 1.21 and 1.14 are the ratios of the conductances of CO_2 to COS for stomata and the boundary layer (Wohlfahrt et al., 2012), resulting from different diffusivity rates of COS and CO_2.

Measurements of LRU have been conducted especially in controlled conditions (Stimler et al., 2010; Stimler et al., 2011) but also under field conditions (Seibt et al., 2010; Sun et al., 2018b; Yang et al., 2018, **Paper III**) using leaf chambers. Stimler et al. (2012), Maseyk et al. (2014), Commane et al. (2015), Sun et al. (2018b), and Yang et al. (2018) hypothesized that LRU is not constant under varying radiation conditions due to different biochemical reactions controlling COS and CO_2 exchange at the leaf level, of which CO_2 reactions are highly light-dependent while COS reactions are not. Still, most $\mathrm{GPP_{COS}}$ estimates have relied on constant LRU estimates both at the ecosystem scale (Asaf et al., 2013) and in global land surface models (Launois et al., 2015; Hilton et al., 2017). The LRU estimation has been found to be one of the largest sources of uncertainty in COS-based GPP estimates (Blonquist et al., 2011). **Papers III** and **IV** address this limitation by providing new formulations for LRU that better describe the stomatal response to environmental conditions and COS exchange, making $\mathrm{GPP}_{\mathrm{COS}}$ less uncertain and of wider use.

3 Measurements at Hyytiälä

All measurements related to this thesis were collected at Hyytiälä boreal Scots pine forest in Southern Finland during years 2013–2017. The forest hosts the Station for Measuring Ecosystem Atmosphere Relations (SMEAR II) and the ICOS atmospheric and ecosystem stations. In this chapter, the site and measurements used in this study are described in more detailed.

3.1 Site description

Hyytiälä forest measurement site is located in Southern Finland (61°51'N, 24°17'E) and is a typical managed Finnish forest. The forest stand is more than 50 years old and is dominated by Scots Pine (*Pinus Sylvestris L.*) with some Norway spruce (*Picea abies L. Karst.*) and deciduous trees (e.g. *Betula sp., Populus tremula, Sorbus aucuparia*) (Hari and Kulmala, 2005). The measurement station is located on a gentle ridge and the homogeneous forest stand reaches at least 200 m in all directions, and maximally extends about 1 km to the north. The canopy height increased from approximately 18 to 20 m during the measurement period (2013–2017) and the all-sided leaf area index (LAI) was ca. 8 m m^{-2}.

3.2 Eddy covariance measurements

EC measurements were done at 23 m height on a tower above the forest (Fig. 3a). The EC instrumentation consisted of a sonic anemometer (Solent Research HS1199, Gill Instruments Ltd., England, UK) for measuring horizontal and vertical wind velocity components and sonic temperature. LI-6262 (LI-COR, Lincoln, NE, USA) closed path infrared gas analyzer measured atmospheric CO_2 and water vapor (H_2O) mole fractions, and an Aerodyne quantum cascade laser spectrometer (QCLS; Aerodyne Research Inc., Billerica, MA, USA) measured COS, CO_2, carbon monoxide (CO) and H_2O mole fractions. All measurements were done at 10 Hz frequency. The sampling tubes were 32 and 12 m long for QCLS and LI-6262, respectively. Both sampling lines were made of PTFE and had inner diameters of 4 mm. Two PTFE filters - one coarse filter (0.45 μm, Whatman) close to the analyzer inlet and a finer filter (0.2 μm, Pall Corporation) at approximately 50 cm distance to the analyzer inlet - were used upstream of the QCLS to prevent any contaminants from entering the analyzer. The tubing outside the instrumentation cabin was heated to prevent condensation on the tubing walls. Background measurements of high-purity nitrogen (N_2) were done every 30 min for 26 s to remove background spectral structures in the QCLS (Kooijmans et al., 2016). In addition, in 2015 a calibration cylinder was sampled each night at 00:00:45 for 15 s. The calibration cylinder consisted of COS at 429.6 ± 5.6 ppt, CO_2 at 408.37 ± 0.05 ppm, and CO at 144.6 ± 0.2 ppb. The water vapor spectral interference of the COS and H_2O absorption lines was corrected for by fitting the COS spectral line separately from the H_2O spectral line, as recommended by Kooijmans et al. (2016). For more details on the EC setup and data logging, see **Paper I**. EC fluxes were calculated using the EddyUH software package version 1.7 (Mammarella et al., 2016).

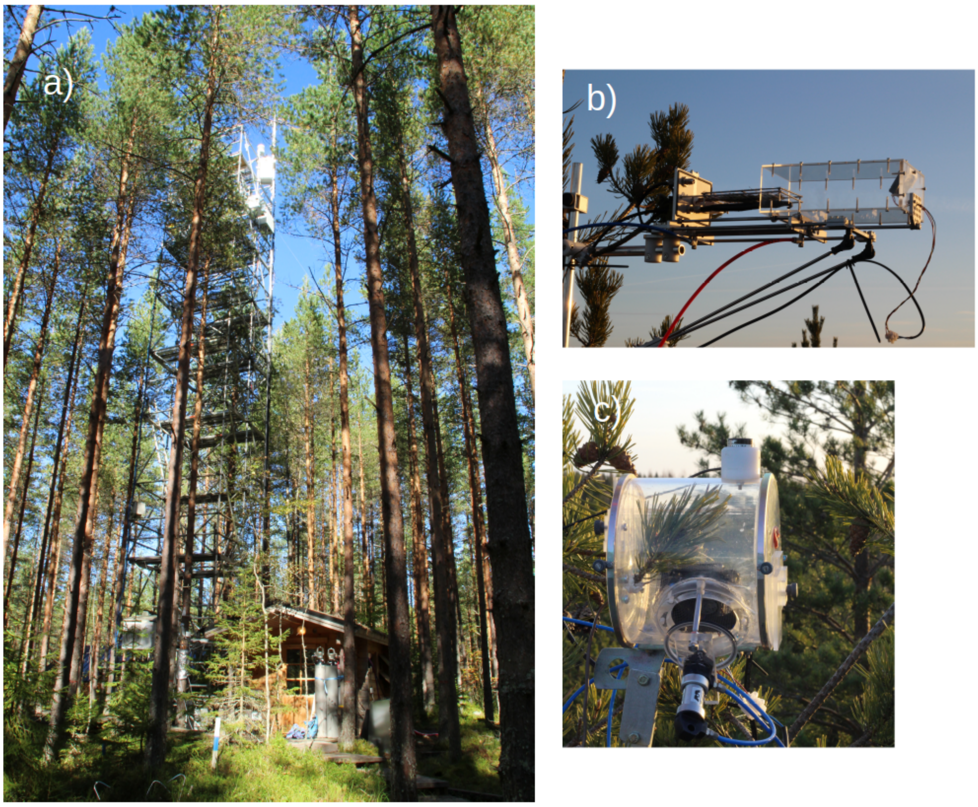

Figure 3: Measurements at Hyytiälä forest: a) tower for EC flux measurements and cabin for instrument housing (**Papers I-IV**), b) rectangular branch chamber (chamber 1, **Papers III** and **IV**) and c) cylindrical branch chamber (chamber 2, **Papers III** and **IV**).

3.3 Chamber measurements

Two automated, transparent chambers were installed on Scots pine branches at the top of the canopy between February 16 and July 17, 2017 (**Paper III**, Fig. 3b-c). Chamber 1 was rectangular with a 2.1 L volume and opened horizontally with an automatically sliding component. Chamber 2 was cylindrical with 1.8 L volume with two lids that opened on two opposing sides. Both chambers were made of acrylic plastic. While open, the branches in chamber 1 were more exposed to ambient meteorological conditions than in chamber 2 due to different chamber structures. In chamber 1 the branch was fastened between two nets such that the needles were arranged as a flat surface, while in the cylindrical chamber the branch was freely spaced. In both chambers, the lids were sealed off with Viton o-rings (Eriks) and fans inside the chambers continuously ventilated the air inside. Photosynthetically active radiation (PAR) and air temperature (T_a) were measured inside and outside the chambers by quantum sensors (Li-Cor LI-190) and thermocouples, respectively.

During measurements, the chambers were closed for 4 min and each chamber was measured once every hour. Air was pumped with a flow of 1–1.5 L min^{-1} through 65 m long Synflex (Decabon) tube (inner diameter 4 mm) from the branch chambers to another QCLS (Aerodyne Research Inc.), that recorded the mole fractions of COS, CO_2, CO, and H_2O at 1 Hz frequency. Ambient air could enter the chambers through small holes on the chamber walls at all times. Similar to EC measurements, the sample tubing outside the instrumentation cabin was heated to prevent condensation on the tubing walls. Calibration cylinder measurements were performed every half hour. Similar to the EC setup, the spectral water vapor interference of COS was corrected for according to Kooijmans et al. (2016).

Branch fluxes were calculated from the change of molar concentrations within the chamber during chamber closure through the mass balance equation:

$$V\frac{\mathrm{d}C}{\mathrm{d}t} = FA + q(C_a - C) \tag{9}$$

where C is the molar concentration of the gas of interest inside the chamber (mol m^{-3}), C_a the atmospheric molar concentration of the gas (mol m^{-3}), V the chamber volume (m^3), F the uptake or emission rate (mol m^{-2} s^{-1}), A the leaf area (m^2) inside the chamber, and q the flow rate (m^3 s^{-1}). The fluxes were calculated from a least-squares fit of the time series of molar concentrations inside the chamber and by solving Eq. (9) for F. C_a was determined a few minutes before chamber closure from the ambient air. For more details on the branch chamber measurements and flux calculation, see **Paper III**.

3.4 Ancillary measurements

Environmental measurements used in the study include T_a at 16.8 m (measured with a Pt100 temperature sensor inside a custom shield), PAR above the canopy (Li-190SZ quantum sensor, LI-COR, Lincoln, NE, USA), relative humidity (RH) at 16.8 m and 33.6 m heights (Rotronic MP102H, Rotronic Instrument Corp., NY, USA), soil temperature (T_{soil}) at 2–5 cm depth (KTY81-110 temperature sensor, Philips, The Netherlands) as a mean of five locations, and soil water content (SWC) in the humus layer (Delta-T ML2 soil moisture sensor, Delta-T Devices, Cambridge, UK). Vapor pressure deficit (VPD) was calculated as the difference between the saturation water vapor pressure (e_s) and the actual atmospheric water vapor pressure (e_a) as

$$\mathrm{VPD} = e_s - e_a \tag{10}$$

where e_s was calculated from air temperature measurements as

$$e_s = 0.618 \exp\left(\frac{17.27T_a}{T_a + 237.3}\right) \tag{11}$$

and e_a derived from RH measurements and e_s as

$$e_a = \frac{\mathrm{RH}e_s}{100} \tag{12}$$

4 Overview of results

4.1 Data processing guidelines

Different processing options (Fig. 2) for COS flux calculation were tested and compared to a reference processing scheme that included 2D coordinate rotation, linear detrending, time lag determination from CO_2 time lag, experimental high frequency spectral correction method and low frequency spectral correction according to Rannik and Vesala (1999).

Different detrending methods resulted in maximum 6.2 % difference in the final COS flux. The best detrending method option depends on measurement site (in case of e.g. large scale transport of COS) and instrument drift and should be determined site specifically from raw data (**Paper I**).

Different methods in determining time lag caused up to 15.9 % difference in the final flux. The most commonly used method of determining time lag from the absolute maximum cross-covariance of w and COS mixing ratio resulted in a "mirroring effect" and fluxes close to zero were not detected (**Paper I**). To avoid this problem, the time lag was determined as the maximum cross-covariance difference to a line between covariance values at the lag window limits (COS_{lag}). Still, the time lag distribution was not as clear as when time lag was determined from CO_2 flux measurements ($CO2_{lag}$, Fig. 4). A running mean cross-covariance was also tested as an alternative for time lag determination (RM_{lag}, Taipale et al., 2010) but did not produce a clearer time lag distribution than COS_{lag}. When time lag was determined as a combination of COS_{lag} and $CO2_{lag}$ ($DetLim_{lag}$) so that COS_{lag} was chosen only if the COS flux was well above the flux detection limit and otherwise from $CO2_{lag}$, the time lag distribution became more clear than with the COS_{lag}. However, as there should not be any reason why COS and CO_2 time lags should differ and as the time lag determination from CO_2 cross-covariance is less uncertain, the recommendation is to use CO_2 time lag for COS flux calculation in the future studies (**Paper I**).

Correcting for high frequency loss with the experimental method resulted in 14.2 % higher COS flux, which was expected and in line with previous studies (Mammarella et al., 2016). Experimental spectral correction approaches with a site specific cospectral model are recommended over the analytical corrections (e.g. Horst, 1997), because they better capture the turbulent characteristics at the site (Aubinet et al., 2000, **Paper I**). These two methods resulted in a 2.7 % difference in the final median COS flux. Moreover, as the COS fluxes have low signal-to-noise ratio, it is recommended to empirically estimate the EC system spectral transfer function based on CO_2 rather than COS cospectra, as also found in Wehr et al. (2017).

The storage change fluxes affected the diurnal variation of COS flux as they account for the delayed capture of fluxes by the EC system under low-turbulence conditions, but were not relevant for budget calculations in time scales larger than one day, as expected (Montagnani et al., 2018). However, storage change fluxes have been widely ignored in previous COS studies even though storage change flux measurements are mandatory in places where the EC system is placed at a height of 4 m or above according to the ICOS protocol for EC flux measurements (Montagnani et al., 2018). It would be best to calculate the storage change flux from concentration profile measurements, but as those are not always available, a good option is to use the EC system COS concentration change at one level and assume a constant concentration profile (**Paper I**).

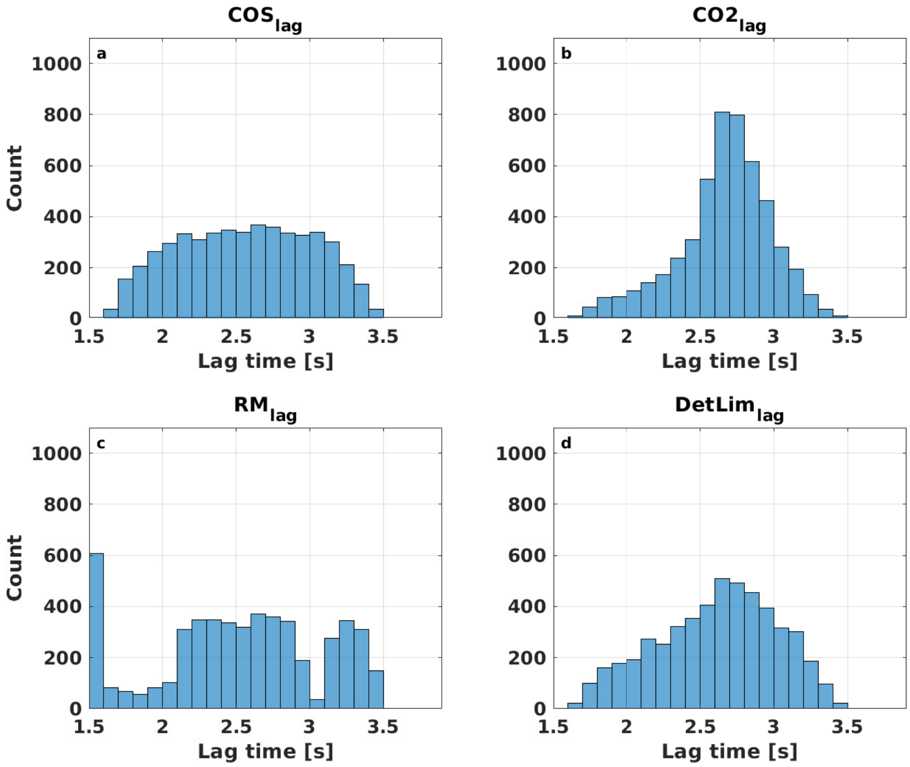

Figure 4: Distribution of time lags derived from different methods: (a) COS time lag from maximum cross-covariance, (b) CO_2 time lag from maximum cross-covariance, (c) COS time lag from a running mean cross-covariance (RM_{lag}), and (d) a combination of COS and CO_2 time lags based on the detection limit of COS flux for each 30 min flux value ($DetLim_{lag}$). Figure from **Paper I**.

The random uncertainty of COS fluxes is high due to the low signal-to-noise ratio and dominates over the systematic uncertainty related to different flux processing options (Fig. 5). The random uncertainty decreased when 30 min fluxes were averaged to daily values, but remained at a similar level for longer averaging periods. The relative uncertainty of COS flux was 5 times higher than that of CO_2 flux at low flux values (absolute COS flux of less than 3 pmol m^{-2} s^{-1}), highlighting the noisy property of COS measurements.

Gap-filling has not been applied in previous COS flux studies due to the lack of good gap-filling strategies. **Paper I** introduces a simple gap-filling function that combines a saturating light response curve and a linear VPD dependency of COS fluxes:

$$FCOS = \frac{aI}{I+b} + cD + d, \tag{13}$$

where I is photosynthetic photon flux density (μmol m^{-2} s^{-1}), D is VPD (kPa) and a (pmol m^{-2} s^{-1}), b (μmol m^{-2} s^{-1}), c (pmol m^{-2} s^{-1} kPa^{-1}), and d (pmol m^{-2} s^{-1}) are fitting parameters that need to be re-evaluated every 15 days against measured FCOS. This function gives a good estimate of the COS flux when a flux measurement is not available and enables e.g. COS budget calculation from site-level EC studies, that has not been possible before.

These EC processing recommendations were used in the data processing in **Papers I-IV** and will hopefully be implemented in the wider COS community and future research.

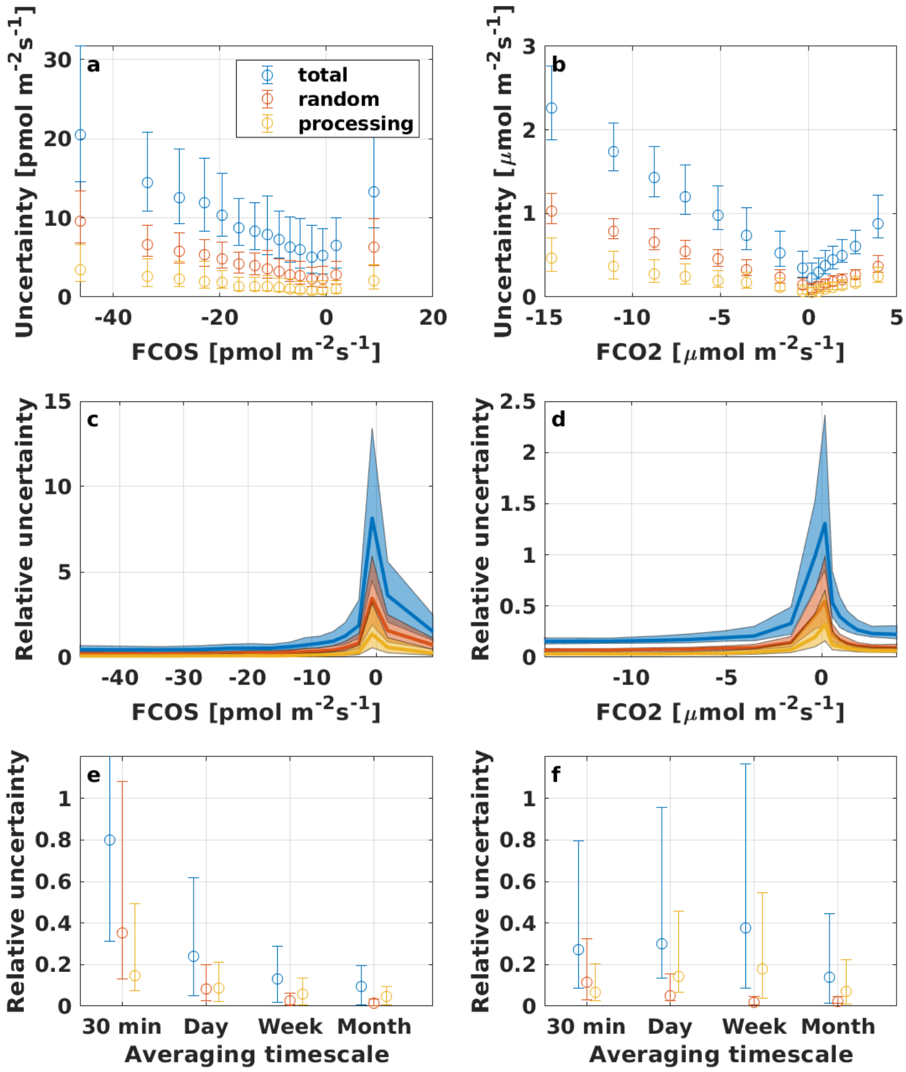

Figure 5: Uncertainty of (a) COS and (b) CO_2 fluxes, binned into 15 equal-sized bins that represent median values. Error bars show the 25th and 75th percentiles. Panels (c) and (d) represent the relative uncertainty, i.e., the uncertainty divided by the flux for COS and CO_2, respectively. Panels (e) and (f) represent the relative uncertainties of time-averaged COS and CO_2 fluxes, respectively. Figure from **Paper I**.

4.2 Interannual variability of FCOS

The variation of FCOS from sub-daily to interannual scales in Hyytiälä was studied during 2013–2017 (**Paper II**). The FCOS budget (from April to August, for best data coverage) varied by 37% from -41.6 gS ha^{-1} in 2014 to -66.4 gS ha^{-1} in 2016. The onset date of the significant uptake after winter dormancy varied by 2 weeks between years and was found to be mostly controlled by air temperature, while the date of the maximum COS uptake in the growing season varied by 6 weeks. The 5 year data set allowed for investigating environmental responses and their time lags in more detail. Multivariate and univariate regression analysis revealed that the main controlling factors of FCOS were temperature, radiation and VPD. The importance of all these variables gained even more weight at longer time scales (weekly and monthly). A 3-hour time lag between FCOS and air temperature was also found at the daily scale and is related to stomatal control (**Paper III**; Maignan et al., 2021).

As the COS exchange is closely linked to CO_2 exchange, a simple parameterization for FCOS was developed based on earlier models of CO_2 exchange (Mäkelä et al., 2008; Dewar et al., 2018; Peltoniemi et al., 2015):

$$FCOS = FPAR \cdot FS \cdot FVPD \cdot FLAI \tag{14}$$

where

$$FPAR = \frac{aPAR}{PAR + b} \tag{15}$$

$$FS = \frac{1}{1 + \exp(cS)} \tag{16}$$

$$FVPD = \frac{d}{1 + \sqrt{VPD}} \tag{17}$$

$$FLAI = \frac{1 - \exp(-eLAI)}{e}, \tag{18}$$

where $a = -341.81$, $b = 1000$, $c = -0.77$, $d = 1.03$, and $e = 0.18$ are fitting parameters that were fitted to minimize the root mean square error of the parameterized FCOS against the measured FCOS. The S parameter describes the stage of physiological development and was calculated according to Pelkonen and Hari (1980). The simple parameterization captured the seasonal variation well, especially in 2015–2017 (Fig. 6). The parameterization was also implemented in the Simple Biosphere Model Version 4

(SiB4, Haynes et al., 2019) and compared to the standard SiB4 FCOS output both over Hyytiälä and over the boreal region evergreen needleleaf forests. While the standard SiB4 output produced too low FCOS especially from July to October each year, the SiB4 parameterization was able to capture the seasonal FCOS variation over Hyytiälä. SiB4 likely lacks a stomatal response in dry conditions, especially in the boreal region (Smith et al., 2020; Kooijmans et al., 2021).

In July 2014 the parameterization overestimated COS uptake compared to measured FCOS. During that period, VPD was about twice as high compared to other years, and so reduction in measured FCOS was likely low due to stomatal regulation that was not captured by the parameterization (**Paper II**). The parameterization could be improved in terms of the VPD regulation during drought. This was not possible to do with the Hyytiälä data set, as there were too few occasions when VPD was very high to produce a reliable parameterization.

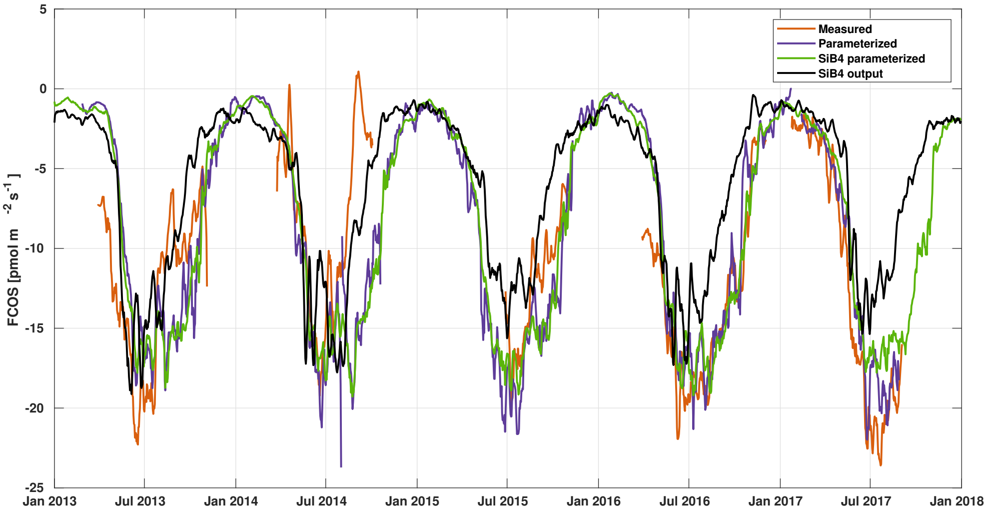

Figure 6: Weekly averaged FCOS from measurements (orange), parameterization (purple), SiB4 parameterization (green) and standard SiB4 output (black) in Hyytiälä. Figure from **Paper II**.

The SiB4 parameterization produced a higher COS sink for the boreal region (-14.6 Gg S yr^{-1}) than the SiB4 standard output (-10.6 Gg S yr^{-1}), in line with a previous estimate by Ma et al. (2021), who also recognized that the boreal COS sink was underestimated in global inverse modelling. The simple parameterization developed in **Paper II** could help future land surface model development for capturing the high latitude COS sink better. It would be beneficial to compare the parameterization with other COS EC flux sites in the boreal evergreen needleleaf forests in order to estimate its accuracy also elsewhere. However, even though such measurement sites do exist (e.g. Rastogi et al., 2018), there are yet none that would have sufficiently long or comprehensive data sets for a proper comparison.

4.3 LRU light-sensitivity

As discussed earlier, COS exchange at the leaf level is closely related to stomatal regulation. As there is always enough CA activity to destroy all available COS (Protoschill-Krebs et al., 1996), the most limiting factor for COS exchange is diffusion through stomata. Both COS and CO_2 diffusion are regulated by stomatal conductance, but CO_2 assimilation is also dependent on RuBisCo activity and light, whereas COS destruction is independent of light. This results in a light (and humidity) dependent LRU. At low light levels LRU approaches infinity while at high PAR (PAR>700 μmol $m^{-2}s^{-1}$) it approaches a constant value (approximately 1 in Hyytiälä pine forest, **Paper III**). However, even at high PAR values, the LRU is still sensitive to stomatal regulation through other factors, such as VPD, and varies through seasons. While the light-dependency of LRU has been noticed before (Commane et al., 2015; Stimler et al., 2011; Sun et al., 2018b), universally accepted expressions for this dependency are still missing. In **Paper III** the measured LRU (following Eq. (7) with measured branch level COS and CO_2 fluxes) was found to have a PAR-dependency following the equation

$$\mathrm{LRU}_{\mathrm{PAR}} = \frac{607.26}{PAR} + 0.57. \tag{19}$$

This $\mathrm{LRU}_{\mathrm{PAR}}$ function works well in GPP estimation at Hyytiälä (**Papers III** and **IV**) and has also been implemented in the land surface model ORCHIDEE providing regional and global estimates (Maignan et al., 2021). However, this empirical relationship is based solely on Hyytiälä measurements and may be site and species specific. Thus, in order to develop a more generic model of LRU, we derived an alternative expression for LRU that is based on the CAP stomatal optimization model (Dewar et al., 2018), according to which stomatal conductance maximises leaf photosynthesis, reflecting a trade-off between stomatal limitations to CO_2 diffusion and non-stomatal limitations to carboxylation capacity. Starting from Eq. (8) and assuming that both the boundary layer conductance and mesophyll conductance to CO_2 and COS are infinite, LRU has the form

$$\mathrm{LRU} = \frac{1}{1.21}\left(1 - \frac{c_i}{c_a}\right)^{-1}. \tag{20}$$

The CAP stomatal optimization model (Dewar et al., 2018), predicts the value of c_i as an analytical function of various environmental and physiological factors. When the CAP model is substituted into Eq. (20), the resulting expression for LRU is given by

$$\mathrm{LRU_{CAP}} = \frac{1}{1.21}\frac{c_a}{c_a - \mathit{\Gamma}^*}\left(1 + \sqrt{\frac{K_{sl}X}{VPD}}\sqrt{1 + \frac{Y}{PAR}}\right) \tag{21}$$

where $\mathit{\Gamma}^*$ is the CO_2 photorespiratory compensation point (mol mol^{-1}), K_{sl} the soil-to-leaf hydraulic conductance (mol m^{-2} s^{-1} MPa^{-1}), $X = \frac{|\psi_c|}{1.6g_c}$ and $Y = \frac{2\mathit{\Gamma}^* g_c}{\alpha}$ where ψ_c is the critical leaf water potential at which non-stomatal limitations reduce photosynthesis to zero (MPa), g_c is the carboxylation conductance in the absence of non stomatal limitations (mol m^{-2} s^{-1}) and α is the photosynthetic quantum yield in the absence of non-stomatal limitations (mol mol^{-1}). In addition to PAR and VPD measurements, $\mathrm{LRU_{CAP}}$ requires soil moisture measurements through the soil component of K_{sl}. Using the literature values (Duursma et al., 2008; Dewar et al., 2018), however, led to an underestimate of LRU at PAR<150 μmol m^{-2}s^{-1} and thus X and Y were also fitted to the smallest mean square error between the modelled and measured LRU as a test. While parameter X (2.64) was close to the literature value (2.5), the optimized Y (0.0033) was three times higher than expected from literature (0.001) (**Paper IV**). This mismatch suggests there may be scope for further model improvement, such as the inclusion of dark respiration in the $\mathrm{LRU_{CAP}}$ model. $\mathrm{LRU_{CAP}}$ captures the measured LRU values well in general, but gives slightly overestimated LRU values (offset of ca. 0.3) at PAR $>$ 1000 μmol m^{-2}s^{-1} (Fig. 7).

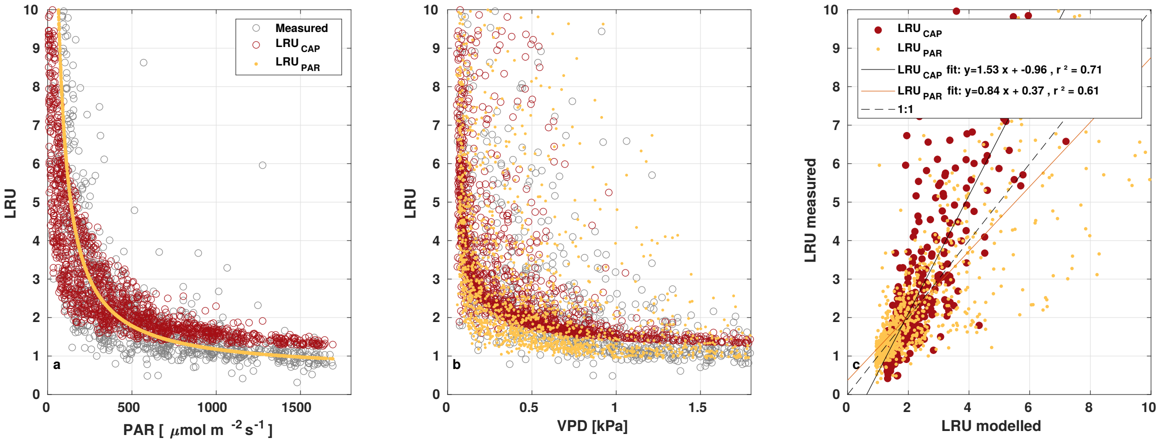

Figure 7: Measured (gray) and modelled LRU (LRU_{CAP}, red; LRU_{PAR}, yellow) against (a) PAR and (b) VPD. In (c), modelled LRU are compared against measured LRU. Note that in reality LRU varies from 0 to infinity, but this analysis is restricted from 0 to 10 for better readability, while 7 % of data fall out of the figure limits. Figure adapted from **Paper IV**.

While LRU_{PAR} is an empirical model describing only the PAR dependence, LRU_{CAP} explains the dependence of LRU on PAR, VPD and soil water, with a wider applicability in other ecosystems. Even though both LRU models developed in this thesis have their shortcomings, both LRU_{PAR} and LRU_{CAP} give a more accurate representation of the leaf scale COS exchange dynamics at sub-daily scales than the assumption of a constant LRU and help improving the GPP_{COS} estimates (**Paper IV**, Sect. 4.4).

4.4 COS as a GPP tracer in Hyytiälä

Two CO_2-based and two COS-based GPP estimates were compared with each other in **Paper IV**. CO_2-based estimates were the traditional CO_2 partitioning, GPP_{NLR}, (Kulmala et al., 2019) and a data-driven partitioning method based on artificial neural networks (Tramontana et al., 2020), GPP_{ANN}. As the GPP_{NLR} method is the most established, it was used as reference. It is to be noted, though, that GPP_{ANN} uses the same CO_2 flux measurements as GPP_{NLR} and is thus not totally independent, even though the partitioning methods differ. COS-based GPP estimates included GPP calculated from LRU_{PAR} ($GPP_{COS,PAR}$, **Paper III**) and LRU_{CAP} ($GPP_{COS,CAP}$, **Paper IV**). Daily GPP_{ANN} did not differ statistically from daily GPP_{NLR} and differences were very small also in the sub-daily and seasonal scales (Figs. 8 and 9). $GPP_{COS,PAR}$ was higher than other GPP estimates from 30 min to monthly timescales and especially during midday (Fig. 8). $GPP_{COS,CAP}$ on the other hand was found to be lower than $GPP_{COS,PAR}$ at midday but closer to the two CO_2-based GPP estimates. $GPP_{COS,CAP}$ also compared best with the traditional GPP_{NLR} at all time scales (Fig. 9), although FCOS measurements are very scattered at 30 min time scale. COS-based GPP was also calculated using a constant LRU=1.6 ($GPP_{COS,const}$) from previous studies (Stimler et al., 2012; Asaf et al., 2013) for comparison with the more developed LRU functions. While $GPP_{COS,const}$ would be an adequate estimate at high radiation, it gives a clearly overestimated GPP during morning and late afternoon (Fig. 8), which may become very important at longer time scales.

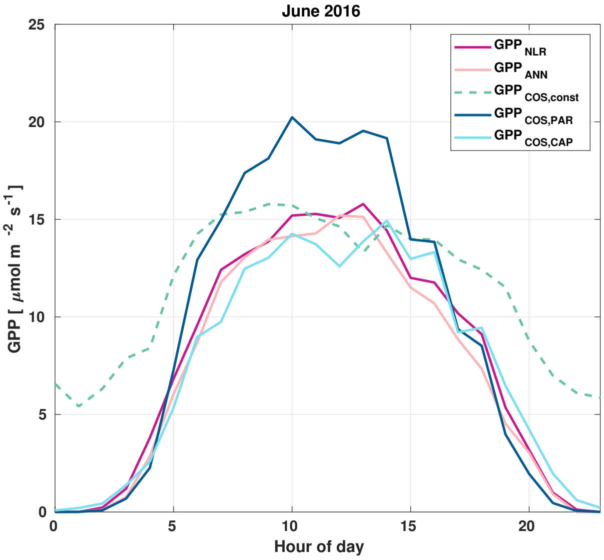

Figure 8: Example of the diurnal variation of GPP derived with different methods in June 2016: GPP_{NLR} (purple), GPP_{ANN} (pink), COS with constant LRU=1.6 ($GPP_{COS,const}$, green dashed line), COS with LRU_{PAR} ($GPP_{COS,PAR}$, dark blue), COS with LRU_{CAP} ($GPP_{COS,CAP}$, light blue). The time is presented in UTC+2 (local winter time).

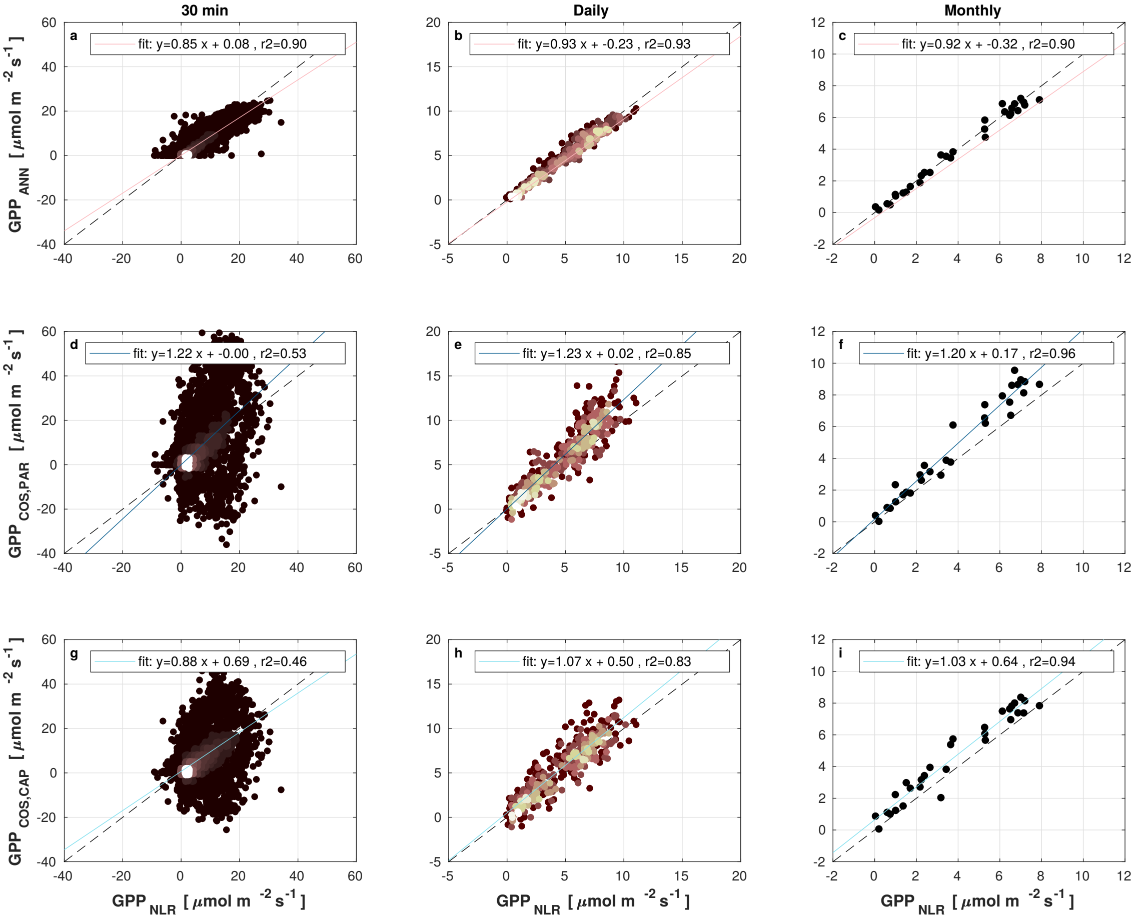

Figure 9: Scatter plots of $\mathrm{GPP_{ANN}}$ (a-c), $\mathrm{GPP_{COS,PAR}}$ (d-f) and $\mathrm{GPP_{COS,CAP}}$ (g-i) against $\mathrm{GPP_{NLR}}$ in 30 min, daily and monthly time scales. The color of data points in 30 min and daily scatter plots indicate the data density, lighter colors indicating higher point density than dark. The fits are least-squares linear fits to the data, fitting details written in the figure legends. Figure adapted from **Paper IV**.

While the $\mathrm{LRU_{PAR}}$ function gives a reasonable estimate of LRU at least in Hyytiälä and results in a better COS-based GPP estimate than the constant LRU method, it gives approximately 20% higher GPP than the traditional partitioning method (Figs. 9, 10). This may be a result of underestimated $\mathrm{GPP_{NLR}}$ and deficiencies in the traditional CO_2 flux partitioning, but may also result from an underestimated $\mathrm{LRU_{PAR}}$ at high PAR.

The new $\mathrm{LRU}_{\mathrm{CAP}}$ formulation on the other hand results in a lower GPP during midday, but higher GPP at longer timescales. This may result from an overestimated $\mathrm{LRU}_{\mathrm{CAP}}$ at high PAR (**Paper IV**) that leads to lower, likely underestimated GPP. However, as the small overestimation was only observed at PAR > 1000 μmol $\mathrm{m}^{-2}\mathrm{s}^{-1}$ it is likely that $\mathrm{LRU}_{\mathrm{CAP}}$ is more reliable than $\mathrm{LRU}_{\mathrm{PAR}}$, especially at longer time scales. It is to be noted, that this PAR threshold probably only applies to Hyytiälä, where the fraction of such high radiation in the data set was 14 %. $\mathrm{GPP}_{\mathrm{COS,CAP}}$ reduced the overall difference to $\mathrm{GPP}_{\mathrm{NLR}}$ compared to $\mathrm{GPP}_{\mathrm{COS,PAR}}$, especially in the peak growing season (Fig. 10). Still both COS-based GPP estimates suggest that GPP should be higher than what was estimated with the $\mathrm{CO_2}$-based methods, in line with a study by Spielmann et al. (2019) who studied COS flux relation to GPP at four different ecosystems. Recent isotopic measurements suggest that traditional $\mathrm{CO_2}$ partitioning would rather bias GPP estimates too high than too low (Wehr et al., 2016), supported by Keenan et al. (2019) who show respiration inhibition during daytime, not captured by the traditional nighttime method of $\mathrm{CO_2}$ partitioning. However, as the reference GPP, $\mathrm{GPP}_{\mathrm{NLR}}$, was based on a combination of nighttime and daytime $\mathrm{CO_2}$ flux partitioning methods, it is not expected to be biased due to daytime respiration inhibition, as suggested by Keenan et al. (2019).

It is also likely that LRU changes throughout the canopy, as the leaf scale COS and $\mathrm{CO_2}$ exchange ratio may change with leaves more adapted to varying light penetration conditions and more scattered solar radiation inside the canopy, which is not taken into account with neither of the presented LRU models. This would serve as a good possibility for future research to investigate, as all previous COS branch chamber measurements have been made on the top of the canopy (Seibt et al., 2010, **Paper III**).

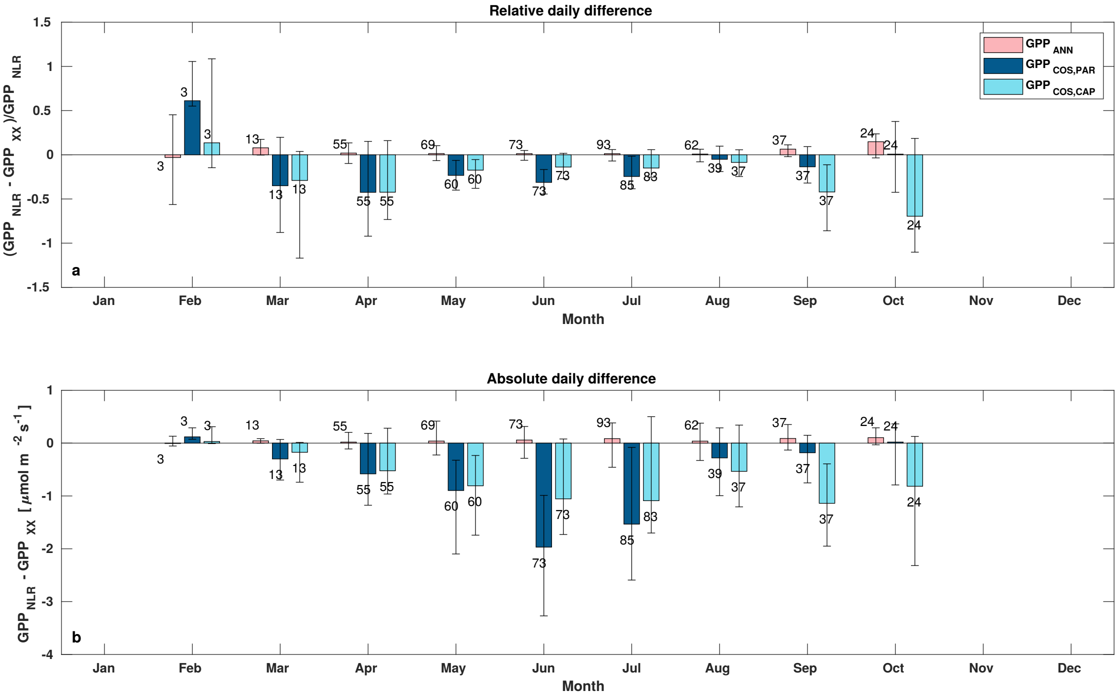

Figure 10: Relative (a) and absolute (b) differences of daily $\mathrm{GPP}_{\mathrm{ANN}}$ (pink), $\mathrm{GPP}_{\mathrm{COS,PAR}}$ (dark blue) and $\mathrm{GPP}_{\mathrm{COS,CAP}}$ (light blue) to $\mathrm{GPP}_{\mathrm{NLR}}$ in different months, averaged over the whole measurement period 2013–2017. Bars represent the median difference, and whiskers show the 25th and 75th percentiles. Numbers on top of the bars indicate how many daily flux data points have been used for calculating the medians. Figure adapted from **Paper IV**.

5 Conclusions and outlook

COS has gained more attention in the carbon cycle research during the past decade due to its promising possibility to be used as a proxy for photosynthesis, that could serve to improve process-based models of GPP and respiration. However, there are only few ecosystem scale flux measurement studies covering more than one growing season, and all flux studies so far have used different setups for EC flux processing, reducing their comparability. In addition, no universal function has been found so far for LRU, which is the key parameter for the COS-based GPP estimate.

This thesis aims at refining COS-based GPP estimates by introducing COS EC flux processing protocols for more reliable COS flux measurements, by providing a simple parameterization for COS fluxes in the boreal region, and by developing better LRU formulations for more accurate GPP calculation.

Paper I presents recommendations for COS EC flux processing and introduces a gap-filling function for COS fluxes for the first time, allowing to calculate COS budgets in the ecosystem scale. This gap-filling function worked well at the studied site Hyytiälä, but would benefit from further testing at other flux measurement sites, especially in similar ecosystems. The processing recommendations should also be put to practical use at other measurement sites, in order to test their generalizability. This would further help cross-comparison of COS fluxes from different measurement sites.

Ecosystem scale COS fluxes were found to have high interannual variability that was linked especially to humidity and temperature (**Paper II**). A simple parameterization of the COS fluxes was created for the boreal region based on CO_2 exchange models as these two fluxes are closely related. The parameterization captured the seasonal variation well in Hyytiälä, but overestimated COS uptake during dry periods. The parameterization could be further developed to better account for reduced VPD, for which data availability was not enough in this study. The parameterization was tested in a land surface model in the boreal region and it could help with improving land surface model development, since the current models have been found to underestimate COS uptake in the high latitudes. The parameterization should also be tested against other flux measurement sites in similar ecosystems as the Hyytiälä forest, to better analyze its uncertainties and development needs.

Branch scale COS fluxes were used to develop better LRU estimates (**Paper III** and

IV). While a simple PAR-dependent $\mathrm{LRU}_{\mathrm{PAR}}$ estimate was already put to test in a land surface modelling study (Maignan et al., 2021), the more complex but theory-based $\mathrm{LRU}_{\mathrm{CAP}}$ remains to be tested at other measurement sites. Both LRU formulations given in this thesis should also be compared against measured LRU at other sites. In addition, it would be beneficial to measure COS and CO_2 fluxes at different levels of the canopy in order to see how the scattered radiation and different light-use properties of the lower canopy affect the LRU, and possibly to create a canopy integrated LRU, as so far all LRU measurements have been done on the top of the canopy.

The improved COS-based GPP (with both $\mathrm{LRU}_{\mathrm{PAR}}$ and $\mathrm{LRU}_{\mathrm{CAP}}$) should be tested in other ecosystems and compared against not only the traditional CO_2 flux partitioning, but also to other emerging GPP proxies, such as isotopic flux measurements and solar induced fluorescence (SIF). While all the methods have their uncertainties, a proper comparison could help with detecting their deficiencies and advantages, hopefully finally leading to improved GPP estimates and process-based models.

In conclusion, COS does appear as a promising proxy for photosynthesis, but the method - while improved - still needs deeper analysis and further testing of its pitfalls before wider use.

6 Review of papers and the author's contribution

Paper I investigates the effects of different flux processing options on the final COS EC fluxes and presents recommendations for future COS flux processing. The author was responsible of all data processing and most of the analysis, produced all figures and wrote the manuscript with contributions from all co-authors.

Paper II reports the longest time series of measured COS EC flux data so far. A simple parameterization was created based on COS flux measurements for evergreen needleleaf forests. The author processed and analyzed all EC related data, produced the parameterization and almost all figures. The author wrote the manuscript together with the first author, with contributions from all co-authors.

Paper III presents branch chamber measurements of COS and CO_2 fluxes. The paper links COS exchange to stomatal conductance and reports a light-dependent formulation for LRU. The author participated in setting up and maintaining field measurements and processed all EC flux data. The author contributed to writing the manuscript.

Paper IV investigates the difference between two CO_2-based and two COS-based GPP estimates during five years and introduces a new, stomatal theory -based formulation for LRU. The author processed and analyzed almost all data and together with other co-authors produced a new formulation for LRU. The author wrote the manuscript with contributions from all co-authros.

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