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Stomatal control of leaf fluxes of carbonyl sulfide and CO_2 in a *Typha* freshwater marsh

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Abstract. Carbonyl sulfide (COS) is an emerging tracer to constrain land photosynthesis at canopy to global scales, because leaf COS and CO_2 uptake processes are linked through stomatal diffusion. The COS tracer approach requires knowledge of the concentration normalized ratio of COS uptake to photosynthesis, commonly known as the leaf relative uptake (LRU). LRU is known to vary with light, but the environmental controls over LRU variability in the field are poorly understood due to scant leaf scale observations.

Here we present the first direct observations of the LRU versus light relationship in the field. We measured leaf COS and CO_2 fluxes at a freshwater marsh in summer 2013. Daytime leaf COS and CO_2 uptake showed similar peaks in the mid-morning and late afternoon, separated by a midday depression, highlighting the common stomatal control on COS and CO_2 diffusion. At night, in contrast to CO_2, COS uptake continued, indicating partially open stomata. LRU ratios showed a clear relationship with photosynthetically active radiation (PAR), converging to 1.0 at high PAR, while increasing sharply at low PAR. Daytime integrated LRU ranged from 1 to 1.5, with a mean of 1.2 across the campaign, significantly lower than the mean value reported from laboratory measurements (~1.6). Our results indicate two major determinants of LRU—light and vapor pressure deficit (or evaporative demand). Light is the primary driver of LRU because CO_2 reactions are light limited but the COS reaction is not. In a secondary effect, high evaporative demand tends to reduce LRU values. During periods of high evaporative demand, leaves conserve water by partial stomatal closure. This reduces COS uptake more than CO_2 uptake because stomatal resistance is a more dominant component in the COS diffusional pathway. High evaporative demand usually coincides with high PAR, leading to the lowest observed LRU in the afternoon. Our findings illustrate the stomatal coupling of COS and CO_2 uptake during the most photosynthetically active period in the field, and provide important characterization of LRU, a key parameter to support the use of COS as a photosynthetic tracer.

1 Introduction

Carbonyl sulfide (COS) has been shown as a unique tracer for land photosynthesis (also known as gross primary productivity, GPP) at regional to global scales (e.g., Montzka et al., 2007; Campbell et al., 2008; Berry et al., 2013; Hilton et al., 2017; Campbell et al., 2017). Globally, the largest sinks of COS are uptake by leaves and soils, and the largest sources are ocean emissions, followed by additional emissions from anthropogenic activities (Montzka et al., 2007; Berry et al., 2013; Launois et al., 2015; Campbell et al., 2015). Since vegetation uptake dominates the COS exchange in land ecosystems (Berry et al., 2013), concurrent measurements of COS and CO_2 fluxes can be used to separate photosynthesis and respiration from the net carbon flux (Asaf et al., 2013; Billesbach et al., 2014). The COS tracer approach to photosynthesis is based on the coupling of leaf COS and CO_2 uptake (Sandoval-Soto et al., 2005; Seibt et al., 2010; Stimler et al., 2010, 2011; Wohlfahrt et al., 2012). Understanding the quantitative relationship that ties together leaf COS and CO_2 fluxes is key to obtaining accurate estimates of photosynthesis from COS measurements.

In leaves, COS and CO_2 follow the same stomatal diffusional pathway and similar hydrolytic reactions catalyzed by carbonic anhydrase (CA), with the main difference being that the hydrolysis goes reversibly for CO_2 but one-way for COS (Protoschill-Krebs et al., 1996; Notni et al., 2007). The reaction of COS with CA yields H_2S and CO_2 (Schenk et al., 2004; Notni et al., 2007), without any observed COS (re)emission from leaves (Stimler et al., 2010). In contrast, CO_2 hydration is subject to chemical equilibrium that depends on its diffusional supply versus its demand from fixation, leading to retrodiffusion to the atmosphere. CA-mediated hydrolysis therefore serves as the sink reaction of COS in leaves, but not of CO_2.

The COS hydrolysis via CA has been shown to be light independent (Goldan et al., 1988; Protoschill-Krebs et al., 1996). Since this reaction is also highly efficient (Ogawa et al., 2013), the COS uptake rate should be mostly controlled by the sequence of conductances along the diffusional pathway into leaves, i.e., substrate limited rather than enzyme limited (Goldan et al., 1988; Sandoval-Soto et al., 2005; Seibt et al., 2010; Stimler et al., 2010). Leaf COS uptake should therefore respond to environmental variables that regulate stomatal conductance, including photosynthetically active radiation (PAR), because of the feedback from photosynthesis to stomatal conductance (e.g., Ball, 1988; Collatz et al., 1991). Thus, light regulates leaf COS uptake even though COS hydrolysis itself does not depend on light.

In contrast to the CO_2 flux that turns to emission at night, COS uptake may continue if stomata are not fully closed (Stimler et al., 2010). To understand the relationship between daily integrated COS and CO_2 fluxes for regional flux inversion (e.g., Hilton et al., 2015), nighttime COS uptake needs to be constrained (Maseyk et al., 2014). Nighttime COS uptake has been found in a wheat field (Maseyk et al., 2014), a boreal pine forest (Kooijmans et al., 2017), and temperate forests (Berkelhammer et al., 2014; Commane et al., 2015; Wehr et al., 2017). However, most field studies based their findings upon indirect evidence of nighttime ecosystem COS uptake, with only one study reporting some direct leaf observations of nighttime uptake (Berkelhammer et al., 2014).

The quantitative relationship between leaf COS uptake and photosynthesis required for COS-based photosynthesis estimates—from canopy to regional scales (e.g., Asaf et al., 2013; Campbell et al., 2017)—is commonly expressed in one parameter: leaf relative uptake (LRU). LRU is the ratio of leaf COS : CO_2 fluxes normalized by their respective ambient concentrations

(Sandoval-Soto et al., 2005; Campbell et al., 2008). A mean LRU value of 1.6 has been reported for a wide range of species from leaf scale measurements in the laboratory (Stimler et al., 2010, 2011, 2012) and the field (Berkelhammer et al., 2014). But in the field, lower LRU values have also been observed, e.g., 1.3 in a wheat field (Maseyk et al., 2014) and 1.2 in a temperate forest (Commane et al., 2015), both estimated from ecosystem scale measurements.

For ecosystem and larger scale applications, a constant LRU of 1.6 has been assumed (e.g., Asaf et al., 2013; Hilton et al., 2015) despite the known dependence of LRU on PAR. LRU is found to decrease with light in both laboratory and field observations (Stimler et al., 2010, 2011; Maseyk et al., 2014; Commane et al., 2015). Leaf level measurements in the laboratory show that LRU is stable at PAR above ca. 500 µmol m^{-2} s^{-1}, but increases sharply with decreasing PAR (Stimler et al., 2010, 2011). The stable LRU region is consistent with that of light-saturated photosynthesis and maximal stomatal conductance, and therefore low variations in COS and CO_2 fluxes (Stimler et al., 2011). At low light, the rate at which LRU increases differs among species, with some showing a sharp increase to LRU values of ca. 9, while others show a more gradual or only slight increase. This LRU behavior results from the diverging responses of COS and CO_2 uptake in low light: CO_2 assimilation that is also controlled by light decreases more rapidly than COS uptake that is only controlled by stomatal conductance. Using a light dependent LRU instead of a constant value is therefore necessary for COS-based photosynthesis estimates. But in the field, the LRU–PAR relationship has only been approximated with ecosystem fluxes (Maseyk et al., 2014; Commane et al., 2015), not directly determined from leaf fluxes. For COS-based canopy photosynthesis estimates, we need direct knowledge of how LRU responds to PAR and other possible drivers in the field. Applications for longer timescales would further need daily integrated LRU values.

This study is motivated by two research questions: 1) How does light control instantaneous and daily integrated LRU values? 2) How do stomatal responses to environmental variables regulate leaf COS uptake in the field? We report leaf COS and CO_2 fluxes measured in a *Typha latifolia* freshwater marsh during the peak growing season of June and July 2013. We then examine how environmental variables control fluxes and LRU through stomatal mechanisms, and discuss the implications for COS-based photosynthesis estimates.

2 Methods

2.1 Site description

We measured leaf fluxes of COS, CO_2, and water from 31 May to 6 July 2013 (day of year 151–187) at the San Joaquin Freshwater Marsh (SJFM, 33°39′44.4″ N, 117°51′6.1″ W). The SJFM is located near the campus of the University of California at Irvine, at 3 m above sea level and 8 km northeast of the Pacific Ocean (Goulden et al., 2007). The SJFM is part of the University of California's Natural Reserve System. The site history and management have been described in Goulden et al. (2007). Briefly, the SJFM is a mature freshwater marsh, the remnant of once a 2100 ha wetland along the San Diego Creek. Since the 1960s, the SJFM has been managed by flooding the area annually to a depth of approximately 1 m from December/January to March. The standing water recedes by evapotranspiration and subsurface drainage and eventually disappears by midsummer (Goulden et al., 2007). A flux tower (5 m high) is located on a floating wooden platform near the northeastern edge of the SJFM. The

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platform is surrounded by dense vegetation dominated by *Typha latifolia* (broadleaf cattail). In contrast to most species in a mediterranean climate that grow in the rainy winter or early spring, the growing season of the marsh plants is summer due to the standing water.

2.2 Experimental setup

Leaf fluxes of COS, CO_2, and H_2O were measured with a flow-through (dynamic) chamber. The cylindrical chamber (18 cm diameter, 38 cm height, 10.3 L volume) consisted of PFA Teflon film stretched between two aluminum rings connected by rods. The PFA film was laid inside the structure such that only the Teflon was in contact with the sampled air. The chamber enclosed the upper sections of six tall cattail leaves with an average width of 1.5 cm. The leaves extended above and below the chamber. The total leaf area in the chamber was estimated as 409.5 cm^2. Skirts of Teflon film were wrapped around the leaves to provide a seal at both ends of the chamber. On one end, a high-speed axial fan (D344T, Micronel) was installed to provide ventilation to keep the chamber at ambient conditions (i.e., within 1 p.p.m.v. of ambient CO_2, tested at the start of the campaign). During measurement periods, the fan was turned off and its opening served as the inlet to allow airflow through the chamber. A second, smaller fan (F62, Micronel), attached to a stainless steel rod and placed inside the chamber, ran continuously to mix the air within the chamber.

The chamber was connected via 1/4″ PFA Teflon tubing to a Quantum Cascade Laser (QCL) analyzer (CW-QC-TILDAS, Aerodyne Research Inc., Billerica, MA, USA), with a 1 µm Teflon filter attached at the inlet. The analyzer was placed in an instrument enclosure on the platform. Flow through the analyzer was provided by a Varian TriScroll 600 pump (Agilent Technologies Inc., Santa Clara, CA, USA). Flow rate in the tubing was 6 standard liter per minute (s.l.m.). The pump was placed next to the nearest main power line near the entrance to the marsh site, and connected to the analyzer by a 150 m long 2″ vacuum line. A solenoid valve at the inlet to the QCL was used to switch from the sampling line to a stream of dry N_2 (ultrahigh purity) for a one-minute background correction every hour. Data from the QCL analyzer were recorded at 10 Hz and stored on the QCL hard drive. The RMS noise (1 σ) at 10 Hz was 11–18 parts per trillion in volume (p.p.t.v.) for COS during chamber measurements.

The leaf chamber was measured once per hour. We monitored chamber air concentrations during the five-minute measurement periods (i.e., while the ventilation fan was off), as well as the ambient air for one minute before and after these periods (i.e., while the fan was running). Leaf fluxes were calculated from the transient changes with respect to the interpolated inlet (ambient) concentrations (Fig. 1). The apparent fluxes from blank chambers were characterized and were found to be negligible. Environmental data were obtained from various sensors including photosynthetically active radiation (PAR) (SQ-215, Apogee Instruments), ambient air temperature and humidity (HMP45AC, Vaisala), and chamber air and leaf temperature (type T thermocouples, PFA coated), and were stored at 10 s intervals on a datalogger (CR1000, Campbell Scientific). The datalogger also controlled the operation of the high-speed ventilation fan.

2.3 Calculation of leaf fluxes

A mass balance equation is formulated for the gas species being measured (COS, CO_2, or H_2O),

$$V\frac{\mathrm{d}C}{\mathrm{d}t} = q\left(C_\mathrm{a} - C\right) + FA$$

where C [mol m^{-3}] is the chamber headspace concentration of the gas, C_a [mol m^{-3}] is the inlet (ambient) concentration, q [m^3 s^{-1}] is the inlet flow rate, V [m^3] and A [m^2] are the chamber volume and leaf area, respectively, and F [mol m^{-2} s^{-1}] is the flux rate to be calculated. Solving the mass balance equation with the initial condition $C(t = 0) = C_\mathrm{a}$, we obtain

$$C(t) = -\frac{FA}{q}\exp\left(-qt/V\right) + C_\mathrm{a} + \frac{FA}{q}$$

The flux rate F is

$$F = \frac{q}{A} \cdot \frac{C - C_\mathrm{a}}{1 - \exp\left(-qt/V\right)}$$

Let $\hat{y} = C - C_\mathrm{a}$ and $\hat{x} = \exp\left(-qt/V\right)$ be the variables for the regression, hence,

$$\hat{y} = \frac{FA}{q}\left(1 - \hat{x}\right)$$

The flux rate F is then solved from the slope of the regression $\hat{y} \sim (1 - \hat{x})$. The standard error of the estimated F is also obtained from the regression. The flux calculation method described above does not require a steady state to be reached in the chamber. A typical example of the chamber measurement period for COS with the fitted curve of concentration changes is shown in Fig. 1.

2.4 Data quality control

All leaf flux and meteorological data have been quality checked and filtered. Conspicuously unrealistic data points in the meteorological data have been removed. For the flux data, we used several independent criteria to filter out bad measurements. First, measurement periods with serious misfit of the shape of concentration changes during chamber closure or with strong drift in the ambient concentrations were discarded. Second, flux estimates associated with large RMSEs between fitted and observed concentrations were also filtered out. Then, outliers in flux data were detected using the well-established Tukey's interquartile range method (Wilks, 2011). In addition, strongly positive CO_2 fluxes during the day and strongly negative CO_2 fluxes at night were also removed. Only the data points that passed all these filtering procedures were kept in the final data for analysis.

2.5 Calculation of leaf relative uptake (LRU)

Leaf COS : CO_2 relative uptake ratio (LRU) is defined as the ratio of COS and CO_2 fluxes (F_COS and F_{CO_2}) normalized by their respective concentrations (χ_COS and χ_{CO_2}),

$$\mathrm{LRU} = \frac{F_\mathrm{COS}}{F_{\mathrm{CO}_2}} \cdot \frac{\chi_{\mathrm{CO}_2}}{\chi_\mathrm{COS}}, \text{ where } F_\mathrm{COS} < 0 \text{ and } F_{\mathrm{CO}_2} < 0$$

LRU is a dimensionless quantity. We confine our LRU analysis to occasions where both COS and CO_2 fluxes are negative (i.e., showing net uptake). Hence, LRU is only calculated during the daytime and is always positive.

2.6 Fitting light response curves for leaf COS and CO_2 fluxes and LRU

We used the LOWESS (locally weighted scatterplot smoothing) regression method to obtain smooth light response curves for COS flux, CO_2 flux, and LRU (see Fig. 5). The LOWESS regression method is a nonparametric method that does not require any a priori known relationship between the predictor (here, PAR) and the response variables (COS flux, CO_2 flux, and LRU). At each point in the range of the predictor, a low-degree polynomial is fitted to all the neighboring points to estimate the least squares response, weighted by the distances between the neighboring points and the current point (Cleveland et al., 1992). The calculation was performed with the Python `statsmodels` package (Seabold and Perktold, 2010).

3 Results

During the campaign period in June 2013 covering the peak growing season of *Typha latifolia*, meteorological conditions changed little except for a few cloudy days (day of year 159, 160, and 181, Fig. 2d), and the diurnal patterns of leaf COS, CO_2, and H_2O fluxes therefore also remained similar (Fig. 2). The diurnal patterns of leaf fluxes and related variables are visualized with hourly binned medians and quartiles (Fig. 3). During the day, leaf uptake of COS and CO_2 showed similar patterns (Fig. 3a, b), with uptake peaks in the morning and afternoon separated by a midday depression around local noon (13:00). The midday depression was up to 36% for COS (5.5 pmol m^{-2} s^{-1} at 14 h versus 8.5 pmol m^{-2} s^{-1} at 11 h) and 40% for CO_2 (3.7 µmol m^{-2} s^{-1} at 13 h versus 6.1 µmol m^{-2} s^{-1} at 17 h), respectively. The morning peaks coincided for the two fluxes at around 11:00, whereas the afternoon peak occurred slightly later for COS (18:00) than for CO_2 (17:00). The afternoon peak of CO_2 flux was slightly stronger than its morning peak (Fig. 3b, c), probably because the chamber received more light in the afternoon than in the morning (Fig. 3e) due to a wider gap in the canopy to the west of the chamber than to other directions. Leaf transpiration showed a decline at 11:00 (Fig. 3c), but with an earlier afternoon peak (16:00) that coincided with the maximum vapor deficit (Fig. 3f). Contrary to COS and CO_2 fluxes, the diurnal pattern of water flux was strongly asymmetric due to the high vapor deficit in the afternoon (Fig. 3f), although the midday depression in stomatal conductance was roughly symmetric as indicated by COS uptake.

In contrast to daytime fluxes, nighttime fluxes of COS and CO_2 showed diverging patterns. At night, CO_2 was emitted from leaf respiration (Fig. 3b), whereas COS uptake continued (Fig. 3a). Both fluxes had significantly smaller magnitudes than during the day, with CO_2 emissions of around 1 µmol m^{-2} s^{-1}, and COS uptake of around 2–3 pmol m^{-2} s^{-1}. Note that although COS emissions were occasionally observed at night (Fig. 2a), they were likely caused by the measurement uncertainty from high flow rates (~6 s.l.m.), and the hourly medians indeed showed a robust pattern of nighttime COS uptake (Fig. 3a). When averaged over the whole campaign, nighttime COS uptake was 23% of the total daily COS uptake by leaves. Nighttime transpiration was minimal (Fig. 3c) as the vapor deficit was close to zero at night (Fig. 3f).

Leaf relative uptake (LRU), the ratio of COS to CO_2 uptake normalized by their respective concentrations in the chamber, showed an asymmetric U-shape diurnal pattern (Fig. 3d). The LRU had highest values of 2–3 (medians binned by the hour) near dawn or dusk, with a gradual decrease throughout the morning and early afternoon, and had minima around 0.9 at 15:00 coinciding with the dip in COS uptake (Fig. 3d). LRU was stable in the late afternoon until an abrupt increase at 19:00 before sunset.

Overall, COS flux was well correlated with CO_2 flux, with an r^2 of 0.49 (Fig. 4a), reaffirming the shared stomatal control on both fluxes. The correlation between COS and water fluxes was lower: r^2 = 0.32 (Fig. 4b), and showed a wide spread during the day due to the asymmetric diurnal pattern of water fluxes (Fig. 3c). At night, COS fluxes showed larger variability than water fluxes as the vapor deficit was small (Fig. 3f).

The diurnal pattern of LRU (Fig. 3d) was consistent with the LRU response to PAR (Fig. 5c). The LRU values decreased with increasing PAR (Fig. 5c) to around 1.0 at PAR above around 500–600 µmol m^{-2} s^{-1}. Surprisingly, the lowest LRU values during the day did not occur at the time of the highest PAR (Fig. 3d), but rather at the time of the highest vapor deficit (Fig. 3f) and moderately strong PAR (1000–1400 µmol m^{-2} s^{-1}) due to the stronger stomatal limitation on fluxes as a response to the high evaporative demand.

4 Discussion

4.1 Stomatal control is responsible for the similarity in daytime leaf COS and CO_2 uptake

Leaf fluxes of COS and CO_2 showed similar light responses, increasing with PAR until they become light saturated, and decreasing at high light and high evaporative demand (Fig. 5a, b). However, the similarity in fluxes is not due to a common light response of the biochemical reactions that consume COS and CO_2 in leaves, since COS hydrolysis is light independent. Instead, underlying the similar diurnal patterns and light responses (Figs. 3a, b, 5a, b) is the shared response of leaf COS and CO_2 uptake to stomatal conductance, which increases with light because of the feedback between stomatal conductance and photosynthesis (Cowan, 1978; Farquhar and Sharkey, 1982; Ball, 1988; Collatz et al., 1991). At high light, when CO_2 assimilation is light saturated, leaf COS and CO_2 uptake is controlled by stomatal conductance in a similar way: both decline as stomatal conductance is reduced in response to high evaporative demand (Fig. 3a, b). At low light, COS and CO_2 diffusions are both reduced by low stomatal conductance, but CO_2 assimilation is additionally reduced by low light, causing a stronger decrease in CO_2 uptake than COS uptake (Fig. 5a, b).

The most striking feature in the diurnal patterns of leaf COS and CO_2 uptake was the concurrent midday depression in the early afternoon (Fig. 3a–c), also affecting the light response curves of fluxes (Fig. 5a, b). From the smoothed light response trends (Fig. 5a, b), we found that COS uptake reached the maximum of 7.5 pmol m^{-2} s^{-1} at PAR = 493 µmol m^{-2} s^{-1} and decreased to 4.7 pmol m^{-2} s^{-1} at PAR = 1800 µmol m^{-2} s^{-1} (the typical PAR level at local noon), whereas CO_2 uptake reached the maximum of 5.3 µmol m^{-2} s^{-1} at PAR = 740 µmol m^{-2} s^{-1} and decreased to 3.7 pmol m^{-2} s^{-1} at PAR = 1800 µmol m^{-2} s^{-1}. The respective 37% and 31% reductions in COS and CO_2 uptake at typical midday light (1800 µmol m^{-2} s^{-1}) with respect to their peak uptake indicate that stomatal conductance exerted a stronger control on COS uptake than CO_2 uptake (see sect. 4.3). This behavior was driven by the stomatal response to high vapor deficit that always coincided with high PAR (Fig. 2d, e).

The reduction of stomatal conductance under high vapor deficit is a well-documented behavior that serves to curb excessive loss of water and optimize water use against carbon gain (Tenhunen et al., 1984; Ball, 1988; Collatz et al., 1991; Leuning, 1995). Previously, the midday depression in plant COS uptake has been inferred from canopy scale measurements in a Mediterranean pine forest in the winter (Asaf et al., 2013) and in a temperate forest in the summer (Commane et al., 2015), but has not been investigated directly at the leaf level. The current study, to our knowledge, offers the first field observations of the influence of midday depression on COS uptake at the leaf scale and reaffirms stomatal conductance as the dominant control of COS uptake.

4.2 COS uptake is an indicator of nocturnal stomatal conductance

The coupling between leaf COS and CO_2 fluxes breaks down at night because leaves produce CO_2 due to respiration, whereas COS uptake may continue if stomata are not fully closed. At this site, nocturnal uptake contributed 23% of the total daily leaf COS uptake. This fraction is comparable to those reported from a wheat field (29 ± 5%, Maseyk et al., 2014), an alpine temperate forest (25–30%, Berkelhammer et al., 2014), a boreal pine forest (17%, Kooijmans et al., 2017), and a New England mixed forest (< 20% after subtracting soil uptake, Commane et al., 2015; Wehr et al., 2017). Collectively, these studies indicate that nocturnal uptake is typically 17–30% of the total canopy COS budget, a fraction that is too large to ignore in ecosystem and regional COS budget studies. Understanding nocturnal COS uptake will therefore be necessary for COS-based photosynthesis estimates at daily and longer timescales.

For the *T. latifolia* leaves here, we obtained a mean value of 5 ± 1 mmol m^{-2} s^{-1} for the nocturnal stomatal conductance to COS ($g_{s,COS}$) if internal conductance ($g_{i,COS}$), the combination of mesophyll conductance and biochemical reaction coefficient, is ignored ($g_{s,COS} \ll g_{i,COS}$). This translates to 10 ± 2 mmol m^{-2} s^{-1} for the stomatal conductance to water (g_s), after accounting for the different diffusivities of water and COS in the air with a ratio of 2.0 (Seibt et al., 2010). The nocturnal $g_{s,COS}$ is at the lower end of values reported for other ecosystems, ranging from 1.6 mmol m^{-2} s^{-1} for a New England mixed forest (Wehr et al., 2017) to 5–20 mmol m^{-2} s^{-1} for a Scots pine forest (Kooijmans et al., 2017), 11.5 mmol m^{-2} s^{-1} for a wheat field (Maseyk et al., 2014), and 13–20 and 22–66 mmol m^{-2} s^{-1} for pine and poplar trees, respectively, in an alpine temperate forest (Berkelhammer et al., 2014).

Although these observations span a wide range of values across plant species and ecosystem types, the fraction of nocturnal uptake in the daily canopy COS budget lies in a much narrower range of 17–30%. This convergence indicates that nocturnal values may be directly coupled to daytime stomatal conductance. Hence, it may be beneficial for large scale applications to relate nocturnal stomatal conductance to daytime observable parameters, e.g., 5.5% of the light saturated value for a wheat field (Maseyk et al., 2014) or 2.5% of the daytime maximum value in a New England mixed forest (Wehr et al., 2017).

In land biosphere models, nocturnal stomatal conductance has been typically parameterized with a small fixed value regardless of plant type, for example, 10 mmol m^{-2} s^{-1} in the Community Land Model v4.5 (Oleson et al., 2013). This fixed-value parameterization may introduce biases in the nighttime COS fluxes and long-term COS budget in regional simulations, which in turn propagate into the COS-based photosynthesis estimates. For better estimates of nighttime COS fluxes and transpiration, the variability of nocturnal stomatal conductance, and its links to daytime values, need to be quantified across plant species and ecosystem types. COS measurements are well suited for this purpose since COS uptake continues as long as stomata are open, whereas water fluxes become very small as the ambient air typically gets close to saturation at night. We expect COS measurements to be particularly beneficial in tropical rainforests and other environments that experience high humidity.

4.3 The environmental determinants of leaf relative uptake (LRU)

Leaf COS to CO_2 relative uptake (LRU) is an important parameter that links plant COS uptake with GPP. Observations at leaf and ecosystem scales show that LRU is primarily controlled by light, following an asymptotically decreasing trend with increasing PAR (Fig. 5c; Stimler et al., 2010, 2011; Maseyk et al., 2014; Commane et al., 2015). Such a pattern originates from the differential responses of COS and CO_2 uptake to light, because unlike photosynthesis, COS uptake responds only indirectly to light through changes in stomatal conductance (Stimler et al., 2011). Using the nonparametric LOWESS fit without assuming an a priori relationship between LRU and PAR, we found an LRU–PAR relationship (Fig. 5c) similar to the decaying power law ($\mathrm{LRU} = a \cdot \mathrm{PAR}^{-b}$) reported by Maseyk et al. (2014). Based on this and previous studies, the light response of LRU may be generalized empirically with a decaying power law fit (Stimler et al., 2010, 2011; Maseyk et al., 2014; Commane et al., 2015).

We identified vapor deficit as secondary environmental driver of LRU, resulting from the differential effects of low humidity induced stomatal closure on COS and CO_2 fluxes (Fig. 5a, b; see also sect. 4.1). High vapor deficit tends to reduce LRU values in mid-afternoon, when LRU is expected to reach light-saturated values according to the LRU–PAR relationship. This is because stomatal conductance is a more dominant component in the diffusional pathway for COS than for CO_2. Using the resistance analog (the inverse of conductance, i.e., $r_\mathrm{s} = g_\mathrm{s}^{-1}$), we can combine all sub-stomatal terms (mesophyll and chloroplast wall conductances and biochemical reaction coefficient) into a single internal resistance term ($r_\mathrm{i,COS}$ or $r_\mathrm{i,CO_2}$). Because of the strong affinity of β-CA for COS (Ogawa et al., 2013), COS is more readily consumed at the CA active site than CO_2 is at the carboxylation site of RuBisCO (Stimler et al., 2010; Berry et al., 2013), leading to a much smaller contribution of internal resistance to the COS diffusional pathway,

$$\frac{r_\mathrm{i,COS}}{r_\mathrm{s,COS} + r_\mathrm{i,COS}} < \frac{r_\mathrm{i,CO_2}}{r_\mathrm{s,CO_2} + r_\mathrm{i,CO_2}}$$

For example, based on rough estimates of light-saturated values of stomatal conductance ($g_\mathrm{s,H_2O}$ = 80 mmol $\mathrm{m^{-2}\ s^{-1}}$) and COS and CO_2 fluxes (Fig. 5), for a relative decrease in stomatal conductance ($g_\mathrm{s,COS}$ and $g_\mathrm{s,CO_2}$) of 50% at high vapor deficit, the total resistance of COS uptake increases by 37% whereas that of CO_2 uptake only increases by 28%. Thus, when CO_2 uptake is light saturated, a decrease in stomatal conductance due to high vapor deficit will reduce COS uptake more than CO_2 uptake, and result in a lower LRU (7% for the examples above, from 1.07 to 1.0).

Previous laboratory studies have not found any significant response of LRU to relative humidity (Stimler et al., 2010, 2011), but it is possible that the vapor deficit in the experiments was not strong enough to initiate partial stomatal closure. At our site, the influence from vapor deficit causes the lowest LRU values to occur in the early afternoon (15:00), when vapor deficit is the highest, instead of at noon when PAR is highest (13:00).

The asymptotic LRU value at high light (PAR > 600 µmol m^{-2} s^{-1}) at our site was around 1.0 (Fig. 5c). This value is lower than the mean LRU of 1.61 ± 0.26 from laboratory measurements across a range of species (Stimler et al., 2012), which has been used as a representative LRU in regional GPP inversion studies from COS measurements (e.g., Hilton et al., 2015). The low asymptotic LRU value reported here is, however, similar to values seen in some grasses and shrub species (Stimler et al., 2012). Lower LRU values have also been reported from field studies, for example, 1.3 in a wheat field (Maseyk et al., 2014) and 1.2 in a mixed temperate forest at high PAR (Commane et al., 2015). The discrepancy between LRU values measured under laboratory and field conditions may come from variations in environmental drivers, for example, vapor deficit, or plant water status that regulates stomatal responses. The LRU responses to environmental conditions can also differ by plant species (Stimler et al., 2012). In ecosystem or regional scale applications, LRU values that are diagnosed from process-based models (Berry et al., 2013; Hilton et al., 2015) may be preferable to an assumed value of 1.6.

4.4 Daily integrated leaf relative uptake ratio and its implications for regional flux estimates

Beyond the ecosystem scale, daily values of LRU can be useful for large scale COS applications. The daily (24 h) mean LRU at this site showed large day-to-day variations (1.4–3.6) and also had large uncertainty due to the variability and measurement uncertainty in nighttime CO_2 fluxes (Fig. 6). In contrast, the daytime mean LRU, averaged over the day length of 14 hours, did not show strong variability (1.0–1.8) and had an average value of 1.2 across the campaign. The daytime mean LRU was consistently lower than the daily (24 h) mean LRU, since the latter includes nocturnal COS uptake and CO_2 emissions.

We found a good correlation between daytime mean LRU and daytime mean PAR ($r = -0.525$; Fig. 6b), similar to Maseyk et al. (2014). This indicates that the LRU–PAR relationship is preserved at the daily timescale, supporting the use of COS as a photosynthetic tracer at large scales where measurements are often made at daily or longer intervals. On overcast days, the daytime mean LRU values were higher than on clear days (Fig. 6a), as expected from the light response of LRU. We expect the relationship between daytime means of LRU and PAR to be useful for calculating daytime mean LRU empirically from meteorological conditions for GPP estimates. Since the use of COS as a GPP tracer in an inverse modeling framework requires the uncertainty in LRU to be smaller than that in the a priori GPP estimates (Hilton et al., 2015), future studies should be dedicated to understanding LRU variability in the field for accurate COS-based GPP estimates.

5 Conclusions

From direct field observations at the leaf scale, our study has shown that leaf COS and CO_2 fluxes share broadly similar diurnal patterns driven by the common stomatal responses to light and vapor deficit. In the early morning and late afternoon, the increase of COS uptake with light is caused by increasing stomatal conductance, since the COS reaction with CA is light independent. Around midday, vapor deficit becomes a limiting factor of stomatal conductance and drives the midday depression in COS and CO_2 uptake.

We have identified three distinct physiological regimes that control LRU variability over the course of a day:

1. In the early morning when both PAR and vapor deficit are low, biochemical reactions of CO_2 are light limited. As a result, leaf CO_2 uptake is more restricted than COS uptake that is only stomatal conductance limited, causing LRU to be high and to decrease with PAR.

2. Around midday and in the early afternoon when both PAR and vapor deficit are high, midday depression occurs and both CO_2 and COS diffusion processes are limited by the low stomatal conductance. Since COS uptake is more sensitive to stomatal conductance, vapor deficit becomes the key driver of LRU at this time of the day.

3. In the late afternoon when PAR declines but vapor deficit is still quite high, stomatal conductance is more limited by vapor deficit compared to the morning. This causes COS uptake and LRU to be lower than in the corresponding morning time with the same PAR, and leads to the asymmetric diurnal pattern of LRU.

We have validated the previously reported light dependence of LRU directly at the leaf scale in field conditions. At high light, LRU converges to 1.0, much lower than the typical value of 1.6 reported from laboratory conditions. In addition, we identified vapor deficit as a secondary but non-negligible effect on LRU when it begins to limit stomatal conductance. The LRU–PAR relationship also holds between the daytime mean LRU and PAR values. The coupling between leaf COS and CO_2 fluxes during the peak growing season of the *Typha latifolia* vegetation lends strong support to the use of COS as a quantitative tracer for canopy photosynthesis.

Data availability. Data presented here can be found in the University of California Curation Center (UC3) Merritt data repository at https://doi.org/10.15146/R37T00.

Author contributions. U.S. designed the research. All authors conducted the fieldwork. W.S. and U.S. performed data analysis. W.S., U.S., and K.M. wrote the paper with contributions from all co-authors.

Competing interests. The authors declare no conflict of interest.

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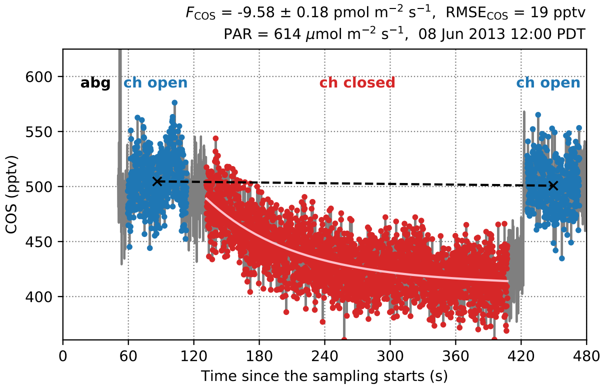

Figure 1. A typical sampling period on the leaf chamber illustrated with COS concentration measurements. The first minute is for auto-background spectral correction (abg) using N_2 gas. The sampling system then switches to the chamber line with the ventilation fan turned on (ch open) for one minute. Then the ventilation fan is turned off for five minutes (ch closed) to observe flux signals in the chamber, and after that is turned on again for one minute (ch open). The fitted curve for concentration changes is shown in light pink. The black dashed line represents the zero-flux baseline correction to account for any drift in the measured ambient concentrations.

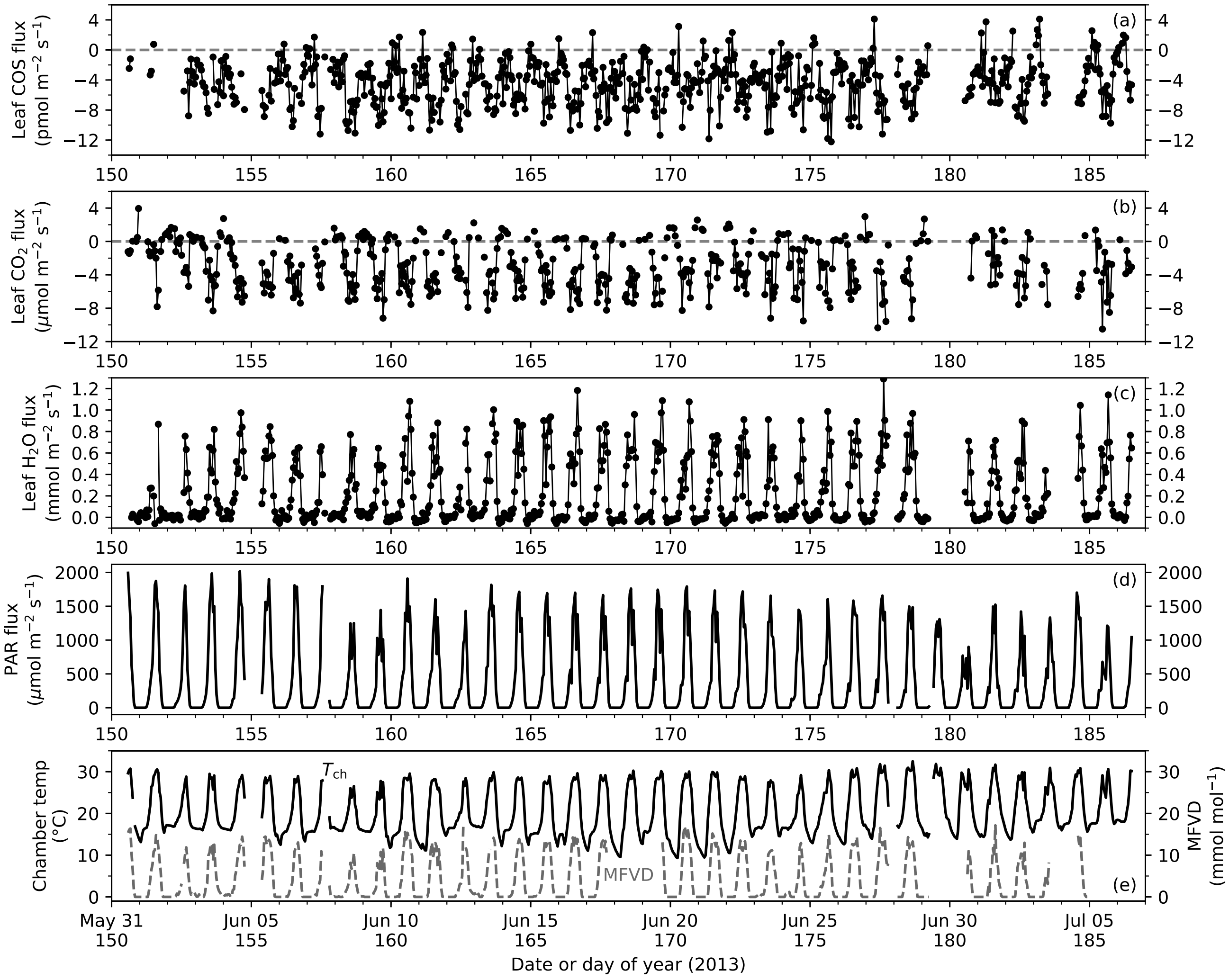

Figure 2. Time series of leaf COS (a), CO$_2$ (b) and water (c) fluxes, photosynthetically active radiation (PAR) at the leaf chamber (d), air temperature (e, black solid line; T_{ch}) and saturation vapor deficit in mole fraction (e, gray dashed line; MFVD) in the chamber. Ticks on x-axes indicate the start of the days (0000 h).

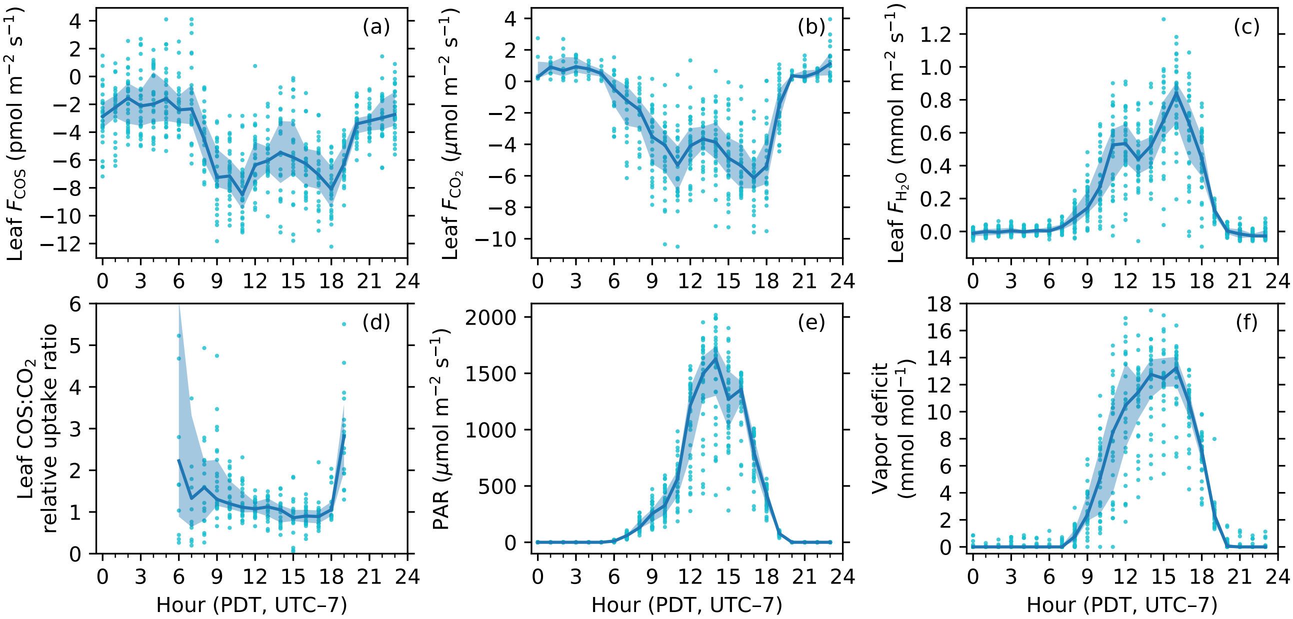

Figure 3. Diurnal patterns of leaf COS (a), CO_2 (b) and water (c) fluxes, leaf COS : CO_2 relative uptake ratio (d), PAR at the leaf chamber (e), and vapor deficit inside the leaf chamber (f). The solid curves show medians binned by the hour of the day (Pacific Daylight Time, UTC–7), and the upper and lower shaded areas are 25th and 75th percentiles, respectively.

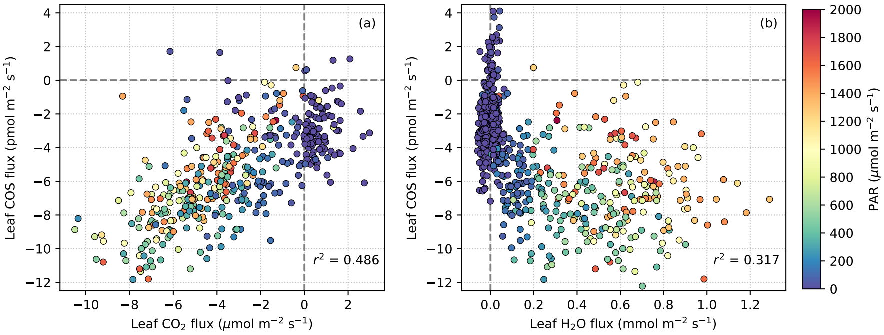

Figure 4. (a) Leaf COS vs. CO_2 fluxes, and (b) leaf COS vs. H_2O fluxes. Data points are colored by the PAR level.

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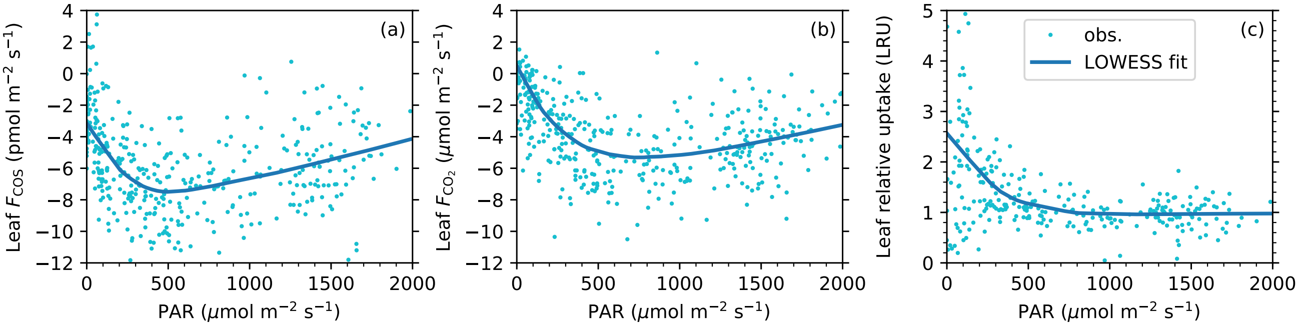

Figure 5. Light responses of leaf COS flux (a), CO_2 flux (b) and LRU, the COS : CO_2 relative uptake ratio (c). Data are shown as dots, and the smoothed curves are fitted with the nonparametric LOWESS method.

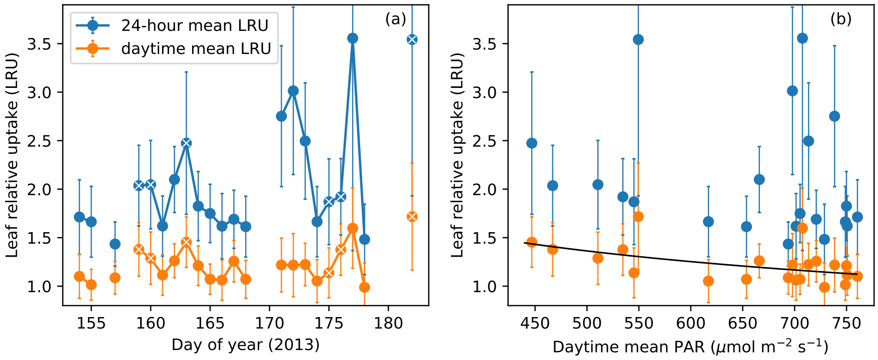

Figure 6. (a) 24-hour mean (blue) and daytime mean (orange) leaf relative uptake (LRU) ratios during the campaign. Data points from overcast days (daytime mean PAR < 550 μmol m^{-2} s^{-1}) are labeled with additional white cross signs. (b) 24-hour mean and daytime mean LRU values vs. daytime mean PAR. Daytime mean LRU vs. PAR follows a response curve (black): LRU = 24.0689 PAR$^{-0.4620}$. Error bars in both panels show ranges of ±1 standard error.