Dear Editor,

We have addressed all concerns raised in the comments of both reviewers in the revision. Per your request, below is a concise list of relevant changes made in the manuscript. For the detailed point-by-point response, please see Page 3. We appreciate your consideration of the revised manuscript.

List of changes in the revised manuscript

"R1" and "R2" refer to concerns raised by Reviewers #1 (T.E.G) and #2 (M.E.W.), respectively. Line and page numbers refer to locations in the revised manuscript, not the marked-up document for change tracking.

1. Abstract
   - The second paragraph has been revised to give an accurate account of the role of stomatal control (R1).
   - Language correction has been made in P1L4 (R1).
2. Introduction
   - The first paragraph has been shortened (R1). See P2L2–L8.
   - Language corrections have been made (R1).
   - The research objectives have been redefined in terms of hypotheses in P3L14–L20 (R1).
3. Methods
   - A schematic figure of the chamber (Fig. 1a) has been provided (R1).
   - We have clarified that the chamber was not operated as a static enclosure during the measurement period (R1). See also Fig. 1b.
   - Details on how the fans inside the chamber were operated have been added in P4L8–L13 (R1).
   - The flow rate and the chamber turnover time have been added in P4L17–L18 (R1).
   - We have added blank chamber effects in P4L32–L34, with more details provided also in §S2 of the Supplement (R1 & R2).
   - A description of the water correction of QCL measurements has been added in P4L23–L27 (R1 & R2). More details have been supplied in §S1 of the Supplement.
   - Leaf temperature data have been shown in Fig. S3 in the Supplement and added to the online dataset (R1).
   - §2.5 has been added to describe the calculations of various flux-derived variables, including the stomatal conductance and time-integrated LRUs (R1 & R2).

- Language corrections have been made (R1).

4. Results
   - Stomatal conductance estimates have been added and described in details (R1 & R2). See Fig. 6 and §3.2.
   - A distinction between the instantaneous LRU and time-integrated LRUs has been made in §2.5.2 and §3.3 (R1).

5. Discussion
   - Redundant texts in this section have all been removed (R1). Paragraphs that belong to the Results section have been relocated there (R1).
   - The former §4.1 has been removed (R1).
   - The main idea in former §4.3 has now been addressed in the new §4.1, which has been completely rewritten to give a proper mechanistic discussion of the environmental controls on LRU (R1 & R2).
   - An explanation of why high VPD drives LRU lower has been given in P10L25–L29 in §4.1 (R1).
   - §4.2 and §4.3 have been condensed significantly (R1).
   - The calculation of nighttime stomatal conductance has been documented in §S4 of the Supplement (R1).
   - We have given a mechanistic explanation of the low LRU observed on *T. latifolia* in P11L33–P12L3 in §4.3 (R1).
   - The rationale behind the use of all-day mean LRU has been discussed in P12L7–L15 (R1).
   - The confusion about 'midday' and 'early afternoon' has been eliminated (R1).
   - The limitation of the LRU method in large-scale GPP estimation has been discussed in P12L7–L15 in §4.3 (R2).

6. The Conclusion has been completely rewritten.

7. Figures
   - A schematic figure of the chamber is added to Fig. 1a.
   - Fig. 3: The y-axis range in panel d has been changed to emphasize LRU variation; in panel f, vapor deficit has been corrected with respect to leaf temperature.
   - Fig. 4 has been revamped for better visualization of the colored data points.
   - Fig. 6 has been added to show stomatal conductance data.

8. Table 1: A list of variable symbols has been added.

9. The Supplement includes additional information on the water correction of QCL measurements (§S1), blank chamber effects (§S2), leaf temperature data (§S3), and estimation of the nighttime stomatal conductance (§S4).

Response to the comments on "Stomatal control of leaf fluxes of carbonyl sulfide and CO_2 in a *Typha* freshwater marsh"

Wu Sun, on behalf of all coauthors

In this response, the text is formatted as: referees' comments (indented blocks), authors' response, **applied changes in the manuscript**. Locations in the revised manuscript are referenced by "P{#X}L{#Y}", meaning "Line Y on Page X".

Reply to comments by Teresa E. Gimeno (Referee #1)

> Sun et al. present here the first field dataset for COS and CO_2 leaf relative uptake (LRU) collected in situ during continuous measurement over the peak of a growing season. The authors chose a typical wetland plant (*Typha latifolia*) and report continuous measurements of CO_2 and COS uptake under varying environmental conditions, mainly light (photosynthetically active radiation) and vapour pressure deficit (VPD). They demonstrate that the strong dependency of LRU with PAR observed under laboratory conditions is also observed under natural conditions. The authors explain that strong stomatal control of both processes (COS and CO_2 uptake) underlies the observed patterns. Interestingly, the authors report lower LRU values in natural conditions than those previously measured under laboratory conditions. This constitutes a very valuable contribution as it is the first dataset of LRU collected at the leaf level, in situ, under natural conditions and for more than a month. The paper is very clearly written and the figures and results are nicely presented.

We thank Dr. Gimeno for her evaluation of our manuscript. We have made corrections and clarifications to concerns raised in the comments. Below please find a detailed point-by-point response.

> Yet, I do not believe that this paper deserves to be published as regular 'research paper', rather these results would be more appropriately presented as a technical note or rapid report. The reason is that the authors report data from one chamber that measured continuously one single set of six leaves. Their results and conclusions are relevant as they constitute a strong proof of concept, but continuous measurements

over a period with limited climatic variability (one campaign with homogenous meteorological conditions, P6L11–15) on a single set of leaves from the same plant (presumably) are not sufficient to constitute a whole research paper. Even more so taking into account the environmental heterogeneity of the light environment (P6L19–21).

We acknowledge these limitations in data collection; however, none of them should weaken the main conclusions or disqualify the manuscript from a full research paper. In fact, the experiments were designed to characterize leaf relative uptake (LRU) variability in response to environmental controls, particularly on the diurnal timescale. It represented the first continuous measurement of leaf fluxes under field conditions, and therefore the first validation of theory and lab measurements. This experimental design in turn served the higher purpose of COS-based ecosystem GPP estimation by providing accurate LRU parameters.

An ideal experimental design entails randomization and replication, yet field conditions and the resources available can often be restrictive. We were limited by the sampling time on the QCLS analyzer, because in each hour, 45 minutes were allotted to eddy covariance measurements (unpublished) and the rest was divided between a soil chamber (unpublished) and a leaf chamber (reported here). To support COS-based GPP estimation *on the hourly timescale*, LRU measurements must have the same resolution in time. This was the main reason that a high sampling frequency was chosen at the expense of having multiple leaf chambers. Nevertheless, we had a large sample size ($N > 300$) to support a robust analysis of LRU variability.

The similarity in day-to-day meteorological conditions was a blessing rather than a defect of the study, because it means that, other than PAR and vapor deficit, little else was changing, creating an ideal situation for testing LRU responses to PAR and vapor deficit. Indeed, diurnal variations of fluxes and LRU in response to PAR and vapor deficit were well characterized with a high sampling frequency. Besides, there were a few overcast days that caused the daytime mean LRU to increase; this was made clear in Fig. 7. The PAR sensor used in the study was collocated with the chamber (see P5L3–L4 added in the revised text), and this should have properly accounted for the light microenvironment around the chamber.

In addition I have some major technical concerns and another major concern related to the result interpretation and theoretical framing of the study.

We have made revisions and added the requested information in the Methods section to address these technical concerns. We have provided stomatal conductance estimates to

4

improve data interpretations and to better support the main messages of this study.

In the methods, the authors claimed that they used a 'flow-through (dynamic) chamber' (P4L5). Yet, during the 5-minute measurement period the chamber acted as a static enclosure (P4L13) and the authors calculated COS and CO_2 uptake and transpiration from the slope of the progressive drawdown (or accumulation) of the different species over time (P5L4–15). This approach should be valid provided good mixing, but that is hard to achieve for a > 10 L chamber without a fan. The authors need to provide the flow rate entering the cuvette over the measurement period and discuss to what extent they can warranty thorough mixing inside their chamber. In addition, the authors report that they characterised the blank fluxes of (presumably) the same chamber and that these were negligible (methods P4L27). Still, they do not specify how often were these characterised and under what conditions. More important, although it is not stated specifically, it appears that they authors calculated transpiration rates from H_2O vapour concentration measured with the QCLS. If that is the case, I assume the authors did not operate their QCLS coupled to a Nafion drier (or other type of water trap) and thus they need to correct for the interference associated with the water absorption line (Kooijmans et al. 2016 Atmospheric Measurements Techniques 9: 5293–5314).

These technical concerns have been addressed in §2.2 Experimental setup.

The leaf chamber was not operated as a static enclosure. There was always airflow passing through the chamber, supplied by a vacuum pump. During the measurement phase, the flow rate entering the enclosure was the same as that leaving. To clarify that the chamber was always an open system, **the label of the measurement phase has been changed from "ch closed" to "ch meas" in Fig. 1b**.

There were two fans running in the chamber, one for ventilation, and the other for mixing. During the measurement phase indicated in Fig. 1b, the ventilation fan was turned off, but the chamber nevertheless was still a flow-through system, because (i) the pump was pulling air from the chamber and (ii) the opening of the ventilation fan served as the inlet. The mixing fan was kept running continuously to make sure the air inside the chamber was always mixed. **This paragraph has been rewritten.** See P4L8–L13 in §2.2 Experimental setup.

The median flow rate through the chamber was 6.4 slm, which translated to a chamber turnover

time of 1.5 minutes. **This information has been added in P4L17–L18.**

Blank chamber effects were negligible: 0.05 ± 0.29 pmol m^{-2} s^{-1} for COS and 0.02 ± 0.15 µmol m^{-2} s^{-1} for CO_2. **This information has been added in P4L32–L34.** Please also see the Supplement for a detailed description.

We did not use a Nafion dryer or any other water trap. We applied the water broadening corrections supplied by TDLWintel—a data acquisition software on the QCL—using default correction factors. **We have now described the water correction procedure in P4L23–L27.** In addition, we have also discussed the potential influences of the uncertainty in the CO_2 water correction factor (see the Supplement).

> The authors claim that simultaneous stomatal control of both CO_2 and COS uptake underlies the coupling between these processes and the changes in LRU observed under low light and high VPD. Indeed, stomatal control lies at the heart of the discussion and the theoretical framing of the paper, but no data are shown. Also, the authors claimed that they monitored leaf temperature (P4L29–30) and they also had transpiration fluxes (Figure 3c). Still, no calculations of stomatal conductance have been performed. Later in the discussion, some calculations of stomatal conductance are mentioned (P8L20, P9L24), but the authors do not detail how these were obtained. Given that the authors have all the ingredients to calculate stomatal conductance, but yet these are missing, I wonder if this is due to poor mixing inside the chamber, which would have affected all other measurements. This needs to be clarified. In addition, comparing estimates of stomatal conductance derived from COS-uptake measurements with independent quantifications of stomatal conductance from transpiration and leaf temperature would allow to further demonstrate the tight stomatal control of COS uptake. These issues need to be clarified.

Diurnal patterns of the stomatal conductance of H_2O and the total conductance of COS have now been presented in the new Figure 6. Interpretations and discussions of the results have been added. See §3.2 in the Results and §4.1 in the Discussions. We have also described how stomatal conductance of H_2O and the total conductance of COS are calculated in §2.5.1 in the Methods.

> In addition to these major issues, I have some additional concerns:

Title Remove the term 'Stomatal control' unless you decide to include stomatal conductance measurements, otherwise I suggest "Effects of light and vapour pressure deficit on the coupling of leaf fluxes of carbonyl sulphide and CO_2 in a *Typha* freshwater marsh under natural conditions", or something similar.

We have included stomatal conductance estimates. The title is kept unchanged.

Abstract

P1L3–4 I think, here, you could be more specific with respect to what we have learned so far: 'LRU is known to increase under low light'.

Revised. See P1L4.

P1L15–17 reduce the emphasis on the role of stomatal control.

Since stomatal conductance data have been added to the revised manuscript, the emphasis on the role of stomatal control is appropriate.

Introduction

This section is interesting and very clearly written.

P2L2–10 maybe consider shortening this section, these concepts have already been amply discussed in the literature.

We have shortened this paragraph by 25%. See P2L2–L8.

P2L2 'COS has been shown to be a unique tracer'.

Changed to "Carbonyl sulfide (COS) is a unique tracer for . . .". See P2L2.

P2L8 'The approach to estimate photosynthesis from COS fluxes'

This sentence has been removed for conciseness.

P2L12 'COS and CO_2 follow the same diffusional pattern'

We think that 'pathway' is a more suitable word. A search in Google Ngram (`https://books.google.com/ngrams/`) finds no result of the phrase 'diffusional pattern'.

P2L22 'environmental variables that regulate diffusional limitations, mainly stomatal conductance, including photosynthetically active radiation (PAR) (. . .) and vapour pressure deficit (VPD)' Also provide a citation here (e.g. Leuning 1995 that you already cite).

Revised according to the reviewer's suggestion. See P2L18–L21.

P2L25 'In contrast to the CO_2 flux, at night, COS uptake might continue. . .'

Revised to "At night, in contrast to the CO_2 emission, COS uptake may continue . . .". See P2L22.

P2L27–28 'Night time COS uptake has been observed..'

Revised: 'found' —> 'observed'. See P2L24.

L29–31 This is not entirely clear. I think here what you mean is that the cited studies inferred vegetation COS uptake from ecosystem-scale measurements instead of direct measurements.

The sentence has been improved to clarify the point. See P2L26–L27.

Also, please note that both Maseyk et al. (2014) and Commane et al. (2015) found not only evidence for COS uptake, but also emission, this should be briefly mentioned here.

Emissions reported in Maseyk et al. (2014) came from soils and mature grain heads. And those in Commane et al. (2015) were not found in subsequent years of their campaign (Wehr et al., 2017). Since the scope of this study is leaf scale COS exchange, non-foliar sources of COS are only of peripheral importance and are hence not elaborated here.

P3L16 'We need direct measurements of how LRU...'

Revised. See P3L12.

P3L19–23 Please try to specify the research objectives more clearly, or even better formulate two hypotheses (e.g. LRU will decrease under low light in natural conditions) instead of stating the questions that motivated the study.

The research objectives have been rephrased in terms of clearly defined hypotheses. See P3L14–L20.

Methods

This section is also very clear and nicely written, but some key details are missing (see major concerns above).

The missing details have been added.

P4L5–14 Could you please provide a schematic drawing of the gas-exchange chamber?

A schematic diagram of the chamber has been added in panel (a) of the new Figure 1.

P4L29–30 Where are the data for leaf temperature?

Leaf temperature data are now shown in Figure S3 in the Supplement and are added to the online dataset. In addition, vapor deficit shown in Fig. 3f has been corrected with respect to leaf temperature.

P5L17–18 'Conspicuously unrealistic data points in the meteorological data were removed.'
P5L18 'independent criteria to filter measurements'
P5L21 'were also discarded'
P5L23 'these filtering criteria'

Revised following the referee's suggestions. See P5L21, L22, L25, and L27.

Results

P6L2 so if LRU was only calculated during the daytime, why do present the 24-h mean LRU in figure 6?

We have now clarified how the instantaneous LRU (i.e., the commonly referred 'LRU' in the literature) and the time-integrated LRU are calculated in §2.5.2 in the Methods. The use of time-integrated LRU is relevant to large-scale applications, as is discussed in §4.3 in the Discussions.

The results section is very clear and I only have one minor comment: no need to repeat the definition of LRU (P7L1).

We have removed the redundant definition.

Discussion and conclusions

In my opinion, this section turned out to be the least interesting of the paper. It is nicely written, but it only consists on a mere repetition of the results and ideas previously presented in the introduction. It can be shortened significantly and I believe the results and discussion section should be merged into one, which would be a much more adequate format for a technical paper. I provide some further specific details below.

We have restructured and greatly abridged the discussion to strive for a balance between conciseness and clarity. The former §4.1 has been removed, because most of its original contents are now addressed in the Results. The former §4.3 on LRU environmental control has been completely rewritten, explained in terms of the stomatal vs. internal conductance competition. Other parts of the discussion have been condensed significantly.

For the optimal flow of the text, we did not merge the Discussion into the Results. This is simply because each part of the Discussion may rely on multiple pieces of information from the Results.

P7L19 Provide a citation to support light-independency of COS hydrolysis.

Added Protoschill-Krebs et al. (1996). See P10L15.

P7L17–26 This paragraph is a long compilation of ideas presented already in the results and in the introduction.

Removed.

P7L27–P8L2 this paragraph belongs to the results section.

Moved to §3.1 in the Results. See P8L28–L33.

P8L20 provide the details for these calculations in the methods.

This is intended as a back-of-the-envelope calculation for discussion only. Strictly speaking, the obtained value is an estimate derived from the data, so it is not appropriate to document the calculations in the methods. **We have detailed the calculations in the Supplement instead.**

P9L6–10 Shorten this section, most of these ideas are repeated elsewhere in the paper.

Removed.

P9L16–22 Again repeated ideas, this belongs to the introduction.

This part has been completely rewritten. See P10L20–L30 in §4.1.

P9L23 The discussion is not a section appropriate for introducing new equations, move this to the methods.

P9L24 detail how this was calculated in the methods.

This part has been removed since it is no longer essential for the discussion. However, generally, there is no rule or guideline to discourage the use of equations in the discussion, if they are well explained.

P10L8–10 this discussion on the variation of LRU among species is very relevant. Note that *T. latifolia* has a very particular physiological behaviour, often exhibiting very

high rates of carbon uptake (e.g. Yavitt & Knapp 1998, 139:495–503 or Jespersen et al. 2017 Functional Plant Biology 44:774–784). Thus it is not surprising to find lower LRU value than those previously reported for other plants. Maybe also consider comparing your measurements of leaf CO_2 uptake with previous measurements as you seem to have measured much lower values than those previously reported, although this might be simply due to the differences in environmental conditions among studies, most likely light environment.

The reviewer raised an interesting point regarding the link between LRU and photosynthetic parameters. **We have added a brief explanation to the low LRU of the *T. latifolia* in P11L33– P12L3 in §4.3.**

P10L11–24 I do not think it is relevant to discuss the differences between day-time LRU and 24-h averaged LRU. The parameter LRU is useful to estimate GPP from COS uptake, thus it is only relevant during day-time. Please remove this section and the corresponding values from figure 6.

The all-day mean LRU is relevant to large-scale applications, because regional COS drawdown patterns are time-integrated features. **This is discussed in P12L7–L15 in §4.3.**

P11L2 remove 'that is only stomatal conductance limited'.

Removed.

P11L4–6 rephrase, are 'midday' and 'early afternoon' the same? Because you use them interchangeably here!

This sentence has been removed from the conclusion. We have taken care to use these terms consistently in other parts.

P11L7–9 I am not quite sure I understand the logic behind this statement. In the afternoon, presumably, PAR does not limit stomatal opening, instead stomatal opening would be limited by high VPD and thus COS and CO_2 would both be constraint and hence LRU would not respond to VPD.

This is because COS uptake is more stomatal-conductance-limited than CO_2 uptake due to the

much higher enzyme activity of CA in catalyzing COS hydrolysis (k_{cat}/K_m of CA $> k_{cat}/K_m$ of RuBisCO). **We have added a discussion of this issue in P10L25–L29 in §4.1.**

> In fact, I cannot appreciate a change in LRU at midday in figure 3d. I think this conclusion might be a bit misguided by an earlier interpretation of the measurements.

The y-axis range of Figure 3d has been adjusted to emphasize the variations of LRU. A "dip" of LRU between 15:00 and 18:00 should be clearly visible now.

> P11L10–15 this should be the opening, not the closing paragraph of the discussion.

This paragraph no longer exists. **The conclusion has been rewritten.**

> Figure 4. The data points do not appear colored.

The figure has been revamped to resolve the issue experienced by the reviewer. The problem was likely caused by the aliasing of the edges of data points under low-resolution conditions.

Reply to comments by Mary E. Whelan (Referee #2)

> Leaf relative uptake (LRU) of COS and CO_2 is a parameter that is often used to estimate plant CO_2 uptake from observed ecosystem fluxes of COS. There are other sources and sinks of COS in ecosystems, though they are typically small compared to uptake through plant stomata. One important exception is wetland soils, which tend to be a relatively large source of COS. In non-wetland or agricultural systems, measurements of net CO_2 and COS concentrations and fluxes are sufficient to make an estimate of GPP with an approximation of LRU.

We thank Dr. Whelan for her helpful and insightful comments. Indeed, COS fluxes from wetland soils—potentially large sources—need to be carefully constrained when using COS measurements to infer GPP. In this study, the chamber enclosure created a separate system for leaf gas exchange that was free from soil interference. When scaled up to the canopy, with soil COS budget constrained, the COS method for GPP estimation can still work reliably in a wetland ecosystem. The

treatment of soil COS budget in GPP estimation is out of the scope of this paper, but will be demonstrated in a manuscript on ecosystem-scale COS fluxes by our group (Seibt et al., in prep.).

> Here, Sun et al. present a dataset of H_2O, COS, and CO_2 flux and concentration measurements from a single leaf chamber in a wetland over about 36 days. This type of data is an important contribution and will be undoubtedly useful for other studies. However, the interpretation would be aided by greater attention to stomatal conductance, as the title implies, rather than LRU.

We have provided data and a figure of stomatal conductance estimates at the request of both reviewers. See Figure 6 and §2.5.1 in the revised manuscript.

We acknowledge that the previous version might have created misleading expectations for the study of LRU. **We have rewritten most of the Results and the Discussions to reorient the manuscript on how LRU varies in field conditions and how such behavior manifests stomatal responses.**

> The trouble with focusing on LRU is the matter of scale and applicability. Work by Hilton et al. (2015) demonstrated that, for regional GPP estimates, LRU is not the most important source of uncertainty. On the leaf scale, a direct measurement of CO_2 uptake can be made, though it includes photorespiration. At the tower-level scale (1 km^2), I am not sure that COS-based GPP estimates are more accurate than recent approaches relying on CO_2 measurements alone, though the Wehr et al. (2017) study in a temperate forest demonstrated COS-based estimates of canopy stomatal conductance were consistent with other measurement approaches in that system. In short, LRU is not the most important question on large scales, not employed in and of itself on leaf scales, and has some applicability still under development at the site scale. While having a better description of LRU variation with PAR would be an improvement, it is not the urgent next step that the text here describes.

At the ecosystem scale (~1 km^2), the COS-based method for GPP estimation is meant to supplement rather than replace conventional CO_2-based methods. In terms of accuracy, it is true that previous studies that applied the COS method on the ecosystem scale ended up getting similar—but not more accurate—results compared with the CO_2-based methods. Part of the reason was that LRU variability was unable to be treated properly due to the lack of concurrent leaf-level measurements. The uncertainty in LRU would further propagate into the GPP estimates. Recog-

nizing the problem, our study aims to contribute to its solution rather than circumvent it.

Yet the actual value-added benefit of COS tracer lies in the fact that it provides GPP estimates that are *independent* of assumptions on the temperature response of respiration and on the light response of photosynthesis—at least one of which is required in CO_2-based methods (Reichstein et al., 2005; Lasslop et al., 2010). In other words, uncertainties in the built-in assumptions of CO_2-based methods cannot be assessed unless other *independent constraints*—such as COS—are introduced. For example, COS-based GPP estimates may allow us to obtain daytime respiration straightforwardly, which further opens the possibility of studying the Kok effect (i.e., light inhibition of leaf respiration). Various ecophysiological applications of COS form an evolving frontier, and the usefulness of COS could not be overstated.

At large scales, currently available datasets are limited in spatial and temporal coverage, and the uncertainty in remotely retrieved COS concentrations would likely overwhelm the uncertainty of LRU in GPP-oriented applications (Whelan et al., 2017). But the research field likely would not stay there. Were better COS data products to be available in the future to allow for data assimilation at finer spatial and temporal scales—like a 'NOAA CarbonTracker' for COS—then LRU would become an issue. LRU responses to light and VPD would mean that synoptic weather events may shift regional estimates of daily averaged LRU. Without accounting for the relevant effects on LRU, GPP products derived from COS measurements could be biased. Although models like SiB can simulate LRU ab initio, the simulated LRU has yet to be validated with field studies and it is too early to put complete trust in model-generated LRU values.

In short, the outstanding issues around LRU have been underappreciated; but it does not mean that LRU is well understood and it no longer begs for questions, nor would LRU be less useful with the presence of process-based models. LRU is still an indispensable tool linking COS and CO_2 uptake, because it is simple enough to provide an understanding of the relationship between COS and CO_2 uptake, which would otherwise be inscrutable.

> The second issue is applicability to other ecosystems. This dataset was collected from a chamber containing leaves of a plant typically found in wetlands. The COS–GPP tracer technique is not usually applied at the site level in wetlands because of often substantial COS production from wetland soils. Also, some wetland plants have interesting adaptations to tolerate suboxic soil environments. For example, *Typha* have well developed aerenchyma to allow oxygen to diffuse into the root zone. Aerenchyma can also transport reduced gas compounds to the surface, circumventing oxidation

in the water column. This has been shown for methane and Whelan et al., (2013) suggested a similar route for carbonyl sulfide. The data do not necessarily show COS release from the parts of the leaves enclosed in the chamber, but teasing apart uptake from other sources of COS in the system would probably be a challenge. It is confusing to carry out an LRU study in one of the few ecosystems where applying LRU to back out GPP is an exception to the simplicity of the approach.

During the same campaign, we had a soil chamber installed to characterize soil COS emissions. We have already attempted COS-based GPP estimation at the site. The COS-based GPP estimates (GPP_{COS}) agree well with traditional CO_2-based GPP estimates (GPP_{NEE}). Results from that study have been presented at the 2016 AGU Fall Meeting, and are currently being written up as a manuscript (Seibt et al., in prep.).

As for the aerenchymal COS transport, we did not have the means to measure its contribution to COS fluxes. However, the close resemblance between GPP_{COS} and GPP_{NEE} suggests that the aerenchymal COS transport does not constitute a significant missing source of COS, although its presence cannot be ruled out.

While using LRU is probably the most popular method of calculating GPP from COS measurements, it is not the only method. The SiB model, for instance, has a "mechanistic" uptake representation that does not rely on an LRU number. The applicability of COS measurements to carbon cycle studies does not depend solely on LRU.

This is a valid point. But the advantages of SiB shine better in large-scale applications, especially when a representative LRU is difficult to determine from the upscaling of field data. **We have revised the related discussion in the manuscript to reflect this point (P12L7–L15).**

Motivating this study interpretation with the vagaries of leaf conductances would be of greater interest. Already, Sun et al. show that nighttime stomatal conductance is occurring and that daytime conductances change with evaporative demand. Sect. 4.2 should be expanded to include the broader literature on nocturnal stomatal conductance, rather than restricting the discussion to focus only on COS studies. Graphically comparing an established method to the COS-based method of estimating stomatal conductance could reveal possible mismatches and highlight the strengths of each approach, even if leaf temperature was not measured precisely. Re-working the figures to this effect would be beneficial.

We thank Dr. Whelan's suggestions for improvement. The following changes have been made to address these issues:

- **Figure 6 (new) has been added to show diurnal trends of the stomatal conductance of water and the total conductance of COS.**
- **In §4.2, the nighttime stomatal conductance estimate has been corrected for an erroneous assumption that internal conductance is negligible. The discussion has also been improved.**

Small technical concerns include publishing chamber blank results and also the exact equation that was used for the QCL water correction. There are a growing number of researchers using this make of QCL and water is a problem for the older models.

Blank chamber effects are now provided in §2.2 Experimental setup. See P4L32–L34. Please also see the Supplement for more details on the blank chamber effects.

We have added information on the QCL water correction. See P4L23–L27 in §2.2. A detailed description of the equations used for water vapor correction and their effects on flux uncertainty is given in the Supplement.

In short, this is a good dataset, but the interpretation could perhaps avoid the concept of LRU entirely.

We have explained why LRU is useful in assessing the relationship between COS and CO_2 leaf uptake. Please see the reply to a previous comment on Pages 14–15 of this response.

Stomatal control of leaf fluxes of carbonyl sulfide and CO$_2$ in a *Typha* freshwater marsh

Wu Sun[1], Kadmiel Maseyk[2,a], Céline Lett[3,a], and Ulli Seibt[1,a]

[1]Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA 90095-1565, USA
[2]School of Environment, Earth and Ecosystem Sciences, The Open University, Milton Keynes MK7 6AA, United Kingdom
[3]Laboratoire des Sciences du Climat et de l'Environnement, Université Paris Saclay, 91191 Gif-sur-Yvette, France
[a]formerly at Institute of Ecology and Environmental Sciences, Université Pierre et Marie Curie Paris 6, France

Correspondence: Wu Sun (wu.sun@ucla.edu) and Ulli Seibt (useibt@ucla.edu)

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 [..[1]]increase under low light, but the environmental controls over LRU variability in the field are poorly understood

5 due to scant leaf scale observations.

Here we present the first direct observations of [..[2]]LRU responses to environmental variables 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 [..[3]]separated by a prolonged midday depression, highlighting the common stomatal control on [..[4]]diffusion. At night, in contrast to CO$_2$, COS uptake continued, indicating partially open stomata. LRU ratios

10 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 (calculated from daytime mean COS and CO$_2$ uptake) ranged from 1 to 1.5, with a mean of 1.2 across the campaign, significantly lower than [..[5]]previously reported laboratory mean value (~1.6). Our results indicate two major determinants of LRU—light and vapor [..[6]]deficit. Light is the primary driver of LRU because CO$_2$ [..[7]]assimilation capacity increases with light, while COS consumption capacity does not. Superimposed upon the

15 light response is a secondary effect [..[8]]that high vapor deficit further reduces LRU, causing LRU minima to occur in the afternoon, not at noon. The partial stomatal closure [..[9]]induced by high vapor deficit suppresses COS uptake more strongly than CO$_2$ uptake because stomatal resistance is a more dominant component in the [..[10]]total resistance of COS. Using stomatal conductance estimates, we show that LRU variability can be explained in terms of different patterns of

---

[1]removed: vary with

[2]removed: the LRU versus light relationship

[3]removed: ,

[4]removed: COS and CO$_2$

[5]removed: the mean value reported from laboratory measurements

[6]removed: pressure deficit(or evaporative demand)

[7]removed: reactions are lightlimited but the COS reaction is not. In

[8]removed: , high evaporative demand tends to reduce LRUvalues. During periods of high evaporative demand, leaves conserve water by

[9]removed: . This reduces

[10]removed: COS diffusional pathway. High evaporative demand usually coincides with high PAR, leading to the lowest observed LRU in the afternoon.

stomatal vs. internal limitations on COS and CO_2 uptake. Our findings illustrate the [..[11]]stomata-driven coupling of COS and CO_2 uptake during the most photosynthetically active period in the field [..[12]]and provide an in-situ characterization of LRU—a key parameter required for the use of COS as a photosynthetic tracer.

5 **1 Introduction**

Carbonyl sulfide (COS) [..[13]]is a unique tracer for land photosynthesis ([..[14]]i.e., gross primary productivity, GPP) at regional to global scales [..[15]](e.g., Montzka et al., 2007; Campbell et al., 2008; Berry et al., 2013; Campbell et al., 2017). Globally, [..[16]]COS is mainly emitted from the ocean and anthropogenic activities and consumed by leaves and soils (Berry et al., 2013; Launois et al., 2015; Campbell et al., 2015; Whelan et al., 2017). Since ecosystem COS exchange is
10 dominated by plant uptake (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 [..[17]](e.g., Asaf et al., 2013; Billesbach et al., 2014). Understanding the quantitative relationship [..[18]]between leaf COS and CO_2 fluxes is [..[19]]therefore critical to estimating canopy and regional photosynthesis from COS measurements.

In leaves, COS and CO_2 follow the same stomatal diffusional pathway and similar hydrolytic reactions catalyzed by carbonic
15 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)[..[20]]-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.

---

[11]removed: stomatal

[12]removed: , and provide important characterization of LRU, a key parameter to support

[13]removed: has been shown as

[14]removed: also known as

[15]removed: (e.g., Montzka et al., 2007; Campbell et al., 2008; Berry et al., 2013; Hilton et al., 2017; Campbell et al., 2017)

[16]removed: 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

[17]removed: (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; **?**).

[18]removed: that ties together

[19]removed: key to obtaining accurate estimates of

[20]removed: emission

20   The COS hydrolysis via CA [..[21]]is light independent (Goldan et al., 1988; Protoschill-Krebs et al., 1996). Since this reaction is also highly efficient (Ogawa et al., 2013), [..[22]]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 [..[23]]diffusion—mainly stomatal diffusion—including photosynthetically active radiation (PAR), because of the feedback from photosynthesis to stomatal conductance [..[24]](Ball, 1988; Collatz et al., 1991), and vapor deficit (Leuning,

5   1995). Thus, light regulates leaf COS uptake even though COS hydrolysis itself does not depend on light.

    [..[25]]At night, in contrast to the CO_2 [..[26]]emission, 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 [..[27]]observed in a wheat field (Maseyk et al., 2014), a boreal pine forest (Kooijmans et al., 2017), and temperate forests

10 (Berkelhammer et al., 2014; Commane et al., 2015; Wehr et al., 2017). [..[28]]Most field studies base their findings of nighttime COS uptake upon ecosystem scale observations, with only one study reporting [..[29]]nighttime COS uptake at the leaf scale (Berkelhammer et al., 2014).

    The quantitative relationship between leaf COS uptake and photosynthesis required for COS-based photosynthesis estimates— from canopy to regional scales [..[30]](e.g., Asaf et al., 2013; Hilton et al., 2017)—is commonly expressed in one parameter:

15 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.

20   For ecosystem [..[31]]scale applications, a constant LRU of 1.6 has been assumed [..[32]](e.g., Asaf et al., 2013) 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

---

[21] removed: has been shown to be

[22] removed: the

[23] removed: stomatal conductance, including

[24] removed: (e.g., Ball, 1988; Collatz et al., 1991)

[25] removed: In

[26] removed: flux that turns to emissionat night

[27] removed: found

[28] removed: However, most field studies based their findings upon indirect evidence of nighttime ecosystem COS uptake

[29] removed: some direct leaf observations of nighttime uptake

[30] removed: (e.g., Asaf et al., 2013; Campbell et al., 2017)

[31] removed: and larger

[32] removed: (e.g., Asaf et al., 2013; Hilton et al., 2015)

variations in COS and CO_2 fluxes (Stimler et al., 2011). At low light, the [..[33]]extent to 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 [..[34]]measurements of how LRU responds to PAR and other possible drivers in the field. Applications [..[35]]at longer timescales would further need daily integrated LRU values.

This study [..[36]]aims to characterize how light and vapor deficit drive variabilities in leaf COS uptake and LRU and to probe the stomatal mechanism that underlies LRU responses to these drivers. Here, we hypothesize that (i) light dependence of instantaneous LRU is analogous to that reported in laboratory conditions, and this relationship is also preserved in daily integrated LRU[..[37]]; and (ii) strong diurnal variation of vapor deficit will have observable effects on COS uptake and LRU, due to stomatal response to vapor deficit. 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[..[38]], 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 [..[39]]tall) is located on a floating wooden platform near the northeastern

---

[33]removed: rate at

[34]removed: knowledge

[35]removed: for

[36]removed: is motivated by two research questions: 1) How does light control instantaneous and

[37]removed: values? 2) How do stomatal responses to environmental variables regulate leaf COS uptake in the field?

[38]removed: at

[39]removed: high

edge of the SJFM. The 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 [..[40]](Fig. 1a). 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 [..[41]]film was in contact with the sampled air. The chamber enclosed the upper sections of six tall [..[42]]*T. latifolia* 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.

[..[43]]

Two fans were installed in the chamber for ventilation and mixing, respectively. On the inlet end, a high-speed axial fan (D344T, Micronel[..[44]]; 40×40 mm) provided ventilation to keep the chamber at ambient conditions (i.e., within 1 [..[45]]ppmv of ambient CO_2, tested at the start of the campaign). [..[46]]A second, smaller flat fan (F62, Micronel; 16×16 mm), attached to a stainless steel rod, was placed near the center of the chamber for air mixing. During the measurement period, the ventilation fan was turned off and its opening served as the inlet to allow airflow through the chamber. [..[47]]The mixing fan, in contrast, was kept running at all times.

The chamber was connected via [..[48]]a 0.25-inch 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 of the analyzer. 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 [..[49]]sampling tube was 6.4 standard liter per minute ([..[50]]slm), which corresponded to a chamber air turnover time of around 1.5 minutes. 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 [..[51]]2-inch 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

---

[40]removed: .

[41]removed: Teflon

[42]removed: cattail

[43]removed: On one

[44]removed:) was installed to provide

[45]removed: p.p.m.v.

[46]removed: During measurement periods, the

[47]removed: 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

[48]removed: 1/4″

[49]removed: tubing was 6

[50]removed: s.l.m.)

[51]removed: 2″

stored on the QCL hard drive. The [..[52]]root-mean-square deviation of COS measurements at 10 Hz was 11–18 parts per trillion in volume ([..[53]]pptv).

Correction for water vapor effects on the dry mixing ratios of COS and CO_2 was done in the TDLWintel data acquisition software on the analyzer (Nelson, 2012). We did not use the same correction factors reported in Kooijmans et al. (2016) for the same make of QCL analyzer; however, a mock run of data processing with CO_2 concentration recalculated using their correction factor value resulted in a potential bias of only 0.12% ($r^2 = 0.999$). Thus, the flux uncertainty associated with the correction factor of water vapor effects was negligible (see the Supplement for details).

The leaf chamber was measured once per hour. Chamber operations were programmed on a CR1000 datalogger (Campbell Scientific, Inc., Logan, UT, USA). We monitored chamber air concentrations [..[54]]for a five-minute measurement [..[55]]period (i.e., while the ventilation fan was off), as well as the ambient air for one minute before and after [..[56]]measurement periods (i.e., while the ventilation fan was running). Leaf fluxes were calculated from the transient changes with respect to the interpolated inlet (ambient) concentrations (Fig. 1b). The apparent fluxes from [..[57]]the chamber material (PFA), characterized post hoc, were negligible—the blank effects translated to apparent fluxes of 0.05 ± 0.29 pmol m^{-2} s^{-1} for COS and 0.02 ± 0.15 µmol m^{-2} s^{-1} for CO_2 when normalized against the leaf area (see the Supplement).

Various sensors were installed to record environmental data, 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)[..[58]]. These data were recorded at 10 s intervals on [..[59]]the CR1000 [..[60]]datalogger. The PAR sensor was placed near the chamber to measure the light microenvironment of the chamber. All sensor data are released alongside the flux data (see Data Availability).

2.3   Calculation of leaf fluxes

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

$$V \frac{\mathrm{d}C}{\mathrm{d}t} = q\left(C_\mathrm{a} - C\right) + FA \tag{1}$$

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

---

[52]removed: RMS noise (1 σ)

[53]removed: p.

p. t.v.)for COS during chamber measurements

[54]removed: during the

[55]removed: periods

[56]removed: these

[57]removed: blank chambers were characterized and were found to be negligible.

Environmental data were obtained from various sensors

[58]removed: , and were stored

[59]removed: a datalogger (

[60]removed: , Campbell Scientific). The datalogger also controlled the operation of the high-speed ventilation fan.

the flux rate to be calculated. Solving the mass balance equation with the initial condition $C(t = 0) = C_a$, we obtain

$$C(t) = -\frac{FA}{q}\exp(-qt/V) + C_a + \frac{FA}{q} \qquad (2)$$

The flux rate F is

$$F = \frac{q}{A} \cdot \frac{C - C_a}{1 - \exp(-qt/V)} \qquad (3)$$

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

$$\hat{y} = \frac{FA}{q}(1 - \hat{x}) \qquad (4)$$

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 [..[61]]with the fitted curve of COS concentration changes is shown in Fig. 1b.

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 [..[62]]were removed. For the flux data, we used several independent criteria to filter [..[63]]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 [..[64]]root-mean-square errors between fitted and observed concentrations were also [..[65]]discarded. Then, outliers in flux data were detected using the [..[66]]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 [..[67]]criteria were kept in the final data for analysis. After the filtering, 73.9% of COS flux observations and 54.3% of CO_2 flux observations were retained.

2.5 Calculation of [..[68]]flux-derived variables

[..[69]]

---

[61]removed: for COS
[62]removed: have been
[63]removed: out bad
[64]removed: RMSEs
[65]removed: filtered out
[66]removed: well-established
[67]removed: procedures
[68]removed: leaf relative uptake (LRU)
[69]removed: Leaf COS : CO

2.5.1 Stomatal conductance of water and total conductances of CO_2 and COS

Stomatal conductance of water (g_{s, H_2O}, mol m^{-2} s^{-1}) is calculated from water flux measurements,

$$g_{s, H_2O} = \frac{F_{H_2O}}{D} \tag{5}$$

where F_{H_2O} is the water flux (mmol m^{-2} s^{-1}), D is the leaf-to-air water vapor deficit expressed in mole fraction (mmol mol^{-1}). The mole-fraction vapor deficit D is calculated from

$$D = \frac{e_{sat}(T_{leaf})}{p} - \chi_{H_2O} \tag{6}$$

where e_{sat} (Pa) is the saturation water vapor pressure as a function of temperature (Goff and Gratch, 1946), T_{leaf} (°C) is the leaf temperature (see the Supplement for details), p (Pa) is the ambient pressure, and χ_{H_2O} (mmol mol^{-1}) is the water vapor mixing ratio in the chamber air.

The total conductances of COS ($g_{tot, COS}$, mol m^{-2} s^{-1}) and CO_2 [..[70]](g_{tot, CO_2}, mol m^{-2} s^{-1}) are calculated from:

$$g_{tot, COS} = -\frac{F_{COS}}{\chi_{COS}} \tag{7}$$

$$g_{tot, CO_2} = -\frac{F_{CO_2}}{\chi_{CO_2}} \tag{8}$$

where F_{COS} (pmol m^{-2} s^{-1}) and F_{CO_2} (µmol m^{-2} s^{-1}) are leaf COS and CO_2 fluxes, χ_{COS} (pmol mol^{-1}) and χ_{CO_2} (µmol mol^{-1}) are mixing ratios of COS and CO_2 in the chamber air, respectively. Note that the intercellular concentrations of COS and CO_2 are canceled out from these equations by approximating their biochemical reaction rates with hypothetical (but mathematically convenient) 'biochemical conductances' (Stimler et al., 2010; Berry et al., 2013), which are then included in the total conductances.

2.5.2 Instantaneous and time-integrated leaf relative uptake ratios

Instantaneous leaf COS : CO_2 relative uptake (LRU) is defined as the ratio of COS and CO_2 fluxes [..[71]]normalized by their respective [..[72]]mixing ratios (Sandoval-Soto et al., 2005; Campbell et al., 2008; Whelan et al., 2017),

$$LRU = \frac{F_{COS}}{F_{CO_2}} \cdot \frac{\chi_{CO_2}}{\chi_{COS}}, \text{ where } F_{COS} < 0 \text{ and } F_{CO_2} < 0 \tag{9}$$

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.

---

[70]removed: relative uptake ratio

[71]removed: (F_{COS} and F_{CO_2})

[72]removed: concentrations (χ_{COS} and χ_{CO_2}),

We also calculate the all-day mean LRU ($LRU_{\text{all-day}}$) and the daytime mean LRU (LRU_{daytime}) of each day using

$$LRU_{\text{all-day}} = \frac{\left(\sum\limits_{i=0}^{23} F_{\text{COS}}^i\right) \cdot \left(\sum\limits_{i=0}^{23} \chi_{\text{CO}_2}^i\right)}{\left(\sum\limits_{i=0}^{23} F_{\text{CO}_2}^i\right) \cdot \left(\sum\limits_{i=0}^{23} \chi_{\text{COS}}^i\right)} \tag{10}$$

$$LRU_{\text{daytime}} = \frac{\left(\sum\limits_{i=6}^{19} F_{\text{COS}}^i\right) \cdot \left(\sum\limits_{i=6}^{19} \chi_{\text{CO}_2}^i\right)}{\left(\sum\limits_{i=6}^{19} F_{\text{CO}_2}^i\right) \cdot \left(\sum\limits_{i=6}^{19} \chi_{\text{COS}}^i\right)} \tag{11}$$

where i is the truncated hour number (integer), in local daylight-saving time (UTC–7). The daytime period is determined with solar elevation angle > 0°, which translates roughly to between 06:00 and 20:00. In each period of calculation, missing data points are gap-filled with the mean in that period.

2.5.3 Contributions of stomatal component to the total resistance

To assess the relative importance of the stomatal limitation on COS and CO_2 uptake with respect to internal limitations (mesophyll conductance and biochemical reactions), we calculate the ratios of stomatal resistance to total resistance for COS (r_{COS}^*) and CO_2 ($r_{\text{CO}_2}^*$),

$$r_{\text{COS}}^* = \frac{r_{s,\text{COS}}}{r_{\text{tot,COS}}} = \frac{g_{\text{tot,COS}}}{g_{s,\text{COS}}} = \frac{g_{\text{tot,COS}}}{g_{s,\text{H}_2\text{O}}/2.01} \tag{12}$$

$$r_{\text{CO}_2}^* = \frac{r_{s,\text{CO}_2}}{r_{\text{tot,CO}_2}} = \frac{g_{\text{tot,CO}_2}}{g_{s,\text{CO}_2}} = \frac{g_{\text{tot,CO}_2}}{g_{s,\text{H}_2\text{O}}/1.66} \tag{13}$$

where 2.01 is the water-to-COS ratio of diffusivity in air, and 1.66 is the water-to-CO_2 ratio of diffusivity in air (Seibt et al., 2010). The reason to switch from conductance to its reciprocal—resistance—is simply that different resistance components are additive.

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

3.1 Leaf fluxes of COS, CO$_2$, and water

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 ([..[73]]8, 9, and 30 June 2013 in Fig. 2d), and the diurnal patterns of leaf COS, CO$_2$, and H$_2$O fluxes therefore also remained similar (Fig. 2a–c). The diurnal patterns of leaf fluxes and related variables are visualized with hourly binned medians and quartiles (Fig. 3).

[..[74]]

In the daytime, leaf uptake of COS and CO$_2$ showed similar patterns (Fig. 3a, b), with uptake peaks in the morning and afternoon separated by a prolonged 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 [..[75]]a bit 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 slightly 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)[..[76]].

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 [..[77]]random error due to high flow rates (~6 [..[78]]slm), 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).

[..[79]]

---

[73]removed: day of year 159, 160, and 181,

[74]removed: During the day

[75]removed: slightly

[76]removed: , although the midday depression in stomatal conductance was roughly symmetric as indicated by COS uptake

[77]removed: the measurement uncertainty from

[78]removed: s.l.m.

[79]removed: 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.

[..[80]]COS flux was overall 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[..[81]], $r^2 = 0.32$ (Fig. 4b), and showed a wide spread [..[82]]in the daytime due to the asymmetric diurnal pattern of water fluxes (Fig. 3c). At night, COS fluxes showed larger variability than water fluxes because vapor deficit that drives transpiration was small (Fig. 3f).

The midday depression was also evident in the light responses of fluxes. Both COS and CO_2 uptake rates increased with PAR until they became light saturated, and then decreased at high light and high vapor deficit (Fig. 5a, b). According to the smoothed light response curves, at a typical midday light level (1800 µmol m^{-2} s^{-1}), COS uptake drops by 37% from the peak value of 7.5 pmol m^{-2} s^{-1} (at PAR = 493 µmol m^{-2} s^{-1}) to 4.7 pmol m^{-2} s^{-1}, while CO_2 uptake drops by 31% from the peak value of 5.3 µmol m^{-2} s^{-1} (at PAR = 740 µmol m^{-2} s^{-1}) to 3.7 pmol m^{-2} s^{-1}. This indicates that stomatal conductance exerted a stronger control on COS uptake than CO_2 uptake.

3.2 Diurnal patterns of stomatal conductance and total conductance

Stomatal conductance (g_{s,H_2O}) derived from water measurements showed a distinct period of midday depression in its diurnal pattern (Fig. 6a). g_{s,H_2O} was the highest in the early morning after daybreak, but started to drop quickly as the vapor deficit [..[83]]picked up, reaching its minimum at local noon (13:00). In the late afternoon, stomatal conductance slowly rebounded and remained relatively stable, but was still lower than the early morning level. Nighttime stomatal conductance was unable to be estimated from water measurements due to large uncertainty introduced by low vapor deficit and water flux.

The total conductance of COS ($g_{tot,COS}$) exhibited broadly similar diurnal pattern to that of g_{s,H_2O}, but lagged by 1 hour (Fig. 6a). This difference may be attributed to changes in internal conductance terms entailed in $g_{tot,COS}$, namely, mesophyll conductance and biochemical activities. A midday depression period was also visible in the diurnal trend of $g_{tot,COS}$. At night, $g_{tot,COS}$ remained at a stable, low level.

The ratios of stomatal resistance to total resistance of COS (r^*_{COS}) and of CO_2 ($r^*_{CO_2}$) indicated that stomatal limitation was the dominant component in the diffusional pathways of both gases during most of the daytime (Fig. 6b). For COS, stomatal limitation is always a much stronger component compared with that of CO_2. However, at around 15:00 the difference between stomatal limitation on COS uptake and that on CO_2 uptake was small (Fig. [..[84]]6b).

3.3 Leaf relative uptake ratios

The instantaneous leaf relative uptake (LRU) showed an asymmetric U-shape diurnal pattern (Fig. 3d). 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 then had minima around 0.9 at 15:00.

---

[80]removed: Overall, COS flux was

[81]removed: :

[82]removed: during the day

[83]removed: was

[84]removed: 3f).

5   The diurnal pattern of LRU (Fig. 3d) was consistent with the LRU response to PAR (Fig. 5c). [..[85]]With increasing PAR, LRU decreased to around 1.0 at PAR above [..[86]]500–600 μmol m^{-2} s^{-1} [..[87]](Fig. 5c). 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 [..[88]]

10 **4   [..[89]]**

3.1   [..[90]]

[..[91]]vapor deficit. The timing of the lowest LRU (Fig. 3d), around 15:00, was when the difference between stomatal limitation on COS uptake and that on CO_2 uptake became the smallest (cf. Fig. 6b). However, this vapor deficit control on LRU was only secondary to the light control and was not evident in the light response of LRU (Fig. 5[..[92]]c).

15   The all-day mean LRU at this site showed large day-to-day variations (1.4–3.6) and also had large uncertainty due to the random error in nighttime CO_2 fluxes (Fig. 7a). In contrast, the daytime mean LRU, averaged over the daylight period 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 all-day mean LRU, since the latter included nighttime COS uptake and CO_2 [..[93]]emissions (Fig. 7a). Daytime mean LRU and daytime mean PAR was moderately well correlated ($r = -0.525$;

20 Fig. 7b), similar to Maseyk et al. (2014). On overcast days, the daytime mean LRU values were higher than on clear days (Fig. 7a), as is expected from the light response of LRU. This indicates that the LRU–PAR relationship is preserved on the daily timescale.

4   Discussion

4.1   Competition between stomatal and internal limitations underlie the responses of leaf relative uptake to light and vapor deficit

---

[85] removed: The LRU values decreased with increasing PAR(Fig. 5c)

[86] removed: around

[87] removed: .

[88] removed: evaporative demand.

[89] removed: Discussion

[90] removed: Stomatal control is responsible for the similarity in daytime leaf COS and CO_2 uptake

[91] removed: 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

[92] removed: a, b).

However, the similarity in fluxes is not due to acommon light response of the biochemical reactions that consume COS

[93] removed: 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

Using the ratio of stomatal resistance to total resistance as a metric of the relative importance of stomatal limitation (Fig. 6b), we can recognize how the dynamics of stomatal vs. internal limitations regulates LRU. At the leaf scale, LRU

5 manifests the ratio between the stomatal limitation on COS uptake (r_{COS}^*) and that on CO_2 uptake [..[94]]($r_{CO_2}^*$) (compare Eqs. 12 and 13 to Eq. 9):

$$LRU \equiv \frac{g_{tot,COS}}{g_{tot,CO_2}} = \frac{0.83 \cdot r_{COS}^*}{r_{CO_2}^*} \tag{14}$$

where 0.83 is the COS-to-CO_2 [..[95]]ratio of diffusivity in air (Seibt et al., 2010). The equation shows that LRU becomes smaller when r_{COS}^* and $r_{CO_2}^*$ get closer, providing a simple mechanistic interpretation of LRU variability.

10 We have reaffirmed in field conditions that LRU decreases with increasing PAR (Fig. 5c), consistent with laboratory studies and ecosystem field studies (Stimler et al., 2010, 2011; Maseyk et al., 2014; Commane et al., 2015). This light response of LRU arises from the difference between the marginal gain (i.e., partial derivative) of COS uptake and that of CO_2 uptake [..[96]]with respect to the same increase of PAR (Fig. [..[97]]5a, b). [..[98]]Increasing PAR drives an increase in CO_2 [..[99]]assimilation rates, which in turn leads to an increase in stomatal conductance to facilitate optimal CO_2 uptake.

15 This increase in stomatal conductance also enables higher COS uptake rates, but as COS hydrolysis is light independent (Protoschill-Krebs et al., 1996), there is a proportionally greater increase in CO_2 [..[100]]than COS uptake[..[101]]

[..[102]]. That LRU light response is chiefly due to differential biochemical limitations on COS and CO_2 uptake [..[103]]is supported by indirect evidence in r_{COS}^* and $r_{CO_2}^*$ (Fig. [..[104]]6b). For instance, from 06:00 to 13:00 with increasing PAR, the higher relative increase of $r_{CO_2}^*$ than that of r_{COS}^* (Fig. [..[105]]6b) indicated that the extent to which non-stomatal resistance reduces—attributed mainly to the increases in biochemical reaction rates—is higher for CO_2 than for COS.

In addition to PAR, vapor deficit has been identified as a secondary environmental driver of LRU. Stomatal response to vapor deficit, such as the midday depression (Fig. [..[106]]6a), is a well-known behavior that serves to optimize water use against carbon gain (e.g., Tenhunen et al., 1984; Collatz et al., 1991). However, the fact that vapor deficit has differential

---

[94]removed: to stomatal conductance, which increases with light because of the feedback between stomatal conductance and photosynthesis (**??**Ball, 1988; Collatz et al., 1991).At high light, when CO

[95]removed: assimilation is light saturated, leaf COS

[96]removed: is controlled by stomatal conductance in a similar way: both decline as stomatal conductance is reduced in response to high evaporative demand

[97]removed: 3

[98]removed: At low light, COS and CO_2 diffusions are both reduced by low stomatal conductance , but CO

[99]removed: assimilation is additionally reduced by low light , causing a stronger decrease

[100]removed: uptake

[101]removed: (Fig. 5a, b).

[102]removed: The most striking feature in the diurnal patterns of leaf

[103]removed: was the concurrent midday depression in the early afternoon

[104]removed: 3a–c), also affecting the light response curves of fluxes

[105]removed: 5a, b) . From the smoothed light response trends

[106]removed: 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

5 effects on COS and CO_2 uptake [..[107]]appears puzzling, since it does not affect differently COS and CO_2 biochemical reactions, and nor is it known to affect mesophyll conductance. A closer scrutiny of the stomatal limitations of COS and CO_2 [..[108]](Fig. 6b) shows that the difference between r^*_{COS} and $r^*_{CO_2}$ became smaller during the period of peak vapor deficit (14:00–17:00). Although vapor deficit has the same effect on $g_{s,COS}$ and g_{s,CO_2}, it can change the proportion of stomatal vs. internal components in the total resistance to the uptake, because COS uptake is always more stomatal-conductance-

10 limited than CO_2 uptake ([..[109]]r^*_{COS} always higher than $r^*_{CO_2}$ in Fig. 6b)—a consequence of the higher catalytic efficiency (k_{cat}/K_m) of β-CA in COS hydrolysis (Protoschill-Krebs et al., 1996; Ogée et al., 2016) than RuBisCO in CO_2 fixation (Tcherkez et al., 2006). Thus, vapor deficit controls LRU variability, but is less influential than PAR.

[..[110]]Since the mesophyll conductance is also a component in the internal conductance, it is worthy of note that the increase of mesophyll conductance with leaf temperature (Bernacchi, 2002) may have contributed to the [..[111]]dynamics

15 of stomatal vs. internal limitations over the course of the daytime, as is shown in Wehr et al. (2017), although we lack relevant data to separate biochemical limitation from mesophyll limitation.

4.2 [..[112]]

[..[113]]

4.2 Nighttime COS uptake is a significant portion of COS budget

During this campaign, nighttime uptake contributed to 23% of the total daily leaf COS uptake. This fraction is comparable

5 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 [..[114]]nighttime uptake is typically 17–30%

---

[107]removed: 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

[108]removed: 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

[109]removed: 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) .

[110]removed: 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

[111]removed: influence of midday depression on COS uptake at the leaf scale and reaffirms stomatal conductance as the dominant control of COS uptake.

[112]removed: COS uptake is an indicator of nocturnal stomatal conductance

[113]removed: 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

[114]removed: nocturnal

14

of the total canopy COS budget, a fraction [..[115]]too large to [..[116]]be ignored in ecosystem or regional COS budget[..[117]].
Understanding nighttime COS uptake is necessary for the success of COS-based photosynthesis estimates [..[118]]on daily
and longer timescales.

[..[119]]The *T. latifolia* leaves showed a mean value of [..[120]]5.0 mmol m^{-2} s^{-1} for the [..[121]]total conductance of COS
($g_{\mathrm{tot, COS}}$) at night (Fig. 6a). Assuming that the internal conductance of COS at night is the same as its daytime average,
we obtain an estimate of nighttime $g_{\mathrm{s, COS}}$, 6.4 mmol m^{-2} s^{-1} [..[122]](see the Supplement for detailed calculations). This
estimate of the nighttime $g_{\mathrm{s, COS}}$ is at the lower end of values reported [..[123]]from other ecosystems: 1.6 mmol m^{-2} s^{-1} for
a New England mixed forest (Wehr et al., 2017)[..[124]], 5–30 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). The nighttime stomatal conductance shows a large
variability among different species.

[..[125]]

In land biosphere models, [..[126]]nighttime stomatal conductance is often a fixed value regardless of plant type [..[127]
]and water status, e.g., $g_{\mathrm{s, H_2O}}$ = 10 mmol m^{-2} s^{-1} in the Community Land Model v4.5 (Oleson et al., 2013). [..[128]]The
fixed-value parameterization may introduce biases [..[129]]to the nighttime COS fluxes and long-term COS budget in regional
simulations, which may in turn propagate into the COS-based photosynthesis estimates. [..[130]]To constrain nighttime COS
uptake requires an understanding of the variability of [..[131]]nighttime stomatal conductance among plant species and

---

[115] removed: that is

[116] removed: ignore in ecosystem and

[117] removed: studies. Understanding nocturnal COS uptake will therefore be necessary for

[118] removed: at

[119] removed: For the *T. latifolia* leaves here, we obtained

[120] removed: 5 ± 1

[121] removed: nocturnal stomatal conductance to COS ($g_{\mathrm{s, COS}}$) if internal conductance ($g_{\mathrm{i, COS}}$), the combination of mesophyll conductance and biochemical
reaction coefficient, is ignored ($g_{\mathrm{s, COS}} \ll g_{\mathrm{i, COS}}$). This translates to 10 ± 2

[122] removed: 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 $g_{\mathrm{s, COS}}$

[123] removed: for other ecosystems, ranging from

[124] removed: to 5–20

[125] removed: 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).

[126] removed: nocturnal stomatal conductance has been typically parameterized with a small

[127] removed: , for example,

[128] removed: This

[129] removed: in

[130] removed: For better estimates of nighttime COS fluxes and transpiration,

[131] removed: nocturnal stomatal conductance , and its links to daytime values, need to be quantified across

10 ecosystem types. [..[132]]Water and COS flux measurements need to be used in conjunction to derive robust estimates of nighttime stomatal conductance. We expect COS measurements to be particularly [..[133]]useful for stomatal conductance estimates in tropical rainforests and other environments that experience high humidity conditions, provided that the variability of the internal conductance of COS is well understood.

4.3 [..[134]][..[135]]Implications on COS-based GPP estimation

LRU is an important [..[136]]empirical parameter used to derive GPP from COS measurements on spatial scales ranging from the ecosystem to the continent (Asaf et al., 2013; Commane et al., 2015; Hilton et al., 2015). Choosing a represen-
5 tative LRU for COS-based GPP estimation is crucial and challenging.

[..[137]][..[138]][..[139]]

[..[140]]

---

[132]removed: 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

[133]removed: beneficial

[134]removed: The environmental determinants of leaf relative uptake (LRU)

[135]removed: Leaf COS to CO_2 relative uptake (LRU)

[136]removed: 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 (LRU $= a \cdot \text{PAR}^{-b}$) 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).

[137]removed: 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., $r_s = g_s^{-1}$), we can combine all sub-stomatal terms (mesophyll and chloroplast wall conductances and biochemical reaction coefficient) into a single internal resistance term ($r_{i,COS}$ or r_{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,

[138]removed: $\dfrac{r_{i,COS}}{r_{s,COS} + r_{i,COS}} < \dfrac{r_{i,CO_2}}{r_{s,CO_2} + r_{i,CO_2}}$

[139]removed: For example, based on rough estimates of light-saturated values of stomatal conductance ($g_{s,H_2O} = 80$ mmol m^{-2} s^{-1}) and COS and CO_2 fluxes (Fig.

5), for a relative decrease in stomatal conductance ($g_{s,COS}$ and g_{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).

[140]removed: 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).

[..141]In addition to its environmental controls, LRU also varies among plant species (Stimler et al., 2012). For the *T. latifolia*, the asymptotic LRU value at high light (PAR > 600 μmol m^{-2} s^{-1}) [..142]is around 1.0 (Fig. 5c). This value

10 is much 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 [..143]ecosystem-scale (e.g., Asaf et al., 2013) and regional-scale GPP inversion studies [..144](e.g., Hilton et al., 2015). The low asymptotic LRU [..145]of *T. latifolia* is, however, [..146]not surprising according to the mechanistic LRU model in Seibt et al. (2010), which describes that LRU is positively related to the ratio of intercellular CO_2 to the ambient CO_2 (C_i/C_a). Since *T. latifolia* often has a high photosynthetic capacity

15 (e.g., Tinoco Ojanguren and Goulden, 2013; Jespersen et al., 2017), as a result, its C_i/C_a ratio may be lower than other species, thus contributing to the low LRU. Relatively low LRU values have also been reported from [..147]other ecosystems, 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). [..148]This suggests that for the success of COS-based GPP estimation, LRU needs to be locally constrained on the dominant species in an ecosystem, rather than assumed to be a constant.

5 **4.4 [..149]**

[..150]For regional scale applications, the time-integrated LRU can be [..151]more relevant than the instantaneous LRU. Large scale patterns of COS and CO_2 drawdown imprinted in an air parcel are spatiotemporally integrated features, because the transport of surface uptake signals to the planetary boundary layer takes time and may be affected by the entrainment with other parcels along the way. Our results of time-integrated LRU show that although daytime mean LRU

10 [..152]

---

[141] removed: The

[142] removed: at our site was

[143] removed: regional

[144] removed: from COS measurements

[145] removed: value reported here

[146] removed: similar to values seen in some grasses and shrub species(Stimler et al., 2012). Lower

[147] removed: field studies

[148] removed: 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 ecosystemor 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

[149] removed: Daily integrated leaf relative uptake ratio and its implications for regional flux estimates

[150] removed: Beyond the ecosystem scale , daily values of

[151] removed: 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

[152] removed: was consistently lower than the daily (24 h) mean LRU, since the latter includes nocturnal COS uptake and CO_2 emissions.

[..[153]]and PAR are correlated, nighttime leaf respiration and COS uptake create large variability in the all-day mean LRU, which decouples it from PAR (Fig. [..[154]]7b). This suggests that a bottom-up scaling is unlikely to offer reliable daily LRU values for regional scale applications. Instead, LRU that is diagnostically calculated from biosphere models such as the [..[155]]Simple Biosphere model (Berry et al., 2013; Hilton et al., 2015) would be more appropriate for COS–GPP inversion studies, provided that model parameterizations are validated against observations.

5 Conclusions

[..[156]]Our field study has shown that leaf COS and CO_2 fluxes share [..[157]]similar diurnal patterns driven by the common stomatal responses to light and vapor deficit[..[158]], showing dual peaks of uptake separated by a prolonged midday depression period. We have validated the light dependence of LRU directly at the leaf level in field conditions. LRU converges to around 1.0 at light-saturated conditions for *Typha latifolia*, much lower than many other species due possibly to its high photosynthetic capacity. In addition to light, vapor deficit is identified as a secondary driver of LRU, acting to reduce LRU further in the afternoon (15:00–17:00) from its light-saturated value.

[..[159]][..[160]]Stomatal conductance derived from water measurements has provided process-level insights into the diurnal variability of LRU. Since the biochemical sink of COS is light independent, COS uptake is less reaction-limited compared with CO_2 uptake. With increasing light, the assimilation capacity for CO_2 increases but is unchanged for COS, causing LRU to [..[161]][..[162]][..[163]]decrease regardless of the stomatal coupling between COS and CO_2. The reduction

---

[153]removed: We found a good correlation between daytime mean LRUand daytime mean PAR ($r = -0.525$;

[154]removed: 6b), similar to Maseyk et al. (2014). This indicates that

[155]removed: 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

[156]removed: From direct field observations at the leaf scale, our

[157]removed: broadly

[158]removed: . 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

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

[160]removed: 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 COSuptake that is only stomatal conductance limited

[161]removed: be high and to decrease with PAR.

[162]removed: 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.

[163]removed: 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.

in stomatal conductance induced by high vapor deficit affects COS uptake more than CO_2 uptake, since COS uptake is more stomatal-conductance-limited, causing a further reduction in LRU. In a word, LRU variability is regulated by the relative influences of stomatal limitation vs. internal limitation on COS and CO_2 uptake.

[..[164]]The coupling between leaf COS and CO_2 fluxes [..[165]]and the predictability of LRU lend strong support to the use of COS as a quantitative tracer [..[166]]of canopy photosynthesis. More unknowns exist in the process-level controls of LRU, especially the variability of internal conductance. We expect that future studies may find the use of LRU as a diagnostic of stomatal processes to be interesting.

Author contributions. U.S. designed and supervised 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.

---

[164] removed: 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.

[165] removed: during the peak growing season of the *Typha latifolia* vegetation lends
[166] removed: for

References

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., and Yakir, D.: Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux, Nature Geoscience, 6, 186–190, https://doi.org/10.1038/ngeo1730, 2013.

Ball, J. T.: An analysis of stomatal conductance, Ph.D. thesis, Stanford University, 1988.

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., Provencal, R., Chen, H., and Yakir, D.: Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide, Global Biogeochemical Cycles, 28, 161–179, https://doi.org/10.1002/2013GB004644, 2014.

Bernacchi, C. J.: Temperature response of mesophyll conductance. Implications for the determination of Rubisco enzyme kinetics and for limitations to photosynthesis in vivo, Plant Physiology, 130, 1992–1998, https://doi.org/10.1104/pp.008250, http://dx.doi.org/10.1104/pp.008250, 2002.

Berry, J., Wolf, A., Campbell, J. E., Baker, I., Blake, N., Blake, D., Denning, A. S., Kawa, S. R., Montzka, S. A., Seibt, U., Stimler, K., Yakir, D., and Zhu, Z.-X.: A coupled model of the global cycles of carbonyl sulfide and CO_2: A possible new window on the carbon cycle, Journal of Geophysical Research: Biogeosciences, 118, 842–852, https://doi.org/10.1002/jgrg.20068, 2013.

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., Abu-Naser, M., and Campbell, J. E.: Growing season eddy covariance measurements of carbonyl sulfide and CO_2 fluxes: COS and CO_2 relationships in Southern Great Plains winter wheat, Agricultural and Forest Meteorology, 184, 48–55, https://doi.org/10.1016/j.agrformet.2013.06.007, 2014.

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., Blake, N. J., Vay, S. A., Collatz, G. J., Baker, I., Berry, J. A., Montzka, S. A., Sweeney, C., Schnoor, J. L., and Stanier, C. O.: Photosynthetic Control of Atmospheric Carbonyl Sulfide During the Growing Season, Science, 322, 1085–1088, https://doi.org/10.1126/science.1164015, 2008.

Campbell, J. E., Whelan, M. E., Seibt, U., Smith, S. J., Berry, J. A., and Hilton, T. W.: Atmospheric carbonyl sulfide sources from anthropogenic activity: Implications for carbon cycle constraints, Geophysical Research Letters, 42, 3004–3010, https://doi.org/10.1002/2015GL063445, 2015GL063445, 2015.

Campbell, J. E., Berry, J. A., Seibt, U., Smith, S. J., Montzka, S. A., Launois, T., Belviso, S., Bopp, L., and Laine, M.: Large historical growth in global terrestrial gross primary production, Nature, 544, 84–87, https://doi.org/10.1038/nature22030, 2017.

Cleveland, W. S., Grosse, E., and Shyu, W. M.: Chapter 8 Local Regression Models, in: Statistical Models in S, edited by Chambers, J. M. and Hastie, T. J., Wadsworth & Brooks/Cole, Pacific Grove, California, USA, 1992.

Collatz, G. J., Ball, J. T., Grivet, C., and Berry, J. A.: Physiological and environmental regulation of stomatal conductance, photosynthesis and transpiration: a model that includes a laminar boundary layer, Agricultural and Forest Meteorology, 54, 107–136, https://doi.org/10.1016/0168-1923(91)90002-8, 1991.

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., Templer, P. H., Juice, S. M., Zahniser, M. S., and Wofsy, S. C.: Seasonal fluxes of carbonyl sulfide in a midlatitude forest, Proceedings of the National Academy of Sciences, 112, 14 162–14 167, https://doi.org/10.1073/pnas.1504131112, 2015.

[..[167]][..[168]]

Goff, J. A. and Gratch, S.: Low-pressure properties of water from −160 to 212°F, in: The 52nd Annual Meeting of the American Society of Heating and Ventilating Engineers, pp. 95–122, New York, USA, 1946.

---

[167]removed: Cowan, I. R. : Stomatal Behaviour and Environment, Advances in Botanical Research, 4, 117–228,

[168]removed: , 1978.

[..[169]][..[170]][..[171]][..[172]]

Goldan, P. D., Fall, R., Kuster, W. C., and Fehsenfeld, F. C.: Uptake of COS by growing vegetation: A major tropospheric sink, Journal of Geophysical Research: Atmospheres, 93, 14 186–14 192, https://doi.org/10.1029/JD093iD11p14186, 1988.

20   Goulden, M. L., Litvak, M., and Miller, S. D.: Factors that control *Typha* marsh evapotranspiration, Aquatic Botany, 86, 97–106, https://doi.org/10.1016/j.aquabot.2006.09.005, 2007.

Hilton, T. W., Zumkehr, A., Kulkarni, S., Berry, J., Whelan, M. E., and Campbell, J. E.: Large variability in ecosystem models explains uncertainty in a critical parameter for quantifying GPP with carbonyl sulphide, Tellus B, 67, 26 329, https://doi.org/10.3402/tellusb.v67.26329, 2015.

25   Hilton, T. W., Whelan, M. E., Zumkehr, A., Kulkarni, S., Berry, J. A., Baker, I. T., Montzka, S. A., Sweeney, C., Miller, B. R., and Campbell, J. E.: Peak growing season gross uptake of carbon in North America is largest in the Midwest USA, Nature Climate Change, 7, 450–454, https://doi.org/10.1038/nclimate3272, 2017.

Jespersen, E., Brix, H., and Sorrell, B. K.: Acclimation to light and avoidance of photoinhibition in Typha latifolia is associated with high photosynthetic capacity and xanthophyll pigment content, Functional Plant Biology, 44, 774–784, https://doi.org/10.1071/fp16356,
30   http://dx.doi.org/10.1071/FP16356, 2017.

Kooijmans, L. M. J., Uitslag, N. A. M., Zahniser, M. S., Nelson, D. D., Montzka, S. A., and Chen, H.: Continuous and high-precision atmospheric concentration measurements of COS, CO_2, CO and H_2O using a quantum cascade laser spectrometer (QCLS), Atmospheric Measurement Techniques, 9, 5293–5314, https://doi.org/10.5194/amt-9-5293-2016, 2016.

Kooijmans, L. M. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., Kolari, P., Aalto, J., Franchin, A., Vecchi, R., Valli, G.,
35   and Chen, H.: Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest, Atmospheric Chemistry and Physics, 17, 11 453–11 465, https://doi.org/10.5194/acp-17-11453-2017, 2017.

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

5   Leuning, R.: A critical appraisal of a combined stomatal–photosynthesis model for C3 plants, Plant, Cell & Environment, 18, 339–355, https://doi.org/10.1111/j.1365-3040.1995.tb00370.x, 1995.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., and Seibt, U.: Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains, Proceedings of the National Academy of Sciences, 111, 9064–9069, https://doi.org/10.1073/pnas.1319132111, 2014.

10   Montzka, S., Calvert, P., Hall, B., Elkins, J., Conway, T., Tans, P., and Sweeney, C.: On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2, Journal of Geophysical Research, 112, D09 302, https://doi.org/10.1029/2006JD007665, 2007.

Nelson, D.: TDLWintel User's Manual, Aerodyne Research, Inc., Billerica, MA, USA, 2012.

Notni, J., Schenk, S., Protoschill-Krebs, G., Kesselmeier, J., and Anders, E.: The missing link in COS metabolism: a model study on the
15   reactivation of carbonic anhydrase from its hydrosulfide analogue, ChemBioChem, 8, 530–536, https://doi.org/10.1002/cbic.200600436, 2007.

---

[169]removed: Farquhar, G. D. and Sharkey, T. D.:

[170]removed: Stomatal conductance and photosynthesis

[171]removed: , Annual Review of Plant Physiology, 33, 317–345,

[172]removed: , 1982.

Ogawa, T., Noguchi, K., Saito, M., Nagahata, Y., Kato, H., Ohtaki, A., Nakayama, H., Dohmae, N., Matsushita, Y., Odaka, M., Yohda, M., Nyunoya, H., and Katayama, Y.: Carbonyl sulfide hydrolase from *Thiobacillus thioparus* strain THI115 is one of the β-carbonic anhydrase family enzymes, Journal of the American Chemical Society, 135, 3818–3825, https://doi.org/10.1021/ja307735e, 2013.

20 Ogée, J., Sauze, J., Kesselmeier, J., Genty, B., Van Diest, H., Launois, T., and Wingate, L.: A new mechanistic framework to predict OCS fluxes from soils, Biogeosciences, 13, 2221–2240, https://doi.org/10.5194/bg-13-2221-2016, 2016.

Oleson, K. W., Lawrence, D. M., Bonan, G. B., Drewniak, B., Huang, M., Koven, C. D., Levis, S., Li, F., Riley, W. J., Subin, Z. M., Swenson, S., Thornton, P. E., Bozbiyik, A., Fisher, R., Heald, C. L., Kluzek, E., Lamarque, J.-F., Lawrence, P. J., Leung, L. R., Lipscomb, W., Muszala, S. P., Ricciuto, D. M., Sacks, W. J., Sun, Y., Tang, J., , and Yang, Z.-L.: Technical description of version 4.5 of the Community
25 Land Model (CLM), NCAR Technical Report NCAR/TN-503+STR, National Center for Atmospheric Research (NCAR), Boulder, CO, USA, https://doi.org/10.5065/D6RR1W7M, 2013.

Protoschill-Krebs, G., Wilhelm, C., and Kesselmeier, J.: Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA), Atmospheric Environment, 30, 3151–3156, https://doi.org/10.1016/1352-2310(96)00026-X, 1996.

Sandoval-Soto, L., Stanimirov, M., Hobe, M. v., Schmitt, V., Valdes, J., Wild, A., and Kesselmeier, J.: Global uptake of carbonyl sulfide (COS)
30 by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO_2), Biogeosciences, 2, 125–132, https://doi.org/10.5194/bg-2-125-2005, 2005.

Schenk, S., Kesselmeier, J., and Anders, E.: How does the exchange of one oxygen atom with sulfur affect the catalytic cycle of carbonic anhydrase?, Chemistry – A European Journal, 10, 3091–3105, https://doi.org/10.1002/chem.200305754, 2004.

Seabold, S. and Perktold, J.: Statsmodels: Econometric and Statistical Modeling with Python, in: The 9th Python in Science Conference,
35 2010.

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U., and Berry, J.: A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation, Biogeosciences, 7, 333–341, https://doi.org/10.5194/bg-7-333-2010, 2010.

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., and Yakir, D.: Relationships between carbonyl sulfide (COS) and CO_2 during leaf gas exchange, New Phytologist, 186, 869–878, https://doi.org/10.1111/j.1469-8137.2010.03218.x, 2010.

Stimler, K., Berry, J. A., Montzka, S. A., and Yakir, D.: Association between carbonyl sulfide uptake and ^{18}O during gas exchange in C_3 and C_4 leaves, Plant Physiology, 157, 509–517, https://doi.org/10.1104/pp.111.176578, 2011.

Stimler, K., Berry, J. A., and Yakir, D.: Effects of carbonyl sulfide and carbonic anhydrase on stomatal conductance, Plant physiology, 158,
5 524–530, https://doi.org/10.1104/pp.111.185926, 2012.

Tcherkez, G. G. B., Farquhar, G. D., and Andrews, T. J.: Despite slow catalysis and confused substrate specificity, all ribulose bis-phosphate carboxylases may be nearly perfectly optimized, Proceedings of the National Academy of Sciences, 103, 7246–7251, https://doi.org/10.1073/pnas.0600605103, http://dx.doi.org/10.1073/pnas.0600605103, 2006.

Tenhunen, J. D., Lange, O. L., Gebel, J., Beyschlag, W., and Weber, J. A.: Changes in photosynthetic capacity, carboxylation efficiency,
500 and CO_2 compensation point associated with midday stomatal closure and midday depression of net CO_2 exchange of leaves of *Quercus suber*, Planta, 162, 193–203, https://doi.org/10.1007/BF00397440, 1984.

Tinoco Ojanguren, C. and Goulden, M. L.: Photosynthetic acclimation within individual Typha latifolia leaf segments, Aquatic Botany, 111, 54–61, https://doi.org/10.1016/j.aquabot.2013.08.007, http://dx.doi.org/10.1016/j.aquabot.2013.08.007, 2013.

Wehr, R., Commane, R., Munger, J. W., McManus, J. B., Nelson, D. D., Zahniser, M. S., Saleska, S. R., and Wofsy, S. C.: Dynamics
505 of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake, Biogeosciences, 14, 389–401, https://doi.org/10.5194/bg-14-389-2017, 2017.

[..[173]]

Whelan, M., Lennartz, S., Gimeno, T., Wehr, R., Wohlfahrt, G., [..[174]]Wang, Y., Kooijmans, L., Hilton, T., Belviso, S., Peylin, P., Commane, R., Sun, W., Chen, H., Kuai, L., Mammarella, I., Maseyk, K., Berkelhammer, M., Li, K.-F., Yakir, D., Zumkehr, A., Katayama, Y., Og[..[175]]é[..[176]]e, J., Spielmann, F., Kitz, F., Rastogi, B., Kesselmeier, J., Marshall, J., Erkkilä, K.-M., Wingate, L., [..[177]]Meredith, L., He, W., Bunk, R., Launois, T., Vesala, T., Schmidt, J., Fichot, C., Seibt, U., Saleska, S., Saltzman, E., Montzka, S., Berry, J., , and Campbell, J. E.: [..[178]]Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles, [..[179]][..[180]]Biogeosciences Discussions, 2017, 1–97, https://doi.org/10.5194/bg-2017-427, 2017.

Wilks, D. S.: Statistical Methods in the Atmospheric Sciences, Academic Press, 3rd edn., 2011.

510

---

[173]removed: Wilks, D. S.: Statistical Methods in the Atmospheric Sciences, Academic Press, 3rd edn., 2011.

[174]removed: Brilli, F., H

[175]removed: ö

[176]removed: rtnagl,

[177]removed: Xu, X., Bingemer, H., Hansel, A., and Loreto, F.

[178]removed: Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: potential and limitations

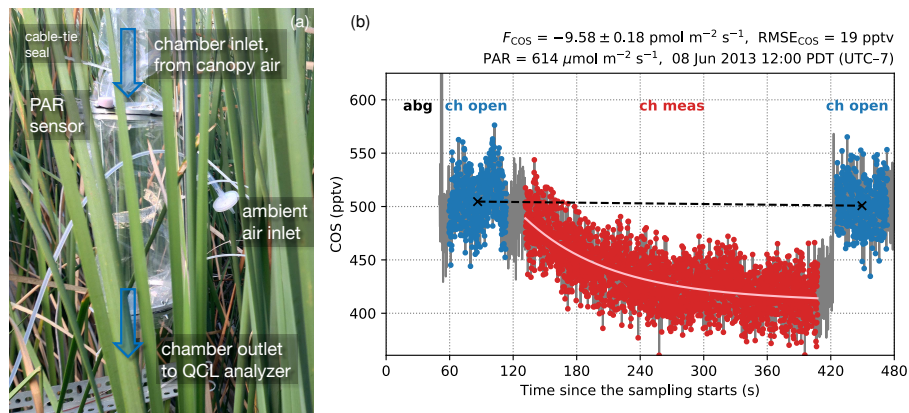[179]removed: Plant, Cell & Environment, 35, 657–667,

[180]removed: , 2012.

Figure 1. (a) A schematic diagram of the leaf chamber. (b) 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 [..181]to [..182]measure flux signals in the chamber (ch meas), 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 [..183]the drift in the measured ambient concentrations.
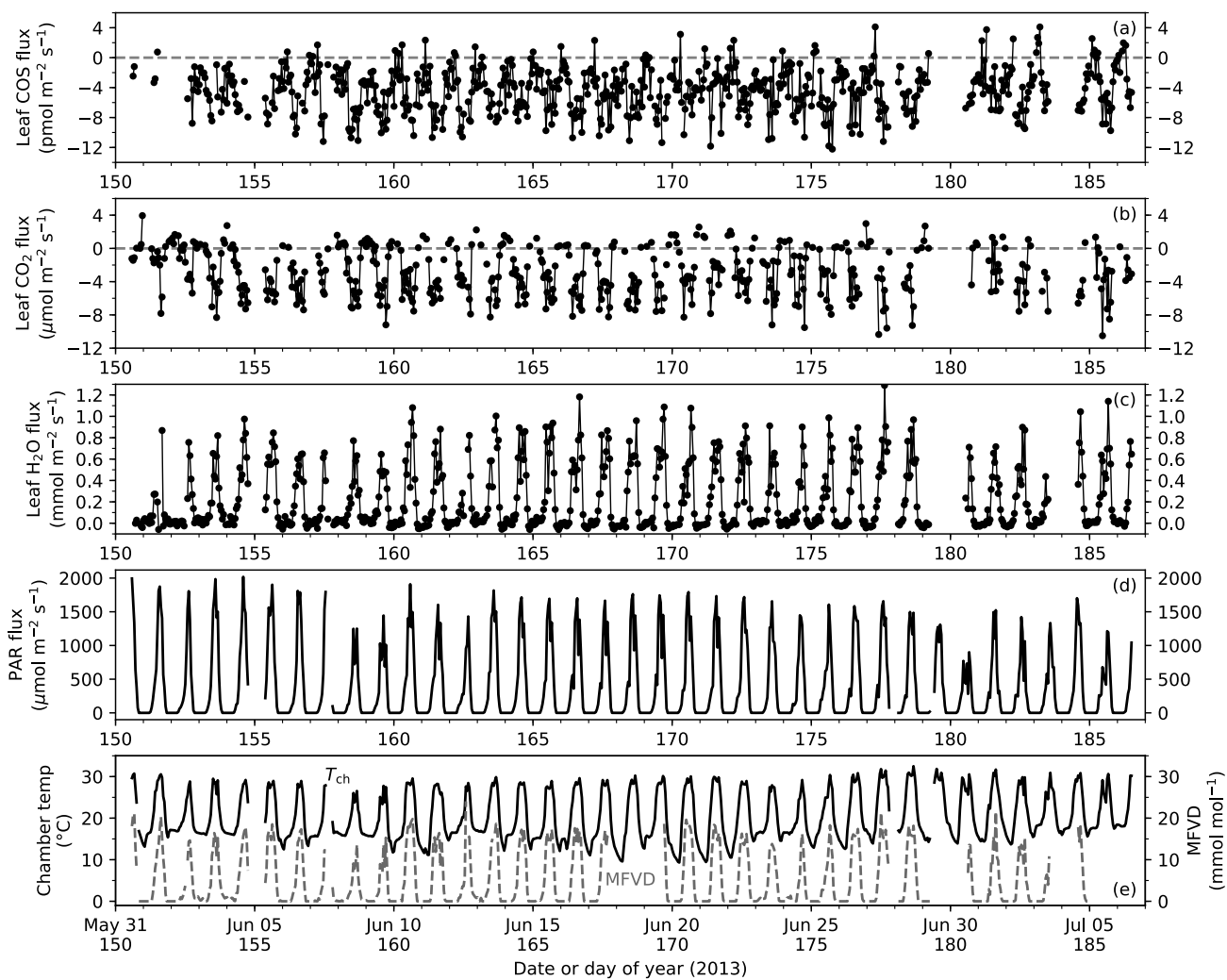
Figure 2. Time series of leaf COS (a), CO_2 (b) and water (c) fluxes, photosynthetically active radiation (PAR) at the leaf chamber (d), chamber air temperature (e, black solid line; T_{ch}) and [..[184]]leaf-to-air vapor deficit in mole fraction (e, gray dashed line; MFVD)[..[185]]. Ticks on x-axes indicate the [..[186]]starts of the days (0000 h).
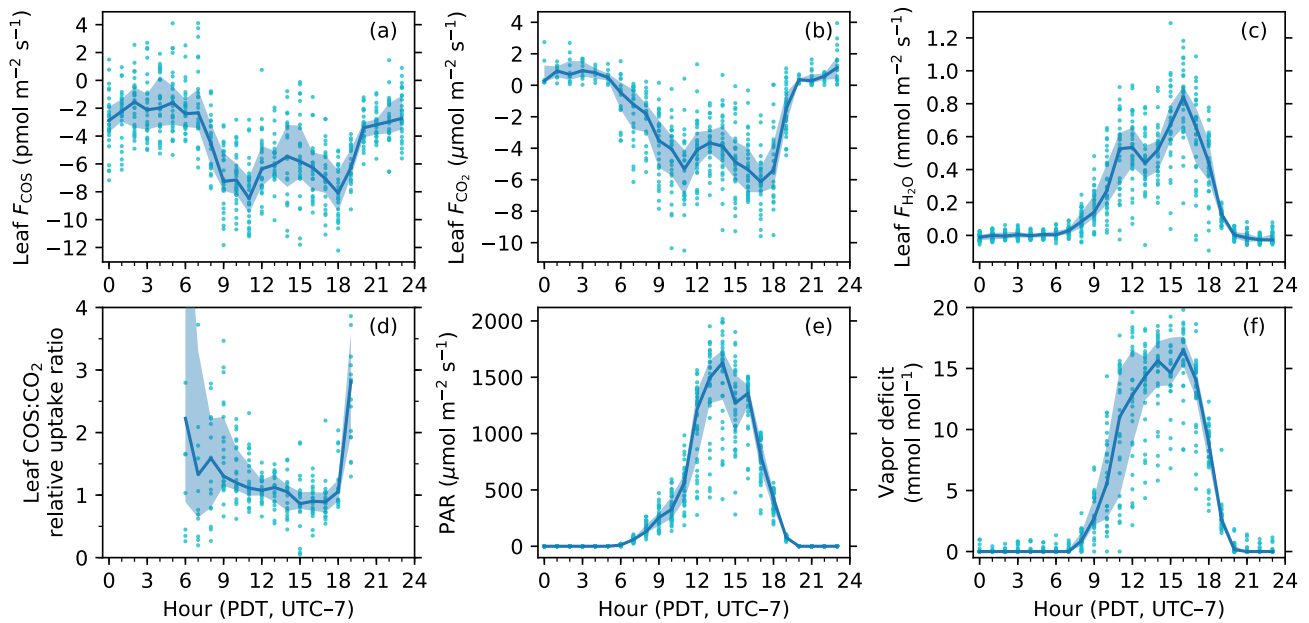
25

Figure 3. Diurnal patterns of leaf COS (a), CO_2 (b) and water (c) fluxes, leaf [..[187]]relative uptake ratio (d), PAR at the leaf chamber (e), and leaf-to-air vapor deficit [..[188]]in mole fraction (f). The solid curves show medians binned by the hour of the day (Pacific Daylight Time, UTC–7), and the upper and lower bounds of shaded areas are 25th and 75th percentiles, respectively.
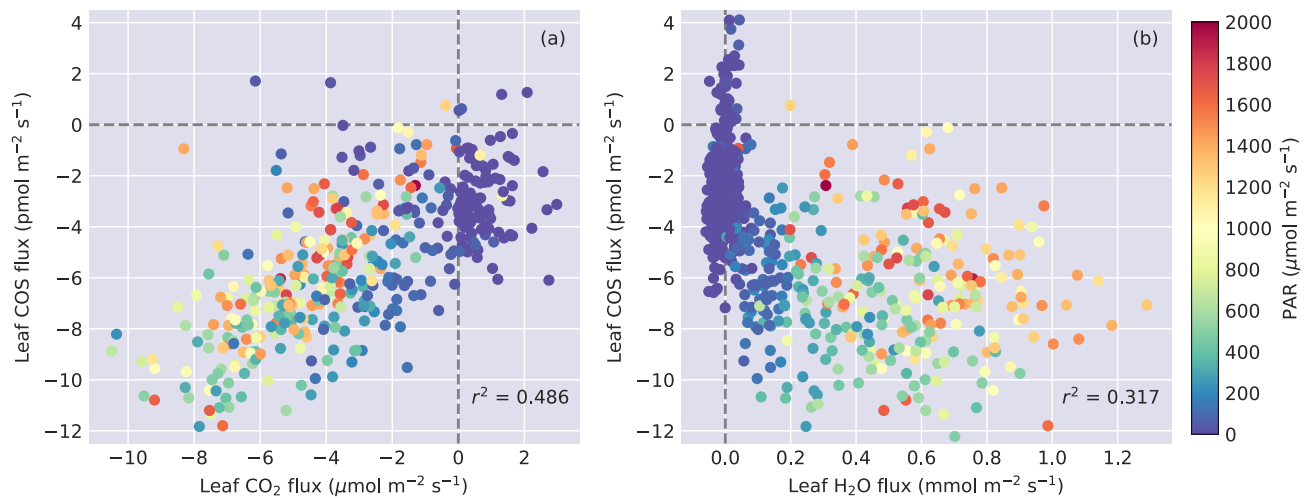
Figure 4. (a) Leaf COS vs. CO_2 fluxes, and (b) leaf COS vs. H_2O fluxes. Data points are colored by the PAR level.
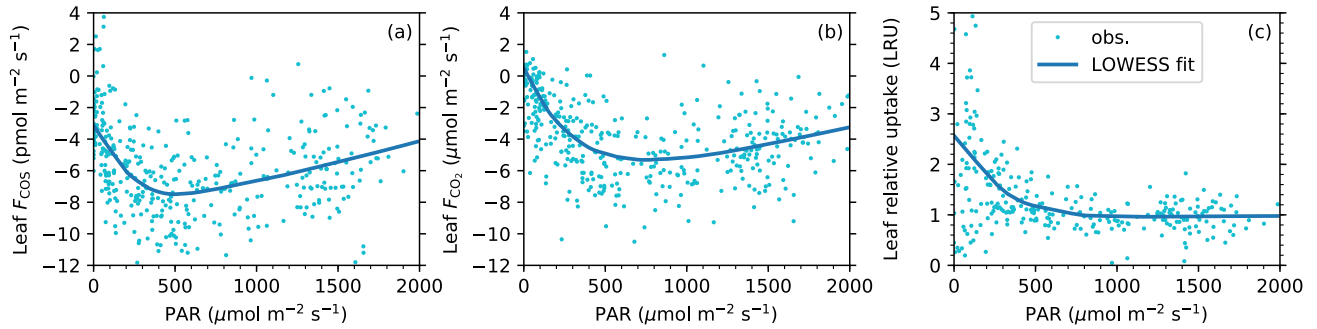
Figure 5. Light responses of leaf COS flux (a), CO_2 flux (b)[..189], [..190]and leaf relative uptake ratio (c). Data are shown as dots, and the smoothed curves are fitted with the nonparametric LOWESS method.
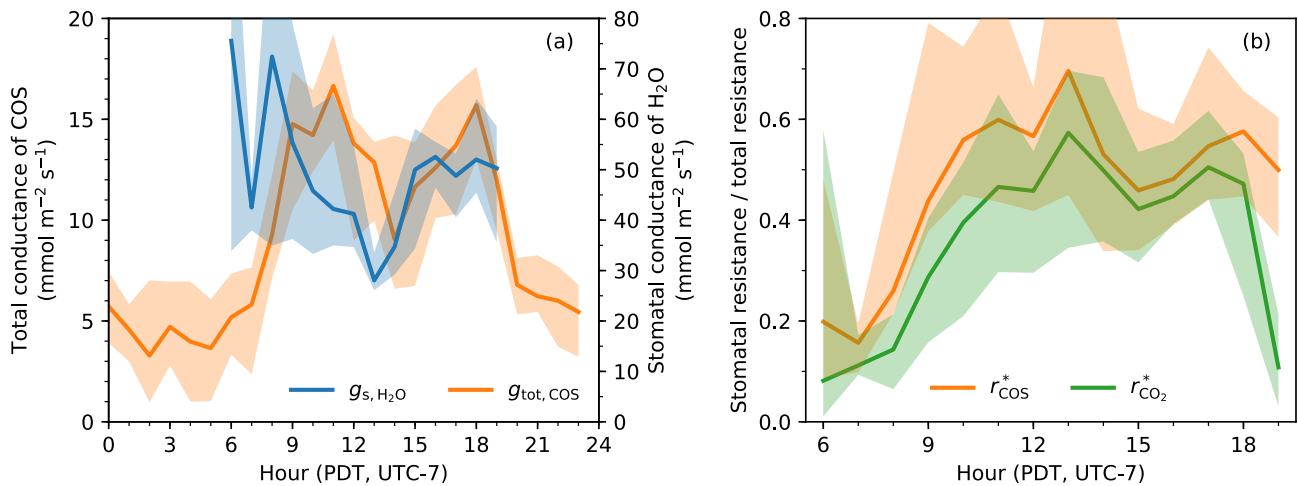

Figure 6. (a) [..191]Diurnal patterns of the stomatal conductance of water (blue, right *y*-axis) and [..192]the total conductance of COS (orange, left *y*-axis)[..193]. Note that the [..194]two variables were on different scales for visual comparison. [..195]([..196]b) [..197]Daytime patterns of the fraction of stomatal resistance in the total resistance for COS ([..198]orange) [..199]and [..200]for CO_2 ([..201]green)[..202]. [..203]Similar to Fig. 3, in both panels [..204]solid curves indicate medians and shaded areas are between 25th and 75th percentiles, binned by the hour of [..205]the day.
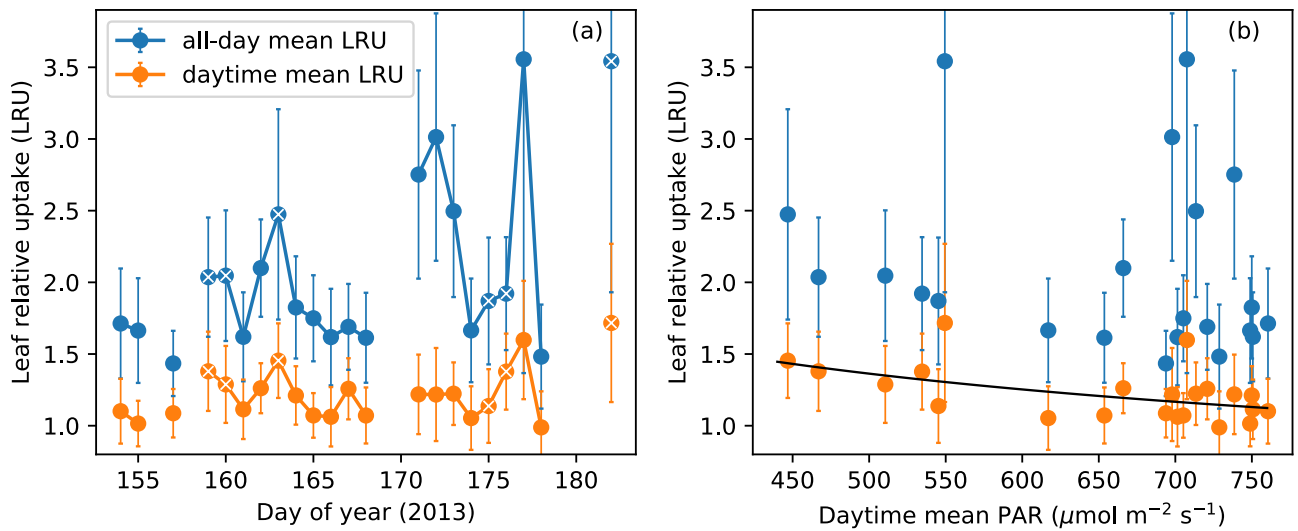
Figure 7. (a) All-day mean (blue) and daytime mean (orange) leaf relative uptake (LRU) ratios during the campaign. Data points from overcast days (daytime mean PAR < 550 µmol m^{-2} s^{-1}) are labeled with additional white cross signs. (b) All-day mean and daytime mean LRU values vs. daytime mean PAR. 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.

Table 1. List of variable symbols

Symbol	Description
χ_{COS}	COS mixing ratio (pptv or pmol mol^{-1})
χ_{CO_2}	CO$_2$ mixing ratio (ppmv or μmol mol^{-1})
χ_{H_2O}	H$_2$O mixing ratio (mmol mol^{-1})
F_{COS}	COS flux (pmol m^{-2} s^{-1})
F_{CO_2}	CO$_2$ flux (μmol m^{-2} s^{-1})
F_{H_2O}	H$_2$O flux (mmol m^{-2} s^{-1})
$g_{s,COS}$	Stomatal conductance of COS (mol m^{-2} s^{-1})
g_{s,CO_2}	Stomatal conductance of CO$_2$ (mol m^{-2} s^{-1})
g_{s,H_2O}	Stomatal conductance of water (mol m^{-2} s^{-1})
$r_{s,COS}$	Stomatal resistance of COS (mol^{-1} m^2 s)
r_{s,CO_2}	Stomatal resistance of CO$_2$ (mol^{-1} m^2 s)
r_{s,H_2O}	Stomatal resistance of water (mol^{-1} m^2 s)
$g_{tot,COS}$	Total conductance of COS (mol m^{-2} s^{-1})
g_{tot,CO_2}	Total conductance of CO$_2$ (mol m^{-2} s^{-1})
$r_{tot,COS}$	Total resistance of COS (mol^{-1} m^2 s)
r_{tot,CO_2}	Total resistance of CO$_2$ (mol^{-1} m^2 s)
$r^*_{CO_2}$	Ratio of stomatal resistance to total resistance of CO$_2$
r^*_{COS}	Ratio of stomatal resistance to total resistance of COS
T_{ch}	Chamber air temperature (°C)
T_{leaf}	Leaf temperature (°C)
e_{sat}	Saturation vapor pressure (Pa)
MFVD or D	Leaf-to-air vapor deficit in mole fraction (mmol mol^{-1})
LRU	Instantaneous leaf relative uptake
LRU$_{all\text{-}day}$	All-day mean leaf relative uptake
LRU$_{daytime}$	Daytime mean leaf relative uptake