

Terrestrial Photosynthesis Inferred from Plant Carbonyl Sulfide Uptake

Jiameng Lai¹, Linda M.J. Kooijmans², Wu Sun³, Danica Lombardozzi⁴, J. Elliott Campbell⁵,

Lianhong Gu⁶, Yiqi Luo¹, Le, Kuai⁷, Ying Sun^{1*}

Affiliations:

¹ School of Integrative Plant Science, Cornell University, Ithaca, New York, USA

² Meteorology and Air Quality, Wageningen University and Research, Wageningen, The Netherlands

³ Department of Global Ecology, Carnegie Institution for Science, Stanford, California, USA

⁴ Colorado State University, Fort Collins, Colorado, USA

⁵ University of California, Santa Cruz, Santa Cruz, California, USA

⁶ Environmental Science Division and Climate Change Science Institute, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

⁷ Jet Propulsion Laboratory, California Institute of Technology

*Corresponding author. Email: ys776@cornell.edu

Abstract: Terrestrial photosynthesis, or gross primary production (GPP), is the largest carbon flux in the biosphere but its global magnitude and spatiotemporal dynamics remain uncertain¹.

The global annual mean GPP is historically thought to be around 120 PgC yr⁻¹ ²⁻⁶, which is ~30-50 PgC yr⁻¹ lower than GPP inferred from the oxygen-18 isotope (¹⁸O)⁷ and soil respiration⁸.

This disparity is a source of uncertainty in predicting climate-carbon cycle feedbacks^{9,10}. Here

we infer GPP from carbonyl sulfide (OCS), an innovative tracer for CO₂ diffusion from ambient

air to leaf chloroplasts through stomata and mesophyll layers. We demonstrate that explicitly representing mesophyll diffusion is important for accurately quantifying the spatiotemporal dynamics of plant OCS uptake. From the estimated plant OCS uptake, we infer a global contemporary GPP of $157 (\pm 8.5) \text{ PgC yr}^{-1}$, which is consistent with estimates from ^{18}O (150-175 PgC yr^{-1}) and soil respiration ($149^{+29}_{-23} \text{ PgC yr}^{-1}$), but with an improved confidence level. Our global GPP is higher than satellite optical observation-driven estimates (120~140 PgC yr^{-1}) that are used for Earth System Model benchmarking. This difference predominantly occurs in the pan-tropical rainforests and is corroborated by ground measurements¹¹, suggesting a more productive tropics than satellite-based GPP products indicated. As GPP is a primary determinant of terrestrial carbon sinks and may shape climate trajectories^{9,10}, our findings lay a physiological foundation on which the understanding and prediction of carbon–climate feedbacks can be advanced.

Main

Terrestrial ecosystems remove carbon dioxide (CO_2) from the atmosphere via photosynthesis, which is the largest carbon flux on Earth and fuels subsequent processes of the terrestrial carbon cycle¹². Despite decades of effort to quantify photosynthetic CO_2 uptake (or gross primary production, GPP), substantial uncertainty remains in its global magnitude, spatial patterns, temporal dynamics, and environmental responses^{6,8,13,14}. This uncertainty cascades into predicting carbon-climate feedbacks¹. The global GPP has been estimated to be around 120 PgC yr^{-1} since the early 1980s^{2,3}, a value that has later been reiterated by remote sensing^{4,5}. However, this value is at odds with independent inferences based on the oxygen-18 isotope (^{18}O) signature of atmospheric CO_2 ⁷ (150-175 PgC yr^{-1}) and soil respiration⁸ ($149^{+29}_{-23} \text{ PgC yr}^{-1}$). Such

uncertainties present challenges for projecting the future trajectories of terrestrial carbon sinks¹⁵ and call for novel constraints on GPP and its spatiotemporal patterns¹.

Carbonyl sulfide (OCS or COS) is a trace gas in the atmosphere, whose concentration is six orders of magnitude lower than that of CO₂¹⁶. Plants take up OCS through a diffusion pathway shared with CO₂ and consume it via carbonic anhydrase (CA) within leaves. As the hydrolysis of OCS by CA is irreversible, plant OCS uptake, unlike CO₂ exchange, is not offset by any production process and thereby tracks GPP. Moreover, the plant uptake, the dominant sink of atmospheric OCS, is spatially separated from its major sources (i.e., ocean and industrial sources)¹⁷. Consequently, the continental-scale uptake of OCS and CO₂ (i.e., GPP) are coupled^{10,17}.

Quantifying GPP from OCS fluxes requires a realistic representation of OCS diffusion (from ambient air to leaf chloroplasts) and reaction processes (consumption by CA) along the soil-plant-atmosphere continuum¹⁶, as implemented in Terrestrial Biosphere Models (TBMs). The OCS consumption via CA (g_{CA}^{OCS}) is generally not considered a limiting factor for OCS exchange¹⁸. OCS diffusion parallels CO₂ diffusion, as they share the pathway from ambient air through the leaf boundary layer, stomata, mesophyll layers, and to their respective reactive sites¹⁶. Along this pathway, the boundary layer conductance g_b and stomatal conductance g_s for CO₂ ($g_b^{CO_2}$ and $g_s^{CO_2}$ respectively) have been represented in most TBMs¹⁹. Such formulations can be adapted to represent the counterparts for OCS (i.e., g_b^{OCS} and g_s^{OCS}), after accounting for the different molecular diffusivities of OCS and CO₂ in air¹⁶. However, the mesophyll conductance

(g_{mes}) has long been neglected in TBMs, even though mesophyll layers act as a major barrier (with a magnitude comparable to g_s) to the movement of both CO_2 and OCS inside leaves of C_3 plants^{20,21}. Here $g_{\text{mes}}^{\text{OCS}}$ is assumed equal to $g_{\text{mes}}^{\text{CO}_2}$, as the aqueous diffusivities of CO_2 and OCS are similar^{22,23}. Unless otherwise specified, we use g_{mes} to denote mesophyll conductance for both CO_2 and OCS.

An explicit implementation of g_{mes} is therefore essential to mechanistically resolve the internal drawdown of CO_2 and OCS along the mesophyll diffusion pathway. Although *ad hoc* compensating strategies via parameter tuning were employed (or g_{mes} -implicit) and have appeared reasonable for estimating the “mean” for contemporary periods over limited spatial areas, such strategies may fall short in characterizing seasonal, interannual, or long-term trends and spatial variability²⁴. The impact of g_{mes} on the temporal and spatial dynamics of plant OCS uptakes and on OCS-inferred GPP estimates remains unclear.

In this study, we quantify global plant OCS uptake and GPP and map their spatiotemporal dynamics using a bottom-up, process-based approach. We incorporate mechanistic models of g_{mes} ²⁴ and OCS diffusion¹⁶ into the National Center for Atmospheric Research (NCAR) Community Land Model (CLM5) (Methods). We verify estimates of both OCS uptake and GPP against independent measurements and inferences from the field to the global scale. A key advantage of our approach is to resolve the spatiotemporal patterns of GPP, with new insights beyond a single global constraint offered by ^{18}O ⁷ or soil respiration⁸.

Impact of g_{mes} on OCS flux (F_{OCS})

Compared with the g_{mes} -implicit treatment, an explicit mechanistic representation of g_{mes} improves agreement in ecosystem OCS fluxes (F_{OCS} ; negative for net uptake) with *in-situ* measurements at both Hyytiälä Forest, Finland (FI-Hyy) and Harvard Forest, USA (US-Ha1) (Methods), the only two sites where multi-year, continuous ecosystem OCS flux measurements are available (Fig. 1 & fig. S1). In particular, the g_{mes} -explicit simulation better captures not only the peak-season magnitude but also the seasonal dynamics of F_{OCS} . For example, at FI-Hyy, *in-situ* F_{OCS} reveals that OCS uptake may start as early as the end of January (e.g., in 2017) (fig. S1). This early start is unlikely a consequence of soil OCS uptake since the soil temperature was too low to stimulate soil uptake (fig. S2). The g_{mes} -explicit simulation more realistically captures this early start of active F_{OCS} uptake. Moreover, in the spring and fall at both FI-Hyy and US-Ha1, the g_{mes} -explicit simulated F_{OCS} agrees well with measurements; in contrast, the g_{mes} -implicit simulation underestimates F_{OCS} in both spring and fall at both sites.

The improved model-observation consistencies in F_{OCS} result from an explicit consideration of g_{mes}^{OCS} . This is confirmed by examining the internal conductance of OCS from leaf substomatal cavity to the OCS consumption site (g_i^{OCS}) and the overall conductance of OCS from ambient air to the OCS consumption site (g_t^{OCS}) (Methods). The g_{mes} -implicit strategy bundles g_{mes}^{OCS} and g_{CA}^{OCS} to form an apparent internal OCS conductance (g_i^{OCS}) and ties it empirically to the maximum carboxylation rate (V_{cmax}) through a fixed scaling factor α (Methods)¹⁶. However, the actual relationship between g_i^{OCS} and V_{cmax} may vary with environmental conditions and phenological stages²⁵ beyond what the limited existing observations of gas exchange can constrain¹⁶. Taking the two sites as an example, the V_{cmax} -scaled g_i^{OCS} and the resulting g_t^{OCS} tend to be smaller than those calculated from g_{mes}^{OCS} and g_{CA}^{OCS} explicitly considered throughout the

year, especially in the dormant and shoulder seasons (fig. S3). In contrast, the g_{mes} -explicit g_t^{OCS} more closely matches *in-situ* measurements (fig. S3). These results suggest that parameter adjustment cannot compensate for a lack of mechanistic representation of $g_{\text{mes}}^{\text{OCS}}$ (fig. S4). Although the peak F_{OCS} can be matched by tuning the scaling factor α^{25} , such tuning cannot reproduce the seasonal variations of F_{OCS} (fig. S1), particularly in the shoulder and dormant seasons because V_{cmax} decreases faster than g_i^{OCS} does (fig. S4). A similar phenomenon occurs at night when carboxylation pauses while leaf stomata remain partially open, allowing sizable plant OCS uptake that amounts to 20–30% of the total daily uptake^{26–28}. Such nighttime plant OCS uptake cannot be captured by the g_{mes} -implicit strategy, but can be reproduced by the g_{mes} -explicit simulation (fig. S5). Note that both g_{mes} -implicit and g_{mes} -explicit simulations assume that OCS is predominantly consumed by CA within leaf chloroplasts²⁹.

Globally, g_{mes} -implicit and g_{mes} -explicit simulations of F_{OCS} show remarkable differences in time and space (Fig. 2 and fig. S6). Implicit g_{mes} modeling leads to a weaker F_{OCS} for almost all plant functional types (PFTs; Fig. 2) but C_3 arctic grass. From 2000 to 2010, the g_{mes} -implicit simulation yields a global average OCS sink of 752 GgS yr⁻¹, consistent with the SiB4 estimate of 753 GgS yr⁻¹²⁵. The g_{mes} -explicit simulation yields a global F_{OCS} of 967 GgS yr⁻¹, which is still within the range of 368–1279 GgS yr⁻¹ (with a mean of 917 GgS yr⁻¹) reported previously (fig. S6). Differences between the g_{mes} -explicit and implicit simulations (ΔF_{OCS}), generally around 30%~50%, persist throughout the year for temperate and tropical regions but exhibit the largest seasonal variation in boreal forests of the northern hemisphere (NH). The distinct seasonal variation of ΔF_{OCS} in boreal forests indicates a longer active OCS uptake period by g_{mes} -explicit than g_{mes} -implicit simulations, consistent with *in-situ* measurements at FI-Hyy (Fig.

1 & fig. S1). The most pronounced g_{mes} impact on F_{OCS} is concentrated in NH boreal forests because of their stronger mesophyll diffusion limitation (i.e., smaller g_{mes}) than other PFTs²⁴ (fig. S7). For these PFTs, g_{mes} acts as a strong barrier to both OCS and CO_2 diffusion, decreasing F_{OCS} by 10% to 50% (fig. S8) and potentially reducing photosynthesis by 25% to 75% according to leaf-level studies³⁰. Although the arctic C_3 grass is the only PFT to show weaker F_{OCS} in the g_{mes} -explicit simulation, this pattern cannot yet be validated due to scarce measurements from this PFT³¹. Future studies, such as measurements and modeling of g_{mes} dependence on leaf traits, temperature, and other environmental conditions, are required to understand the impact of g_{mes} on F_{OCS} for this PFT.

Our results highlight the importance of mesophyll control, which is of a similar magnitude to stomatal control, but has not received due attention in TBM representation²⁴. The global g_{mes} model employed here formulates g_{mes} as a function of leaf dry mass per unit area (M_a), and considers its vertical variation within canopy depth (driven by light gradient) as well as its response to leaf temperature and water stress. This formulation characterizes the first-order impacts of leaf structure and environmental variations on g_{mes} and demonstrates reasonable performance in estimating contemporary GPP and OCS fluxes across spatial scales. However, future research to improve the g_{mes} model formulation is still needed, especially with regard to the varying relationship between g_{mes} and M_a across different PFTs³², temperature response functions of g_{mes} ³³, complex responses of g_{mes} to soil water stress³⁴, and acclimation to future environmental changes³⁵. These complexities, although challenging to parameterize due to limited measurements, are critical to understanding and predicting the g_{mes} impact on global

carbon and water fluxes under future changing climate scenarios²⁰ (see detailed discussion in Supplementary Text S1).

GPP inferred from OCS fluxes

Further, we used leaf relative uptake (LRU, the concentration-normalized ratio of OCS and CO₂ uptake)^{14,36} to translate plant OCS uptake into GPP. LRU varies with environmental conditions, particularly light intensities, among other factors (e.g., water vapor pressure deficit VPD)^{26,37}. Kooijmans et al.³⁸ developed a parsimonious empirical equation between LRU and photosynthetic active radiation (PAR) based on hourly *in-situ* measurements at FI-Hyy. This unique leaf-scale dataset paired LRU and PAR along a full range of PAR continuum. Its joint use with concurrent canopy-level OCS flux measurements facilitated scaling from leaf to canopy scales. We applied the LRU-PAR equation developed from this dataset (Eq. 25, fig. S9) to translate the simulated plant OCS fluxes ($g_{\text{mes-explicit}}$) into GPP, denoted as $GPP_{\text{OCS_LRU_PAR}}$ (Methods).

We found that $GPP_{\text{OCS_LRU_PAR}}$ mirrors the *in-situ* GPP partitioned from net ecosystem exchange of CO₂ (NEE) at both diurnal (Fig. 3) and seasonal scales (fig. S10). Compared to GPP inferred from plant OCS uptake with a commonly used constant LRU value (1.61 for C₃³⁹) ($GPP_{\text{OCS_LRU_constant}}$, $g_{\text{mes-explicit}}$), GPP derived from PAR-dependent LRU ($GPP_{\text{OCS_LRU_PAR}}$) is higher during daytime and the growing season, but zero at nighttime and lower during the non-growing season as expected. $GPP_{\text{OCS_LRU_PAR}}$ tracks the diurnal and seasonal dynamics of *in-situ* GPP more closely than $GPP_{\text{OCS_LRU_constant}}$. In addition, $GPP_{\text{OCS_LRU_PAR}}$ outperforms GPP

simulated by the default Farquhar, von Caemmerer, and Berry (FvCB) model implemented in CLM5 (GPP_{CLM5_FvCB}). For example, GPP_{CLM5_FvCB} fails to capture the diurnal shape of GPP at FI-Hyy and US-Ha1 (e.g., the hysteresis in the afternoon) (Fig. 3), and markedly underestimates daytime and growing-season GPP at US-Ha1 (Fig. 3b, and fig. S10c).

At the global scale, applying the parsimonious LRU-PAR equation (Methods) leads to an annual GPP estimate of $157 (\pm 8.5) \text{ PgC yr}^{-1}$ ($GPP_{OCS_LRU_PAR}$, g_{mes} -explicit, the 2000–2010 average) (Fig. 4a & fig. S11). Implicit treatment of g_{mes} only slightly changes the global annual mean GPP to 152 PgC yr^{-1} (Table S1), implying that compensatory parameter adjustment might match the present-day global annual GPP magnitude but can distort the simulated seasonal and spatial dynamics of OCS fluxes and thus GPP (Fig. 2). However, a constant LRU value (a simplified strategy adopted in the literature^{10,14}) strongly impacts the global GPP estimates (Fig. 4a, Table S1, detailed discussion in Supplementary Text S2).

The global annual mean GPP inferred from the ^{18}O signature of atmospheric CO_2 was $150\text{--}175 \text{ PgC yr}^{-1}$ ⁷ and that inferred from soil respiration was $149^{+29}_{-23} \text{ PgC yr}^{-1}$ ⁸. Our estimate of $157 (\pm 8.5) \text{ PgC yr}^{-1}$, inferred from plant OCS uptake, falls within these independent constraints but with a considerably narrower uncertainty range. However, all these estimates are much higher than those derived from satellite optical remote sensing, e.g., estimates from upscaling globally distributed flux tower measurements using machine learning^{5,40} or LUE (light use efficiency)-type models^{13,41} (Fig. 4a & fig. S11). Recently, somewhat higher GPP estimates ($120\text{--}140 \text{ PgC yr}^{-1}$) were obtained from satellite solar-induced fluorescence (SIF) remote sensing with the assumption of a linear SIF-GPP scaling⁴², and process-based models driven by satellite optical

data (e.g., LAI, fPAR, vegetation indices VIs)^{43,44}; these estimates are still lower than our OCS-inferred GPP estimates. The generally lower existing estimates likely result from their shared biases or uncertainties such as the spatial representativeness of flux towers, NEE partitioning approaches, and uncertainties in satellite remote sensing products, among others (detailed discussion in Supplementary Text S3). Interestingly, the global annual mean GPP directly simulated by CLM5 with the default FvCB photosynthesis module (GPP_{CLM5_FvCB}) is 126 PgC yr⁻¹, similar to estimates by existing satellite optical data-driven products. This low estimate likely results from parameter tuning to reproduce the widely cited bottom-up GPP estimates (e.g., around 120 PgC yr⁻¹)^{4,5}. Our stronger OCS-inferred GPP estimate is not due to the lack of exceptional El Niño/Southern Oscillation (ENSO) events in the period from 2000 to 2010, as demonstrated by our sensitivity simulation (Supplementary Text S4, fig S12).

Revisiting the spatial GPP patterns

Plant OCS uptake can offer new insights into the spatial and temporal variations of GPP, which previous global constraints such as the ¹⁸O⁷ and soil respiration⁸ were unable to resolve. Our OCS-based approach not only informs global GPP but also pinpoints where and when GPP is likely misrepresented in existing remote sensing based products. To discern the spatiotemporal disparities of GPP from different approaches, we selected four widely used satellite optical remote sensing-driven GPP products (i.e., MODIS⁴⁵, GOSIF⁴⁶, FluxSat⁴¹ and FLUXCOM⁵ GPP) and compared them with our OCS-inferred GPP (Fig. 4b-e, fig. S13). The largest discrepancies occur in the pan-tropical rainforests. This finding is consistent with a recent study¹¹ that estimated GPP from comprehensive plot-scale measurements and detailed carbon budget quantification⁴⁷. The aforementioned study reported that the mature intact rainforests in the tropical Amazon have substantially stronger GPP than what the existing satellite optical remote

sensing driven products indicated. The poor performance of these satellite GPP products in the tropics is likely due to the impacts of frequent clouds and scarcity of flux tower observations which are needed for upscaling in this most productive region of the Earth⁶.

To evaluate the robustness of the OCS-inferred GPP estimates in the pan-tropics, we compared $GPP_{OCS_LRU_PAR}$ against *in-situ* data at four tropical flux tower sites located in the central- and eastern-Amazon⁴⁸ (Table S2). We found a close agreement in both dry and wet seasons at the four sites, particularly at the K67 and CAX towers (Table S2 & fig. S14). Additionally, $GPP_{OCS_LRU_PAR}$ outperforms GPP_{CLM5_FvCB} (both g_{mes} -implicit and explicit), which significantly underestimates GPP at all four sites in both dry and wet seasons (fig. S14). Furthermore, $GPP_{OCS_LRU_PAR}$ reveals substantially higher productivity in the western than central Amazon, as expected from the tropical forest aridity gradient there¹¹. Such a contrast is consistent with OCO-2 SIF observations⁴⁹ and inference from plot-scale measurements¹¹ but not captured by GPP_{CLM5_FvCB} (Fig. 3c & d) or other GPP data products (fig. S13). These emergent patterns have important implications on the carbon sink capacity of tropical rainforests and their resilience to stress under climate change, and thus should be thoroughly evaluated in the future with independent ecosystem-scale measurements of OCS and GPP fluxes. Our findings suggest that *in-situ* measurements of ecosystem-scale OCS uptake with concurrent CO₂ fluxes are critically needed across the pan-tropics to understand their dynamical relationships, which ultimately will help verify the regional-scale GPP magnitude and spatiotemporal variations reported here.

Further, current satellite-driven products also underestimate GPP in NH mid-to-high latitudes, particularly during the growing season (Fig. 4c). This pattern is consistent with previous

findings⁵⁰ that utilized atmospheric OCS concentrations from ground measurements and aircraft campaigns to reveal a stronger GPP than existing TBMs in NH high latitudes.

Impact of LRU on OCS-inferred GPP

LRU, a key parameter for OCS-based GPP inference, varies with VPD^{26,38} and with PFTs^{17,39}; yet this variability cannot be fully constrained due to limited observations. Nevertheless, our simulations and uncertainty quantification indicate that the empirical LRU-PAR equation is broadly applicable across species. For example, GPP estimates based on the LRU-PAR relationship derived at FI-Hyy track the GPP diurnal and seasonal cycles at US-Ha1 reasonably well (Fig. 3b and fig. S10c-d). Even in the tropical Amazon with drastically different environments, this parsimonious equation still leads to a GPP magnitude and dry-wet contrast consistent with *in-situ* measurements (fig. S14). At the global scale, we employed a Monte Carlo approach to quantifying the potential uncertainty from cross-PFT variability in LRU and in the LRU dependency on PAR. We synthesized field and laboratory measurements^{38,39} as a guidance to generate an ensemble of PFT-specific LRU-PAR relationships that mimic a diverse combination of PFT-dependent LRU-PAR relationships (details in Methods and Supplementary Text S5). The ensemble encompasses a wide range of LRU under ambient light conditions (fig. S15), but still yields a highly constrained uncertainty range of global GPP, i.e., $\pm 8.5 \text{ PgC yr}^{-1}$ (Fig. 4). This indicates that the sensitivity of the global annual GPP estimates to the cross-PFT variability in LRU and the LRU-PAR relationship is scale-dependent. At local scales, this sensitivity can be substantial, as documented by chamber and/or canopy-level measurements^{38,51}, but at the global scale, such sensitivity greatly diminishes. The dearth of field observations under varying light intensities and other environmental gradients across diverse biomes or species

prevents a PFT-specific LRU formulation that varies not only with PAR but also with other environmental conditions (e.g., VPD²⁶). Field measurements across a diverse range of biomes and environments are urgently needed to characterize PFT/species-specific LRU dependency on environmental conditions and plant traits.

Conclusions

Taking advantage of the close coupling between OCS and CO₂ diffusion processes, we investigated the impact of mesophyll diffusion on the dynamics of plant OCS uptake, and inferred the global GPP and its spatiotemporal patterns. Our bottom-up estimates of plant OCS fluxes provide robust prior for quantifying the global OCS budget and for ascertaining the sources and sinks of OCS on Earth with inversion approaches^{10,50}. Harnessing the mechanistic constraint from plant OCS uptake on photosynthesis, our study provides a well-constrained contemporary GPP estimate. This new estimate is consistent with independent inferences from ¹⁸O isotope and soil respiration but with a much-improved confidence level and fully resolved spatial and temporal dynamics. Our advances mark a key step toward constraining GPP dynamics. As GPP is a primary determinant of terrestrial carbon sinks and shapes climate trajectories, our findings lay a solid physiological foundation on which the understanding and prediction of carbon–climate feedbacks can be advanced.

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412 Main figure legends

413 **Fig. 1 Comparison of seasonal cycles of terrestrial ecosystem OCS fluxes (F_{OCS}) simulated**
414 **by implicit and explicit representations of mesophyll conductance ($g_{\text{mes}}^{\text{OCS}}$) with *in-situ***
415 **ecosystem-scale measurements at (a) Hyytiälä Forest, Finland (FI-Hyy) and (b) Harvard**
416 **Forest, Massachusetts, USA (US-Ha1). Negative F_{OCS} denotes net OCS uptake by the**
417 **ecosystem.**

419 **Fig. 2. Comparison of F_{OCS} (2000–2010 average) between g_{mes} -implicit and g_{mes} -explicit**
420 **simulations across plant functional types (PFTs). Curves show monthly mean F_{OCS} (the right**
421 **ordinate), and bars denote relative difference in percentage (ΔF_{OCS} , g_{mes} -explicit minus g_{mes} -**
422 **implicit, normalized by g_{mes} -explicit F_{OCS} , the left ordinate). Maps show the seasonal ΔF_{OCS}**
423 **across the globe. A positive ΔF_{OCS} indicates larger ecosystem OCS uptake (or sink) in g_{mes} -**
424 **explicit simulations. Abbreviations: BDS: broadleaf deciduous shrub; BDT: broadleaf deciduous**
425 **tree; BES: broadleaf evergreen shrub; BET: broadleaf evergreen tree; NDT: needleleaf**
426 **deciduous tree; NET: needleleaf evergreen tree. Global PFT distribution is shown in fig. S16.**

428 **Fig. 3. Comparison of GPP inferred from CLM5 OCS simulation with GPP simulated by**
429 **CLM5 implemented with the default FvCB model. a & b, diurnal patterns of CLM5 OCS-**

430 inferred GPP ($GPP_{OCS_LRU_PAR}$ and $GPP_{OCS_LRU_constant}$, both are g_{mes} -explicit) and the CLM5
431 GPP simulations with the default FvCB (GPP_{CLM5_FvCB} , g_{mes} -explicit) in comparison to GPP
432 partitioned from *in-situ* NEE (detailed partitioning methods described in Table S3) at FI-Hyy and
433 US-Ha1 Due to data availability, the mean diurnal cycle from June to mid-July 2017 is shown
434 for FI-Hyy, and that from June to August during 2012 and 2013 is shown for US-Ha1. **c & d**,
435 global annual mean GPP (in 2010) inferred from CLM5 OCS simulations and simulated by
436 CLM5 with default FvCB, respectively.

437

Fig. 4. Intercomparison of GPP estimates from existing approaches. **a**, the global annual mean GPP estimates synthesized from literature⁸. A full list of individual studies under each category is in fig. S11 (with references). Here colors differentiate the broad categories of approaches. GPP estimates from this study are all based on g_{mes} -explicit simulations. GPP estimates inferred from oxygen-18 isotope, soil respiration, and satellite solar-induced fluorescence (SIF) with linear scaling come from single references, thus the error bars (in black) denote their uncertainty ranges provided by each reference; GPP estimates from machine learning-based upscaling and LUE-based upscaling are synthesized from multiple references and the error bars (in red) denote the standard deviation across different studies falling into the same category of approaches. **b** to **e**, zonal variations of GPP from this study and a subset of widely used satellite optical remote sensing-driven products from **a**.

Methods

Model parameterization of ecosystem OCS fluxes

Ecosystem OCS uptake

Terrestrial ecosystem OCS uptake (termed F_{OCS}) is modeled as:

$$F_{OCS} = g_a^{OCS}(OCS_a - OCS_m) \quad (1)$$

where g_a^{OCS} is the aerodynamic conductance for OCS and assumed equal to that for water; OCS_a is the OCS concentration in the canopy air space, updated at each model time step; OCS_m is the OCS concentration at a reference level. We used the global gridded monthly estimations of OCS concentration from Ma et al.⁵².

OCS_a in Eq. (1) was updated at each time step based on simulated plant and soil fluxes as follows:

$$OCS_a = (OCS_{a_prev} + dt/OCS_{cap} \times (OCS_m \cdot g_a^{OCS} - F_{ocs_soil} - F_{ocs_veg})) / (1 + dt \cdot g_a^{OCS}/OCS_{cap}) \quad (2)$$

where OCS_{a_prev} refers to OCS_a in the previous time step (the OCS concentration at the starting time step was set as 450 parts per trillion); dt is the CLM model timestep; OCS_{cap} is the air capacity for the OCS exchange (unit: mol air m⁻²), calculated based on OCS canopy air depth which was assumed to be a constant (i.e., 10 m); F_{ocs_soil} and F_{ocs_veg} are the OCS plant and soil fluxes whose calculation is described below.

OCS Plant uptake

Plant uptake of OCS (termed as F_{ocs_veg}) is modeled as:

$$F_{ocs_veg} = OCS_a \times g_t^{OCS}; \quad g_t^{OCS} = \frac{1}{\frac{1}{g_b^{OCS}} + \frac{1}{g_s^{OCS}} + \frac{1}{g_{mes}^{OCS}} + \frac{1}{g_{CA}^{OCS}}} \quad (3)$$

where OCS_a was updated for each model time step by Eq. (2), g_t^{OCS} is the OCS conductance from the leaf boundary layer to the CA reaction site (unit: mol m⁻²s⁻¹), calculated based on leaf boundary layer conductance (g_b^{OCS}), stomatal conductance (g_s^{OCS}), and mesophyll conductance (g_{mes}^{OCS}), as well as a reaction rate coefficient for OCS hydrolysis by carbonic anhydrase (CA) (g_{CA}^{OCS} , also termed as biochemical conductance).

Although CA is ubiquitous in plants, we only considered the OCS consumption by chloroplast CA, as existing experimental evidence showed that chloroplast CA dominates the total OCS consumption²⁹. Following existing parameterization of plant OCS uptake¹⁶, we assumed that the

pathway for OCS diffusion from ambient air to leaf chloroplast is similar to that of CO₂ as represented in current land surface models. Analogous to CO₂, the boundary layer and stomatal conductance of OCS can be scaled from those of water vapor (denoted as $g_s^{H_2O}$ and $g_b^{H_2O}$ respectively)³⁷ following:

$$g_b^{OCS} = \frac{g_b^{H_2O}}{1.56}, \quad g_s^{OCS} = \frac{g_s^{H_2O}}{1.94} \quad (4)$$

The mesophyll conductance of OCS (g_{mes}^{OCS}) was assumed equal to that of CO₂ ($g_{mes}^{CO_2}$)¹⁸, as a substantial part of mesophyll diffusion is in the aqueous phase, and the aqueous diffusivities of these two gases are similar^{22,23}. However, unlike $g_s^{H_2O}$ and $g_b^{H_2O}$, $g_{mes}^{CO_2}$ was not represented in the standard version of CLM5. In this study, we implemented both implicit and explicit considerations of mesophyll diffusion to model the OCS plant uptake (descriptions will be given below).

CLM is a two-big-leaf model, which resolves canopy leaves into sunlit and shaded leaves.

Therefore, g_t^{OCS} was calculated respectively for sunlit and shaded leaves and aggregated as follows:

$$g_t^{OCS} = g_{t_sun}^{OCS} \cdot LAI_{sun} + g_{t_sha}^{OCS} \cdot LAI_{sha} \quad (5)$$

where $g_{t_sun}^{OCS}$ and $g_{t_sha}^{OCS}$ are the g_t^{OCS} for sunlit and shaded leaves, respectively, and LAI_{sun} and LAI_{sha} are leaf area index (LAI) for sunlit and shaded leaves, respectively.

A: OCS plant model with implicit mesophyll diffusion

Independent studies have shown that both the mesophyll conductance (g_{mes}^{OCS}) and CA activity (g_{CA}^{OCS}) tend to scale with the maximum carboxylation rate of Rubisco (V_{cmax})^{53,54}. Therefore, an

alternative approach was proposed to combine the two processes of g_{mes}^{OCS} and g_{CA}^{OCS} into a single apparent conductance g_i^{OCS} for the calculation of the overall conductance g_t^{OCS} :

$$g_t^{OCS} = \frac{1}{\frac{1}{g_b^{OCS}} + \frac{1}{g_s^{OCS}} + \frac{1}{g_i^{OCS}}} \quad (6)$$

In Eq. (6), g_i^{OCS} represents the internal conductance of OCS diffusion from the intercellular air space to CA reaction sites and is assumed proportional to V_{cmax} ¹⁶:

$$g_i^{OCS} = \alpha \cdot V_{cmax} \cdot f_w(\theta) \cdot \left(\frac{p}{p_0}\right) \cdot \left(\frac{T_{can}}{T_0}\right) \quad (7)$$

where α is a scaling factor (1400 for C₃ species and 8862 for C₄ species²⁵), $f_w(\theta)$ is the water stress function (ranging from 0 to 1) implemented in CLM5, p is the atmospheric pressure, and p_0 is the reference surface pressure (1000 hPa), T_{can} is canopy temperature which is prognostically calculated by CLM5, and T_0 is the reference temperature (273.15 K). The water stress function $f_w(\theta)$ is:

$$f_w(\theta) = \sum_i^n f_{root,i} \cdot w_i(\theta) \quad (8)$$

where $f_{root,i}$ denotes the root fraction within soil layer i ; and w_i refers to the plant wilting factor related to soil water content θ .

B: OCS plant model with explicit mesophyll diffusion

Although mesophyll diffusion was not represented in the standard version of CLM5, attempts have been made to represent the mesophyll conductance of CO₂ (g_{mes}^{CO2})²⁴ in some ways. Here, we assumed g_{mes}^{CO2} equal to g_{mes}^{OCS} ¹⁸, and leveraged a process-based g_{mes} model²⁴ to explicitly calculate g_{mes} . g_{CA}^{OCS} , which depends on CA activity, is assumed constant (0.055 mol m⁻²s⁻¹) following Wehr et al.¹⁸:

$$g_{CA}^{OCS} = 0.055. \quad (9)$$

This value (0.055) was estimated from measurements made at Harvard Forest, a temperate deciduous forest, but works well also at a boreal needleleaf forest site (Hyytiälä Forest, Finland, FI-Hyy) (Fig. 1). This cross-site applicability suggests that the simulated OCS fluxes may not be sensitive to the value of g_{CA}^{OCS} . We also evaluated the impact of the temperature dependence of g_{CA}^{OCS} , using Eq. (10), and found no significant effects on the simulated OCS fluxes (fig. S17).

$$g_{CA}^{OCS} = 0.8 \times 0.055 \times \exp\left(\frac{E_0}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T_L}\right)\right) \quad (10)$$

where E_0 is the activation energy (40 kJ mol⁻¹), R is the ideal gas constant (8.3145 J mol⁻¹K⁻¹), T_{ref} denotes the reference temperature (293 K), and T_L is leaf temperature, prognostically calculated by CLM5.

Process-based g_{mes} model

Sun et al.²⁴ developed the first global process-based g_{mes}^{CO2} model for C₃ plants, which was successfully applied to CLM4.5. The model considered g_{mes}^{CO2} variations with leaf structures and environmental conditions (e.g., temperature and water stress), following:

$$g_{mes}^{CO2} = g_{max0} \cdot f_I(LAI) \cdot f_T(T_L) \cdot f_w(\theta) \quad (11)$$

where g_{max0} is the maximum g_{mes}^{CO2} under non-stressed conditions (i.e., the presence of ample soil water at 25°C); $f_I(LAI)$ refers to the vertical variation of g_{mes}^{CO2} as a function of LAI; $f_T(T_L)$ represents the response function of g_{mes} to leaf temperature (T_L , calculated by CLM5); and $f_w(\theta)$ is the water stress function given in Eq. (8). g_{max0} is given by

$$g_{max0} = a \cdot M_{a0}^b \quad (12)$$

where M_{a0} represents the leaf dry mass per unit area (M_a , unit: g m^{-2}) at canopy top, which can be calculated as two times the inverse of the canopy-top specific leaf area SLA_0 (a parameter in CLM5). In CLM5, M_a differs from $1/SLA_0$ (with a unit of gC m^{-2}) by a factor of two, as the latter only includes carbon fraction; the carbon content is assumed to be 50% of leaf dry mass²⁴. a and b are two constants ($a = 24.240338$, $b = -0.6509$)²⁴. This gives a g_{mes}^{CO2} the unit $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$, which can be converted to $\text{mol m}^{-2} \text{s}^{-1}$ if multiplied by surface pressure.

Since CLM5 divides the canopy leaves into sunlit and shaded fractions, the function f_l in Eq. (11) was also defined for sunlit (f_{l_sun}) and shaded (f_{l_sha}) fractions, respectively:

$$f_{l_sun}(LAI) = \frac{k_b}{k_g + k_b} \cdot \frac{1 - \exp[-(k_g + k_b)LAI]}{1 - \exp(-k_b \cdot LAI)} \quad (13a)$$

$$f_{l_sha}(LAI) = \frac{k_b}{k_g(k_g + k_b)} \frac{k_b - (k_g + k_b)\exp(-k_g LAI) + k_g \exp[-(k_g + k_b)LAI]}{\exp(-k_b LAI) - 1 + k_b LAI} \quad (13b)$$

where LAI is the leaf area index; k_b is the direct beam extinction coefficient; k_g is a composite parameter with an empirical value of 0.08997.

The temperature response function $f_T(T_L)$ in Eq. (11) is given by:

$$f_T(T_L) = \exp\left(\frac{c - \Delta H_a / (R \cdot T_L)}{1 + \exp((\Delta S \cdot T_L - \Delta H_d) / (R \cdot T_L))}\right) \quad (14)$$

where c is a scaling constant (20); ΔH_a is the activation energy ($49.6 \times 10^3 \text{ J mol}^{-1}$); R is ideal gas constant; ΔS is an entropy term ($1.4 \times 10^3 \text{ J mol}^{-1} \text{K}^{-1}$); and ΔH_d is the deactivation energy ($437.4 \times 10^3 \text{ J mol}^{-1}$).

Sun et al.²⁴ also applied the simulated g_{mes}^{CO2} to facilitate a more accurate photosynthetic estimation, as CO₂ concentrations drop considerably along mesophyll diffusion pathways, expressed by Eq. (15):

$$C_c = C_i - A/g_{mes}^{CO2} \quad (15)$$

where C_c and C_i are the CO₂ partial pressure (unit: Pa) inside leaf chloroplasts and that at intercellular air space; A is the net carbon assimilation rate (unit: $\mu\text{mol m}^{-2}\text{s}^{-1}$).

Sun et al.²¹ gave a relationship to estimate the true photosynthetic parameters (i.e., the g_{mes} -including parameters) from the CLM modeled g_{mes} -lacking parameters once g_{mes}^{CO2} is known:

$$y = w \cdot \exp \left(p \frac{w^u}{(g_{mes}^{CO2})^{q+v}} \right) \quad (16)$$

where y denotes parameters for a g_{mes} -explicit representation (including V_{cmax} , J_{max} at a reference temperature of 25°C) and w denotes their counterparts in a g_{mes} -implicit representation; p , q , u , and v are empirical constants: they are 0.034, 1.1253, 0.8787, and 0.4801 for V_{cmax} while are 0.2935, 1.4838, 0.0858, and 0.1726 for J_{max} .

OCS soil flux

We used a mechanistic model⁵⁵ to simulate the soil flux of OCS (F_{ocs_soil}). This model described the OCS uptake or production together with the OCS diffusion, respectively, for each soil column of a uniform temperature, soil moisture, and porosity. The Ogée soil model has been used to infer reaction rate parameters across a range of biomes and land cover types in several laboratory studies^{56,57}. It has also been applied to SiB4, showing a good performance²⁵.

The Ogée soil model simplifies the soil OCS flux (F_{ocs_soil}) as:

$$F_{ocs_soil} = \sqrt{kB\theta D} \left(OCS_{s_a} - \frac{z_1^2 P}{D} \left(1 - \exp\left(\frac{-z_p}{z_1}\right) \right) \right) \quad (17)$$

where k is the first-order rate constant for CA-mediated OCS hydrolysis (unit: s^{-1}); B is the non-dimensional solubility of OCS in water (unit: $mol\ m^{-3}\ H_2O/mol\ m^{-3}\ air$); θ is volumetric soil water content (unit: $m^3\ m^{-3}$); D is soil OCS diffusivity (unit: $m^3\ air\ m^{-3}\ soil\ s^{-1}$); OCS_{s_a} is the OCS mole fraction at the soil-air interface, assumed to be identical to the OCS mole fraction at the canopy air space; z_1 is $D/(kB\theta)$; P is the OCS production rate (unit: $mol\ m^{-3}\ s^{-1}$); z_p is soil depth ($= 1.0\ m$). Various functions in Eq. (17) are modeled as follows.

The rate constant k in Eq. (17) is given by:

$$k = f_{CA} \cdot k_{uncat} \cdot \frac{x_{CA}(T)}{x_{CA}(T_{ref})} \quad (18)$$

where f_{CA} is the CA enhancement factor (see Table S4 for its values across different plant function types (PFTs)); k_{uncat} is the uncatalyzed reaction rate; $x_{CA}(T)$ and $x_{CA}(T_{ref})$ are temperature response functions. The uncatalyzed reaction rate k_{uncat} depends mostly on the temperature T and pH (assume constant at 4.5):

$$k_{uncat} = 2.15 \times 10^{-5} \left(-10450 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) + 12.7 \times 10^{-pK_w + pH} \exp \left(-6040 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad (19)$$

where pK_w is the dissociation constant of water (i.e., 14.0). For agricultural patches, the k_{uncat} value was designated as 1/5 of the value calculated from Eq. (19) as agricultural soil was reported to have a lower k_{uncat} ⁵⁸.

The temperature response function $x_{CA}(T)$ in Eq. (18) is given by:

$$x_{CA}(T) = \frac{\exp(-\Delta H_a/RT)}{1 + \exp(-\Delta H_d/RT + \Delta S_d/R)} \quad (20)$$

where ΔH_a , ΔH_d , and ΔS_d are thermodynamic parameters with values of 40 kJ mol⁻¹, 200 kJ mol⁻¹, and 660 J mol⁻¹K⁻¹, respectively

The non-dimensional solubility B of OCS in water in Eq. (17) is related to Henry's law constant K_H (unit: mol m⁻²Pa⁻¹) and depends on temperature:

$$B = k_H \cdot R \cdot T; k_H = 2.1 \times 10^{-4} \cdot \exp\left(\frac{24900\left(\frac{1}{T} - \frac{1}{298.15}\right)}{R}\right) \quad (21)$$

The soil OCS diffusivity D in Eq. (17) is calculated as²⁵:

$$D = D_{eff,a} + D_{eff,l} \cdot B; D_{eff,a} = D_{0,a}(T) \cdot \tau_a \cdot \varepsilon_a; D_{eff,l} = D_{0,l} \cdot \tau_l \cdot \theta \quad (22)$$

where $D_{eff,a}$ and $D_{eff,l}$ are the effective diffusivities of gaseous OCS and dissolved OCS through the soil matrix, respectively; $D_{0,a}$ refers to the binary diffusivity relative to temperature as: $D_{0,a}(T) = D_{0,a}(298.15K)(T/298.15K)^{1.5}$ where $D_{0,a}(298.15 K)$ (or $D_{0,a}(25^\circ C)$) equals to $1.27 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$; $D_{0,l}$ is also relative to temperature: $D_{0,l}(T) = D_{0,l}(T_0)(T/T_0 - 1)^{1.5}$ where T_0 is 216 K ($-57.15^\circ C$) and $D_{0,l}(T_0)$ can be calculated as $D_{0,l}(298.15K)/(298.15K/T_0 - 1)^{1.5}$ with $D_{0,l}(298.15 K)$ equal to $1.94 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; τ_a and τ_l are the tortuosity factors used to describe the tortuous movement through the air- or water- filled pore space. We selected the τ_a function⁵⁹ formed as $(0.2(\varepsilon_a/\phi)^2 + 0.004)/\phi$ where ε_a is the volumetric air content and ϕ is total soil porosity, and τ_l function⁶⁰ formed as $\theta^{7/3}/\phi^2$ where θ is the volumetric water content as they are independent of pore-size distribution²⁵.

The OCS production rate P in Eq. (17) is assumed uniform from the surface to depth z_p (= 1.0 m) and controlled by soil temperature T_{soil} (in $^\circ C$):

$$P = j \cdot \exp(m \cdot T_{soil}) \quad (23)$$

where j and m are empirical parameters whose average values across different PFTs are given in Table S4.

Inference of GPP from plant OCS fluxes

OCS plant uptake is used to infer GPP, once the concentration-normalized ratio of OCS and CO₂ uptake (LRU, leaf relative uptake) is known:

$$GPP = F_{ocs_veg} \frac{[CO_2]_a}{[OCS]_a} \frac{1}{LRU} \quad (24)$$

where $[CO_2]_a$ denotes the ambient concentration of CO₂. For inferring GPP from site-level simulations, site measurements of $[CO_2]_a$ and $[OCS]_a$ were used herein; whereas for inferring GPP at the global scale, model simulation of $[CO_2]_a$ and $[OCS]_a$ were used.

LRU has been estimated in some experimental studies¹⁷. Measurements carried out in 22 C₃ plant species reported cross-species ranges of LRU with a mean value of 1.61 (± 0.26)³⁹, which has been adopted by previous studies in evaluating GPP-OCS relationships at sites or globally^{14,61}. However, a constant LRU is not able to accurately translate plant OCS uptake to GPP, as LRU was observed to decrease with increasing photosynthetically active radiation (PAR) at both leaf and ecosystem scales^{38,51}. Here, we applied two approaches to calculating the LRU for C₃ species (a constant LRU of 1.16 was used for C₄ species for both approaches, as C₄ species were reported to have a much lower LRU^{29,61}) and obtained two estimates of OCS-inferred GPP from Eq. 24. First, a constant LRU value of 1.61 was adopted, leading to a GPP estimate termed as $GPP_{OCS_LRU_constant}$. Second, we considered the LRU variations in response to light intensity, and adopted the empirical equation between LRU and PAR proposed by

Kooijmans et al.³⁸ at Hyytiälä, Finland (Eq. 25). The applicability of the LRU-PAR relationship in estimating GPP (the resulting GPP is termed as $GPP_{OCS_LRU_PAR}$) was evaluated at two sites in different biomes (Fig. 3 & fig S10). The two OCS-inferred GPP were compared with each other and also with that directly simulated by the CLM5 with the default FvCB model (termed GPP_{CLM5_FvCB}) (Table S5).

$$LRU = 607.2623/PAR + 0.5705 \quad (25)$$

Comparison of OCS-inferred GPP with in-situ canopy-scale GPP in Amazon rainforests

Both OCS-inferred and CLM5 FvCB-simulated GPP were compared with *in-situ* GPP partitioned from *in-situ* NEE measurements at four tropical sites located in central and eastern Amazon. Here the GPP dataset came from the Large-Scale Biosphere-Atmosphere Experiment in the Amazon - Ecology dataset (LBA-ECO)⁶², which has been harmonized across projects with additional quality control checks performed, and aggregated to several time intervals. The four sites were selected (following Restrepo-Coupe et al.⁴⁸) because: (1) they represent mature intact tropical forests in Amazon that are highly productive, and (2) they span a range of dry-season intensities and lengths. The simulation design and model-data comparison at these four sites are provided in Supplementary Text S6.

Monte Carlo simulations of uncertainties in GPP estimates arising from cross-PFT variabilities in LRU and its light dependency.

GPP uncertainty may arise from cross-species/PFT variabilities in LRU and its light dependency. To systematically assess this uncertainty, we combined best available field measurements with Monte Carlo simulations to generate ensemble estimates of GPP based on diverse combinations

of PFT-specific LRU-PAR relationships. The core of this approach is to construct diverse combinations of PFT-specific LRU-PAR relationships guided by field measurements. To achieve this, we generated ensemble LRU-PAR relationships by randomly sampling data points from two types of field datasets to mimic cross-species variability (Supplementary Text S5). The two field datasets employed here are: 1) leaf-level measurements of Kooijmans et al.³⁸, so far the only publicly available leaf-scale dataset with paired LRU-PAR along a full range of PAR continuum and with concurrent canopy-level OCS flux measurements that can facilitate scaling from leaf to canopy scales, and 2) datasets compiled by Stimler et al.³⁹, so far the only dataset available that have LRU measurements under multiple standardized PAR levels across diverse PFTs/species. Kooijmans et al.³⁸ provided continuous and paired LRU-PAR measurements in the full PAR range. It offers the baseline “shape” (functional relationship) between LRU and PAR that all plant species may follow, i.e., a linear relationship between LRU and 1/PAR (or a hyperbolic relationship between LRU and PAR). Then we applied the cross-PFT variability by varying slopes and intercepts of the baseline linear shapes. This was achieved by imposing random variations (representing cross-species variability) to the “baseline” shape, with the random variation generated from the dataset of Stimler et al.³⁹. We chose measurements from Stimler et al.³⁹ (synthesized in their Table II) to represent species variability in LRU and its PAR dependency, primarily because: (1) it covered LRUs from 22 species in total belonging to four different biome types; (2) it provided LRU values for each species at three different (and standardized) light levels, i.e., 179, 352, and 1889 $\mu\text{mol m}^{-2}\text{s}^{-1}$, which allowed us to quantify LRU variability arising from species differences under multiple light levels, and (3) these LRUs were measured at the same environmental conditions including CO₂ concentration, air

temperature, and humidity, ensuring that the LRU variability primarily comes from PAR for each species.

Although there are other studies that synthesized LRU values across species from literature (e.g., Whelean et al.¹⁷), these values came from different studies under diverse combinations of environmental conditions, without standardizing PAR levels or controlling other environmental factors, precluding the possibility to systematically quantify the variability of LRU-PAR dependency across species. There are also attempts to employ the optimization theory to generate global mapping of LRU (e.g., Wohlfahrt et al.⁶³), but challenges still remain with this approach in quantifying LRU-PAR relationships under unsaturated light conditions. More field measurements are needed to better characterize LRU variability with light across PFTs.

Design of CLM5 Model Simulations

We used the CESM (Community Earth System Model) CLM5 as the TBM for OCS simulation. Four simulations were carried out, with different parameterizations of g_t^{OCS} (Table S6). For simulation 1 (S1, g_{mes} -implicit simulation), we implemented the OCS plant model with implicit mesophyll diffusion¹⁶. For simulation 2 (S2, g_{mes} -explicit simulation), the OCS plant model with explicit mesophyll diffusion was implemented, with g_{mes} calculated by a process-based model²⁴. Comparison between S1 and S2 shows the impact of mechanistic consideration of mesophyll diffusion in OCS flux simulation. For simulation 3 (S3, g_{mes} -excluding simulation), we assumed g_{mes} infinite (i.e., ignoring mesophyll resistance) and computed g_t^{OCS} only with g_b^{OCS} , g_s^{OCS} and g_{CA}^{OCS} . Comparison between S2 and S3 shows the effect of mesophyll diffusion on OCS fluxes.

For simulation 4 (S4), we implemented explicit g_{mes} while employing a temperature response function for g_{CA}^{OCS} (Eq. 10). Comparison between S2 and S4 shows the impact of g_{CA}^{OCS} parameterization on OCS simulation.

Each simulation was run with active biogeochemistry (BGC) and crop models and was preceded by a spin-up for 100 years. We performed both global simulations and point simulations. For global simulation, all scenarios from S1 to S4 were performed from 2000 to 2010. Meteorological data from GSWP3 (Global Soil Wetness Project Phase 3) NCEP (National Centers for Environmental Prediction) dataset on a 3-hour interval (available from 1901 to 2014) was used as meteorological forcing. Point simulation was run at two field sites: Hyytiälä, Finland (FI-Hyy) (2013–2017) and Harvard Forest (US-Ha1) (2012–2013), where OCS observations exist across most months within a year^{38,51} and partitioned GPP estimates were also available for growing seasons^{38,64} (Table S3). For each site, the plant function type (PFT) in model simulation was set as consistent with the site land cover type, and site observations of meteorological conditions were used as meteorological forcing.

Data and materials availability: The CLM5 simulation output related to this study is available at <https://doi.org/10.7298/mxg9-7176>.

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Author contributions:

778 Y. S. and J. L. conceived of the study. J. L. and Y. S. developed the methodology. J. L.
779 conducted the analyses. J. L. and Y. S. interpreted the results, L. M., W.S., D. L., E. C., L. G., Y.
780 L., and L. K. helped the interpretation. J. L. and Y. S. constructed the initial draft, and L. M.,
781 W.S., D. L., E. C., L. G., Y. L., and L. K. contributed critically to the subsequent revision of
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785 **Supplementary Materials**

786 Text S1-S6

787 Tables S1-S6

788 Figs. S1 to S20