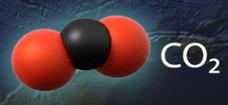


Detecting Climate Carbon Feedbacks: Next-Generation Approach for Space-Based Integration of OCS, CO₂, and SIF



**Detecting Climate-Carbon Feedbacks:
Next-Generation Approach for
Space-Based Integration of OCS, CO₂, and SIF**

Study Report prepared for the W. M. Keck Institute for Space Studies (KISS)

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Director: Prof. Tom Prince

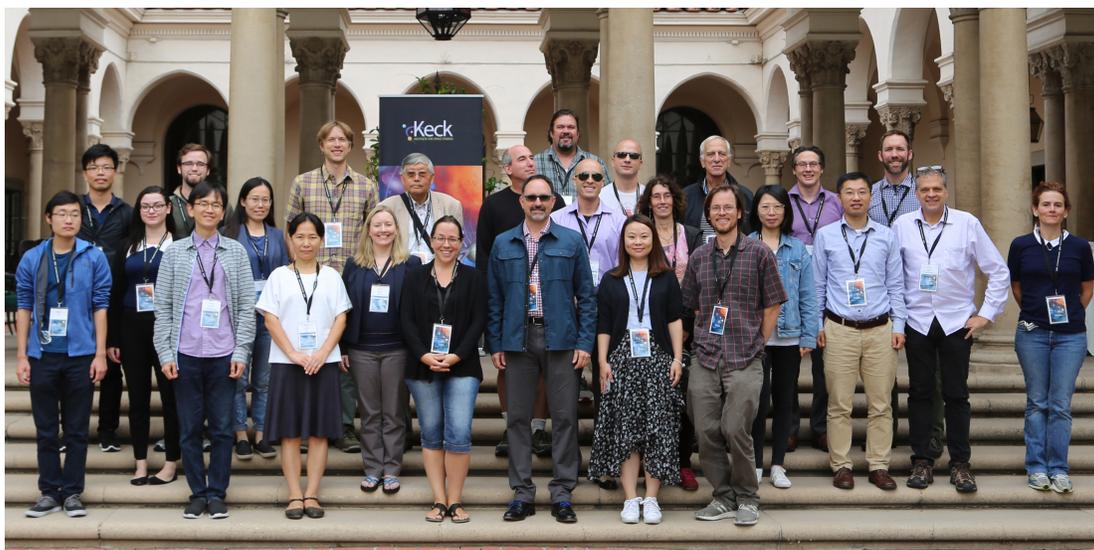
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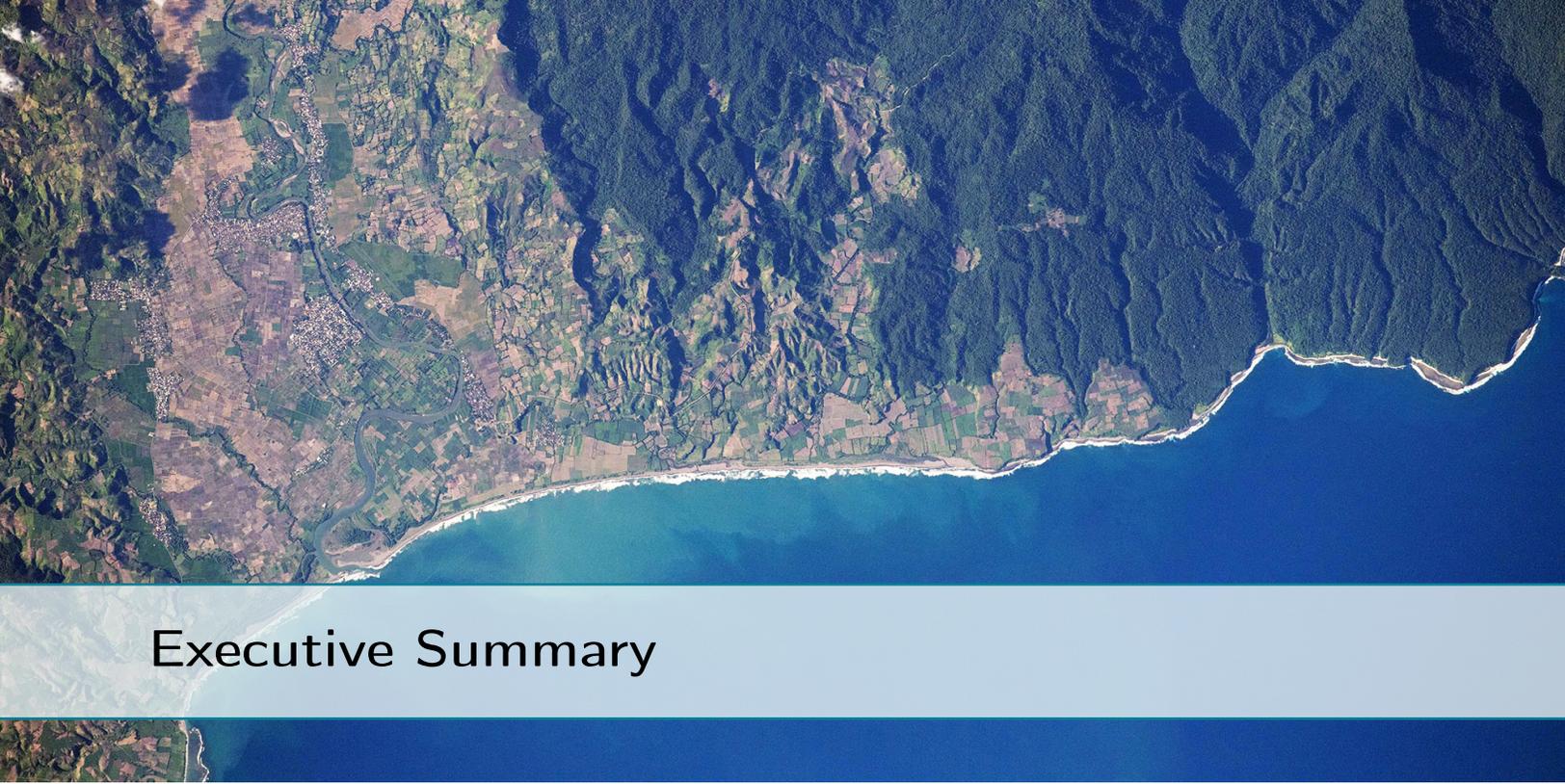
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Executive Summary

Photosynthesis is a keystone process for the Earth system. The emergence of photosynthesis transformed Earth's geologic, geochemical, and biologic evolution, and today, virtually all life on Earth depends on this process as a direct or indirect food source. Photosynthesis controls a fundamental link between the global carbon, water, and energy cycles, which underlies central scientific mysteries of the Earth system. In particular, post-industrial growth in global photosynthesis is responsible for one of the largest and most uncertain feedbacks to anthropogenic climate change.

Despite its importance, photosynthesis cannot be measured directly at scales larger than the leaf. Historically, measurements of CO_2 gas exchange are suitable for leaf chambers, but at larger scales, this technique is confounded by CO_2 emissions from soils. Theories of global photosynthesis are largely in the realm of computer simulations. Thus, measurement technology limits our ability to pursue questions that are essential to understanding the processes governing the Earth system and impacting our future.

To confront this key scientific challenge, the workshop "Next-Generation Approach for Detecting Climate–Carbon Feedbacks: Space-Based Integration of OCS, CO_2 , and SIF" assembled a multi-disciplinary team to conceive a new integrated technique for measuring photosynthesis at regional to global scales. The participants merged perspectives from the fields of ecology, biogeochemistry, atmospheric chemistry, and space science to focus on how a rapidly emerging technique with carbonyl sulfide sensors (OCS or COS) could be integrated with existing CO_2 and satellite observations of solar-induced chlorophyll fluorescence (SIF) platforms.

The workshop discussions leveraged recent findings from atmospheric OCS observations and plant gas exchange studies that reveal a robust relationship between regional variation in photosynthesis and atmospheric variation in OCS. Plant leaves consume atmospheric OCS gas through a one-way hydration sink, which is controlled by stomatal conductance that is also a primary control on photosynthesis. Atmospheric OCS observations, such as the satellite detection of a massive depletion in OCS over the Amazon, can then provide a measurement-based estimate of photosynthesis.

These OCS findings were analyzed within the context of recent breakthroughs from spaceborne SIF analysis. SIF platforms record the electromagnetic energy released from plant leaves during photosynthesis. Strong correlations between SIF and photosynthesis suggest an alternative means of assessing global photosynthesis from space.

The key result of this workshop is that these alternative methods fill critical, yet different, methodological gaps, suggesting the need for a unified, space-based, photosynthesis observation platform. First, the highly complementary temporal and spatial scales of SIF analysis provide instantaneous, spatially resolved data and OCS provides spatially and temporally integrated data. Second, the independent photosynthesis processes that need to be constrained include the biochemical SIF constraint and stomatal conductance OCS constraint. Third, the Amazon basin is identified as an ideal domain where the temporally integrated OCS analysis could confront cloud contamination problems of alternative approaches.

These outcomes has been used to develop a roadmap for near-, mid-, and long-term activities to achieve this vision for a unified global photosynthesis observing system. Proof-of-concept studies, including an airborne field experiment in the Amazon and an observing system simulation experiment, will provide critical evidence for the proposed satellite observations. The workshop team will collaborate on perspective articles in diverse disciplinary journals and develop a research coordinating network to communicate this new approach to the broad community of scientists and technologists who would be impacted by enabling a large-scale understanding of global photosynthesis.



1. Introduction

1.1 The Central Enigma of the Carbon, Energy, and Water Cycles

Terrestrial photosynthesis is the fundamental coupling between global cycles of energy, carbon, and water (Figure 1.1). Photosynthesis is driven by incoming radiation and water availability, modulates atmospheric carbon, and in turn releases water vapor that can drive cloud distributions and rainfall.

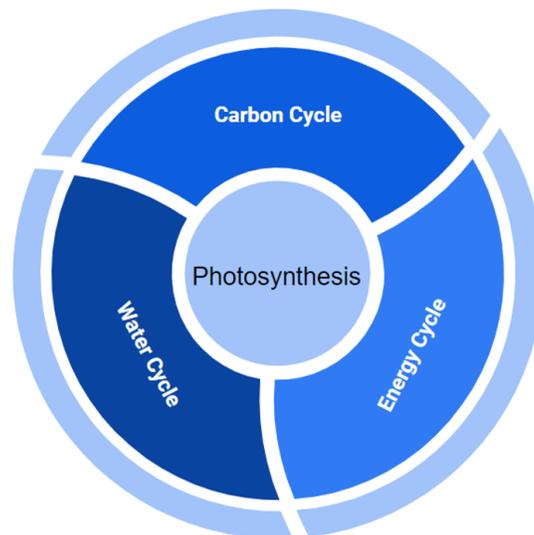


Figure 1.1: Photosynthesis is a critical Earth system process that links the carbon, energy, and water cycles. In particular, photosynthesis processes control the exchange of latent heat, CO₂, and water vapor between the atmosphere and terrestrial biosphere.

Despite this central importance of photosynthesis, **the most biologically productive region on Earth, tropical rainforests, remains a critical blind spot** in our attempts to understand this process. Even groundbreaking satellite observations of solar-induced chlorophyll fluorescence (SIF) are largely obscured by the persistence of tropical clouds (Magney et al., 2019a). What lies beneath these clouds is the central enigma of the carbon cycle.

The mystery of the tropical biosphere leads to profound questions for the global carbon, water, and energy cycles. For example, rising atmospheric CO₂ levels stimulate terrestrial photosynthesis, which in turn causes the terrestrial biosphere to sequester as much as a third of anthropogenic CO₂ emissions every year. This highly fortuitous negative feedback to climate change is called the CO₂ fertilization effect and is thought to be one of the largest global feedbacks in the climate system. Most climate models, and theory due to scaling with gross primary production (GPP), predict that the CO₂ fertilization effect should be concentrated in the tropics [(Schimel et al., 2015)]. However, without a cloud-penetrating measurement of tropical photosynthesis, there is no way to confirm this model-driven hypothesis.

Tropical forests are also the domain of a heavily debated positive feedback. Some climate models forecast a powerful positive feedback as drying and warming reduce tropical photosynthesis, initiating the dieback of tropical forests and the subsequent emissions of vast quantities of CO₂. Again, we lack robust large-scale constraints on photosynthesis that are needed to resolve this debate.

The root of the uncertainty in tropical photosynthesis is spatial. Photosynthesis in the tropics has been measured at the leaf to site level (< 1 km²). However, we lack robust measurement of tropical photosynthesis at regional scales. A space-based approach could provide regional measurements, but is currently lacking. While satellite CO₂ data provide information on net ecosystem processes, CO₂ is not a useful tracer of photosynthesis because the signal from photosynthesis is obscured by co-located CO₂ sources. Satellite vegetation indices (e.g., Normalized Difference Vegetation Index, or NDVI) provide insights on vegetation structure, but they do not provide a direct measurement of photosynthesis rates and are subject to saturation effects in the tropics. And although SIF data have already revealed new patterns in global photosynthesis, they bring little to the table in tropical regions due to interference by persistent cloud cover.

1.2 A New Line of Evidence

Since the 1970s, carbonyl sulfide (OCS) has been a focal point in atmospheric science due to its role in influencing climate and stratospheric ozone (Crutzen, 1976). Unlike space-based CO₂ observations, which cannot separate photosynthesis and respiration processes, atmospheric OCS provides a tracer of photosynthesis (Figure 1.2).

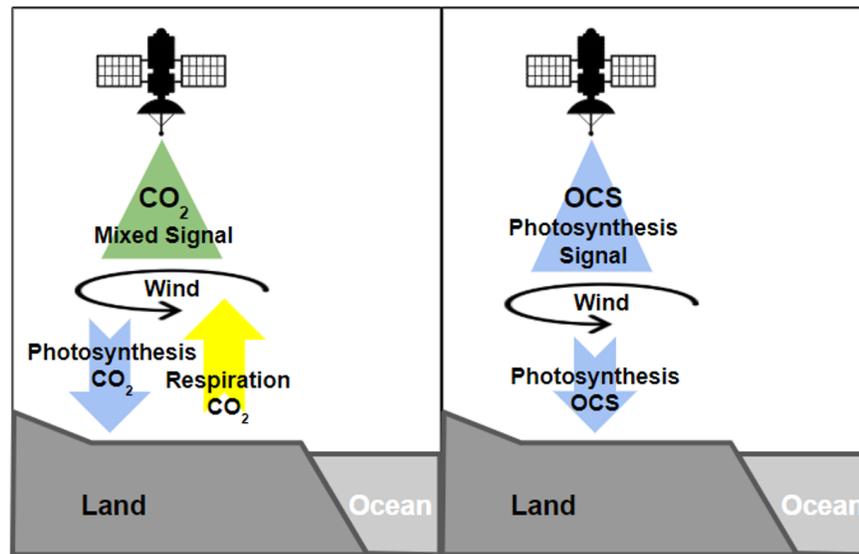


Figure 1.2: Satellite measurements of CO₂ provide valuable information on net ecosystem exchange, but CO₂ measurements are not useful for monitoring photosynthesis because winds mix the photosynthesis signal with the co-located respiration signal (left). However, continental OCS is dominated by a process closely related to stomatal conductance, providing a measurement-based tracer of this critical photosynthesis process.

However, the proposed use of OCS as a photosynthesis tracer has only been seriously investigated over the last decade. The proposal was based on the exciting discovery of a massive biosphere signal (Figure 1.3). Large seasonal variations in the Northern Hemisphere (Figure 1.3, left) and depletions of OCS in the continental boundary layer (Figure 1.3, right) were found to be quantitatively consistent with a priori knowledge that related OCS plant uptake to photosynthesis.

An explosive growth in OCS measurement capabilities followed. This included the first global satellite maps, global air-monitoring, sensors capable of continuous measurements at ambient levels, and global mechanistic models, leading to an unprecedented advance in the understanding of OCS budgets (e.g., Berkelhammer et al., 2014; Berry et al., 2013; Campbell et al., 2015; Fisher et al., 2014; Glatthor et al., 2015; Kremser et al., 2015; Krysztofiak et al., 2015; Kuai et al., 2015; Lejeune et al., 2017; Maseyk et al., 2014; Stimler et al., 2010a; Vincent and Dudhia, 2017; Wang et al., 2016).

The global atmospheric flask sampling network described in Montzka et al., 2007 served as a basis for understanding the distribution and seasonality of OCS concentrations in both hemispheres at Earth's surface, and from regular aircraft profiles, through much of the troposphere over North America. With the advent of commercially available quantum cascade laser spectrometers (Commane et al., 2015; Kooijmans et al., 2019; Stimler et al.,

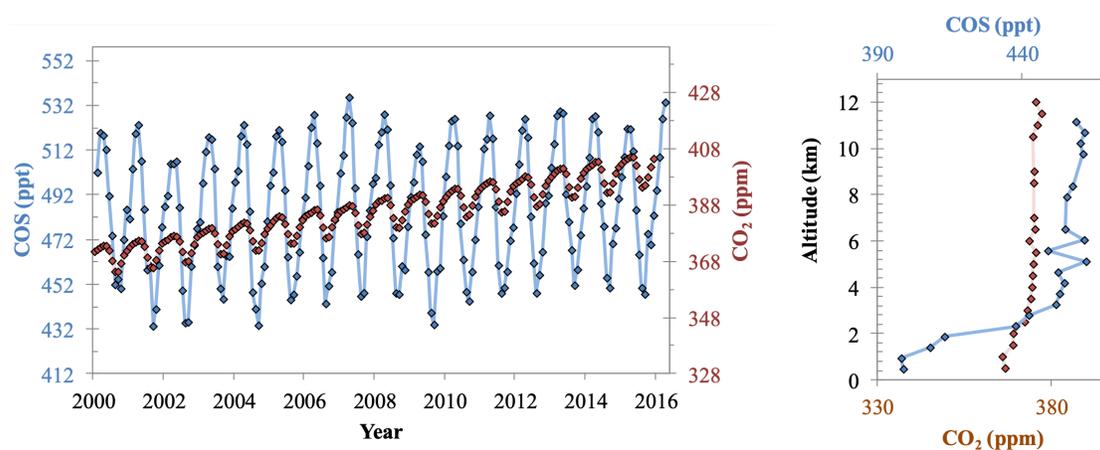


Figure 1.3: There is a striking difference in the variability of tropospheric OCS (blue) and CO₂ (orange). The NASA tropospheric drawdown (right) and NOAA seasonal cycle (left) are persistent signals due to terrestrial plant uptake of atmospheric CO₂ and OCS. The normalized variation in these data are 6 times larger for OCS than CO₂, because of the shorter lifetime for OCS. Data sources: (Campbell et al., 2008; Dlugokencky et al., 2001; Montzka et al., 2007).

2010b) and off-axis integrated cavity output spectroscopy analyzers (Berkelhammer et al., 2014), continuous atmospheric concentration measurements of OCS allowed for a mechanistic understanding of OCS sinks and sources in the laboratory and a refined understanding of the correlation between GPP (gross primary production or CO₂ uptake during photosynthesis) and OCS fluxes at the leaf and ecosystem scales (Belviso et al., 2020; Commane et al., 2015; Kooijmans et al., 2019).

Total column measurements of OCS with ground-based Fourier transform infrared spectroscopy (FTIR) largely improved the global coverage of OCS measurements (Kremser et al., 2015; Wang et al., n.d.). Besides this, intensive aircraft campaigns provide both atmospheric profile measurements and large-scale transects that allow for detailed studies on OCS, CO₂ and other tracers. OCS measurements from aircraft, FTIR, and AirCore samples could provide important data for validating satellite measurements of OCS.

Multiple factors contribute to the close relationship between atmospheric OCS abundance and photosynthesis. The dominant global sink of atmospheric OCS is a one-way hydration reaction in terrestrial plant leaves that is modulated by stomatal conductance (Stimler et al., 2010a). The dominant global sources are from oceans and Chinese industry (Berry et al., 2013; Campbell et al., 2015; Zumkehr et al., 2018). Many other sources and sinks have been observed, but they are a relatively small fraction of the global budget.

The spatial separation of the OCS dominant sink (tropical biosphere) and sources (ocean and anthropogenic) as well as the relatively moderate seasonal variation in the sources creates the strong relationship between atmospheric OCS concentrations over land and the photosynthesis activity below (Figure 1.4). Furthermore, unlike CO₂, the deep ocean is not a reservoir for OCS and does little to buffer changes in atmospheric OCS (Campbell et al., 2017a). This suggests that long-term OCS trends may be related to photosynthesis trends. Alternatively, the CO₂ exchange with the deep ocean results in a CO₂ relaxation time that is at least two orders of magnitude longer, obscuring the relationship between the atmospheric CO₂ change and ecosystem change.

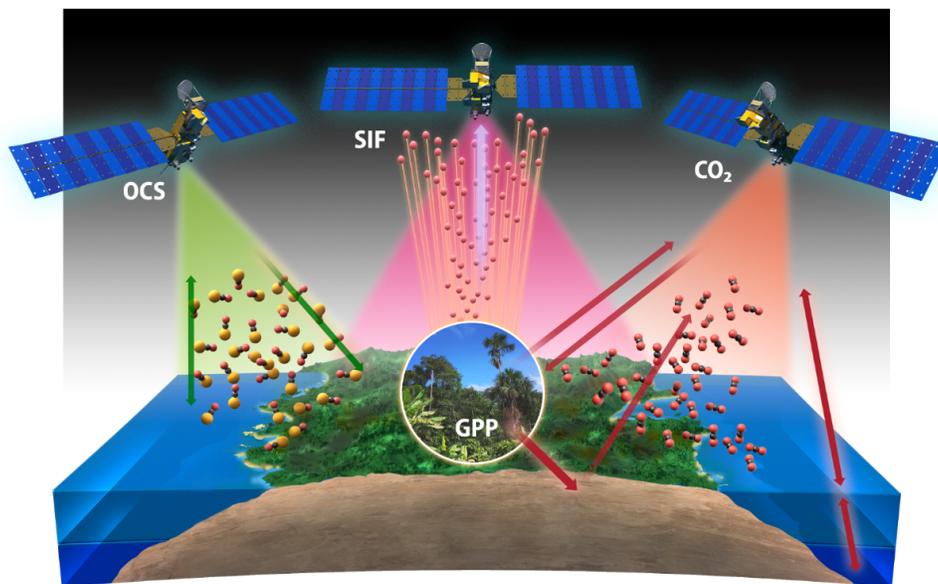


Figure 1.4: Natural sources and sinks for remote sensing of OCS, SIF, and CO₂. The natural carbon cycle (red) is dominated by exchanges between terrestrial photosynthesis (GPP), ecosystem respiration (Re), and the surface and deep oceans. The dominant global OCS fluxes (green) are the plant sink and surface ocean source. SIF is directly emitted from leaves. These three signals provide highly complementary views into net ecosystem exchange (CO₂) and controls on photosynthesis that are biophysical (OCS) and biogeochemical (SIF).

The key distinction between spaceborne SIF and OCS approaches is temporal coverage. SIF is an instantaneous measurement of light emitted from leaves that provides a snapshot of spatial variation in photosynthesis only at the time of the satellite overpass (Jeong et al., 2017). The satellite measurements of SIF are taken only once a day at any given location (Frankenberg et al., 2011). Integrating instantaneous SIF measurements over daily to monthly scales requires an understanding of its sensitivity to light and weather from dawn to dusk

across diverse plant functional types (Qiu et al., 2018). Furthermore, when optically thick clouds are present, as is often the case in the tropics, the ability to accurately measure SIF is lost (Figure 1.5, top).

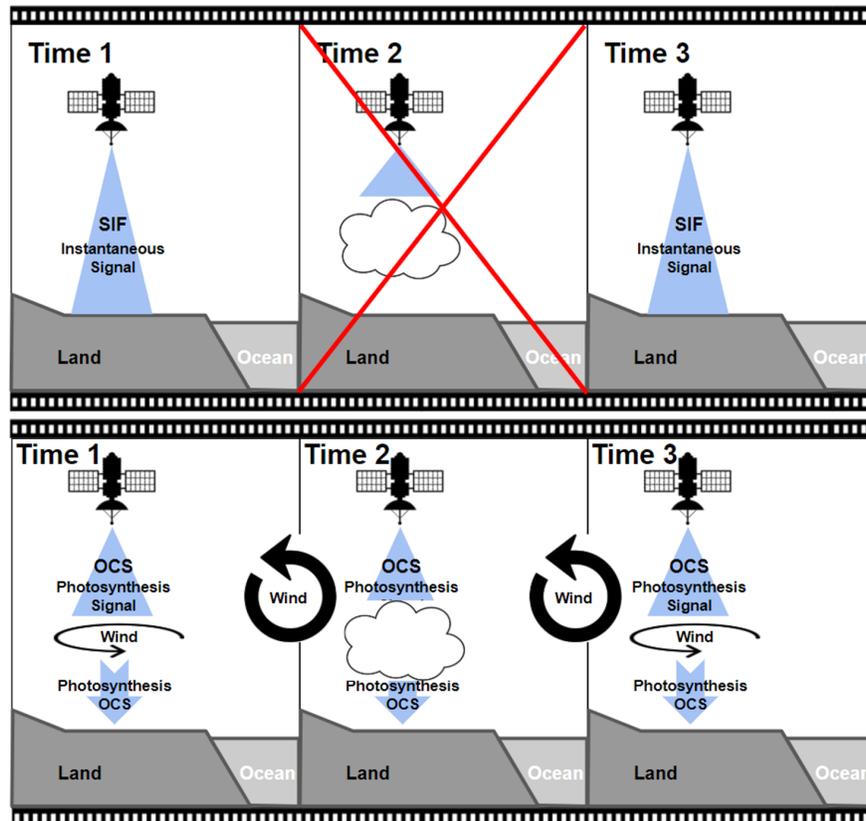


Figure 1.5: Temporal data, visualized as a filmstrip, for measurements of SIF (top) and atmospheric OCS (bottom). SIF provides an instantaneous snapshot of photosynthesis, providing detailed information during clear conditions but missing information during cloudy conditions. Atmospheric OCS provides a time integrated measurement due to wind-driven mixing of different air masses. The strength of SIF is the ability to identify short-term variation, but at the expense of losing information when clouds are present. OCS fills this critical gap by capturing a photosynthesis signal that is integrated in time to include both cloudy periods and clear periods.

The temporal and spatial attributes of the OCS approach help fill these critical temporal gaps in the SIF analysis, creating necessary and complementary measurement (Figure 1.5, bottom). The atmospheric OCS tracer is related to a temporally and spatially integrated signal from photosynthesis that is upwind of the OCS measurement. When clouds are present, the ability to accurately measure OCS is lost. However, the photosynthesis signal is preserved in time as the accumulated atmospheric OCS signal. When observed in clear sky conditions, OCS provides an integral view of the photosynthesis fluxes that were upwind

of the OCS measurement. Thus, the atmospheric OCS variation provides an archive of the photosynthesis activity that can be collected by satellites at times and locations that are not contaminated by clouds. **This unique temporal integration of the OCS method could have a transformative effect on our ability to quantify photosynthesis feedbacks to climate in the tropics.**

1.2.1 Emerging Awareness of Limitations of Conventional Measurement-based Methods

While new measurements in the past have faced strong resistance from the scientific community, now is a key time when an emerging community awareness may enable the realization of the potential of OCS and SIF measurements. Until recently, intellectual inertia was a critical roadblock to OCS and SIF science, with many members of the community considering more conventional techniques adequate for diagnosing the Earth system. And as with all new and complex techniques, initial skepticism in the larger community presented roadblocks to reaching a critical mass of research to fully leverage the technique. Such an outlook inhibits the development of new tools for practical reasons such as a reluctance to fund new initiatives. More importantly, this outlook is a barrier to the widespread collaborations that are needed to integrate members of the OCS and SIF community with experts focusing on conventional techniques and independent tracers that are needed to develop the implications of the OCS and SIF science.

Recent research activities, however, have motivated an adjustment in broader scientific perspectives. Awareness of the key contributions of conventional methods are now balanced by a widespread understanding of critical knowledge gaps that are not easily addressed with such techniques. Furthermore, technological breakthroughs and high-impact science on OCS and SIF suggest that the inevitable complications with these new approaches are surmountable.

1.2.2 Technical Motivation and Opportunities

Satellite-based OCS data could provide a time-integrated tracer of photosynthesis that is an indispensable complement for both the net signal related to CO₂ satellite data and the instantaneous signal related to SIF satellite data. Each of the three independent approaches has unique capabilities for detecting carbon–climate feedbacks that were previously not measurable. These independent lines of evidence also have unique limitations, and as with all emerging and complex techniques, hesitation from the larger community may initially prevent necessary research from being done to fully take advantage of the technique. However, leveraging all three independent lines of evidence in an integrated research approach could address both the real uncertainties and community inertia.

The integrated research approach requires a data assimilation framework that has primarily been used with CO₂, but thanks to recent advances could be applied to integrate all three data sources. For example, the 4D variational assimilation model STEM has been used for surface

flux optimization with OCS and CO₂ using ecosystem models that recently have been extended to incorporate mechanistic relationships between photosynthesis CO₂ flux, SIF emission signals, and OCS plant uptake (Campbell et al., 2008; Hilton et al., 2015, 2017). In this framework, the surface fluxes are propagated through the troposphere by observational operators (e.g., interpolating model grid cell results to aircraft profiles), meteorological models, and chemical transport models. The cost function compares the state of the simulated atmosphere and satellite data. The photosynthesis and respiration fluxes would comprise a state vector that is optimally adjusted to minimize this cost function, providing a unique opportunity to obtain process information needed for climate and crop science.

OCS satellite platforms such as Tropospheric Emission Spectrometer (TES), Advanced Composition Explorer (ACE), and Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) are near or past the end of their mission lives and this is an opportune time to explore the potential for future space-based OCS missions. The existing OCS satellite technology is primarily sensitive to the free troposphere, which is a useful constraint on background variability when assimilating surface and airborne data (Figure 1.6). Future missions with greater sensitivity in the boundary layer could improve detection of surface fluxes. The KISS study program explored the potential for follow-on missions to provide this key capability while also considering the integration with SIF (e.g., GeoCARB), CO₂ (e.g., OCO-2), evapotranspiration and skin temperature (e.g., ECOSTRESS), soil water (e.g., SMAP) and other satellite instruments (e.g., A-Train for temperature) to enhance overlap in the time and space domains. Plans for space-based missions will also include validation from OCS airborne (e.g., ACT America) and ground-based column observations (e.g., TCCON and NDACC).

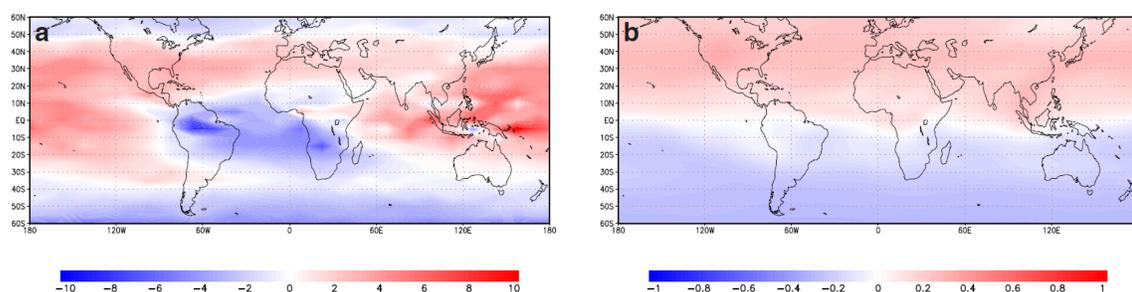


Figure 1.6: Upper troposphere (250 hPa) satellite retrievals of (A) OCS concentration variation from MIPAS (average binned observations, 2002 - 2012) and (B) CO₂ concentration variation from GOSAT (2013). Both plots express changes in concentration as percent deviation from the global annual mean at 250 hPa. Note that the colorbars on these plots are different and the CO₂ signal (-1% to 1%) is an order of magnitude less than that of OCS (-10% to 10%). Source: Stinecipher et al., In Preparation.

1.2.3 Scope of Study

To advance our understanding of OCS and its relationship to regional-scale photosynthesis, the Keck Institute for Space Studies (KISS) convened a workshop on the Caltech campus in September, 2017. The workshop followed on the heels of recent breakthroughs in OCS measurement capability, global budget information, and model development. The first global satellite maps for OCS from TES and MIPAS showed strong similarities with spatial and temporal patterns in a priori global simulations (Glatthor et al., 2015; Kuai et al., 2015). Furthermore, laser-based sensors capable of continuous measurements for the detection of ambient variations have been developed and could enhance future satellite validation campaigns (Stimler et al., 2010a,b). Advances in bottom-up modeling provided the first mechanistic plant flux models, which were successfully implemented in a global atmospheric chemical transport model for interpreting variations in free troposphere mixing ratios (Berry et al., 2013). The ecosystem model is built into the Simple Biosphere Model (SiB) which has mechanistic representations of OCS plant uptake, SIF emissions, CO₂ photosynthesis flux, and CO₂ ecosystem respiration flux. The workshop also leveraged recent collaborative activities within the OCS (EGU/Aerodyne funded workshop, Finland, August, 2016) and SIF communities (KISS, Pasadena, August, 2012).

The study program directly benefited from collaborations between JPL/Caltech Campus and leading experts in OCS modeling and measurements. JPL and Caltech have measurement expertise in satellite and surface-based column OCS measurements and terrestrial ecosystem science. However, the leading scientists in OCS flux measurements and global budget modeling are external. The meeting provided the first workshop to bring these OCS teams together with the added SIF and CO₂ satellite communities.



2. Components of the Study: Schedule and Organization

The success of this workshop required the energetic participation of leading scientists from multiple fields which have historically not been closely connected. We recruited eager participants from three key communities: space science, atmospheric chemistry, and ecology. Forging a deeper connection between these three communities is essential to planning an integrated analysis of CO₂, OCS, and SIF data. The interactions between these communities at the KISS workshop provided a seed from which to develop a vibrant inter-disciplinary research community (e.g., Kuai et al., 2015).

The KISS workshop was used to articulate a vision for coupled analysis of OCS retrievals with satellite-based SIF and CO₂ data, providing a new window into the carbon cycle and a change in our understanding of carbon–climate feedbacks. Key workshop goals were to move beyond the disparate analyses of OCS, SIF, and CO₂, and create a common language, basic understanding of opportunities and uncertainties, shared data sets, and a roadmap for an integrated space-based OCS-SIF-CO₂ mission to address critical outstanding science questions answerable through the intersection of such measurements. The science workshop was 5 days in duration with the scheduled elements listed in the appendix.

Workshop participants included junior members who the team leads had identified as rising stars in the field. The co-leads worked with them to ensure their active participation, particularly in the activities that were focused on junior members (e.g., poster sessions).



3. Outcome of Study: Schedule and Organization

3.1 Conventional Methods and Their Limitations

The new OCS and SIF measurements explored in this workshop represent a fundamental shift from conventional methods. Nevertheless, these critical new techniques are developed within the context of fundamental ecosystem knowledge resulting from conventional methods. These conventional methods include CO₂ inverse analysis, satellite vegetation indices, and eddy flux measurements, which provide a critical reference point for the development of the new OCS and SIF techniques.

Previous studies using these conventional methods suggest that land processes are responsible for much of the variability in the annual airborne fraction (annual CO₂ increase in the atmosphere). Models are unable to reach a consensus around the question of how the natural CO₂ net sink on land, currently estimated to be around 25% of annual anthropogenic CO₂ output, will evolve over the next century. Models do not agree about the magnitude of current photosynthetic uptake on regional to global scales, ecosystem variability across scales (diurnal, synoptic, annual, interannual), or biophysical response to stressors such as drought. Understanding the carbon–climate–water link contained in photosynthesis, whereby evaporation and carbon uptake are linked through stomatal processes, is critical to resolving these gaps in understanding.

These knowledge gaps are not uniform. We seem to have a better ability to describe the behavior of some ecosystems, in the form of equations discretized into computer simulations. These ecosystems are generally those in North America and Europe, due to the fact that they are more scrupulously studied both on the ground and from the air. Other important ecosystems, such as those in the tropics and arctic, are not well understood at all. This

can be due to the remoteness of location, or lack of affluence of the countries where these communities reside.

A fundamental challenge in our knowledge of photosynthesis is that we do not currently possess physics-based equations describing stomatal behavior. Empirically derived equations such as the Ball–Berry equation are used to reasonably reproduce plant behavior at plant- to landscape-scale. These equations take the general form of

$$g_s = mA_n H / C_i + b \quad [1]$$

where

g_s = stomatal conductance

m = empirically derived slope parameter

A_n = net photosynthesis

H = relative humidity at the leaf surface

C_i = intercellular partial pressure of CO₂

b = empirically-derived intercept parameter

We can think about the stomatal opening as an optimization, whereby carbon uptake (A_n or GPP) is maximized for a minimal water loss. New observations may provide insight into both sides of our stomatal regulation parameterization.

Observation networks of global CO₂ concentration, satellite vegetation indices, and eddy covariance flux estimates have helped to fill these knowledge gaps. The current state of these methods and their limitations with respect to understanding photosynthesis were explored during the workshop and are reported below.

3.1.1 CO₂ Inverse Analysis

CO₂ concentration has been observed at the Earth's surface since the late 1950s, although the number of stations was very few prior to the 1980s. Particularly significant measurements for large-scale carbon cycle assessment are those made from airborne profiles and surface-based observatories that gather point measurement (e.g., NOAA tall towers) or retrieve atmospheric column data (e.g., Total Column Carbon Observing Network).

The first satellite measurements of carbon dioxide with sensitivity to the lower troposphere were provided by SCIAMACHY on Envisat, which was launched in 2002. The poor precision and accuracy of the XCO₂ measurements made the interpretation of these data difficult, but they proved that such an approach held great promise. Additional satellite missions including the Orbiting Carbon Observatory (OCO), Greenhouse Gases Observing Satellite (GOSAT), and the Orbiting Carbon Observatory 2 (OCO-2) were designed with the high spectral resolution and wide spectral coverage needed for measuring greenhouse gases from space (Crisp et al., 2017, 2008; Eldering et al., 2017a; Eldering et al., 2017b, 2019).

These atmospheric CO₂ measurements are used as input to inverse models in order to infer land surface processes such as photosynthesis rates. Inverse models account for atmospheric winds to create a relationship between land surface processes and the chemical fingerprints that these land surface processes leave in the atmosphere. The inverse models take the CO₂ atmospheric concentration measurements and wind estimates as input, and in turn, output estimates of the net land surface CO₂ flux.

3.1.2 Satellite Vegetation Indices

Remote sensing provides an opportunity to observe biophysical behavior globally, including poorly understood regions. With vegetation indices such as NDVI, we have been able to observe the 'breathing' of the terrestrial biosphere in the form of changes in vegetation reflectance across synoptic to interannual scales. Higher spectral resolution data (as in the MODIS instrument) have allowed refinement of NDVI to generate models of Leaf Area Index (LAI) and GPP.

Remote sensing of vegetation indices, such as NDVI and EVI (Enhanced Vegetation Index), enabled the first global scale, regionally resolved maps of photosynthesis estimates, opening a new era of photosynthesis science based on remote sensing. By interpreting reflected light from the land surface in different wavebands as indices of substrates for photosynthesis (such as chlorophyll content, via the red edge spectrum, and amount of canopy structural material or Leaf Area Index, via the near-infrared spectrum), and combining these with estimates of drivers such as sunlight, researchers were able to estimate photosynthetic activity (Turner et al., 2006). The VIs by themselves also proved to be effective at tracking changes in vegetation over the weeks to months following climatic events, such as droughts and heat waves, at high temporal and spatial resolution (Peters et al., 2002). Work continues to refine the VIs, particularly on increasing the representativeness of NIR (i.e., NIRv), to improve the link to GPP.

3.1.3 Eddy Covariance (EC) Flux Measurements of CO₂ and Water

Eddy flux towers have proved to be a critical point of reference (ground truth) for all other larger-scale methods, and a real-world laboratory for exploring and testing our understanding of processes. Eddy flux towers are used to estimate spatial and temporal variations of carbon, water vapor, and energy surface fluxes across a range of ecosystems from the tropics to the arctic (currently, 914 sites registered to FLUXNET: <http://fluxnet.fluxdata.org/sites/site-summary>).

These estimates have been combined with machine learning models to produce continuous global maps of GPP, as well as evapotranspiration and respiration (Beer et al., 2010; Jung et al., 2010, 2017). The resulting flux data has led to the discovery of novel ecosystem processes, such as enhanced light use efficiency with increases in diffuse radiation fraction, as well as tight correlation between GPP and ecosystem respiration (Baldocchi et al., 2001).

A direct connection has been detected between carbon and water fluxes, which enables the investigation of water use efficiency (Keenan et al., 2013). These data also provide information on the relative control that abiotic and biotic variations have on trends in GPP (Keenan et al., 2013; Zscheischler et al., 2016). Previous work has also used eddy flux data as reference data to evaluate satellite-based GPP (Running et al., 1999). This technique has also been applied to OCS trace gas measurements yielding estimates of GPP, water fluxes, and ecosystem stress at the canopy scale (Commane et al., 2015; Maseyk et al., 2014; Wehr et al., 2017).

3.1.4 Methodological Limitations of Conventional GPP and ET Observations

While CO₂ inverse analysis, satellite vegetation indices, and eddy flux approaches have led to profound advances in knowledge of ecosystem processes, these three techniques have critical limitations with respect to photosynthesis studies that call for the development of new, complementary measurement-based techniques to address persistent knowledge gaps. A key limitation of CO₂ inverse analysis for understanding photosynthesis is due to the co-location of photosynthesis and respiration. Uptake of CO₂ by photosynthesis is of similar magnitude to the co-located CO₂ emission by ecosystem respiration. Thus, the inverse method is an analysis of an atmospheric CO₂ concentration signal that is a very small residual resulting from two relatively large gross surface fluxes from the GPP sink and the respiration source. The CO₂ inverse analysis cannot easily separate these two processes due to their close proximity in time and space. CO₂ inverse analysis is a useful technique for understanding net ecosystem exchange ($NEE = \text{photosynthesis} - \text{respiration}$), but an independent line of measurements would be needed to partition this net CO₂ signal for an understanding of the underlying photosynthesis and respiration components that are needed to resolve carbon–climate feedbacks. This inverse analysis is also limited by the uncertainty of prior fluxes and atmospheric mixing.

Satellite NDVI data are more closely associated with GPP than NEE, but NDVI senses the structural substrates of photosynthesis rather than activity associated with photosynthesis itself. Photosynthesis can critically diverge from photosynthetic-associated structures due to changes in physiological states that are not directly detected (although they may in some cases be inferred from changes in drivers). For example, NDVI is a measurement of ecosystem structure (e.g., Leaf Area Index – quantity of leaves) and function (e.g., leaf level photosynthetic assimilation capacity – quality of leaves), rather than GPP. More leaves can coincide with higher rates of photosynthesis but other factors must be accounted for in models that extrapolate from vegetation index data to photosynthesis estimates, such as ambient temperature, light, and soil moisture. Thus, while remotely sensed vegetation indices provide advances in observable vegetation structure, they do not provide a measurement-based estimate of photosynthesis. Furthermore, cloud contamination and high aerosol loadings increase the uncertainty of NDVI data, particularly in the tropics. An additional challenge is the saturation of the NDVI signal in the tropics and other high LAI ecosystems. Sun–sensor

geometry influences the accurate interpretation of satellite data and requires a Bidirectional Reflectance Distribution Function (BRDF) to obtain adjusted reflectance.

The critical limitation of eddy flux data in the context of global change is spatial scale. Eddy flux data provide information at the spatial scale on the order of 1 km², but due to spatial heterogeneity, global Earth system models require validation data at much larger spatial scales (regional to global). This limits the global representativeness of such data, and biome representativeness (no disturbance, bias towards growing ecosystems). Complimentary observation techniques are needed to provide information at regional scales that are relevant to Earth system models and the resulting simulations of carbon–climate feedbacks.

3.1.5 Implications of Methodological Limitations

These methodological limitations have led to persistent and critical knowledge gaps in the global Earth system. The continuing elevated fossil fuel emissions and their impact on climate affect the magnitude and spatial distribution of terrestrial GPP in fundamental (Norby et al., 2005) but uncertain ways (Friedlingstein et al., 2006, 2014; Huntingford et al., 2013). This uncertainty constitutes a critical limitation in the accuracy of model predictions of future atmospheric CO₂, crop production, and carbon–climate feedbacks (Friedlingstein et al., 2006, 2014; Schimel et al., 2015).

The uncertainties are focused in the tropics. There is a large spread in estimates of GPP from tropical rainforests. Important sources of uncertainty are V_{cmax} , leaf demography, and Leaf Area Index. Models fail to capture the seasonal GPP dynamics and decoupling of evapotranspiration (ET) and GPP, which are driven by hydrology and leaf demography. Models also fail to capture the interannual variations of GPP which are driven by meteorology, hydrology, and phosphorus limitation. There is a particularly large spread in the estimates of the CO₂ fertilization effect on GPP in the tropics (Schimel et al., 2015).

3.2 OCS Inverse Analysis

To inform the global Earth system models for a more realistic and reliable projection for the future, it is necessary to provide a new source of measurement-based data that can fill the critical knowledge gaps left by conventional methods. To meet this critical need, we propose the inverse analysis of satellite retrievals of tropospheric OCS mixing ratios as a new tool for observing GPP at regional to global spatial scales.

Plant uptake of OCS is closely related to photosynthesis. Different rates of photosynthesis create different chemical OCS signals in the Earth's troposphere. Measuring this observable OCS signal with satellites and interpreting this measured OCS signal with inverse atmospheric models in order to infer GPP has the potential to transform our understanding of photosynthesis.

3.2.1 Three OCS Attributes for Carbon Cycle Applications

It was proposed that **three attributes** of OCS budgets create the opportunity for OCS applications to regional photosynthesis studies (Campbell et al., 2017a):

1. **Regional Attribute – Spatial Separation of Sources and Sinks:** The dominant global OCS sources are tropical oceans and Asian industry, which are generally spatially separated from the dominant global sink due to terrestrial plant uptake. This spatial separation of the sources and sinks causes plant uptake of OCS to leave a robust chemical signature in the continental atmospheric boundary layer (Figure 3.1b). Thus, regional GPP could potentially be estimated from OCS inverse analysis over the continents. For comparison, atmospheric CO₂ has co-located GPP CO₂ sinks and respiration CO₂ sources, which are similar in magnitude but opposite in sign, preventing the use of CO₂ inverse analysis as a regional tracer of GPP. Examples of applications that leverage this OCS regional attribute include studies of the vertical drawdown in the continental boundary layer using NASA airborne intensive campaign data (Campbell et al., 2008) and NOAA airborne monitoring data (Hilton et al., 2017).
2. **High-Latitude Attribute – Seasonality of Sources and Sinks:** Global chemical transport simulations suggest that the terrestrial OCS plant sink drives the seasonal cycle of atmospheric OCS concentrations in Northern Hemisphere high-latitudes (Figure 3.1). This feature is due to the relatively small seasonal amplitude of the ocean and industrial sources and the relatively large seasonality of the OCS plant sink. Because the OCS plant sink drives the seasonal amplitude, it may be possible to use OCS inverse analysis to infer Northern Hemisphere GPP from the seasonal or secular changes in atmospheric OCS concentration. Studies that leverage this high-latitude attribute are underway now.
3. **Global Attribute – Fast Response of OCS Source:** The lifetime of atmospheric OCS has been estimated using both budget and Junge approaches to be between 1 and 3 years (see supporting online material of Campbell et al., 2008). This 1- to 3-year lifetime hits a sweet spot for inferring global GPP from long-term records (e.g., decadal records). In particular, this 1- to 3-year lifetime is long enough for OCS to be globally well-mixed, but not so long as to obscure the dynamics of sources and sinks over the industrial era. An application that has leveraged this global attribute of OCS budgets is a study of long-term records from solar spectrum and Antarctic firn data to estimate a high rate of global GPP growth over the industrial era (Campbell et al., 2017b).

While a number of studies have already leveraged these three OCS attributes to answer persistent questions about GPP, more refined questions about GPP will require a more refined understanding of the global OCS budget. We review the sources and sinks in the global OCS budget as follows.

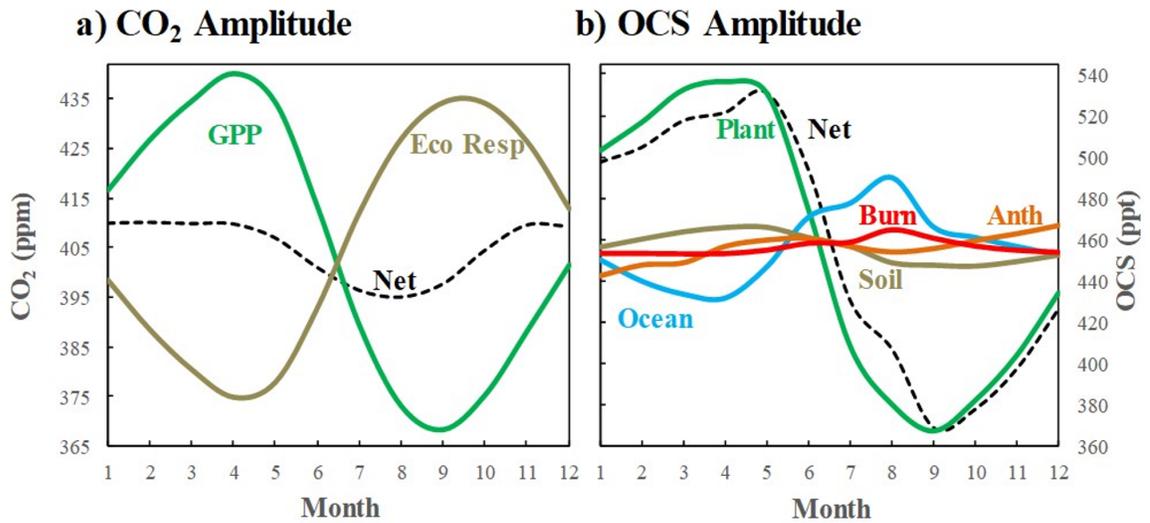


Figure 3.1: Simulations of the seasonal cycle of tropospheric (a) CO₂ and (b) OCS mixing ratios at the Barrow Atmospheric Baseline Observatory. The net signal (dotted black line) is obtained from a global atmospheric transport simulation using all the dominant sources and sinks while the signal components (colored lines) are obtained by running the global atmospheric simulation with one component flux at a time. The CO₂ seasonality at this background observatory is characterized by two large and offsetting components from GPP and ecosystem respiration. The OCS signal, however, is dominated by the plant uptake component. (Source: Campbell et al., In Prep.)

3.2.2 OCS Global Budgets

It has been demonstrated that plant uptake of OCS is strongly related to stomatal conductance (g_s) which in turn is closely related to GPP, particularly at integrated scales in space and time (Hilton et al., 2017). OCS is increasingly being observed at flask stations, by eddy covariance towers, and, increasingly, by satellites (Barkley et al., 2008; Commane et al., 2015; Glatthor et al., 2017; Kuai et al., 2014; Maseyk et al., 2014; Wehr et al., 2017). This provides a potential window into 'front end' (the left-hand side of Equation 1) processes on the plant scale.

While this relationship between OCS and stomatal conductance is essential to the OCS method, a number of other OCS sources and sinks must be accounted for in robust applications of OCS inverse analysis. We review these other OCS sources and sinks below.

3.2.2.1 OCS Sources

The major sources of atmospheric OCS are derived from oceans and Asian industrial emissions. Sources include direct emissions of OCS to the atmosphere (e.g., coal combustion) as well as indirect sources from the emissions of chemical precursors that are rapidly oxidized to OCS

in the atmosphere (e.g., CS₂ emitted from rayon production). Characteristics of the spatial, seasonal, and interannual variability of these sources are essential to the applications of the OCS method in understanding global photosynthesis.

The surface oceans emit OCS and OCS precursors to the atmosphere. When the concentrations of OCS in regions of the surface ocean dip below saturation, the ocean can act as a sink, but on the whole the ocean is a large source to the atmosphere (Kettle et al., 2002). Bottom-up inventories using ocean cruise data estimate this source at 345 Gg S y⁻¹ (both direct and indirect sources) (Lennartz et al., 2017, 2020). Ocean models and top-down atmospheric studies find larger estimates of 465 to 1,089 Gg S yr⁻¹ (Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2014). Additional cruise data and top-down studies are needed to resolve this budget gap.

The largest continental source is emissions from anthropogenic activities which have been quantified globally over the industrial era (Campbell et al., 2015) and extrapolated in space in regional gridded inventories and global gridded inventories (Whelan et al., 2018; Zumkehr et al., 2018). The most recent estimate of the global source is 406 Gg S y⁻¹ (range of 223–586 Gg S y⁻¹), which is highly concentrated in China (Zumkehr et al., 2018). Rayon production and coal combustion (both residential and industrial) are the two largest source sectors. Bottom-up estimates of the source are consistent with Antarctic firn, global air-monitoring, and satellite measurements (Campbell et al., 2017b; Zumkehr et al., 2018).

Biomass burning contributes a significant global source that has recently been estimated at 116 ± 52 Gg S y⁻¹, including open burning, agriculture waste, and traditional biofuels (Campbell et al., 2015; Stinecipher et al., 2019). While emission factors embedded in these bottom-up inventories have large uncertainties, recent top-down studies provide consistent results (Stinecipher et al., 2019).

3.2.2.2 OCS Sinks

The dominant global sinks of atmospheric OCS include uptake by terrestrial plants, soils, and in situ atmospheric chemical reactions. The plant uptake has been explored in biochemical studies that reveal a one-way hydration sink of OCS in leaves, catalyzed by the enzyme carbonic anhydrase (Sandoval-Soto et al., 2005; Stimler et al., 2010b). Extrapolation of these empirical relationships using a mechanistic biosphere model yields a global sink of 740 Gg S y⁻¹ (Berry et al., 2013), while the use of the full range of global GPP models yields and parameter estimates provides a range of 400 to 1,360 Tg S y⁻¹ (Campbell et al., 2017b). The large uncertainty in GPP drives the uncertainty in the OCS plant uptake and in turn provides the opportunity to use OCS observations to constrain GPP. These physiological studies indicate that the OCS plant uptake flux is largely controlled by stomatal conductance—which is also a strong control on GPP. Analysis of eddy flux data (Asaf et al., 2013) and planetary

boundary layer observations (Berry et al., 2013; Campbell et al., 2008) are consistent with this biochemical theory.

An additional plant sink that is not closely related to GPP is nocturnal plant uptake. Incomplete closure of stomata at night results in OCS plant uptake (Berkelhammer et al., 2014; Kooijmans et al., 2019; Wehr et al., 2017). The air in the lower canopy is depleted of OCS at night. When the sun comes up and the nighttime residual layer breaks down in the canopy (Fisher et al., 2007), there is low concentration OCS flushing out into the planetary boundary layer. This can create artifacts of strong uptake in the early morning in eddy flux experiments (Harvard Forest, U.S.; La Selva, Costa Rica) (Wehr et al., 2017).

Soil chamber experiments in the field have found that the exchange between soils and the atmosphere generally results in a sink (Commane et al., 2015; Kesselmeier and Merk, 1993; Whelan et al., 2016). Extrapolating to the global scale yields a soil sink of between 70 and 180 Gg S y⁻¹ from the atmosphere (based on a standard exchange rate of 10 pmol m⁻² s⁻¹ and correction factors for soil water content, temperature, and atmospheric OCS concentration) (Campbell et al., 2017b).

The atmospheric in situ sink of OCS is primarily through oxidation by OH. This gas-phase chemical sink has been estimated at a global scale for present conditions to be between 82 and 110 Gg S y⁻¹ based on climatological OH concentration data and a temperature dependent chemical rate coefficient (Kettle et al., 2002).

3.2.2.3 Balancing the OCS Global Budget

The global OCS budget is dominated by the plant sink and the ocean and Asian anthropogenic sources. Attempts to balance the budget with a priori estimates suggest that the largest uncertainty in the global budget is associated with the ocean source. As noted above, additional ocean cruise experiments, particularly in the tropical Western Pacific, may be needed to resolve this uncertainty.

3.2.3 OCS Measurements

The understanding of these OCS sources and sinks has been advanced through a wide range of field and laboratory experiments. Here we review the key sources of measurement data from satellite, airborne, ground-based, and laboratory experiments. The observation data are also summarized in the Appendix (Table A1).

3.2.3.1 Satellite OCS Measurements

Up until now, there has been no satellite mission dedicated to the measurement of OCS from space. Nonetheless, various groups have exploited the fact that existing thermal infrared sensors measure near the 2050 cm⁻¹ spectral region, and have used these measurements to retrieve OCS at this wavelength. This has so far been done for measurements from the satellites including ACE-FTS (Barkley et al., 2008), TES (Kuai et al., 2015), MIPAS

(Glatthor et al., 2017), and IASI (Vincent and Dudhia, 2017). Only ACE-FTS and IASI are still operational. TES and IASI are nadir-viewing instruments but ACE and MIPAS are both limb-viewing instruments. Therefore only ACE and MIPAS provide upper tropospheric and stratospheric observations of OCS. TES and IASI measurements have similar averaging kernels that are representative of the mid- to upper troposphere. Figure 3.2 shows the GEOS-Chem model simulations driven by the updated tropical ocean flux with the constraint by TES OCS observations that result in an elevated tropical west Pacific OCS source. The HIPPO aircraft campaign data also indicate higher tropical Pacific OCS than mid and high latitude regions (Kuai et al., 2015).

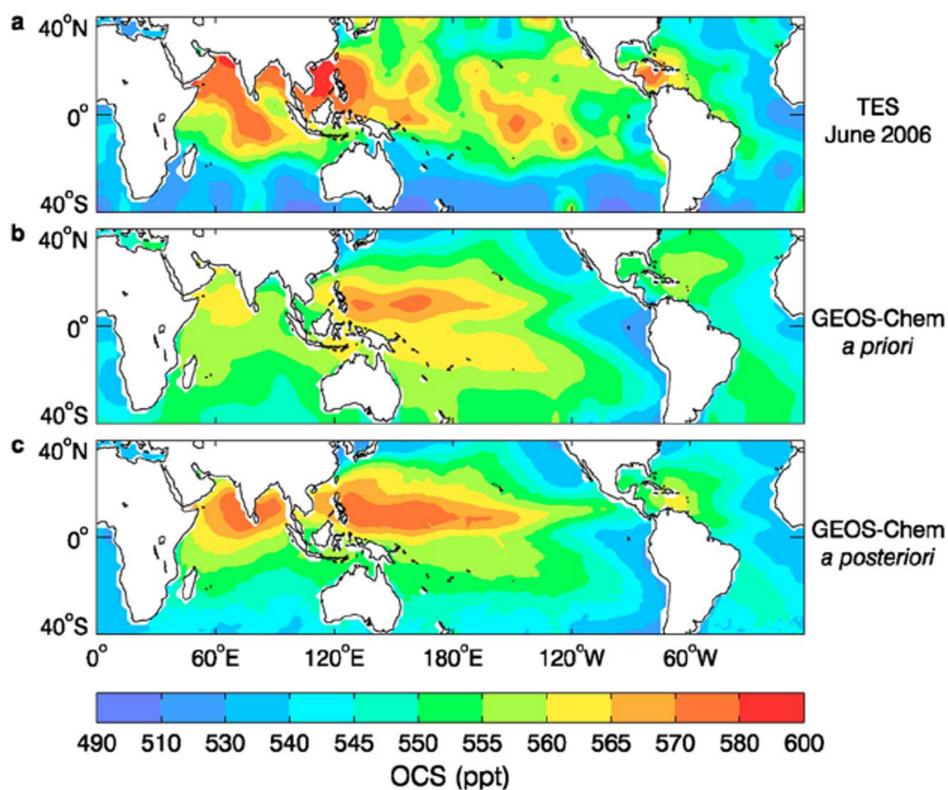


Figure 3.2: Maps of free troposphere OCS (ppt) for (a) TES observations from space in June 2006, (b) GEOS-Chem simulated OCS driven by baseline fluxes, and (c) simulated OCS driven by TES optimized tropical fluxes.

Retrieval over cold surfaces is more difficult due to the poorer thermal contrast between the surface and the atmosphere, and validation and calibration data over land are very limited. Here the ground-based FTIR network of NDACC and TCCON could play an important role, but these experimental retrievals also first require calibration. Once these measurements have been calibrated, they can more easily be incorporated into an OCS inverse modeling framework to estimate surface fluxes.

The averaging kernel weighting in the upper troposphere means that application of these measurements for the estimation of surface fluxes is not uncomplicated. Satellite measurements of trace gas concentrations that are intended for use in surface flux estimation can be designed to have averaging kernels that are representative of the lower troposphere to increase their sensitivity to surface processes. While existing OCS satellites are more sensitive to the mid- to upper troposphere, which makes them less sensitive to surface processes in regions with more stable boundary layers such as North America, these higher altitude measurements may provide useful information to surface processes in regions with high rates of deep convection, such as the tropics. For example, MIPAS data from the upper troposphere show a deep depression in OCS mixing ratios over tropical rainforests due to the presence of deep convection. Lower altitude measurements from tall towers and small aircraft would not see this high-altitude signal, which contains important information relevant to photosynthesis at the surface.

3.2.3.2 Solar Spectra OCS Measurements

A global FTIR network has obtained solar spectra at numerous sites, the first beginning in 1978 (Kesselmeier et al., 1999; Kremser et al., 2015; Lejeune et al., 2017; Rinsland et al., 2008; Wang et al., 2016). The total mass of OCS in an atmospheric column can be retrieved from these spectra. Column OCS mass has been retrieved using a range of algorithms to partition the column into partial troposphere, full troposphere, and stratosphere components.

A limitation for the use of the FTIR OCS retrievals is the lack of calibration. However, FTIR data can be used without calibration to estimate relative changes in OCS (Campbell et al., 2017b). Furthermore, calibration data is now available. The ATOM-1 airborne campaign flew over NDACC network sites Eureka and Lauder, and can be used to calibrate the OCS profile retrievals.

3.2.3.3 Airborne OCS Measurements

There are three types of flights that have measured OCS by flask sampling and GC-MS over the past number of years. These include flights that cover global latitudinal gradients (HIPPO, ATOM), regular survey flights at set locations (NOAA network), less frequent survey flights (ABOVE, CARVE), and intensive regional airborne campaign studies (e.g., ACT-AMERICA, CalNex, DC3, INTEXA/B, TC4, TRACEP, etc.). Airborne flask measurements are made by a number of groups and consistent calibration scales have not been applied to all projects. Comparisons between projects require careful consideration of the calibration scales used.

The NOAA vertical profiles are flown on approximately monthly intervals at many global sites and shorter intervals at select sites (www.esrl.noaa.gov/gmd/ccgg/aircraft/index.html) (Campbell et al., 2008; Hilton et al., 2017; Montzka et al., 2007). These data have shown vertical drawdown in the continental boundary layer that is quantitatively consistent with regional atmospheric models of OCS plant uptake (Campbell et al., 2008; Hilton et al., 2017).

Data covering large latitudinal transects have include several multi-year, pole-to-pole flightpath plans. The HIPPO campaign included five sub-campaigns between years 2009 and 2011 (January, March, June, August, October). A similar approach was taken by the ATOM campaign with four sub-campaigns for years 2016 through 2018 (February, May, August, October).

Intensive airborne campaign data have been used to provide spatially dense data that complement the long-term NOAA data. These intensives provide information on regional terrestrial plant uptake (Campbell et al., 2008), but also targeted source characterization such as emission factor information in the outflow from Asian anthropogenic activities (Blake et al., 2004).

3.2.3.4 Ground-Based OCS Measurements

Tall towers provide temporally dense, sustained, and long-term sampling of trace gases throughout the atmospheric boundary layer. Measurements can be collected at multiple levels from the surface to the top of the tall tower high above the plant canopy, providing vertical profiles with sensitivity at local and regional scales. Continuous coverage at diurnal, synoptic, seasonal, and interannual scales offers integral constraints of atmosphere–land trace gas exchange over multiple years. Only a few strategically placed towers, such as from the North America network, are needed to resolve annual carbon budgets at the continental scale. Thus, tall towers complement eddy covariance and aircraft data by filling spatial gaps in eddy covariance networks and filling in temporal gaps from aircraft sampling networks.

Long-term observations of OCS at tall towers and other boundary layer sites are provided through the NOAA global air-monitoring network (Montzka et al., 2007). While most of the sites are in North America, global coverage includes a wide breadth of latitudinal bands. To complement NOAA measurements, new campaigns are being conducted at towers in the Hyttiälä reserve in Finland and the ATTO tall tower in Brazil.

To extend this long-term record back in time, studies of firn air and ice core samples have been used to create a 54,000-year record (Aydin et al., 2016). These data are relevant to modern studies of global change due to the large changes in global GPP and OCS concentrations that are apparent in interglacial records (Aydin et al., 2016).

Much of our knowledge about OCS has come from eddy flux tower measurements. OCS eddy covariance flux estimates generally trace well the diurnal and seasonal trends in NEE at flux tower sites. Estimates of leaf relative uptake (LRU) provide an empirical-based relationship to understand covariations in the concentration of CO₂ and OCS as controlled by individual leaf stomates. Despite leaf-level variations in LRU, the canopy relative uptake (GPP/FOCS) tends to converge to the vicinity of 1.6.

To obtain reliable GPP estimates from OCS, fluxes associated with soil emissions and nighttime uptake must be characterized properly. Soil flux must be characterized properly with a soil chamber. Although recent work has demonstrated small seasonality in soil flux, high sensitivity to temperature and soil moisture suggested that continuous soil chamber measurements under varying environmental conditions are needed (Whelan et al., 2016). For example, soils from agricultural and other managed lands may become strong sources under high temperature/solar radiation conditions (Maseyk et al., 2014). In those types of ecosystems, the soil source of OCS may coincide with the signal of plant uptake at local and potentially regional spatial scales under widespread environmental stress, and thus needs to be characterized with collocated soil chambers. Nighttime OCS uptake by the canopy (not including soil) has been observed at diverse locations and ecosystems. Long-term nighttime OCS budgets must be characterized at the site scale, in order to properly include this fraction of OCS uptake in the interpretation of large-scale OCS flux inversion estimates.

At flux tower scale, OCS is potentially well suited as a tracer for canopy conductance, as well as stomatal conductance on single leaves. Using the information provided by OCS, we can shed light on carbon–water cycle coupling. A direct application would involve using OCS flux to optimize canopy conductance, and then using the canopy conductance to partition evapotranspiration into transpiration and evaporation (Wehr et al., 2017). Following the extraction of canopy conductance information from OCS flux, we can then use OCS to falsify or validate the findings about canopy conductance changes during eddy covariance experiments.

In addition to tall tower and flux tower observations, field measurements in leaf and soil chambers provides important OCS flux information. Soil fluxes measured in the field often do not show the same, ideal behavior observed in the laboratory settings. For example, Kesselmeier et al., 1999 and Diest and Kesselmeier, 2008 reported a relationship between soil OCS uptake and soil moisture, temperature and ambient OCS. But in contrast, in Sun et al., 2017, there was no clear relationship between soil OCS flux and ambient OCS.

In an analogy to LRU, Berkelhammer et al., 2014 showed from soil chamber measurements that soil relative uptake (SRU) can be a useful construct to represent the empirical relationship between the soil OCS sink and the soil CO₂ respiration source. The different temperature responses of OCS soil uptake and CO₂ soil respiration give rise to a relationship between SRU and soil temperature: SRU (negative values) usually increases with temperature and asymptotically approach a high-temperature value. This relationship can be used to model soil OCS flux empirically.

Similar to soil chambers, leaf chamber observations of OCS flux in the field also show features deviating from the lab. In the laboratory settings, experimental plants are usually kept in happy conditions (well watered, incubated in artificial light, VPD not high, etc.), which is only

a subset of the possible conditions in the field. In leaf OCS flux measurements conducted at a freshwater marsh site, leaf OCS flux is strongly suppressed in the middle of the day by high VPD condition (Sun et al., 2018). Complementary measurements from both lab and field settings provide a comprehensive understanding of the dynamics of leaf OCS exchange.

3.2.3.5 Laboratory OCS Measurements

Much laboratory work has already been done on leaf and soil fluxes. The first researchers who attempted to quantify the flux of OCS between natural land and the atmosphere mistakenly used sulfur-free sweep gas in dynamic enclosures (Kuhn et al., 1999). This biased results because the mechanisms that control fluxes are often dependent on ambient concentrations. This error put into doubt years of data regarding the flux of sulfur-containing gases, particularly from soils where chamber-based methods dominated data collection. With the advent of commercially available quantum cascade lasers for detecting OCS, many datasets on OCS fluxes from soils have been generated (Whelan et al., 2018).

Laboratory experiments of leaf fluxes use flow-through leaf cuvettes made of relatively inert materials that will not provide a source or sink of OCS. A wide range of experiments have been conducted with respect to plant species, age, humidity, light, temperature, ambient OCS concentration, and ambient CO₂ concentration. These experiments find a relatively robust relationship between GPP and OCS plant uptake that is critical to the intended application for photosynthesis studies.

Laboratory experiments have resulted in a fairly straightforward approach to anticipating OCS fluxes from soils in the field. When dry, all non-desert soils generate OCS emissions that grow exponentially larger with temperature. The absolute magnitude of these fluxes varies with ecosystem: agricultural soils appear to have the largest emissions, followed by forests (both temperate and tropical) and then savannahs. There is no evidence yet to identify the chemical precursor to OCS soil production in soil; however, we have determined that it is not any of the variables found in soil reanalysis products.

All living soils exhibit some OCS uptake when wet, including desert soils. Soil uptake follows a temperature and a soil moisture optimum, indicating that it is a biotic process driving OCS uptake. This is further bolstered by carbonic anhydrase (CA) suppression studies, where soil uptake was reduced after adding CA inhibitors to soil samples (Kesselmeier et al., 1999).

These two pieces of knowledge allow us to approach the problem of OCS soil exchange in a practical way. When making OCS measurements at the site level, installing several automatic soil chambers and observing fluxes over seasonal change (for example, rainy season to dry season) will often generate enough data to model soil OCS fluxes with the biotic uptake/abiotic production framework. Even when OCS fluxes are at their highest, in hot dry agricultural soils, ignoring OCS soil fluxes introduces at most a 20% error in GPP estimates made with OCS (Whelan et al., 2016). Thankfully, most soils are not hot and dry, and

therefore this correction is always small. For the site level, the detail of the soil fluxes may be important to the overall calculation of fluxes. For the regional scale, the strict accuracy of soil fluxes is much less important (Hilton et al., 2017) and a larger effort to quantify the contribution of soil is probably not needed.

3.2.4 Regional and Global Application of OCS Analysis to the Carbon Cycle

While new insights into OCS budgets are rapidly evolving, the current state of OCS knowledge has already proven to be sufficient for early applications to the regional and global carbon cycle. At the regional scale, NOAA airborne OCS observations were used as a benchmark for North American GPP estimates from global ecosystem models (Hilton et al., 2017). This study leveraged the regional attribute of the global OCS budget (Section 4.2.1)—the dominant sources (oceans and Asian industry) are spatially separated from the dominant sink (plant uptake). The results suggest that North American GPP is concentrated in the mid-continent, which provides a benchmark for ecological models that have a wide range of spatial distributions for North American GPP.

At the global scale, long-term trends in Antarctic firn and FTIR data were used to estimate the percent increase in global GPP during the industrial era (Campbell et al., 2017b). This study was possible due to the global attribute of OCS (Section 4.2.1)—the lifetime of OCS is long enough for atmospheric OCS to be well-mixed but not so long to obscure the dynamics of sources and sinks. The long-term increase in GPP in global ecosystem models creates one of the largest and most uncertain feedbacks in climate change forecasts. In this OCS study, the long-term increase in GPP was found to be near the high end of the CO₂ fertilization rates simulated by global ecosystem models.

3.3 Space-based SIF Retrievals

Satellite retrievals of SIF have been used to better understand and predict the dynamics of terrestrial ecosystems from regions to the globe. Examples include: 1) inferring GPP to constrain the terrestrial carbon budget by combining SIF with process-based ecosystem models (Parazoo et al., 2014), 2) improving crop yield monitoring (Guan et al., 2016; Guanter et al., 2014), 3) interpreting the seasonal dynamics of the terrestrial carbon exchange with the atmosphere in tropical rainforests (Lee et al., 2013; Parazoo et al., 2013), 4) depicting vegetation phenology across a variety of ecosystems (Joiner et al., 2014), and 5) understanding ecosystem responses to climate extremes (e.g., drought and heat waves) and the underlying mechanisms of such responses (Parazoo et al., 2015; Sun et al., 2015; Yoshida et al., 2015).

These efforts demonstrate the potential of applying satellite SIF to directly monitor vegetation functioning, complementing the more conventional approaches of optical remote sensing of vegetation 'greenness' based on spectral reflectance (Huete et al., 2002). These advances have spurred research to mechanistically understand the coupling of SIF and GPP under

various canopy structures and environmental regimes (Porcar-Castell et al., 2014). Multiple site comparisons show that satellite SIF measurements fit linearly with GPP estimates from flux network data products (Sun et al., 2017). Towards smaller scales, the linear relationship between GPP and SIF tends to break down and shifts to nonlinearity (Magney et al., 2017).

The continuous global SIF observations by multiple satellites, e.g., Global Ozone Monitoring Instrument (GOME), Orbiting Carbon Observatory 2 (OCO-2), TROPospheric Monitoring Instrument (TROPOMI), etc. (Figure 3.3 and Figure 3.4) since 1996 provide the opportunity for a multi-decadal SIF record for overlapping instruments. How to reconcile multi-sensory measurements with different instrument characteristics and retrieval algorithm is key to using the multi-satellite global record for studying long-term change in photosynthesis (Parazoo et al., 2019).

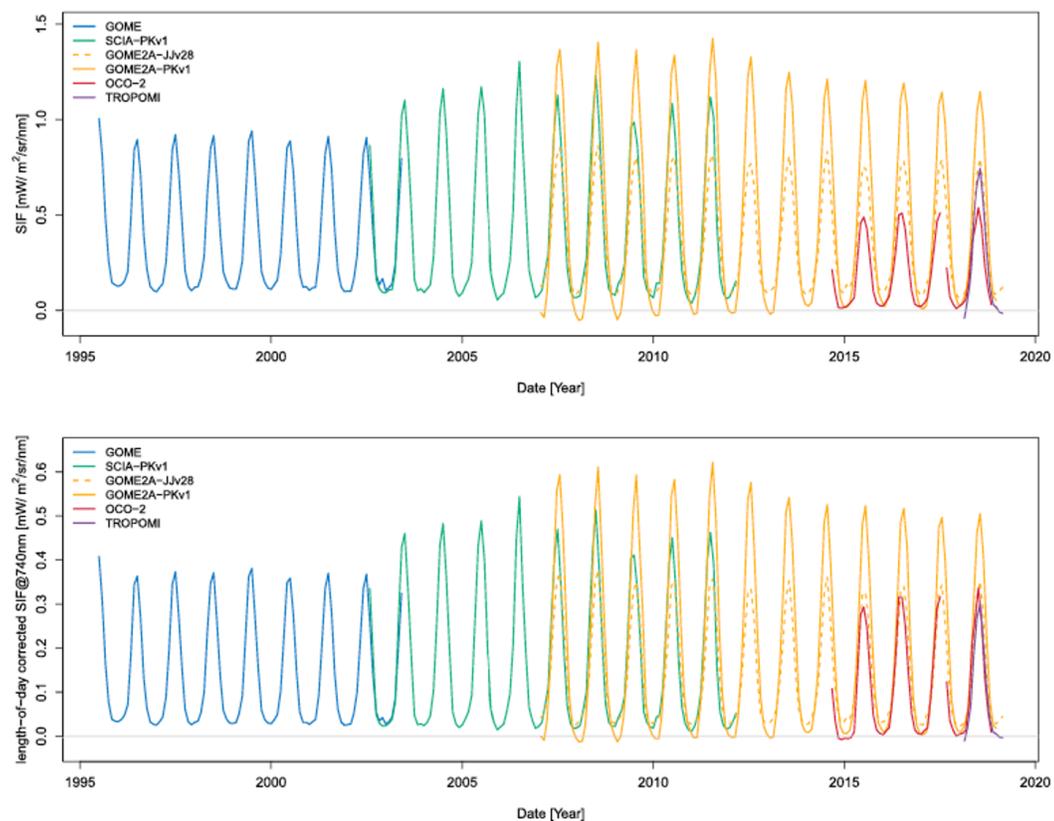


Figure 3.3: Time series of (top) instantaneous and (bottom) corrected (length-of-day and wavelength) SIF for all sensors averaged from 30 to 60°N over the period 1995–2018.

3.3.1 Site-Level SIF Observations

Making site-level observations of SIF is challenging. Currently, Li-Cor sells a leaf chamber that has a PAM fluorescence capability. In other words, SIF on the leaf level is trivial, but SIF

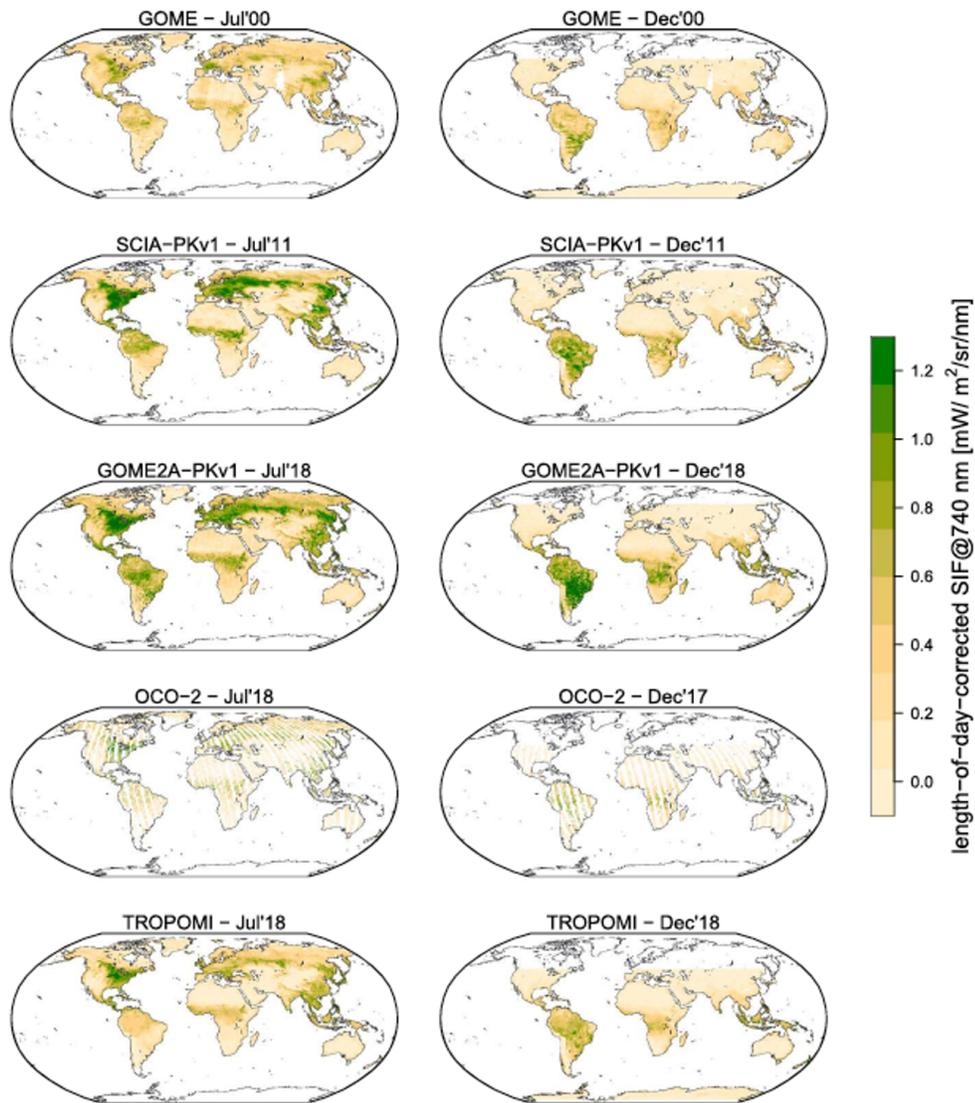


Figure 3.4: Monthly mean maps of length-of-day corrected SIF for all satellite sensors averaged for (left) July and (right) December. This shows differences between sensors in spatial coverage, spatial resolution, and magnitude.

on the site level is harder. Site level observations need a calibration target that the sensor looks at over time, that also happens to be weatherproof.

In order to observe and understand the process-level SIF dynamics in ecosystems, it is useful to isolate components in the field or extract components and manipulate them in a laboratory setting. Identical leaf chambers can be used in different settings to look at light transfer from leaves. Soils do not fluoresce at the same wavelengths as chlorophyll and do not need to be included in SIF measurements.

Several challenges to SIF observations remain to be addressed. Before making connections between airborne SIF with flux tower GPP, it is essential to evaluate airborne and satellite SIF against tower based SIF, which is the critical gap at this moment. Different groups measure canopy SIF in different ways (e.g., field of view, retrieval method, spectral bands, etc.). It is important to organize these in-situ SIF efforts into a network to share lessons and move forward together.

3.4 Integrating OCS and SIF into Multi-Tracer Analysis

Ultimately, we need multiple, independent lines of evidence to understand GPP. Any individual approach to estimating large-scale photosynthesis will suffer from unique uncertainties. For such a complex problem, there will likely be no silver bullet that can provide information about GPP. However, multiple lines of evidence may provide a tractable path for addressing this pressing concern in carbon–climate projections. In the case of OCS and SIF analysis, the approaches for constraining GPP are not only independent, but they address the problem in highly complementary ways with respect to the processes, temporal scales, and spatial scales.

3.4.1 Stomatal Conductance (Front End) vs. Biochemistry (Back End)

Simultaneous acquisition of OCS and SIF observations gives separate constraints on distinct parts of the photosynthetic chain process: OCS is consumed at the "front end" (after regulation by stomatal conductance OCS is consumed by reaction with carbonic anhydrase at the point of hydration within the leaf, before CO₂ carboxylation by Rubisco). SIF, on the other hand, is an indication of electron transport, the "back end" photochemistry (Figure 3.5). This allows, for the first time, large-scale separate constraints on different parts of photosynthesis.

Photosynthesis and transpiration are coupled through stomata, which regulate the carbon and water exchange between ecosystems and the atmosphere, effectively controlling water use efficiency. SIF can provide information on the electron transport rate, which is tightly coupled to photosynthesis. OCS fluxes are more directly related to the ambient OCS concentration and the bulk stomatal conductance, which are also closely related to photosynthesis but orthogonal to the SIF constraints.

A mechanistic modeling framework is needed to fully take advantage of the joint availability of SIF and OCS to constrain GPP, stomatal conductance, and water use efficiency estimates. So far, the promising SIF–GPP relationship obtained from observations is empirical and correlative in nature, and largely based on SIF products at coarse spatial and temporal resolutions. A mechanistic model built upon extensive ground measurements of SIF and GPP at high frequency will help elucidate how the true SIF–GPP relationship scales from leaf to canopy to landscape, and from diurnal to seasonal. In this front, the theoretical framework developed by (Gu et al., 2019) established the mechanistic ground on how to use SIF to estimate GPP from the light-reaction side will potentially guide future research in

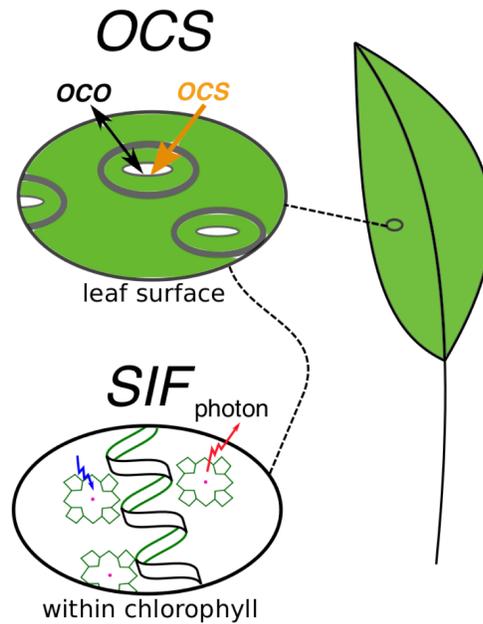


Figure 3.5: Measurements of OCS and SIF reflect different components of the photosynthesis process. OCS is most closely related to stomatal conductance which is a key constrain on photosynthesis while SIF is closely related to biochemical constraints. Diagram source: Whelan et al., 2020.

modeling GPP. On the other hand, to use OCS to constrain stomatal conductance, a key unknown factor is mesophyll conductance, which has been largely overlooked in the current photosynthesis-stomatal conductance model. The methodological framework built by Sun et al., 2014 and (Knauer et al., 2019) will potentially be incorporated into the OCS model to better estimate stomatal conductance. These modeling frameworks could be further refined and validated with existing ground measurements of OCS collected by this report. Finally, the SIF-based GPP model and mesophyll conductance resolved OCS-based stomatal conductance model can be integrated together to iteratively solve GPP and stomatal conductance.

3.4.2 Complementary Spatial and Temporal Attributes of OCS and SIF

SIF provides an instantaneous and spatially resolved snapshot of GPP at the time of the retrieval. These maps of GPP can be used to identify detailed spatial variability and, due to the time resolution, can be used to relate GPP to very specific environmental conditions. A limited number of satellite retrievals for a region may be available if the retrievals are constrained by how often the satellite overpass occurs or by the presence of clouds at the time of a snapshot. Extending these snapshots in time to create temporally integrated results such as monthly GPP or annual GPP estimates will require an ecosystem model and other environmental data (e.g., temperature, humidity, soil moisture, light) as input to that

model. This model-dependency of upscaling the temporal dimension of the SIF estimates may introduce biases.

Alternatively, OCS provides a record of GPP that is integrated over a range of time that precedes the OCS retrieval and over a region of space around the OCS retrieval. This time and space integration is caused by the turbulent mixing of atmospheric winds. As the OCS plant uptake affects the OCS ambient concentrations in the canopy air, turbulent mixing causes this canopy air mass to be mixed up into the continental boundary layer with air masses that were more heavily influenced by OCS plant fluxes from hours to days earlier and from tens of km away from the retrieval. The satellite retrievals of tropospheric OCS concentrations are capturing a photosynthesis record that is an integration over these time- and spatial scales. These tropospheric OCS concentrations are used as input to OCS inverse analysis, which in turn creates output that is a time-integrated GPP estimate.

The temporal and spatial attributes of the OCS and SIF approaches are highly complementary. While SIF can identify spatial variation in GPP such as hot spots, OCS can characterize the total regional GPP over a large time step, which is particularly relevant to global ecosystem models. Crucially, while cloud contamination of a SIF retrieval causes the loss of information at that time, an OCS satellite retrieval at a subsequent time when the clouds are not present may still allow information of the cloud contaminated period because the OCS approach is a time integrated analysis. This is particularly important in the tropics where persistent cloud presence means that is ecologically important to know GPP during cloudy period. SIF (and all other remotely sensed vegetation parameters) thus enable great spatial coverage and resolution at the expense of the lack of temporal and spatial integration; OCS acts orthogonally.

3.4.3 Canopy Integration

SIF observations on the canopy focus more on the upper canopy and may not give a canopy-integrated signal. OCS, however, may provide canopy-integrated information.

3.4.4 Amazon Application

We can use an example from the Amazon to illustrate the potential value of OCS and SIF. This region straddles the equator, and therefore has little seasonality in temperature. Radiation at all times of the year is sufficient to maintain canopy status. Precipitation, therefore, provides the largest driver of seasonality. From the extremely wet northwest corner of the Amazon Hydrologic Basin (annual precipitation 3,500 millimeters or more, little or no dry season) to the drier southeast (annual precipitation 1,500 millimeters, 6–7 month dry season, defined as months with less than 100 millimeters precipitation), precipitation is the forcing behind large gross fluxes of photosynthesis and respiration that define the net flux of CO₂.

Regionally, the Amazon Hydrologic Basin can be thought of as light- or water-limited. In water-limited areas, the net CO₂ flux will be into the atmosphere during dry periods, due to photosynthetic decreases in response to drying. In light-limited areas, the soil is always wet, and moisture availability is not an issue. In the light-limited case, photosynthesis is suppressed by lack of light during consistently cloudy periods. When the rain ends and clouds are relatively sparse, an increase in sunlight results in increased GPP and net CO₂ uptake. In reality, the distribution of light and water limitation across the Amazon is heterogeneous, with many locales expressing characteristics of both light and water limitation throughout the year.

The annual cycle of SIF can provide a window into the annual cycle of GPP. There will be no dormant period (as there would be in regions that experience winter), but we may be able to determine a cycle of relative maximum and minimum. Respiration will also be consistently large, but we do not have the ability to remotely sense variability in respiration. OCS and CO₂ concentrations may provide a means to determine this flux.

With an aircraft, we can sample CO₂ and OCS concentrations of air entering the Amazon Hydrologic Basin (off the east coast of Brazil, perhaps) at relatively low levels (PBL or just above). We can then sample again in the interior of the continent, after the air has had a chance to move inland and be exposed to biological processes. OCS will be drawn down, as it is taken up by photosynthesis without a compensating efflux. CO₂ will also be influenced by the biosphere, but in this case by large photosynthetic and respiratory fluxes. If OCS and CO₂ are positively correlated (both smaller concentrations inland), then the region is a sink. If they are negatively correlated (inland the OCS is smaller and CO₂ larger), then the region is a source.

The savvy reader may point out that you can make this determination without OCS; CO₂ will tell you the net flux story. However, the amplitude of the OCS drawdown gives a correlation to the amplitude of the GPP flux, and therefore allows an estimate of the large photosynthetic and respiratory fluxes to be made.

3.4.5 Integrating OCS and SIF with other Earth System Observations

In a comprehensive carbon–climate data assimilation system, OCS and SIF can be integrated in parallel with other data constraints that provide complementary information on the underlying processes. Here we examine the complementary data from hydrogen deuterium oxide, carbon monoxide, and surface properties.

3.4.5.1 Hydrogen Deuterium Oxide (HDO)

Hydrogen deuterium oxide (HDO) is a water isotope that can provide information on the recent source of water, partitioning between transpiration or evaporation, due to fractionation effects (Wright et al., 2017). This insight into the role of stomatal conductance on the water

cycle is analogous to that of OCS into stomatal conductance in general, and together these independent atmospheric measurements can provide a more robust data constraint.

3.4.5.2 Carbon Monoxide (CO)

Another atmospheric tracer that provides information about relevant processes is carbon monoxide (CO), which, like OCS and HDO, can be measured both in situ or via remote sensing (Deeter et al., 2017). In this case, the process in question is biomass burning. Like OCS, the CO signal may be overwhelmed or complicated by anthropogenic sources in some regions, but in less industrialized tropical regions where the carbon cycle variability is significantly influenced by biomass burning, CO signals in the atmosphere are strongly correlated with fire emissions. Most fire emission databases rely upon remotely sensed surface properties such as the burned area (e.g., GFED) (Van der Werf et al., 2010) or the fire radiative power (e.g., GFAS) (Kaiser et al., 2012), and convolve these with estimates of the available biomass and emission ratios based on total carbon for different biomes (Akagi et al., 2011; Stockwell et al., 2016). Here CO is different in that it provides a direct measure of the actual emissions of one tracer with a relatively large dynamic range (compared to CO₂), and emission ratios can be applied directly to the plume to estimate the impact on other tracers such as CO₂ and OCS.

Because OCS, CO, and HDO are all atmospheric tracers that undergo similar advection in the atmosphere, the correlation between them can be exploited in the statistical treatment of the measurement correlations. This is somewhat more complicated for HDO due to loss from precipitation, but the advective and convective processes apply nonetheless.

3.4.5.3 Surface Properties

Surface-based properties are also important for integration into an Earth system simulation. Some of these are comparatively stable in time, such as land cover, while others represent instantaneous information on processes (such as SIF) or meteorological drivers (e.g., photosynthetically active radiation, surface temperature, soil moisture). Many of these surface properties are required drivers of biosphere models that are integrated into the modeling framework, either as initial conditions or with optimizable parameters in the case of CCDAS approaches. These driver data are often taken from meteorological reanalyses, which in turn have assimilated remote sensing and in-situ measurements, or they can be assimilated directly. Biosphere models generally provide not only net carbon fluxes, but also partition these fluxes into uptake (GPP) and respiration. As the surface property SIF gives instantaneous information related to GPP, this can be used to assess and constrain the model's estimation of this flux partitioning.

3.4.6 Multi-Scale, Multi-Platform Approach

Because the processes that we need to constrain are happening on a variety of spatial and temporal scales, the measurements and interpretation need to span these same scales. These measurements include leaf-scale chemical fluxes and fluorescence; chamber chemical fluxes;

tower-based measurements of chemical fluxes, chemical concentrations, and fluorescence; aircraft-based measurements of chemical fluxes, concentrations, and fluorescence; and global measurements of concentrations and fluorescence using satellites. No single modeling system will resolve all scales simultaneously, but the process knowledge gained on the leaf and site scale is crucial for the interpretation of larger-scale measurements at regional scales.

Flux towers have been long used as a way to directly measure the exchange of energy, water, and trace gases between the land surface and the atmosphere. These site-level measurements are used to constrain the relationships and parameters in process-based models, which in turn can be applied over regional domains or the whole globe in an effort to understand and predict the future behavior of the carbon–water–climate system. However, because these measurements represent such a local scale, they are often difficult to reconcile with Earth system models operating on coarser-resolution global scales.

Satellites have proven to be an invaluable platform for Earth observation due to their ability to cover these larger spatial scales that are simply not achievable with other approaches. Though the accuracy and precision of the measurements is generally poorer than that measured on site scales, the spatial scale the measurement represents is often more compatible with the scale of global models, specifically when considering atmospherically advected tracers such as CO₂, OCS, CO, or HDO. A measurement in the atmosphere reflects the integral of fluxes that have influenced that parcel of air over a larger spatial and temporal domain. A similar column-integrated measurement is provided by ground-based spectrometers, which, while sparse in space, provide better coverage in time. In the case of OCS, the fact that historical thermal infrared spectra can be reprocessed to retrieve OCS also means that these measurements provide a temporal record going more than two decades into the past.

A key bridge between the site-level measurements and the space-based measurement is provided by aircraft measurements, which simultaneously provide the precision and accuracy of in-situ measurements with a broader spatial representation. These measurements are typically available on a campaign basis, over regional spatial scales.

A first step toward a multi-scale platform would be the development of hourly data of OCS, CO₂, CO, and fluorescence at an existing tower observatory. At Niwot Ridge, for example, a PhotoSpec has been placed at the top of a tower since June 2017 (Magney et al., 2019b). The observing strategy is focused on targeting multiple plant species over diurnal cycles (dawn-to-dusk). Overlapping SIF and OCS can be used to investigate how SIF and GPP covariance changes at different time scales and environmental conditions. Tracer–tracer correlation of gas species would provide process and regional attribution of carbon flux.

3.4.7 Multi-Species, Multi-Scale Data Assimilation Framework

Analysis of the multi-scale data will require the development of a multi-species, multi-scale data assimilation framework (MSMS-DA) (Figure 3.2) to incorporate OCS, SIF, CO, and CO₂ observations from multiple observing platforms to address key science goals: 1) regional scale GPP, respiration, fire, and net CO₂ flux estimates; 2) the responses of regional carbon cycle fluxes to climate variability; and 3) the observing requirements to reduce uncertainties of regional GPP estimates. These approaches can build off of successful carbon cycle data assimilation systems such as the Carbon Monitoring System Flux (CMS-Flux) (Liu et al., 2014). CMS-Flux incorporates multiple species to infer the relative contribution of carbon cycle processes to surface atmosphere exchange. These data have been used to assess the impacts of El Niños on the tropical balance Bowman et al., 2017; Liu et al., 2017, impacts of droughts, in North America (Liu et al., 2018), and the uncertainty in carbon–climate models (Quetin et al., 2020).

Similarly, the MSMS-DA will use the SIF constrained GPP and uncertainty structure (including spatiotemporal correlation) as a prior flux, and the CO₂, CO, and OCS will be assimilated simultaneously to constrain net biome exchange (NBE), fire, and GPP, respectively. The error covariance structure between NBE and GPP will be incorporated in the prior error covariance, so that CO₂ and OCS can inform both GPP and NBE during data assimilation. Since SIF represents the instantaneous signal of photosynthetic activity and OCS are indicative of an integrated signal of GPP, assimilating OCS while using SIF–GPP as a prior will propagate the discrete SIF signal through space and time.

MSMS-DA includes a global coarse-resolution and a regional high-resolution assimilation framework that can assimilate and utilize observations from platforms including tall towers, aircraft, FTIR, and satellites. The global coarse-resolution assimilation assimilates observations from satellite, FTIR, and NOAA surface flask to constrain fluxes on the scale of hundreds of kilometers, and provides boundary conditions for regional high-resolution assimilations. Tall tower observations will be used to calibrate a high-resolution biosphere model, which will be used as a prior biosphere flux estimate for the high-resolution assimilation framework that can incorporate aircraft PBL observations.

MSMS-DA will be first used to assimilate existing observations, and then be used in the Observing System Simulation Experiments (OSSEs) to design future observing networks (Figure 3.6).

3.4.8 Integration Across Agencies and PIs

A fundamental challenge in understanding the role of photosynthesis in driving carbon and water cycles within the Earth system is the diversity of spatial scales and observational techniques that are within the purview of a number of agencies including NASA, NOAA, NSF, DOE as well as European, Brazilian, and other science agencies. Basic science support is

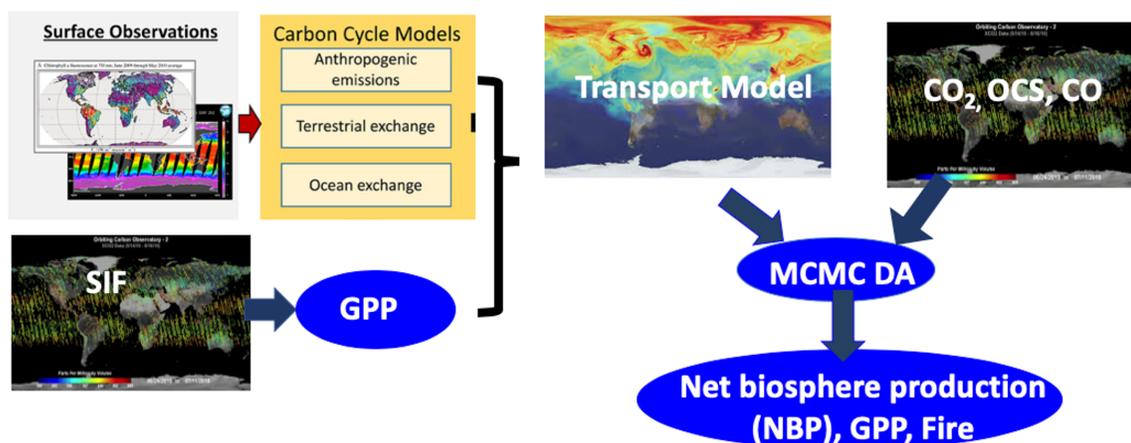


Figure 3.6: Multi-Species, Multi-scale data assimilation (MSMS-DA) framework for assessing biogeochemical process and trace gas fluxes using space-based observations. (adapted from Bowman et al., 2017)

needed to understand leaf-level biophysical processes relating air-leaf exchange through photosynthetic activity. However, these studies need to incorporate quantities such as OCS and SIF that can be observed at regional scales. Development and deployment of sensors at towers should be supported by NSF and analog international agencies. These in turn can be related to satellites. For example, validation of space-borne SIF measurements, which are supported by NASA, JAXA, and the EU, are critical across a wide variety of biomes in regions such as North America, Brazil, and Australia with tower measurements supported in part by host agencies. TCCON and NDACC networks comprising of uplooking column and associated in-situ flask samples are needed to provide well-calibrated CO₂, OCS, and SIF measurements to support an observing system of photosynthesis.

Photosynthetic processes acting on regional scales are amenable to focused process-based aircraft missions supported by field measurements and satellite observations. Coordinated campaigns between agencies, e.g., FIREX (NOAA) and FIRECHEM (NASA), are crucial for quantifying these processes in sensitive tropical (e.g., Brazil) and extra-tropical (e.g., California) regions. Global-scale impacts of photosynthetic variability require coordination, planning, and development of satellite observations. ACC-CEOS could incorporate this theme as part of its carbon and water cycle foci to identify gaps in measurements and vantage points. Integration of these observations across scales is vital to accurately assess and predict one of the major drivers of the Earth system. Innovative Earth system assimilation methods and models that can ingest OCS and SIF observations in the context of other Earth observations (e.g., CO₂, HDO, and VPD) need to be developed and supported.

One possible organizational instrument could be a research coordination network (RCN), funded through the DOE or NSF. These grants support meetings and cross-calibrations between disparate groups.

For the most likely success of this cross-coordination, it would make sense to hire a dedicated director, even part time, to organize and facilitate research efforts. Having an outside support person who is not jockeying for publications but is dedicated to the advancement of the collaboration would be best. Either that, or some very well-established scientist with exceptional leadership skills. Our best intentions can sometimes fall to the wayside when human logistics impede progress. Another possible avenue would be a dedicated workgroup and identity, e.g., COSANOVA for the OCS community, with regular annual or bi-annual meetings. Often a website format is easiest for the collection and dissemination of new information. This is an aspect where FLUXNET fell down, where even the best laid plans of standardization did not yield satisfactory results in terms of standardized data. In truth, each ecosystem really deserves its own treatment, and what can be done is a standardized way of reporting the data treatment for that particular flux dataset.

It is important to share data with a special treatment of meta-data to avoid misinterpretation or "data abuse". For example, if one group releases satellite data, it is important to make the data uncertainty as accessible as the reported data values themselves.

On a final note, we will get into some trouble when the satellite products have to be validated with ground-based products. The calibration scale between certain flights and flask sampling is not consistent. As a result, there will be deviations in the data that are attributable to the calibration scale rather than anything happening in the ecosystem. While NIST does not make a standard mix of OCS, many members of the international OCS community have agreed to use the NOAA scale. Making a gravimetric standard can lead to big problems, so as our community grows, even the most careful atmospheric scientist should not report values with their lab-specific calibration scale. We do not agree that the NOAA scale is accurate; we agree that it is consistent, and that is the only thing that really matters in terms of this calibration scale (since we don't actually care about the absolute mass of sulfur in the atmosphere).



4. Future Plans and Development

4.1 Roadmap for Technical Development

In order to develop a robust understanding of the Earth's coupled carbon–energy–water system, new tools are needed that can observe the key biogeochemical processes at regional to global scales. Space-based OCS observations could play a critical role in addressing this challenge if integrated with remote sensing of SIF and vegetation indices. However, no current satellite instrument has the capabilities to retrieve these trace gas concentrations in the required domain (e.g., continental boundary layer). Given the lack of capable instrumentation, the following steps must be taken for the technical development of a space-based OCS spectrometer:

- Assess the potential of committed satellites to estimate OCS (e.g., Sentinel 5/IASI-NG, MTG-IRS)
- Validate existing OCS satellite data using global transport models and in-situ and aircraft data.
- Coordinate a meeting between scientists and instrumental engineers to discuss future remote sensing observations with an emphasis on the potential for retrievals that are over land, tropical, and in the continental boundary layer.
- Develop Observing System Simulation Experiments (OSSEs) to elucidate design constraints for future satellite mission. The OSSE will be based on synthetic future satellite observation to determine the sensitivity of inverse analysis to surface fluxes.

4.2 Recent and planned papers

4.2.1 Published papers

Bowman, K. W. et al. Global and Brazilian carbon response to El Niño Modoki 2011-2010. *Earth and Space Science*, 4, 2017. doi: 10.1002/2016EA000204. <http://dx.doi.org/10.1002/2016EA000204>.

Campbell, J. E., et al. "Assessing a new clue to how much carbon plants take up." *Eos* 98 (2017).

Campbell, J. E., et al. "Plant uptake of atmospheric carbonyl sulfide in coast redwood forests." *Journal of Geophysical Research: Biogeosciences* 122.12 (2017): 3391-3404.

Campbell, J. E., et al. "Large historical growth in global terrestrial gross primary production." *Nature* 544.7648 (2017): 84-87.

Hilton, T. W. "Photosynthesis in high definition." *Nature Climate Change* 8.1 (2018): 20-21.

Hilton, T. W., et al. "Peak growing season gross uptake of carbon in North America is largest in the Midwest USA." *Nature Climate Change* 7.6 (2017): 450-454.

Kooijmans, L. MJ, et al. "Influences of light and humidity on carbonyl sulfide-based estimates of photosynthesis." *Proceedings of the National Academy of Sciences* 116.7 (2019): 2470-2475.

Lejeune, B., et al. "Optimized approach to retrieve information on atmospheric carbonyl sulfide (OCS) above the Jungfraujoch station and change in its abundance since 1995." *Journal of Quantitative Spectroscopy and Radiative Transfer* 186 (2017): 81-95.

Lennartz, S., et al. "Direct oceanic emissions unlikely to account for the missing source of atmospheric carbonyl sulfide." *Atmospheric Chemistry and Physics* 17 (2017): 385-402.

J. Liu, et al, Carbon monitoring system flux estimation and attribution: impact of ACOS-GOSAT XCO₂ sampling on the inference of terrestrial biospheric sources and sinks. *Tellus B*, 66(0), J.

Liu, J. et al, Contrasting carbon cycle responses of the tropical continents to the 2015–2016 El Niño. *Science*, 358(6360), 10 2017. <http://science.sciencemag.org/content/358/6360/eaam5690.abstract>.<http://www.tellusb.net/index.php/tellusb/article/view/22486>.

Liu, J. et al, Detecting drought impact on terrestrial biosphere carbon fluxes over contiguous US with satellite observations. *Environmental Research Letters*, 13(9):095003, 2018. <http://stacks.iop.org/1748-9326/13/i=9/a=095003>.

Quetin, G., Bloom, A. A., Bowman, K. W., & Konings, A. (2020). Carbon flux variability from a relatively simple ecosystem model with assimilated data is consistent with terrestrial biosphere model estimates. *Journal of Advances in Modeling Earth Systems*, 12, e2019MS001889. <https://doi.org/10.1029/2019MS001889>.

Spielmann, F. M., et al. "Gross primary productivity of four European ecosystems constrained by joint CO₂ and COS flux measurements." *Geophysical research letters* 46.10 (2019): 5284-5293.

Stinecipher, J. R., et al. "Biomass burning unlikely to account for missing source of carbonyl sulfide." *Geophysical Research Letters* (2019): 46, 14912–14920. <https://doi.org/10.1029/2019GL085567>.

Wehr, R., et al. "Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake." *Biogeosciences* 14.2 (2017): 389-401.

Whelan, M., et al. "Reviews and syntheses: Carbonyl sulfide as a multi-scale tracer for carbon and water cycles." (2018).

Wohlfahrt, G., et al. "Sun-induced fluorescence and gross primary productivity during a heat wave." *Scientific reports* 8.1 (2018): 1-9.

Zumkehr, A., et al. "Gridded anthropogenic emissions inventory and atmospheric transport of carbonyl sulfide in the US." *Journal of Geophysical Research: Atmospheres* 122.4 (2017): 2169-2178.

4.2.2 Papers resulting from meeting

The workshop team has recently published or will soon publish papers related to the key findings of this meeting on the potential for unified observations of global photosynthesis. These papers will focus on the multiple dimensions of photosynthesis that can be probed when multiple satellite signals are integrated into the analysis including OCS, SIF, CO₂, and other tracers. The focus of these articles will be on the broad cross-section of scientific disciplines that are needed to achieve this goal. Two papers have been submitted and additional papers are discussed in the roadmap sections below.

Campbell, J.E., et al. "Checking nature's brakes: A review of regional photosynthesis measurements from satellite vegetation indices, solar induced fluorescence, and carbonyl sulfide." *New Phytologist*, In Preparation.

Hilton, T.W. Photosynthesis in high definition. *Nature Clim Change* 8, 20–21 (2018). <https://doi.org/10.1038/s41558-017-0040-6>.

Kuai, L., N. Parazoo, M. Shi, C. Miller, I. Baker, A. , K. Bowman, M. Lee, Z. Zeng, J. Berry, R. Commane, Y. Yung: Benchmarking the regional-scale Gross Primary Productivity (GPP) through Carbonyl Sulfate (OCS), manuscript finalizing.

Parazoo, K. Bowman, J. Liu, M. Lee, L. Kuai, B. Baier, Y. Shiga, I. Baker, M. Whelan, S. Feng, M. Krol, J. DiGangi, Colm Sweeney, K. Davis, Covariation of airborne biogenic tracers (CO₂, COS, and CO) supports widespread plant CO₂ uptake throughout the eastern United States, and stronger than expected growing season uptake in the southeast, manuscript finalizing.

Stinecipher J., P. Cameron-Smith, L. Kuai, N. Glatthor, M. Hopfner, I. Baker, C. Beer, K. Bowman, M. Lee, S. Miller, N. Parazoo, E.J. Campbell, Remotely-sensed Carbonyl Sulfide Constrains Model Estimates of Amazon Primary Productivity, manuscript finalizing.

Stinecipher, J. R., Cameron-Smith, P. J., Blake, N. J., Kuai, L., Lejeune, B., Mahieu, E., et al. (2019). Biomass burning unlikely to account for missing source of carbonyl sulfide. *Geophysical Research Letters*, 46, 14912–14920. <https://doi.org/10.1029/2019GL085567>.

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4.3 How the Team Will Continue to Move Forward

The workshop activities developed strong working and social relationships between the participants that pave the way for ongoing activity at multiple levels. First, two of the team leads, Elliott Campbell and Elva Kuai, will continue to meet weekly in order to coordinate the ongoing collaborative activities of the workshop participants. These weekly meetings will be held using Zoom webconferencing and will involve the regular participation of one graduate student research assistant. Second, the leads will incorporate input from all project participants into the writing of the final report. Third, sub-groups of the workshop team will pursue several proof-of-concept research activities and publications described in the roadmap below in order to leverage the most exciting incites emerging from the workshop discussions.

4.4 Roadmap

Short-term activities are focused on completion of the report, perspectives publications to multi-disciplinary audiences, and outreach. The final report will be developed using the writing assignments from the final day of the workshop as a foundation. Campbell and Kuai will develop the core draft based on these writing pieces and will coordinate a small team of project participants to fill out additional sections, including Nick Parazoo and Meemong

Lee. This draft will then be circulated through individual outreach by the four report leads to each project participant for further development. The key findings of the report will be distilled by Campbell and Kuai into a 1-slide and a 4-slide outreach presentation and circulated to the project participants for incorporation into seminars, conference presentations, and teaching. These findings will also be communicated through two perspective articles written by a postdoc supported by the team leads (Mary Whelan, now faculty at Rutgers) and by Campbell to atmospheric science and ecological science communities.

Mid-term activities will be the development of proof-of-concept studies that leverage the critical concepts that emerged from the workshop discussions. The first paper will provide the first demonstration of large-scale integration of SIF and OCS constraints. This activity, led by Elva Kuai, Nick Parazoo, and Kevin Bowman, will derive an OCS vegetation sink from the existing global SIF observations, in addition to using ecosystem model SiB. The model simulation of OCS mixing ratios will be constrained with TES satellite retrievals and in-situ observations from the NOAA air-monitoring network and HIPPO airborne campaigns, with a focus on the latitudinal gradient between hemispheres in the free troposphere and boundary layer. Additionally, Mary Whelan and Elva Kuai will leverage an ECOSTRESS grant to interface OCS with the ECOSTRESS project.

The mid-term research will also include a focus on a critical regional experiment in the Amazon using upcoming OCS in-situ observations and atmospheric transport simulations. While the Amazon is the key frontier for global photosynthesis research where the OCS–SIF integration could provide essential advances, few OCS measurements have been made in the tropical continental boundary layer. This study will constrain global atmospheric transport simulations with airborne and tower OCS observations and MIPAS satellite free troposphere retrievals. Boundary conditions will be provided by TES-constrained atmospheric fields. This activity is led by Elliott Campbell, Joe Berry, and Ulli Seibt.

The outreach of the short-term activities and the proof-of-concept research of the mid-term activities will in turn be leveraged to pursue the long-term goal of developing a space-based OCS observing system that is integrated with SIF, CO₂, and multi-tracer platforms. In pursuit of this goal, we will develop a research coordinating network to build on the collaborative team established at the KISS workshop, engage these interdisciplinary scientists with instrumental engineers to plan future OCS space-based sensing systems, and pursue NASA and NSF grants to extend the scientific applications of these satellite data.

4.5 Conclusions

Our workshop, "Next-Generation Approach for Detecting Climate-Carbon Feedbacks: Space-Based Integration of OCS, CO₂, and SIF" was instrumental in bringing distinct communities together to conceive a global photosynthesis observing platform for transforming our under-

standing of the Earth system. While multiple lines of evidence have been used to uncover key aspects of photosynthesis processes, a unified observing system that is grounded in the spatially and temporally integrated OCS tracer offers the unique capability to detect the climate–carbon feedbacks that are essential to understanding climate change. The multi-disciplinary workshop brought scientists together from distinct communities, including ecologists who understand the exchange of trace gases and energy fluxes between terrestrial ecosystems and the atmosphere, space scientists who measure the signature of these gases and energy sources from satellites, and atmospheric chemists who integrate atmospheric observations with Earth system models in order to uncover the underlying ecological processes.

The workshop presentations focused on the relationship between OCS and photosynthesis and the value of integrating OCS with SIF and CO₂ data that could lead to unprecedented scientific advances. These discussions prompted further exploration of regions of critical interest where simultaneous OCS/SIF/CO₂ capabilities are most needed. The outcome of these discussions was an Amazon experimental design that could address the persistent challenges of cloud contamination in satellite data by combining the instantaneous biochemical information from SIF with the temporally integrated conductance information from OCS. While no OCS measurements in the boundary layer have been attempted in the Amazon, the satellite OCS retrievals for the free troposphere over the Amazon show a massive depression in mixing ratio that is indicative of a remarkably robust relationship between the variability of OCS and photosynthesis.

Perhaps most importantly, the discussions extended the scientific applications of an OCS/SIF/CO₂ platform beyond the carbon cycle applications that were most apparent at the outcome of workshop. Critical applications to hydrology, atmospheric circulation, and boundary layer dynamics were revealed through the breakout group discussions that mixed ecologists, atmospheric chemists, and space scientists. These critical applications are due to the fact that photosynthesis creates a link between the global cycles of carbon, energy, and water. A unified photosynthesis platform offers an unparalleled opportunity to pursue the mysteries of these fundamental Earth system processes.



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Appendix

Project Name	Variable	Platform	Spatial Characteristics	Temporal Characteristics	Publication
Air Monitoring					
NOAA GMD HATS	Concentration	Ground-based	Flask sampling at surface sites and airborne	T2000–Present, ~Twice per month	Montzka et al., 2007
Website: https://www.esrl.noaa.gov/gmd/hats/gases/OCS.html					
Remote Sensing					
FTIR (NDACC/TCCON)	Total column/profile	Ground-based	Sites	Mid-1990s–Present	Wang et al., 2016
Website: https://www.ndaccdemo.org/					
TES	Free troposphere concentration	Satellite	40°S–40°N, Ocean only (current)	Monthly, 2002–2012	Kuai et al., 2015
Website: https://tes.jpl.nasa.gov/					
MIPAS	Upper troposphere and stratosphere	Satellite	60°S–60°N	Monthly	Glatthor et al., 2015
Website: https://earth.esa.int/					
IASI-NG	OCS (pptv)	Sentinel 5	15 km	Daily global	Crevoisier et al., 2014, AMT
Website: http://www.eumetsat.int/website/home/Data/index.html					

Project Name	Variable	Platform	Spatial Characteristics	Temporal Characteristics	Publication
MTG-IRS	OCS (pptv)	Eumetsat/ MTG	Europe/ 4 km	Diurnal/ geostationary	
Website: https://www.ecmwf.int/sites/default/files/elibrary/2017/17227-science-applications-and-and-product-plans-mtg-irs.pdf					
Aircraft					
HIPPO	Concentration	Aircraft	Pole-to-pole, Pacific Ocean	January 2009, November 2009, March 2010, June 2011, August 2011	Wofsy et al., 2011
Website: http://hippo.ornl.gov/data_access					
ATOM	Concentration	Aircraft	85°S to 85°N, Pacific and Atlantic	August 2016, February 2017, October 2017, May 2018	Wofsy et al., 2018
Website: https://doi.org/10.3334/ORNLDAAC/1581					
ARCTAS/ARCPAC					
CARVE	Concentration	Aircraft	55°N to 72°N, -134°W to -155°W, Alaska	April–November 2012–2015	
Website: https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1404					
TC4	OCS (pptv) Blake scale	DC8		Aug 2007	
Website: https://espoarchive.nasa.gov/archive/browse/tc4/DC8					
TC4	OCS (pptv) Atlas	WB-57		Aug 2007	
Website: https://espoarchive.nasa.gov/archive/browse/tc4/WB57					
ATTREX	OCS (pptv) Atlas	Global Hawk	Pacific Ocean	Feb 2013, Feb 2014	
SONEX	OCS (pptv) Blake	DC8	Atlantic Ocean	October 1997	
KORUS-AQ	OCS (pptv) Blake	DC8	Korea	May 2016	
SEAC4RS					
DC3					
NOAA GMD HATS	Concentration	NOAA Flights	U.S.		Montzka et al., 2007
Website: https://www.esrl.noaa.gov/gmd/hats/gases/OCS.html					

Project Name	Variable	Platform	Spatial Characteristics	Temporal Characteristics	Publication
COS-OCS	Concentrations	Balloon	Arctic/ mid-latitude/ tropics	2018–2022	
Ground-Based					
HYYTIALA	Eddy fluxes/ Concentrations, leaf fluxes, soil fluxes	Tower, chambers		2013–2017	Kooijmans et al., 2017; Sun et al., 2017
Summen Project	Concentration, Flux	Tower con- centration, Soil Chamber Flux, Branch Chamber Flux Website: www.fogsci.com	Northern California, Coastal, Lagrangian watershed sampling, Vertical profiles	2015–Present, Continuous and Discrete Flasks	Campbell et al., <i>JGR Biogeosciences</i> , In Review
SGP	Eddy flux, soil flux	Tower, chamber	Agriculture, Midwest	April–June 2012	Billesbach et al. 2014; Maseyk et al. 2014; Sun et al. 2015
La Selva	Eddy flux, leaf fluxes, soil fluxes	Tower, chambers	Tropical rainforest	Oct 2013–Feb 2014	
Irvine Marsh	Eddy flux, leaf flux, surface flux	Tower, chambers	Freshwater marsh	June–July 2013	
Stunt Ranch	Leaf fluxes, soil fluxes	Chambers	Oak woodland	March–May 2013	Sun et al. 2016
Harvard Forest	Eddy Flux, Gradient Fluxes Website: doi:10.6073/pasta/5a3a88182fb9aebc0385aeda3535a3de	Towers	Mid-latitude forest	2011–2013, 2019	Commane et al., 2015; Wehr et al., 2017

Table A.1: OCS Observations

Project Name	Platform	Spatial Characteristics	Temporal Characteristics	Publication
National Research Foundation of Korea	Tower QEPro spectrometer	~20 m (5 m height with cosine corrector)	Half-hourly	In progress...
Global	OCO-2, GOME-2, GOSAT			Sun et al., 2015, 2017a, b
Cornell Research farm	Tower QEPro spectrometer	Site, cosine corrector	Varies: few seconds to few minutes, optimized integration time	In progress...
GOAmazon, etc.	Towers K34-Manaus, K67-Santarem, ATTO			
Coles Field and Brooks Field near Ames, Iowa (Corn and Soy)	PhotoSpec on mobile Tower	2D scanning, 0.7degrees FOV	20 seconds per FOV	Starting
Niwot Ridge	PhotoSpec on Fluxtower	2D scanning, 0.7degrees FOV	20 seconds per FOV	Starting
La Selva, Costa Rica	PhotoSpec on mobile Tower	PhotoSpec		
Toolik, Alaska	Fluospec2 on flux tower	Fixed, 25 deg FOV	5 sec integrating time, 5 minute measurement cycle	Data collection started July 2017
Old Black Spruce, Canada	PhotoSpec on flux tower	2D scanning, 0.7degrees FOV	20 seconds per FOV	Data collection planned March 201
Old Black Spruce, Canada	Fluospec2 on flux tower	Fixed, 25 deg FOV	5 sec integrating time, 5 minute measurement cycle	Data collection planned March 201
Charlottesville, Virginia	Fluospec2 on flux tower	Fixed, 25 deg FOV	5 sec integrating time, 5 minute measurement cycle	Data collection started July 2017
Northern New Mexico (MPJ field site)	Fluospec2 on flux tower	Fixed, 25 deg FOV	5 sec integrating time, 5 minute measurement cycle	Data collection planned March 201

Table A.2: SIF Data

Model Name	Model type	Key variables	Publication
STEM	Regional chemical transport model Website: http://campbell.sites.ucsc.edu	OCS concentration, CO ₂ concentration, other tracers	Campbell et al., 2017; Hilton et al., 2015, 2017
GEOSChem	Global chemical transport model	OCS concentration, CO ₂ concentration, other tracers	Kuai et al., 2015
CLM	Ecosystem model	SIF, OCS, mesophyll conductance, carbon isotope	Campbell et al., 2017; Hilton et al., 2015, 2017
SiB	Ecosystem model Website: willbeputonGitHubinthefuture	T _{soil} , SWC, [COS], etc.	Sun et al. (2015); Sun et al. (2016)
LRU model	Leaf; semi-empirical	PAR, RH, and Ball–Berry parameters	Sun and Seibt, in review.

Table A.3: Models