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Innovations in Carbon Cycle Science

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ABSTRACT: Where does the carbon released by burning fossil fuels go? Currently, ocean and land systems remove about half of the CO_2 emitted by human activities; the remainder stays in the atmosphere. These removal processes are sensitive to feedbacks in the energy, carbon, and water cycles that will change in the future. Observing how much carbon is taken up on land through photosynthesis is complicated because carbon is simultaneously respired by plants, animals, and microbes. Global observations from satellites and air samples suggest that natural ecosystems take up about as much CO_2 as they emit. To match the data, our land models generate imaginary Earths where carbon uptake and respiration are roughly balanced, but the absolute quantities of carbon being exchanged vary widely. Getting the magnitude of the flux is essential to make sure our models are capturing the right pattern for the right reasons. Combining two cutting-edge tools, carbonyl sulfide (OCS) and solar-induced fluorescence (SIF), will help develop an independent answer of how much carbon is being taken up by global ecosystems. Photosynthesis requires CO_2, light, and water. OCS provides a spatially and temporally integrated picture of the "front door" of photosynthesis, proportional to CO_2 uptake and water loss through plant stomata. SIF provides a high-resolution snapshot of the "side door," scaling with the light captured by leaves. These two independent pieces of information help us understand plant water and carbon exchange. A coordinated effort to generate SIF and OCS data through satellite, airborne, and ground observations will improve our process-based models to predict how these cycles will change in the future.

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Photosynthesis is the largest flux of the global carbon cycle, and yet the amount of carbon being fixed by plants is highly uncertain. At scales larger than a single leaf, measuring CO_2 uptake is complicated by the release of CO_2 via respiration at the same time and place. We can observe the net effect of photosynthesis and respiration by measuring CO_2 alone, via satellites like NASA's *Orbiting Carbon Observatory 2 (OCO-2)* and *OCO-3* or the long record from the NOAA Cooperative Air Sampling Network (e.g., Fig. 1). Two approaches have emerged capable of isolating the carbon uptake from photosynthesis at large spatial scales: measurements of atmospheric carbonyl sulfide (OCS) and solar-induced fluorescence (SIF). The strength of both SIF and OCS is the ability to scale measurements up to vast regions. However, perhaps because these methods rely on different parts of the photosynthetic machinery, the communities developing these techniques have had limited overlap.

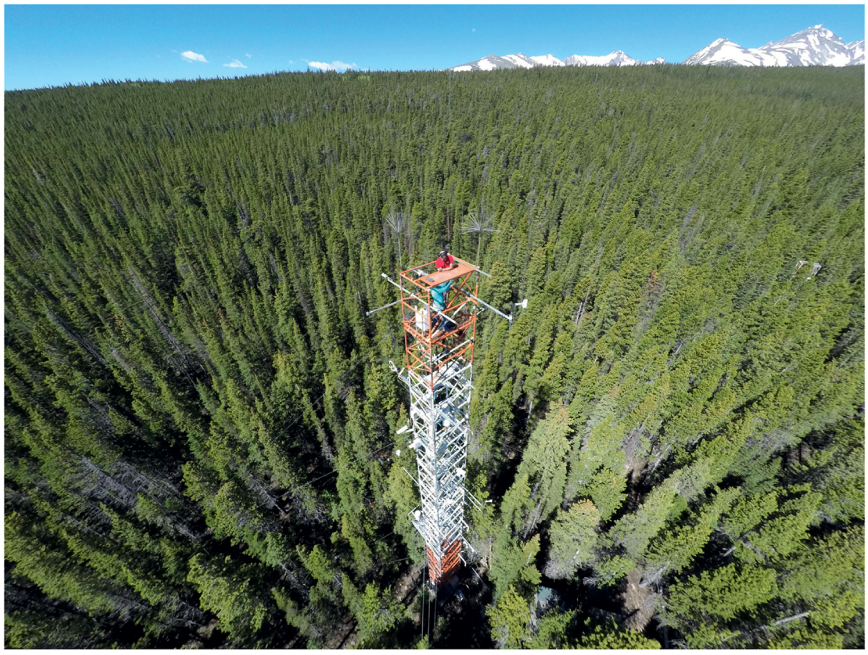

Fig. 1. Troy Magney and Katja Grossmann maintain an SIF-enabled spectrometer on a tall tower used to measure CO_2 at Niwot Ridge, Colorado. Surface trace-gas exchange measurements using a combination of techniques allow us to compare traditional to cutting-edge datasets and benchmark new observations from satellites. Photo courtesy of Christian Frankenberg.

Low daytime concentrations of atmospheric OCS indicate that nearby plants are consuming CO_2. The first step for plants to remove CO_2 from the atmosphere is the physical movement of the gas through stomata, tiny openings on leaves, usually at the cost of losing water (Fig. 2). Plants open and close their stomata to regulate carbon and water exchange. While we have a good understanding of the chemistry behind photosynthesis, we still have a limited understanding of the mechanisms

behind this stomatal functioning. OCS has a similar structure to CO_2 and interacts with the same enzymes, independent of light conditions. Most OCS is made in the oceans or emitted from certain industries like rayon manufacturing. Most OCS is consumed in plant leaves after diffusing through stomata. Observing the lowered concentrations of OCS over vegetated areas tells us how wide the "front door" of photosynthesis is open (Whelan et al. 2018).

When leaves absorb light, a small fraction is reemitted at a longer wavelength through fluorescence. SIF is a measure of new photons emitted from the excited state of chlorophyll-a, a chief player in photosynthesis, after absorption of solar light, thereby providing insight into the light reactions of photosynthesis (Fig. 2). Some SIF photons are produced in parts of the spectrum where solar light is absent. Using high-resolution spectrometers, the SIF photons can be distinguished from reflected sunlight. In practice, the magnitude of SIF is proportional to the amount of light intercepted by light-dependent machinery, or the "side door" of photosynthesis. Measuring the amount of light reemitted by leaves gives us an idea of how much light is getting through the door and ultimately used to power photosynthesis (Porcar-Castell et al. 2014).

Both SIF and OCS tools together cover spatial and temporal domains that elude other measures of photosynthesis. We can already quantify carbon uptake instantaneously on the individual leaf scale with small leaf chambers attached to water and CO_2 gas analyzers. With eddy covariance flux towers (Baldocchi 2020), we can estimate photosynthesis on the half-hourly and 1-km^2 scales by observing the net CO_2 exchange and subtracting out modeled respiration from observations at nighttime or periods when photosynthesis is small or absent. SIF data from satellites expand our purview to instant snapshots of multiple square kilometers, as often as the satellite can sample. On the ground and from aircraft, SIF spectrometers can give us canopy level estimates that relate directly to the leaf biochemistry, rather than involving the uncertainty of respiration estimates. Where SIF data are sparse because of thick clouds or limited satellite overpasses, OCS observations can represent the integrated signal of carbon uptake over a much larger landscape. Leveraging the power of both a light-based and a gas-based tracer fills important gaps in our knowledge of how much carbon our terrestrial ecosystems can pull out of the air.

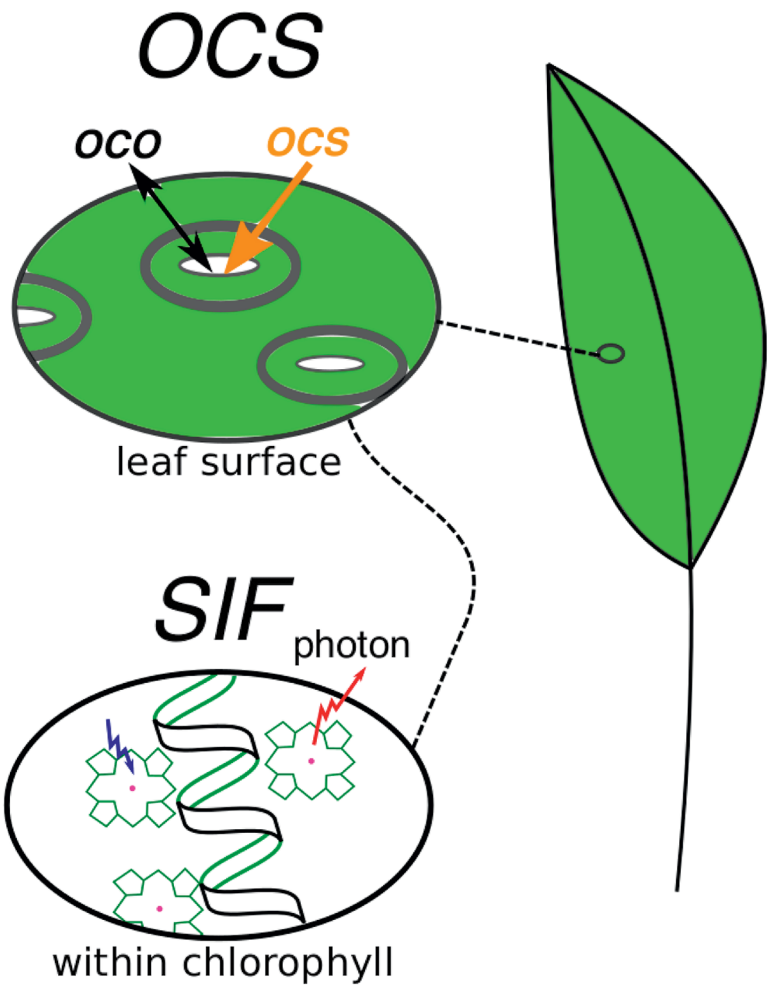

Fig. 2. OCS is a gas present everywhere in the troposphere at around 0.5 parts per billion. OCS is destroyed in plant leaves by the same enzymes as CO_2 and in proportion to how wide the stomata or "front door" of photosynthesis is open. SIFs are new photons produced when leaves receive more light than can be used. Some of these photons have wavelengths the sun does not make and can be distinguished from reflected sunlight.

Separate uncertainties

The uncertainties of SIF and OCS measurements are eclipsed by our remaining process-level questions about

photosynthesis and respiration on the continental to global scales. As with any observational approach, there are systematic uncertainties in either. Luckily, OCS and SIF are used to estimate the same parameters while being affected by separate sources of uncertainty. By using both OCS and SIF to constrain our estimates of carbon fluxes, we will reduce our total uncertainties.

Most photons intercepted by chlorophyll go to either photochemistry (for food) or nonphotochemical quenching (for protection), with only 1%–2% reemitted as SIF. Subtle variations in this efficiency, termed fluorescence yield, contain detailed information about leaf-level biochemistry (Weis and Berry 1987). Reducing the signal further, some of those newly emitted photons are intercepted by other leaves in the canopy. This can actually be turned to our advantage: the variations in SIF measured by canopy scanning spectrometers give us information about plant canopy structure, providing additional information about whole-plant productivity that appears to be mostly independent from concerns of fluorescence yield or light absorption (Zeng et al. 2019). SIF holds the promise of not only providing a new boon of information about leaf-level biochemistry, but also an entirely new way to study canopy structure and within-canopy light absorption

Remotely sensing SIF still has challenges; however, we can take solace in the fact that none of the satellite missions from which SIF is currently derived were specifically designed for dedicated SIF measurements. Rather, satellite-based SIF observations were enabled in a fortuitous manner as SIF emissions share a similar spectral range to that needed for cloud and trace-gas detection. For SIF, this has led to issues such as low signal-to-noise and coarse satellite pixels, which have complicated scientific interpretation. Fortunately, new technologies and observing strategies are likely to overcome many of these challenges.

Since OCS is an atmospheric tracer, a different set of issues introduce error into its measurement. OCS is present in the atmosphere at a level of a million times less than CO_2 and signal-to-noise detection is challenging. The uncertainty of atmospheric transport modeling makes it difficult to attribute changes in atmospheric signal to changes in surface uptake. Fortunately, we can measure OCS and CO_2 at the same geographic point to remove some uncertainty of atmospheric transport, which affects both gases equally, and help interpret the observations.

Many OCS-specific problems incidentally produce useful data. Though not as significant as plant uptake, soils can produce or consume OCS, governed principally by soil temperature and moisture content. The uptake of OCS is light independent and the ratio at which OCS is taken up relative to CO_2 changes with light levels: at low light, plants can still take up OCS while photosynthesis starts shutting down. This means that OCS draw down is controlled by stomatal conductance regardless of light. Nighttime stomatal conductance is an important parameter for studying the water cycle. OCS observations can give us more information about how much water escapes out of plant stomata during the dark night.

Data serendipity

Now is the right time for getting into measurements of SIF and OCS, thanks to recent technical innovations. It is notable how much new information we have already extracted with SIF and OCS with the little data collected. Both SIF and OCS global, long-term datasets were generated by instruments that were designed to measure other phenomena. OCS concentrations were included in the NOAA Global Flask Network data on a detector originally configured to quantify other low-concentration atmospheric gases. New commercially available detectors are targeted specifically at OCS, addressing some of the measurement problems that plagued the pioneers of these observations. SIF observations require a high spectral resolution spectrometer to distinguish "additive" fluoresced photons from "reflected" photons in reflected sunlight, and high-spatial-resolution footprints to distinguish land types. Thankfully, several

existing and planned satellites collect such data, but the small signal of SIF is difficult to extract from the noise.

The fluorescence of leaves has been known since the 1870s, but fluorescence observable as distinct from sunlight was not demonstrated until 1990. Spectrometers are now available to make this measurement remotely in the air and on the ground; however, some manufacturers do not prioritize consistency between instruments. The observation of SIF requires careful calibration of a spectrometer: most calibrations will lead to a reported concentration of photons that correlates to carbon uptake, but intercomparison of absolute measurements is important.

Currently, quantum cascade lasers can be configured to measure OCS concentrations frequently enough for ecosystem flux measurements. OCS is present in the atmosphere at a concentration around half a part per billion. Before 2010, OCS had to be measured via a complicated preconcentration step before injection into a gas chromatograph with an appropriately sensitive detector. Early studies suffered from high labor cost and method-process mismatches. These initial studies of leaf and soil OCS exchange fueled the desire to try and extract OCS signals out of noisy satellite spectroscopic data.

New satellite observations of SIF and OCS provide a more comprehensive look into the regions of the world, such as the tropics, where feedbacks among climate, carbon, radiation, clouds, and water are moderated by photosynthesis. The satellite-based SIF measurements, when paired with other satellite measurements of carbon cycle tracers such as CO_2 and CO, have transformed our understanding of how climate perturbations such as ENSO affect the tropical carbon cycle. The satellite OCS data, when paired with aircraft measurements, provide direct evidence for a substantive tropical oceanic source; updating the OCS budgets is an important step toward using these data to quantify seasonal photosynthesis variability. Current OCS and SIF satellite data over tropical regions are relatively sparse and likely to remain so, underscoring the importance of combining space-based methods with airborne and tower-based measurements to reduce fundamental uncertainties in the processes controlling the carbon cycle.

Challenges remain, but the future looks bright

The scientific community would benefit from space-based sensors specifically designed to measure OCS and SIF, coordinated with ground measurements. SIF has had a head start, and two recent articles in Science demonstrate how satellites such as Greenhouse Gas Observing Satellite (GOSAT) and *OCO-2* are being used to address remaining challenges. Sun et al. (2017) used the power of *OCO-2* SIF to distinguish gross primary production (GPP) across land uses and coordinated airborne measurements to validate satellites and capture within pixel variability. Liu et al. (2017) leveraged GOSAT and *OCO-2* SIF and CO_2 to break down the tropical carbon cycle into a discrete set of ecosystem processes, which interact with carbon and climate in unique, and previously unknown, ways.

Additionally, a new satellite was just launched and two others are planned for SIF measurements. The Tropospheric Monitoring Instrument (TROPOMI) spectrometer on board *Sentinel-5 Precursor (Sentinel-5P)* has already collected nearly two years of data continuously in time (daily) and space (7 km x 3.5 km) combining the strengths of approaches used for previous satellite missions (Köhler et al. 2018). The OCO-3 sensor has been measuring SIF on the International Space Station (ISS) with other ecosystem tracers [biomass from Global Ecosystem Dynamics Investigation (GEDI), evapotranspiration from Ecosystem Spaceborne Thermal Radiometer Experiment on Space Station (ECOSTRESS)] since June 2019. The Geostationary Carbon Cycle Observatory (GeoCarb) is targeted for launch in 2022 and will be the first geostationary satellite to measure SIF.

OCS measurements have been retrieved from satellite spectrometers that were already launched, but no OCS-specific space-based sensors are planned for the future. Several satellite

products report OCS measurements in the upper troposphere and stratosphere: NASA's Tropospheric Emission Spectrometer (TES; Kuai et al. 2014), ESA's Michelson Interferometer for Passive Atmospheric Sounding (MIPAS; Glatthor et al. 2017) and IASI (Vincent and Dudhia 2017) and the Canadian Space Agency's recently improved Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS; Kloss et al. 2019). This latter product can also be used to estimate ratios of OCS isotopologues (Yousefi et al. 2019). For ecosystem science applications, OCS boundary layer measurements are needed to supplement satellite observations, particularly over land. A targeted satellite approach could make OCS estimates nearer to Earth's surface possible and open up a wider field of questions that OCS data can answer.

Combining both SIF- and OCS-based tools is a very powerful method of measuring global plant activity. This article was conceived at the OCS, CO_2, and SIF study funded by the W. M. Keck Institute for Space Studies in 2017. At the time, we did not have enough data analyzed to harmonize the two approaches and compare estimates of photosynthesis on large scales. This will be the goal of an upcoming workshop in 2022. With a suite of other more established tracers, like heavy water, we can get a better picture of how much carbon is flowing into ecosystems and how much water is escaping back into the atmosphere. When we have a more accurate map of ecosystem function, we can explore and improve our existing process-based ecosystem models. We need to understand how Earth is breathing now to know how resilient it will be to future change.

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