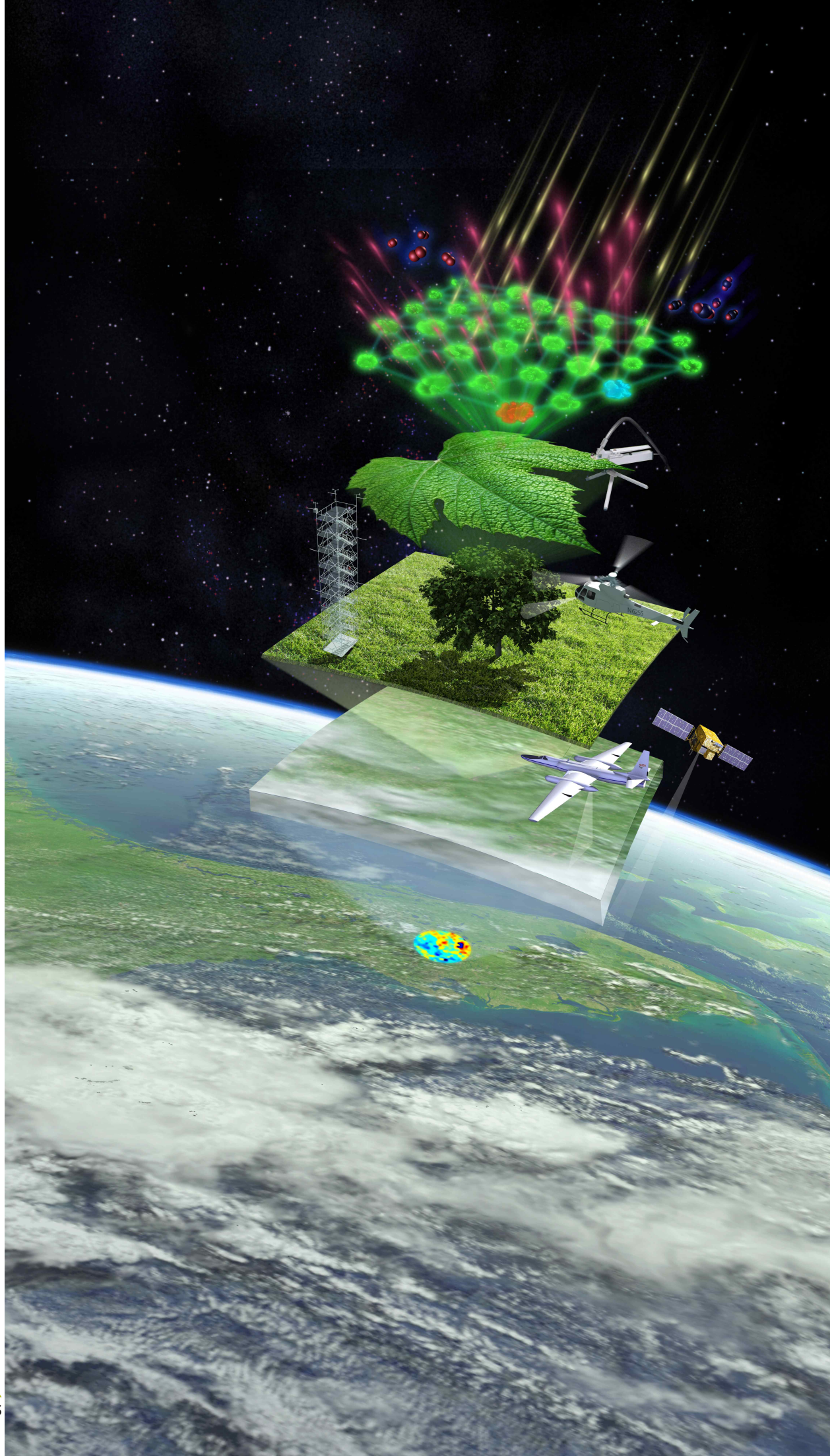


New Methods for Measurements of Photosynthesis from Space





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Study start date: August 26, 2012

Study end date: August 31, 2012

Final Report submission date: April 1, 2013

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Acknowledgments

The research described in this paper was sponsored by the Keck Institute for Space Studies (KISS) and was carried out in part at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

This report is a joint effort of all the people and organizations who participated in the KISS-sponsored study, and we greatly acknowledge everyone's involvement at the workshop and the report. This workshop would have been—speaking euphemistically—very different without the support of the KISS team, most importantly Michele Judd and Tom Prince. Owing to Michele's organizational and herding skills, the team leads could focus on the workshop itself and not worry about logistics.

Further, we thank Pat Rawlings for creating the professional cover art and Susan Foster for her tremendous help (and patience) in editing and getting the final report together.

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Acronyms and Abbreviations

AGCM	atmospheric general circulation models
APAR	absorbed photosynthetically active radiation
ASD	ASD Inc.
Cab	chlorophyll content
CarbonSat	Carbon Monitoring Satellite
CASA	Carnegie, Stanford, Ames Approach
CEFLES	CarboEurope, FLEX, and Sentinel 2
CLN	cropland
CP	chlorophyll-protein complex
CSM	climate systems model
DBFN	deciduous broadleaf forest in northern latitudes
DGVM	dynamic global vegetation models
DNFN	deciduous needleleaf forest in northern latitudes
EBFS	evergreen broadleaf forest in southern latitudes
ECMWF	European Centre for Medium-Range Weather Forecasts
ENVISAT	Environmental Satellite
ESA	European Space Agency
EVI	enhanced vegetation index
FAPAR	fraction of absorbed photosynthetically active radiation
FLEX	FLuorescence EXplorer
FLUXNET	a network of regional flux tower site networks
FPAR	fractional absorptance of sunlight
fs	femtoseconds
FTS	Fourier Transform Spectrometer
FWHM	full width at half maximum
GCC	global carbon cycle
GLN	grasslands in northern latitudes
GOME	Global Ozone Monitoring Experiment
GOSAT	Greenhouse Gases Observing Satellite
GPP	gross primary production
HyPlant	Hyperspectral Plant Imaging Spectrometer
IGBP	International Geosphere-Biosphere Programme
IPCC	Intergovernmental Panel on Climate Change
JAXA	Japan Aerospace Exploration Agency

KISS	Keck Institute for Space Studies
KM	Kubelka-Munk
LAI	leaf area index
LHCII	light-harvesting complexes
LUE	light-use efficiency
MERIS	MEdium Resolution Imaging Spectrometer
MODIS	Moderate Resolution Imaging Spectroradiometer
MOE	Ministry of the Environment (Japan)
MPI-BGC	Max Planck Institute for Biogeochemistry
NCAR	National Center for Atmospheric Research
NDVI	normalized difference index
NDVI	normalized difference vegetation index
NEE	net ecosystem exchange
NEON	National Ecosystem Observatory Network
NIES	National Institute for Environmental Studies (Japan)
NPP	net primary production
NPQ	nonphotochemical quenching
OCO	Orbiting Carbon Observatory
PAM	Pulse Amplitude Modulated
Pg C	petagrams (one billion metric tonnes) of carbon
PROSPECT	A radiative transfer model describing the optical properties of plant leaves from 400 nm to 2500 nm
PSI	photosystem 2
PSII	photosystem 1
RCI	reaction center 1
RCII	reaction center 2
Reco	ecosystem respiration
Rh	soil heterotrophic respiration
RT	radiative transfer
SAIL	Scattering by Arbitrarily Inclined Leaves, a vegetation canopy reflective model
SCIAMACHY	SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY
SCOPE	Soil-Canopy Observation of Photosynthesis and Energy
SiB	Simple Biosphere Model
SIF	sun-induced fluorescence

SpecNet	Spectral Network
SVAT	soil-vegetation-atmosphere
SVN	Savannas
SZA	sun zenith angle
TCCON	Total Carbon Column Observing Network
TOA	top of atmosphere
TOC	top of canopy
VPD	vapor pressure deficit
ZEA	zeaxanthin

1. Executive Summary

Our ability to close the Earth's carbon budget and predict feedbacks in a warming climate depends critically on knowing where, when, and how carbon dioxide (CO₂) is exchanged between the land and atmosphere. In particular, determining the rate of carbon fixation by the Earth's biosphere (commonly referred to as gross primary productivity, or GPP) and the dependence of this productivity on climate is a central goal. Historically, GPP has been inferred from spectral imagery of the land and ocean. Assessment of GPP from the color of the land and ocean requires, however, additional knowledge of the types of plants in the scene, their regulatory mechanisms, and climate variables such as soil moisture—just the independent variables of interest!

Sunlight absorbed by chlorophyll in photosynthetic organisms is mostly used to drive photosynthesis, but some can also be dissipated as heat or re-radiated at longer wavelengths (660–800 nm). This near-infrared light re-emitted from illuminated plants is termed solar-induced fluorescence (SIF), and it has been found to strongly correlate with GPP. To advance our understanding of SIF and its relation to GPP and environmental stress at the planetary scale, the Keck Institute for Space Studies (KISS) convened a workshop—held in Pasadena, California, in August 2012—to focus on a newly developed capacity to monitor chlorophyll fluorescence from terrestrial vegetation by satellite. This revolutionary approach for retrieving global observations of SIF promises to provide direct and spatially resolved information on GPP, an ideal bottom-up complement to the atmospheric net CO₂ exchange inversions.

Workshop participants leveraged our efforts on previous studies and workshops related to the European Space Agency's FLuorescence EXplorer (FLEX) mission concept, which had already targeted SIF for a possible satellite mission and had developed a vibrant research community with many important publications. These studies, mostly focused on landscape, canopy, and leaf-level interpretation, provided the ground-work for the workshop, which focused on the global carbon cycle and synergies with atmospheric net flux inversions.

Workshop participants included key members of several communities: plant physiologists with experience using active fluorescence methods to quantify photosynthesis; ecologists and radiative transfer experts who are studying the challenge of scaling from the leaf to regional scales; atmospheric scientists with experience retrieving photometric information from space-borne spectrometers; and carbon cycle experts who are integrating new observations into models that describe the exchange of carbon between the atmosphere, land and ocean. Together, the participants examined the link between “passive” fluorescence observed from orbiting spacecraft and the underlying photochemistry, plant physiology and biogeochemistry of the land and ocean.

This report details the opportunity for forging a deep connection between scientists doing basic research in photosynthetic mechanisms and the more applied community doing research on the Earth System. Too often these connections have gotten lost in empiricism associated with the coarse scale of global models. Chlorophyll fluorescence has been a major tool for basic research in photosynthesis for nearly a century. SIF observations from space, although sensing a large footprint, probe molecular events occurring in the leaves below.

This offers an opportunity for direct mechanistic insight that is unparalleled for studies of biology in the Earth System.

A major focus of the workshop was to review the basic mechanisms that underlie this phenomenon, and to explore modeling tools that have been developed to link the biophysical and biochemical knowledge of photosynthesis with the observable—in this case, the radiance of SIF—seen by the satellite. Discussions led to the identification of areas where knowledge is still lacking. For example, the inability to do controlled illumination observations from space limits the ability to fully constrain the variables that link fluorescence and photosynthesis.

Another focus of the workshop explored a “top-down” view of the SIF signal from space. Early studies clearly identified a strong correlation between the strength of this signal and our best estimate of the rate of photosynthesis (GPP) over the globe. New studies show that this observation provides improvements over conventional reflectance-based remote sensing in detecting seasonal and environmental (particularly drought related) modulation of photosynthesis. Apparently SIF responds much more quickly and with greater dynamic range than typical greenness indices when GPP is perturbed. However, discussions at the workshop also identified areas where top-down analysis seemed to be “out in front” of mechanistic studies. For example, changes in SIF based on changes in canopy light interception and the light use efficiency of the canopy, both of which occur in response to drought, are assumed equivalent in the top-down analysis, but the mechanistic justification for this is still lacking from the bottom-up side.

Workshop participants considered implications of these mechanistic and empirical insights for large-scale models of the carbon cycle and biogeochemistry, and also made progress toward incorporating SIF as a simulated output in land surface models used in global and regional-scale analysis of the carbon cycle. Comparison of remotely sensed SIF with model-simulated SIF may open new possibilities for model evaluation and data assimilation, perhaps leading to better modeling tools for analysis of the other retrieval from GOSAT satellite, atmospheric CO₂ concentration. Participants also identified another application for SIF: a linkage to the physical climate system arising from the ability to better identify regional development of plant water stress. Decreases in transpiration over large areas of a continent are implicated in the development and “locking-in” of drought conditions. These discussions also identified areas where current land surface models need to be improved in order to enable this research. Specifically, the radiation transport treatments need dramatic overhauls to correctly simulate SIF.

Finally, workshop participants explored approaches for retrieval of SIF from satellite and ground-based sensors. The difficulty of resolving SIF from the overwhelming flux of reflected sunlight in the spectral region where fluorescence occurs was once a major impediment to making this measurement. Placement of very high spectral resolution spectrometers on GOSAT (and other greenhouse gas-sensing satellites) has enabled retrievals based on in-filling of solar Fraunhofer lines, enabling accurate fluorescence measurements even in the presence of moderately thick clouds. Perhaps the most interesting challenge here is that there is no readily portable ground-based instrumentation that even approaches the capability of GOSAT and other planned greenhouse gas satellites. This strongly limits

scientists' ability to conduct ground-based studies to characterize the footprint of the GOSAT measurement and to conduct studies of radiation transport needed to interpret SIF measurement.

The workshop results represent a snapshot of the state of knowledge in this area. New research activities have sprung from the deliberations during the workshop, with publications to follow. The introduction of this new measurement technology to a wide slice of the community of Earth System Scientists will help them understand how this new technology could help solve problems in their research, address concerns about the interpretation, identify future research needs, and elicit support of the wider community for research needed to support this observation.

Somewhat analogous to the original discovery that vegetation indices could be derived from satellite measurements originally intended to detect clouds, the GOSAT observations are a rare case in which a (fortuitous) global satellite dataset becomes available before the research community had a consolidated understanding on how (beyond an empirical correlation) it could be applied to understanding the underlying processes. Vegetation indices have since changed the way we see the global biosphere, and the workshop participants envision that fluorescence can perform the next indispensable step by complementing these measurements with independent estimates that are more indicative of actual (as opposed to potential) photosynthesis. Apart from the potential FLEX mission, no dedicated satellite missions are currently planned. OCO-2 and -3 will provide much more data than GOSAT, but will still not allow for regional studies due to the lack of mapping capabilities. Geostationary observations may even prove most useful, as they could track fluorescence over the course of the day and clearly identify stress-related down-regulation of photosynthesis. Retrieval of fluorescence on the global scale should be recognized as a valuable tool; it can bring the same quantum leap in our understanding of the global carbon cycle as vegetation indices once did.

2. Introduction

The invention of oxygenic photosynthesis by cyanobacteria more than 2 billion years ago remade the Earth. In changing the redox chemistry of the ocean, atmosphere, and land, oxygenic photosynthesis completely altered Earth's geological and biological evolution. The quantity of photosynthesis taking place on planet Earth places an ultimate limit on the quantity and activity of organisms that can be supported by Earth's biosphere.

The growth of the human population has been made possible by appropriating an ever-increasing fraction of Earth's productivity for human use (Vitousek et al., 1986). Over the short term it can be argued that some things man has done—such as improved agricultural practices and increased nitrogen fertilization—have increased productivity, while other things—such as de-forestation, top soil loss, and climate change—may lead to decreasing global photosynthesis. As we contemplate the transition to a sustainable population size and economic model, it is of importance to have an answer to key questions: What is the photosynthetic productivity of Earth? Is it changing? However, current technology limits our ability to answer these questions directly.

The *New Methods for Measurements of Photosynthesis from Space* workshop centered on a new technique to quantify photosynthesis; namely, using solar-induced chlorophyll fluorescence as a direct probe into the photosynthetic process itself. The study leveraged from decades of fluorescence research in the laboratory and on the leaf-level as well as preparatory studies for the European FLuorescence EXplorer (FLEX) satellite mission proposal. In addition, chlorophyll fluorescence data on a global scale became recently available from the Japanese Greenhouse Gases Observing Satellite (GOSAT) using a technique that was previously not thought possible (using solar absorption lines to derive fluorescence estimates). The workshop focused on how chlorophyll fluorescence can inform research on the global carbon cycle, especially on how it may benefit us by providing estimates of actual photosynthetic rates, as opposed to estimates of potential photosynthesis that can be derived using classical remote sensing techniques. As with all new techniques, initial skepticism in the larger community needs to be overcome and a critical mass of researchers reached to support this new concept. In this workshop, a diverse group of researchers—ranging from laboratory-scale plant physiologists to remote sensing expert to global carbon cycle modelers—discussed the potential and shortcomings of the current data. Photosynthesis is pivotal for Earth's budgets of carbon, energy, and water. Fluorescence now provides a highly credible opportunity to exploit a by-product of photosynthesis for global studies. We must not miss this opportunity.

2.1 Scientific motivation and opportunities

The primary scientific stimulus for this study was the sudden availability of chlorophyll fluorescence observations from the GOSAT satellite as well as the potential of the upcoming second Orbiting Carbon Observatory (OCO-2) mission to do the same but with much higher spatial resolution and a 100-fold increase in available data. Historically, the GOSAT and OCO-2 satellite community is strongly linked to atmospheric scientists who use atmospheric greenhouse gas abundances to invert spatially resolved net fluxes of CO₂ between the Earth's surface and atmosphere. If the serendipitous fluorescence retrieval can be used as a spatially and temporally explicit constraint on the gross uptake of CO₂ by terrestrial vegetation, then if

may be possible for net flux inversions to disentangle uptake from respiration—a prerequisite for a process-based understanding of the global carbon cycle and its feedback to global warming.

2.2 Technical motivation and opportunities

Similar to the scientific motivation, the technical motivation also had its origin in the GOSAT fluorescence retrievals: GOSAT demonstrated that high spectral resolution enables chlorophyll fluorescence retrievals that are not affected by atmospheric interferences because retrievals are based on in-filling of solar absorption features (Fraunhofer lines). This is a paradigm shift from the traditional application of oxygen lines, which work very well if the distance between the sensor and the fluorescence emitter is small. Atmospheric scattering, however, can be detrimental to this technique, especially from a satellite.

The new method, however, also has drawbacks, mainly related to the required spectral resolution and high single-measurement noise. However, neither GOSAT nor OCO-2 were optimized for fluorescence retrievals, and there are opportunities to substantially improve on these sensors. The lack of current ground-based instrumentation with the high spectral resolution of GOSAT and OCO-2 also warrants further investigation in optimized detector design for long-term monitoring of fluorescence at fixed locations such as flux-tower sites.

2.3 Scope of study

The scope of the study centered on principal themes with respective organizing questions; namely

1. **Basics of chlorophyll fluorescence across spatial scales (molecular, leaf level, canopy, mixed vegetation)**
 - *What are the biophysical mechanisms of fluorescence and its relation to gross primary production (GPP)?*
 - *Is there adequate knowledge of fluorescence principles to relate emission to GPP? Where are the main uncertainties (canopy radiative transfer or relation of fluorescence yield to photosynthesis yield)?*
 - *How can the scale gap from leaf-scale measurements to the satellite footprint be bridged?*
2. **Global carbon cycle modeling (GPP estimates, source/sink inversions)**
 - *Why is there such a large spread in current GPP model estimates?*
 - *How can fluorescence be implemented in terrestrial vegetation models (→ towards carbon cycle data assimilation)*
 - *Can fluorescence and CO₂ net flux inversions derived from atmospheric CO₂ data be used synergistically?*
3. **Retrieval of chlorophyll fluorescence from ground and space**
 - *What are the advantages and disadvantages of the new technique?*
 - *What would an optimal fluorescence sensor look like based on the new knowledge?*

3. Components of the study: schedule and organization

The workshop was a basic, intensive 1-week Keck Institute for Space Studies (KISS) workshop designed to bring together a diverse community of scientists and engineers to work on a new interdisciplinary research field. On the Sunday prior to the core workshop, we held an open short-course with the aim of developing a common language and introducing the main ideas to all workshop participants as well as to interested researchers from the California Institute of Technology (Caltech), Jet Propulsion Laboratory (JPL), and other universities. The short-course lectures were as follow:

1. The global carbon cycle, an overview (Ian Baker, Colorado State University)
2. A Primer into Photosynthesis and Chlorophyll Fluorescence (Joseph Berry, Carnegie Institution for Science, Stanford)
3. Retrieval of Chlorophyll Fluorescence from Space (Christian Frankenberg, JPL)

Videos of the short-course are available at

<http://www.kiss.caltech.edu/workshops/photosynthesis2012/schedule.html>.

The workshop itself was based on introductory talks for each major topic with adequate time allotted for discussions. The overall schedule was kept flexible in case some topics needed additional attention. Towards the end of the workshop, even more free discussion time was available in order to stimulate open discussions and “digestion” of the ideas that came up in the beginning. Generous lunch and coffee breaks as well as dinners and group events were essential for both community building and scientific discussions in subgroups.

4. Outcome of the study

4.1 Basics of chlorophyll fluorescence across spatial scales (molecular, leaf level, canopy, mixed vegetation)

4.1.1 Introduction

The possibility that climate change will affect crop production while population continues to increase has prompted several institutions such as the World Bank to warn of an impending food crisis. While we have excellent infrastructure for reporting crop yield in many countries, a reliable method to assess crop health across broad agricultural areas to anticipate or diagnose problems with crop production is needed (Lobell and Field, 2007). Similarly, our ability to close the Earth's carbon budget and predict feedbacks in a warming climate depends critically on knowing where, when, and how carbon dioxide (CO₂) is exchanged between the land and atmosphere (Le Quéré et al., 2009). A method is needed to study how climate-driven variability in biological processes control this net flux (Friedlingstein et al., 2006) as the future trajectory of atmospheric CO₂ depends on the response of plants to climate change. Even our ability to understand our weather and climate system is tied up with the productive activities of plants. For example, transpiration of water vapor from plants is directly linked to photosynthesis and moistens the atmosphere over the continents, thereby moderating the climate (Lee et al., 2005).

All of the above and more are linked to the photosynthetic activities of the plants that cover the continents, and it follows that we need to have the best tools possible to measure and monitor this key process of the biosphere. The recent demonstration that chlorophyll fluorescence can be monitored from a satellite platform provides a novel and possibly breakthrough tool for studies of photosynthesis. Up to this point our knowledge of vegetation dynamics has been obtained from analysis of sunlight reflected by leaves and other objects at the ground surface. The high spectral resolution of the GOSAT sensor has enabled us to see the light that plant leaves emit as chlorophyll fluorescence. This is an entirely new light arising from within the photosynthetic machinery of plants. Only plants conducting photosynthesis emit this light. In this section we examine how this light is linked to the photosynthetic process.

4.1.1.1 Terrestrial Photosynthesis

While photosynthesis is normally defined as the use of energy from absorbed light to accomplish the uphill synthesis of sugars from CO₂, it is useful here to think of this in the context of plant growth in a terrestrial environment. Photosynthesis on land requires that the plant replace the water that inevitably escapes from its leaves when CO₂ is taken up from the dry atmosphere. Plants also require a supply of nutrients in addition to the water exchanged for carbon, since the ultimate product of photosynthesis is not only carbohydrates but also new plant tissue. Therefore, we will refer to photosynthesis synonymously with gross primary production (GPP). Physiological and developmental mechanisms operate to adjust the rate of GPP to the availability of resources. For example, a recent analysis (Beer et al., 2009) of CO₂ and water vapor exchange measured by eddy covariance from a wide range of ecosystems indicates a loss of about 200±63 mol of water for each mol of C taken up as GPP by the canopy at a sampling of flux sites. This close metering of water use is due in part

to physiological regulation of the stomata, which are valves on the leaf surface that permit the exchange of gases between the leaf interior and the atmosphere. When these close both water loss and GPP are restricted. In addition, there are important indirect effects of water supply on the rate of leaf area expansion and the allocation of new growth to roots vs. shoots that tends to balance the plant's demand for water with its ability to obtain water over its growing season. Similarly, deficiency of an essential nutrient tends to cause plants to suppress expansion of leaf area in favor of forming more roots. Field et al. (1995) point out that evolutionary processes have tuned the physiology and developmental programs of plants to reduce the impact of single limiting factors such that growth can be co-limited by several factors. This is the strategy that would make most efficient use of the specific suites of resources available in different locations, and it has important implications for the way that we view productivity of terrestrial plants.

John Monteith (1972) proposed an equation that has become the paradigm for understanding GPP:

$$\text{GPP} = \text{PAR} \cdot \text{FPAR} \cdot \varepsilon_p \quad (4-1)$$

It is given as proportional to the incident short wave radiation, the fractional absorption of that flux (FPAR) and the efficiency with which the absorbed radiation is converted to fixed carbon, ε_p . There has been a tendency to emphasize one term or the other of this equation. In England, crop physiologists focused on the PAR term that explains the seasonal growth of crops and year-to-year variation in yield. Many in the remote sensing community have focused on the FPAR term (Sellers et al., 1985), and more recently on the light-use-efficiency term as the arbiter of productivity—particularly in strongly seasonal and nutrient-limited forests (Coops et al 2010). From the ecological perspective above, we could argue that much of the long-term spatial variation in productivity is likely to reside in the FPAR term, as it reflects differences between sites in the average availability of resources for plant growth. Variation in ε_p ; however, is likely to be significant over shorter time frames when water or temperature stress develops. The take home message is that this simple equation sits atop a great deal of biological and biophysical complexity. Researchers have developed models of GPP that deal with this complexity in different ways.

4.1.1.2 *Estimating photosynthesis at global scales*

With the development of a global infrastructure for weather forecasting and satellite remote sensing of surface reflectance, it has become possible to specify the environmental conditions that plants experience and the density of plant cover over the continents, and to use these data to drive models of the land surface. Checking these models has always been problematic. Traditionally, GPP has been estimated by measurement of net primary production at a plot scale and correcting for respiratory losses (about half) in converting sugars to new plant material (Field et al., 1995). The development of eddy correlation as a method for quantifying the carbon, water, and energy balance over so-called “flux sites” has given us a wealth of observational data to test and tune models; but these measure net CO₂ exchange, the sum of ecosystem respiration, and GPP. Several approaches are used to estimate GPP (Desai et al., 2008), but these are difficult to verify. In neither case is there sufficient density of sampling to get regional or continental scale GPP. This is the domain of models. Three general types of models are in use:

- 1 *Light-use-efficiency models*, exemplified by the MODIS (Moderate Resolution Imaging Spectroradiometer)-GPP product (Zhao et al., 2005), make direct use of remote sensing to estimate the flux of absorbed light on a grid over the land surface. These models apply Eqn. 4-1 to estimate GPP. This approach uses meteorological data from reanalysis products to modulate ε_p but does not explicitly model the biophysical environment. The CASA (Carnegie, Stanford, Ames Approach) model (Field et al., 1995) has a similar productivity model that is coupled to a multi-pool carbon cycle module to provide a gridded net CO₂ flux as a product.
- 2 *Process models* of the Earth system include a much more complete representation of the biophysical environment that the plant experiences and simulate the plant's physiological responses to the environment. In particular, these models integrate a number of state variables, such as the quantity of water stored in the soil, the soil temperature, and the leaf area index from time step to time step. These models have been developed from climate models, in which the focus is on the exchange of energy between the land surface and the atmosphere. Several models of this type—for example, the National Center for Atmospheric Research's Climate Systems Model (NCAR CSM)—are now being used in Intergovernmental Panel on Climate Change (IPCC) studies to predict the course and impacts of climate change.
- 3 *Diagnostic models* do not attempt to represent the mechanisms occurring on the land surface, but instead use empirical studies to calibrate GPP to potentially limiting resources; for example, can GPP be statistically related to the quantity of precipitation, temperature, leaf-area index (LAI) and other observations? The classic Miami model, which was the first to estimate global productivity, is such a model: Beer et al. (2009) have made use of a machine learning approach to analyze over 1000 site years of flux observations to calibrate a global model of GPP, and they provide a global GPP estimate that they claim is accurate to $\pm 5\%$.

Each of these model types has a niche where it excels. For example, the MODIS-GPP model is directly linked to remote sensing and weather forecast products and can provide near-real time information on productivity and the influence of anomalies such as droughts. However, it can only be run retrospectively; hence, it is not appropriate for “what if” questions. The process models are designed to be predictive and are widely used for studies of the carbon cycle and how it will respond to climate change and for studies of carbon cycle climate feedbacks. The diagnostic models are able to take advantage of the large pool of measurement data, so they have a much stronger statistical basis for estimating GPP. However, since the model does not represent mechanisms, the results should be viewed more as a “climatology” of GPP than as a predictor of the response of GPP to future climate.

The modeling approaches also have specific limitations. Studies with the MODIS-GPP product (Heinsch et al., 2006) highlight its ability to correctly predict observed fluxes at tower sites, but also draw attention to the uncertainty in the MODIS vegetation indices due to cloud and aerosol contamination problems, errors in the re-analysis meteorology, and difficulty constraining the light-use-efficiency term. The process models, while faithful to the mechanisms, have great difficulty with calibration and accumulation of errors in the simulated state variables. For example, an error in calibration of the effective storage capacity for water in the soil can lead to errors in site hydrology impacting the water

available for photosynthesis—even if it was perfect in other respects. Currently process models can only be calibrated at flux sites, and there is very limited capability to assess or correct for errors in state variable integration. The diagnostic models do very well at the flux sites, but there is a lot of space between these that is poorly constrained. Remote sensing approaches that could help fill these gaps would improve the accuracy of both the process models and the diagnostic models. Models inter-comparison studies (Huntzinger et al., 2012) show differences by a factor of nearly 2 in simulated GPP of North America using the same input data. Clearly, there is room for improvement.

One of the primary causes for this large uncertainty in GPP is the fact that it cannot be measured directly on a geographically relevant scale. At the leaf scale, GPP can be determined as the gross CO₂ uptake (i.e., the sum of net CO₂ uptake in the light and respiratory CO₂ release in the dark). As the scale of the measurement goes up, respiration becomes an increasingly important component of the carbon balance, and it becomes more difficult to measure GPP independently of net CO₂ uptake. At the regional or global scale, the two processes—GPP and ecosystem respiration (Reco)—are nearly balanced, but neither is strongly constrained by the observed net CO₂ flux. It is ironic that one of the most important processes of the terrestrial biosphere is hidden from us.

4.1.1.3 Chlorophyll fluorescence

With this background, we will now turn to fluorescence and what it might do for us. Chlorophyll fluorescence has been used in laboratory-scale studies of photosynthesis for several decades (Krause and Weis, 1987) and has been used in studies of the effect of nutrient stress on marine productivity (Behrenfeld et al., 2012). Technical difficulties relating to the variable reflectance of terrestrial vegetation in the band where chlorophyll fluorescence resides has inhibited the use of this approach for studies of photosynthesis on the land. Recently, it was found that chlorophyll fluorescence can be retrieved from high-resolution spectra around 757 nm recorded by GOSAT (Joiner et al., 2011; Frankenberg et al., 2011a,b). The spectral channel used for this retrieval was mainly intended for correcting scattering effects in atmospheric greenhouse gas retrievals. Typically about only 1% of the absorbed photons are re-emitted as fluorescence. This re-emitted light mixes with sunlight and is difficult to detect, but the signal can be resolved using high-resolution spectrometer instruments, by observing the in-filling of solar Fraunhofer lines (Joiner et al., 2011; Frankenberg et al., 2011). The GOSAT satellite has been making measurement of sun-induced fluorescence (SIF) since 2009. This signal is a distinct "glow" from plants at wavelengths between 690 nm and about 800 nm that is quite specific for the presence of green plants. It reports on the flux density of photons absorbed by chlorophyll molecules and on the processing of these photons by photosynthetic reaction centers at the time of satellite observation (approximately noon on clear days). The footprint of the observation is a circle about 10 km in diameter. The retrieval is also very insensitive to atmospheric scattering and clouds (Frankenberg et al., 2012), which is in contrast to conventional reflectance spectroscopy. It is also not influenced by the reflective properties of soil or other materials that may be present in the scene.

As a first approximation, the flux of SIF detected by a radiometer looking down on the land surface can be expressed by an equation that is analogous to the expression for GPP,

$$\text{SIF} = \text{PAR} \cdot \text{FPAR} \cdot \varepsilon_f \quad (4-2)$$

where ε_f is the yield of fluorescence photons at the top of the canopy and $\text{PAR} \cdot \text{FPAR}$ is the flux of absorbed light. Figure 4-1 shows monthly mean of GOSAT-measured SIF aggregated by biome regressed against FPAR (from MODIS) times the cosine of the solar zenith ($\cos(\text{SZA})$) which is essentially the flux of absorbed light at the time of GOSAT overpass. While SIF correlates well with existing absorbed PAR products, it is important to recognize that it is an independent measurement linked to a specific component of APAR: that absorbed by chlorophyll. As such it may provide insight into the way we use vegetation indices. In addition, there is evidence (see section 4.2) that SIF is more dynamic than greenness, indicating that there may be additional control by ε_f .

It is interesting that this expression can be combined with Eqn. 4-1 and rearranged to eliminate the parallel dependence of both processes on APAR to yield

$$\text{GPP} = \text{SIF} \cdot \varepsilon_p / \varepsilon_f \quad (4-3)$$

It is well established that ε_p varies with the level of physiological (water or low temperature) stress. This begs the question, what happens to ε_f under stress? If ε_f and ε_p respond in parallel to stress, then both GPP and SIF will decline under stress; and measurements of SIF could

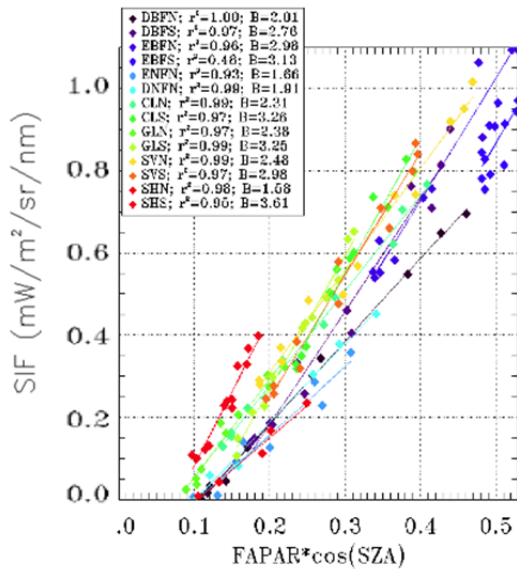


Figure 4-1. Linear regressions of GOSAT SIF vs. $\text{SIF} \cdot \cos(\text{SZA})$ where SZA is the solar zenith angle at the time of overpass (Guanter et al., 2012). Each symbol represents one month (2009–2011). Biomes follow the International Geosphere-Biosphere Programme (IGBP)–based land cover classes: [DBF]=Deciduous Broadleaf Forest, [EBLN(S)]=Evergreen Broadleaf Forest in the northern (southern) hemisphere, [NF]=Needleleaf Forest, [CLN(S)]=Cropland in the northern (southern) hemisphere, [GL]=Grasslands, [SVN(S)]=Savannas in the northern (southern) hemisphere (from Guanter et al., 2012).

also provide a proxy for variation that occurs when stress (in addition to light harvesting) restricts photosynthesis. Research inspired by the European Space Agency's FLuorescence EXplorer (FLEX) mission concept (Meroni et al., 2009, Moya et al., 2006) provides clear evidence for an effect of stress on ε_f . For example, leaf-scale studies show that physiological effects of drought that lead to a decrease of light-use efficiency (LUE) for photosynthesis (ε_p) are associated with decreases in fluorescence yield (ε_f) (Flexas et al., 2002). In a field experiment, measurements of fluorescence during an episode of drought (Figure 4-2 Daumard et al., 2010) demonstrate that fluorescence declines, whereas normalized difference vegetation index (NDVI) (and presumably light interception) in that experiment remained constant (Daumard et al., 2010). Therefore, it seems reasonable to expect that changes in SIF may

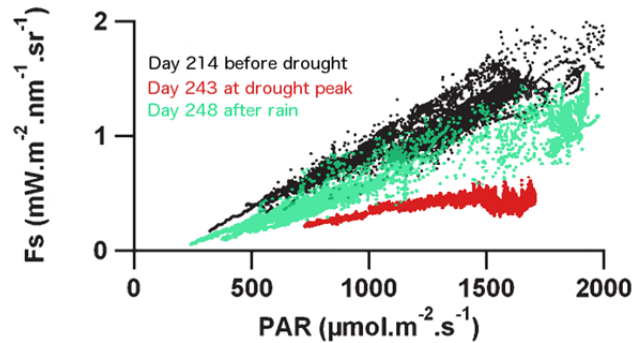


Figure 4-2. A plot of SIF as a function of PAR (the slope is the apparent ϵ_f) made from a radiometer on a tower above a rain fed sorghum crop (adapted from Daumard et al., 2010). The authors note that there was no change in LAI or NDVI, indicating that absorption of light was constant over this interval. Thus, ϵ_f appears to decrease with water stress. Photosynthesis was not measured in these studies, but there is every reason to expect that GPP also declined, leading us to expect that SIF may be used as a proxy for stress effects on GPP.

indicate changes in GPP associated with episodes of stress, and that SIF might sense the development of stress before significant changes in FPAR occur. Satellites are ideally suited for change detection, and deviations of SIF from the expected correlation with absorbed PAR may be a powerful indicator of physiological stress.

There is strong empirical evidence to support this assertion (see Section 4.2). In the remainder of this section, we consider the mechanistic basis for linking photosynthetic rate with satellite observations of SIF.

4.1.2 Modeling fluorescence and photosynthesis from the bottom up

These topics have received abundant attention from researchers interested in basic photosynthetic mechanisms, but the

need to explain SIF presents a new challenge that require changes in existing models. The Soil-Canopy Observation of Photosynthesis and Energy (SCOPE) balance model (van der Tol et al., 2009a,b) is presented here as an example of a model under development for predicting the flux of SIF at the top of a plant canopy (what the satellite observes) from the mechanisms that occur in the chloroplasts and leaves of the canopy. This is by necessity a highly detailed presentation, and many readers may wish to skip over it or refer back to it for information on specific mechanisms.

4.1.2.1 Fluorescence emission at the molecular scale

Chlorophyll molecules are very efficient in absorbing visible light, especially in the blue and red regions. This property is responsible for the green color of chlorophyll and generally of leaves. We begin by considering the interactions of chlorophyll dissolved in an organic solvent. Chlorophyll-a presents two absorption peaks around 430 nm (blue) and 662 nm (red), whereas chlorophyll-b absorption peaks are slightly green-shifted at around 453 and 642. Upon absorption, the energy carried by a photon of blue light is able to excite one of the chlorophyll molecule electrons from the ground state (S_0) to the second molecular orbital (S_2), whereas a photon of red light is able to bring the electron to the first molecular orbital (S_1). From S_2 , the energy is rapidly lost as heat through internal conversion and radiationless decay within a few picoseconds (10^{-12} s) and the electron relaxes to the first molecular orbital (S_1) (Gobets and Grondelle, 2001; Clegg, 2004). It is from the first orbital (S_1) that the excitation energy can take different pathways. Intrinsically, an isolated chlorophyll molecule has three main de-excitation pathways; namely, the electron can relax to the ground state via internal conversion, it can be re-emitted as a photon of light (fluorescence), or it can undergo intersystem crossing and form a chlorophyll triplet state. We can express the fluorescence yield as:

$$\Phi_F(\text{chl}) = k_f / (k_f + k_D + k_{isc}) \quad (4-4)$$

where k_f is the first-order rate constant of fluorescence, k_D the rate constant associated to the constitutive thermal deactivation (radiationless decay), and k_{isc} the rate constant representing the process of intersystem crossing to the triplet state, which is orders of magnitude smaller to that of k_f and k_D (Butler and Kitajima, 1975) for excitation in S_1 . Under these conditions, when chlorophyll is isolated and diluted in a solvent, the fluorescence yield can be very high, e.g., 0.33 or 0.16 for chlorophyll-a and chlorophyll-b, respectively (Latimer et al., 1956; Brody and Brody, 1962; Rabinovitch and Govindjee, 1965). Yet, the chlorophyll-a fluorescence yield in vivo (in the leaf) is more than one order of magnitude smaller because much of the absorbed energy is trapped to do useful work.

4.1.2.2 Fluorescence emission at the scale of chloroplast membranes

During evolution, primordial bacteria, algae—and, later on, higher plants—have evolved structures to efficiently and cost-effectively capture light, and to move its associated energy (exciton) from chlorophyll to chlorophyll and ultimately to a reaction center where the exciton is used to effect a photochemical reaction. Fluorescence yield is strongly suppressed and may be viewed a “leak” from the system rather than a major pathway for de-excitation. These structures are what we now call photosynthetic antennas, a complex multiunit matrix of proteins that bind pigments and that are carefully arranged and distributed to efficiently supply excitation energy to traps, where the excitation energy is converted into more stable form of energy.

There are at least three types of traps for excitons in chloroplast membranes:

- a. Reaction center 2 (RCII) of photosystem 2 (PSII), where photochemical reaction (charge separation) occurs and molecular oxygen is formed from water. The electron liberated in this reaction is passed to electron carriers and photosystem 1 (PSI).
- b. Reaction center 1 (RCI) of PSI, where photochemical reaction (charge separation) also occurs and can be described as the second photo act that uses exciton energy to move the electron produced by PSII to a higher energy level (redox potential) needed to reduce CO_2 .
- c. In addition to PSI and PSII, there may be non-photochemical quenching (NPQ) traps that dissipate excitons harmlessly to heat. The population of these traps at PSII is related to the concentration of a specific carotenoid, zeaxanthin, that is formed when the supply of electrons from PSII exceeds the capacity to use them for reducing CO_2 . NPQ traps are analogous to pressure relief valves on a steam boiler; they only open as much as necessary, and they are specifically associated with PSII.

All of these traps use excitons from the S_1 excited state of chlorophyll. Excitons formed from absorption of blue light are converted to the S_1 state by internal conversion. Thus, a photon of blue and a photon of red light have the same inherent probability of driving photosynthesis; that is why the term “quantum efficiency” is widely used in photosynthesis.

PSII. The supramolecular structure of PSII of higher plants is composed of the following: (1) a core that includes the reaction center chlorophyll pair P680 and two protein complexes (CP43 and CP47) that bind together 38 chlorophyll-a molecules and a number of carotenoids; (2) a peripheral antenna that connects the core to the outer antennas and that is

composed of (a) three different chlorophyll-protein complexes (CP26, CP24, and CP29), each binding chlorophyll-a, chlorophyll-b, and carotenoids, and (b) the main outer antenna that is composed of large protein complexes known as light-harvesting complexes (LHCII), where the gross of the chlorophyll-a and chlorophyll-b is found (Vassiliev and Bruce, 2008). A PSII unit has 180 to 400 chlorophyll molecules, slightly more than found in PSI, although with PSI's having less chlorophyll-b. This number is approximate because the structure of the photosystem and its different complexes has not yet been resolved in vivo, where photosystems with different antenna sizes coexist.

Binding of chlorophyll molecules to a protein and subsequently to a reaction center has a number of important implications. First, unlike in solution, binding of a chlorophyll molecule to a specific site in a protein will affect its electronic properties and thus its absorption and emission (fluorescence) spectra. As a result, the antenna is composed of chlorophylls with different spectral forms that tend to form an energetic gradient for transfer of excitons from the peripheral antenna towards the reaction center (Vassiliev and Bruce, 2008; Novoderezhkin and Grondelle, 2010). Second, the location and orientation of the pigment binding sites in proteins has been highly optimized during evolution to promote fast and efficient energy transfer between neighboring chlorophylls as well as between different protein complexes by means of "link" chlorophylls. Energy transfer in the antenna takes place through different mechanisms: during the first hundreds of femtoseconds (fs); after a chlorophyll absorbs a photon, the excitation energy appears to be delocalized among adjacent chlorophylls in what has been defined as a quantum coherent state (Engel et al., 2007; Ishizaki and Fleming, 2009). This quantum coherence operates at the level of antenna subunit, where neighboring pigments are highly coupled, allowing the excitation to sample the most optimal route for the excitation to be passed downstream. Subsequently, energy transfer takes place through Förster resonance energy transfer (Förster, 1955; Novoderezhkin and Grondelle, 2010); this type of energy transfer would be responsible for the migration of excitation energy from the antenna to the reaction center.

As a result, because chlorophylls are now connected to a reaction center via the antenna, energy transfer (leading to photochemistry) will also compete with fluorescence for de-excitation of energy at the level of chlorophyll molecule. In turn, if we consider the energy partitioning at the level of PSII antennas, and also take into account the regulatory quenching mechanisms by NPQ traps (see item c above) we can update Eqn. 4-4 and express the fluorescence yield in the photosystem as

$$\Phi_F(\text{PSII}) = k_f / (k_f + k_D + k_P + k_{\text{NPQ}}) \quad (4-5)$$

where k_P is the rate constant of the photochemical process by which excitation energy is bound chemically and k_{NPQ} is the rate constant associated to the regulated thermal dissipation mechanisms (NPQ). Figure 4-3 is a schematic diagram of photon processing in PSII.

In vivo, most of the fluorescence comes from PSII. By comparing Eqn. 4-4 and Eqn. 4-5, it is obvious that the yield of chlorophyll-a fluorescence in vivo will be lower than that of chlorophyll in solutions because we now have two more processes competing for excitation energy with fluorescence; namely, k_P and k_{NPQ} . Yet, if we estimate the fluorescence yield upon a saturating light pulse that momentarily "blocks" electron transport and photochemistry

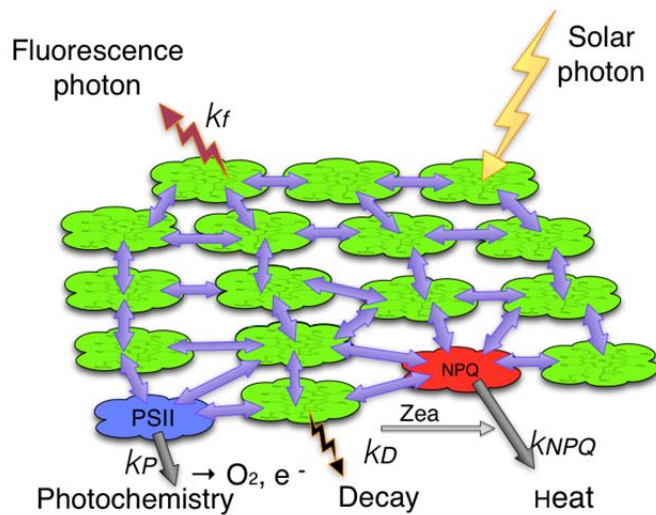


Figure 4-3. A schematic representation of the processing of absorbed photons (excitons) in the chlorophylls associated with a PSII reactions center (PSII) and a non-photochemical trapping center (NPQ). The absorbed photons can be lost as radiationless decay (k_D), re-emitted as a fluorescent photon (k_f), used for photochemistry (k_p), or quenched by NPQs (k_{NPQ}), or as given by Eqn. 4-5. The concentration of Zeaxanthin (Zea) modulates the level of NPQ.

($k_p=0$) and in dark-acclimated samples that do not present any NPQ ($k_{NPQ}=0$), the yield fluorescence at this so called F_m level is still smaller than that obtained in solution. One of the reasons for the lower yield in vivo is the reabsorption of red chlorophyll-a fluorescence by the high local concentration of chlorophyll in the membranes. The spectra of emitted fluorescence extends from 650 nm to well beyond 800 nm; thus, fluorescence in the range 650 nm to 700 nm can be re-absorbed by chlorophylls associated to PSI and PSII and used in photochemistry. For this reason, in addition to the factors expressed in Eqn. 4-5, the yield of fluorescence in the red region (650 nm to 700 nm) will also depend on the chlorophyll content of the leaf. In fact, this phenomenon has been exploited as a means to

estimate leaf chlorophyll content and has been shown to correlate very well with the $F(\text{red})/F(\text{far-red})$ ratio (Gitelson et al., 1999).

PSI. Similarly, the emission of fluorescence in the far-red region occurs from PSI. The fluorescence yield in PSI is generally assumed to be much lower than that of PSII, and it is also assumed to remain constant given that the reaction center of PSI is an effective excitation trap independently of its redox state. For this reason, fluorescence from PSI does not exhibit the dynamics of PSII, and it has typically been considered as something to be corrected from the otherwise “photosynthesis-sensitive” signal coming from PSII. The fluorescence yield in PSI could be expressed as

$$\Phi_F(\text{PSI}) = k_f / (k_f + k_D + k_{P700}) \quad (4-6)$$

where k_{P700} is the rate constant of energy trapping by the PSI reaction center P700 (named P700 after the chlorophyll in its reaction center that absorbs light at 700 nm, in contrast to PSII reaction center chlorophyll P680, which absorbs at 680 nm). The contribution of PSI fluorescence to total fluorescence has been estimated in different species and using different methods, and it has been found to be as high as 30% to 50% in the far-red regions (>700 nm) (Genty et al., 1991; Pfündel et al., 1998, and Franck et al., 2002). The contribution to F_o fluorescence by PSI and PSII varies with wavelength (Figure 4-4). Much of the work on chlorophyll fluorescence has ignored the contribution of PSI because it does not contribute to dynamic changes in fluorescence yield. However, it is a significant, albeit rather constant,

component. Subtracting the PSI component may simplify interpretation of the dynamics of fluorescence.

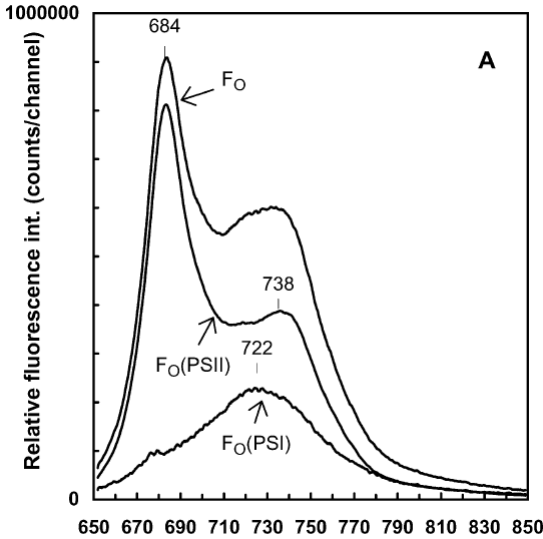


Figure 4-4. Emission spectra for fluorescence from PSI and PSII at the F_0 level (from Frank et al., 2002)

4.1.2.3 CO_2 fixation and fluorescence at the leaf scale

Photosynthesis is a sequence of linked reactions starting with the absorption of light by chlorophyll molecules associated with quantum mechanical processes occurring at reaction centers to biochemical processes that take carbon dioxide from the air to form sugars. The photochemical reactions use the energy of absorbed photons to remove an electron from water-making O_2 and raising the electron to the higher energy level needed to reduce carbon-oxygen bonds in the formation of sugars from CO_2 . The first steps are dependent on the flux of absorbed light and the efficiency with which it is use in photochemistry, while the latter steps are largely independent of light but strongly dependent on enzymatic reactions governed by

the concentration of CO_2 available in the chloroplast and temperature. These reactions become strongly inhibited when water stress develops (Collatz et al., 1991). To maintain redox balance, the rate at which electrons are produced in PSII must balance the rate at which these are consumed in CO_2 reduction. Regulatory processes have evolved to manage the coordination between photochemical and biochemical processes in photosynthesis such that the overall rate approaches the maximum permitted by the available light or the biochemical fixation, whichever is most limiting (Farquhar et al., 1980; Woodrow and Berry, 1988). For the processes considered here, it is only important to understand that there is an interaction between the carbon fixation steps and photon processing in the antenna of PSII. When biochemical reactions are slowed but light absorption continues, feedback mechanisms rebalance the two processes by reducing k_P and/or increasing k_{NPQ} (see Figure 4-3), and this impacts the yield of fluorescence.and photochemistry per absorbed photons. After Eqn. 4-5 we may write that

$$\Phi_F(PSII) = k_f / (k_f + k_D + k_P' + k_{NPQ}') \quad (4-7)$$

and

$$\Phi_P(PSII) = k_P' / (k_f + k_D + k_P' + k_{NPQ}') \quad (4-8)$$

where $\Phi_P(PSII)$ is the corresponding yield of photochemistry and the primes indicate new values of the k 's under the new condition. These equations provide a framework for relating fluorescence and photochemical yields, but the problem is complicated by the contradictory effects of changes in k_P and k_{NPQ} . From eqns. 4-7 and 4-8, we can deduce that: if the feedback increases k_{NPQ} , keeping all else constant, Φ_P and Φ_F decrease together; but if the feedback were to decrease k_P , Φ_P would decrease but Φ_F would increase. Whether Φ_P and Φ_F respond

in parallel or in opposite directions depends on how the feedback is partitioned. To resolve this, we need to examine what happens in laboratory experiments where the exchange of CO₂ and fluorescence are monitored while factors influencing the balance between CO₂ fixation and photochemistry (light levels, CO₂ concentration, or stress) are changed (e.g., Weis and Berry, 1987). These experiments employ a special type of fluorometry that differs from the passive observations we have been discussing.

In the 1980s Schreiber and Shilwa (1986) developed an approach referred to as PAM (Pulse Amplitude Modulated) fluorometry, which uses rapid manipulations of the light regime together with a modulated measuring light to infer the values of the rate constants k_P and k_{NPQ} during steady-state photosynthesis. The use of a constant level of modulated light permits direct measurement of Φ_F independent of the level of unmodulated (DC) light present. Figure 4-5 shows a typical PAM experiment, and the diagnostic fluorescence levels are defined in the legend. These can be used to infer the values of rate constants during steady-state photosynthesis.

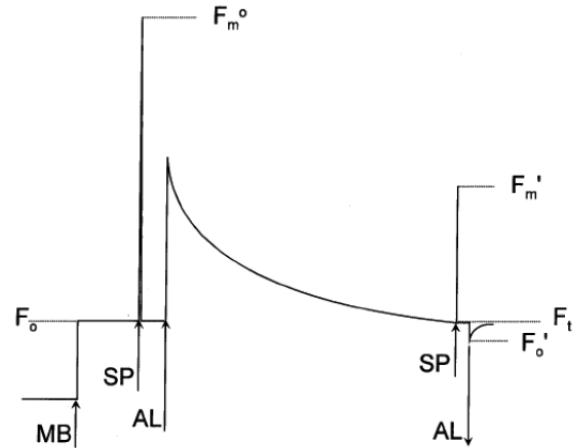


Figure 4-5. A typical sequence of fluorescence measurements of a dark adapted leaf with a PAM fluorometer. The measuring beam is turned on at MB↑ yielding the F_o level (all photochemical traps open $k_{NPQ}=0$). Exposing the leaf to a saturating pulse of light at SP↑ closes nearly all of the photochemical traps yielding F_m^o . Turning on an actinic light at AL↑ activates photosynthesis and feedback mechanisms bring the fluorescence level to a steady-state level F_t . Application of another saturating pulse SP↑ results in a lower maximum fluorescence, F_m' , which reflects the presence of non-photochemical quenching. Turning off the actinic light AL↓ gives the F_o' level, which is typically lower than the dark adapted F_o . (from Maxwell et al., 2003)

Genty et al. (1989) developed an expression from theory that relates the photochemical yield of electrons ($\Phi_P(\text{PSII}) = \text{mol electrons transported/mol quanta absorbed}$) to the fluorescence yields measured at steady state illumination (F_t) and in the pulse (F_m').

$$\Phi_P(\text{PSII}) = (F_m' - F_t) / F_m' = \Delta F / F_m'$$

and

$$J_e = 0.5 \cdot Q \cdot \Phi_P(\text{PSII})$$

Where J_e is the flux of electrons from PSII, Q is the flux of absorbed photons, and the constant 0.5 is included to account for the fact that only half of the absorbed photons are used by PSII. The other half is used by PSI. This can be understood in terms of the formalism developed above by noting that the fluorescence yield (F_m') measured by PAM fluorometry (Figure 4-5) is given by,

$$F_m' = \Phi_{Fm'}(\text{PSII}) = k_f / (k_f + k_D + k_{NPQ}') \quad (4-9)$$

and that F_t is given by Eqn. 4-5. (Note that k_P' is missing from 4-6 because it is forced to zero by the saturating flash, but k_{NPQ} remains the same). This gives us two expressions for fluorescence yield. Substituting these into $\Phi_F(\text{PSII}) = (F_m' - F_t)/F_m'$, and collecting terms we get

$$(F_m' - F_t)/F_m' = k_P/(k_f + k_D + k_P' + k_{NPQ}') = \Phi_F(\text{PSII}) \quad (4-10)$$

This is identical to Eqn. 4-8.

PAM fluorometry at the leaf scale provides a robust basis for evaluating the LUE for electron transport, and it can be used to solve for values of k_P' and k_{NPQ}' during steady-state photosynthesis. It has been widely used to study responses to stress, and leaf measurements of $\Phi_P(\text{PSII})$ will be very useful for scaling up to the canopy.

SIF measurements can be related to the yield at steady state obtained with a PAM fluorometer, (F_t , Figure 4-5),

$$\text{SIF} = \Phi_{Ft} \cdot \text{APAR} \quad (4-11)$$

Most of the studies reported in the literature use the PAM approach. PAM measurements are not possible from a satellite platform since we are only to make a passive measurement, but PAM measurements at the leaf scale can be used to better understand the mechanisms that control SIF.

4.1.3 Equations for interpreting SIF

4.1.3.1 Predicting fluorescence and photosynthesis yields

The key question of passive, solar induced fluorescence is thus to obtain information from a single measurement: the fluorescence at steady state Φ_{Ft} . To interpret the steady state fluorescence we need to know how the two variable rate coefficients, k_P (photochemical quenching) and k_{NPQ} (non-photochemical quenching), vary with stress conditions. The term stress is broadly defined: it can be any factor that lowers the carboxylation rate below the potential rate sustained by light absorption.

Figure 4-6 illustrates this. The figure shows measured and modeled light response curves of gas exchange and active measurements of cotton leaves. The model of Collatz et al. (1991) was fitted to these measurements. Photosynthesis A and electron transport rate J_e increase with irradiance, but the relationship saturates as factors other than fluorescence start to limit photosynthesis. As photosynthesis becomes more and more light saturated, the photochemical yield Φ_{PS2} decreases.

The maximum fluorescence Φ_{Fm}' (the fluorescence yield after a brief saturating light pulse) decreases with irradiance as well, but the steady-state fluorescence Φ_{Ft} shows a different pattern: it first increases, and then decreases again with irradiance. The initial increase is caused by the reduction of photosystems and consequent reduction of k_P (the same principle is also used to measure Φ_{Fm}' a saturating light pulse causes $k_P' = 0$). At higher irradiance, the effect of an increasing k_{NPQ} becomes dominant, and both Φ_{Ft} and Φ_P decrease.

If we are able to express the two variable rate coefficients as a function of Φ_{PS2} , then the unknown k_P' can be eliminated from eqns. 4-7 and 4-8, and the equations can be solved. Figure 4-7 (left panel) shows rate coefficients versus the relative reduction of the

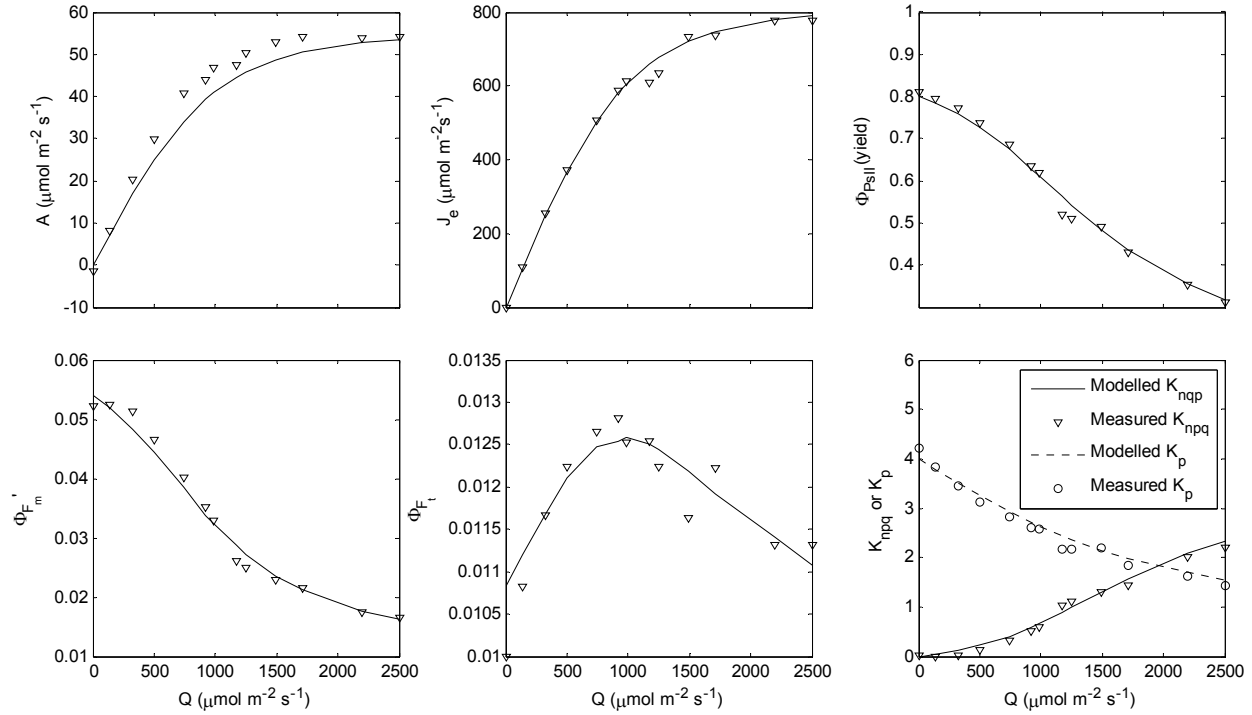


Figure 4-6. Measured (Leaf gas exchange and PAM- symbols) and modeled (Collatz et al., 1991; as implemented in SCOPE- lines) light (Q)response curves of leaf photosynthesis A , electron transport rate J_e , photochemical yield Φ_{PsII} , maximum fluorescence yield Φ_{Fm}' , steady state fluorescence yield Φ_{Ft} , and the rate coefficients k_{NPQ} and k_p k_{NPQ} of cotton leaves.

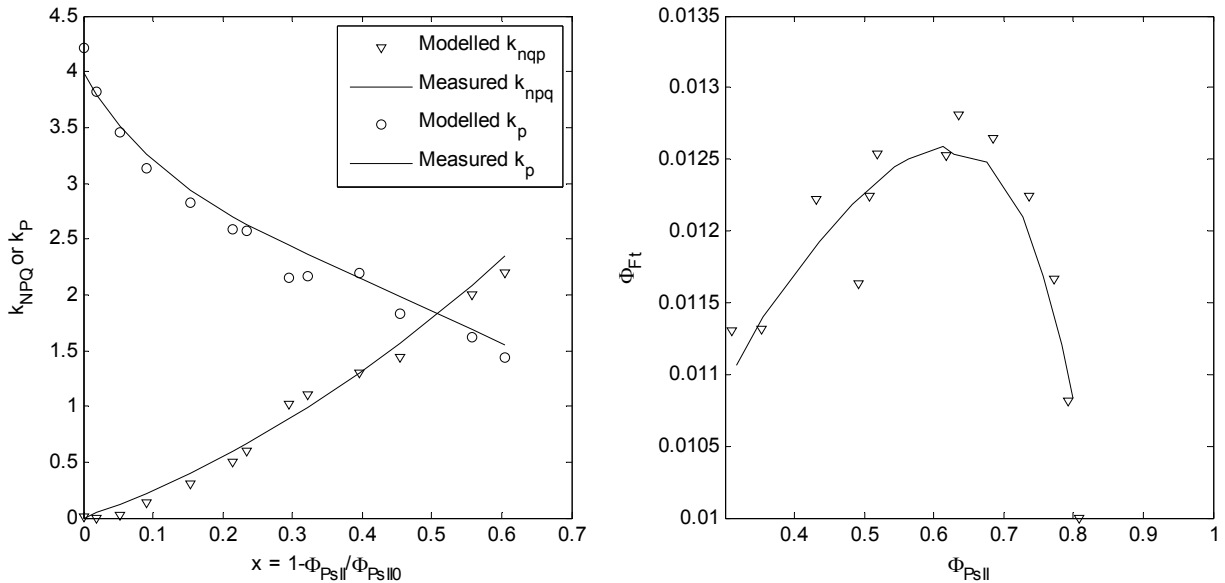


Figure 4-7. For the same experiment as in Figure 4-6, the rate coefficients versus a normalized photochemical yield (x): the relative reduction of photochemical yield below the light limited rate (left), and fluorescence versus photochemical yield (right).

photochemical yield below the light limited rate, $x = 1 - \Phi_{\text{PSII}} / \Phi_{\text{PSII0}}$. There is a clear relation between the relative light saturation and the two rate coefficients. With a simple empirical fit we may obtain a mathematical expression for the relation between Φ_{PSII} and Φ_{Ft} (Figure 4-7, right panel).

The parameter x seems to provide a good metric for parameterizing the behavior of k_p' and k_{NPQ}' , and an empirical calibration can be used to couple carbon fixation models to a fluorescence model. The lines included in these plots were simulated using the photosynthesis model of Collatz et al. (1991). This framework has been included in the SCOPE model and could be adapted for any similar model (for a review see Farquhar et al., 2009).

The relation between steady-state fluorescence yield (bottom row, center panel Figure 4-7) and photochemical yield is difficult to interpret for two reasons: First, the range of fluorescence yield values is relative small; and second, there are two possible corresponding photochemical yields belonging to a single fluorescence yield value. However, GOSAT observations are made near noon on clear days. Under these conditions we observe that Φ_{PSII} and Φ_{Ft} decrease in parallel.

Another question is how universal the relationship between photochemical and fluorescence presented in Figure 4-7 is. In order to answer this question, combined gas exchange and active fluorescence measurements are needed in different conditions: high and low temperature, high and low CO_2 concentration, across a gradient of illumination, and across gradients of nutrient and drought stress. A careful analysis of these experiments could improve our understanding of the relationship between passive fluorescence and photochemistry.

4.1.3.2 From rates to absolute levels at leaf and canopy level

Absolute fluorescence flux at leaf level

Active fluorescence measurements are usually taken at the leaf level. The active fluorescence models discussed above have been used to calculate the photochemical yield from fluorescence yields normalized by the F_m level. For the interpretation of SIF, we need another step since we are interested in the absolute fluorescence flux at some wavelengths at which the retrievals are done. Because the F_m level cannot be measured, normalization is not possible: We can only measure the absolute flux. The absolute rate is expressed in energy units or number of photons per unit of surface area, per unit of time, per unit of wavelength, and per unit of the field of view (radians), so $\text{W m}^{-2} \mu\text{m}^{-1} \text{sr}^{-1}$ or $\mu\text{mol m}^{-2} \mu\text{m}^{-1} \text{sr}^{-1}$. The absolute rate of adapted fluorescence also depends on reabsorption of fluorescence within the leaf, which is mainly determined by the thickness of the leaf and the chlorophyll concentration.

There are at present two radiative transfer models available that quantify this reabsorption and translate fluorescence spectra at photosystem level to the leaf level. FluorMODleaf was developed during a European Space Agency study (Miller et al., 2005), and it has been published by Pedrós et al. (2010). This model uses the analogy of a pile of glass plates to explain scattering and absorption of radiation, similar to the reflectance model PROSPECT (Jacquemoud and Baret, 1990). Since this solution is only possible for integer values of the

leaf mesophyll parameter N (the number of “glass plates”), an interpolation procedure is applied to make the model applicable also for non-integer values of N . The second leaf fluorescence model, Fluspect (Verhoef, 2010), is also based on PROSPECT, but Fluspect calculates fluorescence using a doubling algorithm, by applying a Kubelka-Munk (KM)-type of radiative transfer approach at photosystem level, including fluorescence. The KM-parameters (an absorption and a backscattering coefficient) are derived from leaf reflectance and transmittance as calculated with PROSPECT. Next, the KM model is applied numerically in forward direction using the layer-doubling technique, in which fluorescence is also incorporated. The output consists of (in addition to the spectra of reflectance and transmittance) two excitation-fluorescence matrices, giving the fluorescence at the illuminated side and at the backside of the leaf for each combination of excitation and fluorescence wavelength (Figure 4-8). The input is the (F_o) fluorescence quantum efficiency, and fluorescence spectra for PSI and PSII at photosystem level. Fluorescence is assumed proportional to the absorption by chlorophyll, and fluorescence is assumed isotropic.

Absolute fluorescence rate at canopy level

The scaling of fluorescence to canopy level becomes important when we move from leaf to satellite observations. This scaling is in a way similar to the scaling of fluorescence from chlorophyll in solution to leaf fluorescence in vivo: Similar problems play a role, and these problems may have similar solutions. The two main aspects of the problem are (1) the reabsorption of fluorescence in the canopy and (2) differentiated micro-environmental conditions within the canopy.

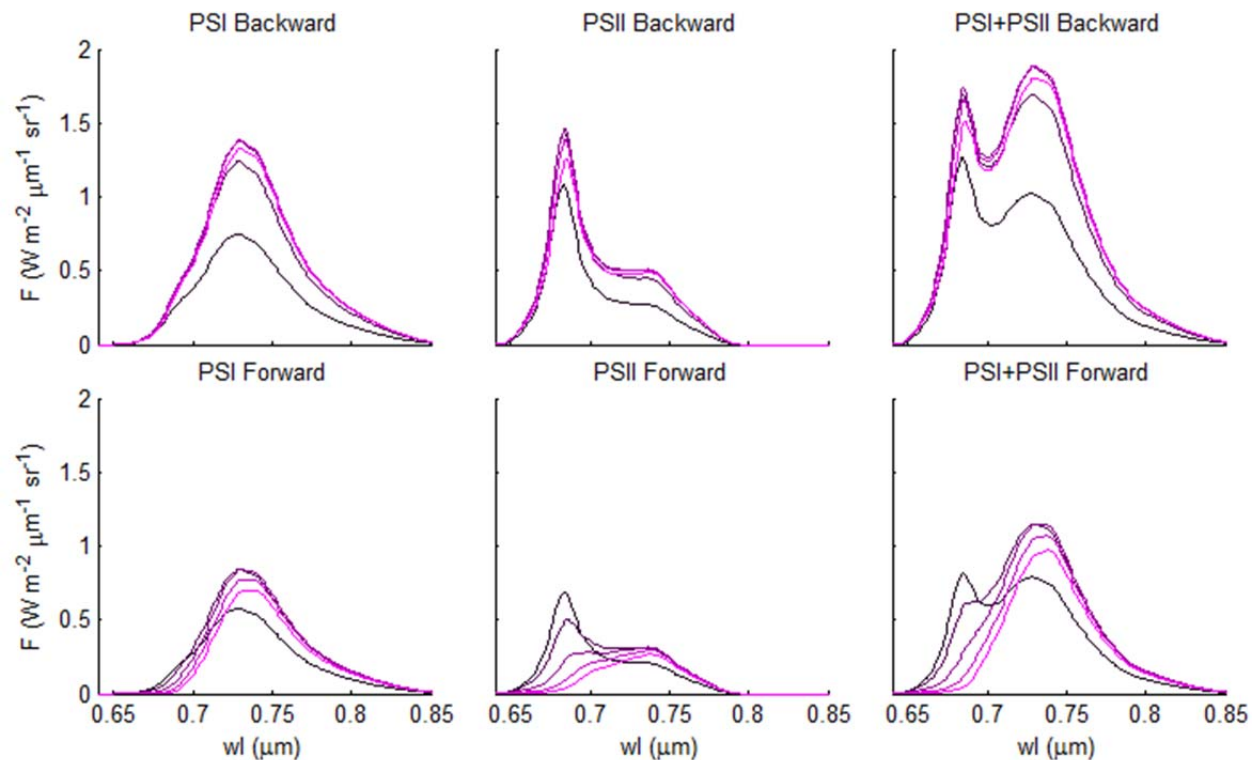


Figure 4-8. Fluspect model output for different values of parameter Cab (10 (black), 30, 50 70 and 90 $\mu\text{g cm}^{-2}$ (purple) of backward (illuminated side of the leaf) and forward (non-illuminated side of leaf) fluorescence spectra of PSI and PSII.

Fluorescence may be reabsorbed not only by leaves or needles, but also by woody material and by the soil. While leaf fluorescence intensity can be used to estimate chlorophyll concentration at leaf level, top-of-canopy fluorescence may be used to estimate chlorophyll content in a canopy. Due to the structure of the vegetation, the top of canopy fluorescence is not isotropic.

The micro-environment is relevant because the illumination of the leaf, the leaf temperature, and the relative humidity in the leaf boundary layer all affect photosynthesis and the quenching of fluorescence. The models that we have for photosynthesis and fluorescence have been developed for situations in which the weather conditions at leaf level are known. In a canopy the environmental drivers are heterogeneous. For example, in clear-sky conditions the irradiance of sunlit leaves can be an order of magnitude higher than that of shaded leaves. In sunlit leaves, photosynthesis may be light saturated, with k_{NPQ} high and k_P low, while in shaded leaves, photosynthesis may be light limited, with k_{NPQ} low and k_P high. The fluorescence as observed from the canopy top is composed of the contributions of all these leaves.

A large number of radiative transfer models are available that calculate the heterogeneity of illumination within the canopy. The simplest of these models differentiate only between sunlit and shaded leaves (De Pury and Farquhar, 1997), while the most complex models simulate the fate of radiance in realistic three-dimensional mathematical models of a canopy (Gastellu-Etchegorry et al., 2004). De Pury and Farquhar (1997) showed that, for the purpose of the calculation of photosynthesis, a simple sun-shade model is sufficient. Much less is known about the reabsorption of fluorescence in the canopy, probably because this is a younger field of research. A literature search on Web of Science with “radiative transfer,” “model,” and “vegetation” as the topics yields more than 1000 results, but when “chlorophyll fluorescence” is added, only 18 papers are found. At present the SCOPE balance model (van der Tol et al., 2009) is, to our knowledge, the only model that calculates irradiance at leaf level, converts this into a fluorescence spectral signature, and translates the fluorescence signal back to the top of canopy.

The radiative transfer model concept in SCOPE is not new: Verhoef (1985) published it as the Scattering of Arbitrarily Inclined Leaves (SAIL) model. The canopy is represented as a number of leaf layers and leaf inclination classes, each with a different probability of occurrence. Four radiative fluxes are calculated in the canopy: the direct solar beam, an upward and downward diffuse radiation, and the radiation in the observation direction. SCOPE is computationally more efficient and simpler to implement than ray tracing models because the fates of radiance are calculated with probabilities. A limitation of the model is that it permits variation only in the vertical dimension; thus, it is only valid for vegetation in which variations in the horizontal dimension are small in comparison to variations in the vertical dimension. This is a significant limitation for many natural canopies.

The innovative element of SCOPE is that the SAIL concept has been applied to incident irradiance, fluorescence, and emitted thermal radiation at the same time, such that the entire radiation budget of each leaf inclination class and each leaf layer is known. This radiation balance has further been coupled with a photosynthesis model and a fluorescence model at leaf level, and an aerodynamic resistance scheme for turbulent fluxes. This combination

made it possible to study the feedback mechanisms between leaf physiology and the “micro-climate” inside the canopy. Thus, the two problems of varying micro-climate and the reabsorption within the canopy are solved within one model.

The primary purpose of SCOPE has been to simulate satellite observations. The model calculates fluorescence, photosynthesis, and the energy balance at instantaneous moments in time: the satellite overpass. It is not a process model in the sense that it does not keep track of “stocks”: It does not calculate biomass accumulation, and it does not calculate a soil water balance, which is different from many soil-vegetation-atmosphere (SVAT) models.

As an example of SCOPE output, Figure 4-9 shows the diurnal cycles of three energy balance components (R_n , λE , and A), modeled net photosynthesis with measured net CO_2 exchange (including soil respiration), and fluorescence derived using the $\text{O}_2\text{-A}$ band between 770 nm

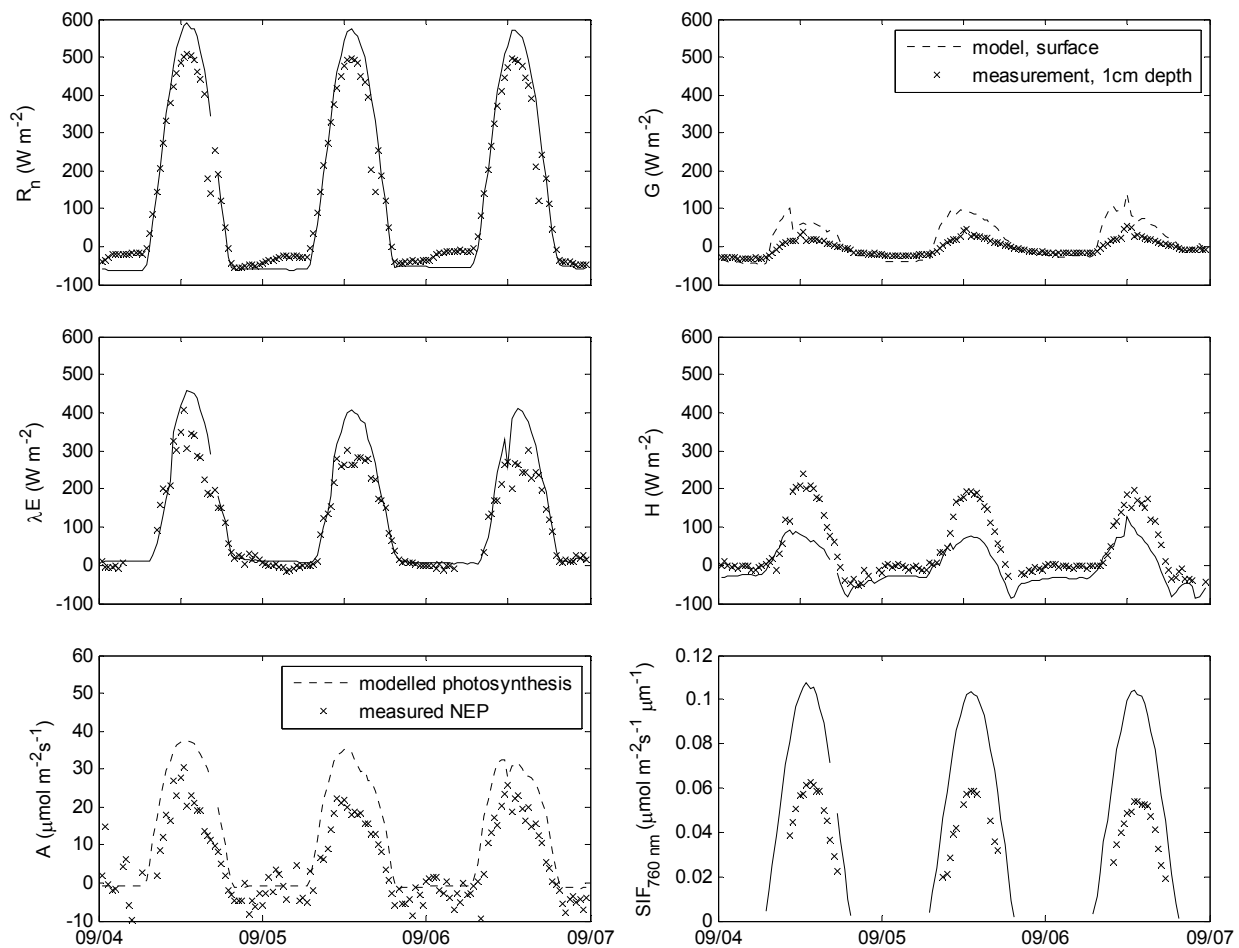


Figure 4-9. Comparison between measured (symbols) and SCOPE modeled (lines) fluxes measured over a maize field during the CEFLES2 campaign (Damm et al., 2010). Solid lines refer to a direct comparison in which the simulated variable was the same as the measured one, while dashed lines refer to an indirect comparison due to the fact that the definition of the simulated variable is different from the measured variable. Clockwise from top left: net radiation, ground heat flux at the surface (modeled) and at 1 cm depth (measured), sensible heat flux, solar-induced fluorescence in the $\text{O}_2\text{-A}$ band (760 nm, aggregated over a FOV of 25°), net photosynthesis of all leaves (simulated), and net ecosystem exchange—including soil respiration (measurements)—and latent heat flux.

and 785 nm, together with measurements. These measurements have been collected with an ASD spectrometer and net CO₂ exchange with an eddy covariance system during the CarboEurope, FLEX, and Sentinel-2 (CEFLES2) campaign over a maize field in Les Landes, France (Damm et al., 2010). SCOPE simulated the fluxes using the available meteorological and crop data collected in the field (LAI=2.8; chlorophyll content (Cab)=~40 mg cm⁻²). Figure 4-9 shows the diurnal cycle of the fluxes for three consecutive days (5–7 September 2007).

The magnitude of the simulated fluxes agrees with the measurements, although fluorescence was overestimated. (We used a Cab of 40 µg cm⁻²; but Damm et al. (2011) describe a vertical profile of Cab with the lowest values at the top.)

Model simulations in combination with carefully designed experiments can answer the relevant key questions: How much of the diurnal variation of the fluxes is caused by the geometry of the vegetation and the solar zenith angle? How much is caused by variations in physiology? We could, for example, investigate the effects of geometry on the top-of-canopy fluorescence. In the case of Figure 4-9, we had a varying solar zenith angle with constant observation angle (nadir in the simulations). Figure 4-10 illustrates the effect of observation angle at a constant solar zenith angle. “Observations” from a large number of angles have been simulated (with a constant solar angle), representing a half-dome of observation zenith (0° to 90°) and azimuth angles (0° to 360°). The results have been interpolated to generate a continuous color map. The hot-spot is clearly visible for all wavelengths, but there are wavelength-dependent variations with observation angles, too. This wavelength dependence is caused by the difference in fluorescence from the sunlit side (backward) and the shaded side (forward) of the leaves. Far away from the hotspot, the shaded sides of the leaves are more visible, where the second peak dominates due to reabsorption within a leaf. This explains the relatively high fluorescence at 755 nm at an azimuth angle of 180° and high zenith angles.

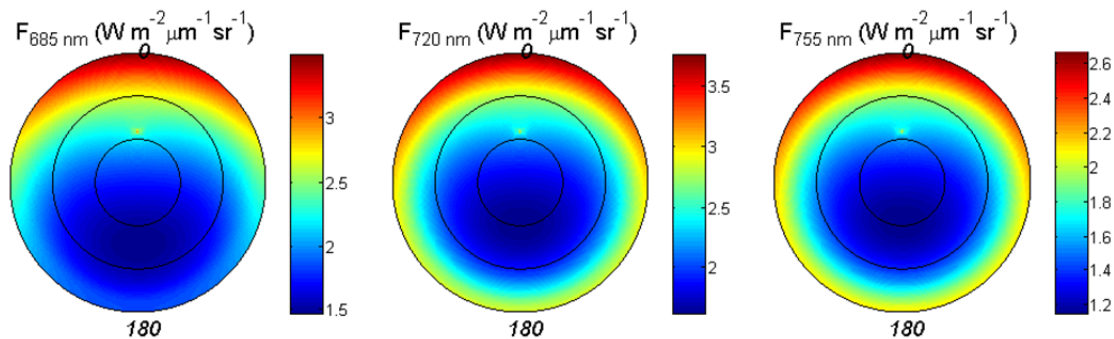


Figure 4-10 SCOPE simulated directional variations of fluorescence at three wavelengths for a canopy with LAI=2 and a spherical leaf inclination distribution. The diagrams represent the angular interpolated directional fluorescence sampled at high resolution of observer zenith (away from the center, solid lines at 30° interval), and the azimuthal difference between solar and observation angles (clockwise from the top). The simulations were carried out for midday light intensity (600 Wm⁻²), a solar zenith angle of 35°.

Absolute fluorescence rate at satellite footprint level

The final step of a bottom-up approach would be to scale SIF to the footprint area of GOSAT. Because the footprint is rather large, we may need to weight the contributions of different land cover types present in the footprint.

An open issue is the effect of the atmosphere on the directionality of fluorescence. Multiple scattering of fluorescence by the atmosphere in clouded conditions may disperse the directionality, because fluorescence originally emitted in a different direction may be redirected towards the sensor, and opposite fluorescence originally directed towards the sensor may “miss” the sensor. In the nadir direction, increased atmospheric scattering will increase fluorescence at 755 nm due to the contribution of fluorescence from higher observation zenith angles (Figure4-10).

Summary

We started off with the idea, supported by leaf-level measurements, that SIF provides much more direct information about the photochemistry than reflectance. We introduced two very simple equations for GPP (4-1) and for SIF (4-2), where both are proportional to the absorbed PAR by green material and a light use efficiency term. Combining these two equations cancels out the absorbed PAR by green material: GPP is then proportional to SIF and the ratio of the light use efficiencies (4-3). This is promising, because absorbed PAR is variable that is not easy to measure. If we also find that the efficiencies correlate (such that their ratio is more or less constant), then SIF may prove a sensitive indicator of photosynthesis.

In order to understand the signal of SIF better, we zoomed in on processes at molecular to canopy level. Based on the simple Eqn. 4-2, we may split the question, what does SIF at canopy level tell us?, into two questions: (1) What does SIF tell us about absorbed PAR? and (2) What does SIF tell us about the light use efficiencies?

Concerning the first question, what does SIF tell us about absorbed PAR?, we found that SIF has a strong positive, but wavelength dependent, correlation with absorbed PAR. Whether SIF does better than existing absorbed PAR products remains to be studied at flux sites and with aircraft measurements. Concerning the second question, what does SIF tell us about the light use efficiencies?, we do not have a definitive answer yet. There is empirical evidence and conceptual understanding of the physiology that indicate that in light saturated conditions the light use efficiencies correlate positively, but it is not known how universal this is, or how large the variations in the fluorescence efficiency are compared to variations in absorbed PAR. There is a clear need for field measurements of top-of-canopy SIF in combination with leaf measurements to validate the presently available modeling tools. Much work has already been done at this scale by the FLEX community, and this represents a possible area of collaboration between the two communities.

4.2 Global carbon cycle modeling (GPP estimates, source/sink inversions)

4.2.1 Application to the global carbon cycle

Coupled carbon-climate models vary widely (Friedlingstein et al., 2006, Heimann et al., 2008) and *"as long as there is no fundamental understanding of the processes involved, simulations of coupled carbon-cycle-climate models can only illustrate the importance of, but do not show, a conclusive picture of the multitude of possible carbon-cycle-climate system feedbacks"* (Heimann et al., 2008). SIF provides the unique option to provide more direct estimates of GPP and especially when combined with net CO₂ fluxes that will eventually be derived based on GOSAT and OCO-2 atmospheric data, which opens up new possibilities of constraining the global carbon cycle with much more process-oriented datasets. This section will briefly discuss results so far and some outlook into the future.

4.2.1.1 Evidence from top-down analysis that supports use for proxy for productivity

From models such as the MPI-BGC model (Beer et al., 2010; Jung et al., 2011) and MODIS derived datasets, Frankenberg et al. (2011a) have observed a very strong linear correlation between SIF retrieved from GOSAT and GPP. We found that the fluorescence emission even without any additional climatic or model information has the same or better predictive skill in estimating GPP as those values derived from traditional remotely sensed vegetation indices using ancillary data and model assumptions.

Figure 4-11 depicts the observed correlations with model GPP products and vegetation indices. Of particular interest are the two rightmost plots in the lower row. Both NDVI and FPAR show a curvilinear relation to fluorescence, but there is a distinct cloud of datapoints that strongly deviates from the general relationship (the cloud at low fluorescence and high NDVI/FPAR). Looking at the surface temperature (color-coded) and vegetation type (symbol), these outliers are clearly dominated by evergreen needleleaf forest at cold temperatures. Photosynthetic activity and fluorescence clearly shuts down at lower temperatures, while the trees still appear green for the classical remote sensing indices. The MODIS GPP product partially corrects for this behavior by using ancillary information on the temperature dependence of GPP. Fluorescence, however, can directly observe the temperature thresholds of photosynthetic activity in evergreen forests.

A more global view of the correlation between fluorescence and GPP is shown in Figure 4-12. Despite the relatively high noise in GOSAT data (related to low sampling density and high single-measurement noise), the spatial correlations are striking: Non-vegetated surface clearly show no fluorescence signal, and the absolute amount of fluorescence appears to be very linearly related to the absolute amount of photosynthetic activity. In Figure 4-13 (from the supplementary of Frankenberg et al., 2011a), we used FPAR from MODIS to derive fluorescence yields for various biomes. An empirical GPP based on fluorescence is calculated from the slope of the linear fit, with the MPI-BGC GPP in the annual average. For needleleaf forest, fluorescence-based GPP is 28% to 32% lower than model estimates, while it is 18% to 48% higher for savannas and croplands. The lower panel in Figure 4-13 shows that the ratios of F_s [normalized by $\cos(\text{SZA})$] with FPAR, are directly proportional to the fluorescence yield.

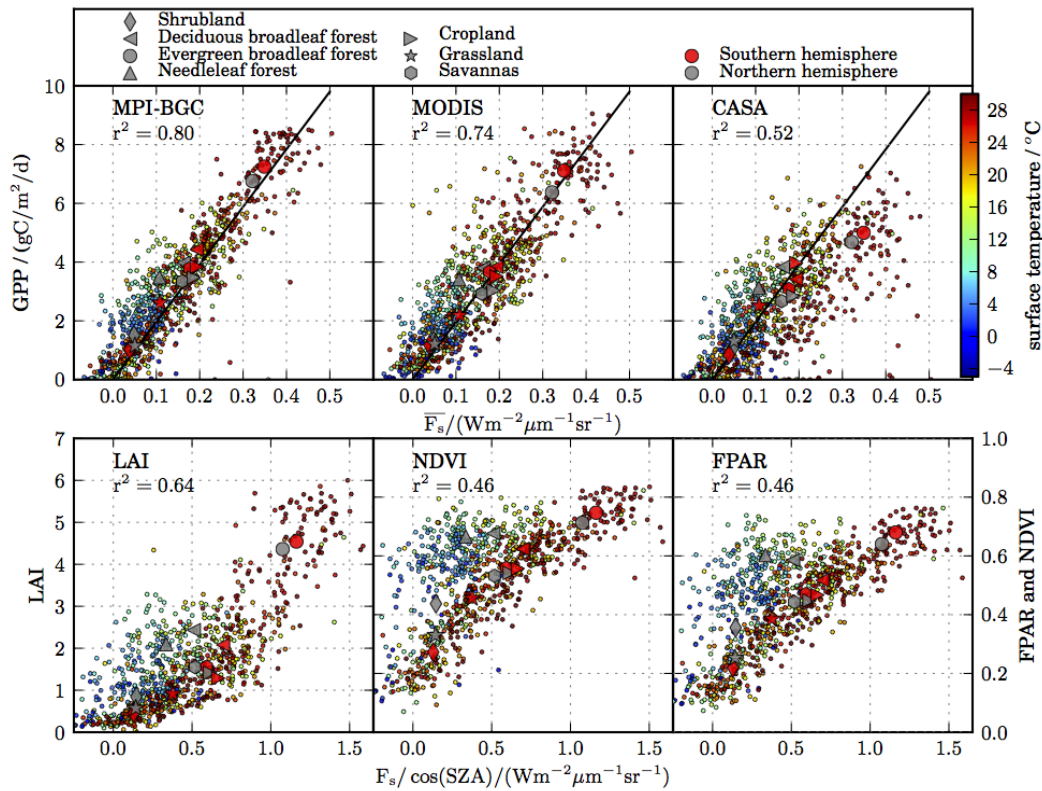


Figure 4-11. Adapted from Frankenberg et al. 2011a: Solar induced fluorescence (annual average gridded on 4×4 degrees) plotted against GPP estimates (top row) and vegetation indices (bottom row).

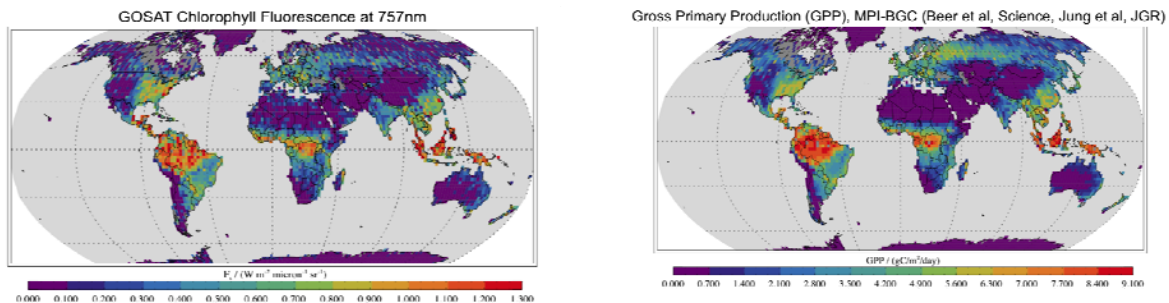


Figure 4-12. Annual fluorescence average from GOSAT (left, Frankenberg et al., 2011b) and GPP model average (right, MPI-BGC model, Beer et al., 2010, Jung et al., 2011).

The observed high variability among different biomes is broadly consistent with an analysis of LUE at flux tower sites (Turner et al., 2003).

For the analysis presented here, we did not take any ancillary information into account; however, the analysis provided strong empirical evidence for a direct correlation between fluorescence and GPP. One of the workshop goals was to move beyond this empiricism and put the relationship on a stronger foundation by taking biophysical modeling (as seen in Section 4.1) into account. The following case studies will leverage from these efforts and provide further evidence on how fluorescence provides a unique opportunity; it is indeed

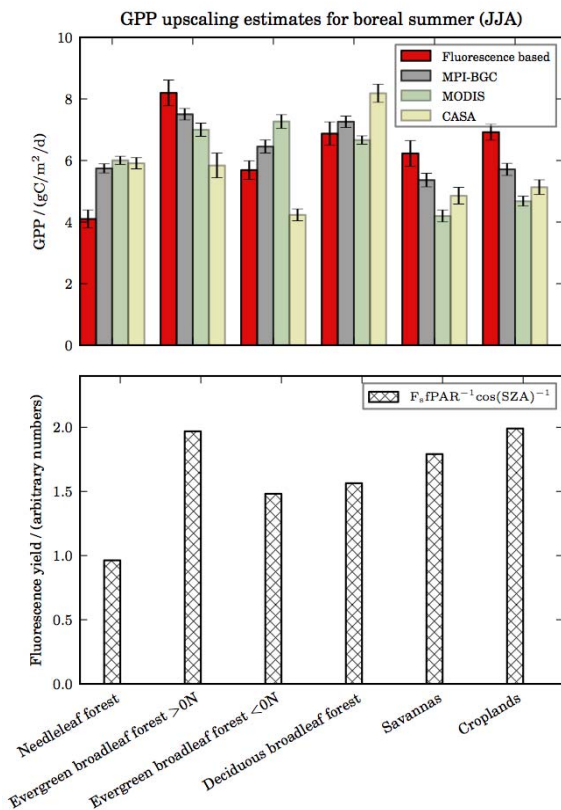


Figure 4-13. Top: Biome specific GPP upscaling estimates. Bottom: Fluorescence yields per biome on an annual average.

Resolution Imaging Spectrometer (MERIS) (Gobron et al., 2007) used in the derivation of the GPP data set has also been used here. APAR has been approximated as $FAPAR \times \cos(SZA)$, with SZA being the sun zenith angle at the time of the GOSAT overpass.

Results of the comparison of SIF with GPP, APAR, and FAPAR for some biomes are displayed in Figure 4-14. The temporal profiles are normalized by the maximum value for the sake of visualization. Visually, GPP compares better to SIF than APAR and FAPAR for deciduous broadleaf forest, grasslands, and deciduous needleleaf forest in northern latitudes (DBFN, GLN, and DNFN, respectively), whereas no clear annual cycle is found for the tropical rainforests (EBFS for evergreen broadleaf forest in southern latitudes). The zero values for DNFN are due to high SZAs, which exceed the maximum SZA allowed to guarantee the proper performance of the retrieval. The comparison between SIF and FAPAR is always significantly worse than for GPP and FAPAR, which is explained by the fact that the annual cycle of SIF is intrinsically modulated by the radiation arriving at the canopy. This also elucidates that the combination of illumination and greenness cycles as in the APAR parameters explains most of the variability in the SIF seasonal cycles. However, it is also observed that APAR cannot explain the trends of SIF and GPP in late winter and spring in DBFN, GLN, and DNFN, which suggests that SIF is able to track the effect of low temperatures on the regulation of

adding value to the current observing system, and in fact, is actually closing a blind spot in the data.

4.2.1.2 Biome specific observed and modeled correlations between SIF and GPP

The potential of the SIF signal as a proxy for GPP has been investigated for different vegetation types and climatic regions. For this purpose, single SIF retrievals have been grouped following the vegetation types defined by International Geosphere-Biosphere Programme (IGBP). SIF was retrieved from GOSAT Fourier transform spectrometer (FTS) data with an algorithm based on a statistical formulation of the top-of-atmosphere radiance (Guanter et al., 2012). Monthly averages of SIF are calculated for each of those clusters. The same has been done for spatially and temporally colocated satellite-based estimates of GPP, absorbed photosynthetically active radiation (APAR) and fraction of APAR (FAPAR). The GPP product used is based on the statistical upscaling of flux tower measurements (Jung et al., 2011). For consistency, the FAPAR product from the Environmental Satellite (ENVISAT) Medium

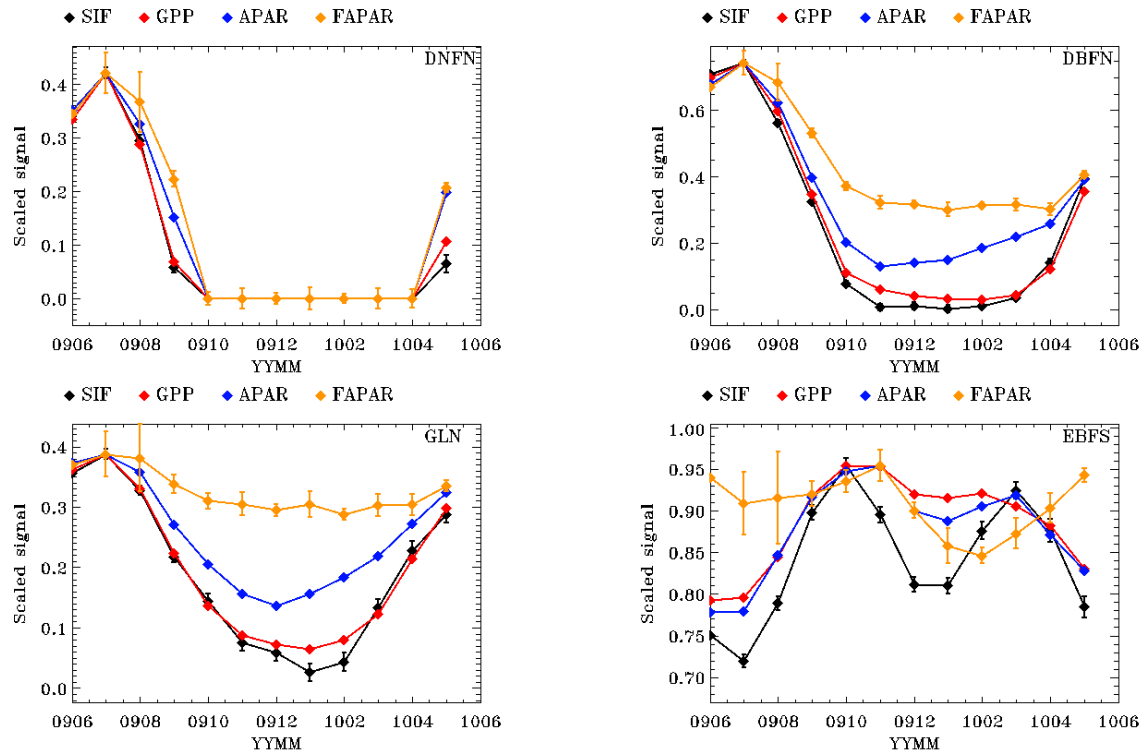


Figure 4-14. Temporal profiles of SIF, GPP, APAR, and FAPAR for different biomes according to the IGBP classification. APAR is calculated as $FAPAR \times \cos(SZA)$, with SZA the sun zenith angle at the time of the GOSAT overpass. Each temporal profile is normalized by the maximum value along the year. [EBF(S)] = Evergreen Broadleaf Forest in the southern hemisphere, [GLN] = Grasslands in the northern hemisphere, [DBFN] = deciduous broadleaf forest in the northern hemisphere, [DNFN] = deciduous needleleaf forest in the northern hemisphere.

photosynthesis. Similar results have been found for evergreen needleleaf forests and shrublands in the north, whereas very small differences between SIF, GPP, and APAR have been found for other biomes.

A different view of these relationships for all biomes is displayed in Figure 4-15. Monthly averages of SIF for different IGBP vegetation types are again compared to GPP, APAR, and FAPAR. An earlier version of these comparisons is provided in Guanter et al. (2012). It can be observed that the comparisons SIF–GPP and SIF–APAR show similar correlation coefficients for each vegetation type, and that these are much higher than for FAPAR for the reason discussed previously. The very high correlations between SIF and GPP and APAR are explained by the common seasonal cycles, but as it is in Figure 4-13, SIF can capture some trends in GPP not apparent in APAR and not traceable in the correlation coefficients in Figure 4-13. However, it is also clear from Figure 4-14 that no single relationship between SIF and GPP exists when the comparisons are performed on a monthly scale. Biome-dependent scaling factors should then be applied for a simple conversion of SIF retrievals to GPP. It must also be remarked that the range of scaling factors between SIF and APAR is smaller than that between SIF and GPP, which could suggest that the SIF on monthly scales might be closer to APAR than to GPP. (However, a length of day correction could also bring the GPP slopes into closer agreement.) This could be explained by the fact that SIF retrievals

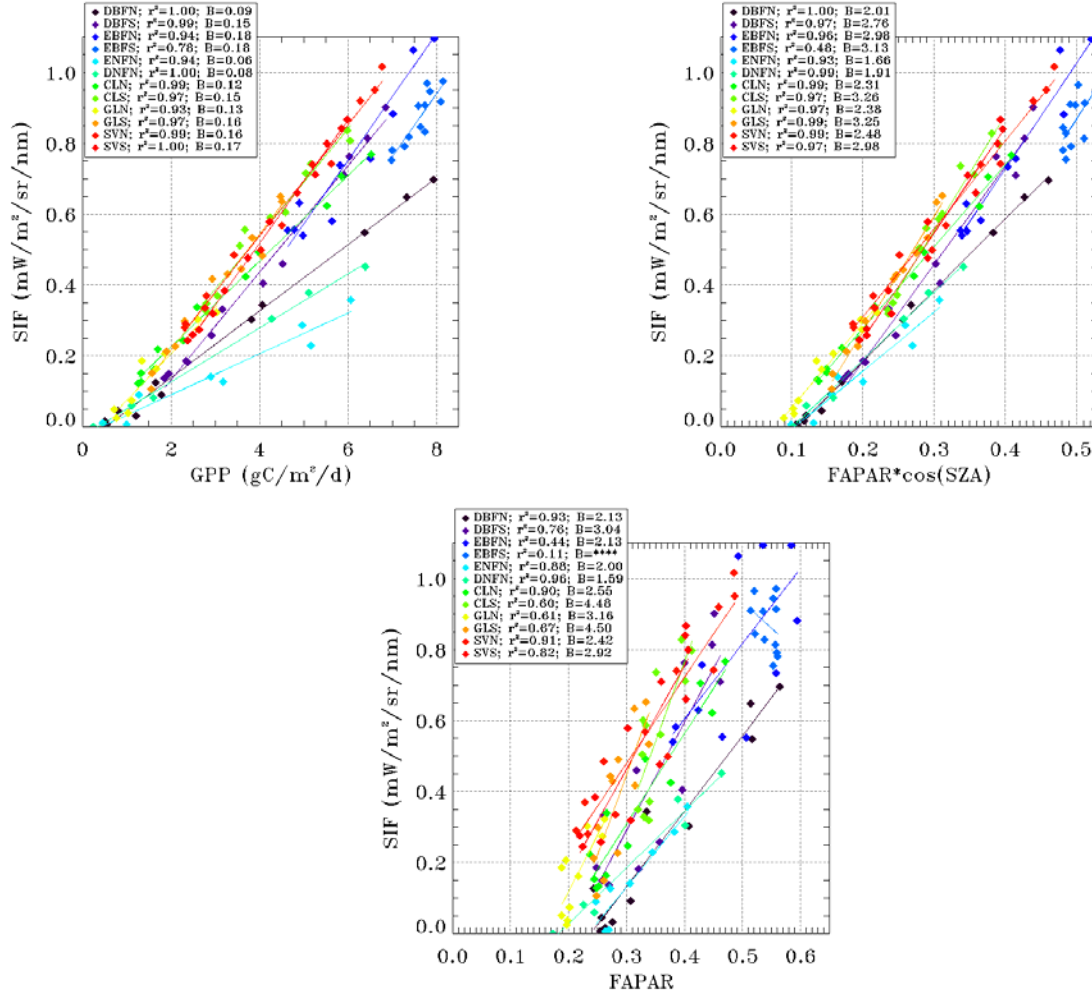


Figure 4-15. Scatter plots between SIF and GPP, APAR and FAPAR. Each symbol represents one month. Biomes follow the IGBP-based land cover classes. In addition to the classes defined in Figure 4-14, [ENF]=Evergreen Needleleaf Forest, [CLN(S)]=Cropland in the northern (southern) hemisphere, [SVN(S)]=Savannas in the northern (southern) hemisphere.

are performed under clear skies at midday; this explanation is consistent with the APAR used in this study but not with the GPP product, which is generated from daily all-sky observations. Modeling these effects might then be necessary for a quantitative mapping of SIF to GPP.

4.2.1.3 Modeling of fluorescence using SiB and comparison with GOSAT observations

We incorporated the Soil Canopy Observation, Photochemistry and Energy fluxes (SCOPE, van der Tol et al., 2009a,b) fluorescence model into the Simple Biosphere Model (SiB). SiB was developed as the lower boundary for atmospheric general circulation models (AGCMs), but with a level of eco-physiological representation that makes it useful for more directed studies. The model was introduced in 1986 (Sellers et al., 1986), and updated to incorporate the inclusion of spectral indices to control model phenology (Sellers et al., 1996a,b; Randall et al., 1996). By coupling SCOPE with SiB (manuscript in preparation), we can perform global comparisons of simulations and observations in an “apples to apples”

manner, with no assumptions about representativeness across diurnal and synoptic cycles. First tentative comparisons of SiB GPP and fluorescence are shown in Figure 4-14. These plots are analogous to Frankenberg et al. (2011), shown in Figure 4-16, but these show the relation between simulated fluorescence and simulated GPP, while those of Frankenberg et al. show measured fluorescence vs. simulated GPP. The SiB results show a wider spread of GPP values with similar fluorescence (i.e., shrub/groundcover). Three reasons for the differences might be as follows: (1) The SiB calculations represent monthly-mean values, while GOSAT takes observations only during its midday flyover. (2) The leaf-to-canopy scaling and canopy radiative transfer scheme (Sellers et al., 1996a,b) may not be appropriate for reproducing a satellite-based diagnostic from the model. (3) Currently only integrated SIF (both across the day and the spectral range) is considered. This work is ongoing and being prepared for publication; hence, we cannot yet display more details.

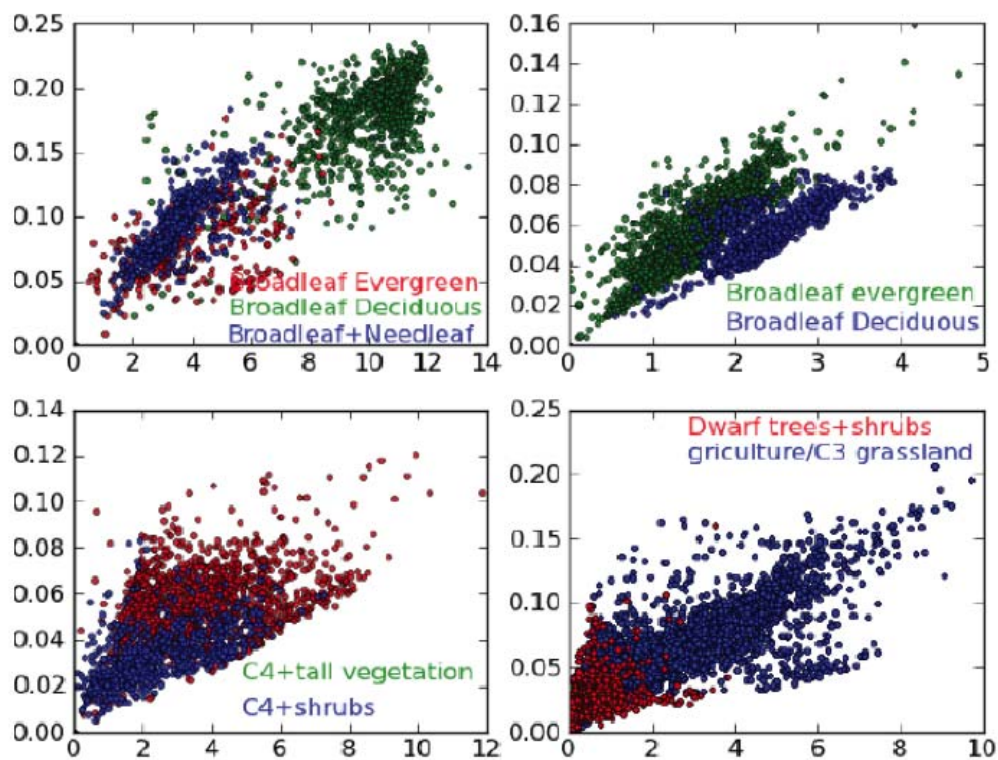


Figure 4-16. Monthly averaged GPP (x-axis) plotted against fluorescence (y-axis) for all land points over 1 year of simulations. Each panel represents a different vegetation type.

4.2.2 Case studies supporting the added value of fluorescence

4.2.2.1 Amazon drought study

The Amazon basin represents more than 50% of tropical rainforest area (Morley, 2000], about half of total terrestrial biomass (120 Pg of C of global 247 Pg C) (Saatchi et al., 2011), and also hosts a quarter of global biodiversity (Dirzo and Raven, 2003). How this system might respond to climate change, such as warming and droughts, has been a recent source of debate (Saleska et al., 2007; Samanta et al., 2010; Myneni et al., 2007; Anderson et al., 2010; Phillips et al., 2010). Water stress is one of the most important forces shaping tropical forests

[Condit et al., 2013, Nepstad et al., 2004]. During extended dry periods, large trees tend to die [Nepstad et al., 2007, Phillips et al., 2009], forest productivity decreases [Brando et al., 2008, Phillips et al., 2009] and wildfires can be triggered over huge forested areas [Alencar et al., 2006, Morton et al., 2008]. Climate models are predicting more frequent and intense droughts due to widespread deforestation and atmospheric CO₂ accumulation. Amazon forests may therefore experience even stronger transformations, with important consequences for global carbon cycle [Cox et al., 2000].

It has been suggested that conventional greenness indices are not sufficient to capture the dynamic response of plants to varying water status over tropical evergreen forests [Asner and Alencar, 2010]. It is known that greenness indices are difficult to interpret over Amazonia for many reasons: saturation over densely forested regions, varying treatments of atmospheric contamination of the MODIS optical bands [Samanta et al., 2010], structural changes of forest canopy [Anderson et al., 2010], and potential variations in the reflectance properties as leaves age [Brando et al., 2010].

Using chlorophyll fluorescence as a proxy for photosynthesis, Lee et al. [accepted] show that fluorescence captures a decrease of photochemical activities as a result of drought, expressed as vapor pressure difference (VPD) between intercellular airspace and the atmosphere over the Amazonian forests that have 3-4 months of dry season (Figure 4-17)—most of Amazonian forests belong to this climate regime. The productivity dependency on VPD is low at low VPD (little water stress), implying other environmental variability such as incoming solar energy variability become more important. The figure also demonstrates that conventional greenness index (EVI in this case) does not capture water stress.

4.2.2.2 *Boreal forest studies: time and space information on productivity*

The potential of SIF to track photosynthetic periods of vegetated areas at high latitudes such as boreal forests has been discussed previously in this text. Since SIF is produced by the photosynthetically active component of the canopy, it is expected to react to environmental stress factors driving vegetation functioning, and at the same time to have a minimum sensitivity to

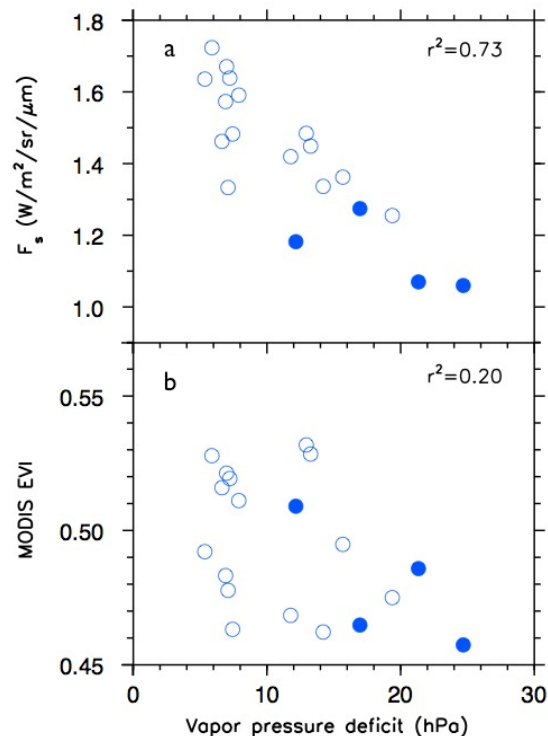


Figure 4-17. The relationship between VPD and GOSAT fluorescence at 755 nm (a) and MODIS EVI (b). Values are monthly means for central Amazon (5°S–5°N, 60°W–50°W), and VPD values have been extracted from the ERA dataset at the time and location of the GOSAT measurement. Filled symbols represent values for months with precipitation lower than 100 mm/month in 2010 during the Amazon drought (June–September). Correlation coefficients are calculated using all values.

perturbing nonphotosynthetic elements such as snow. These features give SIF a high potential to track vegetation dynamics even for evergreen vegetation covers affected by snow.

This claim is strongly supported by Figure 4-18. Biweekly SIF averages from all vegetation areas above 45°N are plotted together with GPP, APAR, and FAPAR. It can be seen how SIF nicely reproduces the seasonality of GPP for this large area, whereas temporal patterns for APAR and FAPAR are somewhat different. In the case of FAPAR, irregular profiles are observed between the end and the start of the phenological cycles, which can be explained by the interaction between vegetation cycles and the presence of snow perturbing the derivation of FAPAR from optical measurements. The seasonal cycles become smoother in APAR through the addition of the illumination cycle, but values in spring overestimate those of GPP and SIF. It can then be concluded that SIF has significant potential to track both vegetation phenological and photosynthetic efficiency cycles over cold climate regions.

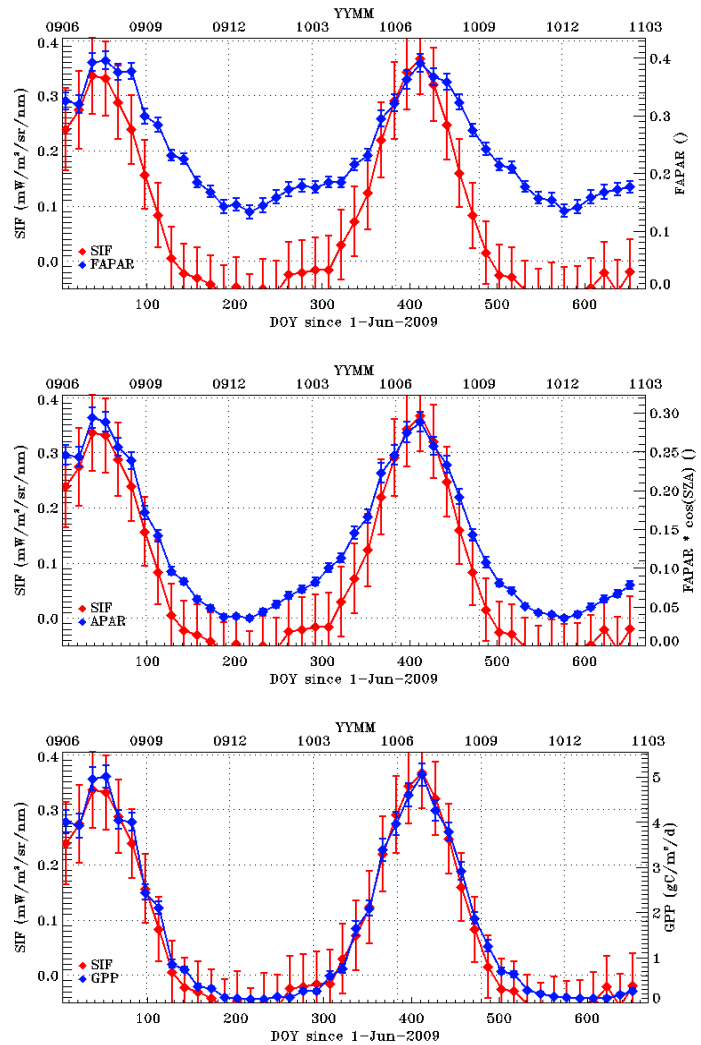


Figure 4-18. Biweekly temporal profiles of SIF from GOSAT together with GPP, APAR, and FAPAR averaged for all vegetated areas at latitude >45°N.

4.2.3 How one imagines implementing SIF in global carbon cycle analysis

One of the fundamental challenges in monitoring the full carbon cycle has been the attribution of changes in atmospheric CO₂ to spatially resolved surface fluxes. New attribution systems such as the NASA Carbon Monitoring System Flux Pilot Project (<http://carbon.nasa.gov>, <http://cmsflux.jpl.nasa.gov>) use 4-D variational assimilation techniques to relate variations in new global observations of xCO₂ from satellites such as GOSAT to surface fluxes (e.g., Ciais et al., 2010). However, xCO₂ is only sensitive to NEE and therefore cannot be used to resolve gross carbon fluxes [GPP and soil heterotrophic respiration (Rh)]. However, the combination of SIF, which is sensitive to GPP, and xCO₂ could in principle provide sufficient information. An approach for implementation SIF within a larger atmospheric carbon attribution system is shown in Figure 4-19. Observations from land, ocean, anthropogenic sources are ingested into respective models. The terrestrial

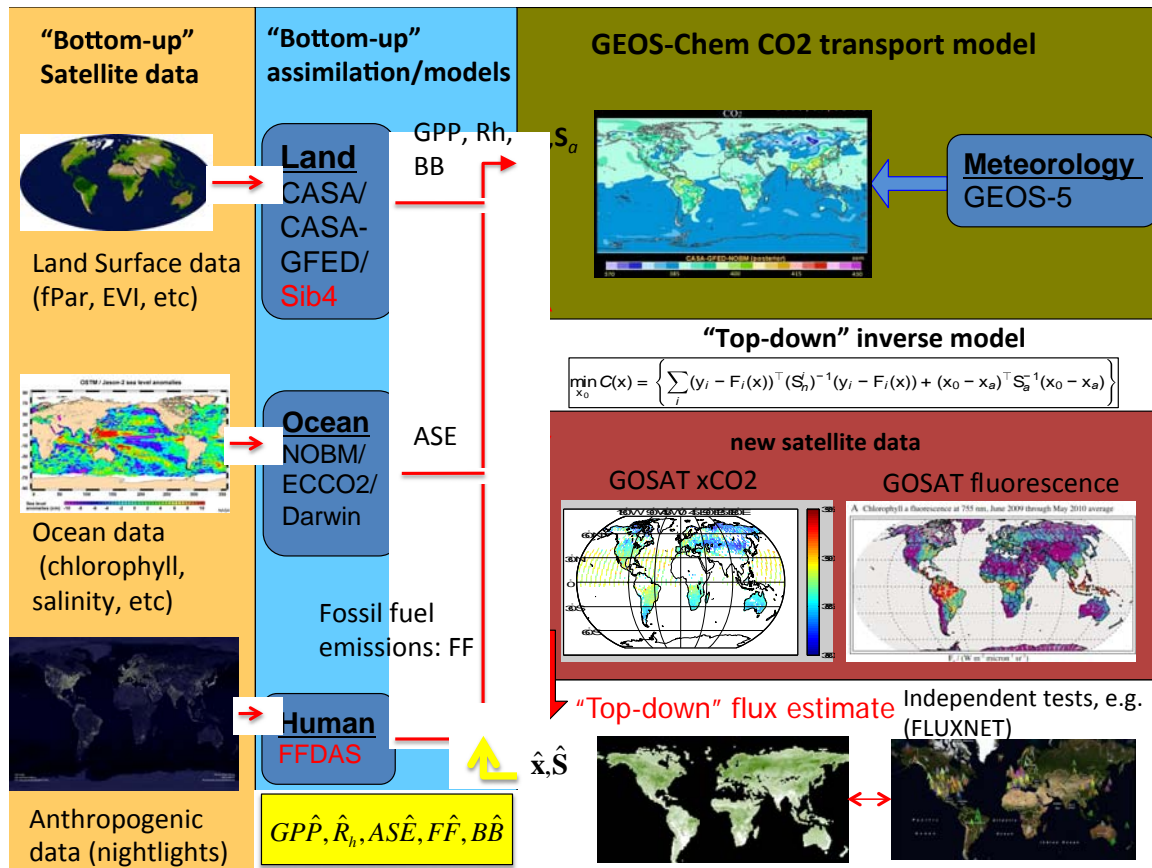


Figure 4-19. Carbon Monitoring Flux System. (Left) Observations that drive land, ocean, and anthropogenic models. These are then used to drive an atmospheric CO₂ transport model. SIF does not require the transport model. CO₂ and SIF from this model are then compared with satellite observations. The optimal GPP and Rh are calculated by minimizing the cost function, $C(x)$.

models will predict GPP, Rh, and biomass burning. Net fluxes will be propagated as atmospheric CO₂. A forward operator, however, would be needed to calculate SIF from GPP. An observation operator would then convert that SIF back to a satellite-retrieved $GPP^r = F(GPP)$. The state vector, x , would then include GPP and Rh, while the observation vector, y , would include GPP^r and xCO₂ at instantaneous satellite observation points. The system would then minimize the cost function, C , in Figure 4-19 with respect to both GPP and Rh.

The biggest technical challenge for the integration of SIF into a CO₂ attribution system is the development of the observation operator and its derivative. These can be implemented simply as in Frankenberg et al. (2011b) but should be developed to include a more mechanistic relationship. This can be done as described in ¶4.2.2.1 with the implementation of SCOPE in a global biosphere model; however, it also requires validation of the fluorescence biophysics while not all of these aspects are fully consolidated.

4.3 Retrieval of chlorophyll fluorescence from ground and space

4.3.1 Introduction

As outlined in the previous sections, SIF provides both complementary and new information compared to common remotely sensed vegetation information. The following are the main differences:

- 1 SIF is an emission signal from the surface, fundamentally different from common remote sensing products based on reflectances.
- 2 SIF is a measure of actual photosynthetic rates, not potential ones
- 3 SIF is directly proportional to absorbed photosynthetic radiation APAR but is only sensitive to APAR seen by chlorophyll; SIF is not sensitive to other, nonphotosynthesizing parts of the plant and/or soil/surfaces. In other words, SIF is a direct measurement of APAR.

The potential of performing remotely sensed chlorophyll fluorescence measurements was first recognized by the European community and triggered by the FLEX mission proposal to ESA in response to the 8th Call for Earth Explorers. FLEX is now competing with Carbon Monitoring Satellite (CarbonSat) in the final selection stage.

The retrieval concept behind FLEX is based on the in-filling of atmospheric oxygen absorption bands (O₂-A band at 760 nm and O₂-B band at 685 nm). At the same time, a new generation of satellites dedicated to accurately measuring greenhouse gases features high-resolution spectrometers covering the O₂-A band. It has been recognized that Fraunhofer lines (solar absorption features) in the vicinity of the O₂-A band can actually be employed to accurately retrieve fluorescence (Joiner et al., 2011; Frankenberg et al., 2011a,b) and thereby also circumvent potential interferences with the impact of atmospheric scattering on the oxygen bands. This led to the first global retrievals of chlorophyll fluorescence from space (Joiner et al. 2011, Frankenberg et al. 2011b, Guanter et al., 2012) using spectra recorded by the Japanese GOSAT satellite (Hamazaki et al., 2005). These measurements, even without explicit biophysical modeling of fluorescence (such as in van der Tol et al., 2009), were found to correlate very well with current best-model estimates of terrestrial GPP (Beer et al., 2010; Jung et al., 2011). This finding—along with GOSAT’s newly found potential of actually using Fraunhofer lines near the O₂-A band for accurate and robust retrievals of fluorescence—were the main motivation for this workshop. Current measurements of fluorescence are far from ideal and cannot yet compete with traditional vegetation remote sensing products (such as EVI or LAI), mostly because of the sparse spatio-temporal sampling of the instruments designed to perform greenhouse gas measurements rather than to identify vegetation characteristics.

In this section, we discuss the capabilities and shortcomings of current measurements of SIF from space, current and future retrieval strategies, differences and complementary aspects to classical remote sensing techniques as well as an outlook on space-borne SIF retrievals into the future.

4.3.2 Retrieval concept

The main challenge of retrieving fluorescence is to disentangle a small additive radiance signal emitted from plant chloroplasts from the much larger contribution by reflected sunlight. The fluorescence signal at 760 nm typically only contributes about 0% to 2% to the continuum level radiance. At the short wavelength side of the red-edge, however, the relative (not absolute) contribution can be much higher, up to more than 10%.

A review of fluorescence retrievals typically used in the field can be found in Meroni et al. (2009).

Ground-based measurements have the advantage that atmospheric scattering between the surface and the sensor is negligible, and that a reference measurement panel can be used to characterize the irradiance flux at the surface, enabling the exploitation of oxygen bands for fluorescence retrievals (thus allowing for much lower spectral resolution and simpler instrumentation). We found, however, that atmospheric scattering and fluorescence signal cannot be unambiguously discriminated if the sensor is at the top of atmosphere (Frankenberg et al. 2011a, 2012). That scenario also obviates the retrieval in strongly scattering scenes. For details, we refer the reader to the workshop presentation videos (<http://www.kiss.caltech.edu/workshops/photosynthesis2012/schedule.html>) and recent publications (Frankenberg et al., 2011a,b; Joiner et al 2011, 2012; Guanter et al., 2012).

In highly heterogeneous scenes with barren soil that can be used as reference targets, the use of the oxygen bands can be feasible (e.g., Guanter et al., 2010) when spatial variability in fluorescence emissions is higher than variability in scattering properties. The future may be in a combination of accurate retrievals based on Fraunhofer lines at coarse spatial scales with the option to provide sub-pixel information based on data with lower spectral resolution; this approach would be constrained by the accurate super-pixel fluorescence retrieval using the high spectral resolution measurement. (Essentially, a zoom into homogeneous scenes where the oxygen bands can be highly biased is not necessary; however, for very inhomogeneous scenes, high spatial resolution using the O₂-A band can be very advantageous.) These effects and potentials should be discussed in the fluorescence research community.

4.3.3 Relation to other reflectance-based remote sensing

Classical remote sensing parameters of biochemical and structural vegetation properties such as EVI, NDVI, or LAI are based on reflectances at different wavelengths, most importantly channels to the short- and long-wavelength side of the red edge (i.e., indicative of chlorophyll content and also LAI). The individual wavelengths bands at which reflectances are measured can be several nanometers wide, allowing for high spatial resolution because the signal level is high. Global measurements of vegetation indices have been instrumental in our understanding of the carbon cycle (e.g., Myneni et al., 2007), for they provide a global picture of greenness at high spatial and temporal resolution.

The use of chlorophyll fluorescence, on the other hand, is based on an entirely different concept, both from a retrieval point of view and an application point of view. Its retrieval is not based on reflectances but rather on direct retrieval of an additive radiance term (on top of a large background), which is emanating from the surface. The discrimination from the large-background radiance requires high spectral resolution, which makes small spatial

footprints a real challenge, especially from space. However, owing to the nature of fluorescence retrievals, even large footprints provide an unbiased estimator of the average fluorescence radiance within a heterogeneous footprint (because nonvegetative areas, in contrast to reflectance-based measurements, do not contribute signal). As fluorescence, in the absence of changes in fluorescence yield, is directly proportional (linearly) to APAR, the APAR estimate is also an unbiased average even for heterogeneous footprints. This is a crucial difference, because heterogeneous footprints (such as agricultural fields or even just patches of snow) can create a challenge for reflectance-based measurements. Ground-based validation of reflectance-based FAPAR and GPP estimates has found significant biases of satellite data, especially over agricultural sites and grassland (Turner et al., 2005).

Another difference is susceptibility to atmospheric disturbance by clouds and aerosols, which can bias reflectances and which thus have to be strongly cloud filtered and/or gap filled with observed maxima (Zhao et al., 2010). Chlorophyll fluorescence retrievals, if based on Fraunhofer lines, have been shown to be very insensitive to atmospheric scattering, even up to few optical depths (as long as aerosols are not strongly absorbing). Fluorescence retrievals even under cloudy conditions can thus provide insights into photosynthesis under rather diffuse illumination. This aspect is of particular interest, as plants and the process of photosynthesis are known to be more efficient when the diffuse irradiance fraction dominates the direct fraction. SIF measurements can hence facilitate systematic investigations of differences in photosynthesis caused by light quality at global scale; SIF measurements could also significantly improve the mechanistic representation of photosynthesis in process models (e.g., DGVM). From a physiological standpoint, the main difference is that fluorescence is directly related to the photosynthesis mechanism. For instance, Daumard et al. (2011) report on a measurement campaign of 38 days that has been carried out over a sorghum field and that continuously measured chlorophyll content and fluorescence. Lack of rainfall during the campaign resulted in water stress, clearly detectable in reduced fluorescence as NPQ-reduced fluorescence and photosynthesis yield. No change in chlorophyll content could be observed, which underlines that vegetation indices can only capture stress signals once senescence starts, at which point the stress may be irreversible. Fluorescence, on the other hand, can be used as an early warning for drought propagation at stages that are essentially blind spots in our current observing system. The dynamic response of fluorescence could be even more fully exploited if measurements are made at various times of day, instead of the current sun-synchronous low Earth orbits. A geostationary platform of a suitable instrument, for instance, could provide fluorescence maps during different stages of stress within a day, showing decreased fluorescence yield in the early afternoon due to increased evaporative demand and subsequent stomatal closure (thus increased NPQ); refer, for example, to Amoros-Lopez (2008) or Damm et al. (2010) for such studies on leaf and canopy scale.

Vegetation indices as fluorescence should not, however, be seen as competing quantities in understanding the global carbon cycle. Both are complementary, and each has its advantages and disadvantages. Reflectance-based vegetation indices are related only to potential photosynthesis, but they can provide a far more detailed picture in space and time because high spectral resolution is not needed. Fluorescence is a much better predictor of actual photosynthetic activity (i.e., actual instead of potential photosynthesis) and is very

responsive to early (or mild) signs of stress. The nature of its retrieval from space, however, does not yet allow for very high spatial resolution in conjunction with global coverage and frequent revisit times. Another aspect is that the various vegetation variables represent different vegetation properties, including biochemical, structural, and functional ones. Considering the time kinetic of plant adaptation processes to changing environmental conditions, the individual vegetation variables are complementary and represent fast regulating processes (e.g., photosynthesis), processes at intermediate time scale (xanthophyll cycle, pigment decomposition), and long term processes (leaf and canopy growth) (Hallik et al., 2012).

4.3.4 Current suite of satellites capable of retrieving fluorescence

Pioneering work in fluorescence retrievals has first been performed by GOSAT (Joiner et al., 2011; Frankenberg et al., 2011a,b; Guanter et al., 2012), using isolated Fraunhofer lines around 757 nm and 770 nm. These are currently the most robust retrievals, especially as these measurements are relatively close to the fluorescence emission peak near 740 nm. Joiner et al. (2012) have shown that even at 866 nm, a weak fluorescence signal can be retrieved using SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) (Bovensmann et al., 1999; Joiner et al., 2012) with moderate spectral resolution [full width at half maximum (FWHM)~0.5 nm] by making use of a rather wide Fraunhofer line. While high spectral resolution is crucial to resolve (and isolate) Fraunhofer lines, these results indicate that satellites similar to SCIAMACHY, such as Global Ozone Monitoring Experiment (GOME, GOME-2), may still have the potential for fluorescence retrievals, albeit at lower accuracy.

4.3.5 Future suite of satellites capable of retrieving fluorescence

In the future, multiple satellites will allow for fluorescence retrievals. Even though there is currently only one mission proposal (FLEX) dedicated to fluorescence retrievals, a suite of satellites dedicated to measuring greenhouse gases will enable fluorescence retrievals as a by-product. (Albeit, the measurements will not be optimized for vegetation remote sensing in terms of spatial resolution and revisit times.) These include OCO-2 (see ¶4.3.6) as well as CarbonSat (ESA), GOSAT-2 [a cooperative mission by Japan Aerospace Exploration Agency, the National Institute for Environmental Studies, and the Ministry of the Environment (JAXA/NIES/MOE)], or the Chinese carbon dioxide observation satellite (TanSAT).

For fluorescence measurements, a geostationary platform (Key et al., 2012) would be very advantageous as fluorescence could be measured multiple times per day at different levels of incoming photosynthetic radiation, opening up new ways to quantify carbon exchange dynamics. OCO-3, if launched as planned on the International Space Station, would also deliver measurements at different times of day owing to its precessing orbit. Multiple measurements per day over the same area, as a geostationary vantage point would allow, are not feasible though.

4.3.6 The orbiting carbon observatory prospects for fluorescence

The main drawback of current GOSAT fluorescence measurements is the sparsity of data in conjunction with relatively high single-measurement noise. OCO-2 covers about the same wavelength range as GOSAT; in other words, it will not extend the wavelength range towards shorter wavelengths where more Fraunhofer lines could be measured and consequently be

used to reduce noise in fluorescence retrievals. Despite somewhat lower spectral resolutions, its higher signal-to-noise ratio will enable fluorescence retrievals with slightly better single-measurement precision than GOSAT. The biggest difference, however, is the data volume: GOSAT records one interferogram every 4 s at widely spaced geolocations, while OCO-2 will record 8 spectra every 0.33 s in a continuous (but narrow) swath (Figure 4-20). This means that OCO-2 will deliver about 100 times more spectra than GOSAT, thereby reducing the standard error in averaged maps by a factor 10.

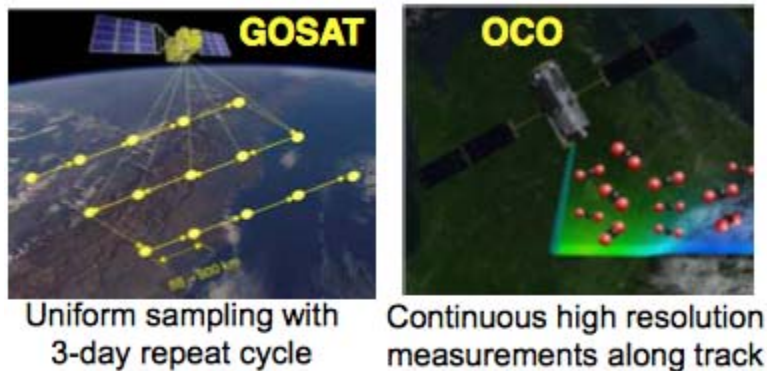


Figure 4-20. Sampling patterns for GOSAT. (Left) Individual footprints recorded in step-and-stare mode. (Right) Continuous narrow OCO-2 swath)

Even though OCO-2 will not map the entire planet (in fact, it will map much less than 5% of it, similar to GOSAT), it will be a step-change from GOSAT, for which high noise currently hampers the exploitation of the full scientific potential. The smaller footprints of OCO-2 as well as the continuous swath will also facilitate potential validation. In addition, the target mode will provide thousands of measurements in

the direct vicinity of Total Carbon Column Observing Network (TCCON) sites at various viewing angles, enabling detailed spatial mapping for a few dedicated sites as well as studies of directional effects of fluorescence emissions. The vegetation community should be made aware of this potential so that these measurements can be fully exploited.

4.3.7 Validation Strategies

Owing to the nature of the GOSAT sampling strategy (see Figure 4-21), validation of fluorescence (SIF) is challenging because there is no continuous swath, and individual measurement samples are noisy.

The challenge for validating retrieved SIF maps is their coarse resolution (monthly averages, 2° grid cell size). Thus, the combined use of observations and models is essential for such a validation, which was the initial intention in the global scale comparisons in Frankenberg et al., 2011b. Observations provide reference SIF measurements and auxiliary data for data interpretation (e.g., structural and functional vegetation variables, meteorological data, other supporting environmental data), whereas models are required not only to extrapolate discontinuous observations to relevant larger temporal and spatial scales, but also to theoretically assess various aspects related to the retrieval performance under controlled conditions.

Applicable observatories to provide spatio-temporal data for validation purposes are satellites, airborne sensors, and in situ instrumentation. At present, GOSAT is the only satellite mission providing global maps of SIF (especially since the ENVISAT failure, with the concurrent loss of SCIAMACHY). Upcoming dedicated missions (i.e., ESA's future Earth Explorer mission FLEX) are under development (Kraft et al., 2012), and no final selection

decision has been made. OCO-2, with a planned launch date in summer 2014, would be the earliest next satellite capable of fluorescence retrievals, so data will not be available for at least 2 years at the earliest. However, various other satellite missions already provide complementary data products (i.e., APAR, chlorophyll content) and estimates of photosynthesis based on different concepts [e.g., the MODIS GPP product (Running et al., 2004)] at respective scales, which can be utilized to assess the sensitivity of SIF for functional changes of vegetation canopies.

Airborne observatories are important at intermediate scale to provide a link between field, regional, and global scale observations. The spatial mismatch between both airborne and GOSAT data hinders a direct comparison but will be feasible for the OCO-2, which provides a continuous swath and footprint sizes on the order of 2 km² to 3 km². The intended use of airborne sensors would be the collection of information of typical SIF ranges over selected ecosystems during the phenological cycle. The combination of snapshots of SIF upscaled with models can be a valuable information source for validating global maps of SIF and linking the process-based understanding on the local scale to the global scale. Only a few airborne instruments are currently suitable to measure SIF [most importantly the Finnish Hyperspectral Plant Imaging Spectrometer (HyPlant)]; there are none in the U.S., and there is no spectrometer world-wide that matches the spectral resolution of GOSAT and OCO-2. The specification of current instruments allows retrieving SIF based on atmospheric absorption bands (i.e., oxygen bands) but limits the application of GOSAT-like SIF retrieval based on Fraunhofer lines. Thus, a validation of SIF retrieved with comparable concepts is currently almost impossible, but at least a relative validation would be possible.

In situ observations of differential atmospheric CO₂ concentrations as proxy for carbon sequestration determined by plant photosynthesis using networks of eddy covariance towers [i.e., FLUXNET, a network of regional networks (Baldocchi et al., 2001)] or other techniques (i.e., TCCON (Wunch et al., 2011)) are valuable to assess the temporal sensitivity of SIF for changes in photosynthesis at ecosystem level. Further, initiatives like the National Ecosystem Observatory Network (NEON) (Keller et al., 2008) provide extensive observations of functional ecosystem properties and environmental conditions to increase knowledge on ecosystem responses to environmental change. Data and the knowledge base of such observatories offer an alternative way to assess the sensitivity of SIF to changes in photosynthesis in general and to better interpret SIF data content wise. To summarize, there is currently no extensive ground-based network that continuously measures fluorescence, and there is no airborne platform that matches the spectral resolution of current satellites. The Fraunhofer lines-based retrieval technique may, however, enable new generations of ground-based measurements (Guanter et al., 2013) as compact high resolution spectrometers are commercially available and integration times can be sufficiently long to reach necessary signal-to-noise ratios. This technique will make continuous monitoring easier as frequent reference target measurements are unnecessary and retrievals even possible under diffuse light conditions.

In addition, coupled radiative transfer (RT), photosynthesis and energy balance models [i.e., SCOPE (van der Tol et al., 2009)] are essential tools to understand the physiological meaning of SIF, its relation to carbon exchange as well as to biochemical and structural plant properties, and its response to environmental conditions. The coupling of SCOPE-like models

with atmospheric RT models allows propagation of emitted SIF radiation from the vegetation canopy through the atmosphere to the sensor level and, consequently, enables us to simulate apparent SIF at satellite level. This capability is interesting as it is an independent validation. However, further work is needed to consolidate the representation of fluorescence in such models across multiple biomes and also complex canopy structures. (For example, canopy radiative transfer currently has to be largely simplified.) Models (e.g., biosphere models or DGVMs) are at present the only tool to predict photosynthesis at ecosystem level globally. The comparison of photosynthesis (GPP) and retrieved SIF offers an alternative way to empirically validate the sensitivity of SIF as proxy for photosynthesis (Frankenberg et al., 2011b). Other important analytical tools are end-to-end-like simulators in combination with local/global sensitivity analysis to quantify SIF retrieval uncertainties related to instrumentation and methodology.

The validation of the GOSAT SIF product is challenging, but several strategies that combine observations and models are possible to assess its respective accuracy and reliability. Validation strategies can be categorized three ways, as described below., .

- 1 The assessment of SIF signal itself (absolute accuracy; consistency of spatio-temporal pattern)

The validation of retrieved SIF itself requires models in combination with systematic observations covering a wide range of SIF emissions at relevant spatio-temporal scales. At present only airborne observations and in situ instrumentation are applicable, but cross comparison with OCO-2 will be possible in the future. Test sites across various ecosystems considering latitudinal diversity should be identified and investigated to obtain typical variations of SIF. Existing sites and infrastructure in frame of, for example, the Spectral Network [SpecNet (Gamon et al., 2006)], could be evaluated and, if required and possible, could complement relevant fluorescence instrumentation or be adapted with specific measurement protocols. Dedicated flight experiments using airborne observatories are important not only to provide additional validation data, but also as a knowledge base for exceptional findings caused by, for example,, extreme environmental conditions. This option eventually requires the development of a new airborne sensor if available instruments are evaluated as unsuitable. The site measurements itself have to be aggregated or extrapolated using specific models (e.g., SCOPE) for validating GOSAT SIF; however, we see potential for the OCO-2 mission, as the swath is continuous, footprints much smaller, and data amount 100× higher (largely reducing the precision error in aggregated maps).

- 2 The evaluation of the causal relationships between retrieved SIF and environmental variables or ecosystem properties

Underlying physiology makes remotely measured SIF more sensitivity to the process of plant photosynthesis compared to greenness based variables. A second strategy to validate GOSAT SIF can focus on the sensitivity of SIF to changes in the functional status of ecosystems. This requires extended spatio-temporal measurements of ecosystem and environmental variables as available from various satellites (e.g., AVHRR, MODIS) or measurement networks (e.g., FLUXNET, NEON). Statistical analysis between GOSAT SIF and measured environmental properties that considers underlying physiological mechanisms could be applied to reveal the plausibility of SIF and the added value compared to common

greenness-based remote sensing approaches. Complementary to this, DGVMs can be used to simulate photosynthesis at ecosystem scale; the results can be then compared to GOSAT SIF and eventually allow for carbon cycle data assimilation using actual state variables. Findings and observed mechanistic relationships can be cross checked with models such as SCOPE.

- 3 The quantification of factors influencing and potentially disturbing the SIF retrieval (e.g., atmospheric absorption and scattering, surface anisotropy, applied methods, and used instrumentation)

A third strategy applicable to gathering evidence on retrieved SIF is a theoretical assessment of uncertainties related to the various retrieval steps and instrumental effects based on sensitivity analysis (Frankenberg et al., 2012; Guanter et al., 2012) in combination with end-to-end-like simulators. The most straightforward validation approach currently used for GOSAT is to ensure that vegetation-free areas indeed exhibit zero fluorescence signal, even under various signal level and viewing geometry conditions. The zero-level offset in GOSAT O₂-A band spectra and its time dependence currently make this a challenging task if small variations in fluorescence are to be interpreted.

5. Future plans and development

5.1 Roadmap for technical development

In order to enhance current photosynthesis measurement capabilities, we must address the lack of consistent ground-based long-term datasets. No current ground-based or airborne instrument has a spectral resolution that matches GOSAT or OCO-2 performance; i.e., there is no instrument currently available that can easily apply the robust algorithms now developed for satellites. Current measurements are mostly based on retrievals using the O₂ bands, which provide highly accurate relative fluorescence levels at short distances but that are much less accurate when the plant–observer distance is greater (e.g., from aircraft or helicopters). Therefore, technical development is needed to establish a consistent ground-based spectrometer system that matches the spectral resolution of satellites. In order to validate the absolute fluorescence levels observed from space as well as to consolidate fluorescence-GPP modeling. The following steps must be taken to develop high-spectral resolution spectrometers for ground-based long-term measurements as well as for airborne system (aircraft or helicopter):

- Design high-spectral resolution spectrometers covering the entire red-edge and fluorescence emission spectrum (either 2D push-broom grating spectrometers or rely on the proven GOSAT FTS system if full mapping is not required).
- Evaluate potential of existing (e.g., Ocean Optics, Avantes) high-resolution spectrometers for operational ground-based studies.

5.2 Recent and planned papers

5.2.1 Published papers

Frankenberg, C., Butz, A., and Toon, G. C. (2011). Disentangling chlorophyll fluorescence from atmospheric scattering effects in O-2 A-band spectra of reflected sun-light. *Geophysical Research Letters*, 38(3), L03801. doi:10.1029/2010GL045896.

Frankenberg, C., Fisher, J., Worden, J., Badgley, G., Saatchi, S., Lee, J.-E., et al. (2011). New global observations of the terrestrial carbon cycle from GOSAT: Patterns of plant fluorescence with gross primary productivity. *Geophysical Research Letters*, 38(17), L17706.

Frankenberg, C., O'Dell, C., Guanter, L., and McDuffie, J. (2012). Remote sensing of near-infrared chlorophyll fluorescence from space in scattering atmospheres: implications for its retrieval and interferences with atmospheric CO₂ retrievals. *Atmospheric Measurement Techniques*, 5(8), 2081–2094. doi:10.5194/amt-5-2081-2012.

Guanter, L., Frankenberg, C., Dudhia, A., Lewis, P. E., Gómez-Dans, J., Kuze, A., et al. (2012). Retrieval and global assessment of terrestrial chlorophyll fluorescence from GOSAT space measurements. *Remote Sensing of Environment*, 121, 236–251. doi:10.1016/j.rse.2012.02.006

Guanter, L., Rossini, M., Colombo, R., Meroni, M., Frankenberg, C., Lee, J.-E., and Joiner, J. (2013). Using field spectroscopy to assess the potential of statistical approaches for the

retrieval of sun-induced chlorophyll fluorescence from ground and space. *Remote Sensing of Environment*, 133, 52–61. doi:10.1016/j.rse.2013.01.017

Joiner, J., Yoshida, Y., Vasilkov, A. P., Yoshida, Y., Corp, L. A., and Middleton, E. M. (2011). First observations of global and seasonal terrestrial chlorophyll fluorescence from space. *Biogeosciences*, 8(3), 637–651. doi:10.5194/bg-8-637-2011.

Joiner, J., Yoshida, Y., Vasilkov, A. P., Middleton, E. M., Campbell, P. K. E., Yoshida, Y., et al. (2012). Filling-in of near-infrared solar lines by terrestrial fluorescence and other geophysical effects: simulations and space-based observations from SCIAMACHY and GOSAT. *Atmospheric Measurement Techniques*, 5(4), 809–829. doi:10.5194/amt-5-809-2012.

Lee, J. E., Frankenberg, C., van der Tol, C., Berry, J., Guanter, L., Fisher, J., Boyce, K., Morrow, E., Asefi, S., Badgley, G., Saatchi, S. (in press). Amazonian productivity to seasonal water stress: observations from GOSAT chlorophyll fluorescence, *Proceedings of the Royal Society B*.

5.2.2 Planned papers

The workshop team plans to write and publish papers related to a general review of the underlying mechanics of the SIF-GPP linkage, papers related to exploiting the GOSAT dataset, and papers describing the use of future space-based measurements.

5.3 How team will continue to move work forward

The workshop team was very diverse, both in terms of nationalities and basic science background. The workshop facilitated new collaborations between several team members that will allow participants to explore scientific possibilities and common interests as well as to develop proposals for future technical development.

5.4 Lessons learned

In order to develop a common language and introduce the main ideas to all workshop participants, the workshop began with a short course on the global carbon cycle, photosynthesis and chlorophyll fluorescence, and retrieval of chlorophyll fluorescence from space. During the workshop, each speaker presented material to introduce the topic to colleagues who specialized in other fields. Nevertheless, we realized that we should have spent somewhat more time on the basics (e.g., the sudden jump into the details of photosynthesis and fluorescence confused many people, who lost track of the link between SIF and GPP). To some degree, this is also true for the field in general, where skepticism may arise because the problem is complex. However, most other plant-related research, even if based on simple vegetation indices, is at least as complex, which is now often forgotten just because the product is established. Therefore, in future workshops, we will focus on the basics first before discussing potential pitfalls in interpretation.

6. Conclusions

The *New Methods for Measurements of Photosynthesis from Space* workshop focused on a newly developed capacity to monitor chlorophyll fluorescence from terrestrial vegetation by satellite. This revolutionary approach for retrieving global observations of SIF promises to provide direct and spatially resolved information on GPP, an ideal bottom-up complement to the atmospheric net CO₂ exchange inversions and a valuable addition to the tool box for monitoring and modeling of the terrestrial biosphere. Workshop participants included key members of several communities: plant physiologists with experience using active fluorescence methods to quantify photosynthesis; ecologists and radiative transfer experts who are studying the challenge of scaling from the leaf to regional scales; atmospheric scientists with experience retrieving photometric information from space-borne spectrometers; and carbon cycle experts who are integrating new observations into models that describe the exchange of carbon between the atmosphere, land and ocean.

The difficulty of resolving SIF from the overwhelming flux of reflected sunlight in the spectral region where fluorescence occurs was once a major impediment to making this measurement. Placement of very high spectral resolution spectrometers on GOSAT (and other greenhouse gas-sensing satellites) has enabled retrievals based on in-filling of solar Fraunhofer lines, enabling accurate fluorescence measurements even in the presence of moderately thick clouds. Perhaps the most interesting challenge here is that there is no readily portable ground-based instrumentation that even approaches the capability of GOSAT and other planned greenhouse gas satellites. This strongly limits scientists' ability to conduct ground-based studies to characterize the footprint of the GOSAT measurement and to conduct studies of radiation transport needed to interpret SIF measurement.

Workshop presentations reviewed the basic mechanisms that underlie this phenomenon, and examined modeling tools that have been developed to simulate SIF in land surface and carbon cycle models. Another focus of the workshop explored a "top-down" view of the SIF signal from space. Early studies clearly identified a strong correlation between the strength of this signal and our best estimate of the rate of photosynthesis (GPP) over the globe. New studies show that this observation provides improvements over conventional reflectance-based remote sensing in detecting seasonal and environmental (particularly drought related) modulation of photosynthesis. Apparently SIF responds much more quickly and with greater dynamic range than typical greenness indices when GPP is perturbed.

It is noted that this topic represents an opportunity for forging a deep connection between scientists doing basic research in photosynthetic mechanisms and the more applied community doing research on the Earth System. Too often these connections have gotten lost in empiricism associated with the coarse scale of global models. Chlorophyll fluorescence has been a major tool for basic research in photosynthesis for nearly a century. SIF observations from space, although sensing a large footprint, probe molecular events occurring in the leaves below. This offers an opportunity for direct mechanistic insight that is unparalleled for studies of biology in the Earth System.

Appendix A: Workshop participants

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¹ Scott Denning was, unfortunately, unable to attend the workshop

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Appendix B: Workshop agendas

Sunday, August 26, 2012—Hameetman Auditorium—Cahill Building, open to all		
Time	Short Course	Speaker
12:30–1:00	Coffee and refreshments	
1:00–1:05	Introduction	Team Leads
1:05–2:20	<i>The global carbon cycle, an overview</i> (includes 15 minutes for Q+A)	Ian Baker
2:20–2:30	Mini-break for stretching between lectures	
3:30–4:45	<i>A primer into photosynthesis and chlorophyll fluorescence</i> (includes 15 minute for Q+A)	Joe Berry
4:45–5:15	Short break	
5:15–6:30	<i>Retrieval of chlorophyll fluorescence from space</i> (+ 15 minutes for Q+A)	Christian Frankenberg
6:30–7:45	On site, informal dinner provided by KISS for all short course attendees (not only core participants)	
7:45	Short Course concludes	
Monday, August 27, 2012—Third Floor—Keith Spalding Building Theme: Chlorophyll fluorescence across spatial scales (molecular, leaf level, canopy, mixed vegetation)		

Time	Workshop	Speaker
8:00–8:30	Coffee and refreshments	
8:30–9:00	Introduction to the Institute and to KISS	Michele Judd
9:00–10:15	Short presentations of participants (max 2–3 minutes each)	All
10:15–10:45	Break	
10:45–11:45	<i>Biophysical mechanisms of fluorescence and its relation to GPP (incl. 15 min Q+A)</i>	Joe Berry + Bernard Genty
11:45–12:45	<i>Recap of fluorescence retrieval techniques from ground and space (incl. 15 min. Q+A)</i>	Luis Guanter + Joanna Joiner
12:45–2:15	KISS Lunch at the Athenaeum	
2:15–3:15	<i>Fluorescence scaling from the leaf to the canopy level (incl. 15 min Q+A)</i>	Christiaan van der Tol
3:15–3:45	<i>Open issues: Do we have adequate knowledge of fluorescence principles to relate emission to GPP, where are the uncertainties? (incl. 10 min Q+A)</i>	Albert Porcar-Castell

Time	Workshop	Speaker
3:45–4:15	Break	
4:15–4:45	<i>Group Discussion: Do we have adequate knowledge of fluorescence principles to relate emission to GPP, where are the uncertainties?</i>	Moderator: Christiaan van der Tol
4:45–5:45	<i>Fluorescence: Lessons learned from ground-based and airborne studies (for FLEX mission preparation and others). (incl. 15 min Q+A)</i>	Alexander Damm
6:00–9:00	opening KISS Dinner on the Athenaeum Lawn	
Tuesday, August 28, 2012—Keith Spalding Building—Third Floor Theme: Global carbon cycle modeling of GPP and atmospheric inversions of net fluxes.		
8:00–8:30	Coffee and refreshments	
8:30–9:30	<i>Stress responses of terrestrial vegetation and their manifestation in fluorescence and GPP. (incl. 15 min Q+A)</i>	Jaume Flexas
9:30–10:30	Introduction into terrestrial vegetation modeling on the global scale (incl. 15 min Q+A)	Josh Fisher
10:30–11:00	Break	
11:00–12:00	Statistical GPP up-scaling approaches (incl. 15 min Q+A)	Martin Jung
12:00–12:30	Group Discussion: Vegetation modeling	Moderator: Ian Baker
12:30–2:00	KISS Lunch at the Athenaeum	
2:00–2:45	<i>How should/could fluorescence be integrated into carbon cycle models? (incl. 10 min Q+A for each)</i>	Christiaan van der Tol (SCOPE)
2:45–3:30		Jung-Eun Lee and Ian Baker (SiB)
3:30–4:00	Break	
4:00–4:30	Atmospheric CO ₂ data, lessons learned from ground-based data, TCCON and satellites	Paul Wennberg
4:30–5:00	Source/sink inversions based on atmospheric CO ₂ data, statistical tools	Anna Michalak
5:00–5:30	Source/sink inversions based on atmospheric CO ₂ data, general inversions	Kevin Bowman
6:00–8:00	No-Host Dinner in Pasadena	

Time	Workshop	Speaker
Wednesday, August 29, 2012—Keith Spalding Building—Third Floor Theme: Linking interdisciplinary boundaries: How do we best combine chlorophyll fluorescence from space with atmospheric CO₂ observations in a carbon cycle perspective		
8:00–8:30	Coffee and refreshments	
8:30–9:15	<i>Potential ancillary data products: Photochemical Reflectance Index (PRI) and others (incl. 10 min Q+A)</i>	Thomas Hilker (PRI)
9:15–10:00	<i>What other observations are needed in addition to fluorescence (e.g., from MODIS, MERIS, vegetation types, meteorology, etc.) for a robust GPP estimate? Lessons learned from FLEX, path to potential future missions.(incl. 10 min Q+A)</i>	Luis Guanter
10:00–10:30	Break	
10:30–11:30	Group Discussion: Given what we know now, what would the ideal fluorescence mission look like?	Moderator: Christian Frankenberg
11:30–1:30	Poster session combined with on-site Pizza lunch	All
1:00–5:30	<i>Team activity (Griffith Observatory or Mount Wilson)</i>	All
6:00–8:00	No-Host Dinner in Pasadena	
Thursday, August 30, 2012—Keith Spalding Building—Third Floor Theme: Linking fluorescence and atmospheric CO₂ + breakout sessions		
8:00–8:30	Coffee and refreshments	
8:30–9:15	<i>How can we combine the complementary information from fluorescence and atmospheric CO₂? (incl. 15 min Q+A)</i>	Kevin Bowman
9:15–10:00	<i>How can we combine the complementary information from fluorescence and atmospheric CO₂? (incl. 15 min Q+A)</i>	Anna Michalak
10:00–10:30	Group Discussion: How can we combine the complementary information from fluorescence and atmospheric CO ₂ ? Missing pieces?	Moderator: Scott Denning
10:30–11:00	Break	
11:00–12:30	Breakout sessions (Fluorescence Modeling, Fluorescence retrieval, use of fluorescence in global carbon cycle models)	All
12:30–2:00	No-host lunch break	
2:00–2:30	Breakout sessions continued	All

Time	Workshop	Speaker
2:30-3:30	Group Discussion: Breakout session feedback from the larger group	All
3:30-4:00	Break	
4:00-5:00	Preparation of breakout session results + discussion material	All
6:00-8:00	Dinner at The Athenaeum	
Friday, June 29, 2012—Keith Spalding Building—Third Floor		
8:00-8:30	Coffee and refreshments	
8:30-9:30	Summary + discussion of carbon cycle breakout session	Moderator: Paul Wennberg
9:30-10:30	Summary + discussion of fluorescence principles session	Moderator: Joe Berry
10:30-11:00	Break	
11:00-12:00	Summary + discussion of fluorescence retrievals and "the optimal measurement"	Moderator: Christian Frankenberg
12:00-1:00	Informal lunch on site	
1:00-2:30	Open discussion: Identify open issues needed to be addressed to fully exploit the fluorescence potential from space, also wrt to the OCO-2 mission or dedicated mission proposals All: Plan future activities, scientific collaborations.	Moderator: Team Leads
2:30-3:00	Break	
3:00-4:30	Prepare report outline	All
4:30	Workshop concludes	

Appendix C: References

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