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# Using spectral chlorophyll fluorescence and the photochemical reflectance index to predict physiological dynamics

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Observations of terrestrial chlorophyll fluorescence and the Photochemical Reflectance Index (*PRI*) from space have the potential to improve estimates of global carbon exchange. However the relationship between photosynthetic rate and these measurements is complicated by several factors that relate to the dissipation of absorbed light energy via both photochemical (photosynthesis) and non-photochemical pathways. Numerical simulations of physiological remote sensing signals require the coupling of physically-based radiative transfer models with models of physiological dynamics. These schemes provide the quantitative frameworks from which physiological information can be extracted from remote sensing observations of vegetation, helping to resolve the aforementioned complexities. We present such a framework that links physiological fluorescence theory with spectral remote sensing type measurements at the leaf scale. We show how a simple expression can be used to predict the quantum yield of photochemistry ($\Phi_{PSII}$), a proxy for photosynthetic efficiency, from spectral measurements and modelled non-photochemical quenching (*NPQ*). We tested two alternate models of *NPQ*; one process-based (*PHOTOII*) and the other empirical, based on visible region reflectance changes (the *PRI*). We used a Monte Carlo Radiative Transfer (*MCRT*) model to retrieve the separated yields of chlorophyll fluorescence from photosystems II and I. Measurements of dynamic spectral fluorescence, the *PRI*, hemispherical reflectance and transmittance, saturation pulse integrated fluorescence and pigment contents were collected from maple leaves and used to calibrate and validate the modelling framework. Both *NPQ* models reproduced the observed photochemical and non-photochemical dynamics. Future work is recommended to scale the framework across space, time and species.

## 1. Introduction

Vegetation drives carbon exchange at the Earth's surface via photosynthesis. Therefore accurately measuring terrestrial photosynthesis from space is a key aim of Earth observation science. Two remote sensing signals that have shown particular promise for measuring changes in photosynthesis from space are i. solar induced chlorophyll fluorescence (*SIF*) (Moya et al., 2004; Meroni et al., 2009) and ii. dynamic changes in green reflectance (close to 531 nm) as measured by the Photochemical Reflectance Index (*PRI*) (Gamon, Peñuelas, & Field, 1992).

By absorbing light, chlorophyll molecules provide the energy needed to fuel the photosynthetic reactions. However not all of the energy absorbed by chlorophyll is used in photosynthesis. A small amount (typically <5%) is re-emitted as a double-peaked spectrum of chlorophyll fluorescence in the visible to near infrared wavelengths (approximately 650 nm–820 nm). The shape of the chlorophyll fluorescence spectrum is controlled by both physical (scattering and re-absorption) and physiological (photosynthesis) processes (Buschmann, 2007).

Chlorophyll fluorescence originates from deep within the photosynthetic machinery of the leaf, in the photosystems of the thylakoid membranes. Therefore a significant proportion of the chlorophyll fluorescence signal is reabsorbed within the leaf prior to escaping. This effect is particularly evident in the red wavelengths where chlorophyll reaches peak absorption efficiency (Lichtenthaler, Wenzel, Buschmann, & Gitelson, 1998). Physically-based radiative transfer models can correct for re-absorption, thereby recovering an estimate of the true, internal fluorescence spectrum. Codes such as *FlourMODleaf* (Pedrós, Goulas, Jacquemoud, Louis, & Moya, 2010) and *fluspect* (Verhoef, 2011), based on plate theory and Kubelka–Munk theory respectively, propagate spectral fluorescence from the thylakoid to the leaf surface and include some parametrisation of scattering as well as absorption. Monte Carlo integration of the radiative transfer equation has also been used to simulate combined spectral fluorescence, reflectance and transmittance for single leaves (Susila & Naus, 2007). Leaf scale models provide deterministic links between parameters of physiological importance (e.g. chlorophyll content) that constrain re-

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absorption and the measure-able fluorescence spectrum. In addition leaf scale models are also the building blocks for more complicated canopy scale schemes such as *FlourMOD* (Zarco-Tejada, Miller, Pedrós, Verhoef, & Berger, 2006) that can be used to simulate remote sensing observations (Middleton, Corp, & Campbell, 2008).

Remote sensing studies typically employ some variant of Fraunhofer Line Depth method (Plascyk, 1975; Plascyk & Gabriel, 1975) to retrieve sun-induced fluorescence (*SIF*) across dark regions of the electromagnetic spectrum (caused by solar or telluric absorption of light). Progress in the remote sensing of chlorophyll fluorescence has been driven by the selection of the FLuorescence EXplorer (FLEX) mission by the European Space Agency as a candidate for the Earth Explorer programme. As part of the FLEX activities, the HyPlant imaging spectrometer was developed to image *SIF* from airborne platforms with the aim of relating *SIF* to spatial variability in photosynthetic activity. First results (Rascher et al., 2015) from HyPlant indicated that spatial variations in *SIF* were related to differences in light absorption by chlorophyll and also photosynthetic activity. Similar results linking *SIF* and photosynthesis have been shown in earlier studies, for example Damm et al. (2010) used diurnal above-canopy measurements of *SIF* to model Gross Primary Productivity (*GPP*, a measure of photosynthetic activity) of a wheat canopy.

Recent studies have sought to use satellite retrievals of *SIF* to constrain predictions of *GPP* across the landscape (Guanter et al., 2014; Parazoo et al., 2014; Joiner et al., 2014). In a landmark study, Guanter et al. (2014) used *SIF* to model crop *GPP* across the landscape based on an observed linear relationship between eddy covariance measured $CO_2$ fluxes of crops and remote sensing observations in overlying pixels. Guanter et al. (2014) hypothesised that this relationship exists because the *SIF* signal contains information pertaining both to the fraction of light absorbed by the canopy and the efficiency of the fluorescence emission, itself related to the photosynthetic rate. However this is not the case at smaller scales, where the relationship between photosynthesis and fluorescence is non-linear (Porcar-Castell et al., 2014). This is because in addition to fluorescence and photosynthesis a third energy use pathway, termed non photochemical quenching (NPQ), competes for absorbed light energy. Thus NPQ decouples the relationship between photosynthesis and chlorophyll fluorescence.

A number of different processes contribute to NPQ which collectively act to dissipate potentially harmful absorbed light energy (when in excess) as heat (Müller, Li, & Niyogi, 2001). One such NPQ process is the interconversion of a group of carotenoid pigments referred to as the xanthophyll cycle (Müller et al., 2001; Nilkens et al., 2010). This is a reversible series of reactions that is measurable as a subtle change in green reflectance, and is typically formulated in reflectance index form as the *PRI* (Gamon et al., 1992). The *PRI* has been shown to correlate with photosynthetic activity at a range of scales from the leaf to across the landscape (see Garbulsky, Peñuelas, Gamon, Inoue, and Filella (2011) for a review of applications). However the use of the *PRI* for tracking photosynthetic efficiency is complicated by the fact that the *PRI* is correlated with the ratio of carotenoid to chlorophyll pool sizes (Filella et al., 2009; Porcar-Castell et al., 2012; Wong & Gamon, 2015) and that the *PRI* is only partially representative of the multi-temporal dynamics of NPQ.

Gamon and Berry (2012) refer to the reversible, xanthophyll cycle related changes in the *PRI* as the facultative component and the slower pigment pool changes as the constitutive component. Recent studies at the leaf (Hmimina, Dufrene, & Soudani, 2014) and canopy scales (Merlier, Hmimina, Dufrne, & Soudani, 2015; Hmimina, Merlier, Dufrêne, & Soudani, 2015) have focused on dis-entangling these two components, though little work has been done to relate the *PRI* to NPQ. Establishing this link is crucial if the *PRI* and chlorophyll fluorescence are to be combined, as has been proposed by the FLEX mission (Drusch et al., 2008), because it is through NPQ that the two measurements are connected.

The increased interest in measuring *SIF* from space has also led the re-evaluation of the potential of the *PRI* for retrieving physiological information from space (Damm, Guanter, Verhoef, et al., 2015; van der Tol, Berry, Campbell, & Rascher, 2014). Although the *PRI* has previously been used to model *GPP* using satellite retrievals (Drolet et al., 2005; Hilker et al., 2011), canopy *PRI* is particularly sensitive to both structural (Barton & North, 2001) and directional-irradiance (Damm, Guanter, Verhoef, et al., 2015) effects. Hence the *PRI* has remained at the non-operational proof-of-concept stage.

There are clearly a number of physical and physiological factors that disassociate the *PRI* from photosynthesis, and the same is also true for *SIF*. How, then, to solve the problem of using measurements of *SIF* and the *PRI* to retrieve physiologically meaningful information? One solution is to embed radiative transfer schemes within dynamic vegetation models. Such coupled models deterministically link remote sensing observations to physiologically relevant parameters. The Soil Canopy Observation, Photochemistry and Energy Flux model (*SCOPE*) (van der Tol, Verhoef, Timmermans, Verhoef, & Su, 2009; van der Tol et al., 2014) constrains simulated fluorescence yields (and the resulting canopy fluxes) via a feedback mechanism from a model of the carbon reactions of photosynthesis. The benefit of this approach is that there is a direct link between photosynthetic rate and chlorophyll fluorescence, which can then be used to explain satellite observations. For example Lee et al. (2013) used (a modified version) of *SCOPE* to show that satellite retrieved *SIF* was able to track reductions in dry season *GPP* caused by water stress across the Amazon.

*SCOPE* is the current state-of-the art in fluorescence-vegetation modelling. At reduced scales, the dynamic model of Porcar-Castell, Bäck, Juurola, and Hari (2006) (*PHOTOII*) contains a detailed representation of the energy flow through photosystem II and works on short time-scales of seconds to minutes. This means that *PHOTOII* (in contrast to *SCOPE* which operates on longer, steady-state time-steps) has the capability to simulate the short time-scale dynamics of NPQ. Therefore *PHOTOII* is an ideal tool for investigating the physiological mechanisms that control short-timescale changes in chlorophyll fluorescence and the *PRI*. However because *PHOTOII* was developed to simulate dimensionless Pulse Amplitude Modulated (PAM) fluorimeter measured parameters, the original version of *PHOTOII* lacked a radiative transfer component capable of simulating spectral measurements (the PAM fluorimeter is a standard instrument in plant physiology studies from which a number of photosynthesis-related parameters can be derived, such as the quantum yield of photosystem II ($\Phi_p$) (Maxwell & Johnson, 2000)).

Although there is a significant body of literature and theory devoted to understanding the relationships between fluorescence, NPQ and photosynthesis (Porcar-Castell et al., 2014), little modelling or measurement work has been conducted over short time-scales using spectral data acquired from leaves. This issue was recently highlighted by van der Tol et al. (2014) who stated the need for concurrent measurements of active (PAM) fluorimeter and spectral fluorescence for this purpose. In this study we address this need by conducting these measurements. We also develop the theory necessary to relate measurements of spectral fluorescence and the *PRI* to NPQ and photosynthesis parameters derived from active (PAM) fluorescence measurements. In addition we show how *PHOTOII* can be coupled to a radiative transfer scheme.

The objective of this study was to link spectral measurements of fluorescence and the *PRI* to photosynthesis dynamics at the leaf scale and over short time-scales. The physical-physiological linkages are based on active (PAM) fluorescence theory and radiative transfer modelling respectively. By working with leaves we aimed to develop approaches that have the potential to be scaled to the canopy. We used concurrent measurements of spectral fluorescence, reflectance and PAM fluorimeter measured fluorescence to track optical dynamics. We used both a process-based model (*PHOTOII*) and an empirical *PRI* model to estimate the dynamics of NPQ. A radiative transfer scheme