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Key Points:

- Across sky conditions, SIF-PAR relationships converge for Fraunhofer-based but diverge for O₂A-based retrievals, even under clear skies
- The robustness of O₂A-based retrievals under cloudy conditions can be improved by using a narrower fitting window
- These conclusions hold for both bi-hemispherical and hemispherical-conical systems; the latter are less sensitive to atmospheric impacts

Supporting Information:

- Supporting Information S1

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Systematic Assessment of Retrieval Methods for Canopy Far-Red Solar-Induced Chlorophyll Fluorescence Using High-Frequency Automated Field Spectroscopy

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Abstract Remote sensing of solar-induced chlorophyll fluorescence (SIF) offers potential to infer photosynthesis across scales and biomes. Many retrieval methods have been developed to estimate top-of-canopy SIF using ground-based spectroscopy. However, inconsistencies among methods may confound interpretation of SIF dynamics, eco-physiological/environmental drivers, and its relationship with photosynthesis. Using high temporal- and spectral resolution ground-based spectroscopy, we aimed to (1) evaluate performance of SIF retrieval methods under diverse sky conditions using continuous field measurements; (2) assess method sensitivity to fluctuating light, reflectance, and fluorescence emission spectra; and (3) inform users for optimal ground-based SIF retrieval. Analysis included field measurements from bi-hemispherical and hemispherical-conical systems and synthetic upwelling radiance constructed from measured downwelling radiance, simulated reflectance, and simulated fluorescence for benchmarking. Fraunhofer-based differential optical absorption spectroscopy (DOAS) and singular vector decomposition (SVD) retrievals exhibit convergent SIF-PAR relationships and diurnal consistency across different sky conditions, while O₂A-based spectral fitting method (SFM), SVD, and modified Fraunhofer line discrimination (3FLD) exhibit divergent SIF-PAR relationships across sky conditions. Such behavior holds across system configurations, though hemispherical-conical systems diverge less across sky conditions. O₂A retrieval accuracy, influenced by atmospheric distortion, improves with a narrower fitting window and when training SVD with temporally local spectra. This may impact SIF-photosynthesis relationships interpreted by previous studies using O₂A-based retrievals with standard (759–767.76 nm) fitting windows. Fraunhofer-based retrievals resist atmospheric impacts but are noisier and more sensitive to assumed SIF spectral shape than O₂A-based retrievals. We recommend SVD or SFM using reduced fitting window (759.5–761.5 nm) for robust far-red SIF retrievals across sky conditions.

Plain Language Summary Solar-induced chlorophyll fluorescence (SIF) is light energy emitted by photosynthetic machinery which contains information about photosynthetic activity. SIF retrieval accuracy is crucial for properly interpreting SIF dynamics and understanding its relationships with photosynthesis. Different methods have been developed to retrieve SIF from ground-based systems, but to date their consistency has not been evaluated under all sky conditions using field measurements. Here we use a combination of continuous field measurements and synthetic data to evaluate the sensitivity of commonly used SIF retrieval methods to variable atmospheric conditions, measurement noise, and changes in canopy structure and biochemistry. We offer recommendations for optimal retrieval method configurations that can be used by SIF ground systems.

1. Introduction

Rising temperatures and atmospheric CO₂ have significant but varying impacts on the carbon uptake of terrestrial ecosystems across the globe (Cramer et al., 1999; Friedlingstein et al., 2006; Heimann & Reichstein, 2008). Understanding and predicting their differential impacts in time and space are

challenging, due to limited tools available to accurately quantify photosynthesis (i.e., gross primary production [GPP]) beyond the leaf scale. One promising approach to tackle this issue is the remote sensing of solar-induced chlorophyll fluorescence (SIF). Chlorophyll fluorescence is light (650–850 nm) emitted from excited chlorophyll *a* molecules and represents the fraction of absorbed light energy that does not enter photochemical or non-photochemical pathways (Baker, 2008). As such, any measurement of chlorophyll fluorescence intrinsically contains functional information about the performance of photochemistry and non-photochemical quenching (Gu, Han, et al., 2019; Porcar-Castell et al., 2014).

Recent technological advances have enabled the passive detection of SIF for the whole canopy from ground (Grossmann et al., 2018; Gu, Wood, et al., 2019; Guanter et al., 2013; Li et al., 2020; Liu, Guan, et al., 2017; Magney, Bowling, et al., 2019; Magney, Frankenberg, et al., 2019; Miao et al., 2018; Yang et al., 2015, 2017, 2018), airborne (Frankenberg et al., 2018; Rascher et al., 2015) and satellite platforms (Du et al., 2018; Frankenberg et al., 2011; Joiner et al., 2011; Köhler et al., 2015; Köhler, Guanter, et al., 2018; Parazoo et al., 2019; Sun et al., 2018). However, meaningful interpretation of canopy SIF is challenging (Gu, Han, et al., 2019), because the SIF signal detected above the canopy is affected by a multitude of factors related to canopy structure, physiology, and atmospheric conditions. For example, physiological factors include responses of energy quenching processes within leaves, as well as different leaves within a canopy, among species, and over timescales (Atherton et al., 2017; Cendrero-Mateo et al., 2015; Porcar-Castell et al., 2014). Structural factors include leaf angle distribution, canopy architecture, and leaf optical properties that impact light reabsorption and scattering (Van Wittenberghe et al., 2015; Yang & van der Tol, 2018). Lastly, atmospheric conditions such as aerosols, clouds, and highly variable light conditions caused by fast-moving clouds affect the quality of the acquired spectra (Boesche et al., 2006, 2008; Guanter et al., 2010).

Obtaining high-quality SIF retrievals is crucial to meaningfully interpret SIF dynamics, disentangle its physiological and structural contributions, understand its environmental drivers, and finally establish mechanistic relationships between SIF and GPP across biomes, environments, and timescales. In particular, high-frequency ground SIF measurements are critical for underpinning the above questions at different timescales. In recent years, a rapidly growing number of SIF studies have attempted to establish empirical relationships between SIF and GPP for different ecosystems and environments using ground-based systems (synthesized in Table 1). Each of these studies tended to rely exclusively on a single retrieval method, partly due to the constraints of different spectrometer configurations such as spectral resolution and signal-to-noise ratio (discussed by Julitta et al., 2016). Although all SIF retrieval methods originated from the Fraunhofer line discrimination (FLD) principle (Plascyk, 1975), the actual formulation of each method differs in the employed absorption bands (telluric O₂ absorption bands vs. solar Fraunhofer lines), retrieval approaches (physical- vs. statistical-based), spectral channels (multi- vs. hyper-spectral), retrieval window range, and the assumed SIF/reflectance spectral shape (Cendrero-Mateo et al., 2019). Indeed, different SIF retrieval methods and even different parameter selection of the same method can lead to considerable differences in the SIF retrieval (e.g., Damm et al., 2011; Guanter et al., 2013; Meroni et al., 2010). Moreover, existing studies predominantly focused on clear-sky conditions. Although a handful of previous studies have compared the accuracy and robustness of each method to varying levels of instrument noise, they either relied on solely synthetic data (e.g., Cendrero-Mateo et al., 2019; Damm et al., 2011; Meroni et al., 2010) or a limited number of field campaigns under clear-sky conditions only (e.g., Guanter et al., 2013). Other studies such as Julitta et al. (2016) and Zhang et al. (2019) compared multiple system configurations but only employed the standard FLD and/or 3FLD retrieval method.

To date, no efforts have been made to systematically evaluate different SIF retrieval methods under all sky conditions using continuous long-term field measurements from both bi-hemispherical and hemispherical-conical systems. This effort is crucial because (1) accurate SIF retrievals are necessary to interpret SIF dynamics, disentangle physiological and structural contributions, understand its environmental drivers, and finally establish mechanistic relationships between SIF and GPP; (2) there is a need to understand the relative strengths and limitations of each retrieval method; (3) identifying robust methods for SIF retrieval under all sky conditions and across system configurations will greatly enhance the data availability, which are currently biased toward clear-sky conditions (Frankenberg et al., 2012; Grossmann et al., 2018) and may differ among configurations (Zhang et al., 2019); and (4) ground SIF is considered as “ground truth” for validating satellite SIF.

Table 1
Retrieval Methods and System Configurations Used by Recent Ground-Based SIF Studies^a

Reference	Retrieval method	Spectrometer	SNR	Spectral range (nm)	Spectral resolution (nm FWHM)
Guanter et al. (2013)	SVD, SFM	HR4000	300	707–805	0.13
Meroni et al. (2010)	SFM, FLD	n/a (synthetic)	n/a	n/a	n/a
Damm et al. (2011)	FLD versions	n/a (synthetic)	n/a	n/a	n/a
Yang et al. (2018)	SVD	QE Pro	1,000	730–790	0.17
Grossmann et al. (2018)	DOAS ^b	QE Pro	1,000	730–780	0.3
	DOAS ^b	QE Pro	1,000	650–720	0.3
	DOAS ^b	QE Pro	1,000	650–720	0.3
Meroni et al. (2011)	SFM	HR4000	300	700–800	0.1
Cogliati et al. (2015)	SFM	HR4000	300	700–800	0.1
Liu et al. (2015)	SFM	QE Pro	1,000	645–805	0.31
Rossini et al. (2015)	SFM	HR4000	300	700–800	0.1
Yang et al. (2015)	SFM	HR2000+	240	680–775	0.13
Wyber et al. (2017)	SFM	QE Pro	1,000	440–870	0.7
Xu et al. (2018)	SFM	QE65 Pro	1,000	480–850	0.9
Miao et al. (2018)	SFM	QE Pro	1,000	730–780	0.15
Daumard et al. (2010)	FLD	HR2000+	250	630–815	0.5
Liu et al. (2016)	FLD	QE Pro	1,000	645–805	0.31
Julitta et al. (2016)	FLD	HR4000	250	678–857	2
	FLD	HR4000	590	197–1,115	1
	FLD	ASD Fieldspec	1,780	350–2,500	5.5
	FLD	QE Pro	1,080	645–810	0.5
Süß et al. (2016)	FLD	ASD Fieldspec	n/a	350–1,000	3
Du et al. (2017)	FLD	QE Pro	1,000	645–805	0.31
Goulas et al. (2017)	FLD	HR2000+	250	630–815	0.5
Liu, Liu, et al. (2017)	FLD	QE Pro	1,000	645–805	0.31
Yang et al. (2017)	FLD	HR2000+	1,000	680–760	0.13
Liu and Liu (2017)	FLD	QE65 Pro	1,000	480–850	0.9
Gu, Han, et al. (2019)	SFM	QE Pro	1,000	730–786	0.15–0.17
Magney, Frankenberg, et al. (2019)	DOAS ^b	QE Pro	1,000	730–780	0.3
	DOAS ^b	QE Pro	1,000	650–720	0.3
	DOAS ^b	QE Pro	1,000	730–780	0.3
	DOAS ^b	QE Pro	1,000	650–720	0.3
Nichol et al. (2019)	FLD	USB2000+	250	350–1,000	1
Liu et al. (2019)	FLD	QE Pro	1,000	n/a	0.31
Du et al. (2019)	FLD	QE65 Pro	1,000	645–805	0.34
Li et al. (2020)	SFM	QE Pro	1,000	730–785	0.17

Note. Values marked n/a were not provided in the reference. The signal-to-noise ratio (SNR) shown is the maximum value at full signal.

^aA comprehensive review of retrieval methods available for ground, airborne, and satellite platforms is provided by Meroni et al. (2009) and Mohammed et al. (2019). This table focuses on methods that are specifically employed for ground systems. ^bThe retrieval method of Grossmann et al. (2018), Magney, Bowling, et al. (2019), and Magney, Frankenberg, et al. (2019) is based on the concept of DOAS with an additional linearization step for retrieval of red SIF.

To address this knowledge gap, we present a cross-method comparison to evaluate the sensitivity of commonly used SIF retrieval methods, that is, the spectral fitting method (SFM), Fraunhofer line depth (FLD; the 3FLD variant was used in this study), singular vector decomposition (SVD), and differential optical absorption spectroscopy (DOAS), to three different sources of errors:

- atmospheric impacts on the spectral shape of E at the O₂A band and Fraunhofer lines;
- the temporal mismatch between E and L measurements, the effect of which is exacerbated under variable sky conditions; and
- canopy structural and leaf biochemical impacts on the spectral shape of ρ and F at the O₂A band and Fraunhofer lines.

The signal-to-noise (SNR) ratio, spectral resolution, and sampling frequency depend on specific instrument setup and are also critical factors that determine the performance of retrieval methods and hence which type of retrieval methods to apply. However, we do not focus on these factors in this study, as (1) these instrument effects have been extensively studied in previous studies (e.g., Guanter et al., 2010; Joiner et al., 2013, 2016; Köhler, Frankenberg, et al., 2018; Pacheco-Labrador & Martín, 2015) and (2) many recent emerging ground systems, including the systems used in this paper, utilize the same state-of-the-art spectrometer model (Ocean Optics QE Pro), with SNR more or less consistent across different studies.

Satellite-based retrievals of far-red SIF rely upon Fraunhofer lines to avoid contamination by atmospheric scattering and reabsorption due to the O₂ absorption bands (Frankenberg & Berry, 2018). Additionally, while reference measurements from sky or reference panels can be used to constrain ground-based SIF retrievals, no such reference is available for satellite measurements. When the sensor is close to the ground, the interference of the atmospheric column between the vegetation and the sensor is greatly reduced (Liu et al., 2019; Sabater et al., 2018). Therefore O₂A-based methods are usually preferred for ground-based measurements (Meroni et al., 2009); as the O₂A band is deeper and wider than the Fraunhofer lines, a stronger SIF signal can be retrieved from this region by lower-resolution spectrometers (e.g., >0.5 nm FWHM), which are not capable of resolving single Fraunhofer lines. However, the robustness of such practices under diverse sky conditions is still under-investigated; in particular, careful examination of retrieval methods is needed for non-clear conditions with rapidly moving clouds, heavy cloud cover, and hazy skies. To date, no study has examined whether situations exist under which differences across retrievals occur.

Moreover, it is impossible for ground-based SIF measurements to measure incoming and outgoing radiance simultaneously with the same detector, fiber optic, and integration time, although any deviation from this idealized condition may introduce errors (Gu, Wood, et al., 2019). In the majority of recent canopy-level SIF studies (e.g., Cogliati et al., 2015; Damm et al., 2015; Grossmann et al., 2018; Gu, Han, et al., 2019; Li et al., 2020; Liu, Liu, et al., 2017; Miao et al., 2018; Migliavacca et al., 2017; Rossini et al., 2015; Yang et al., 2017), a single instrument is mounted to a stationary tower and used to measure both solar irradiance and canopy reflected radiance in alternating sequence. Thus, the irradiance is inevitably measured at a different time (and therefore different light condition) than the reflected radiance. Furthermore, different integration times have to be used for measuring incoming and outgoing radiance. However, SFM, FLD, and DOAS assume that solar irradiance is measured at the same time as canopy radiance. To account for this assumption, solar irradiance is typically interpolated to the same time as the canopy radiance measurement before solving for SIF (Meroni et al., 2010). While the interpolation approach is generally reliable under clear-sky conditions with only gradual changes in illumination (Gu, Han, et al., 2019), it can introduce further error under cloudy conditions when large, unpredictable fluctuations of illumination occur. The impact of this temporal mismatch on SIF retrieval accuracy and precision may vary depending on the method used and to date has not been evaluated across methods.

In addition to these atmospheric impacts which affect the accuracy of modeling L , changes in spectral shapes of ρ and F also vary across species and over time, due to changes in canopy structure, leaf chlorophyll content (Chl), leaf area index (LAI), and other plant physiological or leaf biochemical properties (Guanter et al., 2013; Joiner et al., 2013; Magney, Bowling, et al., 2019; Magney, Frankenberg, et al., 2019). These shape changes can also affect SIF retrieval accuracy and precision, because most methods rely on a reference shape. While the effects of these shapes have been investigated for individual retrieval methods such as SVD (Guanter et al., 2013; Joiner et al., 2013), a cross-method evaluation has not yet been performed.

The goal of this study is to provide a comprehensive evaluation of retrieval methods for ground-based SIF retrieval. Here we used two continuous SIF systems installed at long-term field experiment stations. The first system is a bi-hemispherical system with high temporal resolution (1–5 s integration time per spectrum, with solar reference spectrum every ~10 s) and high spectral resolution (~0.15 nm FWHM), located in Aurora, New York. The second system is a hemispherical-conical system with lower temporal resolution (20 s total integration time per spectrum, with a sampling of solar reference spectrum every 3–5 min) and moderately high spectral resolution (~0.3 nm FWHM) located in Ames, Iowa. These key features enable us to evaluate the robustness of SIF retrieval methods using both the Fraunhofer lines and the O₂A band across different instrument configurations.

The paper is structured as follows: First, we retrieved SIF from actual field measurements (section 3.1) using parameter specifications from published retrieval methods (SFM, SVD, DOAS, and 3FLD) in order to examine their accuracy and robustness under clear, hazy, variable, or heavy cloud sky conditions. Next, we employed synthetic simulations (section 3.2) to determine which method can most accurately reproduce a true simulated SIF to independently evaluate the impacts of factors that cannot be disentangled from field measurements: (1) exacerbated time mismatch of downwelling and upwelling spectra due to fast-varying light conditions, (2) changes in the spectral shape of reflectance, and (3) changes in the prescribed spectral shape of fluorescence. Lastly, we discussed the implications of our findings for interpreting SIF from

ground-based systems (section 4). Here we will only examine far-red SIF retrieval at the O₂A band (760 nm), which has been demonstrated to be generally more consistent across species and environmental conditions than the red SIF emission peak retrieved at the O₂B band (687 nm) (Magney, Bowling, et al., 2019); red SIF is more challenging to interpret due to within-canopy fluorescence reabsorption and is not available for all ground SIF measurements. For discussion about red SIF retrieval or full-spectrum SIF retrieval (650–800 nm), we refer readers to recent papers (Cendrero-Mateo et al., 2019; Cogliati et al., 2019; Zhao et al., 2018).

2. Methods

In this section, we first give a brief overview of the major retrieval methods that are commonly employed for continuous ground measurements (section 2.1). Previous studies (e.g., Cendrero-Mateo et al., 2019; Meroni et al., 2009; Mohammed et al., 2019) have conducted comprehensive reviews on existing retrieval methods; this paper does not intend to duplicate these efforts but provides such overview with more technical details (e.g., instrument characteristics and retrieval equations) and for the sake of completeness and clarity. We then describe the setup used for the actual field measurements (section 2.2), the experimental design of the simulations (section 2.3), and quality filtering and data processing procedures (section 2.4).

2.1. An Overview of SIF Retrieval Methods Commonly Employed for Ground Measurements

In this study, we evaluated the following major methods which have been established for ground-based SIF retrievals and widely employed for ground SIF systems by previous studies (see synthesis in Table 1). Theoretically, the contribution of chlorophyll fluorescence (F) to irradiance reflected off of a Lambertian surface measured using a cosine corrector can be represented as $L(\lambda) = \rho(\lambda)E(\lambda) + F(\lambda)$, where L is the irradiance upwelling from the surface; E is the incoming solar irradiance; and ρ represents the canopy reflectance (Meroni & Colombo, 2006). All types of retrieval methods require selection of an appropriate spectral fitting window and assumption of shapes for ρ and F . The specific equations for each tested method are listed in Table 2, and specific parameter configurations in each method used in this study are described below. Because several of the methods assume simultaneous acquisition of E and L , we linearly interpolated E to the time of L prior to solving for SIF.

- The Fraunhofer line depth (FLD) retrieval method measures fluorescence by comparing the ratios of the solar continuum to the intensity within the Fraunhofer line for incoming solar radiance and outgoing canopy radiance (Plascyk, 1975; Plascyk & Gabriel, 1975). FLD-based SIF retrieval using solar Fraunhofer lines (caused by absorption of light by molecules in the Sun's atmosphere) is best achieved with instruments capable of high spectral resolution (<0.05 nm; Frankenberg et al., 2011; Guanter et al., 2012; Joiner et al., 2011) which commercially available field spectrometers currently cannot achieve. Thus, in ground-based SIF retrievals, FLD is more commonly applied to wider telluric O₂ absorption features (caused by absorption of light by oxygen in the Earth's atmosphere) such as the O₂A (~759–770 nm, major well depth at 760.5 nm) and O₂B (~686–692 nm, major well depth at 687 nm) bands which are situated near the far-red and red peaks of SIF (Meroni et al., 2009). Many variants of FLD have been developed which have been examined in previous reviews (Cendrero-Mateo et al., 2019; Damm et al., 2011; Meroni et al., 2009); the most commonly assessed are standard FLD, modified FLD (3FLD; Maier et al., 2003), and improved FLD (iFLD; Alonso et al., 2008). In this paper we chose to test the 3FLD retrieval method which is anchored across the O₂A band at three points (759, 761, and 770 nm) (Table 2; Maier et al., 2003) and has been demonstrated to outperform standard FLD (constant ρ and F) and iFLD (nonlinear ρ and F) when used for field measurements (Damm et al., 2011; Ji & Tang, 2018). Specifically, 3FLD was found to be more robust to instrument noise (Ji & Tang, 2018) and less prone to underestimation of SIF (Damm et al., 2011) than both standard FLD and iFLD. Hereafter we refer to this method as 3FLD_{O₂A}.
- The spectral fitting method (SFM) was designed to improve ground-based SIF retrievals for instruments with coarser spectral resolution and spectral sampling intervals by using wide fitting windows to take advantage of the full O₂A or O₂B band features (Meroni & Colombo, 2006). Typically, the ordinary least squares is used to solve for the slope (ρ) and intercept (F) of the linear regression of the recorded incoming solar radiance versus the reflected radiance from the fluorescent target. The simplest form of SFM (Meroni & Colombo, 2006) assumes that ρ and F are constant within the fitting window, but it has also

Table 2
Equations for Retrieval Methods Used in This Paper

Method	ρ and F functions	Equation	Reference
SFM	Polynomial (quadratic)	$L = (b_5\Delta\lambda^2 + b_4\Delta\lambda + b_3)E + b_2\Delta\lambda^2 + b_1\Delta\lambda + b_0$	Meroni et al. (2010)
SVD	Polynomial (variable)	$F = v_1 \sum_{i=1}^{n_{p1}} a_i \lambda^i + v_2 \sum_{i=1}^{n_{p2}} b_i \lambda^i + \sum_{i=1}^{n_r} c_i v_i + F_{760} h_F$	Guanter et al. (2013)
3FLD	Linear	$F = \frac{L_I - \frac{E_I}{W_L E_L + W_R E_R} \times (W_L L_L + W_R L_R)}{1 - \frac{E_I}{W_L E_L + W_R E_R}}$	Damm et al. (2011)
DOAS	Polynomial (6th order Legendre)	$D = \ln\left(\frac{L}{E}\right) \approx \sum_{n=0}^6 P_n\left(\frac{\lambda}{\max(\lambda)}\right) + \frac{h_F}{L}$	Platt and Stutz (2008), Frankenberg et al. (2011), Grossmann et al. (2018)

Note. For SFM, $b_0 - b_2$ represent the coefficients to model the shape of fluorescence; $b_3 - b_5$ represent the coefficients to model the shape of reflectance, $\Delta\lambda$ represents the fitting window used. For SVD, v_1 and v_2 are the first two singular vectors (SVs); $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are arrays of coefficients representing the first, second, and remaining SVs; h_F represents a prescribed shape of F ; F_{760} represents SIF at 760 nm; n_{p1} and n_{p2} are the polynomial degrees used to describe the first and second SVs, respectively; n_r represents the number of SVs used. For 3FLD, subscripts L , I , and R represent fitting windows at the left shoulder, inside the well, and right shoulder of the O_2A absorption band, respectively; W represents a weighting factor calculated as the wavelength range of the left half (W_L) or right half (W_R) of the well (e.g., from L to I , or I to R) normalized by the total wavelength range (e.g., from L to R). For DOAS, D represents the optical density and P_n represents the Legendre polynomial.

been adapted for linear (Meroni & Colombo, 2006) and nonlinear, for example, polynomial or Gaussian (Mazzoni et al., 2012), cases. Here we parameterized SFM using a quadratic polynomial (Table 2), with an initial fitting window of 759–767.76 nm following Meroni et al. (2010); hereafter we refer to this method as SFM_{O₂A}. We examine the impact of changing fitting window size on SFM SIF retrieval in section 3.1.2.

- Statistical methods based on singular vector decomposition (SVD) or principal component analysis (PCA) were developed to improve upon FLD SIF retrieval from satellites (Guanter et al., 2012; Joiner et al., 2013) but have also been applied to ground-based SIF (Guanter et al., 2013; Yang et al., 2018). SVD SIF retrieval is based upon the assumption that the SIF-free spectrum can be represented by a linear combination of orthogonal spectral components (i.e., singular vectors [SVs]) derived from the singular vector decomposition of a given SIF-free training set (Guanter et al., 2012, 2013). Provided sufficient spectra for training with sufficiently high spectral resolution, SVD has been employed to retrieve SIF from either the O_2A band or Fraunhofer lines for ground systems (Guanter et al., 2013; Yang et al., 2018). For example, spectrometers with ≤ 0.15 nm FWHM resolution and 0.02 nm sampling intervals have been demonstrated to successfully detect the Fraunhofer lines although they cannot capture the full depth of these features and therefore produce more noise during retrieval (Guanter et al., 2013). Because the fractional depth of solar Fraunhofer lines is not susceptible to atmospheric impacts, Fraunhofer line-based retrievals are expected to provide the most stable SIF measurements, even under cloudy conditions, if the spectral resolution is sufficiently high (Frankenberg & Berry, 2018). In addition to appropriate selection of the fitting window, SVD requires selecting the number of spectra for training, number of SVs to retain, the polynomial degree (n_p) used to model the first and second SVs, and the shape of the SIF emission spectrum (h_F). Note that existing satellite SIF retrievals tend to avoid applying SVD to the O_2A band as the optical depth can change dramatically under different sky conditions which may result in SIF-like eigenvectors when training with a non-fluorescent spectrum. However, the first GOME-2 retrievals were indeed based on a fitting window containing the O_2A -band (Joiner et al., 2013), whereas a study by Guanter et al. (2013) explored the feasibility of applying SVD to O_2A bands using ground systems; we therefore evaluated the performance of SVD for both Fraunhofer- and O_2A -based retrievals. Here, we followed the SVD method developed by Guanter et al. (2013) (Table 2), initially testing fitting windows that cover the full O_2A band (759–767.76 nm) or the region containing Fraunhofer lines (745–759 nm). Because the optimal combination of n_p and SVs will change depending on the noisiness of the training set, we implemented an automated selection of SVs using a variance cutoff threshold calculated from the SVD matrix (Gavish & Donoho, 2014) and selected the optimal n_p combinations (between 3 and 6, following the findings from Guanter et al., 2013) by minimizing the Bayesian information criterion (BIC) following Köhler

et al. (2015). Additionally, noise can increase due to factors such as variable sky conditions and the fitting window (Köhler et al., 2015). In this paper, we first implemented several fitting windows including the far-red Fraunhofer lines (745–759 nm) as well as the O₂A band (759–767.76 nm) to retrieve field measurements (results in section 3.1.1). We also tested the effects of changing the number of training spectra by either including all spectra from the same day (here denoted SVD_{O₂A} or SVD_{Fraun}) or using a moving window to select a subset of five *E* spectra temporally centered on each *L* spectrum (SVD_{O₂A-local} or SVD_{Fraun-local}). To further test the sensitivity of SVD to the prescribed *h_F* spectral shape, we examined the impact of varying *h_F* shapes (results in section 3.2.3).

- Differential optical absorption spectroscopy (DOAS) was first developed for measuring concentrations of atmospheric trace gases from satellites and is an expansion of Lambert–Beer’s law, which describes the attenuation of radiation as an exponential function of the number of molecules in (*c*) and length (*l*) of the optical path (Platt et al., 1979; Platt & Stutz, 2008). DOAS accounts for the absorption of *j* multiple trace gases with differing absorption cross-sections (*σ*) by calculating the differential optical density of the atmospheric column, $D = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = l \sum_j \sigma_j(\lambda) c_j$ (Platt & Stutz, 2008). DOAS has been adapted for satellite SIF retrieval using the Fraunhofer lines (Frankenberg et al., 2011; Khosravi et al., 2015). More recently, Grossmann et al. (2018) also demonstrated robust results using a variant of DOAS for ground-based SIF retrieval. Unlike the previous methods which model *L*, the SIF application of DOAS models the optical density of the atmospheric column, $D = \ln\left(\frac{L}{E}\right)$ using a combination of polynomials and *h_F* normalized by the reflected irradiance (Table 2). Here, DOAS was configured to model the logarithm of the apparent reflectance for the Fraunhofer fitting window (745–759 nm) using 6th order Legendre polynomials and an assumed *h_F* (Table 2); this is hereafter denoted DOAS_{Fraun}. The impact of incorrect *h_F* assumption on DOAS SIF retrieval is examined in section 3.2.3.

2.2. Field Measurements: Site Descriptions and Spectrometer Setups

2.2.1. Bi-Hemispherical System

Continuous *E* and *L* were measured for retrieving SIF in a 520 m × 290 m rain-fed maize field located at Cornell Musgrave Research Farm, Aurora, NY (42°43′22″N, 76°39′46″W) from 10 July (DOY 191) to 2 October (DOY 275) 2018. LAI, measured using a ceptometer (AccuPAR LP-80, Meter Group Inc., Pullman, Washington), and height were recorded approximately weekly until vegetative maturity (DOY 211). Subsequently, LAI was measured approximately once every 2 weeks (supporting information Table S1). Field soil composition was a mixture of 7.7% Honeoye, 24.1% Kendaia silt, and 68.2% Lima loam. The field was planted with a commercial maize hybrid on 25 May (DOY 145). Rows were planted with north-south orientation, with 30 inches spacing between and 6 inches spacing within rows. For July, August, and September 2018, average daily maximum temperatures were 28.0 °C, 26.3 °C, and 23.1 °C; average daily minimum temperatures were 17.2 °C, 17.6 °C, and 13.5 °C; total monthly precipitation was 5.57, 3.53, and 3.66 inches, respectively.

The core of the SIF system used in this study was a QE Pro spectrometer (Ocean Optics, Dunedin, Florida) which was customized for retrieval of SIF at the far-red range and was equipped with a longpass filter (>695 nm), 25 μm slit, and H15 grating to capture a wavelength range of 730–784 nm with a spectral resolution of ~0.15 nm FWHM (full width at half maximum). The spectrometer was equipped with a weather-proofed and armored fiber optic cable tipped with an opaline glass cosine corrector (CC-3, Ocean Optics). The fore-optic rotated between zenith and nadir positions using a custom-built motor system driven by a 12-volt DC motor controlled using an Arduino, which took approximately 2.8 s to rotate 180°. The fiber optic was secured along the supporting arm to prevent excessive bending past the manufacturer’s recommended bend radius of 30 cm, in order to avoid loss of light (Schermer & Cole, 2007). Raw spectral measurements were collected at integration times optimized to ensure each measurement fell between 75% and 90% of maximum detector saturation of the QE Pros. Measurements of incoming solar irradiance and reflected irradiance (i.e., hemispherical integrated) were sequentially measured at intervals ranging on average from 0.7 s (midday, clear sky) to 2 min (dawn and dusk) per spectral scan, with intervals between sequential measurements ranging from <5 s (midday, clear sky) to a maximum of 10 min. During each QE Pro measurement, incoming and outgoing above-canopy photosynthetically active radiation (PAR), air temperature,

and relative humidity were simultaneously recorded by a CR-1000 data logger (Campbell Scientific Inc., Logan, Utah). The data logger also coordinated the spectrometer, sensors, and motor. The overall instrument design and setup are similar to Gu, Han, et al. (2019) but with a different motor configuration and tower height.

The SIF system was supported with a scaffold at a height of 15 ft (~4.57 m) with the end of the fiber optic positioned 8 ft (~2.43 m) from the scaffold along an arm. At nadir position, the fiber entrance was positioned ~1.5–2 m from the top of the mature crop canopy. The spectrometer and data logger were housed in a dehumidified, temperature-controlled enclosure maintained at 25 ± 0.02 °C. The detector temperature of the QE Pro was kept at -10 °C using the built-in TEC. Radiometric calibrations were performed approximately once a month on-site with an HL-2000-CAL halogen lamp (Ocean Optics), under clear or lightly cloudy days around late morning to reduce environmental effects on the lamp; during these times relative humidity was at or below 60% and temperature was in the mid-20s Celsius. Wavelength calibrations were performed at the beginning and end of the growing season in the laboratory with an HG-1 mercury argon lamp (Ocean Optics).

2.2.2. Hemispherical-Conical System

To evaluate method performance using a hemispherical-conical configured SIF system (i.e., cosine-corrected E and bare fiber L measurement), we also included data sets from the PhotoSpec system installed from 2 May (DOY 122) to 17 September (DOY 260) 2017, over a maize field planted with approximately north-south row orientation located near Ames, Iowa (Magney, Bowling, et al., 2019). The PhotoSpec consists of three temperature-stabilized spectrometers: two QE Pro spectrometers covering the far-red O₂A-band (730–780 nm), the red O₂B-band (650–720 nm), and a FLAME spectrometer covering 350–1,000 nm (Ocean Optics). Here we focused on analyzing the performance of the far-red spectrometer, which was configured with a 0.06 nm diameter fiber optic and 2,400 groove mm⁻¹ grating resulting in a spectral resolution of 0.3 nm FWHM. The PhotoSpec telescope was mounted on top of a 7 m tower with a nadir viewing distance of about 4.5 m to the top of the mature crop canopy. PhotoSpec has a 0.7° field of view (FOV) and was programmed to collect measurements using viewing zenith angles (VZA) from nadir (−90°) to −45°, at 0.7° increments, recording ~20 s at each VZA. This sequence of VZA was repeated for two viewing azimuth angles (VAZ), pointing southeast (132.2°) and southwest (222.2°). More details on the system configuration, site description, and measurement protocol are provided elsewhere (Grossmann et al., 2018; Magney, Bowling, et al., 2019).

2.3. Canopy-Level Synthetic Simulations With SCOPE

In this section, we used simulation experiments to enable evaluation of method precision and accuracy with respect to factors that cannot be easily disentangled using field measurements: (1) variable light conditions induced temporal mismatch between E and L measurements, (2) changes in the spectral shape of ρ , and (3) changes in the spectral shape of h_F , in both O₂A band and Fraunhofer line regions. For all simulation experiments, we used the Soil Canopy Observation Photosynthesis Energy (SCOPE) model version 1.73 (van Der Tol, Berry, et al., 2014, van Der Tol, Verhoef, et al., 2009) to generate the “true known” ρ and F for benchmarking. To achieve this, we first used half-hourly meteorological data collected from an eddy covariance (EC) flux tower positioned ~25 ft south of the bi-hemispherical SIF tower to drive SCOPE simulations. We then linearly interpolated ρ and F to the wavelength and temporal resolution of measurements from the bi-hemispherical SIF tower, assuming a smooth spectral shape of ρ and F . Specific experiments are:

- Experiment 1 was set up to assess the impact of time mismatch of E and L due to variable light conditions. Simulated L spectra were generated using real E measurements from 6 days affected by rapidly moving clouds and three clear days recorded during the peak growing season. To simulate the impacts of rapidly changing illumination on F , we multiplied F by a factor of PAR divided by the maximum seasonal PAR value, using the PAR recorded by the SIF tower at high temporal frequency (<10 s) time steps. To avoid physical artifacts in the measurements caused by sunlight at low solar elevation striking the edge of the cosine corrector (a manufacturing design flaw of the cosine corrector identified by Gu, Han, et al., 2019), we only used measurements when solar zenith angle (SZA) was less than 70°. SCOPE was used to generate various diurnal ρ covering 400–2,400 nm and F covering 650–850 nm with 1 nm spectral resolution. Input driving climate variables (e.g., incoming shortwave and longwave radiation, air temperature, and

vapor pressure) were recorded at the field site over the growing season (Table S2). Leaf parameters such as pigment content, thickness parameters, and leaf angle distribution were set using typical values (Verrelst et al., 2015). SZA and relative azimuth angle were calculated based on latitude, longitude, time of day, and day of year. For this experiment, both LAI and canopy height were taken from weekly field measurements (Table S1) and linearly interpolated to daily values.

- Experiment 2 was designed to analyze the sensitivity of each SIF retrieval method to the spectral reflectance ρ due to changes in chlorophyll (Chl) and LAI. This is because leaf biochemical and canopy structural properties can affect the spectral shape of both ρ and F . In this experiment, instead of using the observed LAI, we tested 30 different scenarios covering different combinations of six Chl levels (10, 20, 30, 40, 50, and 60 $\mu\text{g cm}^{-2}$) and five LAI levels (0.5, 1, 2, 3, and 4 m m^{-2}) (Table S2) for generating ρ . The resulting ρ was then linearly interpolated to the wavelength range and resolution of the QE Pro (730–784 nm) (Figure S1). For this experiment, E was measured on a clear day during the peak growing season (DOY 200), and F was simulated with SCOPE under clear-sky conditions. Canopy height was set at 2 m.
- Experiment 3 was designed to test the influence of varying h_F on the SIF retrievals. Here, ρ was generated using 60 $\mu\text{g cm}^{-2}$ Chl and LAI of 4, representing typical values for maize at peak growing season. E was measured on a clear day during the peak growing season (DOY 200). F was generated using 24 different real leaf-level SIF spectra from Guanter et al. (2013), which were acquired from different plant species and environmental conditions with varying peak wavelengths and spectral slopes (Figures S2 and S3; Guanter et al., 2013). Each h_F shape was normalized by the peak fluorescence value and scaled using diurnal PAR to produce a realistic diurnal SIF pattern.

2.4. Quality Filtering and Data Processing

2.4.1. Quality Control Applied to Both Bi-Hemispherical and Hemispherical-Conical Systems

Quality filtering was performed for each spectrum by retaining only measurements where $\text{SZA} < 70^\circ$, in order to filter out measurements affected by extreme solar angles which are impacted by cosine corrector design (Gu, Han, et al., 2019). Goodness-of-fit was screened using $0.5 \leq \chi_r^2 < 2$, where χ_r^2 is the reduced χ^2 of the retrieval residuals (Guanter et al., 2012; Sun et al., 2018).

Additionally, the clearness index (CI), or the ratio of actual to potential solar irradiance, was used to distinguish clear and cloudy measurements according to Liu and Jordan (1960). To achieve this, we first estimated the potential direct irradiance under clear-sky conditions as $S_p = S_{po}\tau^m$, where S_{po} represents the incident extraterrestrial radiation normal to the solar beam, τ represents atmospheric transmittance, and m represents the optical air mass (Campbell et al., 1998). The total potential shortwave radiation at the ground (S_t) was then calculated as the sum of the direct beam (S_b) and diffuse (S_d) solar irradiance, where $S_b = S_p \cos(\text{SZA})$, and $S_d = 0.3(1 - \tau^m)S_{po}\cos(\text{SZA})$ (Campbell et al., 1998). Potential photosynthetically active radiation (PAR_0) was then calculated using a conversion factor based on the ratio of PAR to shortwave radiation measured on clear days at each field site. Actual PAR values were simultaneously recorded with each spectral measurement using a point quantum sensor (PQS1, Kipp & Zonen B. V., Delft, the Netherlands). The clearness index (CI) at each time of measurement (t) was thus calculated as $\text{CI}_{(t)} = \text{PAR}_{(t)}/\text{PAR}_{0(t)}$.

To identify unstable light conditions, we calculated the coefficient of variation (CV) of incident PAR each

day as $\text{CV} = \frac{\mu(\text{PAR}_{(t-1:t+1)})}{\sigma(\text{PAR}_{(t-1:t+1)})}$ where μ represents the mean and σ represents the standard deviation of PAR

from the immediately preceding to the immediately subsequent PAR measurement. $\text{CV} > 0.05$ indicated presence of rapidly moving clouds which could potentially impact SIF retrieval accuracy. This cutoff threshold was selected based on the maximum CV values that were observed during clear days, when light conditions were stable.

Sky conditions were categorized as follows, based on a combination of CV and CI (Figure S4):

1. Clear sky: $0.9 \leq \text{CI} \leq 1$ and $\text{CV} \leq 0.05$
2. Hazy sky: $0.65 \leq \text{CI} < 0.9$ and $\text{CV} \leq 0.05$
3. Rapidly moving clouds: $\text{CI} > 0.65$ and $\text{CV} \geq 0.05$
4. Heavy clouds: $\text{CI} \leq 0.65$, with no CV constraint

2.4.2. Additional Quality Control Applied for PhotoSpec

From DOY 144–191, PhotoSpec collected one single E for every full cycle of VZA, causing the time difference between E and L for some angles to exceed 10 min. After DOY 191, the protocol was adjusted to record one E for every 10 VZA steps (7°), which constrained the time difference between E and L to approximately 3 min. Thus, we only used PhotoSpec data recorded between DOY 192 and 225, representing the part of the peak growing season that was measured using the higher-frequency E protocol. Because of the complex measuring protocol, the PhotoSpec acquired a comparatively low diurnal frequency of E measurements. We therefore compared the performance of SFM, 3FLD, and DOAS but not SVD between the bi-hemispherical SIF tower and PhotoSpec.

To ensure that the narrow footprint of the PhotoSpec was detecting vegetation rather than soil, we calculated the normalized difference vegetation index (NDVI) from the concurrently measuring FLAME as $(\rho_{\text{NIR}} - \rho_{\text{Red}})/(\rho_{\text{NIR}} + \rho_{\text{Red}})$, where ρ_{NIR} represented wavelengths from 841–876 nm and ρ_{Red} represented wavelengths from 620–670 nm. Spectra were selected for NDVI values ranging between 0.5 and 1.

Spectra collected from VZA -78° to -87° were averaged to approximately mimic the nadir viewing zenith angle of the bi-hemispherical SIF tower. True nadir spectra were avoided because at that angle the PhotoSpec observed a footprint consisting mostly of bare soil and tower interference.

Lastly, spectra obtained from the PhotoSpec occasionally contained anomalous features in the baseline continuum of apparent reflectance (e.g., Figure S5), possibly caused by humidity causing ice formation on the detector. The spectral position of the features was particularly prominent in the 745–759 nm range which would affect Fraunhofer but not O_2A -based SIF retrieval methods. Therefore, to avoid unfairly biasing Fraunhofer retrieval, we screened out these spectra by calculating the coefficient of variation using a window of ± 6 pixels along the apparent reflectance baseline between 745 and 759 nm and removing spectra with outliers greater than two standard deviations from the mean.

3. Results

3.1. SIF Retrievals From Ground Measurements

3.1.1. SIF Retrieved From Bi-Hemispherical System Using Fitting Windows Commonly Employed in Published Literature

Here we compared SIF retrieved from the bi-hemispherical SIF tower with $\text{SFM}_{\text{O}_2\text{A}}$, $\text{SVD}_{\text{O}_2\text{A}}$, $3\text{FLD}_{\text{O}_2\text{A}}$, $\text{SVD}_{\text{Fraun}}$, and $\text{DOAS}_{\text{Fraun}}$ using fitting windows that are commonly utilized in published literature, for example, 759–767.76 nm for O_2A -based and 745–759 nm for Fraunhofer-based methods (Figure 1). Note that for $\text{SVD}_{\text{O}_2\text{A}}$ and $\text{SVD}_{\text{Fraun}}$, retrieval for an L spectra measured on any given day was trained using all E measurements measured during that day. We first checked the goodness-of-fit for all methods (except $3\text{FLD}_{\text{O}_2\text{A}}$, which computes SIF as an analytical solution and does not generate a modeled spectrum) (Figure S6). We found that all methods achieved fitting residuals within 0.5% (Figure S6) and wavelength-independent residuals (except $\text{SFM}_{\text{O}_2\text{A}}$), indicating success in isolating the SIF signal from L . However, an exception was observed for $\text{SFM}_{\text{O}_2\text{A}}$, which showed a larger fitting residual in the 760–761 nm range. Then we examined the relationship between retrieved SIF and PAR across different sky conditions and observed a clear distinction between SIF retrieved using the O_2A band versus the Fraunhofer region (Figure 1). $\text{SFM}_{\text{O}_2\text{A}}$ and $3\text{FLD}_{\text{O}_2\text{A}}$ exhibited an inconsistent relationship with PAR among different sky conditions including many negative SIF values under non-clear conditions (Figures 1a and 1b), while $\text{SVD}_{\text{Fraun}}$ and $\text{DOAS}_{\text{Fraun}}$ exhibited a consistent relationship between SIF and PAR under all sky conditions (Figures 1d and 1e). Interestingly, when SVD was trained using all E spectra measured during each day ($\text{SVD}_{\text{O}_2\text{A}}$), O_2A -based SIF retrieval under non-clear-sky conditions could lead to consistent SIF-PAR relationship across sky conditions, similar to Fraunhofer line-based retrievals (Figure 1c). Note that the nonlinear feature in the SIF-PAR relationship occurs in $\text{SFM}_{\text{O}_2\text{A}}$ and $3\text{FLD}_{\text{O}_2\text{A}}$ even under clear days. Two explanations for this pattern have been proposed: (1) oxygen transmittance can vary due to temperature and air pressure (Sabater et al., 2018); (2) the proportion of contributions between direct and diffuse radiation changes within the O_2A band because of the longer transfer path for diffuse radiation, creating a “direct radiation in-filling effect” (Liu et al., 2019; Liu & Liu, 2017). Both of these effects can produce a bump or trough in the apparent reflectance spectrum that do not indicate presence of SIF and can thus lead to over or underestimation of SIF by O_2A -based retrievals.

Figure 1. The relationship between PAR and SIF_{760} under different sky conditions recorded from a bi-hemispherical system using fitting windows commonly used in published literature. SIF is retrieved using (a) $\text{SFM}_{\text{O}_2\text{A}}$ with fitting window 759–767.76 nm; (b) $3\text{FLD}_{\text{O}_2\text{A}}$; (c) $\text{SVD}_{\text{O}_2\text{A}}$ with fitting window 759–767.76 nm, trained using all E spectra measured during each day; (d) $\text{SVD}_{\text{Fraun}}$, trained using all E spectra measured during each day; (e) $\text{DOAS}_{\text{Fraun}}$. Measurements, recorded during peak growing season (DOY 200–230), are presented as 30-min means. R^2 was calculated for measurements across all sky conditions in each panel; ordinary least squares regression line is fit through origin.

It is also important to mention that while here we are examining the relationship between SIF and PAR, SIF emission is actually driven by the fraction of absorbed PAR (APAR), which is affected by leaf chlorophyll content and canopy structure. Thus, some of the nonlinearity observed in Figures 1 and 5 may be attributed to biochemical or structural factors (discussed by, e.g., Xu et al., 2018; Yang et al., 2018).

Next, we compared retrieval method performance using the bi-hemispherical system by examining the diurnal pattern of SIF across different sky conditions (Figure 2). We found that under all sky conditions, $\text{DOAS}_{\text{Fraun}}$ and $\text{SVD}_{\text{Fraun}}$ are consistently higher than $\text{SFM}_{\text{O}_2\text{A}}$ and $3\text{FLD}_{\text{O}_2\text{A}}$. The lower magnitude of SIF retrieved using $\text{SFM}_{\text{O}_2\text{A}}$ and $3\text{FLD}_{\text{O}_2\text{A}}$ may be caused by high levels of aerosols or other atmospheric factors that influence O_2A -based but not Fraunhofer retrievals, even under clear-sky conditions (Guanter et al., 2010; Sabater et al., 2018). In contrast, $\text{SVD}_{\text{O}_2\text{A}}$ generally retrieved a similar pattern but slightly higher magnitude of SIF compared with both Fraunhofer retrievals (Figure 2a). Paired with the results from Figure 1, these findings demonstrate the robustness of Fraunhofer-based retrieval methods against atmospheric impacts and suggest that $\text{SVD}_{\text{O}_2\text{A}}$ when trained with all spectra from each day may also be more robust against changing atmospheric conditions than other O_2A -based retrieval methods (Guanter et al., 2013). However, $\text{SVD}_{\text{O}_2\text{A}}$ exhibited diurnal distortion, for example, the higher SIF observed during early mornings of clear days (Figure 2a). Using synthetic simulations, we found that the distortion observed for $\text{SVD}_{\text{O}_2\text{A}}$ was due to training the SVD using E sampled across the whole day (typical diurnal measurements were collected over >10 hr), in which artifacts, potentially caused by some source of system drift over time, are propagated to SIF by the SVD (Figure S7). Consequently, we opted to train the SVD with a temporally constrained subset of spectra (collected over 1–2 min), starting from section 3.1.2.

Interestingly, under clear-sky conditions, we also observed a divergence at midday between O_2A -based ($\text{SFM}_{\text{O}_2\text{A}}$, $3\text{FLD}_{\text{O}_2\text{A}}$) and Fraunhofer-based retrievals ($\text{SVD}_{\text{Fraun}}$, $\text{DOAS}_{\text{Fraun}}$), exhibited by a midday dip in the O_2A -based retrievals (Figure 2a). This finding further supports the hypothesis that the discrepancy

Figure 2. The diurnal pattern of SIF_{760} under different sky conditions recorded from a bi-hemispherical system using fitting windows commonly used in published literature. Each point represents the mean across half-hourly intervals with similar sky conditions, recorded during peak growing season (DOY 200–230). The notation of each method is identical to Figure 1.

between Fraunhofer and O_2A -based retrievals is caused by some effect that exclusively impacts the O_2A band, such as the direct radiation in-filling effect (Liu et al., 2019; Liu & Liu, 2017) and/or SIF absorption by O_2 (Sabater et al., 2018). In their study, Sabater et al. (2018) reported the O_2 absorption effect contributed up to 30% overestimation of SIF at the seasonal scale from a 30 m tower. Because our tower was less than 2 m from the canopy surface at peak growing season, diurnal dynamics of temperature and air pressure during the peak growing season period are much smaller in range than seasonal dynamics, and the discrepancy between Fraunhofer and O_2A -based retrievals increased under cloudy (i.e., greater diffuse-to-direct light ratio), we suggest that the direct radiation in-filling effect is a more likely explanation for our observations than the O_2 absorption effect. Importantly, this effect likely impacts many previous ground-based SIF studies, as the majority utilize O_2A -based retrieval methods (Table 1), and can result in incorrect assumptions related to SIF-GPP or SIF-PAR relationships.

3.1.2. Atmospheric Impacts on Spectral Shape at the O_2A Band and Mitigating Such Impacts on SIF Retrieval via Adjustment of Fitting Window

The atmospheric impact on O_2A -based retrievals from the bi-hemispherical system can be observed from the apparent reflectance spectra (Figure 3). Under clear-sky conditions, SIF appears as a bump in the apparent reflectance within the 759–767.76 nm O_2A region (Figure 3a). However, under cloudy or hazy sky conditions, the SIF bump is distorted and may even turn into a trough (Figures 3b and 3d). Consequently, when the full 759–767.76 nm fitting window is used, these depressed regions may have resulted in underestimation or even negative SIF estimates. Note that the affected region does not include the region containing the Fraunhofer lines, confirming that Fraunhofer-based retrievals are robust to atmospheric impacts. The depressed apparent reflectance could be exacerbated by a longer temporal mismatch between the irradiance and canopy radiance due to the lower light intensity under cloudy conditions. However, this does not explain the distortion that occurs under hazy conditions; on hazy days, we still recorded PAR values ranging from 75% to 90% of that recorded on clear days. Thus, we suspect that the distortion is mainly contributed by atmospheric scattering. The apparent reflectance can thus be used to assess measurement quality as recommended by Gu, Han, et al. (2019). Still, for ground sites that do not have the spectral resolution capable of resolving Fraunhofer lines, omitting distorted spectra could result in considerable data availability limitations as well as bias toward clear-sky conditions. Thus, we worked to find a solution for O_2A -based SIF retrieval under cloudy sky conditions.

Due to the strong SIF peak in the main O_2A band and weaker aerosol impacts observed in the 760–761 nm range in previous simulations (Guanter et al., 2010), we tested the effect of narrowing the fitting window size in order to isolate spectral region where SIF affects the O_2A band the most. For this test, we only evaluated the performance of SFM and SVD (denoted as SFM_{O_2A-adj} and SVD_{O_2A-adj} , respectively), since 3FLD requires external anchors at 759 and 770 nm (Figure 4). In addition, as we had identified adverse impacts on SVD_{O_2A} from the inclusion of too many training spectra (Figure S7), we constrained the training set to a moving window of five local spectra (denoted as $SVD_{O_2A-local}$) to reduce such effect.

Figure 3. Apparent reflectance peaks recorded under different sky conditions using a bi-hemispherical system. Here, the apparent reflectance (R_{app}) from 745–780 nm is normalized to 0–1 range as $(R_{app} - \min(R_{app})) / (\max(R_{app}) - \min(R_{app}))$. Black dashed lines highlight 759–767.76 nm fitting window for O_2A band; blue solid lines highlight 759.5–761.5 nm window framing the main SIF excursion peak. Each line represents one apparent reflectance spectrum classified under the corresponding sky condition using the criteria described in section 2.4.

Improved consistency was observed in the magnitude of SIF retrieval with SVD_{Fraun} for both SFM_{O_2A} (Figures 4a–4d) and $SVD_{O_2A-local}$ (Figures 4e–4h) when the fitting window was adjusted to the narrow 759.5–761.5 nm range (hereafter denoted SFM_{O_2A-adj} and $SVD_{O_2A-adj-local}$). This demonstrated that a narrower fitting window may improve the robustness of O_2A retrieval to atmospheric impacts if framing the main SIF bump and avoiding the distorted areas of the O_2A band. SFM_{O_2A-adj} and $SVD_{O_2A-adj-local}$ also achieved fitting residuals below 0.5% (Figure S8). For this adjustment, the fitting window was reduced from 170 to 37 spectral pixels. Note that for effective implementation of any retrieval method, users need to consider both retrieval accuracy (SIF magnitude) and retrieval noise, the latter of which depends on the number of spectral pixels.

Using this narrower 759.5–761.5 nm fitting window, the consistency of the retrieved SIF versus PAR relationships also improved considerably across sky conditions, that is, R^2 improved from 0.29 to 0.87 for SFM_{O_2A} (comparing Figures 1a and 5a). Furthermore, the strong correlation between SIF and PAR was maintained when using temporally constrained SVD with an adjusted O_2A fitting window ($SVD_{O_2A-adj-local}$) with R^2 of 0.84. These findings illustrate the importance of careful selection of the fitting window to minimize impacts of variable sky conditions on ground-based SIF retrieval if using the O_2A band.

No improvement in SIF retrieval under non-clear-sky conditions was observed from adjusting the O_2A fitting window for 3FLD (results not shown). This is likely because 3FLD utilizes anchor points that bridge the left and right continuum in addition to the O_2A well center. Because of the atmospheric absorption of oxygen, light scattering within the O_2A band is differently affected than that along the continuum in the presence of clouds (Boesche et al., 2008). As a consequence, FLD methods, which require use of both within-well and continuum reference points, are inherently more susceptible to atmospheric impacts compared to the other retrieval methods.

Figure 4. Impact of fitting window on O_2A -based SIF retrieval from a bi-hemispherical system under various sky conditions. SIF retrieved using top row (a–d): SFM_{O_2A} ; bottom row (e–h): SVD_{O_2A} trained using a moving window of five local spectra. Markers represent half-hour means averaged across all measurements representing each sky condition recorded during the peak growing season; error bars (759.5–761.5 nm) and shaded regions (SVD_{Fraun} and 759–767.76 nm) represent standard deviation of all half-hour measurements at each time point under each sky condition.

3.1.3. Atmospheric Impacts Using a Hemispherical-Conical System

We assessed retrieval method performance of SFM_{O_2A} , SFM_{O_2A-adj} , $3FLD_{O_2A}$, and $DOAS_{Fraun}$ on a hemispherical-conical system (PhotoSpec, Grossmann et al., 2018; Magney, Frankenberg, et al., 2019; Magney, Bowling, et al., 2019). Similar to the bi-hemispherical system, the hemispherical-conical system also exhibited distortion of the O_2A band under variable and heavy cloud conditions (Figures 6c and 6d). However, the spectral distortion also appeared to be less pronounced than observed for the bi-hemispherical system

Figure 5. Relationship between PAR and SIF_{760} using adjusted O_2A fitting window (759.5–761.5 nm), that is, (a) SFM_{O_2A-adj} and (b) $SVD_{O_2A-adj-local}$, from a bi-hemispherical system. Measurements, recorded during peak growing season (DOY 200–230), are presented as 30-min means. Black: heavy clouds; blue: combined rapidly moving clouds and haze; red: clear sky. R^2 was calculated for measurements across all sky conditions in each panel; regression line is fit through origin.

Figure 6. Apparent reflectance peaks recorded under different sky conditions using a hemispherical-conical system. Here, the apparent reflectance (R_{app}) from 745–780 nm is normalized to 0–1 range as $(R_{app} - \min(R_{app})) / (\max(R_{app}) - \min(R_{app}))$. Each line represents the mean of 13 apparent reflectance spectra recorded across -78° to -87° VZA across two VAZ, classified under the corresponding sky condition using the criteria described in section 2.4.

(Figure 3) under the lighter hazy and variable sky conditions. This suggests that the distortion may be mainly contributed from diffuse light, which could more heavily impact bi-hemispherical systems due to their wider FOV. In contrast with the bi-hemispherical system (Figure 1), SIF retrieved from the hemispherical-conical system displayed a more consistent SIF-PAR relationship under clear and cloudy conditions, although SFM_{O_2A} and $3FLD_{O_2A}$ were still susceptible to retrieving negative SIF values under heavier cloud conditions (Figure 7). Consistent with our results using spectra from the bi-hemispherical system, these negative SIF values were largely absent if retrieving SIF either using the adjusted O_2A fitting window (Figure 7b) or using the Fraunhofer-based DOAS (Figure 7d).

In contrast with the bi-hemispherical system, the diurnal SIF pattern retrieved from the hemispherical-conical system demonstrated consistency across methods under the clear-sky condition. However, similar to the bi-hemispherical system, SIF retrieved from the hemispherical-conical system showed greater divergence under cloudy conditions, such as lower midday SIF under hazy sky and variable conditions from SFM_{O_2A} and $3FLD_{O_2A}$ compared with $DOAS_{Fraun}$ (Figures 8b and 8c). We also found that non-nadir hemispherical-conical systems may distort diurnal SIF dynamics, as they are susceptible to angular effects and shadows that vary in response to both VZA and VAZ (Figure S9).

3.2. Investigating Factors That Impact SIF Retrieval With Simulation Experiments

In the field, a combination of fluctuating light conditions and vegetation targets with dynamic ρ and h_F may introduce SIF retrieval errors over the growing season. In order to disentangle their individual impacts, we designed three synthetic data experiments to evaluate the robustness and accuracy of SIF retrieval methods in response to (1) variable light conditions exacerbating the temporal mismatch between E and L

Figure 7. Relationship between PAR and SIF_{760} from a hemispherical-conical system. Measurements, recorded during peak growing season (DOY 192–225) are averaged over two VAZ, a VZA range of -78° to -87° , and 30 min. Black: heavy clouds; blue: combined rapidly moving clouds and haze; red: clear sky. R^2 was calculated for measurements across all sky conditions in each panel; regression line is fit through origin.

(Experiment 1), (2) variations in the spectral shape of ρ (Experiment 2), and (3) variations in the spectral shape of F (Experiment 3). These experiments are designed to represent a typical ground-based SIF system consisting of a single spectrometer recording alternating E and L measurements (e.g., Grossmann et al., 2018; Gu, Han, et al., 2019; Julitta et al., 2016; Yang et al., 2015). For a consistent comparison with the field measurements presented in section 3.1, in the following synthetic experiments we used the adjusted O_2A fitting window (759.5–761.5), that is, for SFM_{O_2A-adj} and $SVD_{O_2A-adj-local}$.

3.2.1. Sensitivity of Retrieval Methods to Time Mismatch of E and L Under Variable Light Conditions

Fluctuations in light are a frequent occurrence for many ground sites, which can introduce a considerable error source for SIF retrievals through a temporal mismatch between the E and L measurements. As previously mentioned, the common approach for matching E and L for FLD and SFM-based methods is through linear interpolation of E to the L timestamp; we also used this approach here. Such interpolation is generally effective under clear-sky conditions at low SZAs when E is gradually changing (Gu, Wood, et al., 2019) but becomes problematic when clouds introduce unpredictable fluctuations in light between the time of E and L measurements. In Experiment 1, we examined the susceptibility of each retrieval method to frequent changes in E and L magnitude caused by fluctuations in PAR due to presence of clouds observed across the growing season (Figure 9). Specific to SVD-based retrievals, we compared the susceptibility of using all E spectra collected during each day for training versus a local temporal window for training SVD, that

Figure 8. The diurnal pattern of SIF_{760} under different sky conditions recorded from a hemispherical-conical system. Each point represents the mean across two VAZ, a VZA range of -78° to -87° , and half-hourly intervals with similar sky conditions, recorded during peak growing season (DOY 192–225).

Figure 9. Impact of sky variability on SIF retrieval accuracy and retrieval noise due to mismatch of L and E . SIF retrievals are performed using simulated L generated using E recorded from the bi-hemispherical system across the growing season. Top row (a–g) shows raw retrieved SIF and bottom row (h–n) shows half-hourly means. SIF is retrieved using (a, h) SFM_{O_2A-adj} with fitting window of 759.5–761.5 nm; (b, i) $3FLD_{O_2A}$; (c, j) SVD_{O_2A-adj} trained using all daily E with fitting window of 759.5–761.5 nm; (d, k) $SVD_{O_2A-adj-local}$ trained using a five-spectra moving window with fitting window of 759.5–761.5 nm; (e, l) SVD_{Fraun} trained using all daily E with fitting window of 745–759 nm; (f, m) $SVD_{Fraun-local}$ trained using a five-spectra moving window with fitting window of 745–759 nm; and (g, n) $DOAS_{Fraun}$ with fitting window of 745–759 nm. Solid cyan lines and text describe linear regression fit through the origin. Dashed black line indicates 1:1 fit. Different colored markers indicate the sky condition category under which each SIF retrieval was recorded.

is, five spectra including two preceding and two subsequent spectra to the E spectrum associated with the L to be solved. This test was for both O_2A (denoted as $SVD_{O_2A-adj-local}$, also examined in the actual field data) and Fraunhofer-based retrievals (denoted as $SVD_{Fraun-local}$).

Note that the SCOPE simulation cannot reproduce the apparent reflectance peak induced by SIF (Figure 10), because it does not simulate how atmospheric scattering can change the O_2A spectral shape as presented in section 3.1 (Figure 3). As a consequence, Experiment 1 only addresses the impacts of fluctuating light and does not provide a comprehensive analysis of atmospheric impacts on SIF retrieval due to the complexity

Figure 10. Normalized apparent reflectance peaks produced under simulated clear vs. variable sky conditions. As in Figure 3, the apparent reflectance (R_{app}) is normalized to 0–1 range as $(R_{app} - \min(R_{app})) / (\max(R_{app}) - \min(R_{app}))$. Because atmospheric scattering is not reproduced by the simulation, no distortion in SIF excursion is observed.

of light scattering by clouds. However, as we have demonstrated in section 3.1, O₂A-based retrievals are particularly susceptible to atmospheric impacts.

Our simulations showed that DOAS_{Fraun} and SVD_{Fraun} were able to reproduce the simulated SIF with a high accuracy regardless of sky conditions, that is, slope close to 1, but at expense of retrieval precision, that is, high noise level with lower R^2 and higher RMSE (Figures 9e and 9g). Interestingly, SVD_{Fraun-local} can also effectively reduce retrieval noise as compared to SVD_{Fraun} (comparing Figure 9e vs. Figure 9f). In contrast, 3FLD_{O2A} and SFM_{O2A-adj} still exhibited stratification of the reproduction of the true SIF by sky conditions but to a lesser extent compared to the actual field measurements. However, the O₂A-based retrievals tended to generate much lower retrieval noise relative to Fraunhofer line-based retrievals due to the stronger SIF signal extracted from the deeper, wider O₂A well compared with the shallow, narrower Fraunhofer signatures detected by the ground spectrometer. The high noise in Fraunhofer-based retrievals (Figures 9e–9g) and that caused by transient changes in light conditions for the more sensitive O₂A-based methods (Figures 9a–9c) can be effectively averaged out by aggregating retrievals, for example, to half-hour intervals (Figures 9l–9n and 9h–9j, respectively). When light levels were fluctuating under cloudy conditions, however, SFM_{O2A-adj} and 3FLD_{O2A} both exhibited increased retrieval noise, with a particularly wide spread observed in 3FLD_{O2A} under both heavy and lighter cloud conditions (Figure 9b). This susceptibility to fluctuating light observed in SFM_{O2A-adj} and 3FLD_{O2A} reflects their underlying assumption of matching E and L and indicates that a linear interpolation approach to match E and L timestamps may be insufficient for capturing the complexity of the changing light environment under moving clouds (Gu, Han, et al., 2019). Encouragingly, SFM_{O2A-adj-local} exhibited consistent performance whether light conditions were stable or fluctuating under clouds and in the meantime maintained low retrieval noise. The low sensitivity of both O₂A- and Fraunhofer-based SVD to light fluctuations can be explained by the training approach which makes use of multiple E spectra recorded at different times, while both SFM and 3FLD rely on a temporal match.

Overall, the results of Experiment 1 demonstrate the accuracy of both the Fraunhofer fitting window and the SVD method, if using an adjusted O₂A window, to fluctuating light levels that frequently occur in the presence of clouds, and confirm that these methods are more stable for SIF retrieval in comparison with the standard SFM_{O2A} or 3FLD_{O2A} commonly employed in previous literature.

3.2.2. Sensitivity of Retrieval Methods to Changing Reflectance Spectral Shape

This exercise aimed to evaluate the impacts of spectral reflectance (e.g., caused by canopy structure and leaf biochemistry) on the accuracy of SIF retrievals. For example, as shown in Figure 8a, higher levels of Chl lead to a more pronounced curvature at the red-edge, affecting the spectral region of Fraunhofer line-based retrievals (745–759 nm) more than the O₂A region (759–767.76 nm). In contrast, increasing LAI leads to higher reflectivity in the NIR spectral region associated with a shifting red-edge. The influence of ρ on SIF retrieval accuracy has been previously tested for SVD-based methods with a focus on Fraunhofer-based retrievals (Guanter et al., 2013; Joiner et al., 2013) but not across other retrieval methods (i.e., SFM_{O2A}, 3FLD_{O2A}, or DOAS_{Fraun}). To isolate these impacts of fitting window or measurement noise from temporal mismatch, this experiment is performed using clear-sky conditions only, and measurements are presented as half-hourly means.

Our results reveal that variations in the assumed spectral shape of reflectance marginally impact the retrieval accuracy of SIF retrievals to different extents, depending on retrieval algorithms (Figure 11). Model fit residuals for all methods were less than 0.5% (Figure S10). Using reflectance generated using the SCOPE model, we found that such impact is marginal, that is, R^2 greater than 0.996, regression slopes within 2% variation to the perfect fit of 1, except for 3FLD_{O2A} when Chl or LAI were low. SVD_{O2A-adj-local} exhibited the least sensitivity to the spectral shape of reflectance due to changes in LAI or Chl. Here, both Fraunhofer-based methods consistently exhibited slightly decreasing slope and R^2 , and increasing RMSE in response to increasing LAI or Chl. Because SCOPE-generated reflectance has somewhat unrealistic sharp bends at 745 and 770 nm, we also performed the same tests using the PROSAIL model (Jacquemoud et al., 2009) which produces a smooth curve for the whole 730–780 nm region (Figure S11). While the magnitude of response differed (especially for 3FLD_{O2A}), the patterns for each of the other retrieval methods was the same, with minimal impact on O₂A-based retrievals but slightly decreasing slope and increasing noise for Fraunhofer-based retrievals as Chl and LAI increased. Because the magnitude of reflectance generated by PROSAIL is almost twofold that of SCOPE (e.g., comparing

Figure 11. Sensitivity of SIF retrieval accuracy to the assumed spectral shape of reflectance caused by Chl and LAI variation. (a, b) ρ simulated by SCOPE using different levels of Chl and LAI. (c, h) Half-hourly mean SIF retrieved using SFM_{O2A-adj}, 3FLD_{O2A}, SVD_{O2A-adj-local}, SVD_{Fraun-local}, or DOAS_{Fraun} from L spectra simulated using (c, e) different levels of Chl with LAI = 4 m² m⁻² or (f, h) different levels of LAI with 60 $\mu\text{g cm}^{-2}$ Chl. (c, f) Slope, (d, g) R^2 , or (e, h) RMSE is calculated between half-hourly means of retrieved and simulated SIF₇₆₀. For this test, L is generated using 1 day of clear-sky measurements from the bi-hemispherical system obtained during the peak growing season (DOY 200).

Figure 11a with Figure S11a), a larger exacerbation of error was observed among retrieval methods using PROSAIL simulations (Figures S11c–S11h). It is important to note that theoretically, SVD_{Fraun} and DOAS_{Fraun} are both insensitive to changes in reflectance as long as the forward model of the retrieval method can sufficiently model the actual shape. However, 3FLD does not model the reflectance shape but rather assumes a linear slope of reflectance across the spectral window. This results in the comparatively lower performance of 3FLD_{O2A} compared to the other retrieval methods. A more robust FLD alternative could be iFLD (Alonso et al., 2008), which utilizes reflectance within and outside of the absorption band to account for nonlinear reflectance across the spectral window. The generally low

Figure 12. Impact of SIF emission spectrum (h_F) on SIF retrieval magnitude. SIF retrieved using SFM, different configurations of SVD, 3FLD, or DOAS from L generated using 1 day of clear-sky measurements obtained from the bi-hemispherical system during the peak growing season (DOY 200), using LAI of $4 \text{ m}^2 \text{ m}^{-2}$ and $60 \mu\text{g cm}^{-2}$ Chl; y-axis represents the ratio between retrieved and simulated SIF at 760 nm; each point along the x-axis represents a different h_F shape (shown in Figures S2 and S3). (a) SIF retrieved from L spectra generated using different h_F ; for SVD and DOAS, the same h_F is used for simulation and retrieval; (b) SIF retrieved by SVD and DOAS where a different h_F is used for simulation and retrieval. Dashed black line represents 1:1 ratio between simulated and retrieved SIF₇₆₀; solid colored lines indicate average ratio of simulated to retrieved SIF across all 24 h_F for each retrieval method.

retrieval bias due to the assumed spectral shape of reflectance is consistent with previous studies (Guanter et al., 2013; Joiner et al., 2013; Köhler, Guanter, et al., 2018).

3.2.3. Sensitivity of Retrieval Methods to Changes in the Spectral Shape of Fluorescence Emission h_F

The far-red emission peak of SIF has been demonstrated to be considerably more consistent across species and environmental conditions than the red SIF emission peak at the leaf scale (Magney, Bowling, et al., 2019). However, h_F spectra vary across plant species and may also vary on diurnal to seasonal scales due to changes in non-photochemical quenching and leaf Chl (Magney, Bowling, et al., 2019). The influence of h_F on SIF retrieval accuracy has been previously tested for SVD-based methods with a focus on Fraunhofer-based retrievals (Guanter et al., 2013; Parazoo et al., 2019) but not across other retrieval methods (i.e., SFM_{O2A}, 3FLD_{O2A}, or DOAS_{Fraun}). Also, note that these previous studies did not assess the impact of using a local training set for SVD, so we present both SVD_{Fraun} and SVD_{Fraun-local} here for comparison. Among all the retrieval methods that we tested here, SVD and DOAS both explicitly prescribe h_F in their models (Table 2). We therefore tested the effect of using both a correct (Figure 12a) and an incorrect h_F assumption (i.e., the h_F assumed during SIF retrieval is not consistent with the true h_F) on SIF retrieval using SVD_{O2A-adj-local}, SVD_{Fraun}, SVD_{Fraun-local}, and DOAS_{Fraun} (Figure 12b). Note that SFM_{O2A} and 3FLD_{O2A} do not explicitly prescribe h_F and therefore are not included in Figure 12b.

Here we tested 24 different measured h_F (Figures S2 and S3) to evaluate the influence of h_F on SIF retrieval accuracy across SFM_{O2A-adj}, SVD_{O2A-adj-local}, 3FLD_{O2A}, SVD_{Fraun}, SVD_{Fraun-local}, and DOAS_{Fraun} (Experiment 3). When the prescribed h_F shape used for retrieval was identical to the true h_F shape (Figure 12a), all retrieval methods yielded highly accurate results, that is, with retrieval bias within 2%. In particular, the retrieval accuracy for SFM_{O2A} and SVD_{O2A-adj-local} was completely insensitive to the actual h_F shape, while Fraunhofer-based retrievals

and 3FLD_{O2A} were only slightly sensitive to h_F (<1% change in retrieval bias). Among all methods, SVD_{O2A-adj-local} most accurately retrieved SIF with an average retrieved-to-simulated SIF ratio of 1.0 across all h_F tested. When the prescribed h_F shape used for retrieval was not consistent with the true h_F shape (Figure 12b), the true SIF was highly accurately retrieved by SVD_{O2A-adj-local}, while the Fraunhofer-based retrieval methods (SVD_{Fraun}, SVD_{Fraun-local}, and DOAS_{Fraun}) tended to fluctuate with the prescribed h_F shape, indicating that mismatched h_F assumption has a heavier impact on Fraunhofer-based retrievals. Overall, the mean retrieval bias for Fraunhofer-based approaches was within 5% underestimation. However, in the worst case scenario, there could be up to 9% underestimation of SIF for all Fraunhofer-based retrievals, when the far-red peak magnitude of the assumed h_F (Figure S3, spectrum 24) was lower than the peak magnitude of the actual h_F (Figure S3, spectrum 23) and the far-red maxima also did not match between the assumed and actual h_F ; both of these factors affected the curvature of h_F within the 745–759 nm Fraunhofer fitting window.

The underestimation of SIF magnitude by SVD_{Fraun} has been reported previously from ground-based measurements (Guanter et al., 2013), with greater underestimation observed when the lower bound of the fitting window is extended, thereby encompassing more of the curvature at the top of the red-edge. Guanter et al. (2013) reported up to 4% error in SIF magnitude when testing 15 h_F shapes using the 745–759 nm fitting window and also observed exacerbated error if fitting larger Fraunhofer windows. These findings indicate the sensitivity of SVD and DOAS to the choice of h_F and support the use of smaller fitting windows to reduce potential sources of bias. While these two previous studies suggested that the impact of h_F may be negligible (i.e., constitutes <5% error), we caution that error retrieved using SVD_{Fraun} and DOAS_{Fraun} may be

compounded in combination with other sources such as additional underestimation of SIF magnitude under high Chl and LAI (Figures 11b and 11e). This may be an effect caused by the fitting window used for Fraunhofer versus O_2A -based retrievals. h_F is more stable toward the near infrared range because of increased scattering and almost no reabsorption by chlorophyll, while nearer to the red-edge, more chlorophyll reabsorption occurs. Thus, the choice of h_F is more critical for Fraunhofer-based retrievals which are closer to the red edge, especially for high LAI/Chl.

4. Discussion

A complex array of factors governing light scattering contributes to atmospheric impacts on the O_2A band and consequently O_2A -based SIF retrieval. Using the MODTRAN4 atmospheric radiative transfer, Guanter et al. (2010) identified several atmospheric factors that may contribute to this effect in satellite-based radiance measurements under clear-sky conditions, especially surface air pressure, aerosol optical depth, and the height of the aerosol layer. These factors can contribute to a significant mismatch between E and L due to the absorption of SIF in the oxygen column (Sabater et al., 2018) as well as the direct radiation infilling effect (Liu et al., 2019; Liu & Liu, 2017). Recently, corrections for these atmospheric impacts have been proposed for FLD-type and SFM retrieval methods which are particularly recommended for ground-based tower or airborne measurements where E is recorded at a position greater than 10 m above the vegetation target canopy, for example, using reflectance panels or sky-facing sensors (Liu et al., 2019; Sabater et al., 2018). Furthermore, the error in SIF retrieval can be exacerbated for spectrometers with lower spectral resolutions, for example, 0.4–5 nm (Sabater et al., 2018). In our study, we did not correct for a difference in the atmospheric column between E and L because the sensors were positioned between 1.5 to ~4 m (bi-hemispherical) and 4.5 to ~7 m (hemispherical-conical) above the canopy depending on the growth stage, and our spectrometers have high spectral resolution of ~0.15 (bi-hemispherical) and ~0.3 nm (hemispherical-conical). Thus, the atmospheric impact was assumed to be minor. However, based on our findings, we do recommend atmospheric corrections particularly for O_2A -based SIF retrievals.

Changes in air pressure and high aerosols are tightly linked with cloud formation, which can occur as rising air in low pressure induces condensation around aerosol particles (Boucher et al., 2013). Furthermore, aerosol optical depth and altitude can influence light polarization differently within the O_2A absorption band, resulting in considerable differences in light polarization between clear and hazy sky conditions (Boesche et al., 2006, 2008). Spectrometers equipped with gratings, such as the high-resolution QE Pro presently used in many ground-based SIF systems, can be sensitive to polarization effects (Pang et al., 2017). The impact of light polarization can be avoided with the use of a cosine corrector, which is commonly used for measuring downwelling irradiance.

Our findings demonstrate that each SIF retrieval method involves a trade-off between retrieval noise and magnitude bias, with O_2A -based methods (SFM_{O_2A} , $3FLD_{O_2A}$, and $SVD_{O_2A-local}$) highly susceptible to clouds and other atmospheric impacts. When selecting an optimal SIF retrieval method, the user must take into consideration both their system configuration and the site environment. Users with SIF towers operating in locations which commonly experience clear-sky conditions may be able to simply screen out cloudy days and use the full 759–767.76 nm O_2A fitting window for SFM or SVD, or utilize an FLD-based retrieval method, to take advantage of the lower retrieval noise generated from utilizing the whole O_2A band; however, such practice biases seasonal SIF toward clear days, which is not realistic. As we have shown, SIF retrievals under cloudy conditions can be achieved through optimization of the O_2A fitting window to improve performance, or if the spectrometer resolution permits, by utilizing Fraunhofer-based retrieval.

In our study, SIF retrieved using the Fraunhofer region was noisier than O_2A -based retrieval due to the depth of the O_2A band and the spectrometer's spectral resolution (in our case, ~0.15 nm FWHM) which is not ideal to resolve the Fraunhofer line features (~0.01 nm FWHM). Note that even with higher resolution, noise will still be present. A combination of high signal to noise ratios (SNR) and fine FWHM would be ideal for resolving the Fraunhofer lines but technically unrealistic for ground SIF systems. The lower spectral resolution causes a portion of the baseline continuum to be averaged into each absorption feature, thereby decreasing the depth of the well and the strength of the fluorescence signal (Frankenberg & Berry, 2018). The measurement noise can be countered to some extent by averaging multiple

measurements together. In our study, SIF was aggregated to half-hourly means after retrieval, which scaled the SIF retrieval noise with the square root of the number of measurements (e.g., Figure 9 top vs. bottom rows). Still, detection of Fraunhofer lines is only feasible with sufficiently high spectral resolution and SNR. As shown in Table 1, the spectral resolution for some commonly used spectrometers such as the Ocean Optics HR4000 or ASD Fieldspec may be configured for >1 nm and therefore may not be capable of properly resolving the Fraunhofer lines at all. While there is a trade-off between spectral resolution and SNR in different spectrometer systems, a FWHM of <0.5 nm is generally needed for satellite-based Fraunhofer line retrievals (Joiner et al., 2016; Köhler, Frankenberg, et al., 2018). Here we have shown successful Fraunhofer retrievals using systems with FWHM ~ 0.15 nm (bi-hemispherical) and ~ 0.3 nm (hemispherical-conical). In order to reliably utilize Fraunhofer line-based retrieval from a ground system, the spectrometer must be very stable.

Another potential drawback of the SVD and DOAS-based SIF retrieval methods is the necessity of using a prescribed h_F . As shown in section 3.2.3, an incorrect h_F assumption can contribute up to 5% uncertainty for retrievals using the Fraunhofer fitting window but less than 1% for the O_2A fitting window. Currently the h_F is often simply a “best guess” as the true canopy SIF emission spectrum is not known. A valuable future contribution could be the generation of an h_F library consisting of SIF emission spectra over a range of conditions and species such as that performed by Magney, Bowling, et al. (2019) but at the canopy level. Until such data are available, we recommend using the O_2A band with adjusted fitting window for ground-based SIF retrieval.

A number of ground-based SIF studies have used SFM to retrieve SIF under both clear and cloudy conditions and then demonstrate relationships between SIF and GPP and corresponding changes in light use efficiency under diffuse and direct light conditions (e.g., Miao et al., 2018; Yang et al., 2015). Our experiment indicates that O_2A -based retrievals using the full O_2A fitting window may be strongly biased under cloudy and even clear conditions, which can confound the interpretation of the inherent physiological relationship between LUE and SIFyield. To date, only one recent study has tested SVD for ground-based SIF retrieval (Yang et al., 2018), which utilized a fitting window that included both the Fraunhofer lines and O_2A band (745–780 nm). Although this approach is less sensitive to measurement noise because of the larger fitting window, it still leaves SVD susceptible to atmospheric impacts at the O_2A band if the O_2A retrieval window is not properly adjusted. A further caveat of this study is their unconventional analysis which included performing half-hour aggregation of spectra prior to retrieval and using an excessive number of SVs (300) for building the SVD matrix which is not recommended.

Our findings also suggest that the hemispherical-conical setup is less susceptible to cloud impacts, which may be affected by the proportion of direct-to-diffuse light collected using different FOVs. However, the hemispherical-conical configuration has its own drawbacks. For example, changes in canopy footprint during the early growing season would have a larger influence on SIF magnitude retrieved from hemispherical-conical setups than a bi-hemispherical system due to a greater change in the quantity of vegetation captured by its narrower FOV as canopy height increases. Furthermore, if the system is not recording from a nadir VZA, shadow effects within structured canopies may influence the diurnal SIF pattern which are not representative of actual canopy dynamics. Lastly, because the bi-hemispherical configuration has a much larger FOV, it can more easily scale its footprint to match EC towers without drastically changing the height above the canopy, which results in less influence from oxygen reabsorption within the atmospheric column (Liu, Liu, et al., 2017).

These implications must be carefully considered to ensure comparability of SIF data sets collected from different ground systems before they can be utilized for meta-analyses and ground validation.

5. Conclusions

We have examined the sensitivity of different SIF retrieval methods to various sky conditions, time mismatch of E and L , and the choice of ρ and h_F . Based on the metrics of absolute magnitude, diurnal pattern, and retrieval noise, we conclude the following:

- Fraunhofer-based DOAS and SVD retrievals show a strong SIF-PAR relationship and consistent diurnal patterns across different sky conditions.

- In contrast, O₂A-based SFM and 3FLD result in divergent SIF-PAR dependence under different sky conditions, including under clear skies, and can only achieve consistent diurnal shapes with Fraunhofer-based methods under clear skies with stable illumination.
- The robustness of O₂A-based retrievals under cloudy conditions can be improved by using a narrow, for example, 759.5–761.5 nm fitting window to avoid atmospheric-induced artifacts and, for SVD, training with a temporally constrained set of spectra.
- In contrast to O₂A-based retrievals, Fraunhofer-based retrievals are insensitive to atmospheric impacts but are more sensitive to changes in h_F due to the closer proximity of Fraunhofer region to the red-edge which is affected by chlorophyll reabsorption.
- Fraunhofer-based retrievals generate more retrieval noise than O₂A-based retrievals, but this noise can be minimized by measurement aggregation and, for SVD, training with a temporally constrained set of spectra.
- These findings are applicable for both bi-hemispherical and hemispherical-conical systems, although hemispherical-conical systems are less affected by atmospheric scattering.

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