Potential impacts of nonalgal materials on water-leaving Sun induced chlorophyll fluorescence signals in coastal waters

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It has been suggested that Sun induced chlorophyll fluorescence (SICF) signals could be used to estimate phytoplankton chlorophyll concentration and to investigate algal physiology from space. However, water-leaving SICF is also a product of the ambient light field. In coastal waters both algal and nonalgal materials affect the underwater light field. In this study we examine the independent impacts of varying loads of mineral suspended solids (MSS) and colored dissolved organic materials (CDOM) on water-leaving SICF signals using Hydrolight radiative transfer simulations. We show that SICF signals in coastal waters are strongly influenced by nonalgal materials. Increasing concentrations of CDOM and minerals can reduce the water-leaving SICF per unit chlorophyll by over 50% for the concentration ranges explored here (CDOM = 0 to 1 m$^{-3}$ at 440 nm, MSS = 0 to 10 g m$^{-3}$). The moderate-resolution imaging spectroradiometer (MODIS) fluorescence line height algorithm is shown to be relatively unaffected by increasing CDOM, but performance is significantly degraded by mineral concentrations greater than 5 g m$^{-3}$ owing to increased background radiance levels. The combination of these two effects means that caution is required for the interpretation of SICF signals from coastal waters. ©2007 Optical Society of America

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1. Introduction

The optical properties of coastal and shelf seas are determined by the contributions from a variety of constituents, often categorized as phytoplankton, minerals, and colored dissolved organic materials (CDOM), each of whose concentrations varies independently over potentially broad ranges. The resulting optical complexity is a major obstacle to the development of robust algorithms for interpreting data from satellite ocean color sensors. For example, algorithms for estimating chlorophyll concentration (Chl) using simple blue-green reflectance ratios have been found to perform poorly in coastal waters, leading to the development of regionally tuned [1] and water-type specific variants [2] as well as other semi-analytic approaches [3]. Each optical constituent influences radiative transfer in the water column through its inherent optical properties (IOPs), including absorption, scattering, and backscattering. Inelastic scattering processes such as fluorescence by Chl and CDOM as well as Raman scattering by water itself can also play an important role in determining spectral reflectance signals. Of these, chlorophyll fluorescence appears to offer the greatest potential for extracting additional useful information from satellite measurements.

Neville and Gower [4] demonstrated that a peak centered on 685 nm observed in surface leaving reflectance spectra could be attributed to Sun induced chlorophyll fluorescence (SICF). Since then numerous studies have examined the relationship between SICF and chlorophyll concentration [5–9]. Other researchers have worked on determining physiological state or primary production through relationships between fluorescence signals and the quantum yield for fluorescence, $\phi$, and chlorophyll-specific absorption,
Kattawar and Vastano [14] and Maritorena et al. [15] provided a theoretical framework that describes the radiative transfer processes that generate the water-leaving Chl fluorescence signal. Most of the analysis of remote sensing Chl fluorescence signals has concentrated on open ocean Case 1 waters where phytoplankton are the dominant optical constituent along with water itself, for instance [16]. More recently satellite sensors such as the moderate-resolution imaging spectroradiometer (MODIS) and the medium resolution imaging spectrometer (MERIS) [17,18] have been launched with sensors specifically configured to measure chlorophyll fluorescence from space [19]. Regular global coverage is a key benefit of these measurements, but it is important that the user community understands the processes affecting generation of SICF from Case 2 waters, where mineral particles and CDOM may also contribute significantly to the optical properties of the water column. Previous studies have noted some impact of nonalgal materials on fluorescence signals using bio-optical models [20,21] and other radiative transfer methods [22]. Despite this, it has been suggested that Sun induced Chl fluorescence might be used to determine Chl in Case 2 waters where the presence of CDOM and minerals may invalidate other methods [23]. Indeed field results have been presented suggesting that water-leaving Chl fluorescence may be well correlated with Chl over a diverse range of optical environments [24]. Hoge et al. [25] found that the MODIS fluorescence line height (FLH) product was not influenced by CDOM for a range of water types in the western North Atlantic Ocean. Laney et al. [26], referring to work done in coastal waters off Oregon, suggested that SICF might be particularly useful in turbid Case 2 waters. However, since the Sun induced Chl fluorescence signal is a product of the ambient light field as well as the algal population, and the light field is affected by nonalgal materials, there is good reason to investigate the degree to which water-leaving SICF signals are subject to nonalgal influence.

Given the potential benefits of being able to use Chl fluorescence as a diagnostic indicator for phytoplankton, its sensitivity to physiological state, and the availability of global-scale data as a standard product from more than one satellite system, it is appropriate to re-examine the radiative transfer processes underpinning this signal and to examine in detail how these are affected by the presence of significant concentrations of nonalgal materials. In doing so, we can bring to bear on the problem advanced radiative transfer simulations (Hydrolight, Sequoia) and recent estimates of material-specific IOPs obtained from coastal waters using state-of-the-art in situ instrumentation [27]. This radiative transfer simulation technique enables us to systematically analyze the influence of nonalgal materials on Sun induced Chl fluorescence signals, specifically identify absorption and scattering artefacts, and assess the potential performance of the MODIS FLH algorithm for coastal waters.

2. Theory

In this paper we are concerned with radiative transfer processes influencing the generation and propagation to the sea surface of solar-stimulated chlorophyll fluorescence photons and factors affecting our ability to interpret these signals from water-leaving radiometry. A theoretical framework outlining the radiative transfer processes contributing to fluorescence stimulation and emission has been published [14,15] and is summarized here. Note that for this analysis all materials are assumed to be uniformly distributed vertically through the water column.

Chlorophyll fluorescence is excited by absorption of photons by phytoplankton between ~400 and 690 nm (denoted with subscript ex), and is emitted in a broadband with a peak wavelength at 685 nm (denoted by subscript em). The fluorescence quantum yield, \( \phi \), is defined here as the ratio of photons emitted by fluorescence in the 685 nm emission band, \( F_\text{e} \), to photons absorbed by phytoplankton in the 400–690 nm excitation band, \( A_{\text{ex}} \):

\[
\phi = F_\text{e}/A_{\text{ex}}. \tag{1}
\]

We note that this is an effective yield rather than a true physiological yield, and that since we ignore partial reabsorption of fluorescence within algal cells the true physiological yield would be greater than our realized value [7,28].

The number density of photons (\( \mu \text{mol photon m}^{-2} \text{s}^{-1} \)) absorbed by phytoplankton at a given point in the water column can be calculated from

\[
A_{\text{ex}} = \text{Chl} \times \alpha_{\text{ex}} E_\text{e}^\text{ex}, \tag{2}
\]

where Chl is the local chlorophyll concentration (mg m\(^{-3}\)), \( E_\text{e}^\text{ex} \) is the quantum scalar irradiance integrated across the excitation wavelength range (\( \mu \text{mol photon m}^{-2} \text{s}^{-1} \)), and \( \alpha_{\text{ex}} \) is the spectrally weighted chlorophyll-specific algal absorption coefficient, given by

\[
\alpha_{\text{ex}} = \int_\lambda \alpha^*(\lambda) E_\text{e}^\text{ex}^\lambda(\lambda) d\lambda \int \overline{E_\text{e}^\text{ex}(\lambda)} d\lambda. \tag{3}
\]

It has been shown [14,15] that the total quantum fluorescence signal integrated across the emission waveband, \( L_{\text{e}}(\mu \text{mol photon m}^{-2} \text{s}^{-1} \text{sr}^{-1}) \), received by a nadir-viewing sensor from the layers immediately below it, is given by

\[
L_{\text{e}}(z) = \frac{\phi a_{\text{ex}}^\text{Chl} E_\text{e}^\text{ex}(z)}{4\pi (a_{\text{em}} + K_\text{a})}. \tag{4}
\]
Equation (4) shows that the fluorescence signal is dependent on the underwater light field through the diffuse attenuation of scalar irradiance averaged across the excitation wavelengths \( K_{ex}^{\text{w}} \), the absorption of fluorescence emission \( a_{em} \) at \( \sim 685 \) nm (640–730 nm), the scalar irradiance \( E_{ex}^{\text{w}} \) integrated across the excitation wavelengths (400–690 nm), and also through the dependence of \( a_{em} \) on \( E_{ex}^{\text{w}} \) given by Eq. (3). Thus there are four light field parameters that can be influenced by the presence of nonalgal materials and have an impact on fluorescence signal generation. We shall examine the sensitivity of each to nonalgal contributions.

In deriving Eq. (4) it was assumed that \( a_{em} \) would be dominated by water absorption and that scattering would have a negligible effect on the propagation of fluorescence to the surface. It is also assumed that since \( a_{em} \) is relatively large, the fluorescence signal will be received from relatively shallow depths [7] and therefore \( \phi \) and \( K_{ex}^{\text{w}} \) can be assumed to be effectively constant with depth for real-world applications.

3. Materials and Methods

Radiative transfer simulations were performed with Hydrolight v4.2 (Sequoia) using a four component Case 2 model consisting of water, phytoplankton, CDOM, and mineral suspended solids (MSS). All simulations were performed with 2 nm wavelength resolution between 400 and 760 nm, vertically uniform IOPs, surface wind speed of 5 m s\(^{-1}\), zero cloud cover, solar zenith angle of 45°, and above-surface irradiance calculated using the Gregg and Carder model [29]. Simulations were performed to a depth of 40 m and \( K_{ex}^{\text{w}} \) was evaluated to the first optical depth for the excitation waveband. Absorption and scattering values for pure water were taken from Pope and Fry [30] and Smith and Baker [31], respectively. Material-specific IOPs for each nonwater constituent were selected on the basis of consistency with samples obtained from previous fieldwork in the Irish Sea/Bristol Channel [27]. Material-specific absorption spectra are shown in Fig. 1(a). The chlorophyll-specific absorption spectrum was derived from filter pad absorption data and was selected since it had a value of \( a_{\text{chl}}(676) = 0.022 \) m\(^2\) mg\(^{-1}\), consistent with [27]. Mineral-specific absorption was modeled with an exponential function set to 0.05 m\(^2\) g\(^{-1}\) at 440 nm and an exponent of \(-0.010\), also consistent with previously published Irish Sea data. The CDOM absorption was modeled on an exponential function with an exponent of \(-0.014\) and using absorption by CDOM at 440 nm as the principal factor [32]. Chlorophyll- and mineral-specific scattering spectra [Fig. 1(b)] were taken from Table 2 in [27] with typical values of 0.35 m\(^2\) mg\(^{-1}\) and 0.35 m\(^2\) g\(^{-1}\), respectively. As the Hydrolight ABCASE2 model only permits a single scattering phase function for each constituent that cannot be varied with wavelength, wavelength-averaged backscattering ratios were taken for algal (0.013) and mineral (0.040) components based on data in Table 1 of [27]. These backscattering ratios were used to select appropriate Fournier–Forand scattering phase functions for each component [33–35]. A relatively high value of quantum yield for fluorescence (2%) was set for all simulations as this facilitated observation of fluorescence signals in turbid waters (see Subsection 4.E) though it should be noted that this is a strongly variable parameter in nature, e.g. [7].

Hydrolight provides the option of including three inelastic scattering processes within a simulation: algal fluorescence, CDOM fluorescence, and Raman scattering. Three sets of radiative transfer simulations were performed: (a) with all three inelastic scattering processes included, (b) with no inelastic scattering processes included, and (c) with CDOM fluorescence and Raman scattering, but no chlorophyll fluorescence included. The first set of runs provided the most realistic light fields we could achieve. The second set was used to calculate diffuse attenu-
ation coefficients without interference from inelastic processes. The third set provided baselines required for calculating true fluorescence line heights and wavelength-integrated quantum water-leaving fluorescence signals. Each set of runs encompassed two subsets, the first of which saw minerals and chlorophyll varied with CDOM and chlorophyll varied in the second (MSS = 0). The Chl values varied through 0, 0.5, 1, 5, and 10 mg m\(^{-3}\), MSS varied through 0, 0.5, 1, 5, and 10 g m\(^{-3}\), and CDOM absorption at 440 nm varied through 0, 0.05, 0.1, 0.5, and 1 m\(^{-1}\). It is worth noting that both CDOM and MSS absorption increase exponentially into the blue and that absorption at 440 nm (a potential representative for absorption in the broader fluorescence excitation band) is the same for both components when CDOM = 0.5 m\(^{-1}\) and MSS = 10 g m\(^{-3}\). The CDOM (which only absorbs) and MSS (which absorbs and scatters) were varied separately to facilitate investigation into the impacts of absorption and scattering on fluorescence generation and transmission. These constituent ranges were selected to cover moderately turbid coastal water conditions such as those observed in the Irish Sea. It should be noted that they do not represent extreme values, and much broader ranges of constituent concentrations can be found in nature.

Hydrolight simulates chlorophyll fluorescence emission using a Gaussian distribution centered on 685 nm (25 nm FWHM). In this paper we use \(L_{685}\) (see Fig. 2) as our preferred measure of water-leaving fluorescence. This parameter was obtained by subtracting baseline upward radiance spectra (immediately beneath the sea surface) generated without chlorophyll fluorescence from full subsurface radiance spectra with all inelastic processes included. The water-leaving fluorescence radiance, \(L_{685}\) (W m\(^{-2}\) nm\(^{-1}\) sr\(^{-1}\)), can also be expressed in quantum terms as \(L_{q685}\) (\(\mu\)mol photon m\(^{-2}\) s\(^{-1}\) sr\(^{-1}\)) by dividing \(L_{685}\) by \(10^{6} \times (N_{A}h\nu/c/\Delta\nu)\), where \(N_{A}\) is Avogadro’s number, \(h\) is Planck’s constant, \(c\) is the speed of light, \(\nu\) is the wavelength, and \(\Delta\nu\) is the bandwidth. Note: \(L_{q685}\) has to be integrated across the entire emission bandwidth for incorporation into Eq. (4), and \(L_{685}\) should not be confused with the FLH generated from satellite data with limited numbers of discrete wavebands and based on approximate baselines. For example, the MODIS FLH product is calculated by interpolating a baseline to 676 nm between measurements at 667 and 748 nm, and subtracting this approximate baseline from the measured total radiance at 676 nm (see Fig. 2). The

Fig. 2. True water-leaving fluorescence signal, \(L_{685}\), is obtained by subtracting water-leaving radiance calculated from radiative transfer simulations with and without chlorophyll fluorescence. The MODIS FLH algorithm estimates the fluorescence line height at 676 nm by interpolating a linear baseline between neighboring wavebands at 667 and 748 nm. This is off-center from the peak fluorescence emission waveband at 685 nm, but can be compared with true fluorescence line heights at 676 nm derived from radiative transfer simulations.

Fig. 3. (a) In Case 1 waters the subsurface (0') water-leaving fluorescence signal, \(L_{685}\), increases nonlinearly with Chl, while \(L_{685}\) per unit chlorophyll decreases. (b) Increasing Chl raises both \(E_{max}'\) and \(K_{ex}'\) (and also \(a_{em}-\)not shown), which results in the observed decrease in \(L_{685}/\text{Chl}\).
wavelength discrepancy between FLH at 676 nm and $L_{685}$ is necessary for practical reasons (it avoids an atmospheric oxygen absorption band), and is well understood to have both sensitivity and phytoplankton reabsorption issues [6,7,19]. In practice a small offset is added to FLH measurements to account for baseline artifacts [19]. In this paper we shall examine the performance of the FLH baseline procedure over a range of constituent concentrations with realistic material-specific IOPs, comparing FLH values with $L_{676}$, which is calculated in the manner of $L_{685}$, i.e., by subtracting a true baseline from the total radiance signal.

4. Results

In this section, all fluorescence and scalar irradiance signals are taken from immediately beneath the sea surface ($0^{-}$), while $K_{o ex}$ values are evaluated over the first optical depth for the excitation waveband.

A. Water-Leaving Fluorescence—Case 1 Waters

It is instructive to start by examining the generation of Sun induced fluorescence in Case 1 waters where nonalgal materials have zero impact. An initial set of Hydrolight simulations were carried out with chlorophyll varied between 0.1 and 10 mg m$^{-3}$, and with zero CDOM and minerals. Figure 3(a) shows that the relationship between $L_{685}$ and Chl is nonlinear, with $L_{685}$/Chl decreasing as Chl increases, in agreement with previous studies, e.g., [8]. Over this range of Chl concentration, the surface-leaving fluorescence emission per unit chlorophyll reduces by almost a third. It is important to note that although Eq. (4) shows an explicit dependence on Chl in the numerator, Chl also potentially influences the four light field parameters identified in Section 2, with the observed nonlinear relationship a consequence. Figure 3(b) shows that both $K_{o ex}$ and $E_{o ex}$ increase as Chl increases, and $a_{em}$ also increases significantly ($-30\%$) over this range of Chl. The observed nonlinear reduction in subsurface ($0^{-}$) $L_{685}$/Chl as Chl increases [Fig. 3(a)] can be attributed to the impact of absorption and scattering by phytoplankton on the underwater light field, as increases in Chl and $E_{o ex}$ are offset by increases in $K_{o ex}$ and $a_{em}$.

B. Water-Leaving Fluorescence—Case 2 Waters

The impact of increasing concentrations of first CDOM ($0$–$1$ m$^{-3}$ at 440 nm) and then minerals ($0$–$10$ g m$^{-3}$) on the relationship between $L_{685}$ and Chl can be seen in Fig. 4. Increasing concentrations of
CDOM in the water column results in a reduction in $L_{685}$ per unit of Chl, with $L_{685}$ being reduced by up to 57% relative to the Case 1 scenario [Fig. 4(a)]. $L_{685}$/Chl varies by a factor of ~2 for this range of CDOM [Fig. 4(c)]. Since CDOM is assumed to have zero scattering, this behavior must be solely attributable to absorption effects. The addition of up to 10 g m$^{-3}$ of MSS has less impact on $L_{685}$ per unit of Chl, though the trend is again generally downward, with $L_{685}$ being reduced by up to 24% [Fig. 4(b)]. In fact, at low chlorophyll and low ($\leq 1$ g m$^{-3}$) MSS concentrations $L_{685}$/Chl actually increases by up to 6% [Fig. 4(d)]. Given the similarities in the MSS and CDOM absorption spectra, and the fact that similar ranges of absorption are covered (MSS = 10 g m$^{-3}$ is broadly similar to CDOM = 0.5 m$^{-1}$ in absorption terms), the different impact on fluorescence signals of these two materials is presumably due to scattering effects from the mineral particles. Differential effects of CDOM and MSS on water-leaving Chl fluorescence signals can be identified by examining their impact on the light field parameters in Eq. (4).

C. Impact of Nonalgal Materials on Light Field Parameters

We previously identified four parameters in Eq. (4) that depend on the local light field and could potentially be influenced by the presence of nonalgal materials in the water column ($a_{ex}^*, a_{em}, K_{ex}^*$, and $E_{ex}^*$). Analysis of Hydrolight output for all of the simulations performed for this paper shows that $a_{ex}^* = 0.018 \pm 0.001$ m$^{-1}$ for the entire range of sampling conditions. We can therefore effectively remove this parameter as a potential source of the variability observed in Fig. 4, though it should be noted for other applications that this parameter will vary with changes in phytoplankton community composition and physiological state, and with solar angle. The absorption coefficient for the fluorescence emission band, $a_{em}$, varies between $-0.49$ and $0.70$ m$^{-1}$ for these ranges of constituent concentrations, with the water absorption being the greatest contributor, followed by phytoplankton; $a_{em}$ has very little dependence on either CDOM or MSS ($-0.04$ m$^{-1}$ for the full range of either constituent), consistent with both of these materials having absorption spectra that decay exponentially towards longer wavelengths. The impact of both CDOM and MSS is, however, significantly greater on both $K_{ex}^*$ and $E_{ex}^*$. Strong absorption by CDOM in the fluorescence excitation wavebands explains the variability of $K_{ex}^*$ with CDOM [Fig. 5(a)]. However, absorption only partially explains the relationship with MSS in Fig. 5(b) (noting that the MSS range covers less absorption variability than the CDOM range) as backscattering by mineral particles also contributes to the diffuse attenuation coefficient. Mineral backscattering also affects the relationship between subsurface $E_{ex}^*$ and MSS. Whereas increasing CDOM (which absorbs but does not scatter) reduces $E_{ex}^*$ by up to 10% over the chosen range of CDOM [Fig. 6(a)], increasing MSS has the effect of increasing $E_{ex}^*$ by up to 43% [Fig. 6(b)]. It is worth noting that prolonged exposure of phytoplankton cells to the high subsurface (0') scalar irradiance values shown in Fig. 6 could induce significant nonphotochemical quenching. Under these circumstances the quantum yield for fluorescence might vary significantly with depth.

The overall effect of CDOM is to reduce the availability of photons in the excitation waveband by absorbing light traveling in any direction beneath the sea surface. The effect of mineral particles is more complicated. Since these particles are absorbing, they reduce the overall availability in the water column of photons capable of exciting fluorescence. However,
scattering by mineral particles changes photon trajectories through the water column in such a way that the subsurface scalar irradiance increases as mineral particle concentration increases. This results in more excitation photons being available to stimulate fluorescence close to the sea surface, where there is a greater probability of fluorescence reaching the air-sea interface. In effect mineral scattering effects partially compensate for absorption effects, reducing the negative impact on water-leaving Chl fluorescence signals.

D. Effective Quantum Yield Retrieval in Case 2 Waters

Equation (4) provides a computationally efficient alternative to solving the full radiative transfer equation that might be particularly useful for remote sensing. It can also be rearranged to provide an estimate of the effective yield of fluorescence, \( \phi \). We can assess the validity of Eq. (4) for a wide range of Case 2 water conditions, and also its potential for determining \( \phi \) by attempting to retrieve our input value of 0.02 (2%) using light field data supplied from Hydrolight outputs. Figure 7 shows retrieval of \( \phi \) for the ranges of constituent concentrations covered in this paper. In the absence of any nonalgal materials the retrieved value of \( \phi \) varies between \( \pm 10\% \) of the true value. Adding CDOM [Fig. 7(a)] tends to reduce the value of \( \phi \) obtained, with the maximum error being a 12% underestimate (\( \phi_{\text{est}} = 0.0176 \)). Increasing the MSS concentration [Fig. 7(b)] causes overestimates of \( \phi \), with maximum errors of 26% (\( \phi_{\text{est}} = 0.0253 \)). \( \phi \) is known to vary by up to an order of magnitude in response to physiological changes [13,15,16], and so the...
maximum retrieval error using Eq. (4) is considerably less than the natural variability of this parameter. We can conclude that Eq. (4) provides a reasonable representation of the processes contributing to the generation of water-leaving fluorescence signals. The fact that it does not provide a perfect retrieval of \( \phi \), even under these highly idealized circumstances, is a reminder that it is an approximation to a full solution of the radiative transfer equation. It does not fully account for alterations in the geometrical distribution of photons in the water column in response to changes in the balance between absorption and scattering. The limit on its usefulness in practice is likely to be the accuracy with which each of its parameters can be estimated from remote sensing data products.

E. Fluorescence Line Height Baseline Correction in Turbid Case 2 Waters

The differential impacts of the two nonalgal materials on red water-leaving radiance signals are demonstrated in Fig. 8, where it can be seen that for a given chlorophyll concentration: (a) increasing the CDOM absorption generally reduces the radiance signal including fluorescence, (b) increasing the MSS generally raises radiance levels (note the extra factor of 10 on the y axis), and the fluorescence peak becomes less prominent against the raised background signal. The performance of the MODIS FLH calculation procedure can be assessed for turbid waters by comparing FLH values with equivalent values of \( L_{676} \) calculated by subtracting true baselines (Hydrolight runs with no Chl fluorescence) from total radiance spectra (Hydrolight runs with Chl fluorescence). Figure 9(a) shows that MODIS FLH systematically underestimates the true \( L_{676} \) signal by 20%–30% for low Chl values, even in the absence of nonalgal materials,
with the FLH signal reaching only 55% of $L_{676}$ when Chl = 10 mg m$^{-3}$. Adding small concentrations of CDOM has a very limited impact on FLH algorithm performance (there is a slight improvement at low Chl concentrations), which is consistent with Hoge et al. [25]. The FLH algorithm is considerably more affected by the presence of mineral particles. Figure 9(b) shows that FLH underestimates $L_{676}$ when Chl and MSS values are high, reaching only ~30% of the true value when both Chl and MSS are at the high ends of their chosen ranges. However, the most dramatic effect is the overestimation of $L_{676}$ when Chl is low and MSS increases, when FLH values can overestimate $L_{676}$ by an order of magnitude. It should be noted that although these are high percentage errors, the $L_{676}$ values are not high when Chl is low. The FLH algorithm appears to breakdown for MSS values of 5 g m$^{-3}$ and above, due to an inability to resolve the fluorescence peak over raised background irradiance levels in turbid waters. As these radiative transfer simulations were performed with a fluorescence yield of 2%, which is toward the high end of the range found in nature, it is possible that in practice the FLH algorithm performance may degrade at even lower MSS concentrations than these results suggest.

5. Discussion
The ability to observe phytoplankton fluorescence from space has raised the intriguing possibility of surveying variations in phytoplankton concentrations and physiology on unprecedented geographical scales, e.g., [8]. Naturally, most effort has gone into interpreting fluorescence signals from Case 1 waters where the effects of nonalgal materials are negligible. However, it is also important to assess the potential of such techniques for more optically complex coastal waters where a significant proportion of global marine productivity occurs. It is well known that other algorithms, such as blue–green reflectance ratios for chlorophyll, often perform poorly in coastal waters. In this paper we have used radiative transfer simulations based on realistic material specific IOPs to model the impact of varying mineral and CDOM concentrations on water-leaving Sun induced fluorescence signals. This means that our findings are free from the measurement artifacts that inevitably affect the interpretation of in situ data. Using this approach, we have determined that nonalgal materials primarily affect the stimulation of fluorescence by altering the scalar irradiance field, $E_{sc}^\text{ex}$, and the diffuse attenuation of scalar irradiance, $K_s^\text{sc}$. Their impact on the transmission of fluorescence from depth to the surface appears to be limited for the concentration ranges examined. The overall effect of nonalgal materials is to reduce the water-leaving fluorescence signal per unit chlorophyll. This has an effect on the minimum detectable Chl, but it does not prohibit the use of Eq. (4) to interpret the signal. However, to use Eq. (4) with remote sensing data, it is necessary to provide estimates of each of its parameters from the data set available, or make reasonable estimates based on a priori knowledge.

For remote sensing applications, the greatest obstacles to using Eq. (4) in turbid waters appear to be our ability to estimate the fluorescence signal itself when background radiance levels are raised by mineral backscattering [Fig. 9(b)], or when the signal is inhibited due to the presence of high CDOM concentrations [Fig. 4(a)]. Prospects appear to be good for deriving other required parameters, such as $E_{sc}^\text{ex}$ and $K_s^\text{sc}$, from standard MODIS (or equivalent) products [8,36], while the absorption of emitted fluorescence $a_{ex}$ may be approximated by water absorption [15] or water plus phytoplankton absorption [8]. Improved methods for retrieving Chl in turbid coastal waters [1,2] are being developed that could also facilitate using Eq. (4) to estimate effective quantum yields ($\phi$) from remote sensing measurements of FLH. Note that for our simulated data set there is a strong linear relationship between $L_{676}$ and total quantum fluorescence $L_{q}$, $\mu$mol photons m$^{-3}$ s$^{-1}$ sr$^{-1}$—required for Eq. (4) of the form $L_{q} = 223.4 \times L_{676}$. However, our results suggest that FLH measurements may be compromised by the presence of high mineral or CDOM concentrations, and under such circumstances the applicability of Eq. (4) is very much in doubt. Higher concentrations of CDOM or MSS and lower effective fluorescence yields than those considered in this study would all further limit our ability to resolve the water-leaving chlorophyll fluorescence signal.

6. Conclusion
Water-leaving Sun induced Chl fluorescence signals are a product of the phytoplankton population and the surrounding light field. If that light field is subject to nonalgal influence then so is the chlorophyll fluorescence signal. Users of remote sensing products based on SICF should be aware of the potential influence of nonalgal materials, and be particularly careful in interpreting such products from turbid coastal waters.

References