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Wavelength-specific fluorescence coefficients for simulating hyperspectral reflectance signatures of water

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Wavelength Specific Fluorescence Coefficients For Simulating Hyperspectral Reflectance Signatures of Water

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ABSTRACT

A model^{1,2} which describes the transfer of irradiant light in water is used to predict the fluorescence response of the water surface reflectance under solar induced or an artificial light source such as a laser. Formulations for the estimation of wavelength dependent fluorescent coefficients. The techniques allows the description of a fluorescence reflectance response in deep and shallow waters with various bottom reflectance signatures such as submerged vegetation, corals and sand. Recent advances in the model are presented for obtaining wavelength dependent fluorescence spectrum responses from the solutions of the two flow equations following the procedures developed by Bostater^{1,2,3}. Synthetic or modeled signatures are presented using in-situ data from the Space Coast of central FLorida, USA and the southeastern Atlantic waters near Beaufort, South Carolina. The synthetic or modeled signatures are also dependent upon the attenuation length of the water based upon knowledge of the diffuse attenuation coefficient (k), the beam attenuation (c) or the absorption coefficient (a). The model has potential applications for helping to select remote sensing optimal channels or bands useful in near nadir viewing geometry of estuarine or coastal water columns overlying shallow sand, submerged vegetation, or coral reefs. The analytical solution to the two-flow equations developed by Bostater^{1,2} have transferability to complex but important water quality detection problems that can be assisted using fluorescence processes.

Keywords: remote sensing, water, modeling, optical models, fluorescence, absorption, water quality, coral reefs, bottom reflectance, irradiance, collimated sources, lasers, chlorophyll-a, dissolved organic matter, scattering, hyperspectral, submerged aquatic vegetation.

1. INTRODUCTION

An analytical solution^{1,2} to the homogeneous two flow irradiance equations utilized unique Cauchy boundary conditions and resulting sensitivity analyses were used to develop a remote sensing model which contains both diffuse and specular light components with the specular irradiance being specified as a collimated irradiance or source term in the two flow equations (CASE II model²). The equations are in concept similar to model equations called the Suits equations⁷.

The Case II model version used here assumes the direct light (sunlight) and the indirect light (skylight) enters the water (corrected for the presence of the air-sea interface) and all the light is assumed to become part of the downwind irradiance field. This Case II fluorescence model uses equations that explicitly include and have in their derivation and solution a collimated irradiance term and a third ordinary differential equation which explicitly describes the attenuation of this direct sunlight or collimated light in terms of a beam attenuation coefficient. The analytical equations are written in numerical based computer algorithms in order that simulations can be made of the underwater light field and the water surface reflectance based upon specified concentrations of constituents in the water column and associated fluorescence characteristics described below.

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The model is used to test assumptions concerning fluorescence (a) within different homogeneous water column attenuation depths, (b) with varying concentrations of absorbers and scatterers and (c) with different values of specified fluorescence coefficients. The solutions used assumes a steady state fluorescence response over a given time scale of fluorescence and homogeneous water column characteristics.

The equations are introduced for a fluorescence response below. Section three describes the approach and meaning as well as the calculation of the fluorescence conversion coefficient from direct, collimated irradiance to diffuse irradiance that is used in this fluorescence model. Section four describes model output and sensitivity of the model equations. This analytical remote sensing model is also being used to describe vegetation dysfunction in plant canopy research.

2. BACKGROUND

The fluorescence model we are developing utilizes a set of three coupled first order, non-homogeneous differential equations. The additional term for describing the transfer or conversion of the collimated beam to the upward and downwards flowing light fields is specified as $\mathfrak{R}_c(\lambda_x \rightarrow \lambda_m)$ and is assumed constant valued for each transition indicated. Each excitation wavelength given by λ_x has a possible emission wavelength given by λ_m in the model. The \mathfrak{R}_c term (m^{-1}) represents a fluorescence conversion coefficient per unit pathlength (or conversion efficiency matrix) whereby it is possible for the excitation wavelengths from $\lambda_x = 1$ to n , to have associated emission wavelengths given by $\lambda_m = 1$ to n due to inelastic scattering processes dependent upon concentrations of fluorophores (mgL^{-1}). The two resulting diffuse flow field equations along with a third equation describing the attenuation of a diffuse collimated irradiance for the excitation wavelength λ_x as:

$$\frac{dE_d^w(z, \lambda_m)}{dz} = -(a(\lambda_m) + b(\lambda_m))E_d^w(z, \lambda_m) + b(\lambda_m)E_u^w(z, \lambda_m) + \mathfrak{R}_c(\lambda_x \rightarrow \lambda_m)E_x^w(z, \lambda_x) \quad (1)$$

$$\frac{dE_u^w(z, \lambda_m)}{dz} = -(a(\lambda_m) + b(\lambda_m))E_u^w(z, \lambda_m) + b(\lambda_m)E_d^w(z, \lambda_m) + \mathfrak{R}_c(\lambda_x \rightarrow \lambda_m)E_x^w(z, \lambda_x) \quad (2)$$

$$\frac{dE_x^w(z, \lambda_x)}{dz} = -k(\lambda_x)E_x^w(z, \lambda_x) \quad (3)$$

The \mathfrak{R}_c terms represent the fraction of the excitation source $E_x^w(z, \lambda_x)$, (Wm^{-2}) which is converted to the emission wavelength at the excitation wavelength at depth $z = 0$ at the surface to depth $z=h$ at the bottom. The absorption terms $a(\lambda_m)$, (m^{-1}), the backscatter terms $b(\lambda_m)$, (m^{-1}) and the attenuation (absorption plus scattering) term $k(\lambda_x)$, (m^{-1}) applicable to the emission wavelength, as well as the \mathfrak{R}_c terms are assumed to be constants with depth of the environmental medium. Equations 1 and 2 and 3 can be decoupled into two second order, linear, non-homogeneous differential equations. The solutions for the downwelling irradiance $E_d^w(z, \lambda_m)$, (Wm^{-2}) and upwelling irradiance $E_u^w(z, \lambda_m)$, (Wm^{-2}) at emission wavelength λ_m and the excitation wavelength λ_x , for this fluorescence model are:

$$E_d^w(z, \lambda_m) = \frac{[E_d^w(0, \lambda_m) - \eta]\Psi + [\beta_d(0, \lambda_m) + k\eta]e^{\Psi z} + \eta e^{-kz} + [E_d^w(0, \lambda_m) - \eta]\Psi - [\beta_d(0, \lambda_m) + k\eta]e^{-\Psi z}}{2\Psi} \quad (4)$$

$$E_u^w(z, \lambda_m) = \frac{\Psi e^{-\Psi h} \{R_b(h, \lambda_m) [E_d^w(h, \lambda_m) + E_s^w(h, \lambda_m)] - ne^{-kh}\} + e^{-\Psi h} [kne^{-kh} + \beta_u(h, \lambda_m)]}{2\Psi} e^{\Psi z} + \frac{(\Psi e^{\Psi h} \{R_b(h, \lambda_m) [E_d^w(h, \lambda_m) + E_s^w(h, \lambda_m)] - ne^{-kh}\} - e^{\Psi h} [kne^{-kh} + \beta_u(h, \lambda_m)])}{2\Psi} e^{-\Psi z} + ne^{-kh} \quad (5)$$

$$E_s(z, \lambda_x) = E_s^w(0, \lambda_x) e^{-k(\lambda_x)z} \quad (6)$$

Decoupling of the 2 non-homogeneous ODE's above yield a constant ψ and is given by:

$$\psi(\lambda_m) = \sqrt{a(\lambda_m)^2 + 2a(\lambda_m)b(\lambda_m)} \quad (7)$$

The technique for solving the above equations utilize Cauchy type boundary conditions such that:

$E_d(0, \lambda_m)$ = the downwelling irradiance from indirect light or skylight at $z=0$,

$E_d^w(h, \lambda_m)$ = the downwelling light at depth $z=h$,

$\frac{dE_d^w(0, \lambda_m)}{dz}$ = the downwelling slope $\beta_d(\lambda_m)$ or rate of decrease of downwelling light at or near $z=0$,

$\frac{dE_u^w(h, \lambda_m)}{dz}$ = the upwelling slope $\beta_u(\lambda_m)$ or rate of increase of upwelling light at or near the bottom $z=h$,

$dE_x(0, \lambda_x)$ = the magnitude of the excitation source or collimated irradiance at $z=0$ and.

The last 2 terms to be described which are derived from the solution technique are the η and τ constants specified in equations 4 and 5 above. These terms are written as:

$$\eta(\lambda_m, \lambda_x) = \frac{-\Re_c(\lambda_x \rightarrow \lambda_m)(k(\lambda_x) + a(\lambda_m) + 2b(\lambda_m))}{(k(\lambda_x)^2 - \psi(\lambda_m)^2)} E_x^w(0, \lambda_x) \quad (8)$$

$$\tau(\lambda_m, \lambda_x) = \frac{\Re_c(\lambda_x \rightarrow \lambda_m)(k(\lambda_x) - a(\lambda_m) - 2b(\lambda_m))}{(k(\lambda_x)^2 - \psi(\lambda_m)^2)} E_x^w(0, \lambda_x) \quad (9)$$

The above equations thus have embodied within them, absorption coefficients, an elastic backscatter, as well as an inelastic scattering coefficient. The resulting solutions for the upwelling diffuse irradiance

$E_u^w(0, \lambda_m)$ are derived from knowledge of the above surface and in-water downwelling diffuse irradiance

$E_d^w(0, \lambda_m)$ at the surface. Knowledge of reflectance of the water bottom or $R_b(h, \lambda_m)$ can be used to calculate the water surface reflectance or $R_w(0, \lambda_m)$ which is influenced by the indirect light or downwelling skylight, the downwelling specular irradiance from the solar disc, and a collimated irradiant source

term $E_x^w(0, \lambda_x)$ entering the water at $z=0$.

3. METHODS

In this Case III model, a conversion coefficient from direct, specular irradiance to diffuse irradiance is used⁷ and is assumed to represent elastic scattering processes. It is assumed in the Case II model (which is used to estimate the fluorescence conversion) and this new Case III model, that the collimated source is converted equally to the upwards and downward diffuse light fields. Therefore the same value of the conversion coefficient is used. As indicated above, the direct light is converted to the indirect light or diffuse component before reaching the bottom. Thus, if specular collimated irradiance does strike the bottom, the bottom is considered to be a Lambertian surface, and all of the collimated source is converted to diffuse light. Using Petzold's¹¹ volume scattering function for turbid San Diego Harbor water, a backscattering coefficient for the elastic scattering can be found⁶ by integrating and results in a direct, or specular backscattering coefficient which can be multiplied by the mean cosine of the light field to obtain a diffuse backscattering coefficient. For example, in the waters from the Banana River we have estimated $c=b*2.85$ for the Case II model where b is the backscattering coefficient. It is also assumed for this study that the conversion coefficient is the same in both directions, and the \Re_c in equations 1 and 2 are equal. In this Case III fluorescence model, to properly parameterize the fluorescence conversion coefficient or efficiency coefficient one can utilize information on the concentration of the fluorophores as well as information from multiple wavelength excitation and emission spectra of water samples collected at the same time the water surface reflectance is collected and the absorption coefficient is collected. We use data obtained from a field portable long pathlength absorption measurements to obtain the $a(\lambda_m)$ term. Specifically the $\Re_c(\lambda_x \rightarrow \lambda_m)$ conversion term or conversion effi-

ciency term is simplistically conceived as concentration dependent and normalized per unit pathlength (L). The term can be considered as the ratio of the emission signature of the sample for each λ_{m_i} normalized to the magnitude of the excitation at λ_x (thus removing non inelastic scattering effects) and corrected or normalized to the pathlength (L), or:

$$\mathfrak{R}_c(\lambda_x \rightarrow \lambda_m) = [E_u^S(\lambda_{m_i})/E_u^F(\lambda_{x_i})]/L \Rightarrow f\{\text{fluorophores}(\text{mgL}^{-1}), L\} \quad (10)$$

Another parameter needed is k, a kind of beam attenuation coefficient. The beam attenuation coefficient can be defined as the sum of absorption and total scattering (elastic and inelastic), meaning that a relationship between the backscatter coefficient and the total scattering coefficient is needed. The total elastic scattering coefficient for specular irradiance is assumed to be on the order of 53 times the backscattering coefficient¹².

Model runs are generated using the Case II model using a spectral signature of downwelling diffuse and direct skylight derived from a simple atmospheric correction. In addition, we allow for increased downwelling irradiance at 450 nm in order to simulate an artificial light source, such as a laser or broad beam diffuse illuminator as $E_d^W(0, \lambda_x)$. To increase this synthetic line source of collimated downwelling irradiance

$E_d(0, \lambda_m)$ is multiplied by values from 0 (no effects from an artificial source) to 1 which represents increasing the E_d by 100%.

In order to estimate the conversion coefficient for fluorescence, Case II model runs are used to model the downwelling and upwelling natural sunlight and increased downwelling irradiance at wavelength 450nm due to an artificial light source. To increase downwelling irradiance (E_s) the E_s was multiplied by values from 0 (no effects from fluorescence) to 1 which represents transferring 100% of the E_s for laser intensity at 450nm. We have modified a technique originally proposed for calculating the rate of chlorophyll fluorescence (Babin, Morel & Gentili, 1996) to estimate the amount of E_{dw} that would be converted to the fluorescence distribution centered at wavelength 685. Our technique is schematically indicated in figure 1. Using our Case II model we calculate the amount of irradiant fluorescence E_f (Wm^{-2}) as:

$$E_f = E_{\text{Par}(400-700\text{nm})}^d [\text{chl-a}_{\text{ug/L}}] a^* Q_a(685) Q_e(685) Z_{\text{euphotic}} \quad (\text{Wm}^{-2}), \quad (11)$$

where E_{Par}^d (Wm^{-2}) is the Case II model derived irradiance available for absorption from 400-700 nm, and is dependent upon the absorption and backscatter signatures derived from water samples and spectral data collected from waters in Indian River Lagoon, coastal waters off Cape Canaveral, Florida, and estuarine waters in the vicinity of Beaufort, South Carolina. Chl-a (ugL^{-1}) is the chlorophyll- a pigment concentrations assumed for the Case II model runs.

The a^* is the specific absorption coefficients derived from the in-situ data using a long pathlength absorption tube (m^2mg^{-1}). The term $Q_a(685)$ is a factor that accounts for the intracellular reabsorption of fluorescence at wavelength 685 (dimensionless) and is calculated using the following equation $Q_a(685) = 0.549[\text{chl-a}]^{-0.173}$. The term Q_e is the quantum yield of fluorescence (dimensionless); We use 0.035 as the value for the quantum yield per the findings of Kiefer, Chamberland & Booth 1989. $\nabla Z_{\text{euphotic}}$ is calculated from the following equation: $\nabla Z_{90} = 1/k_d + k(685)$ modified after Babin, Morel & Gentili, 1996

When the above technique is used, the Case II model output produces a reflectance signature that includes fluorescence that is dependent on the chlorophyll concentration and the amount of $E_d(z)$ available for absorption by the fluorophores, due to the sum of sunlight and due to an artificial light source, such as a laser.

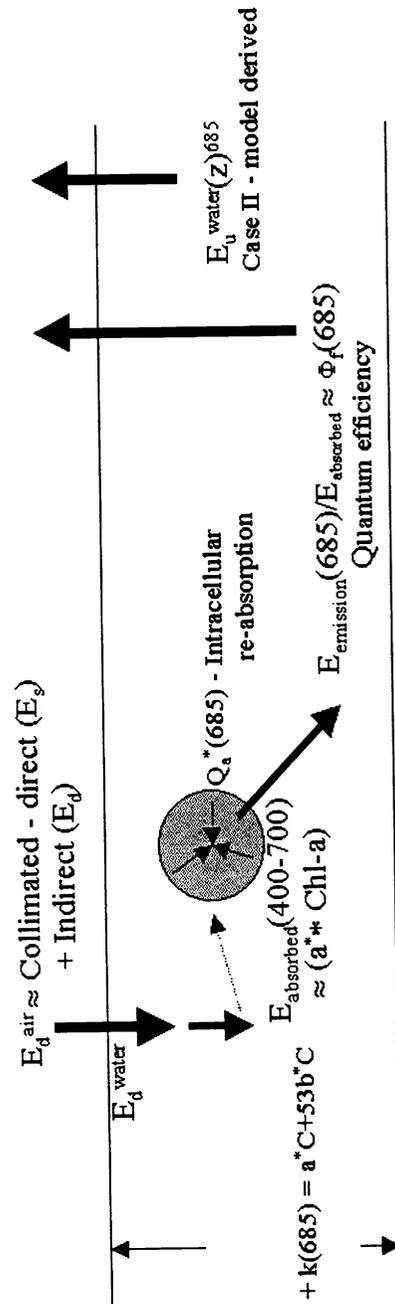


Figure 1. Conceptual model of the Case II model calculations used to estimate the amount of downwelling light $E_d(\lambda)$ available for absorption (400-700 nm) from sunlight and any artificial light (such as a laser). The light absorbed is pigment concentration (Chlor-a μgL^{-1}) dependent according to the specific absorption coefficients $a^*(\lambda)$. The fraction of light emitted as fluorescence is dependent upon the intracellular re-absorption coefficient Q_a at $\lambda=685$, and the quantum efficiency Φ_f at $\lambda=685$. The fluorescence irradiance $E_f(\lambda)$ is then attenuated due to backscatter and absorption over the attenuation depth of the euphotic zone. The resulting reflectance signatures are used to estimate the concentration dependent fluorescence coefficient $\mathfrak{R}(\lambda)$ used in the Case III simplified fluorescence model.

The wavelength dependent fluorescence coefficient \mathfrak{R}_c is then calculated based upon the relation $\mathfrak{R}_c = a^* \text{Chlor-a } Q_e E_d(\lambda) / E_u(\lambda) m$. This idea was occurred to us based upon limited data concerning a chlorophyll natural fluorescence response to upwelling events in the Southern Ocean by Letelier & Abbott 1997. The above relation can be rearranged to $E_u(\lambda) m / \text{chlor-a } (\text{ugL}^{-1}) = (Q_e a^* / \mathfrak{R}_c) E_d(\lambda)$. Note that this has the form of $y = mx + b$ where $(Q_e a^* / \mathfrak{R}_c) = m$ and $b = 0$. Based upon these simplified concepts, a general linear model analysis is performed on $E_d(\lambda)$ vs. $E_u(\lambda) / \text{chlor-a } \text{ugL}^{-1}$ with varying concentrations used in the Case II model runs. The resulting modeled upwelling light with the fluorescence signal can be used to calculate the slope and the slopes used to calculate the wavelength dependent $\mathfrak{R}_c(\lambda)$ from the relation $Q_e a^*(\lambda) / m$ for different wavelengths and model runs with different concentrations of chlorophyll-a. This can be rearranged so that the Case III model rate can be estimated from the Case II model rate (according to figure 1) using $\mathfrak{R}_c = Q_e a^*(\lambda) / m$. To obtain wavelength and concentration dependent fluorescence coefficients the above analysis procedure was performed using E_{dws} at 450 vs. $E_u(\lambda) / \text{chlor-a}$. Note, that for this paper, \mathfrak{R}_c at wavelengths 400 thru 664 are assumed to be 0. The slopes were calculated for chlor-a varying from 0.01, 0.02, 0.05, 1, 2, 5, 10 and 20 ug/L. The resulting \mathfrak{R}_c values were divided by the chlor-a concentration to obtain an f^* , which is assumed to be a specific chlorophyll-a fluorescence coefficient, having units $\text{m}^2 \text{mg}^{-1}$. The resulting f^* 's for each concentration & wavelength are averaged at each wavelength. In other words, each wavelength has one f^* . The f^* is then used in simulations with concentrations to obtain \mathfrak{R}_c using the Case III model.

4. RESULTS

Synthetic reflectance signatures are produced utilizing the fluorescence model with clear water values for absorption and backscatter (Smith & Baker, 1981) as a function of wavelength and our data for chlorophyll-a, specific absorption coefficients from South Atlantic waters and bottom reflectance is assumed constant. A midday light intensity and solar zenith angle is used. The modeled vertical upwelling and downwelling in-water profiles assume a combination of natural sunlight and an additive line source intensity at 450 nm to simulate a laser of collimated excitation light. In Figure 2 and 3 below, we assume a fluorescence response or inelastic scattering process is centered around 685 nm with concentrations of 10 and 20 ugL^{-1} chlorophyll-a and with different levels of collimated excitation intensity 1 to 10 times natural background levels as shown.

Fluorescence at Chlorophyll conc. 10 ug/L

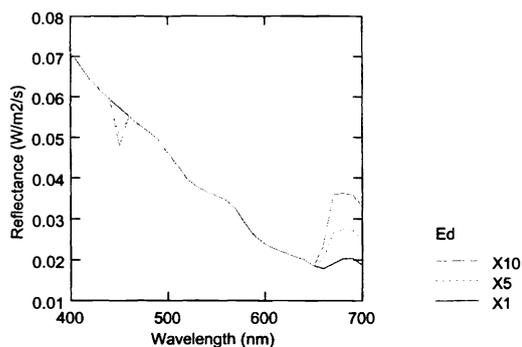


Figure 1. Synthetic reflectance signature under varying excitation levels (5-10) times natural background at a chlorophyll-a concentration of 10 ug/L using the wavelength specific fluorescence coefficients. Absorption coefficients were obtained from Atlantic coastal waters.

Fluorescence at Chlorophyll conc. 20 ug/L

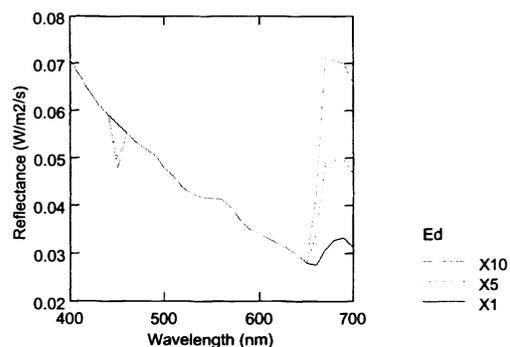


Figure 2. Synthetic reflectance signature under varying excitation levels using the wavelength dependent specific fluorescence coefficients. The reduction of reflectance at 450 nm is due to the line source increase. Bottom reflectance is assumed constant.

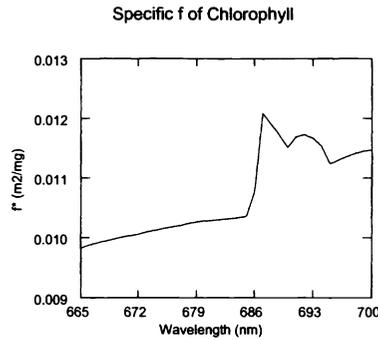


Figure 3. Wavelength dependent fluorescence coefficients based upon the technique of synthetic reflectance signature simulation for chlorophyll-a. Shape of the curve depends upon the downwelling irradiance spectrum, specific absorption and backscatter coefficients used in the procedures described above.

Figure 3 above shows the resulting wavelength dependent fluorescent coefficients calculated using the *in-situ* data the model simulation procedure described above. The magnitude of the emission response observed in figure 4 below is observed to be dependent on the concentration of the fluorophores pigment as described in the model under constant illumination.

Fluorescence at varying Chlorophyll Concentrations

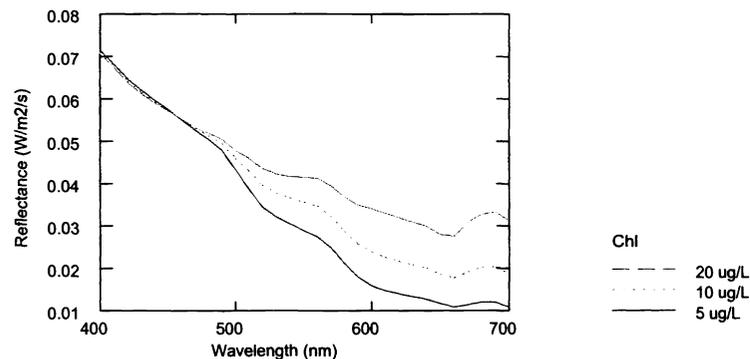


Figure 4. The modeled reflectance signature using wavelength dependent specific fluorescence coefficients in the presence of varying chlorophyll a concentrations with a constant illumination expected due to solar induced fluorescence.

A future application of the model results described above will be in selection of optimal channels for LIDAR based remote sensing of shallow optical water bodies, coral reefs, etc. from satellite, aircraft or shipborne sensors using model runs with realistic bottom reflectance signatures. Bostater^{1,2} has shown the effects of increasing water quality concentrations on reflectance signatures in similar model runs. Increasing the constituent concentrations in the Case II model can also be used to assess the impact on the fluorescence response or emission spectra in the presence of complex mixtures and fluorophores. as described above.

6. SUMMARY & CONCLUSIONS

The two-flow irradiance fluorescence model (Case III) and the technique for using the Case II model described and applied in this paper provides a framework for quantitatively predicted the effects of a collimated source upon water surface reflectance signatures, The model approach requires input not only of the source intensity but also background direct and indirect solar derived energy from the sun and sky for evaluating daytime reflectance conditions. The model requires absorption and backscatter coefficients as well as prior knowledge of the fluorescence conversion or transition efficiency coefficient $\mathfrak{R}_c(\lambda_x \rightarrow \lambda_m)$. If this coefficient is dependent upon the concentration of fluorophores, then these concentrations can be assumed or measured as well as the chlorophyll, seston and DOM concentrations.

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