Theoretical analysis of the *in situ* fluorescence of chlorophyll a on the underwater spectral irradiance

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Abstract: A radiative transfer equation, including the effect of chlorophyll a fluorescence, is derived from a single fluorescence model combined with a two-flow model. The equation is used for investigating the effect of fluorescence upon the upward irradiance in the vicinity of 685 nm where the irradiance peak has been frequently observed. The computational results reveal that the peaks develop at 685 nm and 710 nm at low and high chlorophyll concentrations, respectively. The peak at about 685 nm is due to the fluorescence of phytoplankton, while the peak at about 710 nm is due to spectral properties of absorption and scattering of phytoplankton. Further, the fluorescence peak height in relation to chlorophyll concentration and the effects of both detritus and dissolved organic matter on fluorescence peak height are discussed on the basis of the computational results.

1. Introduction
A strong peak at about 685 nm in the upward irradiance or radiation spectrum in natural waters was observed by NEVILLE and GOWER (1977), GOWER (1980), GOWER and BORSTAD (1981) and KISHINO et al., (1984a). They observed a good correlation between the peak height and the chlorophyll a concentration in each area. This suggests that the chlorophyll fluorescence is responsible for the peak at 685 nm in the upward spectrum. In addition to these experimental results, GORDON (1979) and KATTAWAR and VASTANO (1982) explored this strong peak theoretically and concluded that the peak was attributed to fluorescence of chlorophyll a excited by incident light. However, *in situ* fluorescence is influenced by not only chlorophyll concentration but also by the spectral distribution of the incident light, the turbidity of sea water, the phytoplankton species and the physiological state of phytoplankton (STRICKLAND, 1968, KIEFER, 1973a, 1973b; PÆZELIN and LEY, 1980; KISHINO et al., 1984b). As a result, the effect of fluorescence on the upward spectral irradiance is rather complicated in the vicinity of 685nm and the relationship between the peak height and chlorophyll concentration seems to vary with the season and geographical location.

In order to explore the effect of fluorescence on spectral behavior of irradiance, a single fluorescence model is combined with a two-flow optical model in the present study. By using the developed equation, the variation in downward and upward spectral irradiance in the vicinity of 685nm are calculated for various concentrations of chlorophyll a, detritus and dissolved organic matter.

2. Radiative transfer equation including the effect of the chlorophyll a fluorescence
According to KISHINO et al., (1984a), downward irradiance $E_{d}(z, \lambda)$ and upward irradiance $E_{u}(z, \lambda)$ can be written in the form of a sum of elastic scattering and fluorescence contributions as follows:

$$ E_{d}(z, \lambda) = E_{ds}(0, \lambda)e^{-K(1)z} + E_{fs}(z, \lambda), \quad (1) $$

$$ E_{u}(z, \lambda) = E_{us}(0, \lambda)e^{-K(1)z} + R_{os}(\lambda) + E_{fu}(z, \lambda), \quad (2) $$

where $E_{ds}$ and $E_{fu}$ are downward and upward fluorescence, respectively, given by:

$$ E_{ds}(z, \lambda) = \int_{380}^{680} F_{ds}(\zeta, \lambda, \lambda_{d}) d\zeta, \quad (3) $$

$$ E_{fu}(z, \lambda) = \int_{380}^{680} F_{fu}(\zeta, \lambda, \lambda_{f}) d\zeta, \quad (4) $$

with

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\[
F_d(z, \lambda = \lambda_c) = 2\pi \beta(\lambda_c) \frac{\lambda_c}{\lambda_f} E_d(z, \lambda_c) a_{ph}(\lambda_c) C \times \left[ \exp \left\{ 1 - \frac{\alpha(\lambda_c) - K(\lambda_c)}{\alpha(\lambda_c) - K(\lambda_c) \cos \theta} \right\} \cos \theta \sin \theta d\theta \right] 
\]

\[
F_d'(z, \lambda = \lambda_c) = 2\pi \beta(\lambda_c) \frac{\lambda_c}{\lambda_f} E_d(z, \lambda_c) a_{ph}(\lambda_c) C \times \left[ K(\lambda_c) + \alpha(\lambda_c) \log \frac{\alpha(\lambda_c)}{K(\lambda_c) + \alpha(\lambda_c)} \right],
\]

where \(K\) is the attenuation coefficient for irradiance, expressed by PREISENDORFER (1961) as

\[
K(\lambda) = D_d [a(\lambda) [a(\lambda) + 2b_u(\lambda)]]^{1/2},
\]

and \(R_{\infty}\) is the irradiance reflectance at the infinite depth, given by MOREL and PRIEUR (1977) as

\[
R_{\infty}(\lambda) = 0.33 \frac{b_u(\lambda)}{\alpha(\lambda)}.
\]

The parameters \(D_d, a, b_u\) and \(\alpha\) are the distribution function, the absorption coefficient, the backscattering coefficient, and the beam attenuation coefficient, respectively, \(a_{ph}\) is the absorption coefficient of phytoplankton per unit chlorophyll \(a\) concentration, \(C\) is the chlorophyll \(a\) concentration and \(\beta\) is the volume fluorescence function. If a Gaussian distribution is assumed for the emission peak of chlorophyll at 685 nm, \(\beta\) can be defined by

\[
\beta(\lambda) = \beta(685) \exp \left[ - \frac{1}{2} \left( \frac{\lambda - \lambda_0}{\sigma} \right)^2 \right] = \frac{\phi}{4\sigma \pi^{1/2}} \exp \left[ - \frac{1}{2} \left( \frac{\lambda - \lambda_0}{\sigma} \right)^2 \right],
\]

where \(\phi\) is the quantum yield of fluorescence, \(\sigma\) is the variance of Gaussian distribution and \(\lambda_0\) is 685 nm. It should be noted that the definition of the volume fluorescence function differs from GORDON's model (1979), \(\beta_0\), as follows:

\[
\beta_0(\lambda) = \frac{\lambda_c}{2^{1/2} \lambda_f} a_{ph}(\lambda_c) \beta(\lambda),
\]

where \(\beta_0\) is dependent on \(\lambda_c\) and \(a_{ph}(\lambda_c)\), while \(\beta\) in the present study is independent of \(\lambda_c\) and \(a_{ph}(\lambda_c)\). The theoretical calculations can be simplified by the assumption that \(\beta\) is independent of \(\lambda_c\).

OKAMI \textit{et al.} (1982a, 1982b) express \(b_0(\lambda)\) and \(a(\lambda)\) as the sum of the coefficients for each of the components, respectively. In the present study, it is assumed that the ratio of backscattering in the total scattering coefficient for phytoplankton and detritus is 0.02 (MOREL and PRIEUR, 1977). Denoting the absorption and scattering coefficients for detritus as \(a_d\) and \(b_d\), respectively, and the scattering coefficient for phytoplankton as \(b_{ph}\), we have the following relations:

\[
a(\lambda) = a_w(\lambda) + a_{ph}(\lambda) C + 0.2 b_u \frac{650}{\lambda} + A_v \exp \left[ -0.0167(\lambda - 380) \right],
\]

\[
b_0(\lambda) = \frac{1}{2} b_w(\lambda) + 0.02 [b_{ph} C + b_d],
\]

where \(a_w\) and \(b_w\) are the absorption and the scattering coefficients for optically pure water, respectively, and \(A_v\) is the absorption coefficient of dissolved organic matter at 380 nm. From (11) and (12), \(a(\lambda)\) is expressed as

\[
a(\lambda) = a_w(\lambda) + b_w(\lambda) + e_{ph}(\lambda) C + 0.2 \frac{650}{\lambda} + 1.0 \right\} b_d + A_v \exp \left[ -0.0167(\lambda - 380) \right],
\]

Fig. 1. Optical properties of Chaetoceros socialis.
where $c_{ph}$ is the attenuation coefficient of phytoplankton per unit chlorophyll $a$ concentration.

In the calculation, values of $a_{ph}$, $b_{ph}$, and $c_{ph}$ of *Chaetoceros socialis* given in Fig. 1 are used. The values of $a_{w}$ and $b_{w}$ are taken from Smith and Baker (1981), and $D_{ph}$ and $\sigma$ are assumed to be 1.2 and 10.6 nm, respectively, (Kishino et al., 1984a). Downward irradiance at the surface $E_{d}(0, \lambda)$ is assumed to be $100 \mu W \cdot cm^{-2} \cdot nm^{-1}$ for the entire spectral range.

3. Results and discussion

3.1. Chlorophyll $a$ concentration and fluorescence intensity

In order to investigate the variation in upward spectral irradiance, $C$ is changed on the assumption of $b_{ph} = A_{ph} = 0$ in (11), (12) and (13).

The calculated upward spectral irradiance at depth 0 m is shown in Fig. 2 at various concentrations of $C$. In this calculation, the value of $\beta_{(685)}$ is assumed to be 0.0001 nm$^{-1}$·str$^{-1}$. This value is equal to 0.024 of quantum yield of fluorescence, which corresponds to the mean value in the surface layer in coastal areas (Kishino et al., 1984b). In the figure, dashed line corresponds to the upward irradiance in the absence

Fig. 2. Spectral distribution of upward irradiance at depth of 0 m as a function of chlorophyll $a$ concentration for $\beta=0.0001$ nm$^{-1}$·str$^{-1}$. Dashed line shows $E_{u}$ in the absence of fluorescence ($\beta=0.0$ nm$^{-1}$·str$^{-1}$).

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![Image](image-url)

Fig. 3. Spectral distribution of upward irradiance at depth of 0 m as a function of volume fluorescence function for $C=1.0$ mg·l$^{-1}$ in the left-hand panel and 50.0 mg·l$^{-1}$ in the right-hand panel.
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![Graph](image)

Fig. 4. Correlation between chlorophyll $a$ concentration and upward fluorescence intensity $E_{f\lambda}$ at depth of 0 m for $\beta=0.0001$ nm$^{-1}$·str$^{-1}$.

of fluorescence ($\beta=0.0$ nm$^{-1}$·str$^{-1}$).

A clear peak near 685 nm is recognized in the upward irradiance for $C$ below the 20 $\mu$g·l$^{-1}$.

With the increase of $C$, however, the peak becomes unclear because of the effect of the strong absorption around 680 nm by phytoplankton itself.

This results in a shift of the wavelength of maximum irradiance from 685 nm to about 710 nm. In addition to the absorption effect, the peak around 710 nm is enhanced by the effect of the spectral properties of the scattering coefficient of phytoplankton, which has a maximum at 710 nm as shown in Fig. 1.

If fluorescence by phytoplankton is absent, the peak would appear at lower chlorophyll concentrations, as shown in Fig. 2. Thus, the fluorescence gives an inhibitory effect on the peak around 710 nm.

The fluorescence intensity is proportional not only to $C$ but also to $\beta$ as is clear from Eqn. (3) and (6). The variation of upward irradiance near 685 nm with various $\beta$ at 0 m depth is shown in Fig. 3. When $C$ is 50 $\mu$g·l$^{-1}$ the maximum in upward irradiance at 685 nm is recognized only for $\beta$ larger than 0.0002 nm$^{-1}$·str$^{-1}$. On the other hand, when $C$ is 1.0 $\mu$g·l$^{-1}$, the peak at 685 nm is recognized in all cases except $\beta$ smaller than 0.00001 nm$^{-1}$·str$^{-1}$. As is evident from Figs. 2 and 3, the peak at about 685 nm is due to fluorescence of chlorophyll $a$ and the peak at about 710 nm is due to spectral properties of absorption and scattering of phytoplankton.

The relationship between $E_{f\lambda}(0,685)$ and $C$ at 0 m depth for $\beta=0.0001$ nm$^{-1}$·str$^{-1}$ is shown in Fig. 4. Below 1 $\mu$g·l$^{-1}$ of $C$, the fluorescence intensity increases linearly with the increase in $C$ as is seen in the inset. However, in the ranges from 1 to 20 $\mu$g·l$^{-1}$ of $C$, the relationship between them is not linear but the logarithm of $C$ is proportional to the $E_{f\lambda}$. Above 20 $\mu$g·l$^{-1}$ of $C$, the increasing rate in $E_{f\lambda}$ decreases gradually with increasing $C$ and the $E_{f\lambda}$ tends to approach to the constant value of about 1.2. This pattern of dependence of $E_{f\lambda}$ on $C$ agrees well with observational results of PLATT and HERMAN (1983) and KISHINO et al. (1984b). The saturation in $E_{f\lambda}$ for very high concentration suggests that the remote sensing of $C$ from the fluorescence peak height is rather difficult for very high $C$.

The vertical distributions of fluorescence intensity of $E_{f\lambda}(x,685)$ and $E_{f\lambda}(x,685)$ for $\beta=0.0001$ nm$^{-1}$·str$^{-1}$ and $C=1.0$ $\mu$g·l$^{-1}$, which are assumed constant with depth, are shown in Fig. 5. The intensity of upward fluorescence decreases ex-
 exponentially with depth. On the other hand, the intensity of downward fluorescence increases rapidly with increasing depth and attains a maximum at the depth of 5 m. Below 5 m, it decreases exponentially with depth. The $E_d$ ($z, 685$) below depth of 4 m becomes larger than $E_r$ ($z, 685$). It is interesting to note that the vertical distribution of the fluorescence is analogous to that of radiance generated by elastic scattering (SUGIHARA, 1977). The attenuation of $E_d$ in deeper layer and $E_r$ is nearly equal to that of downward irradiance at the wavelength of maximum transmittance.

The computed spectra $E_d (z, \lambda)$ and $E_u (z, \lambda)$, for the case of $\beta = 0.0001 \text{nm}^{-1}\cdot\text{str}^{-1}$ and $C = 1.0 \text{mg}\cdot\text{l}^{-1}$, are shown in Fig. 6; the irradiance reflectance, defined by $R_d (z, \lambda) = E_u (z, \lambda)/E_d (z, \lambda)$, is shown in Fig. 7, for the same $\beta$ and $C$ assumptions. Because of the strong absorption of pure water at wavelength greater than 685 nm, $E_d$ decreases rapidly with increasing depth. At small depths, the rapid decrease in $E_u$ around 685 nm results in a gradual increase in fluorescence intensity relative to $E_d$ and the shoulder appears near 685 nm. It gradually develops with increasing depth and the peak appears below 15 m.

On the other hand, the sharp peak in upward irradiance is recognized at every depth although the peak becomes sharper at the larger depths. As shown in Fig. 7, the peak in $R_d (z, \lambda)$ appears at various depths for $\beta = 0.0001 \text{nm}^{-1}\cdot\text{str}^{-1}$ and $C = 1.0 \text{mg}\cdot\text{l}^{-1}$.

3.2. The influence of detritus and dissolved organic matter on the fluorescence appearing around 685 nm in upward irradiance

The upward irradiance at the surface was calculated as a function of $b_d$ when $C$ is 1.0 and
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50.0 μg·l⁻¹ in order to investigate the influence of $b_d$ on the spectral fluorescent light around 685 nm. The result is shown in Fig. 8. In this calculation, $A_y$ is assumed to be zero. For $C=1.0$ μg·l⁻¹ $E_d$ increases almost linearly with $b_d$. The fluorescence spectrum, however, becomes smaller and broader with increasing $b_d$.

In the case of $C=50.0$ μg·l⁻¹, on the other hand, the variation of $E_d$ with $b_d$ is rather small; the fluorescence effect is manifested in the upward irradiance as a peak around 700 nm for all values of $b_d$. It is interesting to note that $E_d$ increases and decreases with increasing $b_d$ above and below 615 nm.

The variation of the fluorescence intensity as a function of $b_d$ and $C$ is shown in Table 1. The influence of $b_d$ is very strong for low chlorophyll concentration, while it is weak for

---Fig. 7. Irradiance reflectance $R_d$ at various depths for $\beta=0.0001$ nm⁻¹·str⁻¹ and $C=1.0$ μg·l⁻¹. Dashed line shows $E_d$ in the absence of fluorescence ($\beta=0.0$ nm⁻¹·str⁻¹).

---Fig. 8. Spectral distribution of upward irradiance at depth of 0 m as a function of $b_d$ for $\beta=0.0001$ nm⁻¹·str⁻¹ and $C=1.0$ μg·l⁻¹ in the left-hand panel and 50.0 μg·l⁻¹ in the right-hand panel. Dashed line shows $E_d$ in the absence of fluorescence ($\beta=0.0$ nm⁻¹·str⁻¹).
Table 1. The fluorescence intensity, \( E_{fu} \) (\( \text{w} \cdot \text{cm}^{2} \cdot \text{nm}^{-1} \)) as a function of \( C \) and \( b_{s} \) for \( \beta = 0.0001 \text{nm}^{-1} \cdot \text{str}^{-1} \).

<table>
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<tr>
<th>( C ) (( \text{mg} \cdot \text{l}^{-1} ))</th>
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<th>1.0</th>
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<th>10.0</th>
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<td>0.568</td>
<td>0.323</td>
<td>0.129</td>
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<tr>
<td>50</td>
<td>1.053</td>
<td>0.822</td>
<td>0.571</td>
<td>0.277</td>
</tr>
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</table>

Table 2. The fluorescence intensity, \( E_{fu} \) (\( \text{w} \cdot \text{cm}^{2} \cdot \text{nm}^{-1} \)) as a function of \( C \) and \( A_{y} \) for \( \beta = 0.0001 \text{nm}^{-1} \cdot \text{str}^{-1} \).

<table>
<thead>
<tr>
<th>( C ) (( \text{mg} \cdot \text{l}^{-1} ))</th>
<th>0.0</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
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</thead>
<tbody>
<tr>
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<td>0.993</td>
</tr>
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</table>

Since the spectral absorption coefficient of dissolved organic matter, \( a_{y} \), decreases exponentially with wavelength, the influence of \( a_{y} \) on fluorescence intensity is very small. The variation of \( E_{fu} \) with \( A_{y} \) in the longer wavelength region is computed when \( C \) is 1.0 \( \text{mg} \cdot \text{l}^{-1} \) and is depicted in Fig. 9. The variation of the fluorescence intensity as a function of \( A_{y} \) and \( C \) is shown in Table 2. As shown in Fig. 9 and Table 2, when \( C \) is 1.0 \( \text{mg} \cdot \text{l}^{-1} \), the fluorescence peak in the case of \( A_{y} = 1.0 \text{ m}^{-1} \) decreases down to 30\% of that in the case of \( A_{y} = 0.0 \text{ m}^{-1} \). As \( C \) increases, the influence of \( a_{y} \) decreases more. For example, when \( C \) is 50 \( \text{mg} \cdot \text{l}^{-1} \), the fluorescence intensity in the case of \( A_{y} = 1.0 \text{ m}^{-1} \) decreases down to only 10\% of that in the case of \( A_{y} = 0.0 \text{ m}^{-1} \).

4. Summary

1. The peak at about 685 nm in the upward irradiance is due to the fluorescence of phytoplankton, whereas the peak at about 710 nm is due to spectral properties of absorption and scattering of phytoplankton.

2. A peak appears at about 685 nm when the chlorophyll \( a \) concentration, \( C \), is lower than 20 \( \text{mg} \cdot \text{l}^{-1} \) at the volume fluorescence function, \( \beta \), of 0.0001 \( \text{nm}^{-1} \), and when \( \beta \) is larger than 0.0002 \( \text{nm}^{-1} \cdot \text{str}^{-1} \) at the \( C \) of 50.0 \( \text{mg} \cdot \text{l}^{-1} \).

3. The fluorescence intensity is directly proportional to \( C \) at low concentrations and is proportional to \( \log (C) \) at middle concentrations. It approaches a constant value at high concentrations.

4. The intensity of upward fluorescence decreases exponentially with depth. However, the intensity of downward fluorescence increases rapidly with depth to a maximum value at a depth of 5 m and then decreases exponentially with depth.

5. Below depth of 20 m, the value of irradiance reflectance above 670 nm exceeds 80\%.

6. The fluorescence intensity decreases with increasing detritus.

7. The influence of dissolved organic matter on the fluorescence intensity is weak.

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References


水中分光放射照度におけるクロロフィルα
の蛍光に関する理論的考察

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要旨：一次蛍光モデルと二光束モデルを組み合わせて、クロロフィルαの蛍光の効果を含む放射輸送の理論式を導いた。この理論式を用いて実測の分光放射照度の685nm付近に見いだされる極大特性について調べた。数値計算の結果、クロロフィルα濃度が低い時は685nmに極大が現われ、高くなるにつれて極大は710nmに移動する。685nmの極大は植物プランクトンの蛍光により、710nmの極大は植物プランクトンの吸収と散乱の分光特性により生じた事事が分かった。また、蛍光の強度は、クロロフィルαが低濃度では濃度に比例し、中濃度では濃度の対数に比例し、高濃度では一定値に近づく事が分った。更に、デトリタスや溶存有機物の効果について検討した。その結果、デトリタスが増加すると蛍光強度は減少することと、溶存有機物はクロロフィルの蛍光にはあまり影響しないことがわかった。